Electrochemistry of thin film electrodes via surface modification

Tham, Guo Xiong

2020

Tham, G. X. (2020). Electrochemistry of thin film electrodes via surface modification.
Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/141710>

<https://doi.org/10.32657/10356/141710>

This work is licensed under a Creative Commons Attribution-NonCommercial 4.0
International License (CC BY-NC 4.0).

Downloaded on 26 Apr 2023 08:42:34 SGT

**NANYANG
TECHNOLOGICAL
UNIVERSITY**

SINGAPORE

**ELECTROCHEMISTRY OF THIN FILM ELECTRODES
VIA SURFACE MODIFICATION**

THAM GUO XIONG

SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

2020

ELECTROCHEMISTRY OF THIN FILM ELECTRODES
***VIA* SURFACE MODIFICATION**

THAM GUO XIONG

SCHOOL OF PHYSICAL AND MATHEMATICAL
SCIENCES

A thesis submitted to the Nanyang Technological
University in partial fulfilment of the requirement for
the degree of Doctor of Philosophy

2020

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research done by me except where otherwise stated in this thesis. The thesis work has not been submitted for a degree or professional qualification to any other university or institution. I declare that this thesis is written by myself and is free of plagiarism and of sufficient grammatical clarity to be examined. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

2 Jan 2020

.....
Date

T. Gabriel

.....
Tham Guo Xiong

Supervisor Declaration Statement

I have reviewed the content and presentation style of this thesis and declare it of sufficient grammatical clarity to be examined. To the best of my knowledge, the thesis is free of plagiarism and the research and writing are those of the candidate's except as acknowledged in the Author Attribution Statement. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

2 Jan 2020

.....

Date

RWebster

.....

A/Prof Richard Webster

Authorship Attribution Statement

Please select one of the following; **delete as appropriate*:

~~*(A) This thesis **does not** contain any materials from papers published in peer-reviewed journals or from papers accepted at conferences in which I am listed as an author.~~

*(B) This thesis contains material from **1** paper(s) published in the following peer-reviewed journal(s) / from papers accepted at conferences in which I am listed as an author.

Chapters 1.1, 2.1 and 4 are published as **Tham, G. X.**; Fisher, A. C.; Webster, R. D. A vitamin-based voltammetric pH sensor that functions in buffered and unbuffered media. *Sens. Actuators, B* **2019**, 283, 493–503. DOI: 10.1016/j.snb.2018.12.036

The contributions of the co-authors are as follows:

- A/Prof Webster provided the initial project direction and edited the manuscript drafts.
- I prepared the manuscript drafts. The manuscript was revised by A/Prof Webster.
- I co-designed the study with A/Prof Webster and Dr. Fisher and performed all the laboratory work at the School of Physical and Mathematical Sciences. I also analysed the data.
- The derivative of vitamin E (VEa) was synthesized by Dr. Peng Hong Mei, and the chemical identity was verified with nuclear magnetic resonance by me.

2 Jan 2020

.....
Date

.....
Tham Guo Xiong

This page is intentionally left blank

ABSTRACT

Surface modification of electrodes is an experimental method commonly used in electroanalytical chemistry. The thesis focused on three major areas that involved the surface modification of glassy carbon (GC) electrodes. In the first part of the thesis, a vitamin-based voltammetric pH sensor was developed with the drop cast of riboflavin (VB₂) and a vitamin E analogue (VEa) as the pH-sensitive and pH-insensitive redox active compounds, respectively, on the GC electrode surface. Nernstian responses were observed in deoxygenated and oxygenated buffered media at pH 1–11, and in deoxygenated and oxygenated unbuffered media with the addition of a very small concentration of acidic buffer. In the second part of the thesis, the dispersion of the functionalised carbon nanotubes was utilised with various solvents and drop cast onto GC electrode surfaces. Different classes of surfactants with varying concentrations were also used in the bulk solution to test the cyclic voltammograms of the immersed film electrodes. The analysis of the electrode kinetics was built on and verified with the combination of thin layer diffusion and semi-infinite diffusion *via* interpretation of the current responses of the modified electrodes. Finally, the last part of the thesis covers the electrochemical energy storage capability of the electrochemically co-polymerised PANIMEL/fMWCNT/GCE film electrode. Various factors were explored in the electrosynthesis of individual monomers prior to the electrochemical co-polymerisation. A series of electrochemical tests pertaining to the electrochemical cyclability and stability of the co-polymeric film were performed with a view of stabilizing the daughter polymeric melamine in the co-polymerised film to optimize the capacitor properties.

ACKNOWLEDGEMENTS

I would like to thank my PhD supervisor, Assoc. Prof. Richard D. Webster for his continuous guidance, support and patience in the four-year duration of my graduate education. My PhD journey was definitely enriching and fruitful with the opportunity to explore on the many applications of electrochemistry if not for his immense teaching of electrochemistry. A big thank you to my co-supervisor, Dr. Adrian Fisher for whom I am honored to work with during my course of graduate education.

I am grateful to Nanyang Technological University (NTU), Cambridge CARES (Centre for Advanced Research in Energy Efficiency in Singapore Ltd.) and CREATE (Campus for Research Excellence and Technological Enterprise) for the award of a postgraduate research scholarship and for the financial support to attend an overseas academic conference.

I would like to express my sincere appreciation to my former junior college Chemistry tutor Ms. Goh Chay Hian for her passion and dedication in enriching and inspiring my knowledge in chemistry. Your encouragement and feedback have been valuable to me that pathed my way to obtain a university degree in Chemistry. A big thank you to my former supervisor from the University of Edinburgh Dr. Peter Kirsop who has been supportive of my Chemistry education during my undergraduate and graduate days.

I would like to thank my laboratory mates in the Webster and Pumera groups for their support in the course of my PhD period. I am thankful to Maja, Jazreen and Sherman for offering their valuable advice in my PhD work. A big thank you to Naziah, Farhanah, Nasuha, Hui Ling and Ivan for taking their valuable time in assisting me to source for chemicals and solvents and the operation of various laboratory equipment.

My sincere thanks to Chencheng, Nicholas and Shengliang in Cambridge CARES who have been helpful in my PhD work.

I would also like to express my appreciation to the CBC administration and laboratory staff for their assistance and technical support during my time in NTU. A big appreciation to the corporate and laboratory staff in Cambridge CARES with special mentions of Ms. Khatijah, Ms. Leong Xiang Ning, Mr. John Chan, Ms. Louise Renwick, Ms. Joy Haughton, and Dr. Hugo Schmidt for their unwavering support during my time in Cambridge CARES.

A special thanks to my best friends Daniel Stocks, Roland Todd, Philips Argueta and Nicholas Tan for their unwavering emotional support whenever I am in need of help. Finally, I would like to express my utmost and sincere gratitude to my family who have been patiently in supporting me throughout my education and life. A big thank you to my mother for preparing such delicious and nutritious meals for me even when I have to return home much later than the agreed time. My PhD journey would not have been smooth if not for my family.

This page is intentionally left blank

TABLE OF CONTENTS

Abstract	I
Acknowledgements	II
Table of Contents	V
List of Publications and Scientific Conferences	X
List of Abbreviations	XI
List of Symbols	XIII
CHAPTER 1: Aims and Objectives of the Thesis	1–9
1.1 Aims and objectives	3
1.1.1 A novel vitamin-based voltammetric pH sensor in buffered and unbuffered media	3
1.1.2 Voltammetric studies of functionalised carbon nanotube dispersions in various solvents and surfactants	5
1.1.3 Electrochemical energy storage capability of an electrochemically co-polymerised film electrode	6
1.2 References	8
CHAPTER 2: Introduction to Thin Film Electrodes and Its Applications	10–78
2.1 Voltammetric sensor in the application of pH sensing	12
2.1.1 The science of pH sensing and the glass electrodes	12
2.1.2 Chemical sensors in pH sensing	18
2.1.3 General background on vitamins	20
2.1.3.1 Background of riboflavin	21

2.1.3.2	Background of vitamin E	23
2.2	Dispersion of carbon nanotubes in solvents	25
2.2.1	Background information of carbon nanotubes	25
2.2.2	Literature review of methods to disperse carbon nanotubes	27
2.3	Conducting polymers in electrochemical energy storage	37
2.3.1	Introduction to polymers and conducting polymers	37
2.3.1.1	Background of aniline	40
2.3.1.2	Background of polyaniline	41
2.3.1.3	Background of melamine	45
2.3.1.4	Background of polymelamine	46
2.3.2	Introduction to electrochemical energy storage	48
2.3.2.1	Background of capacitors and supercapacitors	50
2.3.2.2	Types of supercapacitors	53
2.4	References	58
CHAPTER 3: Experimental Methods		79–91
3.1	Overview of electrochemical techniques	81
3.2	Background information of electrochemical techniques	82
3.2.1	Cyclic voltammetry	82
3.2.2	Square-wave voltammetry	83
3.2.3	Electrochemical impedance spectroscopy	84
3.3	References	89
CHAPTER 4: A Novel Vitamin-based Voltammetric pH Sensor in Buffered and Unbuffered Media		92–124
4.1	Literature review of voltammetric pH sensors	94
4.2	Results and discussion	98

4.2.1	Single vitamin systems	98
4.2.2	Dual vitamin system	107
4.2.3	Unbuffered media	110
4.3	Conclusion	117
4.4	Experimental	118
4.5	References	121

CHAPTER 5: Voltammetric Studies of fCNT Dispersions in Various Solvents and Surfactants 125–174

5.1	Literature review of CNT dispersions in solvents	127
5.2	Results and discussion	127
5.2.1	Voltammetric studies of fCNT dispersions in various solvents	127
5.2.2	Effect of scan rate on the electrocatalytic oxidation of the ferri/ferrocyanide redox couple	138
5.2.3	Voltammetric studies of fCNT dispersions in the presence of surfactants	154
5.2.4	Effect of scan rate on the electrocatalytic oxidation of the ferri/ferrocyanide redox couple in the presence of DDAB	161
5.3	Conclusion	165
5.4	Experimental	167
5.5	References	170

CHAPTER 6: Electrochemical Energy Storage Capability of the Electrochemically Co-polymerised Film Electrode 175–219

6.1	Literature review of CPs and CNTs in EES applications	177
6.2	Results and discussion	182
6.2.1	Electrochemical polymerisation of individual monomers	182
6.2.2	Electrochemical co-polymerisation of both monomers	190

6.2.3	Variable scan rates of the electrochemically co-polymerised film electrode	195
6.2.4	Electrochemical stability of the electrochemically co-polymerised film electrode	198
6.2.5	Electrochemical impedance spectroscopy of the various electrodes	201
6.3	Conclusion	211
6.4	Experimental	212
6.5	References	214
CHAPTER 7: Summary and Future Work		220–228
7.1	Summary and future work	222
7.2	References	227
Appendix		229–232

This page is intentionally left blank

LIST OF PUBLICATIONS

CHAPTER 4

Tham, G. X.; Fisher, A. C.; Webster, R. D. A vitamin-based voltammetric pH sensor that functions in buffered and unbuffered media. *Sens. Actuators, B* **2019**, 283, 493–503.

SCIENTIFIC CONFERENCES

Tham, G. X.; Fisher, A. C.; Webster, R. D. Carbon Nanotube Based Electropolymerized Conducting Polymer Films in Potential Applications of Electrochemical Energy Storage. In *The 2nd Chemistry National Meeting Singapore 2019*, Singapore.

Tham, G. X.; Fisher, A. C.; Webster, R. D. An Electrochemical Approach to a Novel and Disposable Vitamin-Based Voltammetric pH Sensor that Functions in Buffered and Unbuffered Media. In *University of Cambridge Chemical Engineering and Biotechnology Research Conference 2017*, Cambridge, United Kingdom.

LIST OF ABBREVIATIONS

ACN	Acetonitrile
BR	Britton-Robinson (buffer)
C step	Chemical step
cmc	Critical micelle concentration
CNTs	Carbon nanotubes
CP	Conducting polymer
CV	Cyclic voltammetry (or voltammogram)
DDAB	Didodecyldimethylammonium bromide
DMF	<i>N,N</i> -Dimethylformamide
E step	Electron transfer (electrochemical) step
EIS	Electrochemical impedance spectroscopy
fCNTs	Functionalised carbon nanotubes
fMWCNTs	Functionalised multi walled carbon nanotubes
FMN	Flavin mononucleotide
fSWCNTs	Functionalised single walled carbon nanotubes
GCE	Glassy carbon electrode
LJP	Liquid junction potential
NMP	<i>N</i> -Methyl-2-pyrrolidone
NMR	Nuclear magnetic resonance
PANI	Polyaniline
PBS	Phosphate buffer solution
PC	Phosphate-citrate (buffer)
PC-K	Phosphate-citrate buffer with potassium chloride (KCl)

PMEL	Polymelamine
SDS	Sodium dodecyl sulfate
SWV	Square-wave voltammetry (or voltammogram)
T20	Tween 20 (Polysorbate 20)
VB ₂	Vitamin B ₂ (riboflavin)
VEa	Vitamin E analogue (or derivative)

LIST OF SYMBOLS

D_0	Diffusion coefficient
E°	Formal potential
E_p^{ox}	Oxidative (anodic) peak potential
E_p^{red}	Reductive (cathodic) peak potential
i_p	Peak current
i_p^{ox}	Peak oxidative current
i_p^{red}	Peak reductive current
k^0	Heterogeneous electron transfer rate constant
M	Molar (concentration)
min	Minute (time)
mg	Milligram (mass)
mL	Millilitre (volume)
mM	Millimolar (concentration)
ms	Millisecond (time)
mV	Millivolt
rpm	Revolutions per minute
s	Second (time)
V	Volt
v	Scan rate
°C	Degree Centigrade
μM	Micromolar (concentration)
ΔE_{pp}	Peak-to-peak potential separation
%wt	Percentage by weight

This page is intentionally left blank

Aims and Objectives of the Thesis

This page is intentionally left blank

1.1 Aims and objectives

The thesis focuses on the electrochemistry of thin film electrodes *via* surface modification and their applications such as voltammetric pH sensing and electrochemical energy storage (EES). In this chapter, the three major research projects and the aims and objectives of each project shall be outlined briefly in each subsection. The fundamental aspects of the project shall be addressed at the beginning of each project with an overview of the related literature followed by the results and discussion.

1.1.1 A novel vitamin-based voltammetric pH sensor in buffered and unbuffered media

Scheme 1.1 Diagrammatic explanation of the square wave voltammetry used for the vitamin-based voltammetric pH sensor when used in solutions of various pH. Within the working pH range, the E_p -values of riboflavin (VB₂) shift with a Nernstian fashion and the E_p -values of a vitamin E analogue (VEa) remain constant (given by the red and blue dotted lines, respectively).

Limited studies have been conducted on the possible capability of developing electrochemical sensors with vitamin compounds acting as redox probes, since they often undergo proton-coupled electron transfer (PCET) reactions.^{1,2} A vitamin-based voltammetric pH sensor can potentially be useful in clinical testing since it can be metabolised safely if the sensor can be made safe for ingestion in the form of a capsule, or injection by hypodermic needle into the blood vessels.^{3,4} Such a sensor could also extend its use in oil drilling industries to determine the pH of the drilling mud as different dissociated forms of hydrogen sulphide are usually trapped in the mud.⁵ If the sensor is used in environmental testing, it can be disposed of safely after use and biodegrade under aerobic conditions.⁶ From a user's perspective, the use of a pH-independent redox couple as an internal standard in pH sensors can be advantageous as other reference electrodes such as the Ag/AgCl or the standard calomel electrodes require a separate solution for the reference electrode that disfavours the miniaturisation of voltammetric pH sensors.⁷ Thus, **Chapter 4** in the thesis examines the possibility of the development of a disposable vitamin-based voltammetric pH sensor that involves a pH-dependent redox active vitamin and a pH-independent redox active modified vitamin to measure the pH in buffered and unbuffered media. In each media, oxygenated and deoxygenated conditions were examined with the aid of voltammetric studies. Results pertaining to unbuffered oxygenated media are of utmost importance as such solutions reflect the type of test solutions being used frequently in pH determination. The pH-independent redox active vitamin acts as the reference compound in the sensor so that pH measurements of a sample solution can be obtained relative to this vitamin. Here, the pH-independent and pH-dependent redox active vitamins studied were a modified form of vitamin E (VEa) and the low water soluble form of vitamin B₂, riboflavin (VB₂) respectively. To determine if a Nernstian response was observed

relative to pH, the difference in the E_p values between the pH-dependent and pH-independent vitamin compounds (**Scheme 1.1**) was plotted against pH to obtain a linear plot based on **equation 4.1**. Such difference in the E_p values also corrects the problem of liquid junction potentials that causes inaccuracy of pH measurements.

1.1.2 Voltammetric studies of functionalised carbon nanotube dispersions in various solvents and surfactants

Scheme 1.2 Chemical structures of (a) DDAB, (b) T20, and (c) SDS.

There have been several works reported in the literature that are dedicated to the study of various agents used in the dispersing of CNTs in solvents. However, voltammetric studies on the comparison of the various solvents and agents used in the dispersion of CNTs are rather limited. **Chapter 5** aims to address these deficiencies by

using cyclic voltammetry as the commonly used voltammetric technique to examine functionalised single-walled carbon nanotubes (fSWCNTs) and functionalised multi-walled carbon nanotubes (fMWCNTs) and their dispersion of three different solvents separately; *N*-methyl-2-pyrrolidone (NMP), *N,N*-dimethylformamide (DMF) and ethanol (EtOH). The effect of varying CNT percentage by weight (%wt) in each solvent on the peak-to-peak potential separation (ΔE_{pp}) of the functionalised carbon nanotube (fCNT) deposited on a glassy carbon electrode (GCE) immersed in a phosphate buffer solution containing a small concentration of ferrocyanide/ferricyanide redox couple was investigated to determine which solvent is preferred for dispersing the fCNTs to give the least ΔE_{pp} value for CNT suspensions with a particular CNT %wt. In addition, the influence of three different classes of surfactants (cationic, non-ionic and anionic) present in the PBS on the ΔE_{pp} of the immersed fCNT/GCE electrodes is discussed, and subsequently compared with the voltammetric results of the corresponding electrodes in the absence of the surfactants. The three surfactants used in this study are didodecyldimethylammonium bromide (DDAB), Tween 20 (T20), and sodium dodecyl sulfate (SDS) as shown in **Scheme 1.2**.

1.1.3 Electrochemical energy storage capability of an electrochemically co-polymerised film electrode

Numerous papers have reported the use of pristine and chemically functionalised CNTs with polymerised aniline (PANI) but with very limited reports on the use of these CNTs with polymerised melamine (PMEL) in EES applications. **Chapter 6** aimed to investigate the possibility of developing a PANIMEL/fMWCNT/GCE co-polymerised film electrode for EES applications that incorporates melamine and aniline *via* an *in-situ* electrochemical co-polymerisation on the fMWCNT/GCE electrode surface.

Melamine, aniline and fMWCNTs were picked due to their ready commercial obtainability, low cost and no work has been done on such combination to the best of the author's knowledge. The use of fMWCNTs is more favoured than its pristine form to reduce the tendency of forming agglomeration and avoid the use of surfactants with pristine CNTs that could cause more inefficiency in industrial processing.⁸ Studies have also indicated that the composite materials that involve heteroatoms with carbons can reduce the band gap between the conduction and valence bands and thereby increase the electrical conductivity of these electrodes.^{9,10} The high nitrogen contents of melamine and aniline in their polymeric forms can potentially induce strong pseudocapacitive effects in the electrochemical performance of supercapacitor electrodes. The use of acids or bases can also activate CNTs by enlarging the micropore volume of the CNTs to enhance charge storage and transport.¹¹ Various factors that may optimise the electrochemical performance of the composite film electrode materials were investigated and evaluated accordingly. In addition, electrochemical impedance spectroscopic studies were performed with its results analysed to offer insights about the nature and extent of the interfacial charge transfer processes occurring in various composite electrodes, and thereby evaluating whether the PANIMEL/fMWCNT/GCE co-polymerised film electrode can be potentially used in the applications of EES.

1.2 References

1. Casimero, C.; McConville, A.; Fearon, J.-J.; Lawrence, C. L.; Taylor, C. M.; Smith, R. B.; Davis, J. Sensor systems for bacterial reactors: A new flavin-phenol composite film for the *in situ* voltammetric measurement of pH. *Anal. Chim. Acta* **2018**, *1027*, 1–8.
2. Hegarty, C.; Kirkwood, S.; Cardosi, M. F.; Lawrence, C. L.; Taylor, C. M.; Smith, R. B.; Davis, J. Disposable solid state pH sensor based on flavin polymer-ferrocyanide redox couples. *Microchem. J.* **2018**, *139*, 210–215.
3. McLister, A.; Davis, J. Molecular Wiring in Smart Dressings: Opening a new route to monitoring wound pH. *Healthcare* **2015**, *3* (3), 466–477.
4. C. McCaffrey, K. Twomey, V. I. Ogurtsov, Development of a wireless swallowable capsule with potentiostatic electrochemical sensor for gastrointestinal track investigation. *Sens. Actuators, B* **2015**, *218*, 8–15.
5. Nasr-El-Din, H. A.; Al-Humaidan, A. Y.; Fadhel, B. A.; Frenier, W. W.; Hill, D. G. Investigation of sulfide scavengers in well-acidizing fluids. *Soc. Petro. Eng. J.* **2002**, *17* (4), 80289–80291.
6. Rontani, J.-F.; Nassiry, M.; Guasco, S.; Mouzdahir, A.; Bonin, P. Aerobic metabolism of vitamin E by marine bacteria: Interaction with free radical oxidation (autoxidation) processes. *Org. Geochem.* **2008**, *39* (6), 676–688.
7. Pöller, S.; Schuhmann, W. A miniaturized voltammetric pH sensor based on optimized redox polymers. *Electrochim. Acta* **2014**, *140*, 101–107.
8. Godara, A.; Vaugien, T. Carbon nanotubes in polymer matrix composite structures. *JEC Compos.* **2009**, *46*, 64–68.
9. Paraknowitsch, J. P.; Thomas, A. Doping carbons beyond nitrogen: an overview of advanced heteroatom doped carbons with boron, sulphur and phosphorus for energy applications. *Energy Environ. Sci.* **2013**, *6*, 2839–2855.
10. Lota, G.; Fic, K.; Frackowiak, E. Carbon nanotubes and their composites in electrochemical applications. *Energy Environ. Sci.* **2011**, *4*, 1592–1605.
11. Frackowiak, E.; Depeux, S.; Jurewicz, K.; Szostak, K.; Cazorla-Amoro, D.; Béguin, F. Enhanced capacitance of carbon nanotubes through chemical activation. *Chem. Phys. Lett.* **2002**, *361*, 35–41.

This page is intentionally left blank

2

Introduction to Thin Film Electrodes and its Applications

This page is intentionally left blank

2.1 Voltammetric sensor in the application of pH sensing

2.1.1 The science of pH sensing and the glass electrodes

The measurement of pH in solutions is of fundamental importance in many industrial and academic environments. Well known modern applications include environmental monitoring to ensure quality in water treatment plants and agricultural farms, marine research in monitoring sea water and aquariums, and clinical testing *via* measurement of blood and other biological fluids in hospitals and clinics. Generally, the measurement of pH can be performed *via* two major classes of experimental methods – either electrochemically or non-electrochemically (**Figure 2.1**).¹ Potentiometry is one of the major electrochemical methods to measure pH and is commonly practised with the glass pH electrode – a pH meter is one such example.^{2,3} There are various other methods to measure pH such as amperometry,^{4,5} and non-electrochemical methods involving the use of litmus paper as a form of colour comparison,⁶ or measuring the wavelength of a pH-sensitive coloured solution photometrically.⁷

The origin of the pH sensing glass electrode was attributed to a German biologist Max Cremer in 1906 whereby an electrical potential difference occurs across the glass membrane with an acid and a base at different sides of the glass membrane.^{8,9} Cremer theorised that such a potential difference was related to the concentration of hydrogen ions in the solution, and the proposal was subsequently further actualised by Professor Fritz Haber and Dr. Zygmunt Klemensiewicz in the successful construction of the first potentiometric glass electrode in 1909.^{9–11} In the same year, the concept of pH was introduced by a Danish chemist Søren Peter Lauritz Sørensen whereby the pH is dependent on the concentration of hydrogen ions.^{12–14} Interestingly, the significance of the letter ‘p’ in the term ‘pH’ is debatable until now due to the ambiguity of Sørensen’s intended meaning, and could possibly refer to the potential of hydrogen, or power.^{15,16}

Moreover, the symbol 'pH' had different forms such as PH, Ph, ph, P_h, P_H but was later formalised by the *Journal of Biological Chemistry* as what it has been used today.¹⁷

Figure 2.1 Various experimental methods involved in the measurement of pH. Reproduced with permission from reference 1.

Theoretically speaking, pH is not directly related to the concentration of hydrogen ions. Shortly after Sørensen's concept of pH, studies by Peter Debye and Erich Hückel in 1923 revealed that pH is actually dependent on the *activity* and not *concentration* of the hydrogen ions. The use of chemical thermodynamics and kinetics explained that ionic interactions should be accounted for in non-ideal solutions.^{18,19} Today, IUPAC defines pH as the negative logarithm of hydrogen ion *activity* in a solution as shown in **equation 2.1**:²⁰

$$\text{pH} = -\log a_{[\text{H}^+]} = -\log \left(\gamma_{[\text{H}^+]} \times [\text{H}^+] \right) \quad (2.1)$$

The activity of an ion refers to its *effective* concentration and arises from ions of the same or different species in the solution interacting with each other. The activity of

an ion is the product of its activity coefficient, γ which is a constant, and its concentration in the solution. Consider an example of a 0.1 M hydrochloric acid that is diluted 100 times to give a 1 mM solution, and that the activity of hydrogen ion increases from 0.860 to 0.967.²¹ With the activity coefficient approaching unity upon successive dilution, the activity (which is the *effective* concentration) is equal to the concentration. Thus, pH can be approximated simply as the negative logarithm of hydrogen ion concentration in a sufficiently dilute solution less than 1 mM as shown in **equation 2.2**. Note that the usage of **equation 2.2** assumes the ideal behaviour of hydrogen ions in an infinitely dilute solution.

$$\text{pH} = -\log [\text{H}^+] \quad (2.2)$$

Typically, the pH values are ranged on a scale from 0 to 14 with 0, 7 and 14 being the values for strongly acidic, neutral and strongly basic solutions respectively. In theory, pH values can fall outside of the pH range if the solution concentration is high enough with 10 M HCl ($\text{pH} < 0$) or 10 M NaOH ($\text{pH} > 14$). Examples of various substances with their characteristic pH values are shown in **Figure 2.2**.¹ Today, the measurement of pH is usually performed with the aid of a pH meter which typically consists of two electrodes – the glass and the reference electrodes as shown in **Figure 2.3**. Owing to the high selectivity of the glass for hydrogen (or more accurately, hydronium) ions, common glass electrodes are usually made as hydrogen-ion selective glass electrodes. A typical glass electrode consists of a glass membrane having an enclosed solution of buffered KCl solution at pH 7 which is in contact with a thin silver wire plated with silver chloride. With the buffered chloride solution enclosed within the glass electrode, the potential inside the glass remains constant. The glass membrane is pH-sensitive as pictured in **Figure 2.4** whereby hydrogen ions from the test solution can form reversible bonding interactions with the anionic silicate sites on the surface of the

glass membrane to form silanol groups. Consequentially, a potential difference across the glass membrane arises due to a change in potential outside of the glass. It is important that the membrane of the glass electrode should have a high electrical resistance which is lower than the input resistance of the meter to ensure accuracy of the pH readings.²²

Figure 2.2 Examples of various substances with their characteristic pH values. Reproduced with permission from reference 1.

Figure 2.3 Glass and reference electrodes of a typical pH meter, and immersed in a test solution.

Figure 2.4 Bonding interactions of free hydrogen ions from the test solution with the anionic silicate sites on the glass membrane.

As for the reference electrode, it contains a piece of silver wire coated with silver chloride that is enclosed by a 3 M potassium chloride filling solution saturated with silver chloride. Similar with the glass electrode, a constant chloride concentration ensures that a constant potential is maintained within the reference electrode. With the porous liquid junction fitted with a porous ceramic diaphragm in the reference electrode, the filling solution interacts with the test solution without contaminating the test solution. With repeated usage of the pH meter, a lowered level of the filling solution requires the replenishing of the same solution so that the device can continue to operate properly.²² If the test solution is poor in buffering capacity or electrolytic concentration, a liquid junction potential (LJP) arises between the reference electrode and the test solution during the pH measurement. A LJP develops when two solutions of dissimilar electrolytic solutions are in contact with each other to result in a potential difference across the solution-solution interface.²³ Factors that influence the extent of LJP include the type and concentration of ions in the test solution.^{22,23} With LJP, pH measurements become erroneous and the usage of a saturated KCl salt bridge can minimise such effect on pH measurements. Before actual pH measurements of the laboratory samples,

calibration of such electrode is usually performed with a few standard IUPAC buffers of known pH that act as a reference standard. The IUPAC defines the operational pH as governed by **equation 2.3**:

$$\text{pH} = \text{pH}_s + (E - E_s) \left(\frac{F}{2.303RT} \right) \quad (2.3)$$

where pH and pH_s are the pH of the test solution and the reference standard solution respectively, E and E_s are the potentials of the test solution and the reference standard solution respectively, and F , R and T referring to the Faraday constant, molar gas constant and thermodynamic temperature respectively.^{24–26} From **equation 2.3**, calibration can negate the influence of LJP and reference electrode potential on pH measurements. Moreover, pH is dependent on cell potentials which in turn are dependent on *activities* and not *concentrations*. Thus, the definition of pH should relate to the *activity* rather than the *concentration* of the hydrogen ion.

The use of hydrogen-ion selective glass electrodes has numerous advantages such as their long shelf life, chemical inertness, allowing rapid measurements, simple to use, and are applicable to pH determination of solutions from clear to turbid and coloured.^{23,27} Moreover, recalibration with standard buffer solutions is not required on a frequent basis for numerous pH measurements that are not too extreme on the ends of the pH scale. However, such glass electrodes have certain drawbacks. Firstly, the glass membrane in glass electrodes is fragile and can degrade with time. The membrane can be damaged irreversibly if pH measurements are performed in strong hydrofluoric acid solutions. Secondly, the “glass pH electrode” is comprised of two electrodes with aqueous internal filling solutions, which makes miniaturization difficult. Thirdly, solutions that are poorly buffered or with low electrolyte concentration suffer from long equilibration time during pH measurements due to a liquid junction potential arising between the reference electrode and the test solution.²³ More importantly, errors in pH

measurements occur when glass electrodes are met with instability and potential drift at very high pH due to alkali errors. Such problems require constant recalibration which render the glass electrodes inconvenient for in-field analysis.^{5,28} Lastly, it may be advantageous for certain applications to have a disposable pH electrode such as for biological samples where cross-contamination needs to be rigorously prevented. The glass pH electrode is relatively expensive to construct which negates its use in a disposable fashion.

2.1.2 Chemical sensors in pH sensing^{29,30}

A chemical sensor is a device that processes chemical information such as the activity of hydrogen ions in the test sample into real-time analytical information. A well-known example of such sensor is the glass electrode for pH determination. Typically, a chemical sensor is comprised of two components – recognition and transduction. Within the recognition component, selectivity is of importance whereby a signal must be stimulated due to the analyte-receptor interaction and not the interferent-receptor interaction. The receptor is a recognition site that allows reversible and noncovalent analyte-receptor interaction. Various forms of recognition may exist such as with ions, enzymes or biological cells and tissues. In the case of the glass electrode, the ion recognition mechanism relies on ion distinctive properties such as electrical charge and size with glass as the recognition site for strong affinity with hydrogen ions. If enzymes are involved, they act as labels in enzymatic sensors for the reversible formation of substrate-enzyme complex to form products with regeneration of the enzymes. Substrate and inhibitor concentrations can be measured from such mechanisms.

For the transducer of a chemical sensor, it detects and translates the signal into useful analytical information. Transduction can be broadly categorised into a few

classes such as thermometric, optical, piezoelectric and electrochemical. Thermometric transduction operates based on temperature change which is commonly used in sensing flammable gases. Spectroscopic data from light propagation and scattering in optical transducers provide luminescence, reflectance and absorbance data which are characteristics of an optical sensor (or more commonly known as optode). For piezoelectric transducers, a change in mass on the surface of a vibrating crystal offers useful analytical information such as pressure and force in terms of voltage. As for electrochemical transduction, three common classes exist – amperometric, potentiometric and voltammetric. Electrochemical sensors involve a two or three-electrode setup. A well-known example of an amperometric sensor is the dissolved oxygen probe that electrochemically reduces oxygen to register a plot of current against time and thereby determine the concentration of dissolved oxygen in a test sample. For potentiometric sensors, negligible current is drawn through the electrochemical cell of high impedance. The concentration (or *activity* in theoretical sense) of the ions is of interest in potentiometric measurements and a well-known common example is the glass electrode that measures the pH of the test sample with the principles discussed earlier. Potentiometric sensors can also be used in lipid membranes, and even as other types of ion-specific sensors such as to detect fluoride ions specifically in the case of a fluoride ion-selective sensor. As for voltammetric sensors, the underlying concept of voltammetry entails the measurement of current as a function of the applied potential to a working electrode. This current is obtained when redox active species are oxidised or reduced on the electrode surface. Different forms of voltammetric techniques are available such as cyclic (CV), square-wave (SWV), differential pulse and linear sweep voltammetry. Voltammetry can provide various insights depending on the type of voltammetric technique used, and usually quantitative information about electroactive

inorganic and organic analytes are the most fundamental observations to be obtained. The use of voltammetric sensors offers numerous advantages such as high sensitivity, short time measurements, simplicity, flexibility and provides insights into the mechanistic and kinetic data associated with the analyte and the reactions involved.³⁰

2.1.3 General background on vitamins

Vitamins are naturally occurring and biologically active compounds which can be absorbed by the human body for human health and well-being if consumed in small amounts.^{31–33,37} Some common sources of vitamins can range from fruits and vegetables to dietary supplements in the form of powder or pills for human consumption. As the human body is unable to synthesize vitamins, a healthy and balanced diet is essential by consuming food from various sources in accordance to the guidelines of the healthy diet pyramid.³⁴ If some of the vitamins in the supplements are non-biologically active, they may undergo certain biochemical reactions in the human body in order to be biologically active. Moreover, some vitamins also function as precursors to coenzymes so that enzymes can be catalytically active to participate in key cellular pathways.³⁵

The presence of vitamins was felt as early as back to 2600 B.C. when the beriberi disease broke out in China. Fruits such as lemons and oranges were used to treat scurvy-infected sea crew in the early 15th century, and the use of cod liver oil to treat rickets in 1824. The underlying causes of these diseases were poorly studied and the consumption of certain food to cure them was widely thought to be a ‘tested and proven prescription’. Despite the occurrence of these vitamin-deficient related diseases, there was still a poor scientific knowledge of the essential vitamins, which is attributed to the general poor scientific advancements.^{36,37} However, research on vitamins gained a breakthrough in the early 20th century. The term “vitamin” originates back to 1912 when a biochemist

Casimir Funk had successfully isolated the active component oryzanin (now known as thiamine) that is present in rice bran. Oryzanin was named as a vitamin because of its presence of the *amine* group and was deemed *vital* to life.³⁸⁻⁴⁰ In the subsequent years, vitamin was renamed to what we know as *vitamin* today with the acknowledgement that not all vitamins may contain an amine group structurally.^{38,41}

To date, there are thirteen essential vitamins for bodily function that are classified into two broad categories – water or fat soluble. Water soluble vitamins include vitamins B complexes and C, while fat soluble vitamins include vitamins A, D, E and K. Water soluble vitamins can function as coenzymes and are easily absorbed into the bloodstream directly. Moreover, they are not stored in the human body except for vitamin B₁₂, and the excess is excreted through urine. As for fat soluble vitamins, they require bile salts and fats for absorption to proceed and are generally stored in the liver and are less readily excreted even with excessive dosage levels. They do not function as coenzymes unlike the water soluble vitamins.^{33,38}

2.1.3.1 Background of riboflavin

Flavins are a class of organic compounds that share a common group based on the aromatic and cyclic base pteridine in their chemical structures. The most commonly known flavin is riboflavin (VB₂, also known as vitamin B₂ or 7,8-dimethyl-10-ribityl-isoalloxazine) (**Scheme 2.1**) which belongs to the family of vitamin B. It appears as a bright orange-yellow powder at room temperature whose colour is characterised by the Latin word *flavus* (yellow).⁴² In addition, riboflavin is fluorescently active and poorly soluble in water.³⁶ As riboflavin is not possible to be synthesized or stored in the human body, various related food sources can be acquired from the diet and include eggs, leafy

vegetables and meats (especially liver and kidney). Notably, riboflavin absorption is enhanced *via* the consumption of animal sources than plant-based food.⁴³

Riboflavin is also the precursor to the two flavin coenzymes – flavin mononucleotide (FMN, or riboflavin-5'-phosphate) and flavin adenine dinucleotide (FAD, or riboflavin 5'-adenosine diphosphate) (**Scheme 2.1**). Both flavin coenzymes are biologically active whose concentration can be enhanced by either oral supplementation of riboflavin or a regular dietary intake of food sources rich in riboflavin in order to correct riboflavin deficiency. Deficiencies associated with riboflavin are very uncommon in urban cities due to the abundance of food sources rich in riboflavin. However, chronic alcoholics are susceptible to such associated deficiency with skin disorders and anaemia and possibly with a higher risk of carcinogenesis owing to their poor dietary habits.⁴⁴ Other conditions associated with riboflavin deficiency may also include poor sensitivity to sunlight, glossitis, and seborrheic dermatitis.^{42,44} On the other hand, riboflavin can bind to proteins to form flavoproteins (also known as flavoenzymes) and participate in key cellular reactions such as signal transduction. This is largely due to the ability of the isoalloxazine ring in riboflavin to accept or transfer electrons is useful in biological processes whereby they can act as mediators in one- or two-electron transfer processes.^{45,46} Moreover, riboflavin can serve as a transformer between obligate two-electron donors (such as NADH to NAD) and obligate one-electron acceptors (such as heme Fe).^{47,48} On the other hand, cofactors such as FAD are essential to flavoproteins in order to facilitate electron transfer.^{45,49}

In general, the core bodily functions of riboflavin include the formation of red blood cells and the metabolism of energy, fats, proteins and carbohydrates. FMN and FAD act as flavoenzymes to facilitate electron transport and the redox conversions of these aforementioned metabolic processes. When riboflavin is ingested and absorbed in

the small intestine, the enzyme riboflavin kinase catalyses the conversion of riboflavin to FMN with the consumption of adenosine triphosphate (ATP). Another enzyme FAD synthase shall then convert FMN to FAD, again with the consumption of ATP.⁴⁹ Excessive bodily consumption of riboflavin is usually excreted in the urine as riboflavin or other flavin metabolites such as lumiflavin.⁵⁰

Scheme 2.1 Chemical structures of (a) riboflavin, and its two cofactor forms (b) flavin mononucleotide (FMN) and (c) flavin adenine dinucleotide (FAD).

