3-dimensional electrode structure for enhanced electrochemical performance of in-plane microsupercapacitors

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**3-DIMENSIONAL ELECTRODE STRUCTURE FOR
ENHANCED ELECTROCHEMICAL PERFORMANCE
OF IN-PLANE MICROSUPERCAPACITORS**

WANG JING YUAN

**SCHOOL OF ELECTRICAL AND ELECTRONICS
ENGINEERING**

2020

**3-DIMENSIONAL ELECTRODE STRUCTURE FOR
ENHANCED ELECTROCHEMICAL PERFORMANCE
OF IN-PLANE MICROSUPERCAPACITORS**

WANG JING YUAN

School of Electrical & Electronic Engineering

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

2020

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The contributions of the co-authors are as follows:

- Prof Qing Zhang provided the initial project direction, discuss all the experimental results and edited the manuscript drafts.
- I prepared the manuscript drafts. The manuscript was revised by Dr Xinghui Wang and A/Prof Seok Woo Lee.
- I co-designed the study with Dr Xinghui Wang and performed all the laboratory work at the School of Electrical and Electronics Engineering. I also analyzed the data.

- All electron microscopy work, including sample preparation, was conducted by me in the Nanyang NanoFabrication Centre and Wintech Nano-Technology Services Pte. Ltd.
- Dr Xinghui Wang and A/Prof Seok Woo Lee assisted in the interpretation and guidance of electrochemical measurements data.

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Summary

This thesis covers the enhancement of electrochemical performance of in-plane microsupercapacitors (MSCs) including electric double layer capacitors (EDLC) and pseudocapacitors. Enhancement was achieved through a facile synthesis method with which electrodes made of 3-dimensional interconnected nanowire networks were obtained. Chapter 1 introduces the background, including literature review, motivations, objectives and major contributions of the thesis. The motivation of the project is to develop a cost-effective template-free 3D electrode nanostructure compatible with foundry processes to realise MSC with enhanced electrochemical performance. Furthermore, the issue of low cycling stability of popular conducting polymer used for supercapacitors, Polypyrrole, is also explored.

Chapter 2 presents the synthesis and optimization process of our developed 3-dimensional interconnected nanowire network (3DINN) structure using copper as the substrate. All solid-state in-plane EDLC microsupercapacitor based on CVD carbon grown on the 3DINN structure were fabricated and showed excellent electrochemical performance.

Chapter 3 describes the application of developed 3DINN structure on pseudocapacitive MSC. Two in-plane pseudocapacitive MSCs based on conducting polymer (polypyrrole) and polymer-metal oxide composite (Polypyrrole@MnO₂) fabricated on the developed 3DINN structure. Both types of pseudocapacitive microsupercapacitors show superior electrochemical performance than most similarly reported microsupercapacitors in literature.

Chapter 4 focuses on the investigation of electrochemical cycling performance of polypyrrole microsupercapacitors based on the use of dopant anions and electrolyte

anions. An anionic size ratio dependency was found which subsequently allowed the synthesis of polypyrrole microsupercapacitors with excellent electrochemical cycling performance. A variety of characterization techniques, especially Time-of-Flight Secondary Ion Mass Spectroscopy, was used to reliably characterize dopant loss as the main reason for capacitance loss.

Lastly, chapter 5 provides for the conclusive remarks and recommendations for possible future work based on the developed 3DINN nanostructure for microsupercapacitors.

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List of Abbreviations

2D	2-Dimensional
3D	3-Dimensional
3DINN	3-Dimensional Interconnected Nanowire Network
AC	Activated carbon
APS	Ammonium Persulfate
CNT	Carbon nanotube
CP	Conducting polymer
CPE	Constant phase element
CVD	Chemical vapour deposition
DI	Deionised
EDLC	Electric double layer capacitor
EDX	Electron dispersive X-ray
EIS	Electrochemical impedance spectroscopy
ESR	Equivalent series resistance
FESEM	Field emission scanning electron microscope
FLG	Few layers graphene
GCD	Galvanic charge-discharge
GO	Graphene oxide
HEV	Hybride electric vehicle
IL	Ionic liquid
IPA	Isopropyl alcohhol
LMB	Lithium micro-battery
MEMS	Micro-electromechanical system
MO	Methyl orange
MSC	Microsupercapacitor
MWCNT	Multi wall carbon nanotube
PAni	Polyaniline
PC	Pseudocapacitor
PEDOT	poly(3,4-ethylenedioxythiophene)

PPy	Polypyrrole
PPyNT	Polypyrrole nanotube
Pth	Polythiophene
PVA	Polyvinyl alcohol
rGO	Reduced graphene oxide
SC	Supercapacitor
SDS	Sodium dodecyl sulfate
SEM	Scanning electron microscope
SWCNT	Single wall carbon nanotube
TEM	Transmission electron microscope
ToF-SIMS	Time-of-flight secondary ion mass spectrometry
VACNT	Vertically aligned carbon nanotube
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

1. Introduction

In this chapter, we explore the literature landscape of supercapacitors and microsupercapacitors. The motivation to develop a cost-effective template-free 3D electrode nanostructure compatible with foundry processes to realise in-plane MSC with enhanced electrochemical performance. Through the development of novel 3-dimensional electrode structure, electroactive materials such as carbon, conducting polymers, and metal oxides can be easily deposited for enhanced electrochemical performance.

1.1 Introduction and Background

1.1.1 Background

With the advent of the transistors back in the 1940s, electronics has steadily become more important in our daily lives. Now, it is indispensable in our fast-moving society where the reliance on electronics is deeply integrated into almost all our important activities.