2.1.3.2 Background of vitamin E

Vitamin E was first discovered in 1922 by Evans and Bishop on its importance in rats with a vitamin E deficient diet that had caused reproductive failure.⁵¹ Ever since, there have been extensive studies on vitamin E that are still ongoing to discover and explain its intricate functions at a cellular and molecular level. To date, vitamin E is generally known as naturally occurring and fat soluble in nature. It is known to exist in two major classes – tocopherols and tocotrienols. Each class can be further subdivided into four different forms (α , β , γ , and δ) depending on the degree of methylation of the polar moiety (**Scheme 2.2**).^{52,53} A major difference between tocopherols and

tocotrienols is that the former contains a fully saturated phytyl chain but not for the latter. All forms of vitamin E have antioxidant properties with α -tocopherol being the most abundant and most biologically active amongst them. Beyond their action as antioxidants, it has been proposed that vitamin E possesses very specific functions by acting as molecules in cell signalling and gene expression. All eight natural occurring forms of vitamin E except α -tocopherol do not count towards meeting the vitamin E requirement due to the inability of the human body to convert them into α -tocopherol.⁵³ When humans ingest tocopherol-containing food, pancreatic esterases and bile acids solubilise tocopherols and other hydrophobic molecules *via* the process of micellar formation. Vitamin E is then absorbed from the intestines into the enterocyte followed by packaging into chylomicrons with triglycerides and phospholipids. The chylomicrons are secreted into the bloodstream to allow catabolism *via* the action of lipoprotein lipase with chylomicron remnants as catabolised product. These remnants contain a large proportion of the vitamin E which are absorbed by the liver and secreted into the blood plasma in the form of very low density lipoproteins (VLDLs).⁵⁴

<i>Saturated</i> phytyl chain			<i>Unsaturated</i> phytyl chain		
Compound	R ₁	R ₂	Compound	R ₁	R ₂
α -tocopherol	CH ₃	CH ₃	α -tocotrienol	CH ₃	CH ₃
β -tocopherol	CH ₃	H	β -tocotrienol	CH ₃	H
γ -tocopherol	H	CH ₃	γ -tocotrienol	H	CH ₃
δ -tocopherol	H	H	δ -tocotrienol	H	H

Vitamin E is mostly present in plant-based foods and various food sources for the human dietary uptake include green vegetables, sunflower seeds, dairy products, nuts, meat and fish.^{53,55} Despite of the divided consensus on the recommended dietary intake of vitamin E across numerous clinical trials and surveys, the recommended intake is generally low ranging from 5 to 13 mg/day worldwide.⁵⁶ However, diseases associated with a deficiency in vitamin E are usually related to a rare genetic condition “*Ataxia with isolated Vitamin E Deficiency*” (AVED). AVED is characteristic of the mutations in the gene coding for the α -tocopherol transfer protein that can cause very poor retainment of vitamin E upon intestinal absorption. It is with oral supplementation of vitamin E that the genetic condition can be suppressed under control.⁵⁵ On the other hand, toxicity of vitamin E in humans are uncommon as an extremely high concentration of α -tocopherol is required to interfere with anticancer signalling and tumour growth arrest associated with breast cancer.⁵⁷

2.2 Dispersion of carbon nanotubes in solvents

2.2.1 Background information of carbon nanotubes

Nanomaterials offer numerous advantages which includes a large surface to volume ratio. Examples of one-dimensional (1D) nanostructures include nanotubes and nanowires. Carbon nanotubes (CNTs) are allotropes of carbon with their diameters in nanoscale and possess excellent electronic, mechanical, chemical, physical and optical properties. They are a class of fullerenes that have sp^2 hybridised carbon atoms stronger than the sp^3 diamond structure.⁵⁸ They are also one-dimensional structures and typically hollow and cylindrical in shape with their ends open for certain types of CNTs. Their large effective surface area, high modulus and high electrical and thermal properties are

of interest in assisting researchers and industries to develop and extend a broad range of applications from rechargeable batteries to biomedical devices.^{58,59}

The history of CNTs goes a long way back to the 1950s when they were first mentioned by Radushkevich and Lukyanovich in 1952 and described as hollow filaments with variable diameters of nanometres size.⁶⁰ In 1991, CNTs were synthesized by Iijima *via* an arc discharge setup and were described as hollow microtubules of graphitic carbon with diameters of 4 to 30 nm and lengths up to 1 μm .⁶¹ These hollow microtubules were thought to be multi walled CNTs (MWCNTs) and stripping them by layer to give a single walled CNT (SWCNT) was then reported by Tsang *et al.* in 1993.⁶² Ever since, the emergence of CNTs led to a rise in interest on the synthesis and their uses. The most popular and conventional methods used to synthesize CNTs include chemical vapour deposition,⁶³ electric arc discharge,⁶⁴ and laser ablation.⁶⁵ Apart from them, liquid electrolysis and plasma torch have been used by various researchers as well.^{66,67} Acid treatment is then proceeded to remove impurities in the CNTs.

Figure 2.5 Diagrammatic representation of (a) SWCNTs and (b) MWCNTs. Reproduced with permission from reference 68.

CNTs can be classified into two major categories: SWCNTs or MWCNTs. SWCNTs exist in the form of a rolled graphene sheet while MWCNTs are multiple layers of concentric single walled graphene cylinders held together by van der Waals interactions (**Figure 2.5**).⁶⁸ This also accounts why MWCNTs have superior mechanical

properties with a measured elastic modulus close to 1 TPa and a tensile strength of 100 GPa that is over ten-fold greater than a typical industrial fibre.⁵⁹ Their characteristics and differences are summarised in **Table 2.1**.⁶⁹

Table 2.1 Differences between SWCNTs and MWCNTs. Reproduced with permission from reference 69.

Single-walled carbon nanotubes (SWCNTs)	Multi-walled carbon nanotubes (MWCNTs)
• Single layer of graphene	• Multiple layers of graphene
• Catalyst is needed for synthesis	• Catalysis is optional for synthesis
• Difficult bulk synthesis due to controlled growth and atmospheric conditions	• Easy bulk synthesis
• Poor purity	• High purity
• Poor dispersion with formed bundled structure	• Homogeneous dispersion with no bundled formation
• High probability of defects during functionalisation	• Minimal probability of defects
• Easy to twist	• Difficulty in twisting due to structure
• Easy characterization and evaluation	• Complex structure renders somewhat difficult characterization and evaluation

2.2.2 Literature review of methods to disperse carbon nanotubes

CNTs are commonly used by researchers in various applications ranging from sensors to energy storage devices.⁷⁰ However, one common problem faced by researchers is the extremely poor dispersion of CNTs in aqueous and organic solvents that can limit their use in many practical applications. The structure of MWCNTs involving the strong van der Waals forces between the side walls can cause agglomeration easily, which inhibits their intended functionality in many practical

applications.⁷¹ As a result, various methods have been adopted by researchers to disperse the CNTs effectively in aqueous and organic solvents. These methods can be either physical or chemical (covalent and noncovalent) functionalisation to disperse CNTs effectively (**Scheme 2.3**).

Scheme 2.3 Summary of physical and chemical methods that are used to disperse CNTs.

Physical functionalisation of CNTs

The following subsection shall briefly describe the common methods of the physical functionalisation of CNTs.

Physical functionalisation: Ultrasonication

One common physical method for CNT dispersion is ultrasonication. This method functionalises the surface of bundled MWCNTs by debundling them with high energy density ultrasound waves with a frequency range from 20 to 106 kHz.⁷² One significant advantage of ultrasonication is the decrease of the agglomeration size of CNTs as compared to without ultrasonication.⁷³ Moreover, it has been reported that ultrasonication can result in the disruption of the tubular CNT length and gas cavities to cause a shorter tubular length with more uniform space and separation that can promote surface functionalisation on the MWCNTs.⁷⁴ However, caution needs to be exercised

with high power ultrasonic oscillation due to irreversible damage to the physical and electronic structures of the CNTs.^{75,76} Instead, mild ultrasonication conditions coupled with the use of surfactants have been reported to minimise structural defects to MWCNTs whilst achieving an effective dispersion of the MWCNTs in suitable solvents.⁷⁷

Physical functionalisation: Plasma treatment

Apart from ultrasonication, plasma treatment is also viable to effectively disperse pristine CNTs in water and to a larger extent with acid treated CNTs.⁷⁸ Such physical treatment works by a plasma reactor to induce the surface modification of MWCNTs with plasma of a particular gas.⁷⁹ Three different gases are often used with oxygen for grafting carboxyl, carbonyl and hydroxyl groups, ammonia for nitriles, amines and amide groups, and tetrafluoromethane for fluoride functionalisation.⁸⁰ Moreover, Trulli *et al* reported that oxygen plasma functionalisation under low pressure of 150 mTorr at a power of 40 W was also more effective in dispersing acid-functionalised MWCNTs than pristine MWCNTs as well.⁸¹ With plasma functionalisation, the process is relatively fast, simple to perform and environmentally friendly as compared to other chemical methods.^{79,80}

Physical functionalisation: Irradiation

Irradiation is a useful physical technique to cause structural changes to the CNTs *via* the means of strong radiation sources such as electrons, protons, ions, or gamma (γ)-rays.⁸² It creates defect sites on the sidewalls of CNTs to promote the introduction of functional groups such as carboxyl groups and therefore enhances dispersibility.⁸³ For instance, γ -irradiated MWCNTs were considerably more dispersed in organic solvents

than its non-irradiated state since more defect sites were created and available for functionalisation for the former. Moreover, increasing the radiation dose had created more defect sites on the MWCNTs to enhance the concentration of functional groups attached to the CNTs.⁸⁴ Apart from the aforementioned radiation sources, UV/ozone irradiation is an alternative and can introduce oxygen-containing functional groups onto the CNT surface. Such process is environmentally friendly which can be performed under ambient conditions and with a relatively low operating cost.⁸⁵ Generally, ozone molecules are generated under UV light and dissociated to form atomic oxygen at higher wavelengths. Carboxylation occurs at the defect sites on MWCNTs by reacting with the highly reactive atomic oxygen. In a study by Kim *et al.*, the dispersibility of UV/ozone-pretreated MWCNTs in organic solvents was better than that of the untreated MWCNTs, and the trend increased with longer pretreatment duration up to 120 minutes.⁸⁶

Physical functionalisation: Mechanical Milling

The process is a solid-state powder processing technique that repeatedly welds and fractures powder particles in a high energy ball mill with a dispersant (such as metallic powder or polymers) optionally added to aid in dispersing the CNTs.^{87,88} To date, various forms of mechanical milling have been explored with *ball milling* and *cryogenic milling* more commonly reported in the literature. With ball milling, CNTs of short tubular lengths with better open tips and surface area are formed to promote homogenous dispersion in base fluids.⁸⁹ Time control is also important whereby SWCNTs were ball milled with an optimum duration of 2 hours to preserve the tubular structure and attain the best specific surface area. Beyond the optimum duration, detrimental disruption of the tubular structures can occur.⁹⁰ However, a caveat with ball milling is recrystallisation which can be avoided by performing *cryogenic milling*

instead. The latter uses liquid nitrogen to perform milling at extremely low temperatures and produces structurally much finer grains.⁹¹ Dispersants involving aluminum powder may also be used to synthesize CNT-reinforced aluminum composite powder too.⁹²

Physical functionalisation: Pulsed Streamer Discharge

Pulsed streamer discharge is commonly used in applications of water and gas purification to remove organic pollutants and bacteria decontamination.⁹³ However, it is also a more unheard of physical technique for CNT solubilisation with a non-thermal plasma that generates high speed electrons, strong electric field, free radicals, ultraviolet rays and shock waves in water.⁹⁴ Imasaka *et al.* applied such a technique to suspensions of SWCNTs and MWCNTs in water and reported functionalisation of hydroxy ($-OH$) groups on the surfaces of the CNTs. The mechanism was proposed with the reactive $O^{\bullet}$ radicals forming bonds on the CNT surface followed by the chemical reaction with $H^{\bullet}$ radicals to form $-OH$ groups. Despite the generation of high energy electrons, the CNT structure experienced no apparent disruption.⁹⁵ Moreover, the technique is simple and time efficient to produce CNTs that are water soluble.^{95,96}

Chemical functionalisation of CNTs

Figure 2.6 Summary of the various common routes of chemical functionalisation of CNTs. Adapted with permission from reference 97.

As pristine CNTs have extremely poor dispersibility in aqueous and organic solvents, they are often chemically functionalised prior to its dispersion. Such functionalisation occurs with the functional groups attached either covalently or noncovalently to the CNTs. In general, chemical functionalisation can proceed *via* a few common routes – covalent defect-group functionalisation, covalent sidewall functionalisation, noncovalent exohedral functionalisation (with polymer or surfactants) and endohedral functionalisation (**Figure 2.6**).⁹⁷

Chemical functionalisation: Covalent defect functionalisation

Structural defects are usually present either at the tube ends and on the sidewalls of the SWCNTs.⁹⁸ They are usually referred to as imperfections or irregularities present in the graphitic carbons of the CNT (**Figure 2.7A and B**). For example, acidic oxidation of CNTs under harsh conditions create defects *via* the covalent attachment of carboxyl groups on the surface and open ends of the CNTs (**Figure 2.7C and D**).⁹⁹ Hence, these defects can be potentially chemically converted or covalently linked with other molecules *via* covalent defect functionalisation. The latter can be best illustrated by having the oxidised CNTs derivatised with thionyl chloride and thereafter undergoing amidation upon the reaction with an amine to form the carboxamide CNTs. In certain occasions, the oxidised CNTs can undergo a more direct synthetic route with dicyclohexylcarbodiimide (DCC) as the coupling reagent to yield the carboxamide CNTs.¹⁰⁰

The solubility of covalent defect functionalised CNTs has been reported in the literature. Functionalisation of the SWCNTs containing acyl chloride groups with biomolecules such as glucosamine resulted in the amide bond formation with a reported solubility of 0.1–0.3 mg/mL between 25–100°C.¹⁰¹ Octadecylamido-functionalised

defect sites on SWCNTs have also been synthesized and reported by Hamon and coworkers to be soluble. These functional entities had about 55% weight percentage which are located mainly at the sidewalls.¹⁰²

Figure 2.7 Possible locations of defects present in a SWCNT. Reproduced with permission from reference 97.

Chemical functionalisation: Covalent sidewall functionalisation

Covalent sidewall functionalisation involves the effect of conjugation loss with a hybridisation change from sp^2 to sp^3 as a functional group is covalently attached to the sp^2 carbon atom of the CNT sidewall. For good dispersibility of the pristine SWCNTs, various reactions for the covalent sidewall functionalisation of these CNTs have been studied and reported by researchers in numerous literature reports.¹⁰³ Typically, reactive species such as carbenes, nitrenes and radicals act as precursors and harsh synthetic conditions are usually required due to the chemical inertness of the CNT sidewalls.^{97,103} Perhaps the most common reaction is the covalent attachment of polar carboxylic acid ($-\text{COOH}$) functional groups on the SWCNT sidewalls. Darabi *et al.* performed a simple one-pot two step synthesis of the COOH -functionalised SWCNTs using *p*-aminobenzonitrile as the precursor.¹⁰⁴ In another instance, Long *et al.* functionalised pristine SWCNTs with $-\text{COOH}$ functional groups in over 90% product yield and the

synthetic route being solvent-free, rapid, and scalable up to the fifth repeat reaction to achieve maximum saturation of the functionalised groups.¹⁰⁵

Apart from the covalent attachment of -COOH groups to CNT sidewalls, other polar functional groups can be used too. Dyke and Tour functionalised SWCNTs *via* sidewall grafting on the basis of the aryl diazonium salt chemistry with *para*-substituted aniline derivatives that carry polar functional entities such as hydroxyl, halogens and nitro groups as precursors. Hence, the solubility of the functionalised SWCNTs in *o*-dichlorobenzene and THF was about four to six-fold better than that of its pristine materials.¹⁰⁶ In another instance, Guo *et al.* prepared MWCNTs with spiropyran covalently functionalised on the CNT sidewall and exhibited good dispersibility in water and common organic solvents such as DMF, DMSO, ethyl acetate and chloroform. The behaviour of such decent dispersion lies with the presence of nitrogen and oxygen heteroatoms to result in the general law of '*like dissolves like*'.¹⁰⁷

Chemical functionalisation: Noncovalent exohedral functionalisation

Noncovalent exohedral functionalisation involves the external wrapping on the CNT surfaces with hydrophilic structures such as polymers or surfactants. In short, the nature of such functionalisation typically relates to π - π interactions, van der Waals forces, hydrogen bonding and electrostatic forces between the surface of the CNTs and the hydrophobic or aromatic structure of the hydrophilic molecules to form supramolecular complexes.^{108–110} Thus, CNTs with such functionalisation can retain their electronic character without affecting its carbon hybridisation unlike their counterparts with covalent chemical functionalisation.¹¹¹ The use of a water-soluble polymer such as polyvinylpyrrolidone (PVP) is a classic example to illustrate how polymer wrapping can happen. By studying the interactions involved in the PVP

wrapping of the SWCNT surface, the free energy required to cause polymeric wrapping of the CNT surface was lesser than the energy gained to overcome the hydrophobic forces between SWCNTs and the surrounding water molecules.¹⁰⁸ Specific monomer structure can also dictate the strength of interaction between the CNTs and the polymers, of which conjugated polymers with aromatic backbone have the strongest interfacial interaction with the parallel alignment of the aromatic rings to the CNT surface.¹⁰⁹ If the interfacial strength is not strong enough to promote sufficient stress transfer, a poor efficiency of interfacial load transfer can happen.¹¹⁰ A word of caution is that not all polymers are structurally similar and may behave dissimilarly during the polymer wrapping of the CNT surface with geometric isomerism of the polymers influencing the extent of dispersing CNTs in organic solvents. Yi *et al.* studied the geometric isomers of a polymer derivative of poly[(*m*-phenylenevinylene)-*alt*-(*p*-phenylenevinylene)] (PmPV) with the *cis* isomer twice as better in the effective dispersion of SWCNTs than the *trans* isomer. The mechanism of such enhanced dispersion was believed to be the *cis* isomer interacting planarly in a π - π fashion with the SWCNT surface, while twisting of the dialkoxybenzene ring away from *co*-planarity in the *trans* isomer was thermodynamically less favourable to facilitate the SWCNT complexation.¹¹²

Apart from polymers, surfactants can also perform a similar dispersibility function by minimising aggregation of CNTs and increasing the π -stacking interactions between the aromatic rings of CNT sidewalls and the surfactant molecules. Surfactants are organic compounds that are structurally characteristic with polar hydrophilic head and non-polar hydrophobic tail to reduce surface tension of suspensions and promote the stable dispersion of solids in the media. They are categorised according to the charge of their polar head with cationic, anionic, nonionic, or zwitterionic.^{113,114} With more than one hydrophilic head and one hydrophobic tail, they are termed as *gemini surfactants*

and able to disperse CNTs in aqueous solvents more efficiently than single-tailed surfactants.^{115,116} Apart from the structure and length of the hydrophilic head or the hydrophobic tail of the surfactant, the dispersibility of CNTs in the media is also influenced by other factors such as the free energy of micellisation, critical micelle concentration and surface tension.¹¹⁷ Due to the various classes of surfactants, various mechanisms can account for the dispersion of CNTs by surfactants in aqueous and organic media across the literature. In an experimental study on the dispersion of SWCNTs by a cationic surfactant such as benzyltrimethylammonium chloride (BTAC), Chen *et al.* deduced that phenyl and ammonium groups of BTAC can interact synergistically with the SWCNTs to induce charge transport.¹¹⁸ On the contrary, a molecular dynamics simulation study of surfactant peptides by Barzegar *et al.* revealed that aromaticity is more crucial than hydrophobicity to support the noncovalent functionalisation of SWCNTs for solubility.¹¹⁹

Chemical functionalisation: Endohedral functionalisation

Endohedral functionalisation of CNTs generally involves the confinement of various molecules or nanomaterials in the interior regions of the CNTs. Such modification would result in an alteration of the physical and chemical properties of the enclosed molecules or nanomaterials.¹²⁰ For instance, computational studies on the endohedral functionalisation of SWCNTs with various polar hydroxyl group-containing amino acid sidechains revealed that the relative orientation of the donor-acceptor can largely influence the extent of proton transfer in the CNT interior upon solvation by water molecules. Hydrogen bonding between the hydroxyl group of the amino sidechain and water molecules are stabilised *via* a fast and efficient proton transfer and thereby lower the free energy of reaction during solvation.¹²¹ On the other hand, CNTs can be

endohedrally doped with metals whereby Matsubara *et al.* synthesized a Li-doped endohedral SWCNT with closed ends with well dispersion in water due to the electron-donating property of Li ions to the surface of the SWCNT bundles. Moreover, the closed ends can prevent water molecules from reacting with Li in the tube channels and preserve the electronic structure of the SWCNT.¹²²

2.3 Conducting polymers in electrochemical energy storage

2.3.1 Introduction to polymers and conducting polymers

According to the International Union of Pure and Applied Chemistry (IUPAC), polymers are described as giant macromolecules with very high molecular weights of at least thousands in magnitude order.¹²³ The term “polymer” is derived from the classical Greek “*poly*” and “*meros*” that mean *many* and *parts* respectively.¹²⁴ Polymers are omnipresent in our daily lives and can be classified into two major categories – natural and synthetic. Natural polymers exist naturally in the environment and examples include cellulose which forms the main structural component of plant cells, and deoxyribonucleic acids (DNA) that contain genetic information which a living organism uses it in replication, encoding, mutation-recombination and gene expression. As for synthetic polymers, they are man-made and common examples include polytetrafluoroethylene which are found in non-stick pans and polyvinyl chloride such as raincoats and water pipes. Generally, polymers can be synthesized *via* chemical or electrochemical polymerisation.^{125,126} Other methods to prepare them may include metathesis,¹²⁷ pyrolysis,¹²⁸ plasma polymerisation,¹²⁹ photochemical polymerisation,¹³⁰ and solid state polymerisation.¹³¹

In the family of polymers, a new subclass on conducting polymers (CPs) has emerged over the recent decades with increased attention from various scientific fields.

CPs are organic polymers that possess electrical conductivity due to the delocalization of π electrons (**Scheme 2.4**).¹³² They also have an extensive and large conjugated structure of sp^2 hybridised carbon with charge transfer able to occur intra and inter-molecularly. The conjugation of π electrons in CPs is not only limited to carbon but sometimes with heteroatoms like nitrogen and sulfur too.¹⁴⁵ Moreover, CPs are generally insoluble in aqueous solutions and serve as relatively cheaper alternatives to carbon-based electrode materials too. Apart from these properties, one of the main motivation behind the strong research interest in CPs is due to its very highly tuneable properties that can be used in a broad range of applications such as actuators,¹³³ sensors,¹³⁴ biosensors,¹³⁵ biomimetics,¹³⁶ photocatalysis,¹³⁷ and EES devices that include batteries,¹³⁸ solar cells,¹³⁹ and supercapacitors.¹⁴⁰ That also explains why the foundation of EES devices is based primarily on the use and fabrication of these high pseudocapacitance CPs with polyaniline (PANI) (775 F g⁻¹) and polypyrrole (PPy) (480 F g⁻¹) having very large specific capacitance values and are comparable to that of the more expensive transition metal oxides like MnO₂ (784 F g⁻¹).^{141–143}

Scheme 2.4 Chemical structures of some common conducting polymers.

The preparation of CPs is somewhat similar with any synthesis of polymers mentioned in the previous paragraph, but the more common methods follow the oxidation of the monomer *via* chemical means with the use of suitable oxidising agents, or electrochemical means by using electrodes to cause anodic oxidation or cathodic reduction of the electroactive functional monomers.^{144,145} However, electrochemical polymerisation has the edge on chemical polymerisation as the former can be performed

at ambient temperatures with the flexibility to control the film thickness of the CP on the electrode surfaces *via* manipulation of the electrochemical conditions.¹⁴⁶

Figure 2.8 Conductivities of insulators, semiconductors, and metals. Increasing doping levels enhances the conductivity of the material. Reproduced with permission from reference 149.

To enhance the conductivity of CPs, doping is performed with the addition of impurities (dopants) acting as donors or acceptors into the intrinsic polymer structure and results in either the addition or removal of charges from the conduction or valence band with a smaller energy band gap. If a CP is not doped, it is referred as a semiconductor or an insulator.¹⁴⁷ Typically, the counter ions of the synthesized CP can act as dopants whereby the electrical conductivity of polyacetylene was greatly enhanced upon doping with halogens such as chlorine, bromine or iodine.¹⁴⁸ Doping of PANI with a protonic acid increased the CP conductivity by several orders of magnitude as compared to its *undoped* form (**Figure 2.8**).¹⁴⁹ Moreover, doping can lead to an electron or hole conductivity which are negatively (n-type) and positively (p-type) charged respectively.^{150,151} A more widely used doping technique by researchers is redox doping *via* the partial redox reactions of the π backbone of the CP: oxidation (p-doping) or reduction (n-doping). The p-dopants such as HCl, H₂SO₄ and I₂ behave as electron acceptor species, while n-dopants such as Na, K and Li behave as electron

donor species.¹⁵² Such doping allows the freedom of altering the mechanical, electrical and electrochemical properties of CPs which include morphology and conductivity.¹⁴⁷ Other doping techniques such as charge injection doping¹⁵³ and photo-doping¹⁵⁴ have been explored on CPs to a less common extent. Moreover, a variety of dopants can be used in the synthesis of CPs such as metal nanoparticles,¹⁵⁵ graphene oxide,¹⁵⁶ CNTs,¹⁵⁷ chalcogenides,¹⁵⁸ or even other polymers.¹⁵⁹ Other advantages of doping include the flexibility to control the doping extent and its reversible nature to allow the original polymer to be regenerated *via* de-doping with minimal to no degradation of the polymer backbone.^{148,149}

2.3.1.1 Background of aniline

Scheme 2.5 Chemical structure of aniline.

Aniline (**Scheme 2.5**) is an organic compound with an amine functional group bound directly to an aromatic phenyl ring. It appears as a colourless oil at room temperature with melting and boiling points of -6 and 184 °C respectively. Back in the 18th century, it was an important and commonly manufactured dye and was thought to be first synthesized in the year 1740 by two French chemists and dye experts Jean Hellot and Lepileur d'Apligny when the leaf of an indigo plant gave a blue dye. The name of aniline was given in 1840 when a German chemist Carl Julius Fritzsche named the product of the acid-base distillation of anthranilic acid as *anilin* which was derived from the Portuguese term *anil* (English: indigo).¹⁶⁰ Today, aniline can be mass manufactured *via* the reduction of nitrobenzene in the presence of a metal catalyst, or the catalytic

amination of phenol with ammonia.¹⁶¹ It is often found in the manufacture of shoe polish, varnish and perfume and also used as an intermediate in dyestuff production.¹⁶²

2.3.1.2 Background of polyaniline

Scheme 2.6 Chemical structure of polyaniline.

Polyaniline (PANI) (**Scheme 2.6**) exhibits numerous characteristics which are of particular interest in the research field. It can be prepared *via* the chemical or electrochemical polymerisation of aniline. Doping with a strong acid such as hydrochloric acid can improve the conductivity of PANI greatly. Various factors such as the strength and concentration of oxidant used, dispersion of the polymer and the extent of polymerisation can result in the conductivity of PANI ranging from as low as 10^{-8} to more than 10^7 S cm^{-1} .^{163,164} Owing to its advantages of low cost, simple synthetic route, stability and tunable electrical properties, PANI is utilised broadly in various applications such as batteries, supercapacitors, sensors and electrochromic devices.^{165–167} It has a general formula and depending on the extent of oxidation, three values of y exist with 0, 0.5 and 1 indicating the states of pernigraniline, emeraldine and leucoemeraldine respectively. When the y -values are full integers, the electrically nonconductive pernigraniline ($y = 0$) and leucoemeraldine ($y = 1$) exist in complete oxidised and reduced forms of aniline respectively. The conducting form of PANI exists in the half oxidised form of emeraldine base when doping of the emeraldine base occurs with a strong protonic acid or suitable anions such as chloride ions.^{168,169} Hence, the doped and protonated states of pernigranilines and emeraldines in strong acids can render themselves as good conductors. In addition, oxidative polymerisation of aniline

is highly dependent on the pH of the reaction medium with PANI best preferred to be prepared in highly acidic ($\text{pH} < 2.5$) conditions to facilitate the release of acidic protons from the amine groups of aniline molecules. This can result in the formation of the protonated states of pernigraniline to participate in chain propagation and form the polymeric PANI chain. The conductivity of PANI is also best achieved with at least $10^{-3} \text{ S cm}^{-1}$ in such similar acidic conditions as well. If polymerisation is performed in a mildly acidic solution ($2.5 < \text{pH} < 7$), short oligomeric chains will be formed instead of a polymeric PANI chain. In neutral and alkaline solution whose pH is greater than the pK_a of aniline (4.6), aniline exists as neutral molecules which are oxidised to form a longer and nonconducting oligomeric chain.^{170,171} Moreover, oligomeric chains may contain aniline units that are coupled in *ortho*- and *para*-positions as compared to the absolute *para*-position coupling with PANI synthesized in strongly acidic solutions.^{170,172}

Chemical polymerisation of aniline

Scheme 2.7 Chemical oxidative polymerisation of aniline with ammonium persulfate.

Chemical polymerisation of aniline can be achieved by mixing acidic aniline in cold bath with the dropwise addition of aqueous ammonium persulfate acting as the reaction initiator to form a green protonated PANI emeraldine (**Scheme 2.7**). The cold bath is essential due to the highly exothermic nature of the polymerisation reaction.¹⁷³ The reaction mechanism of this process is thought to undergo three cyclical steps in repeat – protonation of aniline, formation of singlet ground state phenylnitrenium cation and electrophilic substitution.¹⁷⁴ During the chemical polymerisation, persulfate anions

undergo a two-electron reduction to form sulfate anions. Polymerisation is completed when the reaction mixture has cooled down sufficiently with almost no temperature change. The emeraldine states present in the reaction mixture are then neutralised with a suitable base such as ammonium hydroxide, followed by filtration and purification methods to yield a white powder of leucoemeraldine base PANI.^{164,168}

Electrochemical polymerisation of aniline

Electrochemical polymerisation of aniline was first reported in 1862 whereby aniline was electrochemically oxidised on a Pt working electrode immersed in dilute sulfuric acid.¹⁷⁵ Today, electrochemical techniques such as CV, galvanostatic and potentiostatic methods have been employed to polymerise aniline electrochemically. A distinct difference between chemical and electrochemical polymerisation is that the former does not use any oxidants. If CV is used, a slow scan rate ($10\text{--}50\text{ mV s}^{-1}$) is usually used in an applied potential window with the potential cycling of the working electrode carried out in a three-electrode setup. As for the galvanostatic and potentiostatic techniques, the former is performed under constant current as a function of potential while the latter is performed under constant potential as a function of current. Electrochemical polymerisation of aniline involves the electrodeposition of the polymeric film on the electrode surface in an autocatalysed process,¹⁷⁶ and can be performed on various substrates such as glassy carbon,¹⁷⁷ graphene,¹⁷⁸ platinum,¹⁷⁹ gold,¹⁸⁰ and indium tin oxide (ITO).¹⁸¹

The mechanism of electrochemical polymerisation of aniline in an acidic medium ($\text{pH} < 2.5$) follows the three main stages: initiation, propagation, and termination. In the initiation stage, the neutral aniline is oxidised to form its nitrenium cation radical. With resonance, the nitrenium cation radical can undergo head-to-tail C–N coupling with

another cation radical and subsequent deprotonation and rearomatisation resulting in the dimer formation. In the propagation stage, this dimer undergoes a single-electron oxidation followed by a head-to-tail C–N coupling with the aniline cation radical (Scheme 2.8).^{182,183} Dopants act as counterions in the reaction medium to maintain electroneutrality of the system. It must be noted that the mechanism can vary due to reaction conditions such as electrolyte composition,¹⁸⁴ pH of the electrolyte,¹⁸⁵ nature of dopant anions,¹⁸⁶ electrode material,¹⁸⁷ and switching potential.¹⁸⁸

Anodic oxidation of aniline in acidic medium

Radical-radical coupling

Chain propagation of PANI

Scheme 2.8 Electrochemical polymerisation of aniline in a strongly acidic aqueous medium.

To prepare conductive PANI on electrode surfaces, electrochemical polymerisation of aniline generally occurs in strongly acidic aqueous electrolytes similar with that of chemical polymerisation.¹⁶⁸ The emeraldine form of PANI doped with a protonic acid exhibits an improvement of electrical conductivity up to 10 orders

of magnitude when compared to its corresponding base form.^{164,168} Hence, the manipulation of the redox chemistry of PANI can alter the electronic properties of the electrochemically polymerised film (**Scheme 2.9**).¹⁷³ For example, the treatment of the conductive green protonated emeraldine with a base such as ammonium hydroxide will form a nonconductive blue emeraldine base. Likewise, reduction of the nonconductive violet pernigraniline base in a highly acidic medium can form a highly conductive blue protonated pernigraniline. These flexible and reversible redox conversions in PANI with characteristic colour changes have thus given PANI being used in diverse applications ranging from pH sensors to electrochromic devices and batteries.^{165–167}

Scheme 2.9 Various redox forms of PANI during the electrochemical polymerisation of aniline.

2.3.1.3 Background of melamine

Scheme 2.10. Chemical structure of melamine.

1,3,5-triazine-2,4,6-triamine, also known as melamine (**Scheme 2.10**), is a type of triazine that is omnipresent in our daily lives. The triazine analogue contains three amino groups and its pK_a value is reported as 8.0.¹⁸⁹ Due to its relatively high nitrogen level (67%) by mass, it was been introduced into cattle feed as a dietary non-protein nitrogen (NPN) source in 1958 but was prohibited in 1978 owing to its poor hydrolysis in ruminants. Although it is not carcinogenic, it can react with uric acid in the body to form kidney stones that can lead to acute renal failure and even death.¹⁹⁰ It was also the subject of intentional food adulteration in pet food with thousands of deaths of cats and dogs in the USA during 2007.¹⁹¹ Intentional food adulteration in infant formula during 2008 in China was probably the most prominent scandal of melamine that caused at least 50,000 infants and children hospitalised and 6 children dead.¹⁹²

Melamine can be commercially derived from urea and acts as a raw material in the production of melamine-formaldehyde resins for the manufacture of a wide range of household products such as plastics, commercial filters, adhesives, dishware and kitchenware.¹⁹³ Moreover, its fire-resistant capability has been exploited in the applications of fire resistive coatings.¹⁹⁴ Its capability in organic-aqueous phase separations such as oil and water allow melamine to be used widely as sponges.¹⁹⁵ In the applications of electrochemical energy storage (EES), these melamine sponges can be carbonised with useful applications such as supercapacitors and fuel cells with the corresponding benefits of having low costs and being environmentally friendly.^{196,197}

2.3.1.4 Background of polymelamine

Scheme 2.11 Chemical structure of polymelamine (PMEL).

Although melamine is chemically inert and electrochemically inactive, it can be electrochemically polymerised to produce the electroactive polymelamine (PMEL, **Scheme 2.11**) as the commonly used synthetic route. PMEL is a CP with the electrochemical polymerisation of melamine occurring in aqueous HCl with chloride anions as the main source of dopant.^{198,199} The mechanism is thought to proceed *via* the oxidation of the amino groups in the melamine structure at a sufficiently high potential above 1.3 V to form a radical cation. Subsequently, these generated radical cations are thought to undergo head-to-head coupling at the HN–NH bonds.^{198–200} It is also worthwhile noting that the extent of electrochemical polymerisation of melamine occurs very weakly to almost none on bare GC electrodes due to the absence of oxygen containing surface species,¹⁹⁸ and that the coupling can only proceed *via* head-to-head owing to the structure of melamine (**Scheme 2.12**).¹⁹⁸ Besides the use of acidic medium for electrochemical polymerisation, neutral and basic solutions are possible but less favoured in basic solutions due to the disproportionation of Cl_2 in strongly alkaline solutions.¹⁹⁹

Scheme 2.12 Proposed mechanism for the electrochemical polymerisation of melamine.

Reproduced with permission and modified from reference 198.

Owing to the high nitrogen content and amino functional groups present in PMEL, it had been utilised and reported in various applications such as electrochemical sensing. An electrochemical sensor was reported with the electrochemical deposition of PMEL onto the glassy carbon surface to successfully detect guanine, adenine and epinephrine in the presence of interferents.²⁰⁰ Apart from sensing, PMEL can be used as a potential material for CO₂ capture and separation in the form of a microporous PMEL network owing to the hydrogen bonding between the CO₂ molecules and the vacant nitrogen sites of melamine.²⁰¹

2.3.2 Introduction to electrochemical energy storage

Since the start of the Industrial Revolution in the United States and Europe in the late 18th century, energy became a very valuable and essential commodity in powering the mechanization of industries and the global economy.²⁰² One such example was the widespread activities of coal mining which were essential to power steam engines found in steamboats, locomotives and industries such as steel and textiles.²⁰³ The thermal efficiencies of these steam engines grew substantially from about 0.5% in the early 1700s to 25% in the late 1880s.²⁰⁴ The rapid economic growth in the world has led to an ever-increasing demand for energy. In the present day, electrical energy is primarily obtained from the burning of fossil fuels such as oil, coal and natural gas to power homes and industries around the world. However, numerous problems and challenges arise such as the potential rising costs in oil and gas, increasing pressure of a global population boom to deal with a finite supply of such non-renewable sources. Pollution problems associated with the burning of fossil fuels have caused a sharp increase in greenhouse gas concentration that accelerated global warming and imposed detrimental consequences to the climate and ecosystems.²⁰⁵ Consequentially, there is utmost

importance of using alternative energy sources that are sustainable, pollution free, easy to reproduce and economically affordable to generate electricity and drive the green economy whilst meeting the global energy demand of an ever-increasing world population. Countries around the world have relied on science and technology with the means of cooperating regionally and globally to explore and leverage on renewable energy sources.²⁰⁶ **Figure 2.9** shows that the estimated renewable energy share of global final energy consumption in 2017 was about 19%, which could be further increased and aimed to decrease the heavy reliance on fossil fuels as the main energy source.²⁰⁸ In order to drive the green economy, the use of nanotechnology by scientists from various disciplines to develop into infinite possibility of energy storage applications is part of this green economy.²⁰⁷ Another alternative solution to efficient energy storage is the use of supercapacitors which are electrochemical energy storage (EES) devices. They store very large quantities of energy with high power, virtually high cyclability and are environmentally friendly. Consequentially, research has been ongoing with efforts to develop and optimise the benefits of supercapacitors to cope with the ever-increasing world energy demand *via* a more efficient and cleaner alternative to sustainable energy.

Figure 2.9 Estimated renewable share of global final energy consumption in 2017. Reproduced with permission from reference 208.

2.3.2.1 Background of capacitors and supercapacitors

A capacitor is a form of electronic device that stores electric charge. It operates with very high efficiency and offers a virtually high cycling number.²⁰⁹ It was first developed by a German physicist Ewald Georg von Kleist in 1745 and subsequently was independently invented by a Dutch physicist Pieter van Musschenbroek known as a Leyden jar. The Leyden jar is a setup of a glass jar concealed by conducting tin foil, filled partially with water and a metal wire passing through the jar stopper to result in charge accumulation.²¹⁰ The concept of capacitance was improved when Benjamin Franklin proved the storage of electric charges was on the facing glass surfaces and not the liquid that coined the emergence of the electrostatic capacitor.²¹¹ A simple capacitor that we know today is made up of two flat and conducting plates which are separated in parallel by a dielectric insulator such as glass, ceramic, vacuum or non-ionised air. When a potential difference is applied to the capacitor, an electric field sets up but with zero current across the dielectric to result in a flow of charge around the circuit (**Figure 2.10**).²⁰⁹ If Q is the charge on the plate, ΔV is the potential difference between both plates, ϵ_0 is the absolute permittivity of the dielectric, A is the surface area of the plate and d is the distance between the two plates separated by the dielectric, the capacitance, C , of the parallel plate capacitor can be expressed as **equation 2.4**:

$$C = \frac{Q}{\Delta V} = \frac{\epsilon_0 A}{d} \quad (2.4)$$

Figure 2.10 Schematic diagram of a parallel plate capacitor connected to an external voltage source.

However, there is a major difference between a capacitor and a supercapacitor. A supercapacitor does not require a dielectric material since the electrodes are kept apart with a separator and immersed in the electrolyte solution. With a demand and use of energy much larger than an average individual, supercapacitors are also commonly used as electrochemical energy storage devices with their power and energy delivered much more than conventional portable electronic chargers. They can also be used extensively in applications such as electric automobiles,²¹² military warfare,²¹³ wireless sensors,²¹⁴ and medical care and diagnosis,²¹⁵ thus showing how useful they are as a promising solution to meet the increasing world energy demands.