In this decade, electric vehicles in the transport space and portable devices including wearables are gaining huge momentum. With the world population beyond 7.5 billion in 2017, portable electronic devices are being used globally [17]. One consequence of this proliferation is the demand for better energy storage solutions. The push towards automation where miniature sensors, detectors and energy harvesters also calls for special energy storage solutions.

In the consumer electronics sector, energy storage solution is almost exclusively dominated by batteries (Figure 1-1) due to their capability of storing large amount of

Figure 1-1 Value sales of batteries and supercapacitors for consumer electronics in 2013. Reproduced from Ref. [1].

energy [16, 18]. In the area of supercapacitors, they find extensive use in industrial automation (memory storage, uninterrupted power supply), Power and Energy (Actuators, Wind turbines and photovoltaics), Medical (Defibrillators) and transport (Trains, cranes, cars, buses, elevators, aircrafts and hybrid electric vehicles (HEV) [1]. In the consumer electronics sector, supercapacitors are mostly used as a power management device.

With increasing demand for small-sized portable electronic devices, the need for micropower sources and small-scale energy storage devices must also be developed [19]. Micropower sources are important for future development of sensors, MEMS, portable and wearable electronics, as well as implantable medical devices [20]. Power requirements vary between types of devices and their functions. In general, devices which require communication or transmission of data consume most of the power in wireless devices. For example, a single chip Bluetooth module for use in medical and consumer applications requires the power in the milliwatt range [21]. On the other hand, analog-to-digital signal convertors can be in the low microwatt to sub-microwatt range [22]. A typical pacemaker requires a mean power output of about 10 microwatts [23].

Micropower devices do not need as much energy compared to larger devices and as such, they may be powered by energy harvesters which harvest energy from environment such as solar energy, mechanical vibrations, thermoelectricity etc [21]. Hence, it is important that power management units in these micropower devices can deliver the power required rather than storing large amount of energy with big-sized energy storage devices like batteries or supercapacitors. For these applications, microsupercapacitors are very useful as they can deliver power in the range of milliwatts to hundreds of watts per cm^3 , more than enough for most micropower applications. Supercapacitors are also attractive as they perform very well in applications where batteries are not a very good choice. They could completely negate the need to replace the batteries as supercapacitors can be integrated with energy harvesters which enable the devices to be self-powered and maintenance-free [21]. In area of consumer electronics, supercapacitors also serve to provide long cycle lifetime, enhanced power output, and the ability to charge quickly. Taking mobile phones as an example, batteries increasingly supply energy to more and more functions of the devices where, in the past, mobile phones only had a few functions. The numerous different functions thus demand a variety of energy and power profile from the batteries. Consequently, high power demand functions not only drain the batteries quickly but also stress the batteries, resulting in reduced lifetime of the batteries. The conflict between reducing the size of mobile phones and increasing the capacity of batteries safely is more intense with every generation of new phones. This is where supercapacitors, as an alternate type of energy storage devices, are strong candidates to work with batteries to supply energy to high power consumption functions of the devices. This not only allows the batteries to have a long lifetime, it could also allow physical batteries sizes to be further reduced [24]. One strategy is to embed microsupercapacitors at the actual point of usage inside chips.

This provides numerous advantages such as reduction of energy usage, excellent control of current supplied to each of the different components, heat reduction, scalable energy storage with increasing number of components etc. In-plane microsupercapacitor is an excellent candidate for such applications as they can possibly be integrated into circuit designs and fabricated with existing foundry techniques without a high risk of trace elements contamination like battery does. Furthermore, the very high cycling lifetime of supercapacitors will ensure that they will function for the lifetime of the device.

1.1.2 Principle of Capacitors

In its very basic form, a supercapacitor is a special capacitor which has a much higher area capacitance than that for an ordinary capacitor, which consists of 2 electrodes or parallel plates separated by a dielectric (or electrolyte). During charging, a potential difference is applied across the electrodes. This results in induced positive and negative charges in the dielectric towards the surfaces of the dielectric. . During discharging, electrons flow through the external circuit through the load thereby “releasing” the attracted charges at the interfaces. These induced charges do not inject into the two electrodes. Instead, they stay near the surface of the dielectric so that they are very close to the charges stored in the two electrodes. This electrostatic charge-discharge method is thus the fundamental way in which supercapacitors could store and release electric energy and power in respective field of applications. Figure 1-2 below illustrates how the charges are accumulated and discharged [8]. As this mode of energy storage is non-faradaic (no chemical reactions are involved), certain well-known characteristics of capacitors are:

- Long cycle lifetime of capacitors

- Fast charge and discharge time as electrostatic charges can be quickly accumulated or discharged.
- Fast charge and discharge allow a large amount of energy to be delivered in a short amount of time (high power).
- Energy stored with this electrostatic mechanism is much less than that of energy stored/ released in chemical reactions in the case of batteries.

Figure 1-2: Schematic representation of conventional parallel plate capacitors on how charges are stored. Reproduced from Ref [8].

The capacitance, C , of a capacitor can be defined as the ratio of electric charge, Q , on each electrode to the potential difference between the electrodes, V according to Equation 1.1.

$$C = \frac{Q}{V} \quad (1.1)$$

For a parallel plate capacitor, the capacitance is also proportional to the area of the electrode and inversely proportional to the distance between the electrode plates:

$$C = \frac{\epsilon_0 \epsilon_r A}{D} \quad (1.2)$$

where D is the distance between the electrodes, ϵ_r is the relative dielectric constant of the dielectric material in between the two electrodes and ϵ_0 is the permittivity of free space.