The Ragone plot in **Figure 2.11** illustrates the energy storage performances of four key classes of devices – capacitors, supercapacitors, batteries and fuel cells. Ideally, energy storage should carry high specific power and specific energy and research has been ongoing and focusing on achieving the top right region of the Ragone plot.²¹⁶ Energy storage devices such as batteries and fuel cells have high specific energy but suffer from low specific power. On the contrary, capacitors and supercapacitors have much superior specific power than these aforementioned devices with supercapacitors capable of delivering a large amount of energy in a short timescale. Moreover, supercapacitors can undergo cycles in orders of magnitude up to a thousand more than conventional batteries due to the electrochemical reactions that underline the degradation of the batteries. **Tables 2.2** and **2.3** summarise the key advantages and disadvantages of supercapacitors in energy storage and compare the key performance characteristics of the three major energy storage devices.²¹⁷ Clearly, one can agree that supercapacitors excel better than batteries across all these key characteristics.

Figure 2.11 Ragone plot of various energy conversion and storage systems. Reproduced with permission from reference 218.

Table 2.2 Advantages and disadvantages of supercapacitors in energy storage.

Advantages	Disadvantages
<ul style="list-style-type: none"> • High power density compared with conventional batteries and fuel cells • Virtually unlimited cycles of charging and discharging • Wide operating temperature range • Ease of use and operation • Long shelf life • Environmentally friendly • Safe to operate 	<ul style="list-style-type: none"> • Low working voltage • Low specific energy due to lack of Faradaic processes • High self-discharge with significant impurities present • Can be costly if materials such as metal oxides are used

Table 2.3 Comparison between the key performances of battery, supercapacitor and electrolytic capacitor. Reproduced with permission from reference 217.

Performance characteristic	Battery	Supercapacitor	Capacitor
Charging time	1 ~ 5 h	1 ~ 30 s	$10^{-3} \sim 10^{-6}$ s
Discharging time	> 0.3 h	1 ~ 30 s	$10^{-3} \sim 10^{-6}$ s
Life time (cycle number)	10^3	10^6	10^6
Power density / W kg^{-1}	< 1000	10^5	> 10^6
Energy density / W h kg^{-1}	10 ~ 100	1 ~ 10	< 0.1
Charge/discharge efficiency	0.70 ~ 0.85	0.85 ~ 0.98	> 0.95

For a two-electrode cell, the capacitance, C , of a supercapacitor is defined by **equation 2.5** where Q and V are the coulombic charge and applied voltage respectively. It is usually expressed in Farads (F) with the device typically having electrodes with large surface areas (**equation 2.6**):

$$C = \frac{Q}{V} \quad (2.5)$$

$$C = \epsilon_0 \epsilon_r \frac{Q}{V} \quad (2.6)$$

where ϵ_0 and ϵ_r are the dielectric constants of free space, and the insulating material between both electrodes respectively. Assuming a negligible internal resistance and voltage drop, the energy, E , stored in a supercapacitor is given by **equation 2.7**. Thus, high capacitance of the energy storage device and high cell voltage are essential in order to attain high energy storage in the supercapacitor.

$$E = \frac{1}{2} CV^2 \quad (2.7)$$

2.3.2.2 Types of supercapacitors

Supercapacitors can be broadly classified into three different categories – electric double layer capacitors (EDLC), pseudocapacitors and hybrid capacitors. In this section, each class of capacitor shall be introduced briefly.

I. Electric double layer capacitor (EDLC)

Electric double layer capacitors (EDLCs) have their electrode material electrically conductive, high chemical stability across the pH range and electrochemically inactive such as carbon (for instance carbon aerogels, activated carbon, carbon nanotubes).^{219,220} Supercapacitors have much larger capacitance but smaller voltage limit than conventional capacitors. In addition, they store more energy than solid state electrolytic

capacitors and this energy is stored within the electric double layer at the electrode-electrolyte interface.²²¹

Figure 2.12 Schematic representation of an EDLC (a) during charging, (b) with charging complete, and (c) during discharging.

In an EDLC, two identical electrodes of large specific surface area are separated by a porous membrane to provide high specific power *via electrostatic* charge storage. The principle of such an EDLC works with the movement of cations and anions in the electrolyte across the separator during the process of charging or discharging.^{219–221} Charge transfer does not occur between the electrode and the electrolyte. During charging, a potential difference is applied across both electrodes to result in the migration of cations and anions towards the negative and positive electrodes respectively (**Figure 2.12(a)**). Subsequently, an electric double layer (also known as the Helmholtz layer) is formed at the electrode-electrolyte interface upon charge accumulation (**Figure 2.12(b)**). Upon discharging, the absence of the electric field causes ions of opposite charges in the electrolyte to migrate in the opposite direction and attract each other instead (**Figure 2.12(c)**).²²²

II. Pseudocapacitors

Unlike EDLCs, pseudocapacitors store electrical energy *via electrochemical* charge storage. Thus, the term pseudocapacitance can be simply referred as the

electrochemical processes that occurs at the electrode-electrolyte interface with faradaic charge transfer.²²³ When a potential is applied to a pseudocapacitor, surface redox reactions happen at the electrode-electrolyte interface which are fast, reversible and Faradaic in nature.²²⁴ However, such reactions result in poor stability of these devices upon cycling and have lower power density than supercapacitors. Nevertheless, pseudocapacitors offer great capacitance and energy density. To promote surface redox reactions, the electrodes of pseudocapacitors are usually made of transition metal compounds, particularly oxides such as NiO,²²⁵ RuO₂,²²⁶ MnO₂,²²⁷ Mn₃O₄,²²⁸ V₂O₅,²²⁹ and WO₃,²³⁰ or even carbides,²³¹ hydroxides,²³² nitrides,²³³ and dichalcogenides.²³⁴ Apart from transition metal compounds, CP films such as polypyrrole (PPy),²³⁵ polyaniline (PANI),²³⁶ and poly(3,4-ethylenedioxythiophene) (PEDOT) have been explored as viable electrode materials.²³⁷

Three types of Faradaic processes can occur at the electrodes – reversible adsorption (such as adsorption of hydrogen ions on Pt electrode surface), redox reactions of transition metal compounds, and reversible electrochemical doping/de-doping process with conductive polymer-based electrodes. Transition metal compounds that are used as redox active electrode materials are reduced with the electrolyte cations inserted near the electrode surface (**Figure 2.13**).²³⁸ The discharging process proceeds with a reversal of the aforementioned reaction.²³⁹ For CP-based electrodes, electrochemical doping/de-doping occurs reversibly with CPs storing and releasing charge through redox processes. For instance, electrolyte anions act as dopants to the polymeric chain of the CP with the loss of electrons as an oxidation reaction during the *charging* process. Upon *discharging*, de-doping occurs with these dopants gaining electrons (reduction).^{235–237} What makes pseudocapacitors more attractive than EDLCs is due to their higher capacitance and energy density. However, they can be costly if metal oxide

electrodes are used and can suffer from limited life cycle and lower power density than supercapacitors.

Figure 2.13 Schematic diagram of pseudocapacitor with transition metal compounds as the basis of the electrode materials. M represents the metal atom with the arrows denoting the direction of movement in the electrolyte.

III. Hybrid supercapacitors

Hybrid supercapacitors combine properties from both EDLC and pseudocapacitors whereby its charge storage mechanism can be both *electrostatically* and *electrochemically*. In simple terms, the hybrid supercapacitor can be described as its one-half behaving as an EDLC while the other as a pseudocapacitor.²⁴⁰ Hence the assembly possesses an elevated capacitance with higher energy density and power density than its individual one-half components whilst mitigating their disadvantages and thereby making hybrid assemblies attractive as excellent energy storage devices. A well-known example of a hybrid supercapacitor is the lithium-ion supercapacitor that bridges the gap between high power EDLCs and high energy lithium-ion batteries (LIBs). The lithium-ion supercapacitor operates on the basis of the Li^+ ion intercalation/deintercalation into the cathode with the anions undergoing

adsorption/desorption from the anode surface concurrently (**Figure 2.14**).^{241,242} Moreover, different materials can be employed in the electrodes of either one-half with activated carbon for EDLCs and oxides of transition metals and organic polymers for pseudocapacitors as discussed in the previous subsections.²⁴⁰

Figure 2.14 Schematic diagram of a lithium-ion supercapacitor with the arrows denoting the direction of movement of the lithium ions in the electrolyte.

Generally, three types of electrodes can be used in hybrid supercapacitors, namely the rechargeable battery type, asymmetric and composite.^{240,243,244} These electrodes are classed to highlight the more dominant electrode behaviour in a hybrid supercapacitor. The first type is an assembly of the rechargeable battery type material electrode and the supercapacitor electrode with the capacitor able to withhold the battery's strong power transients and lower the battery discharge current, thereby minimizing the effect of battery degradation.²⁴⁵ For asymmetric hybrid supercapacitors, they are assembled by combining dissimilar electrode materials to facilitate redox reactions with two subclasses in existence: capacitor/capacitor and capacitor/battery. In the case of an asymmetric capacitor/capacitor hybrid, it is assembled as an EDLC electrode behaving as a negative electrode with a pseudocapacitive material (such as CPs) acting as a positive electrode and thus two different charge storage mechanisms can happen *electrostatically* and *electrochemically*. However, there is insufficient work to tackle the complexity of combining an EDLC that uses an inert electrolyte with the other one-half

capacitor component utilizing electrolytes with redox active species such as metal oxides and polymers that are deposited on the electrode surface.^{240,243}

For composite hybrids, the composite assembly is a combination of carbon-based materials such as graphene or CNTs with either electrically CPs or transition metal oxides incorporated in a single electrode.^{240,244} The carbon-based materials offer capacitive charge storage with deposited pseudocapacitive materials that enhance the capacitance of the composite electrode *via* Faradaic reactions. For instance, a composite electrode material with the CP poly(*o*-aminophenol) (POAP) and Sm₂O₃ nanoparticles were used to fabricate the hybrid films of POAP/Sm₂O₃ *via* electrochemical deposition. Its high specific capacitance of 238 F g⁻¹ was attributed to the synergy between the POAP and Sm₂O₃ nanoparticles with the structure of the conjugated polymer promoting charge transfer along the polymer chain.²⁴⁶

2.4 References

1. Vonau, W. pH Electrodes - Industrial, Medical, and Other Applications. In *Encyclopedia of Applied Electrochemistry*; Kreysa, G.; Ota, K.-I., Savinell, R. F.; Springer: New York, 2014; pp 1521–1529.
2. Trivedi, U. B.; Lakshminarayana, D.; Kothari, I. L.; Patel, N. G.; Kapse, H. N.; Makhija, K. K.; Patel, P. B.; Panchal, C. J. Potentiometric biosensor for urea determination in milk. *Sens. Actuators, B* **2009**, *140* (1), 260–266.
3. Novell, M.; Parrilla, M.; Crespo, G. A.; Rius, F. X.; Andrade, F. J. Paper-based ion-selective potentiometric sensors. *Anal. Chem.* **2012**, *84* (11), 4695–4702.
4. Cheng, Q.; Brajter-Toth, A. Permselectivity, sensitivity, and amperometric pH sensing at thioctic acid monolayer microelectrode. *Anal. Chem.* **1996**, *68* (23), 4180–4185.
5. Stred'anskýa, M.; Pizzariello, A.; Stred'anská, S.; Miertuš, S. Amperometric pH-sensing biosensors for urea, penicillin, and oxaloacetate. *Anal. Chim. Acta.* **2000**, *415*, 151–157.
6. Banhidi, M. pH and ORP. *Met. Finish.* **1995**, *93* (1), 544–550.

-
7. Jang, J.; Moon, S.-J.; Hong, S.-H.; Kim, I.-H. Colorimetric pH measurement of animal cell culture media. *Biotech. Lett.* **2010**, *32* (11), 1599–1607.
 8. Cremer, M. Origin of electromotor properties of tissues, and instructional contribution for polyphasic electrolyte chains. *Z. Biol.* **1906**, *47*, 562–608.
 9. Dole, M. The early history of the development of the glass electrode for pH measurements. *J. Chem. Educ.* **1980**, *57* (2), 134.
 10. Haber, F.; Klemensiewicz, Z. About electrical phase boundary forces. *Z. Phys. Chem.* **1909**, *67*, 385–431.
 11. Marczevska, B.; Marczewski, K. First glass electrode and its creators F. Haber and Z. Klemensiewicz – On 100th anniversary. *Z. Phys. Chem.* **2010**, *224* (5), 795–799.
 12. Stock, J. T. Einar Büllmann (1873-1946): pH determination made easy. *J. Chem. Educ.* **1989**, *66*, 910–912.
 13. Sørensen, S. P. L. Enzyme studies II: On the measurement and importance of hydrogen ion concentration in enzymatic processes. *Biochem. Z.* **1909**, *21*, 131–304.
 14. Sørensen, S. P. L. Enzyme studies II: Communication: On the measurement and importance of hydrogen ion concentration in enzymatic processes. *Biochem. Z.* **1909**, *22*, 352–356.
 15. Jensen, W. B. The Symbol for pH. *J. Chem. Educ.* **2004**, *81*, 21.
 16. Nørby, J. G. The origin and the meaning of the little p in pH. *Trends Biochem. Sci.* **2000**, *25* (1), 36–37.
 17. Clark, W. M. *The Determination of Hydrogen Ions*, 2nd Ed.; Williams and Wilkins: Baltimore, MD, 1922; pp 34–47.
 18. Debye, P.; Hückel, E. The theory of electrolytes. I. Lowering of freezing point and related phenomena. *Phys. Z.* **1923**, *24*, 185–206.
 19. McCarty, C. G.; Vitz, E. pH paradoxes: Demonstrating that it is not true that $\text{pH} \equiv -\log[\text{H}^+]$. *J. Chem. Educ.* **2006**, *83* (5), 752–757.
 20. International Union of Pure and Applied Chemistry Gold Book – pH. <https://goldbook.iupac.org/P04524.html> (accessed Feb 06, 2016).
 21. Kielland, J. Individual activity coefficients of ions in aqueous solutions. *J. Am. Chem. Soc.* **1937**, *59* (9), 1675–1678.

-
22. Webster, J. G.; Eren, H. *Measurement, Instrumentation, and Sensors Handbook: Spatial, Mechanical, Thermal, and Radiation Measurement, 2nd Ed.*; CRC Press, New York, **2014**.
 23. Kakiuchi, T. Salt bridge in electroanalytical chemistry: Past, present, and future. *J. Solid State Electrochem.* **2011**, *15*, 1661–1671.
 24. Buck, R. P.; Rondinini, S.; Covington, A. K.; Baucke, F. G. K.; Brett, C. M. A.; Camoes, M. F.; Milton, M. J. T.; Mussini, T.; Naumann, R.; Pratt, K. W.; Spitzer, P.; Wilson, G. S. Measurement of pH. Definition, standards, and procedures (IUPAC recommendations 2002). *Pure Appl. Chem.* **2002**, *74* (11), 2169–2200.
 25. Kristensen, H. B.; Salomon, A.; Kokholm, G. International pH scales and certification of pH. *Anal. Chem.* **1991**, *63*, 885A–891A.
 26. Covington, A. K.; Bates, R. G.; Durst, R. A. Definition of pH scales, standard reference values, measurement of pH and related terminology (recommendations 1984). *Pure Appl. Chem.* **1985**, *57* (3), 531–542.
 27. Zhou, D. D. Microelectrodes for *in-vivo* determination of pH. In *Electrochemical Sensors, Biosensors and their Biomedical Applications*; Zhang, X.; Ju, H.; Wang, J.; Eds.; Academic Press: New York, 2008; pp 261–305.
 28. Streeter, I.; Leventis, H. C.; Wildgoose, G. G.; Pandurangappa, M.; Lawrence, N. S.; Jiang, L.; Jones, T. G. J.; Compton, R. G. A sensitive reagentless pH probe with a *ca.* 120 mV/pH unit response. *J. Solid State Electrochem.* **2004**, *8*, 718–721.
 29. Bănică, F.-G. *Chemical Sensors and Biosensors: Fundamentals and Applications*, 1st Ed.; John Wiley & Sons: United Kingdom, 2012; pp 1–20.
 30. Compton, R. G.; Banks, C. E. *Understanding Voltammetry*, 2nd Ed.; Imperial College Press: London, 2011.
 31. Williams, R. R. Synthetic vitamins and human nutrition. *Ind. Eng. Chem.* **1947**, *39* (4), 464–466.
 32. Wright, L. D. Significance of the vitamins in human nutrition. *J. Agric. Food Chem.* **1954**, *2* (13), 672–678.
 33. Ball, G. F. M. *Vitamins: Their Role in the Human Body*, 1st Ed.; Blackwell Pub.: Oxford, U.K., 2004.
 34. Russell, R. M.; Rasmussen, H.; Lichtenstein, A. H. Modified food guide pyramid for people over seventy years of age. *J. Nutr.* **1999**, *129* (3), 751–753.

-
35. Tauber, H. Vitamins as coenzymes. *J. Chem. Educ.* **1939**, *16* (1), 10–15.
 36. Addinall, C. R. The vitamins. *J. Chem. Educ.* **1942**, *19* (5), 203–214.
 37. Frankenburg, F. R. *Vitamin Discovery and Disasters: History, Science, and Controversies*, Praeger, Santa Barbara, California, 2009, pp 15–32.
 38. Combs, G. F., Jr.; McClung, J. P. *The Vitamins: Fundamental Aspects in Nutrition and Health*, 5th Ed.; Elsevier Academic Press, New York, 2017, pp 7–31.
 39. Griminger, P. Casimir Funk: A biographical sketch (1884–1967). *J. Nutr.* **1972**, *102*, 1105–1113.
 40. Funk, C. The etiology of the deficiency diseases. *J. State Med.* **1912**, *20*, 341–368.
 41. Drummond, J. C. The nomenclature of the so-called accessory food factors (vitamins). *Biochem. J.* **1920**, *14*, 660.
 42. Pettys, B. J.; Frank, E. L. Rapid determination of vitamin B₂ (riboflavin) in plasma by HPLC. *Clin. Chim. Acta* **2011**, *412*, 38–43.
 43. Jamison, J. R. *Clinical Guide to Nutrition & Dietary Supplements in Disease Management*; Churchill Livingstone: London, United Kingdom, 2003; pp 689–691.
 44. Belitz, H.-D.; Grosch, W.; Schieberle, P. *Food Chemistry*, 4th Ed.; Berlin: Springer, 2009, pp 403–420.
 45. Foraker, A. B.; Khantwal, C. M.; Swaan, P. W. Current perspectives on the cellular uptake and trafficking of riboflavin. *Adv. Drug Delivery Rev.* **2003**, *55* (11), 1467–1483.
 46. Massey, V. The chemical and biological versatility of Riboflavin. *Biochem. Soc. Trans.* **2000**, *28*, 283–296.
 47. Niemz, A.; Imbriglio, J.; Rotello, V. M. Model systems for flavoenzyme activity: One-and two-electron reduction of flavins in aprotic hydrophobic environments. *J. Am. Chem. Soc.* **1997**, *119*, 887–892.
 48. Walsh, C. Flavin coenzymes: At the crossroads of biological redox chemistry. *Acc. Chem. Res.* **1980**, *13*, 148–155.
 49. Vitamin B2. *Reference Module in Food Science* [Online]; Elsevier, B. V., Posted 2016. <https://www.sciencedirect.com/science/article/pii/B9780081005965010726> (accessed Oct 21, 2019).
 50. Powers, H. J. Riboflavin (vitamin B-2) and health. *Am. J. Clin. Nutr.* **2003**, *77* (6), 1352–1360.

-
51. Evans, H. M.; Bishop, K. S. On the existence of a hitherto unrecognized dietary factor essential for reproduction. *Science* **1922**, *56*, 650–651.
 52. Mène-Saffrané, L.; DellaPenna, D. Biosynthesis, regulation and functions of tocochromanols in plants. *Plant Physiol. Biochem.* **2010**, *48* (5), 301–309.
 53. Schneider, C. Chemistry and biology of vitamin E. *Mol. Nutr. Food Res.* **2005**, *49*, 7–30.
 54. Herrera, E., Barbas, C. Vitamin E: Action, metabolism and perspectives. *J. Physiol. Biochem.* **2001**, *57* (1), 43–56.
 55. Muller, D. P. R. Vitamin E and neurological function. *Mol. Nutr. Food Res.* **2010**, *54* (5), 710–718.
 56. Galli, F.; Azzi, A.; Birringer, M.; Cook-Mills, J. M.; Eggersdorfer, M.; Frank, J.; Cruciani, G.; Lorkowski, S.; Özer, N. K. Vitamin E: Emerging aspects and new directions. *Free Radicals Biol. Med.* **2017**, *102*, 16–36.
 57. Shibata, A.; Nakagawa, K.; Sookwong, P.; Tsuduki, T.; Asai, A.; Miyazawa, T. α -Tocopherol attenuates the cytotoxic effect of δ -tocotrienol in human colorectal adenocarcinoma cells. *Biochem. Biophys. Res. Commun.* **2010**, *397* (2), 214–219.
 58. Raphey, V. R.; Henna, T. K.; Nivitha, K. P.; Mufeedha, P.; Sabu, C.; Pramod, K. Advanced biomedical applications of carbon nanotube. *Mater. Sci. Eng., C* **2019**, *100*, 616–630.
 59. De Volder, M. F. L.; Tawfick, S. H.; Baughman, R. H.; Hart, A. J. Carbon nanotubes: Present and future commercial applications. *Science* **2013**, *339*, 535–539.
 60. Radushkevich, L. V.; Lukyanovich, V. M. The structure of carbon forming in thermal decomposition of carbon monoxide on an iron catalyst. *Russ. J. Phys. Chem.* **1952**, *26*, 88–95.
 61. Iijima, S. Helical microtubules of graphitic carbon. *Nature* **1991**, *354*, 56–58.
 62. Tsang, S. C.; Harris, P. J. F.; Green, M. L. H. Thinning and opening of carbon nanotubes by oxidation using carbon dioxide. *Nature*, **1993**, *362*, 520–522.
 63. Shah, K. A.; Tali, B. A. Synthesis of carbon nanotubes by catalytic chemical vapour deposition: A review on carbon sources, catalysts and substrates. *Mater. Sci. Semicond. Process.* **2016**, *41*, 67–82.
 64. Su, Y.; Zhang, Y. Carbon nanomaterials synthesized by arc discharge hot plasma. *Carbon* **2015**, *83*, 90–99.

-
65. Chrzanowska, J.; Hoffman, J.; Małolepszy, A.; Mazurkiewicz, M.; Kowalewski, T. A.; Szymanski, Z.; Stobinski, L. Synthesis of carbon nanotubes by the laser ablation method: Effect of laser wavelength. *Phys. Status Solidi B* **2015**, *252*, 1860–1867.
66. Novoselova, I. A.; Oliinyk, N. F.; Volkov, S. V.; Konchits, A. A.; Yanchuk, I. B.; Yefanov, V. S.; Kolesnik, S. P.; Karpets, M. V. Electrolytic synthesis of carbon nanotubes from carbon dioxide in molten salts and their characterization. *Physica E*, **2008**, *40*, 2231–2237.
67. Jašek, O.; Eliáš, M.; Zajíčková, L.; Kudrle, V.; Bublan, M.; Matějková, J.; Rek, A.; Buršík, J.; Kadlečíková, A. Carbon nanotubes synthesis in microwave plasma torch at atmospheric pressure. *Mater. Sci. Eng., C* **2006**, *26*, 1189–1193.
68. Chan, L. Y.; Andrawes, B. Finite element analysis of carbon nanotube/cement composite with degraded bond strength. *Comput. Mater. Sci.* **2010**, *47* (4), 994–1004.
69. Annubhawi, A.; Bhattacharya, B.; Singh, P. K.; Shukla, P. K.; Rhee, H.-W. Carbon nanotube using spray pyrolysis: Recent scenario. *J. Alloys Compd.* **2017**, *691*, 970–982.
70. Lutsyk, P. M.; Shankar, P.; Rozhin, A. G.; Kulinich, S. A. Surface sensitivity of ultrasonically treated carbon nanotube network towards ammonia. *Surf. Interfaces* **2019**, *17*, 100363.
71. Ali, S.; Rehman, S. A. U.; Luan, H.-Y.; Farid, M. U.; Huang, H. Challenges and opportunities in functional carbon nanotubes for membrane-based water treatment and desalination. *Sci. Total Environ.* **2019**, *646*, 1126–1139.
72. Jiang, Y.; Song, H.; Xu, R. Research on the dispersion of carbon nanotubes by ultrasonic oscillation, surfactant and centrifugation respectively and fiscal policies for its industrial development. *Ultrason. Sonochem.* **2018**, *48*, 30–38.
73. Liu, Z.; Bai, G.; Huang, Y.; Ma, Y.; Du, F.; Li, F.; Guo, T.; Chen, Y. Reflection and absorption contributions to the electromagnetic interference shielding of single-walled carbon nanotube/polyurethane composites. *Carbon* **2007**, *45* (4), 821–827.
74. Yang, C.; Hu, X.; Wang, D.; Dai, C.; Zhang, L.; Jin, H.; Agathopoulos, S. Ultrasonically treated multi-walled carbon nanotubes (MWCNTs) as PtRu catalyst supports for methanol electrooxidation. *J. Power Sources* **2006**, *160* (1), 187–193.
75. Cheng, Q.; Debnath, S.; Gegan, E.; Byrne, H. J. Ultrasound-assisted SWNTs dispersion: Effects of sonication parameters and solvent properties. *J. Phys. Chem. C* **2010**, *114* (19), 8821–8827.
-

-
76. Niyogi, S.; Hamon, M. A.; Perea, D. E.; Kang, C. B.; Zhao, B.; Pal, S. K.; Wyant, A. E.; Itkis, M. E.; Haddon, R. C. Ultrasonic dispersions of single-walled carbon nanotubes. *J. Phys. Chem. B* **2003**, *107* (34), 8799–8804.
77. Jung, W. R.; Choi, J. H.; Lee, N.; Shin, K.; Moon, J.-H.; Seo, Y.-S. Reduced damage to carbon nanotubes during ultrasound-assisted dispersion as a result of supercritical-fluid treatment. *Carbon* **2012**, *50* (2), 633–636.
78. Jiang, Y.; Zhu, Y.-F.; Wang, F.-Y.; Chen, W.-J. Effects of plasma and acid treatment on the dispersion of carbon nanotubes in liquids. *Plasma Chem. Plasma Process.* **2011**, *31* (3), 441–448.
79. Chen, C.; Ogino, A.; Wang, X.; Nagatsu, M. Plasma treatment of multiwall carbon nanotubes for dispersion improvement in water. *Appl. Phys. Lett.* **2010**, *96*, 131504.
80. Felten, A.; Bittencourt, C.; Pireaux, J. J.; Van Lier, G.; Charlier, J. C. Radio-frequency plasma functionalization of carbon nanotubes surface O₂, NH₃, and CF₄ treatments. *J. Appl. Phys.* **2005**, *98*, 074308.
81. Trulli, M. G.; Sardella, E.; Palumbo, F.; Palazzo, G.; Giannossa, L. C.; Mangone, A.; Comparelli, R.; Musso, S.; Favia, P. Towards highly stable aqueous dispersions of multi-walled carbon nanotubes: the effect of oxygen plasma functionalization. *J. Colloid Interface Sci.* **2017**, *491*, 255–264.
82. Silambarasan, D.; Surya, V. J.; Iyakutti, K.; Asokan, K.; Vasu, V.; Kawazoe, Y. Gamma (γ)-ray irradiated multi-walled carbon nanotubes (MWCNTs) for hydrogen storage. *Appl. Surf. Sci.* **2017**, *48*, 49–55.
83. Kharissova, O. V.; Kharisov, B. I. Physical Methods. In *Solubilization and Dispersion of Carbon Nanotubes*; Springer, Cham, 2017; pp 5–32.
84. Guo, J.; Li, Y.; Wu, S.; Li, W. The effects of γ -irradiation dose on chemical modification of multi-walled carbon nanotubes. *Nanotechnology* **2015**, *16* (10), 2385–2388.
85. Lee, Y.-I.; Kim, S.; Lee, K.-J.; Myung, N. V.; Choa, Y.-H. Inkjet printed transparent conductive films using water-dispersible single-walled carbon nanotubes treated by UV/ozone irradiation. *Thin Solid Films* **2013**, *536*, 160–165.
86. Kim, S.; Lee, Y.-I.; Kim, D.-H.; Lee, K.-J.; Kim, B.-S.; Hussain, M.; Choa, Y.-H. Estimation of dispersion stability of UV/ozone treated multi-walled carbon nanotubes and their electrical properties. *Carbon* **2013**, *51*, 346–354.
-

-
87. Basariya, M. R.; Srivastava, V. C.; Mukhopadhyay, N. K. Microstructural characteristics and mechanical properties of carbon nanotube reinforced aluminum alloy composites produced by ball milling. *Mater. Des.* **2014**, *64*, 542–549.
 88. Suryanarayana, C. Mechanical alloying and milling. *Prog. Mater. Sci.* **2001**, *46*, 1–184.
 89. Francke, M.; Hermann, H.; Wenzel, R.; Seifert, G.; Wetzig, K. Modification of carbon nanostructures by high energy ball-milling under argon and hydrogen atmosphere. *Carbon* **2005**, *43* (6), 1204–1212.
 90. Pierard, N.; Fonseca, A.; Colomer, J.-F.; Bossuot, C.; Benoit, J.-M.; Van Tendeloo, G.; Pirard, J.-P.; Nagy, J. B. Ball milling effect on the structure of single-wall carbon nanotubes. *Carbon* **2004**, *42*, 1691–1697.
 91. Lavernia, E. J.; Han, B. Q.; Schoenung, J. M. Cryomilled nanostructured materials: Processing and properties. *Mater. Sci. Eng., A* **2008**, *493*, 207–214.
 92. Woo, D. J.; Hooper, J. P.; Osswald, S.; Bottolfson, B. A.; Brewer, L. N. Low temperature synthesis of carbon nanotube-reinforced aluminum metal composite powders using cryogenic milling. *J. Mater. Res.* **2014**, *29* (22), 2644–2656.
 93. Sahni, M.; Locke, B. R. Degradation of chemical warfare agent simulants using gas–liquid pulsed streamer discharges. *J. Hazard. Mater.* **2006**, *137* (2), 1025–1034.
 94. Akiyama, H. Streamer discharges in liquids and their applications. *IEEE Trans. Dielectr. Electr. Insul.* **2000**, *7* (5), 646–653.
 95. Imasaka, K.; Suehiro, J.; Kanatake, Y.; Kato, Y.; Hara, M. Preparation of water-soluble carbon nanotubes using a pulsed streamer discharge in water. *Nanotechnology* **2006**, *17* (14), 3421–3427.
 96. Imasaka, K.; Sun, W.; Tomita, H.; Kato, Y.; Khaled, U.; Suehiro, J. Enhancement and stabilization of pulsed streamer discharge in water by adding carbon nanotubes. *Jpn. J. Appl. Phys.* **2010**, *49* (8), 086203.
 97. Hirsch, A. Functionalization of single-walled carbon nanotubes. *Angew. Chem. Int. Ed.* **2002**, *41* (11), 1853–1859.
 98. Odom, T. W.; Huang, J.-L.; Kim, P.; Lieber, C. M. Structure and electronic properties of carbon nanotubes. *J. Phys. Chem. B* **2000**, *104* (13), 2794–2809.
 99. Patel, A. M.; Gosai, N.; Joshi, A. Y. A review on defects in carbon nanotubes. *Appl. Mech. Mater.* **2015**, *813–814*, 145–150.

-
100. Hirsch, A.; Vostrowsky, O. Functionalization of carbon nanotubes. *Top. Curr. Chem.* **2005**, *245*, 193–237.
 101. Pompeo, F.; Resasco, D. E. Water solubilization of single-walled carbon nanotubes by functionalization with glucosamine. *Nano Lett.* **2002**, *2* (4), 369–379.
 102. Hamon, M. A.; Hu, P.; Bhowmik, P.; Niyogi, S.; Zhao, B.; Itkis, M. E.; Haddon, R. C. End-group and defect analysis of soluble single-walled carbon nanotubes. *Chem. Phys. Lett.* **2001**, *347*, 8–12.
 103. Syrgiannis, Z.; Melchionna, M.; Prato, M. Covalent Carbon Nanotube Functionalization. In *Encyclopedia of Polymeric Nanomaterials*; Kobayashi, S.; Müllen, K. Eds.; Springer, Berlin, Heidelberg, 2014; pp 1–8.
 104. Darabi, H. R.; Tehrani, M. J.; Aghapoor, K.; Mohsenzadeh, F.; Malekfar, R. A new protocol for the carboxylic acid sidewall functionalization of single-walled carbon nanotubes. *Appl. Surf. Sci.* **2012**, *258* (22), 8953–8958.
 105. Long, B.; Wu, T. M.; Stellacci, F. Ultra-fast and scalable sidewall functionalisation of single-walled carbon nanotubes with carboxylic acid. *Chem. Commun.* **2008**, *24*, 2788–2790.
 106. Dyke, C. A.; Tour, J. M. Overcoming the insolubility of carbon nanotubes through high degrees of sidewall functionalization. *Chem. Eur. J.* **2004**, *10* (4), 812–817.
 107. Guo, T.; Wu, J.; Gao, H.; Chen, Y. Covalent functionalization of multi-walled carbon nanotubes with spiropyran for high solubility both in water and in non-aqueous solvents. *Inorg. Chem. Commun.* **2017**, *83*, 31–35.
 108. O'Connell, M. J.; Boul, P.; Ericson, L. M.; Huffman, C.; Wang, Y.; Haroz, E.; Kuper, C.; Tour, J.; Ausman, K. D.; Smalley, R. E. Reversible water-solubilization of single-walled carbon nanotubes by polymer wrapping. *Chem. Phys. Lett.* **2001**, *342*, 265–271.
 109. Yang, M.; Koutsos, V.; Zaiser, M. Interactions between polymers and carbon nanotubes: A molecular dynamics study. *J. Phys. Chem. B* **2005**, *109* (20), 10009–10014.
 110. Chen, J.; Yan, L.; Song, W.; Xu, D. Interfacial characteristics of carbon nanotube-polymer composites: A review. *Composites, Part A* **2018**, *114*, 149–169.
 111. Vizuite, M.; Barrejón, M.; Gómez-Escalonilla, M. J.; Langa, F. Endohedral and exohedral hybrids involving fullerenes and carbon nanotubes. *Nanoscale*, **2012**, *4*, 4370–4381.

-
112. Yi, W.; Malkovskiy, A.; Xu, Y.; Wang, X.-Q.; Sokolov, A. P.; Lebron-Colon, M.; Meador, M. A.; Pang, Y. Polymer conformation-assisted wrapping of single-walled carbon nanotube: The impact of *cis*-vinylene linkage. *Polymer* **2010**, *51* (2), 475–481.
 113. Vaisman, L.; Wagner, H. D.; Marom, G. The role of surfactants in dispersion of carbon nanotubes. *Adv. Colloid Interface Sci.* **2006**, *128–130*, 37–46.
 114. Qiao, M.; Ran, Q.; Wu, S. Novel star-like surfactant as dispersant for multi-walled carbon nanotubes in aqueous suspensions at high concentration. *Appl. Surf. Sci.* **2018**, *433*, 975–982.
 115. Abreu, B.; Rocha, J.; Fernandes, R. M. F.; Regev, O.; Furó, I.; Marques, E. F. Gemini surfactants as efficient dispersants of multiwalled carbon nanotubes: Interplay of molecular parameters on nanotube dispersibility and debundling. *J. Colloid Interface Sci.* **2019**, *547*, 69–77.
 116. Song, X.; Guo, H.; Tao, J.; Zhao, S.; Han, X.; Liu, H. Encapsulation of single-walled carbon nanotubes with asymmetric pyrenyl-gemini surfactants. *Chem. Eng. Sci.* **2018**, *187*, 406–414.
 117. Bricha, M.; El Mabrouk, K. Effect of surfactants on the degree of dispersion of MWNTs in ethanol solvent. *Colloids Surf., A* **2019**, *561*, 57–69.
 118. Chen, Y.; Gunasinghe, R. N.; Wang, X.-Q.; Pang, Y. Selective dispersion of single-walled carbon nanotubes by a cationic surfactant. *RSC Adv.* **2013**, *3*, 25097–25102.
 119. Barzegar, A.; Mansouri, A.; Azamat, J. Molecular dynamics simulation of non-covalent single-walled carbon nanotube functionalization with surfactant peptides. *J. Mol. Graphics Modell.* **2016**, *64*, 75–84.
 120. Parsapour, H.; Ajori, S.; Ansari, R.; Haghighi, S. Tensile characteristics of single-walled carbon nanotubes endohedrally decorated with gold nanowires: A molecular dynamics study. *Diamond Relat. Mater.* **2019**, *92*, 117–129.
 121. Abi, T. G.; Taraphder, S. Proton transfer reactions in carbon nanotubes endohedrally functionalized with selected polar amino acid sidechains. *Chem. Phys.* **2012**, *405*, 107–116.
 122. Matsubara, E. Y.; Luengo, C. A.; Rosolen, J. M. Lithium-doped endohedral single-walled carbon nanotubes can arise during tube growth. *Chem. Phys. Lett.* **2013**, *590*, 175–179.
 123. International Union of Pure and Applied Chemistry Gold Book: Polymer. <http://goldbook.iupac.org/html/P/P04735.html> (accessed Feb 26, 2019).
 124. Jensen, W. B. The origin of the polymer concept. *J. Chem. Educ.* **2008**, *85* (5), 624.
-

-
125. Maiti, S.; Das, D.; Sen, K. Characterization of electro-conductive fabrics prepared by *in situ* chemical and electrochemical polymerization of pyrrole onto polyester fabric. *Mater. Sci. Eng. B* **2014**, *187*, 96–101.
 126. Molina, J.; del Río, A. I.; Cases, B. F. Chemical and electrochemical polymerisation of pyrrole on polyester textiles in presence of phosphotungstic acid. *Eur. Polym. J.* **2008**, *44*, 2087–2098.
 127. Hashimoto, A.; Sogawa, H.; Shiotsuki, M.; Sanda, F. Stabilization of higher-order structure of poly(phenyleneethynylene)s by metathesis polymerization at the side chains. *Polymer* **2012**, *53*, 2559–2566.
 128. Long, Y.; Yu, Y.; Song, B.; Wu, H. Polymerization of glucose during acid-catalyzed pyrolysis at low temperatures. *Fuel* **2018**, *230*, 83–88.
 129. Bitar, R.; Cools, P.; De Geyter, N.; Morent, R. Acrylic acid plasma polymerization for biomedical use. *Appl. Surf. Sci.* **2018**, *448*, 168–185.
 130. Gardiner, J.; Hornung, C. H.; Tsanaktsidis, J.; Guthrie, D. Continuous flow photo-initiated RAFT polymerisation using a tubular photochemical reactor. *Eur. Polym. J.* **2016**, *80*, 200–207.
 131. Darwin, T. P.; Ahmadi, Z.; Taromi, F. A. Biocompatible PLA/PHB coatings obtained from controlled solid state polymerization. *Prog. Org. Coat.* **2019**, *132*, 41–49.
 132. Awuzie, C. I. Conducting polymers. *Mater. Today: Proc.* **2017**, *4*, 5721–5726.
 133. Mukai, A.; Yamato, K.; Asaka, K.; Hata, K.; Oike, H. Actuator of double layer film composed of carbon nanotubes and polypyrroles. *Sens. Actuators, B* **2012**, *161*, 1010–1017.
 134. da Silva, H.; Pacheco, J.; Silva, J.; Viswanathan, S.; Delerue-Matos, C. Molecularly imprinted sensor for voltammetric detection of norfloxacin. *Sens. Actuators, B* **2015**, *219*, 301–307.
 135. Budnikov, H. C.; Evtugyn, G. A.; Porfireva, A. V. Electrochemical DNA sensors based on electropolymerized materials. *Talanta* **2012**, *102*, 137–155.
 136. Hardy, J. G.; Lee, J. Y.; Schmidt, C. E. Biomimetic conducting polymer-based tissue scaffolds. *Curr. Opin. Biotechnol.* **2013**, *24*, 847–854.
 137. Nguyen Cong, H.; El Abbassi, K.; Gautier, J. L.; Chartier, P. Oxygen reduction on oxide/polypyrrole composite electrodes: effect of doping anions. *Electrochim. Acta* **2005**, *50*, 1369–1376.