Hence, the main factors which directly affect the capacitance of a capacitor are [2]:

- Available area, A , for the charge accumulation
- Distance, D , between the electrodes
- Dielectric material used, ϵ_r ,

In practice, the distance between the electrodes are limited by the dielectric material used which relates to the dielectric breakdown of the material. A certain minimum thickness must be maintained such that dielectric breakdown is avoided.

The energy stored, E , in a capacitor is determined by the capacitance and the potential difference between the electrodes:

$$E = \frac{1}{2} CV^2 \quad (1.3)$$

Power is defined by the rate of energy delivered. Although energy stored contributes to the power of the capacitors, other factors such as the internal resistance of the capacitors need to be considered as they affect the charge transfer process which in turn, affects the time needed to deliver the stored energy. The max power that can be delivered from a capacitor to the resistor is defined by:

$$P_{max} = \frac{V^2}{4ESR} , \quad (1.4)$$

where ESR is the equivalent series resistance of the capacitor.

1.1.3 Supercapacitors

A variety of capacitors in capacitor family are illustrated in Figure 1-3. They are mainly differentiated by the specific dielectric used and/ or physical states. Hence, they have different characteristics which cater to different applications from small capacitors for electronics to large power capacitors use in high-voltage power applications [2]. Supercapacitors are alternatively classed as the group of capacitors known as electrochemical capacitors can be further divided into electrochemical double layer capacitors (EDLCs), pseudocapacitors and hybrid capacitors.

In electrochemical capacitors or supercapacitors (SCs), charges are charged and discharged based on the interfaces between the electrodes and the electrolytes involved. Very high surface area of the electrode material is one common characteristic of the SCs [25]. Utilizing very high surface area electrode materials such as activated

Figure 1-3 Common types of Capacitors. Supercapacitors is also known as electrochemical capacitors. Reproduced from Ref. [2]

carbon/nanostructures allows the effective surface area of the SCs to be a few orders higher than that of an ordinary capacitor. Furthermore, the “dielectric distance” in SCs is defined by the thickness of the double layer interface between the electrode and the electrolyte, often in the angstroms level. This allows SCs to have capacitance between 100s to 1000s Farads per device whereas conventional capacitors are rated at micro and milli Farad range.

1.1.4 Electric Double Layer Capacitors

Like a typical capacitor, EDLC capacitors work by accumulating charges/ ions at the interfaces between the electrodes and electrolytes in a non-Faradaic process. This specific interface interaction of stored charges forms the basis of the modern electric-double layer theory to explain the working principle of the EDLC capacitors.

Figure 1-4 illustrates a model of the EDL structure. The theory started off with the Helmholtz model in Figure 1-4a where opposite charges at the surfaces of the electrode and electrolyte are separated by a small distance, H [26]. This model is very similar to the typical parallel plate capacitor where 2 electrodes are separated by a dielectric. This model was later refined by Gouy [27] and Chapman [28] based on the assumption that the charged ions in the electrolyte are mobile, unlike the static charges in solid dielectric. In this model, potential at the surface of electrodes decay exponentially due to the presence of mobile counterions of the electrolyte. This refined model is shown in Figure 1-4b. As opposed to a layer of close-packed ions at the surface of the electrode, the oppositely charged ions form a distribution in a region of space much larger than H . This region of space is termed as the diffused layer. Later in 1924, Stern made further refinement to this model such that H (now termed as Stern layer) and the diffuse layer is incorporated (Figure 1-4c). This new Gouy-Chapman-Stern EDL theory has been widely accepted in the development of EDLC capacitors [11].

In this model, the Stern layer is packed with 1 to a few layers of ions adsorbed near the surface of the electrodes. In the diffuse layer, both anions and cations form a

Figure 1-4 illustration of the (a) Helmholtz model, (b) Gouy-Chapman model and (c) Gouy-Chapman-Stern model showing the Stern layer and the diffuse layer. φ_s is the potential across the double layer. Reproduced from Ref [11].

continuous distribution which is affected by thermal motion [2]. The capacitance of this double layer, C_{dl} can thus be pictured as the total capacitance of the Stern layer, C_H , and diffused layer, C_{diff}

$$\frac{1}{C_{dl}} = \frac{1}{C_H} + \frac{1}{C_{diff}} = \frac{d}{\epsilon_r \epsilon_o A} + \frac{1}{\epsilon_r \epsilon_o \kappa_D A} \quad (1.5)$$

where κ_D is the Debye length of the Gouy-Chapman layer. For highly concentrated electrolyte, $1/\kappa_D$ approaches 0 and the double layer capacitance are contributed by only the Helmholtz capacitance.

1.1.5 EDLC electrode materials

Carbon-based materials like activated carbon (AC), carbon nanotubes (CNTs), graphene, and other carbon allotropes are the most common and dominant electrode material used for EDLC capacitors. Commercially, AC is most commonly used. Carbon materials have numerous chemical and physical characteristics which makes them a choice material for electrodes [29]:

- Reasonably high conductivity
- Very large surface area achievable
- Processable into many forms
- Good corrosion resistance
- Excellent thermal stability
- Controllable pore size distribution
- Compatibility with other materials and systems
- Low cost

There are several types of carbon structures that can be produced which allows much tunability and flexibility in incorporating carbon into many systems. Carbon nanostructures like AC, CNTs and graphene can be processed to have very large surface

area to maximize double layer formation, thereby increasing the energy density of the SCs. An example of a large surface area AC is shown below in Figure 1-5. Table 1-1 also summarizes the specific capacitance of various types of carbon.