-
138. Wei, H.; He, C.; Liu, J.; Gu, H.; Wang, Y.; Yan, X.; Guo, J.; Ding, D.; Shen, N. Z.; Wang, X.; Wei, S.; Guo, Z. Electropolymerized polypyrrole nanocomposites with cobalt oxide coated on carbon paper for electrochemical energy storage. *Polymer* **2015**, *67*, 192–199.
 139. Hong, W.; Xu, Y.; Lu, G.; Li, C.; Shi, G. Transparent graphene/PEDOT–PSS composite films as counter electrodes of dye-sensitized solar cells. *Electrochem. Commun.* **2008**, *10*, 1555–1558.
 140. Rajesh, M.; Raj, C. J.; Kim, B. C.; Cho, B.-B.; Ko, J. M.; Yu, K. H. Supercapacitive studies on electropolymerized natural organic phosphate doped polypyrrole thin films. *Electrochim. Acta* **2016**, *220*, 373–383.
 141. Gupta, V.; Miura, N. High performance electrochemical supercapacitor from electrochemically synthesized nanostructured polyaniline. *Mater. Lett.* **2006**, *60*, 1466–1469.
 142. Fan, L. Z.; Maier, J. High-performance polypyrrole electrode materials for redox supercapacitors. *Electrochem. Commun.* **2006**, *8*, 937–940.
 143. Fan, Z.; Chen, J.; Zhang, B.; Liu, B.; Zhong, X.; Kuang, Y. High dispersion of γ -MnO₂ on well-aligned carbon nanotube arrays and its application in supercapacitors. *Diamond Relat. Mater.* **2008**, *17*, 1943–1948.
 144. Skotheim, T. A.; Reynolds, J. R. *Handbook of Conducting Polymers – Conjugated Polymers: Processing and Applications*, 3rd ed.; CRC Press: New York, **2006**.
 145. Chandrasekhar, P. *Conducting Polymers, Fundamentals and Applications – Introducing Carbon Nanotubes and Graphene*, 2nd ed.; Springer International Publishing AG: Cham, Switzerland, **2018**.
 146. Peng, H.; Zhang, L.; Soeller, C.; Travas-Sejdic, J. Conducting polymers for electrochemical DNA sensing. *Biomaterials* **2009**, *30*, 2132–2148.
 147. Li, C.; Shi, G. Synthesis and electrochemical applications of the composites of conducting polymers and chemically converted graphene. *Electrochim. Acta* **2011**, *56*, 10737–10743.
 148. Shirakawa, H.; Louis, E. J.; MacDiarmid, A. G.; Chiang, C. K.; Heeger, A. J. Synthesis of electrically conducting organic polymers: Halogen derivatives of polyacetylene, (CH)_x. *J. Chem. Soc., Chem. Commun.* **1977**, *16*, 578–580.
 149. MacDiarmid, A. G. “Synthetic metals”: A novel role for organic polymers (Nobel lecture). *Angew. Chem. Int. Ed.* **2001**, *40*, 2581–2590.
-

-
150. Adhikari, A.; Radhakrishnan, S. Dopant induced effect on electrocatalytic reduction of nitrobenzene using conducting polypyrrole thin film electrodes. *J. Appl. Polym. Sci.* **2011**, *120*, 719–724.
 151. Ye, Z.; He, H.; Jiang, L. Co-doping: an effective strategy for achieving stable p-type ZnO thin films. *Nano Energy* **2018**, *52*, 527–540.
 152. Iqbal, S.; Ahmad, S. Recent development in hybrid conducting polymers: Synthesis, applications and future prospects. *J. Ind. Eng. Chem.* **2018**, *60*, 53–84.
 153. Panzer, M. J.; Frisbie, C. D. High carrier density and metallic conductivity in poly(3-hexylthiophene) achieved by electrostatic charge injection. *Adv. Funct. Mater.* **2006**, *16*, 1051–1056.
 154. Elmas, S.; Beelders, W.; Nash, J.; Macdonald, T. J.; Jasieniak, M.; Griesser, H. J.; Nann, T. Photo-doping of plasma-deposited polyaniline (PAni). *RSC Adv.* **2016**, *6*, 70691–70699.
 155. Montoya, P.; Mejía, S.; Gonçalves, V. R.; de Torresi, S. I. C.; Calderón, J. A. Performance improvement of macroporous polypyrrole sensor for detection of ammonia by incorporation of magnetite nanoparticles. *Sens. Actuators, B* **2015**, *213*, 444–451.
 156. Chen, C.; Gan, Z.; Zhou, K.; Ma, Z.; Liu, Y.; Gao, Y. Catalytic polymerization of N-methylthionine at electrochemically reduced graphene oxide electrodes. *Electrochim. Acta* **2018**, *283*, 1649–1659.
 157. Patole, A.; Lubineau, G. Carbon nanotubes with silver nanoparticle decoration and conductive polymer coating for improving the electrical conductivity of polycarbonate composites. *Carbon* **2015**, *81*, 720–730.
 158. Vikulov, S.; Di Stasio, F.; Ceseracciu, L.; Saldanha, P. L.; Scarpellini, A.; Dang, Z.; Krahne, R.; Manna, L.; Lesnyak, V. Fully solution-processed conductive films based on colloidal copper selenide nanosheets for flexible electronics. *Adv. Funct. Mater.* **2016**, *26*, 3670–3677.
 159. Erdoğan, M. K.; Karakışla, M.; Saçak, M. Conductive polyaniline-polythiophene/poly(ethylene terephthalate) composite fiber: Effects of pH and washing processes on surface resistivity. *J. Appl. Polym. Sci.* **2015**, *132*, 41979.
 160. Rappoport, Z. *The Chemistry of Anilines: Part 1*. John Wiley & Sons: New York, **2007**.

-
161. Driessen, R. T.; Kamphuis, P.; Mathijssen, L.; Zhang, R.; van der Ham, L. G. J.; van den Berg, H.; Zeeuw, A. J. Industrial process design for the production of aniline by direct amination. *Chem. Eng. Technol.* **2017**, *40* (5), 838–846.
162. Gad, S. C. *Encyclopedia of Toxicology – Aniline*, 3rd ed.; Elsevier, **2014**, 240–242.
163. Gospodinova, N.; Terlemezyan, L. Conducting polymers prepared by oxidative polymerization: Polyaniline. *Prog. Polym. Sci.* **1998**, *23*, 1443–1484.
164. Chiang, J.-C.; MacDiarmid, A. G. ‘Polyaniline’: Protonic acid doping of the emeraldine form to the metallic regime. *Synth. Met.* **1986**, *13*, 193–205.
165. Seo, C. U.; Yoon, Y.; Kim, D. H.; Choi, S. Y.; Park, W. K.; Yoo, J. S.; Baek, B.; Kwon, S. B.; Yang, C. -M.; Song, Y. H.; Yoon, D. H.; Yang, W. S.; Kim, S. Fabrication of polyaniline-carbon nano composite for application in sensitive flexible acid sensor. *J. Ind. Eng. Chem.* **2018**, *64*, 97–101.
166. Wang, S.; Hu, L.; Hu, Y.; Jiao, S. Conductive polyaniline capped Fe₂O₃ composite anode for high rate lithium ion batteries. *Mater. Chem. Phys.* **2014**, *146* (3), 289–294.
167. Jamdegni, M.; Kaur-Ghumaan, S.; Kaur, A. Study of polyaniline and functionalized ZnO composite film linked through a binding agent for efficient and stable electrochromic applications. *Electrochim. Acta* **2017**, *252*, 578–588.
168. MacDiarmid, A. G.; Epstein, A. J. Polyanilines: A novel class of conducting polymers. *Faraday Discuss. Chem. Soc.* **1989**, *88*, 317–332.
169. Huang, W.-S.; Humphrey, B. D.; MacDiarmid, A. G. Polyaniline, A novel conducting polymer. Morphology and chemistry of its oxidation and reduction in aqueous electrolytes. *J. Chem. Soc., Faraday Trans. 1* **1986**, *82*, 2385–2400.
170. Cooper, C.; Purchase, R. *Organic Chemist's Desk Reference*, 3rd Ed.; CRC Press: New York, 2017, pp 266.
171. Stejskal, J. Polymers of phenylenediamines. *Prog. Polym. Sci.* **2015**, *41*, 1–31.
172. Stejskal, J.; Sapurina, I.; Trchová, M.; Konyushenko, E. N. Oxidation of aniline: Polyaniline granules, nanotubes, and oligoaniline microspheres. *Macromolecules* **2008**, *41*, 3530–3536.
173. Stejskal, J.; Kratochvíl, P.; Jenkins, A. D. The formation of polyaniline and the nature of its structures. *Polymer* **1996**, *37* (2), 367–369.
-

-
174. Sapurina, I.; Stejskal, J. The mechanism of the oxidative polymerization of aniline and the formation of supramolecular polyaniline structures. *Polym. Int.* **2008**, *57*, 1295–1325.
175. Letheby, H. XXIX.— On the production of a blue substance by the electrolysis of sulphate of aniline. *J. Chem. Soc.* **1862**, *15*, 161–163.
176. Zotti, G.; Cattarin, S.; Comisso, N. Cyclic potential sweep electropolymerization of aniline: Their role of anions in the polymerization mechanism. *J. Electroanal. Chem. Interfacial Electrochem.* **1988**, *239*, 387–396.
177. Luo, X.; Killard, A. J.; Smyth, M. R. Nanocomposite and nanoporous polyaniline conducting polymers exhibit enhanced catalysis of nitrite reduction. *Chem. Eur. J.* **2007**, *13*, 2138–2143.
178. Zhao, L.; Zhao, L.; Xu, Y.; Qiu, T.; Zhi, L.; Shi, G. Polyaniline electrochromic devices with transparent graphene electrodes. *Electrochim. Acta* **2009**, *55*, 491–497.
179. Das, I.; Choudhary, R.; Gupta, S. K.; Agrawal, P. Nanostructured growth patterns and chaotic oscillations in potential during electropolymerization of aniline in the presence of surfactants. *J. Phys. Chem. B* **2011**, *115*, 8724–8731.
180. Sabatani, E.; Gafni, Y.; Rubinstein, I. Morphology control in electrochemically grown conducting polymer films. 3. A comparative study of polyaniline films on bare gold and on gold pretreated with *p*-aminothiophenol. *J. Phys. Chem.* **1995**, *99*, 12305–12311.
181. Inamdar, A. I.; Kim, Y. S.; Sohn, J. S.; Im, H. Supercapacitive Characteristics of electrodeposited polyaniline thin films grown on indium-doped tin-oxide substrates. *J. Korean Phys. Soc.* **2011**, *59*, 145–149.
182. Sapurina, I.; Tenkovtsev, A. Y.; Stejskal, J. Conjugated polyaniline as a result of the benzidine rearrangement. *Polym. Int.* **2015**, *64*, 453–465.
183. Hussain, A. M. P.; Kumar, A. Electrochemical synthesis and characterization of chloride doped polyaniline. *Bull. Mater. Sci.* **2003**, *26* (3), 329–334.
184. Choi, S.-J.; Park, S.-M. Electrochemistry of conductive polymers. XXVI. Effects of electrolytes and growth methods on polyaniline morphology. *J. Electrochem. Soc.* **2002**, *149*, E26–E34.
185. Liu, X.-X.; Zhang, L.; Li, Y.-B.; Bian, L.-J.; Su, Z.; Zhang, L.-J. Electropolymerization of aniline in aqueous solutions at pH 2 to 12. *J. Mater. Sci.* **2005**, *40*, 4511–4515.
-

-
186. Hu, C.-C.; Chu, C.-C. Electrochemical impedance characterization of polyaniline-coated graphite electrodes for electrochemical capacitors – Effects of film coverage/thickness and anions. *J. Electroanal. Chem.* **2001**, *503*, 105–116.
187. Dalmolin, C.; Canobre, S. C.; Biaggio, S. R.; Rocha-Filho, R. C.; Bocchi, N. Electropolymerization of polyaniline on high surface area carbon substrates. *J. Electroanal. Chem.* **2005**, *578*, 9–15.
188. Neoh, K. G.; Pun, M. Y.; Tang, E. T.; Tan, K. L. Polyaniline treated with organic acids: Doping characteristics and stability. *Synth. Met.* **1995**, *73*, 209–215.
189. Cao, Q.; Zhao, H.; Zeng, L.; Wang, J.; Wang, R.; Qiu, X.; He, Y. Electrochemical determination of melamine using oligonucleotides modified gold electrodes. *Talanta* **2009**, *80*, 484–488.
190. Newton, G. L.; Utley, P. R. Utley. Melamine as a dietary nitrogen source for ruminants. *J. Anim. Sci.* **1978**, *47*, 1338–1344.
191. Brown, C. A.; Jeong, K.-S.; Poppenga, R. H.; Puschner, B.; Miller, D. M.; Ellis, A. E.; Kang, K.-I.; Sum, S.; Cistola, A. M.; Brown, S. A. Outbreaks of renal failure associated with melamine and cyanuric acid in dogs and cats in 2004 and 2007. *J. Vet. Diagn. Invest.* **2007**, *19*, 525–531.
192. Gossner, C. M.-E.; Schlundt, J.; Embarek, P. B.; Hird, S.; Lo-Fo-Wong, D.; Beltran, J. J. O.; Teoh, K. N.; Tritscher, A. The melamine incident: Implications for international food and feed safety. *Environ. Health Perspect.* **2009**, *117*, 1803–1808.
193. Wu, Y.; Zhang, Y. Analytical chemistry, toxicology, epidemiology and health impact assessment of melamine in infant formula: Recent progress and developments. *Food Chem. Toxicol.* **2013**, *56*, 325–335.
194. Well, E. D. Fire-protective and flame-retardant coatings – A state-of-the-art review. *J. Fire Sci.* **2011**, *29*, 259–296.
195. Lei, Z.; Zhang, G.; Ouyang, Y.; Liang, Y.; Deng, Y.; Wang, C. Simple fabrication of multi-functional melamine sponges. *Mater. Lett.* **2017**, *190*, 119–122.
196. Wang, H.; Liu, X.; Zhang, B.; Yang, J.; Zhang, Z.; Yue, R.; Wang, Z. Highly compressible supercapacitor based on carbon nanotubes-reinforced sponge electrode. *J. Alloys Compd.* **2019**, *786*, 995–1004.
-

-
197. Chou, H.-T.; Lee, H.-J.; Lee, C.-Y.; Tai, N.-H.; Chang, H.-Y. Highly durable anodes of microbial fuel cells using a reduced graphene oxide/carbon nanotube-coated scaffold. *Bioresour. Technol.* **2014**, *169*, 532–536.
 198. Baskar, S.; Liao, C. W.; Chang, J. L.; Zen, J. M. Electrochemical synthesis of electroactive poly(melamine) with mechanistic explanation and its applicability to functionalize carbon surface to prepare nanotube–nanoparticles hybrid. *Electrochim. Acta* **2013**, *88*, 1–5.
 199. Chen, S.; Liu, S.; Wen, A.; Zhang, J.; Nie, H.; Chen, J.; Zeng, R.; Long, Y.; Jin, Y.; Mai, R. New insight into electropolymerization of melamine. I: Chloride promoted growth of polymelamine in different pH medium. *Electrochim. Acta* **2018**, *271*, 312–318.
 200. Liu, X.; Luo, L.; Ding, Y.; Wu, Q.; Wei, Y.; Ye, D. A highly sensitive method for determination of guanine, adenine and epinephrine using poly-melamine film modified glassy carbon electrode. *J. Electroanal. Chem.* **2012**, *675*, 47–53.
 201. Liu, L.; Li, P.-Z.; Zhu, L.; Zou, R.; Zhao, Y. Microporous polymelamine network for highly selective CO₂ adsorption. *Polymer* **2013**, *54*, 596–600.
 202. Chu, S.; Cui, Y.; Liu, N. The path towards sustainable energy. *Nat. Mater.* **2017**, *16*, 16–22.
 203. U.S. Energy Information Administration (EIA): Today in energy dated July 1, 2019. <https://www.eia.gov/todayinenergy/detail.php?id=40013> (accessed July 12, 2019).
 204. Clark, G. *Handbook of Economic Growth – Chapter 5: The Industrial Revolution*, 1st ed.; Elsevier, **2014**, 217–262.
 205. Intergovernmental Panel on Climate Change (IPCC) report on global warming of 1.5°C – Summary for policymakers. https://report.ipcc.ch/sr15/pdf/sr15_spm_final.pdf (accessed Aug 1, 2019).
 206. Chu, S.; Majumdar, A. Opportunities and challenges for a sustainable energy future. *Nature* **2012**, *488*, 294–303.
 207. Clark, W. W.; Cooke, G. *The Green Industrial Revolution: Energy, Engineering and Economics.*; Elsevier B.V., **2015**, 173–190.
 208. Renewables 2019 Global Status Report (REN21) https://www.ren21.net/wp-content/uploads/2019/05/gsr_2019_full_report_en.pdf (accessed August 8, 2019)
 209. Zakeri, B.; Syri, S. Electrical energy storage systems: A comparative life cycle cost analysis. *Renewable Sustainable Energy Rev.* **2015**, *42*, 569–596.
-

-
210. Dummer, G. W. A. *Electronic Inventions and Discoveries*, 4th ed.; Bristol, United Kingdom: Institute of Physics Publishing, **1997**, 74.
 211. Hackmann, W. Lightning rods and model experiments: Franklin's science comes of age. *Studies in History and Philosophy of Science Part A* **1991**, *22*, 679-684.
 212. Libich, J.; Máca, J.; Vondrák, J.; Čech, O.; Sedlaříková, M. Supercapacitors: Properties and applications. *J. Energy Storage* **2018**, *17*, 224–227.
 213. Zopf, S. F.; Manser, M. Screen-printed military textiles for wearable energy storage. *J. Eng. Fibers Fabr.* **2016**, *11*, 1–8.
 214. Lampani, L.; Gaudenzi, P. Innovative composite material component with embedded self-powered wireless sensor device for structural monitoring. *Compos. Struct.* **2018**, *202*, 136–141.
 215. Yang, J.; Wang, H.; Yang, Y.; Wu, J.; Hu, P.; Guo, L. Pseudocapacitive-dye-molecule-based high-performance flexible supercapacitors. *Nanoscale*, **2017**, *9*, 9879–9885.
 216. McCloskey, B. D. Expanding the Ragone plot: Pushing the limits of energy storage. *J. Phys. Chem. Lett.* **2015**, *6*, 3592–3593.
 217. Rafik, F.; Gualous, H.; Gallay, R.; Crausaz, A.; Berthon, A. Frequency, thermal and voltage supercapacitor characterization and modelling. *J. Power Sources* **2007**, *165*, 928–934.
 218. Viswanathan, B. *Energy Sources – Fundamentals of Chemical Conversion Processes and Applications*; Elsevier B.V. **2017**, 315–328.
 219. Kado, Y.; Soneda, Y.; Hatori, H.; Kodama, M. Advanced carbon electrode for electrochemical capacitors. *J. Solid State Electrochem.* **2019**, *23*, 1061–1081.
 220. Kötz, R.; Carlen, M. Principles and applications of electrochemical capacitors. *Electrochim. Acta* **2000**, *45*, 2483–2498.
 221. Sharma, P.; Bhatti, T. S. A review on electrochemical double-layer capacitors. *Energy Convers. Manage.* **2010**, *51*, 2901–2912.
 222. Yuan, H.; Wang, H.; Cui, Y. Two-dimensional layered chalcogenides: From rational synthesis to property control *via* orbital occupation and electron filling. *Acc. Chem. Res.* **2015**, *48*, 81–90.
 223. Simon, P.; Gogotsi, Y.; Dunn, B. Where do batteries end and supercapacitors begin? *Science* **2014**, *343*, 1210–1211.
 224. Conway, B. E.; Birss, V.; Wojtowicz, J. The role and utilization of pseudocapacitance for energy storage by supercapacitors. *J. Power Sources* **1997**, *66*, 1–14.
-

-
225. Kazazi, M. Facile preparation of nanoflake-structured nickel oxide/carbon nanotube composite films by electrophoretic deposition as binder-free electrodes for high-performance pseudocapacitors. *Curr. Appl. Phys.* **2017**, *17*, 240–248.
226. Li, X.; Zheng, F.; Zhou, D. F.; Luo, Y. M.; Li, Y. F.; Lu, F. H. Stable RuO₂-based ternary composite electrode of sandwiched framework for electrochemical capacitors. *Electrochim. Acta* **2018**, *289*, 292–310.
227. Ma, Z.; Shao, G.; Fan, Y.; Wang, G.; Song, J.; Shen, D. Construction of hierarchical α -MnO₂ nanowires@ultrathin δ -MnO₂ nanosheets core-shell nanostructure with excellent cycling stability for high-power asymmetric supercapacitor electrodes. *ACS Appl. Mater. Interfaces* **2016**, *8*, 9050–9058.
228. Shaik, D. P. M. D.; Rosaiah, P.; Ganesh, K. S.; Qiu, Y.; Hussain, O. M. Improved electrochemical performance of Mn₃O₄ thin film electrodes for supercapacitors. *Mater. Sci. Semicond. Process.* **2018**, *84*, 83–90.
229. Kannagi, K. Super critically synthesized V₂O₅ spheres based supercapacitors using polymer electrolyte. *Appl. Surf. Sci.* **2018**, *456*, 13–18.
230. Shao, Z.; Fan, X.; Liu, X.; Yang, Z.; Wang, L.; Chen, Z.; Zhang, W. Hierarchical micro/nanostructured WO₃ with structural water for high-performance pseudocapacitors. *J. Alloys Compd.* **2018**, *765*, 489–496.
231. Tian, J.; Shi, Y.; Fan, W.; Liu, T. Tungsten carbide nanoparticles embedded in electrospun carbon nanofiber membranes as flexible and high-performance supercapacitor electrodes. *Compos. Commun.* **2019**, *12*, 21–25.
232. Jagadale, A.; Guan, G.; Du, X.; Hao, X.; Li, X.; Abudula, A. Cobalt hydroxide [Co(OH)₂] loaded carbon fiber flexible electrode for high performance supercapacitor. *RSC Adv.* **2015**, *5*, 56942–56948.
233. Arif, M.; Sanger, A.; Singh, A. Sputter deposited chromium nitride thin electrodes for supercapacitor applications. *Mater. Lett.* **2018**, *220*, 213–217.
234. Acerce, M.; Voiry, D.; Chhowalla, M. Metallic 1T phase MoS₂ nanosheets as supercapacitor electrode materials. *Nat. Nanotechnol.* **2015**, *10*, 313–318.

-
235. Cao, A.; Chen, Z.; Wang, Y.; Zhang, J.; Wang, Y.; Li, T.; Han, Y. Redox-active doped polypyrrole microspheres induced by phosphomolybdic acid as supercapacitor electrode materials. *Synth. Met.* **2019**, *252*, 135–141.
 236. Eftekhari, A.; Li, L.; Yang, Y. Polyaniline supercapacitors. *J. Power Sources* **2017**, *347*, 86–107.
 237. Patra, S.; Munichandraiah, N. Supercapacitor studies of electrochemically deposited PEDOT on stainless steel substrate. *J. Appl. Polymer Sci.* **2007**, *106*, 1160–1171.
 238. Shi, F.; Li, L.; Wang, X.-L.; Gu, C.-D.; Tu, J.-P. Metal oxide/hydroxide-based materials for supercapacitors. *RSC Adv.* **2014**, *4*, 4191–41921.
 239. Zhang, S.; Pan, N. Supercapacitors performance evaluation. *Adv. Energy Mater.* **2015**, *5*, 1401401.
 240. Muzaffar, A.; Ahamed, M. B.; Deshmukh, K.; Thirumalai, J. A review on recent advances in hybrid supercapacitors: Design, fabrication and applications. *Renewable Sustainable Energy Rev.* **2019**, *101*, 123–145.
 241. Xu, L.; Wang, S.; Zhang, X.; He, T.; Lu, F.; Li, H.; Ye, J. A facile method of preparing LiMnPO₄/reduced graphene oxide aerogel as cathodic material for aqueous lithium-ion hybrid supercapacitors. *Appl. Surf. Sci.* **2018**, *428*, 977–985.
 242. Zhuang, B.; Guo, Z.; Chu, W.; Cao, Z.; Bold, T.; Gao, Y. Mesoporous carbon film inlaid with Li₃V₂(PO₄)₃ nanoclusters through delaying sol-gel method for high performance lithium-ion hybrid supercapacitors. *Electrochim. Acta* **2018**, *283*, 1589–1599.
 243. Afif, A.; Rahman, S. M. H.; Azad, A. T.; Zaini, J.; Islan, M. A.; Azad, A. K. Advanced materials and technologies for hybrid supercapacitors for energy storage – A review. *J. Energy Storage* **2019**, *25*, 100852.
 244. Dubal, D. P.; Ayyad, O.; Ruiz, V.; Gómez-Romero, P. Hybrid energy storage: The merging of battery and supercapacitor chemistries. *Chem. Soc. Rev.* **2015**, *44*, 1777–1790.
 245. Smith, P. H.; Sepe, R. B.; Waterman, K. G.; Myron, L. J. Development and analysis of a lithium carbon monofluoride battery-lithium ion capacitor hybrid system for high pulse-power applications. *J. Power Sources* **2016**, *327*, 495–506.
 246. Shiri, H. M.; Ehsani, A.; Khaled, M. J. Electrochemical synthesis of Sm₂O₃ nanoparticles: Application in conductive polymer composite films for supercapacitors. *J. Colloid Interface Sci.* **2017**, *505*, 940–946.
-

This page is intentionally left blank

Experimental Methods

This page is intentionally left blank

3.1 Overview of electrochemical techniques

In electrochemistry, it allows the study of electron transfer reactions with the aid of electrochemical techniques to offer useful quantitative and qualitative information such as redox potentials, reaction kinetics and electrochemical mechanisms. For all of the experiments performed in the thesis, the main electroanalytical techniques used are cyclic voltammetry (CV), square-wave voltammetry (SWV) and electrochemical impedance spectroscopy (EIS). In each subsection, a general background shall be covered for each electrochemical method. Generally, the electrochemical technique involves a similar experimental setup of the electrochemical cell in a three-electrode configuration with a schematic diagram as shown in **Figure 3.1**. The three-electrode configuration comprises of a 3-mm diameter planar glassy carbon (GC) disk with a platinum wire as the auxiliary electrode along with a silver chloride reference electrode (Ag/AgCl in 3 M KCl).

Figure 3.1 The setup of the fully assembled electrochemical cell in a Faraday cage.

3.2 Background information of electrochemical techniques

3.2.1 Cyclic voltammetry

CV is one of the most popular and commonly used electroanalytical methods in the study of biological, organic and inorganic redox processes. The technique adopts a three-electrode cell configuration, and offers valuable information including electrode kinetics and the ability to elucidate electron transfer mechanisms.¹⁻⁵ It involves a triangular potential sweep with a constant scan rate occurring at the working electrode. During voltammetric measurements, the reaction of interest occurs at the electric double layer near the electrode surface with the current between the working and the auxiliary electrodes measured as a function of potential against the reference electrode to result in a cyclic voltammogram (**Figure 3.2(a)**).⁶ A typical CV provides direct quantitative information such as the anodic and cathodic peak currents, and the anodic and cathodic peak potentials (denoted by i_p^{ox} , i_p^{red} , E_p^{ox} and E_p^{red} respectively). The formal potential of an electrochemically reversible redox couple can be determined by calculating the average of the anodic and cathodic peak potentials. In addition, other qualitative information can also be obtained from the interpretation of the voltammogram. Firstly, electrochemical reversibility can be determined by finding the peak-to-peak potential separation (ΔE_{pp}) which is the absolute difference of E_p^{ox} and E_p^{red} (**equation 3.1**):

$$\Delta E_{\text{pp}} = | E_p^{\text{ox}} - E_p^{\text{red}} | = \frac{0.0592}{n} \quad (3.1)$$

where n is the number of electrons transferred in the redox process at 25°C. If the absolute value of ΔE_{pp} is about 59 mV, the value of n is 1 and thus a reversible single electron transfer is associated with the redox process. Secondly, if the ratio of the anodic and cathodic peak currents equates to one, chemical reversibility is evident of the redox couple. Caution must be taken when using the terms *electrochemical* and *chemical* reversibility as the former refers to the rate of the heterogeneous electron transfer, while

the latter refers to the lifetimes of the oxidised and reduced species in the electron transfer step. If the effect of scan rate is examined, increasing values of ΔE_{pp} with scan rate indicate the occurrence of slow electron transfer kinetics. By comparing both reversible and quasi-reversible electron transfers, the latter is characterised by a greater ΔE_{pp} shown in **Figure 3.2(b)** due to its slow reaction kinetics without a fast equilibrium. Thirdly, the peak current should be directly proportional to the square root of the scan rate for a reversible electron transfer, and is governed by the Randles-Ševčík equation (**equation 3.2**) where i_p = peak current (A), n = electrons involved in the redox process, A = electrode area (cm^2), F = Faraday constant (96485 C mol^{-1}), D = diffusion coefficient of the electroactive species ($\text{cm}^2 \text{ s}^{-1}$), c = bulk concentration (mol/cm^3), v = scan rate (V s^{-1}), R = molar gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$), and T = temperature (K).⁵

$$i_p = 0.4463 n^{3/2} F^{3/2} A c \left(\frac{vD}{RT} \right)^{1/2} \quad (3.2)$$

Figure 3.2 (a) A typical CV of an electrochemically reversible redox couple. (b) CV corresponding to electron transfer reactions which are reversible, quasi-reversible, and irreversible denoted by **I**, **II**, and **III** respectively.⁶

3.2.2 Square-wave voltammetry

Square-wave voltammetry (SWV) is a non-destructive and pulsed voltammetric technique developed by Barker in 1957 with a typical SWV excitation signal

characterised by the superimposition of a staircase waveform and a symmetrical square-wave pulse (**Figure 3.3(a)**).⁷ The current is measured twice during each square-wave cycle, with one at the end of the forward pulse (denoted by I_f) and the other at the end of the reverse pulse (denoted by I_r). A square-wave voltammogram is then given by the difference between the forward and reverse current, Δi against the applied potential E (**Figure 3.3(b)**).^{7–9} Such technique edges over linear sweep voltammetry (LSV) and CV due to its excellent sensitivity, elimination of background currents, and the removal of interference of the electrochemically irreversible reduction of dissolved oxygen in basic conditions.¹⁰ Because of its fast scanning speed, it is also sometimes used in monitoring synthetic reactions, particularly with short-lived intermediate species to study the reaction kinetics with greater accuracy.

Figure 3.3 (a) Schematic representation of the square-wave excitation signal in SWV with potential as a function of time. The symbols ΔE , E_{SW} , E_i , τ and t_p denote the step voltage, square-wave voltage, initial voltage, pulse period and the pulse duration respectively. (b) A typical SWV with the change in current as a function of potential.

3.2.3 Electrochemical impedance spectroscopy

EIS is a useful spectroscopic technique to characterise electrochemical systems in the sciences. Specifically, it can investigate the reaction kinetics of passivated and

porous electrode surfaces especially for studies related to corrosion, adsorption, and energy storage materials.^{11,12} The foundation of EIS was first laid out by an English physicist and mathematician Oliver Heaviside in the late 19th century,¹³ and subsequently further improved and revolutionised into a spectroscopic technique that is being used by scientists today. It is non-destructive, transient, steady state by nature, and adopts an alternating voltage or current as a function of frequency.¹⁴ However, the downside with EIS is that steady state systems are assumed but can be difficult to achieve in practice due to surface adsorption of foreign species. Nevertheless, the technique can offer a wealth of information when applied and analysed appropriately.

Figure 3.4 Graphical representation of EIS data in the form of (a) Nyquist, and (b) Bode plots.

EIS measurements are collected at the open circuit potential *via* applying a small alternating potential or current at a small amplitude over a wide range of frequencies such as 0.01 Hz to 10 kHz. The perturbation point of the alternating potential or current is measured at every frequency point. The results of EIS are then presented graphically usually in the form of Nyquist and Bode plots (**Figure 3.4**).¹⁵ A Nyquist plot is a spectrum of imaginary impedance ($-Z''$) against real impedance (Z') and studies the kinetic control with the semicircle at high frequencies associated with the lower range of Z' . For the Bode plot, it presents the impedance dependence on frequency.

The impedance, Z of a system is expressed in the form of a complex number. For a given coordinate at a known frequency, Z is the sum of Z' and Z'' in the form of $Z = Z' + jZ''$, where j is an imaginary indeterminate. The equivalent expansion of this expression in trigonometric form is given by $Z = |Z| \cos \theta + j |Z| \sin \theta$, where $|Z|$ and θ are the modulus impedance and the phase angle of the system respectively. To determine $|Z|$ and θ , trigonometry shall apply with $|Z| = \sqrt{(Z')^2 + (Z'')^2}$ and $\theta = \tan^{-1} \left| \frac{Z''}{Z'} \right|$.¹⁶ If information on electrode capacitance is required, it can be determined from the linear plot of $\log |Z|$ against $\log f$ when the frequency is approximated to zero (**Figure 3.4(b)**).¹⁶ At infinitely high frequencies, the capacitor behaves like a short circuit with the phase angle and impedance close to zero, and the solution resistance (R_s) dominates the impedance of the resistor. R_s is then determined graphically from the Nyquist plot as the intercept on $Z'(\omega)$. As frequency decreases, an open circuit behaviour is more dominant with resistance contributions from the solution and the charge transfer process to account for the increase in impedance.

Scientifically speaking, impedance refers to the resistance of the impeded flow of electroactive species at the electrode interface.¹⁷ When a signal is generated in the EIS, several factors such as electrode resistance, electrolyte resistivity, electric double layer, ion transport and electron transfer at the electrode-electrolyte interface can affect the intensity and shape of that signal.¹⁸ These factors are represented as electrical elements in a Randles equivalent electrical circuit which models the electric double layer at the electrode interface. Its core electrical elements are charge transfer (or polarisation) resistance (R_{ct}), Warburg impedance (Z_w), and double layer capacitance (C_{dl}), solution resistance (R_s). These elements can be assembled in either series or parallel with an infinite number of possibilities together with the addition of circuit elements and rearrangement of the connection to tailor to the testing needs of the user.¹⁹ For every

element it resembles a certain property of either resistance R , capacitance C , or inductance L that carries an impedance characteristic of itself (**Table 3.1**). For instance, resistance is associated with the conductive pathways in ionic bulk and solid phases, while capacitance is associated with adsorption or polarisation at the interface.¹⁷

Table 3.1 Impedance of the electrical elements R , C , and L .

Electrical element	R	C	L
Impedance	R	$1 / j\omega C$	$j\omega L$

Figure 3.5 (a) The structure of the electrical double layer at the electrode-electrolyte interface. (b) The Randles equivalent electrical circuit that models the structure of the electrical double layer.

When an alternating voltage or current is applied, an electrical double layer is created at the electrode interface (**Figure 3.5(a)**). At the inner Helmholtz plane (ihp), ions are adsorbed onto the electrode surface while the solvated ions migrate freely within the electrolyte at the outer Helmholtz plane (ohp). Capacitive current arises from

the charge accumulation in the Helmholtz region. A common representation of the Randles circuit is shown in **Figure 3.5(b)** whereby a double layer capacitor (C_{dl}) in parallel with the charge transfer resistance (R_{ct}) and Warburg impedance (Z_w), is connected in series with the electrolyte resistance (R_s).^{20,21} In the subsequent paragraphs, each electrical circuit element shall be discussed briefly.

Charge transfer resistance: Also known as *polarization resistance*, it is analogous to the diameter of the semicircle in the Nyquist plot and is directly related to the extent of charge transfer resistance (R_{ct}). Hence, a very small R_{ct} would imply the kinetically facile nature of the charge transfer.^{11,17,18} Charge transfer resistance arises due to the migration of the ionic species in the solution to the electrode surface, and is dependent on various factors such as temperature, potential applied and reactant concentration.^{20,21}

Warburg impedance: The term was first coined by a German physicist Emil Warburg in 1899 that published a paper on the impedance of the *diffusive* electroactive species being transported to the electrode surface.²² Warburg impedance arises due to the mass transfer by *diffusion*-controlled processes at low frequencies as the diffusing species move far from the electrode-electrolyte interface. In the equivalent series circuit, the Warburg impedance is treated as a constant phase element with a constant phase shift of 45° on a Bode plot. In a Nyquist plot, the tailing on the semicircle arc with a straight line of slope 0.5 at low frequencies indicates the presence of Warburg impedance and offers information about the mass transfer by diffusion in the bulk solution. On the contrary, the absence of Warburg impedance is evident on a Nyquist plot with a perfect semicircle that is associated with a relatively slow mass transfer.

Constant phase element (CPE) and double layer capacitance (C_{dl}): In certain circumstances when double layer capacitance is frequency independent, C_{dl} is

approximated by the empirical element CPE. As capacitors do not exhibit ideal behaviour in practice, they behave like CPEs instead of a C_{dl} element. Various theories have been proposed to differentiate between both elements but there is no universal agreement. Generally, the use of CPE may apply to electrode surfaces that are porous and surface-coated with non-uniform surface roughness, thickness and or distribution. Other circumstances such as unequal distribution of resistivity and capacitance of the electrode surface may apply as well.¹³ Both elements CPE and C_{dl} are characterised by a straight line and an arc respectively in the Nyquist plots.¹¹

Solution resistance: In practice, electrochemical cells suffer from solution resistance (R_s). As the term suggests, this resistance arises from the active electrolyte and is influenced by various factors such as the type of ions, ionic concentration, and temperature. However, solution resistance is independent of frequency.^{11,12,17,18,21}

3.3 References

1. Harris, D. C. *Quantitative Chemical Analysis*, 7th ed.; W. H. Freeman and Company: New York, **2007**.
2. Shriver, D.; Atkins, P. *Inorganic Chemistry*, 4th ed.; W. H. Freeman and Company: New York, **2006**.
3. Atkins, P. *Physical Chemistry*, 7th ed.; W. H. Freeman and Company: New York, **2002**.
4. Baldwin, R. P.; Ravichandran, K.; Johnson, R. K. *J. Chem. Educ.* **1984**, *61*(9), 820–823.
5. Zanello, P., *Inorganic Electrochemistry: Theory, Practice and Application*. The Royal Society of Chemistry, United Kingdom, **2003**.
6. Brownson, D. A. C.; Kampouris, D. K.; Banks, C. E. *Chem. Soc. Rev.* **2012**, *41*, 6944–6976.
7. Osteryoung, J. G.; Osteryoung, R. A. *Anal. Chem.* **1985**, *57*(1), 101A–110A.
8. Brookes, B. A.; Ball, J. C.; Compton, R. G. *J. Phys. Chem. B* **1999**, *103*, 5289–5295.
9. Skoog, D. A.; West, D. M.; Holler, F. J.; Crouch, S. R. *Fundamentals of Analytical Chemistry*, 8th Ed., Brooks/Cole-Thomson Learning, New York, **2004**.