Figure 1-5 Surface of activated carbon and pores within activated carbon. Reproduced from Ref [3].

Table 1-1 Various types of carbon materials and their corresponding double layer capacitances. Reproduced from Ref. [30]

Carbon material	Electrolyte	Capacitance ($\mu\text{F cm}^{-2}$)	Remarks
Activated carbon	10% NaCl	19	
Carbon black	1M H ₂ SO ₄ , KOH	8	
Carbon fiber cloth	Et ₄ NBF ₄ in propylene carbonate	6.9	
Basal plane graphite	NaF	3	
Edge plane graphite	NaF	50-70	
Glassy carbon	NaF	13	
Carbon aerogel	4M KOH	23	
Carbon nanostructures	H ₂ SO ₄ , KOH	6 – 24	Including various types of carbon nanotubes, graphenes

Activated Carbon

Activated carbon is most used commercially as it can be produced easily at low cost in a large amount [31]. Their precursors can be obtained from inorganic sources such as pitch and coal, or from organic sources such as cellulosic materials [32]. Many chemicals and/or physical activation processes can be used to activate carbon to form pores of different sizes, obtaining surface areas of up to $3000 \text{ m}^2 \text{ g}^{-1}$. Activation process is the controlled burning and removal of carbon material from the source material which creates the pores. One example is the physical gasification of carbon using CO₂ or steam to react with carbon. On the other hand, chemical activators such as KOH, ZnCl₂ and H₃PO₄ can be used to chemically activate the carbon precursors. Processing

temperatures of chemical activation also tends to be lower than that of physical activation [33].

Carbon Nanotubes

CNT is a class of nanostructured tubular graphitic carbon where certain electrical and physical characteristics are different from the bulk carbon. Various synthesized forms of CNTs have properties ranging from semiconducting to metallic [34]. As an active material for supercapacitors, it is the excellent electrical conductivity property that makes it an attractive active material. However, compared to activated carbon, the specific capacitance of CNT powder still falls short: in the range of about 20 – 80 F g⁻¹ [35]. This is most likely due to the poor porosity of CNTs. Activation of CNTs can be done to increase the pore volume although the capacitance is still comparably lower than that of activated carbon [36]. Another novel characteristic of CNT is that the surface can be functionalised to endow or enhance certain properties of the CNTs such as hydrophilicity/ hydrophobicity. Better electrolyte-CNT interaction can also be fulfilled through oxidative treatment. The capacitance, in this case, is greatly enhanced due to pseudocapacitance contribution, at the cost of cycling life [37].

As opposed to activated carbon where it is produced with subtractive processes, CNTs are produced by additive processes such as chemical vapour deposition (CVD) from the decomposition of hydrocarbons which catalytically grow on substrates. Varying hydrocarbon sources, substrates, gas flows and environment allow different forms of CNTs to be produced, such as multi-walled CNTs (MWCNTs) and single-walled CNTs (SWCNTs). Other synthesis methods such as arc discharge or laser ablation process are also used [38].

Figure 1-6 is an example of a CVD setup to produce CNTs [7]. Transition metal catalysts such as Fe, Co, Ni are normally used and deposited on alumina or silica support as a thin film ranging a few nm thick [39]. The temperature in the reactor is first raised up to 500-1000°C to liquidize the catalyst film, breaking them into islands of particles. Precursor hydrocarbon gas is made to flow through the reactor along with carrier gases. For solid precursor compounds, the material is placed in the furnace itself but at a lower temperature region of the reactor. Depending on a bulk diffusion or surface diffusion process, CNTs will grow in either with the metal at the tip [40] or at the base [41] (Figure 1-7). Generally, when the interaction strengths between the support and metal are strong, the growth proceeds via base-growth, while a weak interaction strength promotes the CNTs to be grown via tip-growth [7].

The properties of CNTs, together with the compatibility of growth process, allow carbon nanostructured electrodes to be fabricated for supercapacitors applications.

Figure 1-6 Growth of CNT via a CVD set up. Reproduced from Ref [7].

Figure 1-7 (a) Base-growth mechanism and (b) tip-growth mechanism of CVD CNT. (c) shows the possibility of tuning CNTs diameter through varying catalyst particles size. Reproduced from Ref. [4]

Graphene

Graphene is another form of carbon allotrope with excellent electrical conductivities ranging from 200 to 3000 S cm⁻¹. A single layer graphene is a 2D material made up of carbon atoms bonded in a hexagonal shape with delocalised π -bonds. It can exist stably in a few layers called few-layer graphene (FLG) [42]. By controlling characteristics like the number of layers, stacking sequence and degree of reduction or oxidation on the surface, the properties of the graphene can be manipulated [43]. Graphene can be produced mechanically through exfoliation of oriented pyrolytic graphite [42]. Other alternatives include the bottom-up approaches such as epitaxial growth of graphene [44] and CVD growth method on metallic substrates [45]. Although graphene is a high surface area and nanostructured material, it was found that the capacitance performance of graphene was more affected by its surface chemistry, rather than the distribution of its pores [46].

In an aggregation of graphene, the graphene layers form an open-pore system which allows electrolyte ions to easily access the surfaces of the graphene. This theoretically allows graphene capacitors to have high power capability. As a carbon material, graphene also shows robustness against chemicals [47]. Furthermore, the layered structure of graphene and its good mechanical behaviour allows them to be used on micropower applications, especially in areas of flexible electronics [48]. Graphene supercapacitors were shown to have specific capacitance of between 117 – 135 F g⁻¹.