-
10. Brett, C. M. A.; Brett, A.M. *Electrochemical Principles, Methods and Applications*. Oxford University Press, Oxford, **1993**.
 11. Pajkossy, T.; Jurczakowski, R. Electrochemical impedance spectroscopy in interfacial studies. *Curr. Opin. Electrochem.* **2017**, *1*, 53–58.
 12. Randviir, E. P.; Banks, C. E. Electrochemical impedance spectroscopy: An overview of bioanalytical applications. *Anal. Methods* **2013**, *5*, 1098–1115.
 13. Unz, H. Oliver Heaviside (1850–1925). *IEEE Trans. Educ.* **1963**, *6* (1), 30–33.
 14. Macdonald, D. D. Reflections on the history of electrochemical impedance spectroscopy. *Electrochim. Acta* **2006**, *51*, 1376–1388.
 15. Stoyanov, Z. B.; Vladikova, D. E. Measurement Methods | Electrochemical: Impedance Spectroscopy. In *Encyclopedia of Electrochemical Power Sources*. Garche, J., Eds.; Elsevier, 2009; pp 632–642.
 16. Park, S.-M.; Yoo, J.-S. Peer reviewed: Electrochemical impedance spectroscopy for better electrochemical measurements. *Anal. Chem.* **2003**, *75*, 455 A–461 A.
 17. Moisel, M.; de Mele, M. A. F. L.; Müller, W.-D. Biomaterial interface investigated by electrochemical impedance spectroscopy. *Adv. Eng. Mater.* **2008**, *10*, B33–B46.
 18. Ram, Y.; Yoetz-Kopelman, T.; Dror, Y.; Freeman, A.; Shacham-Diamand, Y. Impact of molecular surface charge on biosensing by electrochemical impedance spectroscopy. *Electrochim. Acta* **2016**, *200*, 161–167.
 19. Choudhary, Y. S.; Jothi, L.; Nageswaran, G. Electrochemical Characterization. In *Spectroscopic Methods for Nanomaterials Characterization*; Thomas, S.; Thomas, R.; Zachariah, A. K.; Mishra, R. K. Eds.; Elsevier, 2017; pp 19–54.
 20. Orazem, M. E.; Tribollet, B. Electrochemistry. In *Electrochemical Impedance Spectroscopy*; 2nd ed.; Wiley, New Jersey, 2017; pp 89–127.
 21. Chang, B.-Y.; Park, S.-M. Electrochemical impedance spectroscopy. *Annu. Rev. Anal. Chem.* **2010**, *3*, 207–229.
 22. Warburg, E. On the behavior of so-called unpolarised electrodes against alternating current. *Ann. Phys. Chem.* **1899**, *67*, 493–499.

This page is intentionally left blank

A Novel Vitamin-based Voltammetric pH Sensor in Buffered and Unbuffered Media

This page is intentionally left blank

4.1 Literature review of voltammetric pH sensors

Scheme 4.1: A two-proton two-electron transfer quinone/hydroquinone redox couple used as a pH-sensitive electrode by Biilmann in 1921.

Several papers have reported the use of voltammetry using pH-dependent and redox active compounds as the basis of developing pH sensors. A pH sensitive electrode was believed to be first developed as early as in 1921 by a Danish chemist, Einar Biilmann¹ whereby such an electrode relied on the quinone/hydroquinone redox couple to measure the pH of a test solution *via* the reversible transfer of protons between molecules (**Scheme 4.1**). However, the electrode was limited to accurate pH measurements of not more than 8, as well as by the interference from the oxidising or reducing agents.^{1,2}

In a more recent study, Dai *et al.* reported good linear Nernstian potential shifts of various pH-dependent quinone/hydroquinone redox couples such as alizarin, 1,4-dihydroxyanthraquinone (DHAQ), 1,2,3,4-tetrafluoro-5,8-dihydroxyanthraquinone (TFDHAQ) and 2,3-dichloro-5,8-naphthoquinone (DCDHNQ) while monitoring their electrochemical activities in buffered and unbuffered aqueous solutions.^{3,4} The relationship of peak potential and pH can be modelled according to the Nernst equation in **equation 4.1**:

$$E_p = E_{\text{formal}}^0 - 2.303 \left(\frac{mRT}{nF} \right) \text{pH} \quad (4.1)$$

where E_p and E_{formal}^0 are the peak and formal potentials, respectively in V, R is the ideal gas constant, T is the temperature in K, F is the Faraday constant, and m , n are the

number of protons and electrons involved in the redox process, respectively. Hence, a linear relationship can be observed with a plot of peak potential against pH.⁵ **Equation 4.1** is also the encapsulation of proton-coupled electron transfer (PCET) reactions which can be assumed to occur with a concerted nature (simultaneous transfer of electron and proton).^{6–9} It is also possible that PCET reactions can proceed *via* a consecutive mechanism (separate transfer of electron and proton) or a mixed of concerted and consecutive mechanisms.^{10–12} Nevertheless, for a typical $1e^-/1H^+$ redox couple under standard conditions ($T = 298\text{ K}$), a linear negative slope of approximately $59\text{ mV}/\Delta\text{pH}$ is expected based on **Equation 4.1**.

Vitamin compounds have also presented their capability as redox probes in the development of electrochemical sensors. Casimero *et al.* developed a novel composite film of the electropolymer of the phenolic flavin derivative (pPFD) with a sensitivity of $55\text{ mV}/\Delta\text{pH}$ in buffer solutions of pH 2.55 to 8.12.¹³ In a separate study by Hegarty *et al.*, the electropolymer pPFD and ferrocyanide were used as pH-dependent and pH-independent redox active compounds respectively with the former revealing a Nernstian behaviour of $57 \pm 4\text{ mV}/\Delta\text{pH}$ in the range of pH 3 to 8. The redox couple of the pH-independent ferrocyanide served as an internal standard in the measurement of the redox peak potential of pPFD at various pH-values.¹⁴ Similar examples but not limited to vitamin compounds include a mixed self-assembly of 4'-mercapto-*N*-phenylquinone diimine (NPQD) and a macrocyclic nickel complex (MNC) as the pH-dependent and pH-independent compounds respectively. Retna Raj *et al.* reported a Nernstian behaviour of $56 \pm 2\text{ mV}/\Delta\text{pH}$ with NPQD and a relatively constant formal potential of MNC in the physiological pH range of 6.0 to 9.4.¹⁵

Apart from the use of a pair of pH-dependent and pH-independent redox active molecules, a single molecule incorporating the pH-sensing features of the

aforementioned pair of molecules is possible as well. Lafitte *et al.* immobilised anthraquinone-ferrocene (Aq-Fc) as a single molecule pH probe with the potential difference of the pH-dependent anthraquinone moiety and the pH-independent ferrocene moiety as the basis of the pH determination.¹⁶ Besides the common use of the oxygenated quinone species, pH-sensitive polymers have also been used. Pöller *et al.* reported a similar Nernstian behaviour with the modified redox polymers of toluidine blue O (P029-TB) and osmium complex (P032-P231) as the pH-dependent and pH-independent compounds. However, the pH range that was examined in buffered solutions was limited to pH 3–7.5 that falls mostly within the acidic region of the pH scale.¹⁷

Besides the use of conventional glassy carbon working electrodes, voltammetric pH sensing has also been achieved on an *unmodified* edge plane pyrolytic graphite (eppg) electrode. A Nernstian response was obtained upon using such electrode in buffered solutions. This is primarily due to the presence of defect sites on the eppg surface that allows electron transfer processes with dioxygen to form oxo-groups such as carbonyl, hydroxyl and quinyol functional groups.¹⁸

A less common method to immobilise pH-dependent molecules onto the electrode surface is the gentle abrasion on a filter paper with the solid compounds. Streeter *et al.* immobilised two pH-sensitive solid compounds anthraquinone (AQ) and *N,N'*-diphenyl-*p*-phenylenediamine (DPPD) onto a basal plane pyrolytic graphite (bppg) working electrode and reported a consistent Nernstian behaviour for both compounds when examined in buffered solutions at pH 1, 4.6, 6.8 and 9.2. By using two pH-sensitive compounds rather than one, the sensitivity of the pH probe was improved with the tabulation of the Nernstian shift contributed by both compounds.¹⁹

Table 4.1 Summary of the reported literatures that highlight on the use of the pH-dependent and/or pH-independent compound as the basis of voltammetric determination of pH in aqueous media.

pH-dependent compound(s)	pH-independent compound	Working electrode	Potential window (V)	Working pH range	Reference electrode	Reference
alizarin	-	carbon ink (SPE)	[-0.2, 0.9]	2 to 10	Ag/AgCl	3
alizarin, DHAQ, TFDDAQ, or DCDHNQ	-	carbon paste	[0.0, 1.1]	2 to 9	Hg/Hg ₂ Cl ₂	4
pPFD	-	carbon fibre	[-0.8, 1.0]	2 to 8	Ag/AgCl	13
pPFD	ferrocyanide	carbon ink (SPE)	[-0.6, 0.5]	3 to 8	Ag/AgCl	14
NPQD	MNC	Au	[-0.2, 0.7]	6.0 to 9.4	Ag/AgCl	15
AQ-ferrocene	AQ-ferrocene	3-mm GC	[-0.9, 0.8]	2 to 10	Hg/Hg ₂ Cl ₂	16
P029-TB	P032-P231	Au	[-0.4, 1.0]	3.0 to 7.5	Ag/AgCl	17
-	-	eppg	[-0.6, 0.7]	1.0 to 13.0	Hg/Hg ₂ Cl ₂	18
AQ and DPPD	-	bppg	[-1.0, 1.0]	1.0 to 9.2	Hg/Hg ₂ Cl ₂	19

4.2 Results and discussion

4.2.1 Single vitamin systems

Scheme 4.2 Electrochemical oxidation of vitamin E analogue (VEa) in acidic and basic aqueous medium.

The redox chemistry of VEa is shown in **Scheme 4.2** whereby it is oxidised by one-electron to form a cation radical $\text{VEa}^{\bullet+}$ in an electrochemically and chemically reversible process in solution.²⁰ Thus, E_p^{ox} should not change with pH according to **equation 4.1** since no protons are involved in the oxidation mechanism. Such theory fits well with the results of the CV and SWV responses as shown in **Figures 4.1(b)** and **4.2** respectively. In **Figure 4.1(b)**, at pH values ≤ 7 , the voltammetry shows both a forward peak and a reverse peak characteristic of chemically reversible or partially chemically reversible CV. At higher pH-values, the $|i_p^{\text{ox}}/i_p^{\text{red}}|$ ratio is much larger than unity possibly because of hydrolysis of the cation radical. The peak shapes of both the forward and reverse processes are variable because of complications caused by the voltammetric waves being associated with surface confined species. The SWV responses showing the peak potentials of the redox waves at each pH in **Figures 4.2** and **4.3** reveal a relatively constant E_p^{ox} across the pH range measured of +0.85 V versus Ag/AgCl. The detection of a clear voltammetric peak during the SWV experiments indicates that the heterogeneous electron transfer step associated with oxidation of the

surface confined VEa is fast, since SWV is a rapid scanning technique (species undergoing slow electron transfer are difficult to detect by SWV).

Figure 4.1 Cyclic voltammograms obtained at a scan rate of 0.1 V s⁻¹ for the (a) reduction of 2 mM VB₂ and (b) oxidation of 10 mM VEa in DMF, drop cast on a 3-mm diameter planar GC disk, dried in air and then immersed in deoxygenated buffered media at 22 (±2) °C.

Figure 4.2 Square-wave voltammograms obtained for the oxidation of 10 mM VEa in DMF drop cast on a 3-mm diameter planar GC disk and immersed in deoxygenated buffered media at 22 (± 2) °C.

Figure 4.3 Calibration plot of peak potential (from SWV) against pH for the oxidation of 10 mM VEa in DMF drop cast on a 3-mm diameter planar GC disk and immersed in deoxygenated buffered media at 22 (± 2) °C.

To understand the electrochemical behaviour of riboflavin (VB₂) in buffered media, solid state CV was performed in aqueous BR buffers from pH 1–13 with each scan conducted after freshly coating the electrode surface. The redox waves shown in **Figure 4.1(a)** and **Figure 4.4** were observed to shift to more negative potentials as the pH increased. From the CV responses in **Figure 4.1(a)**, the ratio $|i_p^{ox}/i_p^{red}|$ was found to be close to unity between pH 1–13, thereby suggesting a chemically reversible reaction for riboflavin involving the transfer of $2e^-/2H^+$. However, it is interesting to note that larger oxidative and reductive peak currents were observed at pH 12–13 compared to pH 1–11, even though identical amounts of material were placed on the electrode surface at each pH as shown in **Figure 4.1(a)**. A calibration plot based on the SWV responses revealed a negative linear slope of 53.3 mV/ Δ pH from pH 1–11 in **Figure 4.5** that is characteristic of a $2e^-/2H^+$ transfer process (or ne^-/nH^+).

Figure 4.4 Square-wave voltammograms obtained for the reduction of 2 mM VB₂ in DMF drop cast on a 3-mm diameter planar GC disk and immersed in deoxygenated buffered media at 22 ($\pm$ 2) °C.

Figure 4.5 Calibration plot of peak potential (from SWV) against pH for the reduction of 2 mM VB_2 in DMF drop cast on a 3-mm diameter planar GC disk and immersed in deoxygenated buffered media at $22 (\pm 2)^\circ\text{C}$.

A detailed voltammetric and controlled potential electrolysis study on solution phase flavin mononucleotide (FMN) by Tan *et al.* indicated that two protons and two electrons were transferred per molecule in deoxygenated buffered media between pH 3–11.²¹ Since FMN is a derivative of VB_2 and the long hydroxylated chain of VB_2 does not contribute significantly to the electrochemical redox reactions, solid phase VB_2 is postulated to follow an electrochemical square mechanism in buffered media between pH 1–11 (**Scheme 4.3**) and pH > 11 (**Scheme 4.4**) similar to the electrochemical square schemes of solution phase FMN in buffered media between pH 3–13.²¹

As the pK_a of VB_2 is approximately 11, VB_2 exists in its oxidised neutral form Fl_{ox} in acidic buffer between pH 1–11 prior to the electrochemical reduction.^{22,23} Having a sufficiently large proton concentration in the localised environment, the mechanism is postulated to proceed *via* an ECEC mechanism, whereby the symbols E and C refer to

the electron transfer and chemical steps respectively.^{21,24,25} Firstly, VB₂ in its Fl_{ox} state is reduced by one electron to form the anion radical Fl_{rad}^{•-} which in turn is protonated by the buffer to form the neutral radical Fl_{rad}H[•]. This neutral radical undergoes another one electron reduction step to form the anion radical Fl_{red}H⁻ and subsequently becomes protonated by the buffer to form the fully reduced species Fl_{red}H₂ (**Scheme 4.3**). However, only one redox wave is observed in the CV and SWV responses of VB₂ due to the second one-electron transfer step proceeding at a more positive reductive potential than the first one-electron transfer step. Thus, the redox wave involves a single two-electron two-proton transfer step (ECEC mechanism) and a negative linear slope of 53.3 mV/ΔpH from pH 1–11 (**Figure 4.5**) would correspond to a 2e⁻/2H⁺ transfer process.

At pH 12–13, the pH is greater than the pK_a (Fl_{ox}) which results in the deprotonation of the nitrogen atom of the isoalloxazine ring in the oxidised Fl_{ox} and formation of the anion Fl_{ox}⁻ (**Scheme 4.4**).²² The electrochemical reduction mechanism is more complicated than at lower pH values and can also involve the formation of intermediate anionic species that are hydrogen-bonded with H₂O molecules that do not undergo complete protonation.^{21,24,25} Although the reaction still proceeds by two electrons, the number of protons involved in the process can be less than 2, resulting in a lower slope to the potential versus pH curve (**Figure 4.5**). However, the change in mechanism at high pH does not explain why the peak currents are greatest at pH 12 – 13 since the number of electrons involved should be constant over all pH values. Instead, the reason for the change in peak current most likely relates to the percentage of material on the electrode surface that is able to undergo oxidation and reduction. When solids are attached to electrodes, only partial amounts of the solids undergo the redox processes, because the voltammetric processes are limited by the migration of electrolyte counterions into the solid microcrystals.²⁶ Therefore, at high pH, it appears that relatively more

material undergoes the electron transfer reactions, possible due to improved migration within the deposited microcrystals. Nevertheless, this is not detrimental to the operation of the voltammetric electrode as a pH sensor, since the shift in potential is important rather than the peak current.

Scheme 4.3 Proposed electrochemical square-scheme mechanism of VB₂ in buffered media at pH 1 – 11.

Scheme 4.4 Proposed electrochemical square-scheme mechanism of VB₂ in buffered media at pH > 11.

4.2.2 Dual vitamin system

VEa and VB₂ were dissolved in DMF separately and subsequently drop cast on the GC electrode surface prior to voltammetric measurements. After multiple voltammetric trial measurements, the use of 1 mM VB₂ and 10 mM VEa were determined to provide the optimum current heights of both vitamin compounds within the tested pH range. **Figure 4.6** shows the SWV responses when both compounds VEa and VB₂ that were drop cast on the GC electrode surface and immersed in deoxygenated and oxygenated BR buffer, respectively.

Since the peak potential of VEa remained constant with increasing pH as shown in **Figure 4.6**, the peak potential of VB₂ was subtracted against that of VEa at each tested pH to give a plot of peak potential of VB₂ (versus VEa/VEa^{•+}) against pH in deoxygenated and oxygenated buffered media, as shown in **Figure 4.7**. The results indicate a strong linear Nernstian response with negative linear slopes of 54.3 and 53.4 mV/ΔpH observed between pH 1–11 in deoxygenated and oxygenated buffered media respectively, with both conditions indicating a two-electron two-proton transfer mechanism.

There is a slight deviation of the Nernstian slope by 0.9 mV/ΔpH observed in oxygenated buffered media across the tested pH range as compared to that in the deoxygenated buffered media. This could be due to the interference from oxygen reduction reaction (ORR) and the oxidation of the hydroquinone species. Nevertheless, such deviation is very small and can be regarded as insignificant since a strong linear Nernstian response is more crucial to be observed in oxygenated buffered media across a wide pH range.

As the pH increased to above 11, the current response for VEa decreased significantly (**Figure 4.6**). Voltammetric experiments on VEa only attached to the

electrode revealed a drastic decrease of peak current with multiple scans. A possible explanation for such observation could be the irreversible hydrolysis of the $\text{VEa}^{\bullet+}$ cation radical formed from the electrochemical redox reaction at very basic pH. Unlike VEa, VB_2 and its redox species seemed to remain attached onto the electrode surface even at very basic pH conditions since its current height did not drop depreciably with consecutive scans, suggesting a very minimal loss of Fl_{ox} into the solution. However, above pH 11, the reductive response for VB_2 appeared to split into multiple waves which makes it difficult to pick the correct process with which to provide the correct calibration curve. Nevertheless, a sufficiently wide working range of pH 1–11 enables VEa and VB_2 to be used in conjunction as a disposable voltammetric pH sensor.

Figure 4.6 SWVs obtained for the reduction of 1 mM VB_2 and oxidation of 10 mM VEa in DMF drop cast on a 3-mm diameter planar GC disk and immersed in buffered (a) deoxygenated, and (b) oxygenated media at $22 (\pm 2) ^\circ\text{C}$.

Figure 4.7 Calibration plot of peak potential (from SWV) (vs. $\text{VEa}/\text{VEa}^{\bullet+}$) against pH of 1 mM VB_2 in DMF drop cast on a 3-mm diameter planar GC disk and immersed in buffered media under deoxygenated and oxygenated conditions at $22 (\pm 2)^\circ\text{C}$.

4.2.3 Unbuffered Media

The use of a voltammetric pH sensor in unbuffered media is of utmost importance as typical solution samples are usually unbuffered where in-field pH measurements are concerned. Here, voltammetric experiments were investigated in unbuffered media (aqueous KCl solution) with the aim to achieve a linear Nernstian response as a function of pH.

SWV was used without degassing the KCl test solutions and the corresponding results are shown in **Figure 4.8**. The peak potentials of the pH-independent redox compound VEa remained relatively constant (*ca.* 0.79 V versus Ag/AgCl) between pH 1–11. As the pH increased from 1.00 up to 4.00 in the insets of **Figure 4.8(a)** and **4.8(b)**, the peak potential of the VB₂ can be observed to shift with –45.2 and –53.3 mV/pH under deoxygenated and oxygenated conditions respectively. Here, a $2e^-/2H^+$ mechanism is occurring with Fl_{ox} electrochemically reduced to Fl_{red}H₂ as in **Scheme 4.3**. However, a relatively constant peak potential of *ca.* –0.25 V versus Ag/AgCl is observed for VB₂ between pH 4.00–7.00 under both deoxygenated and oxygenated conditions.

The reason that VB₂'s first redox wave remains at a constant potential above pH 4 can be understood based on the total concentration of protons that exist in solution and the extremely high concentration of VB₂ that exists on the electrode surface. Above pH ~ 4 under deoxygenated and oxygenated conditions respectively (**Figure 4.8**), all the localised acidic protons available at the electrode surface will be depleted completely during the reduction process since the concentration of VB₂ on the electrode surface that is able to undergo reduction exceeds the free proton concentration in solution. Therefore, the reduction potential of the VB₂ wave will remain constant as the pH is further increased. The situation is different than exists at a glass pH electrode where the

potential of the glass electrode is determined by the equilibrium reactions of the protons with the silanol groups. For the voltammetric studies described in this work, there must be a proton source available for the equilibrium reaction in **equation 4.1** to occur, which in buffered solutions is able to come from the buffer. In non-buffered solutions at higher $\text{pH} \geq 4$, in the absence of sufficient free protons, the reduced flavins must abstract the proton from water molecules or exist in a hydrogen bonded form, as shown in **Scheme 4.4**. Therefore, the potential remains completely constant since any protonation reactions are coming directly from the water.²⁵

The insufficiency of acidic protons in unbuffered media at higher pH values resulted in no Nernstian shift in the potential of the sensor at $\text{pH} > 4$. Therefore, experiments were attempted by adding a very small concentration of acidic buffer into a 0.1 M KCl solution. The aim of these experiments was to determine whether having a very weakly buffered standard solution that aliquots of the test solution could be added to, would alleviate the problem of needing the solution to be fully buffered for the measurements to work correctly. For these tests, this system can be envisaged as the weakly buffered reference solution containing a miniaturised voltammetric pH sensor, while a separate KCl solution of varying pH is the test solution.

Unlike the buffer used in the previous experiments, phosphate-citrate (PC) buffer was used in substitution of the BR buffer since a sufficiently small acidic buffering capacity is needed to control the extent of the reversible redox conversion of the pH-dependent VB₂. The addition of 0.1 M KCl into the PC buffer in equivalent volumes produced the reference solution (abbreviated as **PC-K**) to ensure a relatively constant ionic strength of KCl, while the test solution was added in equivalent volume to the **PC-K** reference solution. Numerous trials were conducted to achieve the desired

concentration and pH of the **PC-K** reference solution, and it was determined that 1.3 mM at pH 3.9 was ideal for the voltammetric experiments in this section.

Test solutions of various pH were mixed with the **PC-K** reference solution, and the overall pH of the mixture was then measured with the pH meter. Each mixture was subjected to voltammetric scans under deoxygenated and oxygenated conditions as shown in **Figure 4.9**. The linear plots in **Figure 4.10** indicate well-defined Nernstian responses with negative slopes of 50.0 and 50.9 mV/pH under deoxygenated and oxygenated conditions, respectively.

To evaluate the accuracy of the vitamin-based voltammetric sensor, the comparison of voltammetric pH obtained from the voltammetric data against the potentiometric pH obtained from the pH meter was investigated (**Figure 4.11**). Here, strong correlations were noted in both deoxygenated and oxygenated conditions to suggest that both vitamin compounds are potentially viable for use in developing a vitamin-based voltammetric pH sensor.

Figure 4.8 Square-wave voltammograms obtained for 1 mM VB₂ and 10 mM VEa in DMF drop cast on a 3-mm diameter planar GC disk and immersed in unbuffered aqueous KCl solutions (pH 1–7) under (a) deoxygenated and (b) oxygenated conditions at 22 (±2) °C. (Inset): Calibration plot of peak potential (vs. VEa/VEa^{•+}) of VB₂ against pH.

Figure 4.9 SWVs obtained for 1 mM VB₂ and 10 mM VEa in DMF drop cast on a 3-mm diameter planar GC disk and immersed in unbuffered aqueous KCl solutions of varying pH that were mixed in equivalent volumes with the 1.3 mM **PC-K** reference solution to give the pH in parenthesis. (a) Deoxygenated and (b) oxygenated conditions at 22 (±2) °C. The non-parenthesis pH values relate to the acidified/basic KCl test solution prior to the addition of the **PC-K** reference solution.

Figure 4.10 Calibration plot of peak potential (from SWV) (vs. $\text{VEa}/\text{VEa}^{\bullet+}$) of VB_2 against pH across varying unbuffered acidified/basic KCl test solutions mixed in equivalent volumes with 1.3 mM **PC-K** reference solution under deoxygenated (red plot) and oxygenated (blue plot) conditions at $22 (\pm 2) ^\circ\text{C}$.

Figure 4.11 Calibration plot of potentiometric pH against voltammetric pH with experimental data based on the square-wave voltammograms of 1 mM VB₂ and 10 mM VEa in DMF drop cast on a 3-mm diameter planar GC disk and immersed in varying unbuffered acidified/basic KCl test solutions mixed with 1.3 mM **PC-K** reference solution in equivalent volumes under deoxygenated (red plot) and oxygenated (blue plot) conditions at 22 (± 2) °C.

4.3 Conclusion

A vitamin-based voltammetric pH sensor that functions in buffered and unbuffered media that has the potential to be disposable was developed. Redox active compounds drop cast on the electrode surface that were pH dependent (VB₂) and independent (VEa) were investigated concurrently in buffered and unbuffered media across a wide range of pH values. Results from the voltammetric studies of VEa in deoxygenated buffered media indicate the suitability of the compound to be used as a pH-independent redox compound and as a reference compound in a dual vitamin-based voltammetric pH sensor. A linear Nernstian response with a negative slope of close to 59 mV/pH was seen for VB₂ in deoxygenated buffered media. Solid state square-wave voltammetry of VEa and VB₂ simultaneously drop cast on the electrode surface and placed in aqueous solutions yielded a linear Nernstian response in deoxygenated and oxygenated buffered media. However, this was not observed in unbuffered media due to the insufficiency of localised protons at pH values above approximately 4. Further experimental modifications *via* the addition of a very small concentration of acidic buffer (**PC-K** reference solution) into a 0.1 M KCl solution saw a linear Nernstian response achieved in deoxygenated and oxygenated unbuffered media of various pH-values.

4.4 Experimental

4.4.1 Chemicals and reagents

Unless otherwise stated, all chemicals and reagents were used as received. VB₂ (Alfa Aesar) was reagent grade and used as received. VEa was synthesized *via* a reported procedure²⁰, with ¹H and ¹³C NMR spectroscopy confirming the identity of the compound (**Figures A4.1 and A4.2**). Deuterated chloroform (CDCl₃) was obtained from Cambridge Isotope Laboratories Inc. *N,N*-dimethylformamide (DMF) was obtained from VWR and in HPLC grade. Ultrapure water with resistivity >18 MΩ cm was obtained from an ELGA Purelab Option-Q water purification system. Britton-Robinson (BR) buffer was prepared with 0.04 M acetic, phosphoric, and boric acids (Merck), and 0.4 M potassium chloride (Sinopharm Chemical Reagent Co.) for weakly buffered solutions. Phosphate-citrate (PC) buffer was prepared with 0.2 M disodium hydrogen phosphate (Merck) and 0.1 M citric acid (Dae Jung), and dilution was performed with the stock buffer per its required concentration. The required pH of the buffered and unbuffered solutions was adjusted with successive additions of hydrochloric acid (VWR) or sodium hydroxide (Merck). Prior to the first pH measurement of the day, the Metrohm 827 Lab pH meter was calibrated with standard IUPAC buffers to ensure the reproducibility of the pH measurements.

4.4.2 NMR spectra measurements of VEa

VEa was dissolved in CDCl₃ and the ¹H and ¹³C NMR spectra were recorded with the use of a Bruker Avance 300 (300 MHz) NMR spectrometer at room temperature (22 ± 2 °C). Tetramethylsilane (TMS) was used as the internal reference standard in the analysis of the spectra. ¹H NMR (300 MHz, CDCl₃) δ 2.56 (t, *J* = 6.8 Hz, 4H), 2.12 (s,

6H), 1.80 (t, $J = 6.9$ Hz, 4H), 1.28 (s, 12H); $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3) δ 144.7, 123.4, 115.5, 72.3, 32.9, 26.8, 20.1, 11.7.

4.4.3 Preparation of electrode drop castings

The working electrode used was a 3-mm diameter planar glassy carbon (GC) disk (Metrohm). Prior to drop casting the dissolved vitamins on the electrode surface, the GC electrode was polished with 0.3 μm grit alumina oxide powder on the Buehler Ultra-Pad polishing cloth, rinsed thoroughly with ultrapure water to remove any residual powder and then dried with lint-free paper. A stock solution of the vitamins was prepared by dissolving in DMF and subsequently placing a 10 μL aliquot on the surface of the GC electrode with a micropipette and allowing the solvent to evaporate in air for 10 minutes.

4.4.4 Electrochemical procedures

Cyclic voltammetry (CV) and square-wave voltammetry (SWV) experiments were performed with a computer-controlled Eco Chemie Autolab PGSTAT302N potentiostat in a three-electrode cell. The electrochemical cells were dried at 110 $^\circ\text{C}$ for at least an hour prior to use. The auxiliary electrode used in all electrochemical experiments consisted of a platinum wire along with a silver chloride reference electrode (Ag/AgCl in 3 M KCl). The working electrode containing the drop cast vitamin compounds together with the auxiliary and reference electrodes were subsequently immersed in the aqueous buffer at different pH-values. The electrochemical cell was fully assembled in a Faraday cage to minimise any external electromagnetic interference caused while performing the electrochemical scans. A fresh solution was prepared at each desired pH prior to the voltammetric measurement and experiments were conducted at room temperature (22 ± 2 $^\circ\text{C}$). CVs were recorded with a scan rate of 0.1

V s⁻¹ unless otherwise stated, while SWVs were recorded with a pulse period (τ) = 25 Hz, a potential step = 5 mV, and a pulse amplitude = 20 mV.

4.5 References

1. Biilmann, E. The hydrogenation of quinone. *Ann. Chim.* **1921**, *15*, 109.
2. Cullen, E. G.; Biilmann, E. The use of the quinhydrone electrode for hydron concentration determination on serum. *J. Biol. Chem.* **1925**, *64*, 727–738.
3. Dai, C.; Song, P.; Wadhawan, J. D.; Fisher, A. C.; Lawrence, N. S. Screen printed alizarin-based carbon electrodes: Monitoring pH in unbuffered media. *Electroanalysis* **2015**, *27* (4), 917–923.
4. Dai, C.; Chan, C.-W.; Barrow, W.; Smith, A.; Song, P.; Potier, F.; Wadhawan, J. D.; Fisher, A. C.; Lawrence, N. S. A route to unbuffered pH monitoring: A novel electrochemical approach. *Electrochim. Acta* **2016**, *190*, 879–886.
5. Compton, R. G.; Banks, C. E. *Understanding Voltammetry*, 2nd Ed.; Imperial College Press: London, 2010; pp 1–34.
6. Rhile, I. J.; Mayer, J. M. One-electron oxidation of a hydrogen-bonded phenol occurs by concerted proton-coupled electron transfer. *J. Am. Chem. Soc.* **2004**, *126* (40), 12718–12719.
7. Rhile, I. J.; Markle, T. F.; Nagao, H.; DiPasquale, A. G.; Lam, O. P.; Lockwood, M. A.; Rotter, K.; Mayer, J. M. Concerted proton-electron transfer in the oxidation of hydrogen-bonded phenols. *J. Am. Chem. Soc.* **2006**, *128* (18), 6075–6088.
8. Bonin, J.; Costentin, C.; Louault, C.; Robert, M.; Savéant, J.-M. Water (in water) as an intrinsically efficient proton acceptor in concerted proton electron transfers. *J. Am. Chem. Soc.* **2011**, *133* (17), 6668–6674.
9. Mayer, J. M. Understanding hydrogen atom transfer: From bond strengths to Marcus theory. *Acc. Chem. Res.* **2011**, *44* (1), 36–46.
10. Williams, L. L.; Webster, R. D. Electrochemically controlled chemically reversible transformation of α -tocopherol (vitamin E) into its phenoxonium cation. *J. Am. Chem. Soc.* **2004**, *126* (39), 12441–12450.
11. Webster, R. D. New insights into the oxidative electrochemistry of vitamin E. *Acc. Chem. Res.* **2007**, *40* (4), 251–257.
12. Yao, W. W.; Peng, H. M.; Webster, R. D.; Gill, P. M. W. Variable scan rate cyclic voltammetry and theoretical studies on tocopherol (vitamin E) model compounds. *J. Phys. Chem. B* **2008**, *112* (22), 6847–6855.

-
13. Casimero, C.; McConville, A.; Fearon, J.-J.; Lawrence, C. L.; Taylor, C. M.; Smith, R. B.; Davis, J. Sensor systems for bacterial reactors: A new flavin-phenol composite film for the *in situ* voltammetric measurement of pH. *Anal. Chim. Acta* **2018**, *1027*, 1–8.
 14. Hegarty, C.; Kirkwood, S.; Cardosi, M. F.; Lawrence, C. L.; Taylor, C. M.; Smith, R. B.; Davis, J. Disposable solid state pH sensor based on flavin polymer-ferrocyanide redox couples. *Microchem. J.* **2018**, *139*, 210–215.
 15. Raj, C. R.; Okajima, T.; Ohsaka, T. Voltammetric measurement of pH using a mixed self-assembly of macrocyclic nickel(II) complex and diimine on gold electrode. *Electrochem. Commun.* **2002**, *4* (4), 330–335.
 16. Lafitte, V. G. H.; Wang, W.; Yashina, A. S.; Lawrence, N. S. Anthraquinone–ferrocene film electrodes: Utility in pH and oxygen sensing. *Electrochem. Commun.* **2008**, *10* (12), 1831–1834.
 17. Pöller, S.; Schuhmann, W. A miniaturized voltammetric pH sensor based on optimized redox polymers. *Electrochim. Acta* **2014**, *140*, 101–107.
 18. Lu, M.; Compton, R. G. Voltammetric pH sensor based on an edge plane pyrolytic graphite electrode. *Analyst* **2014**, *139* (10), 2397–2403.
 19. Streeter, I.; Leventis, H. C.; Wildgoose, G. G.; Pandurangappa, M.; Lawrence, N. S.; Jiang, L.; Jones, T. G. J.; Compton, R. G. J. A sensitive reagentless pH probe with a *ca.* 120 mV/pH unit response. *Solid State Electrochem.* **2004**, *8*, 718–721.
 20. Peng, H. M.; Choules, B. F.; Yao, W. W.; Zhang, Z.; Webster, R. D.; Long, P. M. W. Long-lived radical cations as model compounds for the reactive one-electron oxidation product of vitamin E. *J. Phys. Chem. B* **2008**, *112* (33), 10367–10374.
 21. Tan, S. L. J.; Kan, J. M.; Webster, R. D. Differences in proton-coupled electron-transfer reactions of flavin mononucleotide (FMN) and flavin adenine dinucleotide (FAD) between buffered and unbuffered aqueous solutions. *J. Phys. Chem. B* **2013**, *117* (44), 13755–13766.
 22. O'Neil, M. J. *The Merck Index – An Encyclopedia of Chemicals, Drugs, and Biologicals*, 14th Ed.; 21, Whitehouse Station, NJ: Merck and Co., Inc., 2006, pp 1413.
 23. Ghasemi, J.; Ghobadi, S.; Abbasi, B.; Kubista, M. Spectrophotometric determination of acidity constants of group B vitamins in different ionic strengths at 25±0.1 °C. *J. Korean Chem. Soc.* **2005**, *49* (3), 269–277.

-
24. Tan, S. L. J.; Webster, R. D. Electrochemically induced chemically reversible proton-coupled electron transfer reactions of riboflavin (vitamin B₂). *J. Am. Chem. Soc.* **2012**, *134* (13), 5954–5964.
25. Tan, S. L. J.; Novianti, M. L.; Webster, R. D. Effects of low to intermediate water concentrations on proton-coupled electron transfer (PCET) reactions of flavins in aprotic solvents and a comparison with the PCET reactions of quinones. *J. Phys. Chem. B* **2015**, *119* (44), 14053–14064.
26. Grygar, T.; Marken, F.; Schröder, U.; Scholz, F. Electrochemical analysis of solids. A review. *Collect. Czech. Chem. Commun.* **2002**, *67* (2), 163–208.

This page is intentionally left blank

Voltammetric Studies of fCNT Dispersions in Various Solvents and Surfactants

This page is intentionally left blank

5.1 Literature review of CNT dispersions in solvents

In **Section 2.2.2**, various methods that are used to disperse carbon nanotubes (CNTs) in solvents have been outlined and described briefly with examples taken from numerous literature reports. The choice of dispersing solvent is also important in the proper dispersion of CNTs. Furthermore, surfactants can serve as good dispersants to CNTs by lowering the surface energy of the nanotubes with relevant examples also outlined in **Section 2.2.2** as well.

5.2 Results and discussion

5.2.1 Voltammetric studies of fCNT dispersions in various solvents

Carbon nanotubes that are functionalised with carboxylic acid groups (fCNTs) were used with their single-walled (fSWCNTs) and multi-walled (fMWCNTs) counterparts in varying percentages by weight (%wt), and subsequently dispersed in three different solvents separately. The bulk solution for testing the modified electrodes was made up of 0.05 M PBS (pH 7.2) with 5 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ redox couple as the quasi-reversible and inner-sphere redox probe.¹ **Figures 5.1, 5.3 and 5.5** show the CVs of the fSWCNT/GCE film electrodes immersed in the bulk solution with various %wt of fMWCNTs that were prepared by dispersing in NMP, DMF and EtOH solvents respectively. Conversely, **Figures 5.2, 5.4 and 5.6** show the CVs of the fMWCNT/GCE film electrodes with various %wt of fMWCNTs that were prepared by dispersing in NMP, DMF and EtOH solvents respectively and subsequently recorded under similar experimental conditions. Based on the observed CV profiles from **Figures 5.1 to 5.6**, the thermodynamics of the redox couple at low scan rates are relatively unaffected by these factors: variation of the fCNTs %wt, type of fCNTs (single or multi-walled), and the choice of the dispersing solvent. This is evidenced by the relatively constant formal

potentials (E^0) of the redox couple between 0.21 to 0.23 V at various fCNTs %wt regardless of the dispersing solvent used.

A quick comparison of the CV profiles between bare GCE and fCNT/GCE film electrodes from **Figures 5.1 to 5.6** suggest that the presence of fCNTs enhances the redox peak currents of the ferri/ferrocyanide couple which is consistent with the findings in literature reports.^{2,3} In addition, the comparison of the CV profiles between fSWCNT/GCE (**Figures 5.1, 5.3 and 5.5**) and fMWCNT/GCE electrodes (**Figures 5.2, 5.4 and 5.6**) across all fCNT %wt and dispersing solvents indicate that the corresponding current heights are higher with the fSWCNT/GCE than the fMWCNT/GCE film electrodes. On the other hand, the observed CV profiles of the fSWCNT/GCE film electrodes across all dispersing solvents in (b)–(f) of **Figures 5.1, 5.3 and 5.5** show that their voltammetric shapes with fSWCNT %wt between 0.05–0.30% at various scan rates are rather similar, and distinct sharp redox waves of the redox couple are noted at their corresponding redox potentials. However, increasing the fCNTs %wt to 0.50%wt in across all dispersing solvents have demonstrated the CV profiles to be more broader and asymmetrical in shape at faster scan rates that is indicative of sluggish kinetics at the electrodes ((f) of **Figures 5.1 to 5.6**). Such difference could be due to the excessively high surface coverage of the electrode area with a high fCNT %wt of 0.50%wt. The interpretation of the kinetics at the film electrodes shall be further discussed in **Section 5.2.2**.

Figure 5.1 CVs of fSWCNT/GCE film electrodes with fSWCNT %wt of (a) 0.00%wt, (b) 0.05%wt, (c) 0.10%wt, (d) 0.20%wt, (e) 0.30%wt, and (f) 0.50%wt dispersed in NMP solvent and drop casted onto a cleanly polished GCE surface. The electrodes are immersed in 0.05 M PBS (pH 7.2) with 5 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ redox couple at 22 (±2) °C.