Electrolyte

Electrolyte is an important component of supercapacitor as it provides the ions for charge accumulation on the surface of the electrodes. Hence, mobility of the ions and chemical compatibility with the active material are crucial in the performance of EDLCs. There are generally 3 classes of electrolytes being used for EDLC as shown in Table 2 [37].

Aqueous electrolytes were adopted the earliest where common acids and bases were utilised. Later, other forms of electrolytes have been explored. New organic and ionic liquid electrolytes are used to achieve higher operating voltages which cannot be done by aqueous electrolyte. A higher operating voltage reduces the need to connect multiple cells in series, and thereby also reduce or eliminate the complexity involved in voltage balancing circuits [37]. A higher operating voltage also increases the specific energy as it is proportional to the square of the operating voltage.

A few factors define the performance and characteristics of the electrolytes. Ionic size determines the mobility of the ions and therefore, the conductivity of the electrolyte. Aqueous electrolytes such as acids (H₂SO₄) and alkalis (KOH) has the

highest ionic conductivity of around 1 S cm⁻¹ [49]. Correspondingly, aqueous solutions allow EDLCs to have higher specific power.

Table 1-2 Comparison table between the 3 classes of electrolyte. Reproduced from Ref. [37, 50, 51].

	Aqueous	Organic	Ionic Liquid
Operating Window	≤1 V	2.5-2.7 V	3-6 V
Conductivity	90 – 540 mS cm ⁻¹	16 – 60 mS cm ⁻¹	0.5 - 15 mS cm ⁻¹
Viscosity	Low	Medium/High	High
Cost	Low	Medium/High	Very High
Assembly environment	Atmosphere	Inert	Inert
Toxicity	Low	Medium/High	Low
Pseudocapacitance	Yes	No	No

The major downside of aqueous electrolyte is the low operating voltage window of about 1 V. This is fundamentally due to the electrochemical breakdown of water which occurs at 1.23 V [52]. Material compatibility of the system, including packaging, must also be well-designed to counter corrosion issues.

Organic electrolyte allows a much higher operating voltage of up to 2.7 V [53]. This allows high specific energy to be achieved. Commercial supercapacitors used in high energy density applications routinely use organic electrolytes. Common organic electrolytes include alkyl ammonium salts dissolved in aprotic solvents such as tetraethylammonium tetrafluoroborate dissolved in acetonitrile or propylene carbonate [37].

Ionic liquids see little use in commercial applications so far [54]. Ionic liquids are a class of organic salts that possess relatively low melting point (e.g. <100°C) [55].

Ionic liquids suitable as an electrolyte for supercapacitors exist as liquid in ambient environment, facilitating ionic movement. The major advantage of ionic liquid electrolytes is the very wide operating voltage window of up to 6V, allowing a larger amount of energy to be stored. Lastly, Ionic liquids are not as flammable and volatile compared to organic electrolytes. Although ionic liquids are stable in performance at ambient and higher temperatures, the viscosity quickly and exponentially increases at lower temperatures, causing a rapid increase in internal resistance and thus a decrease in the power of the supercapacitor [56].

Hence, the advantages and disadvantages must be considered when electrolyte is selected. The ideal electrolyte can vary for different materials, as in the case for different applications. In the case of carbon, size of the electrolyte ions is an important consideration. Smaller ions are better able to access the pores of the carbon

Table 1-3 capacitance performance of different carbon materials in different electrolyte. Reproduced from Ref. [37].

Electrode	Surface area (m ² g ⁻¹)	Capacitance (F g ⁻¹)		
		Aqueous	Organic	ILs
Activated Carbon	1000 – 3000	200-400	100-150	100-150
Template Carbon	500-2500	120-350	120-135	150
Carbon nanotubes	120-500	20-180	20-80	20-45
Carbide derived carbon	1000-1600	-	100-140	100-150
Carbon black	250-2000	300	-	-

Aerogel/ Xerogel	400-1000	20-220	160	-
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and optimally utilise the available surface area. Table 1-3 above compares the capacitance performance of different carbon materials in different electrolyte.

1.1.6 Pseudocapacitors

Despite the numerous advantages of utilizing carbon as an active material for EDLC capacitors, the theoretical capacitance of carbon material is still limited to about $10 \mu\text{F cm}^{-2}$ independent of its pore size [57]. As such, enhancement of electrochemical performance can be achieved by incorporating alternative charge storage mechanism in conjunction with electrostatic charge storage. As opposed to electrostatic charge storage where no faradaic reaction occurs, certain electroactive materials undergo faradaic reaction in which charge transfer occurs. Unlike batteries, its charge and discharge behaviour mirrors that of EDLC capacitors, where voltage is linear to the applied/removed charges [58]. Hence, pseudocapacitance is used to distinguish such mechanism of capacitive charge storage to that of electrostatic charge storage mechanism.

Since carbon is also a chemically versatile material where functionalization or electrodeposition can be carried out on, incorporating electroactive pseudocapacitive materials was the next logical step in enhancing the electrochemical performance of supercapacitors. Modification of EDLC capacitors can be done in the following ways to incorporate pseudocapacitance:

- Addition of heteroatoms (O, N, B, P, S) to carbon for increased surface functionality either through chemical [57] or physical means [59].
- Incorporation of conducting polymers to carbon electrode [60].

- Incorporation of transition metal oxides which are active in changing their charged states through faradaic reactions [61]

Transition Metal Oxides

Transition Metal Oxides have the ability to go through fast faradaic reaction in different electronic states. This makes them ideal material for storing charges [37]. One of the best oxides with high capacitance, decent conductivity, reversibility and cycling life is RuO_2 [5]. However, the high cost and toxicity nature of RuO_2 renders it impractical for mass production given that suitable alternatives are available. MnO_2 is one such alternative which is most popularly used currently [5]. Figure 1-8 compares the specific capacitance performances of RuO_2 and MnO_2 as compared to conducting polymer and pure carbon systems.

In the example of MnO_2 , it undergoes the positive charge insertion and extraction during charging and discharging [62] where electronic charges are passed into or extracted in the supercapacitor:

Figure 1-8 Comparison of capacitance between pseudocapacitance materials. Conducting polymers, and carbon systems. Reproduced from Ref. [5].

Other popular transition metal oxides include Nickel oxide or Cobalt oxide which undergo surface faradaic reactions below [2]:

Transition metal oxides are also versatile in which they can exist in different phases, synthesized in novel nanostructures, and also composited with other metal oxides and materials [63]. Though they possess high theoretical specific capacitances, they are also hindered by comparatively low electrical conductivity due to relatively large band gap, slow ion diffusion in bulk phase, and poor mechanical stability to volume expansion [64, 65]. Table 1-4 below shows some of the recent transition metal oxide based supercapacitors system and their corresponding electrochemical performance.

Table 1-4 Capacitance values associated with the different transition metal oxides-based composite supercapacitors.

Material	Capacitance (F g⁻¹)	Ref.
Ti ₃ C ₂ Tx/Fe ₂ O ₃	405.4	[66]
MnO@C nanofiber	578	[67]
Co ₃ O ₄ @Carbon fiber@Co ₃ O ₄	892	[68]
FeCo ₂ O ₄ @polypyrrole core/shell nanowires	2269	[69]
rGO@NiCo ₂ O ₄ nanowire	1248	[70]
Zn _x Co _{1-x} O oxygen vacancies	450	[71]

Heteroatoms

Functionalization of carbon with heteroatoms such as O, N, B, P, S to enhance capacitance is another method to impart pseudocapacitance. Compared to doping with metal oxides or conducting polymers, this approach is metal-free, lower material cost, and not as limited by cycling stability [72]. These electron-rich heteroatoms allow participation of faradaic reaction with the electrolyte to provide for pseudocapacitance in addition to the electric double layer mechanism. Secondary effects such as improved wettability and conductivity under some circumstances also help to improve the supercapacitor performance [73] [74] [75]. In the example of sulfur, it is thought that sulfur atoms bonded to benzene ring share electrons with the system of conjugated planar delocalized π electrons, rather than existing as discrete localized electrons in their respective single and double bonds [76]. Sulfur atoms functionalized on the carbon can exist in different forms such as sulfonate, sulfide, sulfoxide, and sulfone. They participate in faradaic reactions as below:

Figure 1-9 (a) Sulfone groups functionalised on carbon is first reduced to sulfoxide group (b)) Sulfoxide group is then further reduced to sulfenic acid in a reversible reaction (c) A portion of sulfenic acid can be ionised and adsorb positively charged protons or cations depending on the electrolyte. Reproduced from Ref. [9].

Another advantage of heteroatoms doping is that the dopant precursors can be cheap and sustainable in the form of biomass [72]. For example, peanut shells were directly pulverized and graphitized to form carbon nanosheets containing N, S and O dopants [77]. Electrochemical tests showed that there was appreciable pseudocapacitance contribution from the dopants. Human waste in the form of urine was also used as source material. Drying of urine followed by a carbonization process created porous carbon with heteroatom doping of N, S and P displayed good specific capacitances up to 166 F g^{-1} [78]. Extrinsic doping, on the other hand, involves heat and/or acid treating undoped carbon such as nitric acid [79], monosodium phosphate [80], sulfur powder [81] etc.

Despite the advantages, it can be hard to control the amount or ratio of dopants since they are intrinsically present in the carbon source. The composition of obtained biomass or wastes can differ greatly with time period and geographical locations which makes it challenging to ensure consistent electrochemical performance. On the other hand, extrinsic doping processes such as thermal or acid treatment require very high heat or low pH environment which may be unsuitable for certain supercapacitor fabrication processes.

Table 1-5 below shows the capacitance performance of some supercapacitors which doped with heteroatoms.

Table 1-5 Capacitance performance of various types of doped carbon supercapacitors.

Material	Dopant	Capacitance (F g⁻¹)	Ref.
Graphene nanosheets	N	480	[82]
Graphene	N	390	[83]
Activated Carbon	N	258	[84]
Activated Biomass	S	200	[85]
Carbon nanosheets	S	312	[86]
Activated Carbon	S	332	[87]
Carbon nano-fiber	P	336	[88]
Activated Carbon	P	210	[89]
Graphene	P	320	[90]
Carbon nano-fiber	B	180	[91]
Graphene	B	268	[92]
Activated Carbon	B	197	[93]
Hierarchical Carbon	O, N, S	576	[94]

Activated Carbon	N, S	247	[95]
Carbon Nanowire	B, N	504	[96]

Conducting Polymers

Conducting polymers (CPs) are another class of pseudocapacitive materials which have been widely studied. CPs have similar specific capacitance performance compared to most oxides and are attractive due to their better electrical conductivity, environmental stability, low cost, and ease of processing [97-99]. As they also possess plastic material properties, they can be easily made into complex morphologies [100]. The major downside of CPs is the relatively low cycling stability as they undergo large volume expansion and contraction of their polymer chains during doping and de-doping.