Figure 5.2 CVs of fMWCNT/GCE film electrodes with fMWCNT %wt of (a) 0.00%wt, (b) 0.05%wt, (c) 0.10%wt, (d) 0.20%wt, (e) 0.30%wt, and (f) 0.50%wt dispersed in NMP solvent and drop casted onto a cleanly polished GCE surface. The electrodes are immersed in 0.05 M PBS (pH 7.2) with 5 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ redox couple at $22 (\pm 2)^\circ\text{C}$.

Figure 5.3 CVs of fSWCNT/GCE film electrodes with fSWCNT %wt of (a) 0.00%wt, (b) 0.05%wt, (c) 0.10%wt, (d) 0.20%wt, (e) 0.30%wt, and (f) 0.50%wt dispersed in DMF solvent and drop casted onto a cleanly polished GCE surface. The electrodes are immersed in 0.05 M PBS (pH 7.2) with 5 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ redox couple at $22 (\pm 2) ^\circ\text{C}$.

Figure 5.4 CVs of fMWCNT/GCE film electrodes with fMWCNT %wt of (a) 0.00%wt, (b) 0.05%wt, (c) 0.10%wt, (d) 0.20%wt, (e) 0.30%wt, and (f) 0.50%wt dispersed in DMF solvent and drop casted onto a cleanly polished GCE surface. The electrodes are immersed in 0.05 M PBS (pH 7.2) with 5 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ redox couple at 22 ($\pm$ 2) $^{\circ}\text{C}$.

Figure 5.5 CVs of fSWCNT/GCE film electrodes with fSWCNT %wt of (a) 0.00%wt, (b) 0.05%wt, (c) 0.10%wt, (d) 0.20%wt, (e) 0.30%wt, and (f) 0.50%wt dispersed in EtOH solvent and drop casted onto a cleanly polished GCE surface. The electrodes are immersed in 0.05 M PBS (pH 7.2) with 5 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ redox couple at $22 (\pm 2)$ °C.

Figure 5.6 CVs of fMWCNT/GCE film electrodes with fMWCNT %wt of (a) 0.00%wt, (b) 0.05%wt, (c) 0.10%wt, (d) 0.20%wt, (e) 0.30%wt, and (f) 0.50%wt dispersed in EtOH solvent and drop casted onto a cleanly polished GCE surface. The electrodes are immersed in 0.05 M PBS (pH 7.2) with 5 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ redox couple at $22 (\pm 2)^\circ\text{C}$.

Generally, a lower peak-to-peak potential separation (ΔE_{pp}) value would suggest a greater electrochemical reversibility of the redox process occurring at the electrode. The ΔE_{pp} values of all film electrodes are determined from the CVs in **Figures 5.1 to 5.6** and subsequently plotted as a function of scan rate in **Figure 5.7**. In **Figure 5.7**, the plot of bare GCE was referenced against the plots of fCNT/GCE film electrodes across all fCNT %wt and dispersing solvents in order to deduce the trends of ΔE_{pp} values for two different types of film electrodes at each dispersing solvent.

By comparing all of the fCNT/GCE film electrodes with the use of the same dispersing solvent, the observed ΔE_{pp} values of the fMWCNT/GCE film electrodes are greater than that of the fSWCNT/GCE film electrodes (**Figure 5.7**). Comparison of the fSWCNT/GCE film electrodes with fCNT %wt up to 0.30% across the three different dispersing solvents revealed that the ΔE_{pp} values increase in the order of DMF < EtOH < NMP (**Figure 5.7(a), (c), (e)**). However, such trend is different for the fMWCNT/GCE film electrodes with fMWCNTs %wt up to 0.30%wt, and follows the ascending order of NMP < EtOH < DMF. Clearly, the choice of the dispersing solvent and the type of fCNTs seem to influence the ΔE_{pp} values of the film electrodes. As for the fCNT/GCE film electrodes with 0.50%wt fCNTs, the ΔE_{pp} values increase in the order DMF < EtOH < NMP and EtOH < NMP < DMF for fSWCNT/GCE and fMWCNT/GCE film electrodes, respectively. The reason behind the contrasting trends between both types of film electrodes is unclear, but it is known that some solvent molecules can be trapped within the nanotube film despite the drying of the electrode surfaces after the drop casting. These solvent molecules are surmised to cause some resistance by impeding the diffusion of the ferri/ferrocyanide molecules through and within the nanotube film. In addition, the solvent molecules may also interact with the surface defects on the fCNTs where electron transfer with the electroactive molecules predominantly occurs. In turn,

the $[\text{Fe}(\text{CN})_6]^{3-/4-}$ species of the redox couple are restricted to a lesser coverage of the defect sites on the fCNTs.^{4,5}

Figure 5.7 Effect of varying scan rates on the peak-to-peak potential separation (ΔE_{pp}) of the fCNT/GCE film electrodes with varying fCNT %wt dispersed in (a, b) NMP, (c, d) DMF, and (e, f) EtOH solvents and drop casted onto a cleanly polished GCE surface and immersed in a 0.05 M PBS (pH 7.2) with 5 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ redox couple at 22 (± 2) $^{\circ}\text{C}$.

5.2.2 Effect of scan rate on the electrocatalytic oxidation of the ferri/ferrocyanide redox couple

As far as the drop casting method is concerned, the orientation of the fCNTs in the film may be randomly distributed as the fCNTs were drop casted onto a cleanly polished GC surface. Such a method of drop casting has been commonly used and reported in literature,^{6,7} and poses the likelihood that a randomly distribution of multi-layer film can be formed on the electrode surface due to difficulty in the manipulation of the CNT assembly during the drop casting process.⁸ In order to perform basic theoretical treatments of the experimental results, assumptions are made on the basis that the nanotubes are uniformly spread within the electroactive area of the electrode surface, and with uniform area of the nanotubes during the voltammetric measurements.

The kinetics of the electron transfer occurring at all of the film electrodes in **Figure 5.7** can be inferred by the comparison of the corresponding ΔE_{pp} values. As the film electrodes are loaded with increasing fCNT %wt, the ΔE_{pp} values are noticed to increase which could be due to the uncompensated resistance. It is also imperative to note that sluggish kinetics of the electron transfer processes are due to uncompensated resistance, but not due to the electrocatalytic effect caused by the amount of fCNT %wt loaded on the bare GC surface.¹⁸ An alternative of evaluating the kinetics occurring at the film electrodes is the use of ΔE_{pp} values to acquire approximations of the kinetic parameters such as the heterogeneous electron transfer rate constant, k^0 . Specifically, k^0 is a quantitative kinetic parameter that describes the rate of electron transfer between the electrode surface and the redox active species.⁹ If the extent of the uncompensated resistance is assumed to be constant across all voltammetric measurements, **equation 5.1** can be applied to determine the experimental values of k^0 (cm s^{-1}):

$$k^0 = \psi \sqrt{v \cdot \frac{\pi D_0 n F}{RT}} \quad (5.1)$$

where ψ is a dimensionless parameter based on the Nicholson model, π is the mathematical constant, v is the applied scan rate (V s^{-1}), D_0 is the diffusion coefficient of the analyte ($\text{cm}^2 \text{s}^{-1}$), n is the number of electrons involved in the redox process, F is the Faraday constant ($96\,485 \text{ C mol}^{-1}$), R is the molar gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$) and T is the absolute temperature (K).¹⁰ The Nicholson method involves the experimental values of the dimensionless parameter ψ to be determined from the variation of ΔE_{pp} against ψ by using the experimental ΔE_{pp} values obtained from the CVs in this chapter.¹¹ The value of D_0 for the ferri/ferrocyanide couple reported in the literature is known to be $7.26 \times 10^{-6} \text{ cm}^2 \text{s}^{-1}$.¹² This value is subsequently used in **equation 5.1** together with the collected experimental data to determine the experimental values of k^0 for all of the fCNT/GCE film electrodes. Meanwhile, the experimental ψ values for all of the film electrodes with various fCNT %wt and dispersing solvents are found to be less than 7 which is characteristic of a quasi-reversible electron transfer associated with the ferri/ferrocyanide redox couple in the voltammetric measurements.¹³

The experimental k^0 values are subsequently calculated with the fitting of ψ values in **equation 5.1** and tabulated in **Table 5.1**. The experimental k^0 value of the bare GC electrode is fundamentally smaller as compared to that of the fCNT/GCE film electrodes. This suggests that the presence of nanotubes has an electrocatalytic effect on the rate of electron transfer of the analyte molecules at the electrode.¹⁴ Although the use of fMWCNTs can contribute to greater current densities of the redox couple than that of fSWCNTs, it is risky to attribute to the better electrocatalytic effect of fMWCNTs than fSWCNTs. The small numerical difference of the experimental k^0 values between

fSWCNT/GCE and fMWCNT/GCE film electrodes in **Table 5.1** suggests that the choice of either type of fCNTs dispersed in similar %wt and solvent does not appear to affect the experimental k^0 values in general. In addition, there is no noticeable trend of the experimental k^0 values as the fCNT %wt dispersed in the same solvent increases. Thus, it might be also unfair to infer that increasing the fCNT %wt will enhance the electrocatalysis of the redox couple at the film electrodes. Moreover, the number of oxygen-containing groups present on the tube ends and walls of the functionalised nanotubes does not significantly influence the magnitude of their experimental k^0 values.^{10,15}

Another observation on the choice of solvent influencing the variation of experimental k^0 values is that the use of EtOH to disperse fCNTs gave rather low experimental k^0 values as compared to the use of NMP or DMF for dispersion. The cause for this is surmised to be NMP and DMF serving as better dispersants to fCNTs than EtOH.^{16,17} Although experimental steps have been taken to ensure optimal solubility of the fCNTs in the dispersing solvent, the solubility of fCNTs may still vary across different solvents.

Table 5.1 Experimental heterogeneous electron transfer rate constants (k^0) of various fCNT/GCE film electrodes immersed in 0.05 M PBS (pH 7.2) with 5 mM $[\text{Fe}(\text{CN})_6]^{3-}$ / $^{4-}$ redox couple at 22 (± 2) °C.

Solvent of dispersion	fCNT/GCE electrode		%wt fCNT(in solvent)/GCE					
			0.00	0.05	0.10	0.20	0.30	0.50
NMP	fSWCNT/GCE	$k^0 / \times 10^{-3} \text{ cm s}^{-1}$	0.83	1.80	1.88	1.72	1.98	1.93
	fMWCNT/GCE	$k^0 / \times 10^{-3} \text{ cm s}^{-1}$	0.83	1.84	1.85	1.67	1.26	1.49
DMF	fSWCNT/GCE	$k^0 / \times 10^{-3} \text{ cm s}^{-1}$	0.83	2.02	1.77	1.81	1.95	1.72
	fMWCNT/GCE	$k^0 / \times 10^{-3} \text{ cm s}^{-1}$	0.83	1.89	1.89	2.20	1.82	1.41
EtOH	fSWCNT/GCE	$k^0 / \times 10^{-3} \text{ cm s}^{-1}$	0.83	1.52	1.54	1.55	1.49	1.39
	fMWCNT/GCE	$k^0 / \times 10^{-3} \text{ cm s}^{-1}$	0.83	1.63	1.56	1.71	1.53	1.42

The Randles-Ševčík equation relates to the *purely* diffusional kinetics for an electron transfer-controlled process occurring at 25°C (**equation 5.2**):

$$i_p = 2.69 \times 10^5 A C D^{\frac{1}{2}} \nu^{\frac{1}{2}} n^{\frac{3}{2}} \quad (5.2)$$

where i_p is the peak current (A), A is the electroactive area (cm^2), C is the concentration of the electroactive redox species in the solution (mol cm^{-3}), D is the diffusion coefficient of the analyte ($\text{cm}^2 \text{s}^{-1}$), ν is the applied scan rate (V s^{-1}) and n is the number of electrons involved in the redox process.¹⁸ If **equation 5.2** is applied to the quasi-reversible process of the ferri/ferrocyanide redox couple occurring at the film electrodes, the diffusion-controlled electron transfer kinetics can be verified *via* the linear plots of i_p vs $\nu^{0.5}$ for all film electrode of various fCNT %wt and dispersing solvents (**Figures 5.9**). The coefficients of determination (R^2) of the regression lines plotted in **Figure 5.9** are then presented in **Table 5.2**. Since the corresponding R^2 values are close to 1, diffusion-controlled electron transfer processes are *said* to be dominant at all of the film electrodes.

Figure 5.8 Schematic representation of the two diffusion processes that can occur at the surface-modified electrode with functionalised carbon nanotubes.

However, Streeter and co-workers cautioned that the peak current of the redox couple measured at the surface-modified electrodes with nanotube coverage is due to

the combination of thin layer diffusion and semi-infinite diffusion processes. The former occurs with the electrochemical oxidation of ferrocyanide species confined between the porous nanotubes at the electrode, while the latter involves semi-infinite diffusion towards the electrode surface (**Figure 5.8**).⁶ Thus, the interpretation of the observed peak currents based *only* on diffusion-controlled process is inappropriate.

To verify the occurrence of thin layer diffusion at the electrode, a double-logarithmic linear plot of oxidative peak current (i_p^{ox}) at each film electrode of various fCNT %wt and dispersing solvents against the applied scan rate (ν) can be employed. The direct relationship of i_p^{ox} with ν is governed by **equation 5.3** for an electrochemically reversible process:

$$i_p^{\text{ox}} = \frac{n^2 F^2}{4RT} \nu A \Gamma \quad (5.3)$$

whereby Γ is the surface coverage of the surface-confined process (mol cm^{-2}), and n , F , R , T , ν , and A have been specified previously.¹⁹ On the assumption that A and Γ are constant for all of the film electrodes in the voltammetric measurements, double-logarithmic linear plots of i_p^{ox} versus ν are illustrated in **Figure 5.10**. The slope values of the linear plots are subsequently presented in **Table 5.3**. Most of the observed slope values are close to 0.50 to indicate that semi-infinite diffusion is the main electron transfer process for all film electrodes with fCNT %wt up to 0.30% regardless of the dispersing solvent.²⁰ If a combination of mass transport processes involving thin layer diffusion and semi-infinite diffusion were to happen, the majority of the slope values of the linear plots should lie between 0.6 to 0.9 which did not happen (**Table 5.3**). Perhaps the most noticeable observation in **Table 5.3** is that the fCNT/GCE film electrodes with the highest fCNT %wt of 0.50%wt exhibit the largest slope values at *ca.* 0.60. If the fCNT %wt is assumed to be high enough at 0.50%wt or more, a combination of thin

layer diffusion with semi-infinite diffusion processes is likely to occur at the fCNT/GCE film electrodes.^{21,22}

However, all of these analyses do not justify sufficiently that a combination of thin layer diffusion with semi-infinite diffusion processes can be used to interpret the kinetics of the electron transfer at the film electrodes as proposed by Streeter and co-workers.⁶ For thin layer diffusion, it occurs more appreciably at slower scan rates ($\leq 100 \text{ mV s}^{-1}$). More electroactive species can thus diffuse from the exterior surface of the nanotubes to within the thin layer of the nanotube film on an extended timescale of the potential sweep. On the contrary, electroactive species have a shorter time to undergo thin layer diffusion at faster scan rates ($\geq 100 \text{ mV s}^{-1}$) and semi-infinite diffusion in the exterior region of the nanotube film becomes more prevalent.^{6,23}

To investigate whether such explanations are consistent for film electrodes with increasing fCNT %wt, peak current versus scan rate is plotted at slower scan rates (10 to 100 mV s^{-1})(**Figure 5.11**) while peak current versus square root of scan rate is plotted at faster scan rates (**Figure 5.12**). The corresponding R^2 values of the plots at slower and faster scan rates are then presented in **Tables 5.4** and **5.5** respectively. The R^2 values of all film electrodes at lower scan rates are observed to be very close to unity to indicate that thin layer diffusion has occurred at the film electrodes (**Figure 5.11**). Clearly, this observation is in contrast with the fact that *only* diffusional kinetics happen at most film electrodes with fCNT 0.05–0.30%wt fCNT in **Figure 5.10** and **Table 5.3**. Moreover, the experimental data points at slower scan rates are increasingly well fitted in **Figure 5.11** as the R^2 values generally increase with fCNT %wt up to 0.50%wt (**Table 5.4**). This observation can be inferred that increasing the fCNT %wt up to 0.50%wt gives rise to a greater extent of thin layer diffusion. It was also mentioned earlier in **Section 5.2.1** that regardless of the fCNT %wt and dispersing solvents used, the current heights with

fSWCNT/GCE film electrodes are higher than that of the fMWCNT/GCE film electrodes. Similarly, caution should be taken in the interpretation of the current responses and ΔE_{pp} values between both types of film electrodes. The effects of thin layer diffusion and semi-infinite diffusion processes should be considered, and not due to the fMWCNTs possessing a better electrocatalytic effect than fSWCNTs.^{4,21–23} As for faster scan rates, the R^2 values of all film electrodes in **Table 5.5** have a minimum value of 0.9900 to verify the dominance of the semi-infinite diffusion process. Thus, the kinetics of the electron transfer at all fCNT/GCE film electrodes is best interpreted by the quantitative analysis of the R^2 values in the linear plots at slow and fast scan rates.

Figure 5.9 Linear plots of peak current versus square root of scan rate of the fCNT/GCE film electrodes with varying fCNT %wt dispersed in (a, b) NMP, (c, d) DMF, and (e, f) EtOH solvents and drop casted onto a cleanly polished GCE surface and immersed in a 0.05 M PBS (pH 7.2) with 5 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ redox couple at $22 (\pm 2) ^\circ\text{C}$.

Table 5.2 Coefficients of determination (R^2) of the regression lines for all fCNT/GCE film electrodes plotted in **Figure 5.9**.

Solvent of dispersion	fCNT/GCE electrode	R^2 (i_p^{ox} or i_p^{red})	%wt fCNT(in solvent)/GCE					
			0.00	0.05	0.10	0.20	0.30	0.50
NMP	fSWCNT/ GCE	$R^2 (i_p^{ox})$	0.9999	0.9987	0.9990	0.9986	0.9999	0.9970
		$R^2 (i_p^{red})$	0.9912	0.9943	0.9943	0.9910	0.9970	0.9999
	fMWCNT/ GCE	$R^2 (i_p^{ox})$	0.9999	0.9985	0.9984	0.9990	0.9973	0.9998
		$R^2 (i_p^{red})$	0.9912	0.9934	0.9927	0.9907	0.9818	0.9998
DMF	fSWCNT/ GCE	$R^2 (i_p^{ox})$	0.9999	0.9986	0.9991	0.9986	0.9988	0.9998
		$R^2 (i_p^{red})$	0.9912	0.9940	0.9943	0.9952	0.9949	0.9964
	fMWCNT/ GCE	$R^2 (i_p^{ox})$	0.9999	0.9991	0.9983	0.9987	0.9988	0.9994 [†]
		$R^2 (i_p^{red})$	0.9912	0.9924	0.9882	0.9935	0.9893	0.9991 [†]
EtOH	fSWCNT/ GCE	$R^2 (i_p^{ox})$	0.9999	0.9990	0.9987	0.9987	0.9991	0.9981
		$R^2 (i_p^{red})$	0.9912	0.9917	0.9914	0.9911	0.9979	0.9999
	fMWCNT/ GCE	$R^2 (i_p^{ox})$	0.9999	0.9989	0.9997	0.9999	0.9999	0.9996
		$R^2 (i_p^{red})$	0.9912	0.9924	0.9961	0.9994	0.9996	0.9999

[†] Regression line is extrapolated beyond 500 mV s⁻¹ (22.4 mV^{0.5} s^{-0.5}) due to the unavailability of redox peaks above the aforementioned scan rate.

Figure 5.10 Linear plots of $\log$ oxidative peak current versus $\log$ scan rate of the fCNT/GCE film electrodes with varying fCNT %wt dispersed in (a, b) NMP, (c, d) DMF, and (e, f) EtOH solvents and drop casted onto a cleanly polished GCE surface and immersed in a 0.05 M PBS (pH 7.2) with 5 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ redox couple at 22 (± 2) $^{\circ}\text{C}$.

Table 5.3 Slopes and coefficients of determination (R^2) of the regression line for bare GCE and all fCNT/GCE film electrodes plotted in **Figure 5.10**.

Solvent of dispersion	fCNT/GCE electrode		%wt fCNT(in solvent)/GCE					
			0.00	0.05	0.10	0.20	0.30	0.50
NMP	fSWCNT/GCE	slope	0.4824	0.5071	0.4970	0.4951	0.5544	0.6222
		R^2	0.9999	0.9943	0.9966	0.9973	0.9982	0.9999
	fMWCNT/GCE	slope	0.4824	0.5014	0.5002	0.4706	0.4420	0.5898
		R^2	0.9999	0.9956	0.9941	0.9990	0.9983	0.9974
DMF	fSWCNT/GCE	slope	0.4824	0.5023	0.4848	0.4892	0.5095	0.5600
		R^2	0.9999	0.9955	0.9982	0.9973	0.9955	0.9942
	fMWCNT/GCE	slope	0.4824	0.4703	0.4940	0.5144	0.4945	0.5633 [†]
		R^2	0.9999	0.9996	0.9996	0.9976	0.9975	0.9988 [†]
EtOH	fSWCNT/GCE	slope	0.4824	0.4811	0.4800	0.4784	0.4952	0.5815
		R^2	0.9999	0.9982	0.9982	0.9983	0.9985	0.9992
	fMWCNT/GCE	slope	0.4824	0.4894	0.4943	0.5342	0.5563	0.5807
		R^2	0.9999	0.9981	0.9993	0.9993	0.9986	0.9994

[†] Regression line of the 0.50%wt fMWCNT/GCE electrode is extrapolated beyond 500 mV s⁻¹ (2.70 in *log* value) due to the unavailability of redox peaks above the aforementioned scan rate.

Figure 5.11 Linear plots of peak current versus scan rate of fCNT/GCE film electrodes with varying fCNT %wt dispersed in (a) NMP, (b) DMF, and (c) EtOH solvents and drop casted onto a cleanly polished GCE surface and immersed in a 0.05 M PBS (pH 7.2) with 5 mM $[Fe(CN)_6]^{3-/4-}$ redox couple at $22 (\pm 2) ^\circ C$.

Table 5.4 Coefficients of determination (R^2) of the regression lines for all fCNT/GCE film electrodes plotted in **Figure 5.11** with scan rates from 10 to 100 mV s⁻¹.

Solvent of dispersion	fCNT/GCE electrode	R^2 (i_p^{ox} or i_p^{red})	%wt fCNT(in solvent)/GCE					
			0.00	0.05	0.10	0.20	0.30	0.50
NMP	fSWCNT/ GCE	R^2 (i_p^{ox})	0.9738	0.9545	0.9534	0.9732	0.9791	0.9868
		R^2 (i_p^{red})	0.9627	0.9673	0.9745	0.9703	0.9788	0.9864
	fMWCNT/ GCE	R^2 (i_p^{ox})	0.9738	0.9602	0.9543	0.9696	0.9577	0.9709
		R^2 (i_p^{red})	0.9627	0.9629	0.9685	0.9699	0.9547	0.9884
DMF	fSWCNT/ GCE	R^2 (i_p^{ox})	0.9738	0.9614	0.9655	0.9641	0.9602	0.9662
		R^2 (i_p^{red})	0.9627	0.9646	0.9686	0.9673	0.9658	0.9714
	fMWCNT/ GCE	R^2 (i_p^{ox})	0.9738	0.9713	0.9668	0.9788	0.9708	0.9754
		R^2 (i_p^{red})	0.9627	0.9684	0.9698	0.9753	0.9710	0.9736
EtOH	fSWCNT/ GCE	R^2 (i_p^{ox})	0.9738	0.9654	0.9641	0.9574	0.9688	0.9774
		R^2 (i_p^{red})	0.9627	0.9675	0.9650	0.9707	0.9710	0.9786
	fMWCNT/ GCE	R^2 (i_p^{ox})	0.9738	0.9671	0.9727	0.9677	0.9784	0.9841
		R^2 (i_p^{red})	0.9627	0.9681	0.9734	0.9736	0.9795	0.9836

Figure 5.12 Linear plots of peak current versus square root of scan rate of the fCNT/GCE film electrodes with varying fCNT %wt dispersed in (a, b) NMP, (c, d) DMF, and (e, f) EtOH solvents and drop casted onto a cleanly polished GCE surface and immersed in a 0.05 M PBS (pH 7.2) with 5 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ redox couple at 22 (± 2) °C.

Table 5.5 Coefficients of determination (R^2) of the regression lines for all fCNT/GCE film electrodes plotted in **Figure 5.12** with scan rates from 100 to 1000 mV s⁻¹.

Solvent of dispersion	fCNT/GCE electrode	R^2 (i_p^{ox} or red)	%wt fCNT(in solvent)/GCE					
			0.00	0.05	0.10	0.20	0.30	0.50
NMP	fSWCNT/ GCE	R^2 (i_p^{ox})	0.9999	0.9997	0.9994	0.9999	0.9999	0.9993
		R^2 (i_p^{red})	0.9983	0.9973	0.9979	0.9960	0.9975	0.9999
	fMWCNT/ GCE	R^2 (i_p^{ox})	0.9999	0.9992	0.9994	0.9999	0.9990	0.9999
		R^2 (i_p^{red})	0.9983	0.9983	0.9976	0.9941	0.9953	0.9999
DMF	fSWCNT/ GCE	R^2 (i_p^{ox})	0.9999	0.9997	0.9998	0.9996	0.9997	0.9999
		R^2 (i_p^{red})	0.9983	0.9976	0.9968	0.9982	0.9980	0.9977
	fMWCNT/ GCE	R^2 (i_p^{ox})	0.9999	0.9996	0.9995	0.9995	0.9991	0.9994 [†]
		R^2 (i_p^{red})	0.9983	0.9971	0.9935	0.9962	0.9999	0.9968 [†]
EtOH	fSWCNT/ GCE	R^2 (i_p^{ox})	0.9999	0.9995	0.9992	0.9988	0.9993	0.9987
		R^2 (i_p^{red})	0.9983	0.9961	0.9968	0.9977	0.9994	0.9999
	fMWCNT/ GCE	R^2 (i_p^{ox})	0.9999	0.9995	0.9999	0.9992	0.9999	0.9998
		R^2 (i_p^{red})	0.9983	0.9969	0.9987	0.9980	0.9998	0.9999

[†] Regression line is extrapolated beyond 500 mV s⁻¹ (22.4 mV^{0.5} s^{-0.5}) due to the unavailability of redox peaks above the aforementioned scan rate.

5.2.3 Voltammetric studies of fCNT dispersions in the presence of surfactants

When the film electrodes were immersed in the bulk solution containing the ferri/ferrocyanide redox couple, the use of NMP in the dispersion of 0.30%wt fCNTs led to desirable voltammetric results with the least sluggish kinetics among the dispersing solvents investigated in **Section 5.2.1**. Thus, NMP was used as the dispersing solvent of fCNTs in this section. Cationic, anionic and non-ionic surfactants such as didodecyldimethylammonium bromide (DDAB), sodium dodecyl sulfate (SDS) and Tween 20 (T20) were used to investigate the voltammetry of the film electrodes immersed in the bulk solution that contained varying concentrations of the surfactant. The experimental details of the preparation of fCNT dispersions in the presence of surfactants and the subsequent modified electrodes are outlined in **Section 5.4.2**. A slow scan rate of 20 mV s^{-1} was used in all CV measurements throughout this section to mitigate the ohmic potential (iR) drop.²⁴

Figure 5.13 shows the CVs of the fSWCNT/GCE and fMWCNT/GCE film electrodes immersed in 0.05 M PBS (pH 7.2) with 5 mM of $[\text{Fe}(\text{CN})_6]^{3-/4-}$ as the electroactive redox couple and varying surfactant concentrations at a scan rate of 20 mV s^{-1} . The peak shapes of the initial CVs for fSWCNT/GCE and fMWCNT/GCE film electrodes immersed in the absence of the surfactant were observed to be relatively similar with distinct redox waves noted at a constant formal potential values of *ca.* 0.21 V (**Figure 5.13**).

CVs recorded with fSWCNT/GCE and fMWCNT/GCE film electrodes immersed in the absence and presence of the cationic surfactant DDAB reveal symmetrical shapes with distinct sharp peaks of the redox waves (**Figure 5.13(a) and (b)**). The ratio $|i_p^{\text{ox}}/i_p^{\text{red}}|$ is also close to unity for both types of film electrodes to indicate the nature of the chemically reversible electron transfer process occurring at the electrodes. Comparison

of the peak anodic and cathodic currents for both types of the film electrodes immersed in the bulk solution with three different surfactants demonstrated that the use of DDAB resulted in the greatest peak anodic and cathodic peak currents (**Figure 5.14**). Both types of film electrodes saw their ΔE_{pp} values lowered upon the addition of the bulk DDAB up to its cmc value (**Figure 5.15**). Such observations are due to the electrostatic interaction of the DDAB cations with the anionic species of the ferri/ferrocyanide redox couple and the negatively charged carboxyl group of the nanotube defect sites. With the adsorption of the DDAB cations on the negatively charged active sites of the fCNTs, the surface energy of the fCNTs are lowered to facilitate the electron transfer process.^{25,26} Thus, the current responses due to DDAB should be interpreted based on this combination: (1) diffusion of the ferri/ferrocyanide redox species within the porous layer of fCNT, (2) adsorption of the ferri/ferrocyanide redox species onto the fCNT film, and (3) diffusion of the ferri/ferrocyanide redox species in the diffusing bulk area.

With subsequent increment of the bulk DDAB concentration, there might be some loss of electroactive mass from the electrode surface into the bulk solution during the voltammetric measurements to account for the slightly decreasing peak current upon successive increments of the bulk DDAB concentration. On the other hand, the ΔE_{pp} values of both types of film electrodes are noticed to increase slowly when the bulk DDAB concentration is above the cmc value (**Figure 5.15(a)**). This is likely due to saturation of the active sites on the electrode surface and an increase in the electrode resistance with the formation of more DDAB micelles to interfere the electron transfer occurring at the electrode.^{27,28} Nevertheless, both types of film electrodes saw the least decline of the anodic and cathodic peak currents when they are immersed in the bulk solutions with DDAB than with T20 or SDS due to the effect of electrostatic stability (**Figure 5.14**).

For the non-ionic surfactant T20, the anodic and cathodic waves of the ferri/ferrocyanide redox couple with the fSWCNT/GCE film electrodes are noticed to be broad and split upon increasing the bulk surfactant concentration (**Figure 5.13(c)**). The redox peak potentials and currents associated with fSWCNT/GCE film electrodes are observed to be relatively constant with and without the addition of the non-ionic surfactant T20 into the bulk solution (**Figure 5.14(c) and (d)**). The observed ΔE_{pp} values with the fSWCNT/GCE film electrodes in the absence and presence of increasing bulk T20 concentration remain relatively constant (**Figure 5.15(b)**). In contrast, the voltammetric behaviours of the fMWCNT/GCE film electrodes with increasing T20 concentration are much different as compared to that of the fSWCNT/GCE film electrodes under similar experimental conditions. When the lowest concentration of T20 is added to the bulk solution, the oxidative peak potential of the redox couple shifts cathodically from 0.28 V to 0.49 V, while the reductive peak potential shifts anodically from 0.14 V to -0.02 V with the decrease in intensity for both redox peaks (**Figure 5.14(c) and (d)**). As the T20 concentration continues to increase, the oxidative and reductive peak potentials of the redox couple associated with the fMWCNT/GCE film electrodes remains relatively constant at *ca.* 0.50 V and -0.03 V respectively. Consequentially, the ΔE_{pp} values associated with the fMWCNT/GCE film electrodes increased from 148 mV to 529 mV upon increasing the bulk T20 concentration from zero to between 15 μ M and 240 μ M respectively (**Figure 5.15(b)**). The redox peak currents associated with the fMWCNT/GCE film electrodes decreased by two-third when the bulk T20 concentration was doubled from 120 μ M to 240 μ M. The drastic differences in the potential shift and current change observed with both types of film electrodes are speculated to be the much thicker wall diameter of the fMWCNTs than

fSWCNTs, which in turn adversely affected the electron transfer at the electrode surface upon the increase of the bulk T20 concentration.

As for the anionic surfactant SDS, pre-micelles are formed with electrostatic repulsion between the negatively charged SDS anions, negatively charged groups on the fCNTs, and the negatively charged species of the ferri/ferrocyanide redox couple when the bulk SDS concentration is lesser than the cmc value. Such electrostatic repulsion is expected to persist with no surfactant adsorption on the electrode surface when the SDS bulk concentration is equal or more than the cmc value.²⁹ Thus, the fSWNCT/GCE and fMWCNT/GCE film electrodes are observed with their peak redox currents of the redox couple to remain relatively constant (**Figure 5.14(e)** and **(f)**). As for the anodic and cathodic peak potentials associated with both types of film electrodes, these peaks are observed to shift positively and negatively respectively in general upon the increase of the bulk SDS (**Figure 5.14(e)** and **(f)**). When the bulk T20 concentration increases, the degree of static repulsion is expected to increase which impedes with the redox electron transfer occurring at the electrode surface. Consequentially, both types of fCNT/GCE film electrodes share the similar trend of increasing ΔE_{pp} values with increasing bulk SDS concentration (**Figure 5.15(c)**).

Figure 5.13 CVs of fSWCNT/GCE film electrodes (fCNT %wt = 0.30%wt) immersed in 0.05 M PBS (pH 7.2) with 5 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ redox couple and varying concentrations of surfactants (a, c, e) at a scan rate of 20 mV s^{-1} at $22 (\pm 2) ^\circ\text{C}$. CVs of fMWCNT/GCE film electrodes (fCNT %wt = 0.30%wt) immersed in varying concentrations of surfactants (b, d, f) are also recorded under similar experimental conditions.

Figure 5.14 Effect of varying concentrations of (a, b) DDAB, (c, d) T20, and (e, f) SDS in 0.05 M PBS (pH 7.2) with 5 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ redox couple on the oxidative and reductive peak potentials (left vertical axis, red) and currents (right vertical axis, blue) of the fCNT/GCE film electrodes (fCNT %wt = 0.30%wt) at a scan rate of 20 mV s^{-1} at $22 (\pm 2) ^\circ\text{C}$.

Figure 5.15 Effect of varying surfactant concentrations of (a) DDAB, (b) T20, and (c) SDS in 0.05 M PBS (pH 7.2) with 5 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ redox couple on the peak-to-peak potential separation (ΔE_{pp}) of the fSWCNT/GCE and fMWCNT/GCE film electrodes (fCNT %wt = 0.30%wt) at a scan rate of 20 mV s^{-1} at 22 (± 2) $^{\circ}\text{C}$.

5.2.4 Effect of scan rate on the electrocatalytic oxidation of the ferri/ferrocyanide redox couple in the presence of DDAB

To investigate the nature of the kinetics occurring at the fSWCNT/GCE and fMWCNT/GCE film electrodes, each type of film electrode was immersed separately in the bulk solution with the concentration of the cationic surfactant DDAB equal to its cmc value. The CVs of both types of film electrodes were recorded with variable scan rates as shown in **Figure 5.16**.

Figure 5.16 CVs of (a) fSWCNT/GCE and (b) fMWCNT/GCE film electrodes (fCNT %wt = 0.30%wt) in 0.05 M PBS (pH 7.2) with 80 μ M DDAB and 5 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ redox couple and at scan rates ranging from 10 to 750 mV s^{-1} at 22 (± 2) $^{\circ}\text{C}$.

As the scan rate becomes faster, the anodic and cathodic peak potentials are observed to shift in the positive and negative directions respectively for both types of film electrodes. Reports from literature have shown that diffusion-controlled electron transfer processes occur at electrodes that are surface-modified with CNTs and surfactants.^{30,31} Likewise, linear plots of peak current against the square root of scan rate revealed that the R^2 values of both types of film electrodes are close to unity (**Figure**

5.17(a) and **(b)**).¹⁸ Double logarithmic plot of peak current against scan rate was also plotted for both types of film electrodes with the following linear regression equations:

$$\text{fSWCNT/GCE:} \quad \log i_p^{\text{ox}} = 0.5446 \log \nu + 1.2561 \quad (R^2 = 0.9975)$$

$$\text{fMWCNT/GCE:} \quad \log i_p^{\text{ox}} = 0.4779 \log \nu + 1.4205 \quad (R^2 = 0.9963)$$

The slopes of the linear regression equations for both film electrodes are close to 0.5 to suggest the occurrence of a semi-infinite diffusion at both electrodes.²⁰ However, the quantitative method of comparing the R^2 values at slow and fast scan rates in **Section 5.2.2** needs to be used to confirm if thin layer diffusion happens at film electrodes that are immersed in the bulk solution with DDAB. The R^2 values of both fSWCNT/GCE and fMWCNT/GCE film electrodes at slow scan rates in **Figure 5.18** are close to unity. These values are also compared with their counterpart electrodes which are immersed in the similar bulk solution but in the absence of DDAB under similar experimental conditions (**Table 5.6**). The comparison indicates that the effect of thin layer diffusion at both fSWCNT/GCE and fMWCNT/GCE film electrodes immersed in the bulk solution with DDAB cannot be overlooked.^{6,21,22}

Table 5.6 Coefficients of determination (R^2) of the regression lines for all fCNT/GCE film electrodes immersed in 0.05 M PBS (pH 7.2) containing 5 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ redox couple and with and without DDAB at scan rates from 100 to 1000 mV s^{-1} at 22 (± 2) °C. † R^2 values are taken from **Table 5.4**.

	fSWCNT/GCE		fMWCNT/GCE	
	bulk solution with DDAB	bulk solution without DDAB [†]	bulk solution with DDAB	bulk solution without DDAB [†]
R^2 (i_p^{ox})	0.9750	0.9791	0.9688	0.9577
R^2 (i_p^{red})	0.9936	0.9788	0.9936	0.9547

Figure 5.17 Linear plots of anodic and cathodic peak currents against square root of scan rate of the (a) fSWCNT/GCE and (b) fMWCNT/GCE film electrodes (fCNT %wt = 0.30%wt), and $\log$ anodic peak current against $\log$ scan rate of the (c) fSWCNT/GCE and (d) fMWCNT/GCE film electrodes in 0.05 M PBS (pH 7.2) with 80 μM DDAB and 5 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ redox couple and scan rates ranging from 10 to 750 mV s^{-1} at 22 (± 2) $^\circ\text{C}$.

Figure 5.18 Linear plots of (a, c) peak current versus scan rate, and (b, d) peak current versus square root of scan rate of the fCNT/GCE film electrodes (fCNT %wt = 0.30%wt) with fCNTs dispersed in NMP and drop casted onto a cleanly polished GCE surface and immersed in 0.05 M PBS (pH 7.2) with 80 μM DDAB and 5 mM $[Fe(CN)_6]^{3-/4-}$ redox couple at 22 (± 2) $^{\circ}C$.

5.3 Conclusion

The use of three different solvents in the dispersion of fSWCNTs and fMWCNTs to prepare the respective film electrodes was investigated with CV. Various factors such as the amount of fCNTs, type of fCNTs and variable scan rates were studied upon with further quantitative analysis of the experimental results. Comparison of the calculated experimental k^0 values of the fSWCNT/GCE and fMWCNT/GCE film electrodes has demonstrated that the type of fCNTs and the %wt of the fCNTs used in the dispersion do not affect the rate of heterogeneous electron transfer occurring at the electrodes. The kinetics of the electron transfer at all fCNT/GCE film electrodes is found to be best interpreted by the quantitative analysis of the R^2 values in the linear plots of i_p versus v and i_p versus $v^{0.5}$ at slow and fast scan rates, respectively. The results of the aforementioned interpretation is also consistent with the view that both thin layer diffusion and semi-infinite diffusion should be considered for surface-modified electrodes that involve nanotubes. For all of the fCNT/GCE film electrodes regardless of the fCNT %wt and dispersing solvent, thin layer diffusion and semi-infinite diffusion operate predominantly at slow and fast scan rates respectively. The effect of thin layer diffusion is also investigated to be stronger when the fCNT %wt of all film electrodes increases.