The most popular CPs that are studied are mainly Polyaniline (PAni), Polypyrrole (PPy), Polythiophene (PTh), and poly(3,4-ethylenedioxythiophene) (PEDOT). CPs contain conjugated bonds along the backbone of their polymer chains, and they can be synthesized through chemical polymerization or electrochemical polymerization processes [101]. In the polymerization process, monomers of CPs are oxidized. Oxidation reaction occurs simultaneously on both the monomer as well as the formed polymer chains. Counterions/dopants are also inserted during this process [25]. Hence, physical and electrochemical properties of even similar CP materials can greatly vary depending on the synthesis routes and conditions. During charging and discharging, CPs are either p-doped or n-doped with counterions from the electrolyte which releases electronic charges during the faradaic process, thus realising energy storage. Simplified charging processes are:

The biggest limitation of conducting polymers is its relatively low cycling stability. Due to its polymeric nature, conducting polymers undergo large volumetric changes during charge insertion and extraction in its polymer backbone. In its bulk form, this results in large internal stress which often leads to loss of material after a certain number of cycles [102].

The different electrical conductivities and specific capacitances of various CPs are given in table 1-6 below.

Table 1-6 Theoretical conductivity and specific capacitance of 4 types of conducting polymers. Figures adapted from Ref. [99]

Conducting Polymer	Conductivity (S cm ⁻¹)	Theoretical Specific Capacitance (F g ⁻¹)
Polyaniline	0.1 – 0.5	750
Polypyrrole	10 – 50	620
Polythiophene	300 – 400	485
PEDOT	300 - 500	210

1.1.7 In-plane Microsupercapacitors

With the miniaturization of electronics and the consequent proliferation of portable electronics, reduction in physical size of energy storage systems is crucial. Similarly, for supercapacitors, MSC is a popular research area in the field of supercapacitors. Thin film MSC was first fabricated by Kim et al using W and RuO₂ electrodes with LiPON electrolyte [103]. MSC made from Polyaniline and carbon nanotubes composite fibre was subsequently fabricated by Peng et al [104]. Finally, Gogotsi et al fabricated a carbon based EDLC microsupercapacitor using an interdigital

electrode design for the first time in 2010 [105]. The interdigital electrode design was a breakthrough for MSC as it utilized an in-plane design rather than a sandwich design common to conventional supercapacitors. Carbon MSC of this design proved to be superior in electrochemical performance compared to sandwich-type MSC, paving the way for widespread research in this area.

In the planar electrode design, electron and ion transfer happens in the same plane as the electrodes while similar process proceeds via a top-down approach in a conventional supercapacitor. The major advantage of this change in geometry is that the ionic transport is much more efficient. As observed from Figure 1-10, ion transport in the sandwich geometry is not efficient. In order to penetrate deeply into the active material, ions must travel a longer distance through the bulk of the active material. Hence, active material far from the interface is much more difficult to be utilized

Figure 1-10 (a) The in-plane interdigital electrode design, (b) ion transport in conventional stacked electrodes and (c) ion transport in in-plane interdigital electrode design. Reproduced from Ref. [13].

compared to material at the interface. On the other hand, ions in the planar geometry require only to travel a small distance between the electrode fingers while the width of the electrodes is kept small. Thus, most of the active material can quickly accessed since they directly interface the electrolyte for an effective charge and discharge process. The better utilization of surface area allows planar MSCs to perform better compared to sandwich-type MSC.

In the years since, other designs apart from the interdigital pattern has been explored. Concentric circles and fractal pattern electrodes are examples of such alternative designs [12, 106]. Simulation of the fractal pattern electrode shows that electrical field strength increased significant near the edge of the electrodes. Hence, fractal patterns with increased length of edges allows better electrochemical performance of the MSC compared to interdigital electrodes [12]. Figure 1-11 illustrates the concentric circle and fractal pattern design MSC electrodes and its electric field strength simulation.

Figure 1-11 (a) The concentric circle pattern MSC electrode, (b) fractal pattern electrodes and (c) – (d) respective electric field strength simulation showing increased electric field strength at the edges of the electrodes. Reproduced from Ref [12].

While planar electrodes MSCs may exhibit high power density and cycling ability, the total energy stored is limited by the small areal footprint in several mm². The current challenge by planar MSCs is to improve its energy density in a given limited areal footprint.

Below are the recent advances and performance review of various MSCs fabricated using different types of material.

Carbon-based MSCs

In MSCs, the most common carbon-based materials used are graphene, graphene oxide, CNTs, and porous carbon which have high specific area. Graphene has been most extensively used due to its large specific area and excellent electrical conductivity.

For example, Kaner et al. fabricated graphite oxide based MSC in 2013 using the scalable method of direct laser writing. The MSCs displayed excellent capacitance and power density with a capacitance of 1.35 mF cm⁻² at a high discharge current of 1.84 x 10⁴ mA cm⁻³[107]. Ding et al fabricated CNT-based MSC in 2017 using a 3D printing method and achieved an areal capacitance of 4.69 mF cm⁻² at a scan rate of 50 mV s⁻¹[108]. Mesoporous carbon which can be obtained from biological sources has also been a popular synthesis method. Yadav et al fabricated a MSC based on mesoporous derived from mushroom. Pyrolysis of the mushroom allowed the formation of mesoporous carbon with controllable pore size in which the author used to deposit on substrates. Direct laser writing was used for patterning of the MSC. A large areal capacitance of 9 mF cm⁻² at a discharge current density of 0.05 mA cm⁻² was obtained [109].