The use of various types of surfactants in the bulk solution was studied as well. CV results suggest that the use of the cationic surfactant DDAB offers the best current responses when fSWCNT/GCE and fMWCNT/GCE film electrodes are immersed in the bulk solution. The effect of increasing bulk surfactant concentration was also investigated with both types of film electrodes. Optimum current responses with the least ΔE_{pp} values were obtained with the film electrodes immersed in bulk solutions containing bulk DDAB concentrations at the cmc value. Caution should also be taken

in the interpretation of the peak currents measured at both fSWCNT/GCE and fMWCNT/GCE film electrodes immersed in the DDAB-containing bulk solution. This is confirmed by the occurrence of thin layer diffusion and semi-infinite diffusion processes at slow and fast scan rates *via* the quantitative analysis of the R^2 values in the corresponding linear plots at slow and fast scan rates.

5.4 Experimental

5.4.1 Chemicals

Unless otherwise specified, all chemicals and reagents were of analytical grade and used as received. Both single (90%, 1–2 nm diameter, and 5–30 μm length) and multi walled carbon nanotubes with carboxylic acid functionalisation (95%, 50–80 nm diameter, and 10–20 μm length) were obtained from Nanostructured and Amorphous Materials Inc. in Texas, USA and used as received. Sodium dihydrogen phosphate ($\geq 98\%$), disodium hydrogen phosphate, ($\geq 99.0\%$), potassium hexacyanoferrate(II) trihydrate ($\geq 98.5\%$) and potassium hexacyanoferrate(III) ($\geq 99.0\%$) were purchased from Merck. The solvents *N*-methyl-2-pyrrolidone (NMP) (99+%), *N,N*-dimethylformamide (DMF) (99.0%) and ethanol (EtOH) were obtained from Alfa Aesar, VWR Chemicals, and Fisher Chemical respectively. The surfactants didodecyldimethylammonium bromide (DDAB) (98%) and Tween 20 (T20) (cmc 0.06) were purchased from Merck, while sodium dodecyl sulfate (SDS) was obtained from Hoefer, Inc. All solutions were prepared using ultrapure water obtained from an ELGA Purelab Option-Q water purification system with a resistivity of not less than 18 M Ω cm at 25 °C. Phosphate buffer solution (PBS) at pH 7.2 was prepared with sodium dihydrogen phosphate, disodium hydrogen phosphate and ultrapure water and used as the supporting electrolyte. Prior to the first pH measurement of the day, the Metrohm 827 Lab pH meter was calibrated with standard IUPAC buffers to ensure the reproducibility of the pH measurements.

5.4.2 Preparation of the fCNTs suspensions and modified electrodes

Prior to the addition of the solvent to the fCNTs, the fSWCNTs and fMWCNTs were pre-weighed accordingly to make up a suspension in %wt present in the solvent.

The fCNT suspensions were ultrasonicated for 15 minutes at room temperature (22 ± 2 °C) with the use of an ultrasonicator (Elmasonic E30H) having an ultrasonic frequency of 37 kHz. Subsequently, the suspensions were transferred to a Vortex-Genie 2T vortex mixer (Scientific Industries) at 2700 rpm for 45 to 60 minutes at room temperature (22 ± 2 °C) to ensure homogeneity with uniform diffusion of the fCNTs in the solvent.

Prior to the drop casting of the fCNT suspension on the electrode surface, the GC electrode was polished with 0.3 μm grit alumina oxide powder on the Buehler Ultra-Pad polishing cloth, rinsed thoroughly with ultrapure water to remove any residual powder and then dried clean with lint-free paper. A 10 μL aliquot of the fCNT dispersion was then deposited on the surface of the GC electrode with a micropipette and the solvent then left to evaporate in the air prior to the immersion of the dried electrode in the voltammetric glass cell. As the NMP solvent took a much longer time to desorb from the electrode surface at room temperature than DMF and EtOH, a heat gun with the lowest fan speed was positioned at a far distance to expedite the air drying time of the aliquot on the electrode surface.

5.4.3 Electrochemical procedures

Electrochemical experiments were performed with PBS as the background electrolyte. Cyclic voltammetry (CV) was carried out with a computer-controlled Eco Chemie Autolab PGSTA128N. The electrochemical cells were dried at 110 °C for at least an hour prior to use. The auxiliary electrode used in all electrochemical experiments consisted of a platinum wire along with a silver chloride reference electrode (Ag/AgCl in 3 M KCl). The working electrode used was a 3-mm diameter planar GC disk (Metrohm). For each electrochemical experiment, the working electrode containing the dried drop cast functionalised CNTs (fCNTs) was subsequently immersed in the test

solution together with the auxiliary and reference electrodes. The electrochemical cell was fully assembled in the Faraday cage to minimise any external electromagnetic interference caused while performing the electrochemical scans. A fresh solution was prepared for each voltammetric experiment and deoxygenated by purging with high purity argon gas prior to all voltammetric measurements. All experiments were conducted at room temperature (22 ± 2 °C).

5.5 References

1. Xiong, L.; Batchelor-McAuley, C.; Ward, K. R.; Downing, C.; Hartshorne, R. S.; Lawrence, N. S.; Compton, R. G. Voltammetry at graphite electrodes: The oxidation of hexacyanoferrate (II) (ferrocyanide) does not exhibit pure outer-sphere electron transfer kinetics and is sensitive to pre-exposure of the electrode to organic solvents. *J. Electroanal. Chem.* **2011**, *661* (1), 144–149.
2. Antiochia, R.; Lavagnini, I. Magno, F.; Valentini, F.; Palleschi, G. Single-wall carbon nanotube paste electrodes: A comparison with carbon paste, platinum and glassy carbon electrodes *via* cyclic voltammetric data. *Electroanalysis* **2004**, *16* (17), 1451–1458.
3. Perenlei, G.; Tan, W. T.; Yusof, N. A.; Goh, J. K. Voltammetric detection of potassium ferricyanide mediated by multi-walled carbon nanotube/titanium dioxide composite modified glassy carbon electrode. *Int. J. Electrochem. Sci.* **2011**, *6* (2), 520–531.
4. Robinson, J. A.; Snow, E. S.; Bădescu, Ș. C.; Reinecke, T. L.; Perkins, F. K. Role of defects in single-walled carbon nanotube chemical sensors. *Nano Lett.* **2006**, *6* (8), 1747–1751.
5. Lau, C. H.; Cervini, R.; Clarke, S. R.; Markovic, M. G.; Matison, J. G.; Hawkins, S. C.; Huynh, C. P.; Simon, G. P. The effect of functionalization on structure and electrical conductivity of multi-walled carbon nanotubes. *J. Nanopart. Res.* **2008**, *10*, 77–88.
6. Streeter, I.; Wildgoose, G. G.; Shao, L. D.; Compton, R. G. Cyclic voltammetry on electrode surfaces covered with porous layers: An analysis of electron transfer kinetics at single-walled carbon nanotube modified electrodes. *Sens. Actuators, B* **2008**, *133* (2), 462–466.
7. Henstridge, M. C.; Dickinson, E. J. F.; Aslanoglu, M.; Batchelor-McAuley, C.; Compton, R. G. Voltammetric selectivity conferred by the modification of electrodes using conductive porous layers or films: The oxidation of dopamine on glassy carbon electrodes modified with multiwalled carbon nanotubes. *Sens. Actuators, B* **2010**, *145* (1), 417–427.
8. Pumera, M. Voltammetry of carbon nanotubes and graphenes: Excitement, disappointment, and reality. *Chem. Rec.* **2012**, *12* (1), 201–213.
9. Sandford, C.; Edwards, M. A.; Klunder, K. J.; Hickey, D. P.; Li, M.; Barman, K.; Sigman, M. S.; White, H. S.; Minter, S. D. A synthetic chemist's guide to electroanalytical tools for studying reaction mechanisms. *Chem. Sci.* **2019**, *10*, 6404–6422.

-
10. Pumera, M.; Sasaki, T.; Iwai, H. Relationship between carbon nanotube structure and electrochemical behavior: Heterogeneous electron transfer at electrochemically activated carbon nanotubes. *Chem. Asian J.* **2008**, *3*, 2046–2055.
 11. Nicholson, R. S. Theory and application of cyclic voltammetry for measurement of electrode reaction kinetics. *Anal. Chem.* **1965**, *37* (11), 1351–1355.
 12. Konopka, S. J.; McDuffie, B. Diffusion coefficients of ferri- and ferrocyanide ions in aqueous media, using twin-electrode thin layer electrochemistry. *Anal. Chem.* **1970**, *42* (14), 1741–1746.
 13. Randviir, E. P. A cross examination of electron transfer rate constants for carbon screen-printed electrodes using electrochemical impedance spectroscopy and cyclic voltammetry. *Electrochim. Acta* **2018**, *286*, 179–186.
 14. Ambolikar, A. S.; Guin, S. K.; Neogy, S. An insight into the outer- and inner-sphere electrochemistry of oxygenated single-walled carbon nanohorns (o-SWCNHs). *New J. Chem.* **2019**, *43*, 18210–18219.
 15. Banks, C. E.; Ji, X.; Crossley, A.; Compton, R. G. Understanding the electrochemical reactivity of bamboo multiwalled carbon nanotubes: The presence of oxygenated species at tube ends may not increase electron transfer kinetics. *Electroanalysis* **2006**, *18* (21), 2137–2140.
 16. Sun, G.; Liu, Z.; Chen, G. Dispersion of pristine multi-walled carbon nanotubes in common organic solvents. *Nano* **2010**, *5* (2), 103–109.
 17. Bergin, S. D.; Sun, Z.; Rickard, D.; Streich, P. V.; Hamilton, J. P.; Coleman, J. N. Multicomponent solubility parameters for single-walled carbon nanotube-solvent mixtures. *ACS Nano* **2009**, *3* (8), 2340–2350.
 18. Taurino, I.; Carrara, S.; Giorcelli, M.; Tagliaferro, A.; De Micheli, G. Comparison of two different carbon nanotube-based surfaces with respect to potassium ferricyanide electrochemistry. *Surf. Sci.* **2012**, *606* (3–4), 156–160.
 19. Hallam, P. M.; Banks, C. E. A facile approach for quantifying the density of defects (edge plane sites) of carbon nanomaterials and related structures. *Phys. Chem. Chem. Phys.* **2011**, *13* (3), 1210–1213.
 20. Salehzadeh, H.; Ebrahimi, M.; Nematollahi, D.; Salarian, A. A. Electrochemical study of fenitrothion and bifenox and their simultaneous determination using multiwalled carbon nanotube modified glassy carbon electrode. *J. Electroanal. Chem.* **2016**, *767*, 188–194.

-
21. Sims, M. J.; Rees, N. V.; Dickinson, E. J. F.; Compton, R. G. Effects of thin-layer diffusion in the electrochemical detection of nicotine on basal plane pyrolytic graphite (BPPG) electrodes modified with layers of multi-walled carbon nanotubes (MWCNT-BPPG). *Sens. Actuators, B* **2010**, *144* (1), 153–158.
 22. Henstridge, M. C.; Dickinson, E. J. F.; Aslanoglu, M.; Batchelor-McAuley, C.; Compton, R. G. Voltammetric selectivity conferred by the modification of electrodes using conductive porous layers or films: The oxidation of dopamine on glassy carbon electrodes modified with multiwalled carbon nanotubes. *Sens. Actuators, B* **2010**, *145* (1), 417–427.
 23. Keeley, G. P.; Lyons, M. E. G. The effects of thin layer diffusion at glassy carbon electrodes modified with porous films of single-walled carbon nanotubes. *Int. J. Electrochem. Sci.* **2009**, *4* (6), 794–809.
 24. Elgrishi, N.; Rountree, K. J.; McCarthy, B. D.; Rountree, E. S.; Eisenhart, E. T.; Dempsey, J. L. A practical beginner's guide to cyclic voltammetry. *J. Chem. Educ.* **2018**, *95* (2), 197–206.
 25. Zhang, K.; Liu, Y. D.; Choi, H. J. Surfactant effect on functionalized carbon nanotube coated snowman-like particles and their electro-responsive characteristics. *Mater. Res. Bull.* **2012**, *47* (10), 2752–2755.
 26. Jiang, Y.; Song, H.; Xu, R. Research on the dispersion of carbon nanotubes by ultrasonic oscillation, surfactant and centrifugation respectively and fiscal policies for its industrial development. *Ultrason. Sonochem.* **2018**, *48*, 30–38.
 27. Wu, X.-Y.; Niu, W. J.; Cosnier, S.; Deng, S.-Y.; Zhang, X.-J.; Shan, D. Ferricyanide confined into the integrative system of pyrrolic surfactant and SWCNTs: The enhanced electrochemical sensing of paracetamol. *Electrochim. Acta* **2015**, *186*, 16–23.
 28. Hajduković, M.; Samardžić, M.; Galović, O.; Széchenyi, A.; Sak-Bosnar, M. A functionalized nanomaterial based, new, solid state cationic-surfactant-selective sensor with fast response and low noise. *Sens. Actuators, B* **2017**, *251*, 795–803.
 29. Ziyatdinova, G.; Ziganshina, E.; Budnikov, H. Electrooxidation of morin on glassy carbon electrode modified by carboxylated single-walled carbon nanotubes and surfactants. *Electrochim. Acta* **2014**, *145*, 209–216.
 30. Manjuntha, J. G.; Jayaprakash, G. K. Electrooxidation and determination of estriol using a surfactant modified nanotube paste electrode. *Eurasian J. Anal. Chem.* **2019**, *14* (1), 1–11.
-

-
31. Thomas, T.; Mascarenhas, R. J.; D'Souza, O. J.; Detriche, S.; Mekhalif, Z.; Martis, P. Pristine multi-walled carbon nanotubes/SDS modified carbon paste electrode as an amperometric sensor for epinephrine. *Talanta* **2014**, *125*, 352–360.

This page is intentionally left blank

Electrochemical Energy Storage Capability of the Electrochemically Co- polymerised Film Electrode

This page is intentionally left blank

6.1 Literature review of CPs and CNTs in EES applications

CNTs are known to possess excellent physical and chemical properties and have been widely investigated by scientists from different disciplines to conduct extensive research work related to applications such as catalysis, sensors and EES.¹ Generally, EES involves current (electron) flow between two conducting electrodes separated by an ionic medium (electrolyte) to facilitate the occurrence of redox chemical reactions at the surfaces of both electrodes. Reduction and oxidation reactions occur at the cathode and anode respectively.² In the field of EES, CNTs display promising potential for their use owing to their excellent electrical conductivity and the function to increase pore accessibility. However, the energy density of CNTs can be further enhanced by the combination of CNTs and CPs that are commonly used to fabricate composites ranging from micro to nanosize in thickness. The specific capacitance of purified CNTs lies in the range of 20–80 F g⁻¹ and is enhanced if interactions occur with a pseudocapacitive material such as CPs.³ For instance, the PANI-CNT composite electrode had a greater specific capacitance than its sole PANI electrode which makes the former commonly used as electrode materials for supercapacitors.⁴ The use of CNTs can also overcome the limitation of cyclability lifetime associated with several CPs that experience swelling and shrinking during charging/discharging processes. Moreover, electrically conductive CNTs help to decrease polymer resistance and enhance the porosity and specific surface area of the polymer-CNT composites for charge transport. With such excellent inherent characteristics, CNTs and CPs are commonly and widely co-used to fabricate electrodes of EES devices including supercapacitors and lithium-ion batteries (LIBs) to enhance their power density.^{5,6}

For EES devices to work well, their electrode materials should generally possess the merits of high electrical conductivity, high chemical and physical stabilities, high

specific surface area and high porosity for fast diffusion to the electrode material.⁷ To date, several research studies have reported on a combination of CPs and CNTs that are used as electrode materials *via* various methods to synthesize them. Chemical and electrochemical polymerisation are more commonly used, while less common methods such as mechanical mixing⁸ and layer-by-layer assembly have been reported.⁹ Although the chemical functionalisation of CNTs creates structural defects to affect the conductivity of composite electrodes, the use of electroactive materials with these CNTs can still alleviate this problem. In particular, MWCNTs are usually preferred more than SWCNTs as the capacitance is twice as much as for the former than the latter due to the highly mesoporous structure for more charge accumulation at the electrode-electrolyte interface.¹⁰ For instance, Hui *et al.* prepared a composite material that was electrodeposited with PANI nanowire arrays and carboxylic acid functionalised MWCNTs (fMWCNTs) on a GC electrode in a layered configuration and reported high specific capacitance (160 F cm^{-2}) and excellent cycling stability.¹¹ Gupta *et al.* synthesized a PANI/SWCNT/graphite composite electrode that was prepared *via* electrochemical polymerisation and reported a high specific capacitance of 485 F g^{-1} .¹² Lee *et al.* fabricated a composite electrode of a ceramic fabric surface with the combination of polypyrrole (PPy) and fMWCNTs in 1 M LiClO₄/propylene carbonate (PC) and reported a high specific capacitance of 152.78 F g^{-1} as the ceramic fabric and fMWCNTs offered the composite electrode a high surface area for charge storage.¹³ Lota and coworkers co-polymerised melamine (Mel) and formaldehyde (F) with MWCNTs *via* carbonisation and the pseudocapacitance property of the nitrogen-rich melamine was found to enhance the capacitance of the P(Mel-F)@MWCNT composite up to 126 F g^{-1} at 5 A g^{-1} .¹⁴ Hosseini *et al.* investigated the effect of electrochemical polymerisation on the supercapacitive properties of the composite electrode poly(*o*-

anisidine) (POA)/MWCNTs *via* three different electrochemical methods: potentiodynamic, potentiostatic and galvanostatic. The results revealed that the potentiostatic method offered the highest specific capacitance (323 F g^{-1}), coulombic efficiency (93%), and cyclability ($\sim 93\%$ at 500 cycles) among all the tested methods.¹⁵ Yang *et al.* reported the use of pristine MWCNTs with 5%wt mixture of PEDOT doped with poly(styrene sulfonate) (PEDOT:PSS) and that its specific capacitance becomes stable after 100 cycles of potential cycling.¹⁶

Apart from using each of a CP and CNTs in the fabrication of the composite electrode material, co-polymers can be used in place of a conducting homopolymer. Dhibar *et al.* synthesized a P(An-*co*-Py)@CuCl₂/fMWCNT nanocomposite material with the transition metal compound as the dopant in the copolymer synthesized chemically from aniline (An) and pyrrole (Py). The CuCl₂-doped copolymer interacts strongly with the fMWCNTs to result in a better specific capacitance (383 F g^{-1}) than its analogue without the fMWCNTs (324 F g^{-1}).¹⁷

In other circumstances, CNTs can be combined with two different classes of pseudocapactive materials (CP and an oxide of transition metal) to form a composite electrode. Sk *et al.* fabricated a PANI/MnO₂/fMWCNT composite material whose specific capacitance (517.1 F g^{-1}) was six-fold greater than the pure MWCNT electrode material (83.7 F g^{-1}) at 1 mA constant current. This was largely due to the EDLC properties of fMWCNTs and the enhanced pseudocapacitance through the redox processes of PANI, MnO₂ and the carboxyl group of the fMWCNTs.¹⁸ Apart from the use of GC and Pt as the conventional working electrodes, novel electrode substrates have also been explored with two different CPs used together with CNTs. Sun *et al.* synthesized a composite material PPy/PEDOT:PSS@MWCNT on a silk fabric substrate *via* surface loading of the CP mixture PEDOT:PSS and reported a specific capacitance

of 2664 mF cm⁻² which was better than that of the control electrode material PPy/PEDOT:PSS.¹⁹ Zhou *et al.* constructed a composite electrode material MnO₂/fMWCNT/PPy which combined MnO₂, PPy and MWCNTs that are chemically functionalised with oxygenated functional groups (fMWCNT*). The core-shell nanostructure of the composite material had a high specific surface area to facilitate charge transfer with its remarkably high cycling retention of 98.5% at 5 A g⁻¹ for 1000 cycles.²⁰

Table 6.1 Summary of the reported literatures that highlight the fabrication of electrode materials with the use of CPs and CNTs, and that they can be potentially used in EES applications.

Composite electrode material ^a	Working electrode	Electrolyte	Potential window (V)	Current density ^b	Cyclability ^c	Specific capacitance ^d	Reference electrode	Reference
PANI/fMWCNT	GC	0.5 M HCl/O ₄	[-0.2, 1.0]	0.1 mA cm ⁻²	1000 (~90.0%)	160 F cm ⁻²	Ag/AgCl	11
PANI (73%wt)/SWCNT	graphite	1 M H ₂ SO ₄	[0.00, 0.75]	5 mA cm ⁻²	500 (95%)	485 F g ⁻¹	Hg/Hg ₂ Cl ₂	12
PPy/fMWCNT	ceramic ^e	1 M LiCl/O ₄ /PC	[-1.0, 1.0]	1 mA cm ⁻²	5000 (97%)	153 F g ⁻¹	Ag/AgCl	13
P(Mel-F)@MWCNT	not specified	1 M H ₂ SO ₄	not specified	not specified	5000 (93.3%)	126 F g ⁻¹ at 5 A g ⁻¹	not specified	14
POA/MWCNT	GC	0.5 M H ₂ SO ₄	[-0.3, 1.1]	0.6 A g ⁻¹	500 (~93.0%)	323 F g ⁻¹	Ag/AgCl	15
PEDOT:PSS(5%wt)/MWCNT	platinum	1 M Na ₂ SO ₄	[0.0, 0.8]	not specified	300 (~87.0%)	13.2 F g ⁻¹	Ag/AgCl	16
P(An-co-Py)@CuCl ₂ /fMWCNT	GC	1 M KCl	[-0.8, 0.8]	-	1000 (81%) at 1 A g ⁻¹	383 F g ⁻¹ at 0.5 A g ⁻¹	Hg/Hg ₂ Cl ₂	17
PANI/MnO ₂ /fMWCNT	GC	1 M KCl	[0.0, 1.0]	1 mA g ⁻¹	1000 (90%)	517 F g ⁻¹	Ag/AgCl	18
PPy/PEDOT:PSS@MWCNT	silk fabric	1 M Na ₂ SO ₄	[-0.4, 0.6]	-	5000 (94.3%) at 60 mA cm ⁻²	2664 mF cm ⁻² at 10 mA cm ⁻²	Ag/AgCl	19
MnO ₂ /PPy/fMWCNT*	stainless steel mesh	1 M Na ₂ SO ₄	[0.0, 1.0]	-	1000 (98.5%) at 5 A g ⁻¹	529 F g ⁻¹ at 0.1 A g ⁻¹	Ag/AgCl	20

^a Unless otherwise specified, fMWCNT shall refer as *carboxylic acid* functionalised MWCNT. ^b Cyclability and specific capacitance are measured at the given current density value unless otherwise specified in their respective columns. ^c Cyclability is determined as a percentage of the specific capacitance retention after a tested variable of the cycle number. ^d Specific capacitance is measured in a three-electrode configuration.

6.2 Results and discussion

6.2.1 Electrochemical polymerisation of individual monomers

Choice of working electrode

In order to select the best working electrode for this chapter, the characteristics of the electrodes as supercapacitors were studied and aligned to the aims of the project. Generally, the electrodes used should be physically hard and strong, environmentally friendly, highly conductive, resistant against corrosion and have good chemical and temperature stability. A 3-mm GC electrode (GCE) as the base material to support the composite materials was picked over its platinum counterpart with the former lower in cost as the main deciding factor.

Choice of supporting electrolyte

It is well known that the right electrolytes can enhance the specific capacitance of the electrode materials. Therefore, the choice of a supporting electrolyte is essential to contribute to the proper electrochemical performances of the electrochemical capacitor electrodes. Aqueous electrolytes have their operating voltage window significantly narrower than the organic forms and thereby can limit the energy density of the electrode materials.^{21,22} Nevertheless, aqueous electrolytes are preferred over their organic counterparts to address the goal of developing a green electrode material, as most organic electrolytes are classified as toxic and carcinogenic. Moreover, their advantages of having higher ionic conductivity and lower viscosity offer faster cycling rates of charging and discharging.²³ Low cost and simplicity of preparing aqueous electrolytes can also reduce the cost of constructing the electrodes used in EES as well.

Various aqueous electrolytes such as hydrochloric acid and sulfuric acid are explored. These aqueous electrolytes have high ionic concentration and low resistance,

but hydrochloric acid was best suited for the electrochemically co-polymerisation of aniline and melamine. In a strongly acidic medium ($\text{pH} < 2.5$), aniline can be electrochemically polymerised to give an electrically conductive PANI due to the doping of the emeraldine form of the polymer species with the protonic acid.^{24,25} Moreover, the strong affinity of the chloride anions as dopants to PMEL enhances the polymer conductivity with the chloride anions acting as counterions of the positively charged species of the electrosynthesized polymers.²⁶

Choice of applied scan rate

In most electrochemical polymerisation processes, a slow scan rate is required to allow a slower rate of potential change to generate more charge carriers and insert more anions (or dopants) into the polymeric backbone for charge neutrality, enhanced doping levels and better polymer conductivity.²⁷ Thus, a scan rate of 20 mV s^{-1} was applied to every successive potential cycling for the electrochemical polymerisation processes in this chapter.

Choice of fMWCNTs

Aniline can be electrochemically polymerised with and without the fMWCNTs being drop casted on the bare GCE surface. On the contrary, electrochemical polymerisation of melamine was discussed in **Section 2.3.1.4** and it was indicated that it can only occur strongly when functionalised carbon nanotubes (fCNTs) are used.²⁸ The presence of the fCNTs promotes interactions with the organic polymer species and offers a pathway for charge transfer to occur across the interconnected fCNT-polymer network. To verify this theory, a bare GC electrode was used in this chapter for potential cycling in 1.0 M HCl solution as the supporting electrolyte with a switching potential

of 1.4 V at a scan rate of 20 mV s⁻¹. Indeed, there is very weak to no electrochemical polymerisation with almost constant redox peak currents at *ca.* 0.70 V during the successive potential cycling. However, the use of fMWCNTs indicates that electrochemical polymerisation of melamine has occurred with the increasing anodic and cathodic current heights during the potential cycling which shall be described in the following subsection on the choice of switching potential. Thus, fMWCNTs were used to drop cast onto a clean GC working electrode prior to the electrochemical polymerisation in this chapter.

Choice of switching potential

Figure 6.1 shows the CVs of the electrochemical polymerisation of 2 mM melamine on the surface of the fMWCNT/GCE film electrode at various switching potentials of 0.8, 1.0, 1.2, 1.4, 1.5 and 1.6 V *vs.* Ag/AgCl in 1.0 M HCl with an applied scan rate of 20 mV s⁻¹ for 20 successive potential cycles. In these aforementioned switching potentials, the electrochemical polymerisation of melamine occurred in the potential range of 0.4 to 0.8 V. In addition, the corresponding anodic and cathodic current densities increased as the cycle number increased from 0 to 20 for any switching potential between 0.8 to 1.6 V. Moreover, the anodic and cathodic waves between 0.4 to 0.8 V are noted to shift in the positive and negative directions respectively which implied an increase in the internal resistance of the electrode due to the increased thickness of the polymerised layer caused by the electrochemical polymerisation of melamine on the surface of the fMWCNT/GCE film electrode.

When the switching potential was ≤ 1.2 V, electrochemical polymerisation of melamine was noted at an oxidative potential of 0.45 V. Upon increasing the switching potential to 1.4 V (**Figure 6.1(d)**), the corresponding anodic peak potential shifted

positively to 0.74 V with its current density increased by approximately 56 times more than that of the switching potential at 0.8 V (**Figure 6.1(a)**). Thus, we can determine that a switching potential of 1.4 V is ideal for the electrochemical polymerisation of melamine to occur.

While comparing the CVs at switching potentials of 1.5 and 1.6 V (**Figures 6.1(e)** and **(f)**) against that of 1.4 V (**Figure 6.1(d)**), three observations can be made. Firstly, the anodic current densities of the final (20th) potential cycle at switching potentials of 1.5 and 1.6 V (**Figures 6.1(e)** and **(f)**) are smaller than that of 1.6 V (**Figure 6.1(f)**). Such extremely poor current density at a switching potential of 1.6 V is likely due to the overoxidation of the electrosynthesized polymer on the surface of the fMWCNT/GCE film electrode. To ensure the proper electrochemical polymerisation of melamine, radical cations must be formed upon the oxidation of the monomer during the potential cycling to result in radical coupling.

Secondly, the peak-to-peak potential separation (ΔE_{pp}) of the final (20th) potential cycling is observed to be wider as the switching potentials begin to increase gradually from 1.4 to 1.6 V (**Figures 6.1(d)** to **(f)**). The increasing trend is characteristic of an increasing extent of the sluggish electron transfer kinetics on the timescale of the potential sweep.

Thirdly, there is a pronounced reduction wave of the electrolyte in the range of 0.8 to 1.0 V coupled with a cathodic shift when the switching potential was increased from 1.4 (**Figure 6.1(d)**) to 1.6 V (**Figure 6.1(f)**). The overpotential for oxygen evolution due to water decomposition at strongly acidic pH-values with the use of GC electrodes can occur up to 0.5 V, and the switching potentials (1.4 to 1.6 V) used in the experiments is about 0.2 to 0.4 V more than the theoretical decomposition potential of acidic water (+1.23 V) that is still permissible within the overpotential range.²⁹ Hence,

the preferred switching potential for the electrochemical polymerisation of melamine is selected at 1.4 V. Such electrochemical behaviour of the potential cycling of melamine is also essentially similar to that reported in the literature.^{26,28}

Figure 6.1 CVs for the electrochemical polymerisation of 2 mM melamine on the surface of a 3-mm diameter fMWCNT/GCE film electrode in 1.0 M HCl solution with a scan rate of 20 mV s^{-1} for 20 cycles at $22 (\pm 2) ^\circ\text{C}$. Switching potentials: (a) 0.8 V, (b) 1.0 V, (c) 1.2 V, (d) 1.4 V, (e) 1.5 V and (f) 1.6 V. The solid (—) and dashed (---) lines represent the 1st and 20th cycle of the potential cycling respectively.

Figure 6.2 CVs for the electrochemical polymerisation of 2 mM aniline on the surface of a 3-mm diameter fMWCNT/GCE film electrode in 1.0 M HCl solution with a scan rate of 20 mV s^{-1} for 20 cycles at $22 (\pm 2) ^\circ\text{C}$. Switching potentials: (a) 1.0 V and (b) 1.4 V. The solid (—) and dashed (---) lines represent the 1st and 20th cycle of the potential cycling respectively.

The electrochemical polymerisation of aniline in 1.0 M HCl was also investigated in 1.0 M HCl as the supporting electrolyte. It was reported in literature that the formation of a nonconductive nanosized layer with aniline oligomers can passivate the electrode during the initial electrochemical oxidation of aniline (anodic scan).³⁰ Indeed, CVs of the electrochemical polymerisation of 2 mM aniline with switching potentials of 1.0 and 1.4 V in **Figure 6.2** exhibit no oxidative waves at 0.55 V in their first potential cycle. Depassivation follows in the reverse (cathodic) scan due to the reduction of the nonconducting oligomers to form conducting and charged radical cations with a surface confined electrochemical nature on the electrode surface.³⁰ The chloride anions of the electrolyte also serve as dopants with a main purpose of intercalation/decalation to

facilitate charge transfer across the electrochemically polymerised PANI on the surface of the fMWCNT/GCE film electrode.

Although the CVs at both switching potentials reveal an increase in the current density of the redox peaks as the potential cycling progressed up to the 20th cycle, different electrochemical behaviours are noted with both switching potentials (**Figure 6.2**). A quasi-rectangular shape of the CV curve characteristic of a pseudocapacitive material is observed with a switching potential of 1.0 V. At a switching potential of 1.4 V, a faradaic pseudocapacitance behaviour is noted with a pair of redox peaks between 0.4 to 0.6 V. The peaks are believed to involve the intercalation and decalation of chloride anions to cause electrochemical charge transfer and storage in the electroactive sites of the charged PANI radical species during the course of electrochemical polymerisation. Hence, the switching potential of the potential cycling is determined at 1.4 V in order to facilitate the electrochemical co-polymerisation of aniline and melamine.

6.2.2 Electrochemical co-polymerisation of both monomers

Choice of monomeric ratio

To electrochemically co-polymerise both melamine and aniline monomers onto the surface of the fMWCNT/GCE film electrode successfully, various monomeric concentration ratios were investigated. The CV in **Figure 6.3** revealed that the ideal monomeric concentration ratio of aniline to melamine is 1:3 with 1.0 M HCl solution as the supporting electrolyte. The green and red arrows at the respective redox peak potentials of both monomers in **Figure 6.3** denote the increase in current density upon successive potential cycling. At this monomeric ratio, the redox current heights corresponding to the electrochemical polymerisation of aniline and melamine are observed to be relatively proportionate. When different monomeric ratios are examined, the redox current heights corresponding to melamine are much suppressed as compared to that of aniline. In other words, the extent of the electrochemical co-polymerisation is dependent on the concentration of melamine in the bulk solution. In addition, the distinct peak oxidative potentials of aniline and melamine are noted at 0.55 and 0.71 V respectively. When the potential scan is reversed, the cathodic peaks of aniline and melamine appear at 0.48 and 0.65 V respectively. The ΔE_{pp} values of the electrochemical co-polymerisation are then calculated to be 69 and 50 mV for aniline and melamine respectively, which are consistent with a $2e^-/2H^+$ transfer process associated with both monomers.^{28,31} In terms of the electrochemical behaviour, the increase in redox current heights and the potential shifts of the redox potentials during the electrochemical co-polymerisation (**Figure 6.3**) are largely similar with that of the electrochemical polymerisation of the individual monomers (**Figures 6.1 and 6.2**) as described in **Section 6.2.1**.

Figure 6.3 CV for the electrochemical co-polymerisation of 1 mM aniline and 3 mM melamine monomers on the surface of a 3-mm diameter fMWCNT/GCE film electrode in 1.0 M HCl solution with a scan rate of 20 mV s^{-1} for 8 cycles at $22 (\pm 2) ^\circ\text{C}$. Inset: The solid (—) and dashed (---) lines represent the 1st and 8th cycle of the potential cycling in zoom-in respectively.

In order to verify that the CV profile of the electrochemical co-polymerisation is similar with that of the individual electrochemical polymerisation of each monomer, the latter was performed under similar experimental conditions with 1 mM aniline and 3 mM aniline in separate glass cells. The CVs recorded during the individual electrochemical polymerisation of both monomers (**Figure 6.4**) reveal similar voltammetric profiles with that of the electrochemical co-polymerisation in terms of the redox peak potential values and the gradual increase in current heights with successive potential cycling. Therefore, we can confirm that there is electrochemical co-polymerisation onto the modified surface of the fMWCNT/GCE film electrode.

However, the current heights associated with the individual electrochemical polymerisation of both monomers are higher than that of the electrochemical co-polymerisation. Such an observation is likely to be the competition for the electrochemical co-polymerisation of two monomers rather than the sole electrochemical polymerisation of a monomer on an identical geometric electrode area. The presence of the fMWCNTs plays an important role during the electrochemical co-polymerisation by promoting noncovalent interactions with the co-polymer species *via* π - π stacking, van der Waals, hydrogen bonding and/or electrostatic interactions. The presence of the surface functional groups ($-\text{COOH}$) on the fMWCNTs promotes these interactions to occur during the electrochemical co-polymerisation of melamine and aniline in the presence of the acidic medium.³² Firstly, π - π stacking could occur between the fMWCNTs and the co-polymers.²⁸ Hydrogen bonding can also occur between the $-\text{COOH}$ functional group of the fMWCNTs and the amine group of the co-polymer species.^{28,33} It is also important to note that these noncovalent interactions are more desired than the covalent interactions since the former does not cause modifications to the primary structure of the functionalised MWCNTs that can affect the voltammetric profile of the electrochemical co-polymerisation.³⁴

Choice of number of potential cycles

To control the degree of electrochemical co-polymerisation of aniline and melamine, the optimum number of successive potential cycles can be controlled by selecting the cycle number that results in the highest current density upon successive potential cycling in the monomer-containing electrolyte. The CV recorded during the electrochemical co-polymerisation of aniline and melamine in a 1:3 monomeric ratio (**Figure 6.3**) revealed that 8 potential cycles was the optimum number to register the

maximum current heights associated with both monomers. Beyond the 8th potential cycle, the current height of the daughter polymeric melamine did not increase and instead began to decrease very minimally. A slight increase in the composite film resistance could be the cause of the peak current decline to prevent further electron transfer. Repeats of the electrochemical co-polymerisation process under similar conditions reproduced the same result of 8 potential cycles as the optimum number for potential cycling as well.

Figure 6.4 CVs for the electrochemical polymerisation of (a) 1 mM aniline, and (b) 3 mM melamine monomers on the surface of a 3-mm diameter fMWCNT/GCE film electrode in 1.0 M HCl solution with a scan rate of 20 mV s^{-1} for 8 cycles at $22 (\pm 2) ^\circ\text{C}$. Inset: The solid (—) and dashed (---) lines represent the 1st and 8th cycle of the potential cycling in zoom-in respectively.

6.2.3 Variable scan rates of the electrochemically co-polymerised film electrode

The influence of variable scan rates on the electrochemical response of the electrochemically co-polymerised PANIMEL/fMWCNT/GCE film electrode was investigated in a 1.0 M HCl solution in the absence of the monomers. From **Figure 6.5**, the redox peak currents of the co-polymerised film electrode are observed to increase with the scan rate.

Figure 6.5 Scan rate dependent CVs of the 3-mm diameter PANIMEL/fMWCNT/GCE film electrode immersed in 1.0 M monomer-free HCl solution at $22 (\pm 2) ^\circ\text{C}$.

In addition, the anodic and cathodic peak currents obtained from **Figure 6.5(a)** were found to be linearly related to the applied scan rate with the correlation coefficient (R^2) values of their linear regression equations very close to unity shown in **Figure 6.6(a)**. The following result thus entails a typical surface-confined electron transfer process that has occurred at the electrode-electrolyte interface which is necessary for a high specific capacitance of the modified electrode due to the pseudocapacitive

properties of the CPs. Moreover, the result also confirmed that both aniline and melamine monomers were electrochemically co-polymerised onto the surface of the fMWCNT/GCE film electrode. To further verify the dominance of a surface-confined electron transfer process, a linear plot of $\log$ anodic peak current (i_p^{ox}) versus $\log$ scan rate (ν) is needed with its theoretical slope equal to a value of 1, while a dominant diffusion-controlled process is given by a slope value of 0.5.^{35,36} From **Figure 6.6(b)**, the dependence of the $\log i_p^{\text{ox}}$ on $\log \nu$ can be expressed by the following linear equations:

$$\log i_p^{\text{ox}} = 0.9653 \log \nu - 2.4198 \quad \text{for daughter polymeric aniline (dPANI)}$$

$$\log i_p^{\text{ox}} = 1.1117 \log \nu - 2.3320 \quad \text{for daughter polymeric melamine (dMEL)}$$

with their correlation coefficient values of 0.9930 and 0.9905 corresponding to the daughter polymeric aniline and melamine respectively. These linear equations have thus suggested that their slope values were approximately close to unity and confirmed that a dominant adsorption kinetics has occurred during the electrochemical co-polymerisation process.

It is also important to note that the oxidative peak potentials of the daughter polymeric aniline and melamine shifted to more positive values as the scan rate increased, which could have possibly curtailed the kinetics occurring at the electrode-electrolyte interface. In addition, the ΔE_{pp} value in **Figure 6.6** increased as the applied scan rate was increased gradually, which could have indicated the effect of film resistance. An increase in the scan rate can cause a poorer facilitation of the ion transport to the electrode interface to result in lesser occupation of the active sites and pore structures in the electrochemically co-polymerised film.

Figure 6.6 Linear plots of (a) peak current versus scan rate, and (b) $\log$ peak oxidative current versus $\log$ scan rate for the PANIMEL/fMWCNT/GCE film electrode immersed in 1.0 M monomer-free HCl solution at 22 (± 2) $^{\circ}\text{C}$.

6.2.4 Electrochemical stability of the electrochemically co-polymerised film electrode

If the electrosynthesized film electrode exhibits poor cycling stability, its specific capacitance would be poor and result in a short cycle life. In order to investigate the electrochemical stability of the electrochemically co-polymerised PANIMEL/fMWCNT/GCE film electrode, the newly electrosynthesized electrode was removed from the solution carefully and its surface rinsed gently with 1.0 M HCl to remove any monomer species. The electrode was subsequently transferred to a fresh 1.0 M HCl solution in the absence of the monomers to investigate the electrochemical stability of the electrochemically co-polymerised film.

Figure 6.7 CVs of the 3-mm diameter PANIMEL/fMWCNT/GCE electrode immersed in 1.0 M monomer-free HCl solution with a scan rate of 20 mV s^{-1} at $22 (\pm 2) ^\circ\text{C}$. The legend depicts the particular cycle number of the stability test.

Figure 6.7 shows the CV recorded during the successive potential cycling of the PANIMEL/fMWCNT/GCE electrode in a monomer-free 1.0 M HCl solution. The decrease in the peak current characteristic of the daughters of the electrosynthesized co-polymers can be explained with the possible loss of the active mass caused by the degradation of the electrochemical co-polymerised film at the electrode-electrolyte interface.

On quick inspection of **Figure 6.7**, the magnitude of the current densities related to the daughter polymeric melamine seems to decrease relatively faster than that related to the daughter polymeric aniline. **Table 6.2** presents the cycle numbers related to the daughter polymeric monomers (aniline and melamine) which are determined graphically from **Figure 6.7** at which the percentile of the anodic or cathodic peak current of the first potential cycling occurs. Indeed, the loss of conductivity was significantly much larger for the daughter polymeric melamine than the daughter polymeric aniline. The daughter polymeric monomers for aniline and melamine are observed to have 75% of their peak anodic current density occurring at the 211th and 38th potential cycle respectively. The extremely low potential cycle number with the daughter polymeric melamine is in contrast with supercapacitors having a virtually unlimited cycling life that is usually a minimum of 500 000 cycles. Hence, more work needs to be done on stabilizing the daughter polymeric melamine in order to mitigate the effect of large volumetric swelling-shrinkage behaviour of the fMWCNT-CP composite caused by repetitive doping/de-doping with continuous cycling, and lead to an undesired poor capacitance.³⁷ Another reason for the poor cyclability could be due to the excessive nitrogen enrichment of the electrode film material that can lead to the properties of the film material such as conductivity, capacitance and cyclability being compromised.³⁸ Poor porosity of the electrosynthesized film can also happen and

present with an apparently weak cycling stability of the polymeric melamine too.^{39,40} On the other hand, one might not rule out that the bulk co-polymer chains might have compromised the surface area of the fMWCNTs available for melamine to be electrochemically co-polymerised on the modified electrode surface due to the head-to-head coupling as the only option for co-polymerisation. Hence, the electrolyte ions may not diffuse efficiently into the fMWCNT network and thereby limit the capacitance of the PANIMEL/fMWCNT/GCE film electrode.⁴¹

Table 6.2 Cycle number related to the daughter polymeric monomers (aniline and melamine) at which the percentile of the anodic or cathodic peak current of the first potential cycling occurred.

	Percentile of the anodic peak current (first potential cycling)		Percentile of the cathodic peak current (first potential cycling)	
	75%	50%	75%	50%
Cycle number related to the daughter polymeric aniline	211	> 800	170	> 800
Cycle number related to the daughter polymeric melamine	38	77	24	51

6.2.5 Electrochemical impedance spectroscopy of the various electrodes

In order to understand the interfacial properties of the electrode surfaces, electrochemical impedance spectroscopy (EIS) was performed with different electrodes in a three-electrode cell configuration. The frequency range used was within 0.1 Hz to 60 kHz with the use of a redox probe of 5 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ and 1.0 M HCl as the supporting electrolyte. **Figure 6.8(a)** shows the Randles equivalent circuit model used in all EIS experiments of this study, whereby the solution resistance (R_s) is in series with the parallel connection of the constant phase element (CPE) and the charge transfer resistance (R_{ct}). In practice, the impedance of the electrosynthesized film electrodes deviates from the purely capacitive behaviour and thus CPE was used in place of the single element C_{dl} (double layer capacitance). The EIS results are illustrated in the form of Nyquist plots in **Figure 6.8(b)** with the real Z' and imaginary Z'' components indicative of the Ohmic and capacitive behaviours of the electrode respectively.⁴² The R_e , R_{ct} , specific capacitance C_{sp} , relaxation time constant τ and phase angle θ were determined by fitting the impedance data with the use of the Randles equivalent circuit as summarised in **Table 6.3**.

Figure 6.8 (a) The Randles equivalent circuit model used in the EIS measurements. (b) Nyquist plots of various electrodes immersed in 1.0 M HCl solution with 5 mM $[\text{Fe}(\text{CN})_6]^{3-/4-}$ redox couple at $22 (\pm 2) ^\circ\text{C}$. Inset: Zoom-in of the Nyquist plots showing the three film electrodes PANI/fMWCNT/GCE, PMEL/fMWCNT/GCE and PANIMEL/fMWCNT/GCE and their knee frequency values.

Table 6.3 Impedance parameters of the various electrodes obtained from the fitting of the equivalent electric circuit to the experimental impedance data.

Electrodes	$R_s / \Omega \text{ cm}^{-2}$	$R_{ct} / \Omega \text{ cm}^{-2}$	$C_{sp} / \text{mF cm}^{-2} \text{ }^a$	$-\theta / ^\circ \text{ }^b$
Bare GCE	13.37	115.20	0.08	62.2
fMWCNT/GCE	9.55	0.05	1.32	85.2
PANI/fMWCNT/GCE	10.00	2.05	0.68	75.0
PMEL/fMWCNT/GCE	12.04	97.42	6.29	57.2
PANIMEL/fMWCNT/GCE	12.20	17.10	4.94	70.0

^a Areal capacitance values were determined at the lowest frequency of 0.05 Hz. ^b Phase angles were determined from the Bode plot at the lowest frequency of 0.05 Hz.

The solution resistance (R_s) is given by the point of intersection with the real axis of the Nyquist plot at the high frequency region.⁴³ It is mainly caused by uncompensated solution resistance and the R_s values of the electrodes in **Figure 6.8** are noted to be very close with each other.

By comparing the semi-circle diameter of multiple Nyquist plots in **Figure 6.8**, one can infer the extent of charge transfer resistance (R_{ct}) across all electrodes. The R_{ct} values of the various electrodes are observed to increase in the ascending order of fMWCNT/GCE < PANI/fMWCNT/GCE < PANIMEL/fMWCNT/GCE < PMEL/fMWCNT/GCE < bare GCE. A number of explanations could account for this observed trend. Firstly, the semi-circle of the fMWCNT/GCE film electrode is extremely small owing to the high porosity of the fMWCNT network that allows free diffusion of the electrolyte ions to the electrode surface. Secondly, surface-modified film electrodes have smaller R_{ct} values than the bare electrode which highlight the

importance of the porous fMWCNTs in facilitating charge transfer to the electrode surface and thereby lowering their R_{ct} values. Thirdly, successive potential cycling could have resulted in a greater thickness of the polymeric film being electrodeposited on the electrode surfaces that are associated with the electrosynthesized film electrodes PANI/fMWCNT/GCE, PMEL/fMWCNT/GCE and PANIMEL/fMWCNT/GCE. Consequentially, these three electrosynthesized film electrodes would have larger R_{ct} values than the fMWCNT/GCE film electrode. If these electrosynthesized film electrodes are compared with each other, the PANIMEL/fMWCNT/GCE co-polymerised film electrode has a larger R_{ct} value than the PANI/fMWCNT/GCE film electrode, but smaller than that of the PMEL/fMWCNT/GCE film electrode. This observation is consistent with the result of the poor electrochemical stability of the daughter polymeric melamine discussed in **Section 6.2.4**. A poor ion insertion/de-insertion mechanism with the polymeric melamine species is then likely to cause a larger R_{ct} value associated with the PMEL/fMWCNT/GCE film electrode than the electrosynthesized co-polymer film electrode. On the other hand, the presence of the more conductive and porous PANI species in the PANI/fMWCNT/GCE film electrode is believed to contribute a more efficient charge transfer than that in the electrosynthesized co-polymer film electrode. Thus, the R_{ct} value of the PANI/fMWCNT/GCE film electrode is lower than that of the electrosynthesized co-polymer film electrode followed by the PMEL/fMWCNT/GCE film electrode.

Figure 6.9 shows the corresponding Bode plots with the negative phase angles of these electrodes at the lowest frequency of 0.05 Hz in the ascending order of fMWCNT/GCE < PANI/fMWCNT/GCE < PANIMEL/fMWCNT/GCE < bare GCE < PMEL/fMWCNT/GCE. An ideal capacitor has a 90° negative phase angle characteristic of an EDLC while having a range from 65 to 80° in reality.⁴³ The phase angle values of

the electrosynthesized fMWCNT/GCE, PMEL/fMWCNT/GCE and PANIMEL/fMWCNT/GCE film electrodes are close to the ideal value and also fall within the theoretical range to suggest their good pseudocapacitive behaviour.^{44,45} One key observation is that the negative phase angles of both PANIMEL/fMWCNT/GCE and PANI/fMWCNT/GCE film electrodes were rather close with each other by a small difference of 5°.

Figure 6.9 Bode plots of various electrodes as a function of frequency at 22 (±2) °C.

In general, the impedance of a device, Z is defined by **equation 6.1**:

$$Z(\omega) = \frac{1}{j\omega C(\omega)} \quad (6.1)$$

where j is the unit imaginary number equal to the square root of -1 , ω is the angular frequency with the mathematical expression $\omega = 2\pi f$, and C is the capacitance of the device. The areal (or specific) capacitance, C_{sp} of the electrode (**equation 6.2**) can be

calculated by using the experimental data obtained from the Nyquist plots in **Figure 6.8(b)**:

$$C_{sp}(\omega) = \frac{1}{-Z''} \cdot \frac{1}{2\pi fA} \quad (6.2)$$

where $-Z''$ is the imaginary impedance, A is the surface area of electrode covered by active mass, and f is the frequency (in Hz) within the semi-circle region of the Nyquist plot.^{46,47} By comparing these electrodes with the use of a plot of areal capacitance as a function of frequency (in logarithmic scale) in **Figure 6.10**, the PMEL/fMWCNT/GCE film electrode is noticed to have the highest C_{sp} value at high frequency amongst all of the electrodes. The C_{sp} values of the electrodes at high frequency follow the trend in an ascending order of PMEL/fMWCNT/GCE < PANIMEL/fMWCNT/GCE < PANI/fMWCNT/GCE < fMWCNT/GCE < bare GCE. Electrodes with film materials enriched in nitrogen have a significant impact on the electron donor-acceptor properties of the film material and the contribution of the heteroatom to the delocalised π -electron system.³⁸ With more nitrogen content, the C_{sp} value is expected to be greater.^{48,49} However, there is competition for both aniline and melamine to be electrochemically co-polymerised on the surface of the fMWCNT/GCE film electrode. Moreover, melamine has a much higher nitrogen content by mass than aniline. Thus, the C_{sp} value of the PANIMEL/fMWCNT/GCE co-polymerised film electrode is observed to be lower than that of the PMEL/fMWCNT/GCE film electrode, but higher than that of the PANI/fMWCNT/GCE film electrode.

Figure 6.10 Plot of areal capacitance (C_{sp}) of various electrodes as a function of frequency at $22 (\pm 2) ^\circ\text{C}$.

In practice, the device does not have perfect efficiency and energy losses must be accounted for. The capacitance, C of the device is the sum of its real and imaginary capacitances expressed by **equation 6.3**:

$$C = C' - jC'' \quad (6.3)$$

where the real part C' relates to the effective capacitance that the device can deliver, while the imaginary part C'' accounts for the irreversible energy loss in the charge storage process. The real and imaginary capacitances are governed by **equations 6.4** and **6.5** respectively:

$$C'(\omega) = \frac{-Z''(\omega)}{\omega |Z(\omega)|^2} \quad (6.4)$$

$$C''(\omega) = \frac{Z'(\omega)}{\omega |Z(\omega)|^2} \quad (6.5)$$

where $Z'(\omega)$, $Z''(\omega)$ and $|Z(\omega)|$ are the real, imaginary and modulus impedances respectively as a function of angular frequency.⁵⁰ Using the experimental data obtained from the EIS measurements in **Figure 6.8(b)**, C' and C'' are then plotted separately against the frequency f (in logarithmic scale) as shown in **Figures 6.11** and **6.12**. The latter plot is used to determine the relaxation time constant, τ of the device graphically as given by **equation 6.6**:

$$\tau = \frac{1}{f_{\max}} \quad (6.6)$$

where $f_{\max}$ is the knee frequency (in Hz) at which the device possesses negligible resistive behaviour with maximum capacitance and energy dissipation. τ describes the rate capability of the electrode material and typically ranges from a few to tens of seconds with lower values favouring the higher power delivery of the device.^{50,51} In addition, the electrode is ideally preferred with the lowest τ value coupled a highest $f_{\max}$ value in the Nyquist plot that is characteristic of a rapid discharge of the stored energy.⁵² **Figure 6.12** and **Table 6.4** show that the PANIMEL/fMWCNT/GCE co-polymerised film electrode (8.44 s) presented a τ value smaller than the PMEL/fMWCNT/GCE film electrode (15.0 s), but 74 times greater than the PANI/fMWCNT/GCE film electrode (0.27 s). This result coincides well with the trend of R_{ct} and C_{sp} values observed in **Figures 6.8(b)** and **6.10** respectively. In addition, it also re-confirms the likelihood of a greater diffusion resistance through the pores with a less efficient ion intercalation-decalation mechanism associated with the co-polymerised film electrode than the PANI/fMWCNT/GCE film electrode.

Table 6.4 Values of the knee frequency and relaxation time constant for each electrode.

Electrodes	$f_{\max} / \text{Hz}$	τ / s
Bare GCE	6.61	0.15
fMWCNT/GCE	3.72	0.27
PANI/fMWCNT/GCE	8.80	0.11
PMEL/fMWCNT/GCE	0.067	15.0
PANIMEL/fMWCNT/GCE	0.118	8.44

Figure 6.11 Plot of real capacitance (C') of various electrodes as a function of frequency at $22 (\pm 2) ^\circ\text{C}$.

Figure 6.12 Plot of imaginary capacitance (C'') of various electrodes as a function of frequency at $22 (\pm 2) ^\circ\text{C}$.

6.3 Conclusion

A series of factors such as the choice of working electrode, electrolyte, switching potential, applied scan rate and fMWCNTs were investigated and evaluated during the individual electrochemical polymerisation of aniline and melamine *via* successive potential cycling. The optimum monomeric ratio for the electrochemical co-polymerisation was subsequently determined as 1:3 aniline and melamine respectively. Variable scan rates of the electrosynthesized co-polymer film electrode confirmed the dominance of the surface-confined electron transfer process at the electrode-electrolyte interface. The electrochemical stability of the co-polymer film electrode was also assessed and demonstrated a poor cyclability of the daughter polymeric melamine which was attributed to the excessive nitrogen content and the low porosity with the daughter polymeric melamine that possibly led to a poor ion intercalation-decalation mechanism. EIS measurements were performed to study the interfacial properties of the electrode materials and compared with the control electrodes. Further analysis of the EIS experimental data revealed that the co-polymerised film electrode was more electrochemically superior to the PMEL/fMWCNT/GCE film electrode but was much inferior to the PANI/fMWCNT/GCE film electrode. The electrochemical energy storage capability of the electrochemically co-polymerised film electrode would require more work on stabilising the daughter polymeric melamine upon electrochemical co-polymerisation in order to enhance the cyclability and charging-discharging properties of the electrode material.

6.4 Experimental

6.4.1 Chemicals

Aniline (> 99%) and melamine (99%) were obtained from Alfa Aesar. Potassium hexacyanoferrate(II) trihydrate ($\geq 98.5\%$) and potassium hexacyanoferrate(III) ($\geq 99.0\%$) were ACS reagent grade and obtained from Merck. Hydrochloric acid (37%) was obtained from VWR Chemicals. Ultrapure water with resistivity not less than 18 M Ω cm was obtained from an ELGA Purelab Option-Q water purification system. 1.0 M HCl solution was prepared from the dilution of stock solution with ultrapure water. Multi walled carbon nanotubes with carboxylic acid functionalization (fMWCNT) (95%, 50–80 nm diameter, and 10–20 μ m length) were obtained from Nanostructured and Amorphous Materials Inc. in Texas, USA. Ethanol (Fisher Chemical) was reagent grade and used as received.

6.4.2 Preparation of the modified electrodes

Prior to the drop casting of the fMWCNT suspension on the electrode surface, the GC electrode was polished with 0.3 μ m grit alumina oxide powder on the Buehler Ultra-Pad polishing cloth, rinsed thoroughly with ultrapure water to remove any residual powder and then dried clean with lint-free paper. A fMWCNT suspension was prepared by dissolving 4 mg of fMWCNT in 4 mL ethanol and subsequently ultrasonicated at room temperature (22 ± 2 °C). A 10 μ L aliquot of the fMWCNT dispersion was then deposited on the surface of the GC electrode with a micropipette and the solvent then left to evaporate in the air for 5 to 10 minutes. The drop casting process was repeated for another two times before immersing in the solution that was contained in a voltammetric glass cell for voltammetric scans.

6.4.3 Electrochemical procedures

CV and EIS experiments were performed with a computer-controlled Eco Chemie Autolab PGSTAT302N and PGSTAT203N potentiostat respectively in a three-electrode cell. The electrochemical cells were dried at 110 °C for at least an hour prior to use. The auxiliary electrode used in all electrochemical experiments consisted of a platinum wire along with a silver chloride reference electrode (Ag/AgCl in 3 M KCl). The working electrode containing the drop cast of fMWCNT suspension together with the auxiliary and reference electrodes were subsequently immersed in the solution contained in the glass cell. The electrochemical cell was fully assembled in a Faraday cage to minimise any external electromagnetic interference caused while performing the electrochemical scans. A fresh solution was prepared at each desired pH prior to the voltammetric measurement and experiments were conducted at room temperature (22 ± 2 °C). CVs were recorded with a scan rate of 20 mV s^{-1} unless otherwise stated. EIS measurements were recorded with a frequency range from 0.1 Hz to 60 kHz.

6.5 References

1. Pumera, M. The electrochemistry of carbon nanotubes: Fundamentals and applications. *Chem. Eur. J.* **2009**, *15*, 4970–4978.
2. Buckley, D. N.; O'Dwyer, C.; Quill, N.; Lynch, R. P. Electrochemical energy storage. In *Energy Storage Options and Their Environmental Impact*; Hester, R. E.; Harrison, R. M., Eds.; Royal Society of Chemistry Publishing, 2018; pp 115–149.
3. Pandolfo, A.; Hollenkamp, A. G. Carbon properties and their role in supercapacitors. *J. Power Sources* **2006**, *157*, 11–27.
4. Eftekhari, A.; Li, L.; Yang, Y. Polyaniline supercapacitors. *J. Power Sources* **2017**, *347*, 86–107.
5. De Volder, M. F. L.; Tawfick, S. H.; Baughman, R. H.; Hart, A. J. Carbon nanotubes: Present and future commercial applications. *Science* **2013**, *339*, 535–539.
6. Wei, H.; He, C.; Liu, J.; Gu, H.; Wang, Y.; Yan, X.; Guo, J.; Ding, D.; Shen, N. Z.; Wang, X.; Wei, S.; Guo, Z. Electropolymerized polypyrrole nanocomposites with cobalt oxide coated on carbon paper for electrochemical energy storage. *Polymer* **2015**, *67*, 192–199.
7. Cao, Z.; Wei, B. Q. A perspective: carbon nanotube macro-films for energy storage. *Energy Environ. Sci.* **2013**, *6*, 3183–3201.
8. Lota, K.; Khomenko, V.; Frackowiak, E. Capacitance properties of poly(3,4-ethylenedioxythiophene)/carbon nanotubes composites. *J. Phys. Chem. Solids* **2004**, *65*, 295–301.
9. Hyder, M. N.; Lee, S. W.; Cebeci, F. Ç.; Schmidt, D. J.; Shao-Horn, Y.; Hammond, P. T. Layer-by-layer assembled polyaniline nanofiber/multiwall carbon nanotube thin film electrodes for high-power and high-energy storage applications. *ACS Nano* **2011**, *5*, 8552–8561.
10. Frackowiak, F.; Jurewicz, K.; Delpeux, S.; Béguin, F. Nanotubular materials for supercapacitors. *J. Power Sources* **2001**, *97–98*, 822–825.
11. Hui, N.; Chai, F.; Lin, P.; Song, Z.; Sun, X.; Li, Y.; Niu, S.; Luo, X. Electrodeposited conducting polyaniline nanowire arrays aligned on carbon nanotubes network for high performance supercapacitors and sensors. *Electrochim. Acta* **2016**, *199*, 234–241.
12. Gupta, V.; Miura, N. Polyaniline/single-wall carbon nanotube (PANI/SWCNT) composites for high performance supercapacitors. *Electrochim. Acta* **2006**, *52*, 1721–1726

-
13. Lee, H.; Kim, H.; Cho, S. M.; Choi, J.; Lee, Y. Fabrication of polypyrrole (PPy)/carbon nanotube (CNT) composite electrode on ceramic fabric for supercapacitor applications. *Electrochim. Acta* **2011**, *56*, 7460–7466.
 14. Lota, G.; Lota, K.; Frackowiak, E. Nanotubes based composites rich in nitrogen for supercapacitor application. *Electrochem. Commun.* **2007**, *9*, 1828–1832.
 15. Hosseini, S. R.; Ghasemi, S.; Vahdat, Y. The effect of electro-polymerization method on supercapacitive properties of poly (*o*-anisidine)/CNT nanocomposites. *Synth. Met.* **2018**, *246*, 16–22.
 16. Yang, Q.; Pang, S.-K.; Yung, K.-C. Study of PEDOT–PSS in carbon nanotube/conducting polymer composites as supercapacitor electrodes in aqueous solution. *J. Electroanal. Chem.* **2014**, *728*, 140–147.
 17. Dhibar, S.; Bhattacharya, P. Hatui, G.; Das, C. K. Transition metal doped poly(aniline-co-pyrrole)/multi-walled carbon nanotubes nanocomposite for high performance supercapacitor electrode materials. *J. Alloys Compd.* **2015**, *625*, 64–75.
 18. Sk, M. M.; Yue, C. Y.; Jena, R. K. Non-covalent interactions and supercapacitance of pseudo-capacitive composite electrode materials (MWCNT–COOH/MnO₂/PANI). *Synth. Met.* **2015**, *208*, 2–12.
 19. Sun, C.; Li, X.; Zhao, J.; Cai, Z.; Ge, F. A freestanding polypyrrole hybrid electrode supported by conducting silk fabric coated with PEDOT:PSS and MWCNTs for high-performance supercapacitor. *Electrochim. Acta* **2019**, *317*, 42–51.
 20. Zhou, J.; Zhao, H.; Mu, X.; Chen, J.; Zhang, P.; Wang, Y.; He, Y.; Zhang, Z.; Pan, X.; Xie, E. Importance of polypyrrole in constructing 3D hierarchical carbon nanotube@MnO₂ perfect core–shell nanostructures for high-performance flexible supercapacitors. *Nanoscale* **2015**, *7*, 14697–14706.
 21. Béguin, F.; Presser, V.; Balducci, A.; Frackowiak, E. Carbons and electrolytes for advanced supercapacitors. *Adv. Mater.* **2014**, *26*, 2219–2251.
 22. Ruiz, V.; Blanco, C.; Raymundo-Piñero, E.; Khomenko, V.; Béguin, F.; Santamaria, R. Effects of thermal treatment of activated carbon on the electrochemical behaviour in supercapacitors. *Electrochim. Acta* **2007**, *52*, 4969–4973.

-
23. Fletcher, S. I.; Sillars, F. B.; Hudson, N. E.; Hall, P. J. Physical properties of selected ionic liquids for use as electrolytes and other industrial applications. *J. Chem. Eng. Data* **2010**, *55*, 778–782.
 24. Chiang, J.-C.; MacDiarmid, A. G. ‘Polyaniline’: Protonic acid doping of the emeraldine form to the metallic regime. *Synth. Met.* **1986**, *13*, 193–205.
 25. MacDiarmid, A. G.; Epstein, A. J. Polyanilines: A novel class of conducting polymers. *Faraday Discuss. Chem. Soc.* **1989**, *88*, 317–332.
 26. Chen, S.; Liu, S.; Wen, A.; Zhang, J.; Nie, H.; Chen, J.; Zeng, R.; Long, Y.; Jin, Y.; Mai, R. New insight into electropolymerization of melamine. I: Chloride promoted growth of polymelamine in different pH medium. *Electrochim. Acta* **2018**, *271*, 312–318.
 27. Wei, H.; Wang, Y.; Guo, J.; Yan, X.; O’Connor, R.; Zhang, X.; Shen, N. Z.; Weeks, B. L.; Huang, X.; Wei, S.; Guo, Z. Electropolymerized polypyrrole nanocoatings on carbon paper for electrochemical energy storage. *ChemElectroChem* **2015**, *2* (1), 119–126.
 28. Baskar, S.; Liao, C. W.; Chang, J. L.; Zen, J. M. Electrochemical synthesis of electroactive poly(melamine) with mechanistic explanation and its applicability to functionalize carbon surface to prepare nanotube–nanoparticles hybrid. *Electrochim. Acta* **2013**, *88*, 1–5.
 29. Bichat, M. P.; Raymundo-Piñero, E.; Béguin, F. High voltage supercapacitor built with seaweed carbons in neutral aqueous electrolyte. *Carbon* **2010**, *48*, 4351–4361.
 30. Hong, S.-Y.; Park, S.-M. Electrochemistry of conductive polymers 40. Earlier phases of aniline polymerization studied by Fourier transform electrochemical impedance spectroscopy. *J. Phys. Chem. B* **2007**, *111*, 9779–9786.
 31. Sapurina, I.; Tenkovtsev, A. V.; Stejskal, J. Conjugated polyaniline as a result of the benzidine rearrangement. *Polym. Int.* **2015**, *64*, 453–465.
 32. Fan, H.; Wang, H.; Zhao, N.; Zhang, X.; Xu, J. Hierarchical nanocomposite of polyaniline nanorods grown on the surface of carbon nanotubes for high-performance supercapacitor electrode. *J. Mater. Chem.* **2012**, *22*, 2774–2780.
 33. Wei, H.; Gu, H.; Guo, J.; Wei, S.; Guo, Z. Electropolymerized polyaniline nanocomposites from multi-walled carbon nanotubes with tuned surface functionalities for electrochemical energy storage. *J. Electrochem. Soc.* **2013**, *160* (7), G3038–G3045.
 34. Wu, K.; Hu, S. Deposition of a thin film of carbon nanotubes onto a glassy carbon electrode by electropolymerization. *Carbon* **2004**, *42*, 3237–3242.

-
35. Patil, A. M.; Lokhande, A. C.; Shinde, P. A.; Lokhande, C. D. Flexible asymmetric solid-state supercapacitors by highly efficient 3D nanostructured α -MnO₂ and h-CuS electrodes. *ACS Appl. Mater. Interfaces* **2018**, *10*, 16636–16649.
 36. Ramohlola, K. E.; Monana, G. R.; Hato, M. J.; Modibane, K. D.; Molapo, K. M.; Masikini, M.; Mduli, S. B.; Iwuoha, E. I. Polyaniline-metal organic framework nanocomposite as an efficient electrocatalyst for hydrogen evolution reaction. *Composites Part B* **2018**, *137*, 129–139.
 37. Sivakkumar, S. R.; Ko, J. M.; Kim, D. Y.; Kim, B. C.; Wallace, G. G. Performance evaluation of CNT/polypyrrole/MnO₂ composite electrodes for electrochemical capacitors. *Electrochim. Acta* **2007**, *52* (25), 7377–7385.
 38. Lota, G.; Fic, K.; Frackowiak, E. Carbon nanotubes and their composites in electrochemical applications. *Energy Environ. Sci.* **2011**, *4*, 1592–1605.
 39. Jurewicz, K.; Babel, K.; Żiółkowski, A.; Wachowska, H.; Kozłowski, M. Ammoxidation of brown coals for supercapacitors. *Fuel Process. Technol.* **2002**, *77–78*, 191–198.
 40. Jurewicz, K.; Babel, K.; Żiółkowski, A.; Wachowska, H. Ammoxidation of active carbons for improvement of supercapacitor characteristics. *Electrochim. Acta* **2003**, *48* (11), 1491–1498.
 41. Malik, R.; Zhang, L.; McConnell, C.; Scott, M.; Hsieh, Y.-Y.; Noga, R.; Alvarez, N. T.; Shanov, V. Three-dimensional, free-standing polyaniline/carbon nanotube composite-based electrode for high-performance supercapacitors. *Carbon* **2017**, *116*, 579–590.
 42. Kumar, A.; Kumar, N.; Sharma, Y.; Leu, J.; Tseng, T. Y. Synthesis of free-standing flexible rGO/MWCNT films for symmetric supercapacitor application. *Nanoscale Res. Lett.* **2019**, *14*, 266.
 43. Elmezayyen, A. S.; Guan, S.; Reicha, F. M.; El-Sherbiny, I. M.; Zheng, J.; Xu, C. Effect of conductive substrate (working electrode) on the morphology of electrodeposited Cu₂O. *J. Phys. D: Appl. Phys.* **2015**, *48* (17), 175502.
 44. Krishnamoorthy, K.; Pazhamalai, P.; Kim, S. J. Ruthenium sulfide nanoparticles as a new pseudocapacitive material for supercapacitor. *Electrochim. Acta* **2017**, *227*, 85–94.
 45. Kolathodi, M. S.; Palei, M.; Natarajan T. S. Electrospun NiO nanofibers as cathode materials for high performance asymmetric supercapacitors. *J. Mater. Chem. A* **2015**, *3*, 7513–7522.
 46. Chen, K.; Liu, F.; Xue, D.; Komarneni, S. Carbon with ultrahigh capacitance when graphene paper meets K₃Fe(CN)₆. *Nanoscale* **2015**, *7* (2), 432–439.

-
47. Dettlaff, A.; Das, P. R.; Komsiyńska, L.; Osters, O.; Łuczak, J.; Wilamowska-Zawłocka, M. Electrode materials for electrochemical capacitors based on poly(3,4 ethylenedioxythiophene) and functionalized multi-walled carbon nanotubes characterized in aqueous and aprotic electrolytes. *Synth. Met.* **2018**, *244*, 80–91.
 48. Frackowiak, E. Carbon materials for supercapacitor application. *Phys. Chem. Chem. Phys.* **2007**, *9*, 1774–1785.
 49. Frackowiak, E.; Depeux, S.; Jurewicz, K.; Szostak, K.; Cazorla-Amoro, D.; Béguin, F. Enhanced capacitance of carbon nanotubes through chemical activation. *Chem. Phys. Lett.* **2002**, *361*, 35–41.
 50. Portet, C.; Taberna, P. L.; Simon, P.; Flahaut, E.; Laberty-Robert, C. High power density electrodes for carbon supercapacitor applications. *Electrochim. Acta* **2005**, *50* (20), 4174–4181.
 51. Lewandowski, M.; Orzyłowski, M. Fractional-order models: The case study of the supercapacitor capacitance measurement. *Bull. Pol. Ac.: Tech.* **2017**, *65* (4), 449–457.
 52. Ghosh, A.; Le, V. T.; Bae, J. J.; Lee, Y. H. TLM-PSD model for optimization of energy and power density of vertically aligned carbon nanotube supercapacitor. *Sci. Rep.* **2013**, *3*, 2939.

This page is intentionally left blank

Summary and Future Work

This page is intentionally left blank

7.1 Summary and future work

This thesis focused on the electrochemistry of thin film electrodes *via* surface modification with drop casting as the main preparation method. A comprehensive investigation was conducted in three major areas: electrochemical sensing, dispersion of functionalised carbon nanotubes (fCNTs) in various solvents and the influence of various surfactants, and electrochemical energy storage.

In Chapter 4, two redox-active vitamin compounds vitamin B₂ (VB₂) and vitamin E analogue (VEa) were used to develop a vitamin-based voltammetric pH sensor that can function in buffered and unbuffered media. The pH-sensitive property of VB₂ was exploited as the working vitamin compound against the pH-insensitive VEa to allow the pH determination in various solutions. Individual voltammetric studies of both vitamin compounds suggested that VB₂ in deoxygenated buffered media at pH 1–11 undergoes an ECEC mechanism with a Nernstian response close to 59 mV/pH that is indicative of a $2e^-/2H^+$ transfer process, while the relatively constant peak potentials of VEa in deoxygenated buffered media at pH 1–11 confirmed its suitability as a pH-insensitive compound. The drop casting of both vitamin compounds on the same glassy carbon (GC) electrode surface was also studied to mirror the conditions of an ideal voltammetric pH sensor. Voltammetric results from the drop casting confirmed a linear Nernstian response in deoxygenated and oxygenated buffered media. The Nernstian behaviour was not observed in unbuffered media at pH values above 4 due to a deficiency of localised protons. Experimental modifications were taken *via* the addition of a very small concentration of acidic buffer (PC-K reference solution) into a 0.1 M KCl solution produced a good Nernstian behaviour in deoxygenated and oxygenated unbuffered media of various pH-values.

In Chapter 5, functionalised single-walled (fSWCNTs) and multi-walled carbon nanotubes (fMWCNTs) were dispersed in various solvents and various factors were studied such as the amount of fCNTs, type of fCNTs and variable scan rates on the kinetics occurring at the electrodes. The ferri/ferrocyanide couple was employed as the redox probe in the bulk solution for all voltammetric measurements. The heterogeneous electron transfer rate constants, k^0 of all the fSWCNT/GCE and fMWCNT/GCE film electrodes were calculated and compared, which indicated that the k^0 values were apparently unaffected by the type of fCNTs and the wt% of the fCNTs used in the dispersion. The interpretation of the electron transfer kinetics at all film electrodes was proven to be useful with the quantitative analysis of the coefficients of determination (R^2) values that were obtained from the linear plots of i_p versus ν and i_p versus $\nu^{0.5}$ at slow and fast scan rates, respectively. Such quantitative analysis provided evidence to correct the use of the Randles-Ševčík equation that can present misleading information of diffusion-controlled processes at surface-modified electrodes with CNT coverage. The discussion of both thin layer diffusion and semi-infinite diffusion was also proven valid with the fCNT/GCE film electrodes, and the stronger effect of thin layer diffusion upon the increase of fCNT wt% in all of the film electrodes. The use of various types of surfactants in the bulk solution was also studied with the CV results indicating that the cationic surfactant DDAB offered the best current responses when fSWCNT/GCE and fMWCNT/GCE film electrodes are immersed in the bulk solution. The effect of increasing bulk surfactant concentration was also investigated whereby the fCNT/GCE film electrodes immersed in bulk solutions that contained bulk DDAB concentrations at the cmc value were found to register optimum current responses and the least ΔE_{pp} values. CV with variable scan rate was studied with film electrodes immersed in the DDAB-containing bulk solution to confirm that thin layer diffusion and semi-infinite

diffusion processes need to be taken into account. Again, the inference was made *via* the quantitative analysis of the R^2 values in the corresponding linear plots at slow and fast scan rates.

In Chapter 6, the electrochemical energy storage capability of the electrochemically co-polymerised PANIMEL/fMWCNT/GCE film electrode was studied. A number of factors such as the choice of working electrode, electrolyte, switching potential, applied scan rate and fMWCNTs were investigated and evaluated during the individual electrochemical polymerisation of aniline and melamine *via* successive potential cycling. The electrochemical co-polymerisation of aniline and melamine was then studied with an ideal monomeric ratio of 1:3 that gave optimal ratio of the current heights with distinguishable redox peak potentials. Variable scan rate CV of the electrosynthesized co-polymer film electrode confirmed the dominance of the surface-confined electron transfer process at the electrode. The electrochemical stability of the co-polymer film electrode was also assessed and revealed a poor cyclability of the daughter polymeric melamine. The observation was hypothesized to be an excessive nitrogen content and the low porosity with the daughter polymeric melamine that possibly led to a poor ion intercalation-decalation mechanism. Electrochemical impedance spectroscopy (EIS) was also performed to evaluate the electrochemical performance of the co-polymerised film electrode with other control electrodes. The corresponding EIS results suggested that the co-polymerised film electrode was electrochemically superior than the PMEL/fMWCNT/GCE film electrode but was much inferior to the PANI/fMWCNT/GCE film electrode. Optimization of the cyclability and charging-discharging properties of the co-polymerised electrode material is required due to the need for strong electrochemical stability of the daughter polymeric melamine in the co-polymerised film upon high potential cycling.

Despite the huge amount of effort dedicated to the work described and explained in the thesis, future work may be recommended to improve the reported findings. In Chapter 4, temperature is a factor in determining whether the pH sensor can work in various temperatures. From the Nernst equation in **equation 4.1**, the redox wave will shift negatively in potential as a function of temperature. By performing SWV measurements at a higher temperature such as 398 K as a function of pH, one would be able to conclude if a similar Nernstian response is obtained compared to at 298 K. To ensure minimal loss of electroactive reference compounds from the electrode surface, carbon pasting can be employed by preparation of a carbon paste made up of graphite powder, mineral oil, VB₂ and VEa.¹ Such method is also suitable for mass production when screen printed electrodes on the disposable sensor are required. In Chapter 5, voltammetric studies on the dispersion of fCNTs in various solvents can be conducted with the electrochemically reversible outer-sphere hexaamineruthenium(III/II) redox couple apart from the quasi-reversible inner-sphere ferri/ferro-cyanide redox couple.² Such examination would provide useful insights and comparisons of the film electrodes between two different redox couples. In Chapter 6, the poor electrochemical stability and conductivity of the daughter polymeric melamine may be improved with the use of silicon carbide.³ Silicon carbide is a semiconductor that is low in cost and electrically conductive which can undergo n-doping with nitrogen-rich compounds such as melamine.⁴

In conclusion, the surface modification of electrodes has been presented with the similar method of drop casting. The drop casting of various substrates onto a GC electrode surface together with the aid of voltammetric studies can bring a wealth of knowledge on the nature and feasibility of the proposed electrochemical reactions that

occur at the interface of the electrode and electrolyte. Ultimately, these can open up a plethora of possible applications that can be of relevance and valuable in future studies.

7.2 References

1. Dai, C.; Chan, C.-W. I.; Barrow, W.; Smith, A.; Song, P.; Potier, F.; Wadhawan, J. D.; Fisher, A. C.; Lawrence, N. S. A route to unbuffered pH monitoring: A novel electrochemical approach. *Electrochim. Acta* **2016**, *190*, 879–886.
2. Ambolikar, A. S.; Guin, S. K.; Neogy, S. An insight into the outer- and inner-sphere electrochemistry of oxygenated single-walled carbon nanohorns (o-SWCNHs). *New J. Chem.* **2019**, *43*, 18210–18219.
3. Scholz, R.; dos Santos Marques, F.; Riccardi, B. Electrical conductivity of silicon carbide composites and fibers. *J. Nucl. Mater.* **2002**, *307–311* (2), 1098–1101.
4. Wang, X.; Li, C.; Zhao, T. Fabrication and characterization of poly(melamine-formaldehyde)/silicon carbide hybrid microencapsulated phase change materials with enhanced thermal conductivity and light-heat performance. *Sol. Energy Mater. Sol. Cells* **2018**, *183*, 82–91.

This page is intentionally left blank

Appendix

CHAPTER 4

A Novel Vitamin-based Voltammetric pH Sensor in Buffered and Unbuffered Media

This page is intentionally left blank

Figure A4.1 ^1H NMR spectrum of vitamin E analogue (VEa).

Figure A4.2 ^{13}C NMR spectrum of vitamin E analogue (VEa).

This page is intentionally left blank