Carbon materials were also modified to further enhance their MSC performance. For example, boron-doped graphene MSC was fabricated by Peng et al in 2015 using

boric acid dissolved in polyamic acid as a precursor, followed by laser direct writing to produce boron-doped graphene. The doped graphene MSC obtained an areal capacitance of 16.5 mF cm^{-2} at a discharge current density of 0.05 mA cm^{-2} . This was 4 times higher than the non-doped counterpart [110].

Conducting Polymers

Similar to traditional supercapacitors, conducting polymers are also popularly used in MSCs as pseudocapacitive materials. Wang et al. fabricated a MSC using PANI nanowires in 2011 using an in-situ polymerization approach. The MSC showed an excellent volumetric capacitance of 588 F cm^{-3} [111]. In 2015, Kurra et al. used electropolymerized PEDOT on patterned MSC using photolithography process and obtained an areal capacitance of 9 mF cm^{-2} with high capacitance retention of 80% after 10000 cycles [112]. In 2017, Zhu et al. made use of PPy nanowires synthesized on patterned MSC using electropolymerization. The MSC displayed an areal capacitance of 8.15 mF cm^{-2} at a scan rate of 60 mV s^{-1} [113].

Electrode materials combining conducting polymers and carbon was also explored. Raj et al deposited PPy on graphite flakes in MSC pattern and obtained at areal capacitance of 6 mF cm^{-2} [114]. In the same year, Wu et al, fabricated an MSC using alternating stack layers of graphene and PPy resulting in an areal capacitance of 37.8 mF cm^{-2} at a scan rate of 10 mVs^{-1} [115].

1.1.8 Electrochemical Characterization

Performance of electrochemical capacitors are usually evaluated with 3 characterization techniques: The cyclic voltammetry (CV), galvanic charge-discharge (GCD), and the electrochemical impedance spectroscopy (EIS). The former two are useful in evaluating capacitance performance, specific energy and power density performance while EIS allows researchers to delve deeper and evaluate the kinetics of fabricated MSC device through a fitting of equivalent circuit corresponding to the Nyquist plot.

Cyclic Voltammetry (CV)

In the CV analysis, a linear potential sweep, dV/dt , is applied to the MSC electrode within a potential window. The corresponding current response is recorded as the output. Once the upper limit of the potential limit is reached, a similar magnitude potential sweep in the opposite direction is done to obtain its corresponding current response. This charge-discharge cycling through a potential window allows us to understand the capacitive and stability behaviour of the MSC.

For ideal capacitors, capacitance is constant at all voltages given by $Q = CV$. Hence, given that:

$$I = \frac{dQ}{dt} \quad (1.8)$$

Then,

$$I = \frac{dQ}{dt} = C \frac{dV}{dt} \quad (1.9)$$

Hence, given a linear potential sweep of fixed scan rate, the current response will also be constant. A CV cycle should result in rectangular-shaped current response curve.

Indeed, this is one of the defining characteristics of supercapacitors. A CV analysis on batteries will yield both anodic and cathodic redox peaks corresponding to the redox chemical reactions instead.

Practically, the current response of supercapacitors may deviate from a perfect rectangle in a few ways. Figure 1-12 illustrates how CV curves may deviate from the ideal shape due to various factors. Firstly, there exists some resistance in both the electrodes and electrolyte and this is represented by the equivalent series resistance (ESR). In a circuit diagram, ESR is represented in series to the capacitor. With the existence of ESR, some amount of time is required before a constant capacitive current response is reached. This is known as the time constant where, $\tau = RC$. In this case, the sides of the rectangle in the CV curve will be more rounded and tapered. Secondly, undesired redox reactions and self-discharge of a capacitor are represented as the leakage resistance. It is represented in a circuit diagram to be in parallel with the capacitor. Ideally, capacitors should have infinite leakage resistance. Presence of leakage resistance is reflected in the CV plot as a non-perfect horizontal slope parallelogram instead of a zero-slope rectangle. In reality, all supercapacitor will contain both ESR and leakage resistance, however negligible, in which they are factored in during the fitting of equivalent circuit. Other factors such as pore size distribution of electrode also affect the shape of the CV plot.

It is also possible to calculate the capacitance of MSC from CV plot. Capacitance is directly proportional to the integrated area:

$$C = \frac{\int i v dv}{2\mu\Delta V} \quad (1.10)$$

Figure 1-12 Cyclic Voltammetry diagram of (a) ideal capacitor, (b) capacitor with an equivalent series resistance, (c) capacitor with leakage resistance in parallel, and (d) combination of both resistance. Reproduced from Ref. [6]

Where $\int iv \, dv$ is the integrated area of the CV curve, μ is the scan rate, and ΔV is the potential window. Specific capacitance can be found by dividing the calculated capacitance with either the mass, area, or volume of the active material.

Galvanic Charge-Discharge (GCD)

The GCD technique, as opposed to CV, supplies a constant current while the voltage response is measured. Like CV, capacitance can be calculated from obtained GCD plot from:

$$C = \frac{I\Delta t}{\Delta V} \quad (1.11)$$

This applies to GCD plots where V-t cure profile is linear. For non-linear plots, the integration of discharge curve is used instead. Specific capacitance can be found by dividing the total capacitance with either mass, area, or volume of active material. Besides capacitance, it is also possible to deduce the series resistance of the device using GCD technique. A voltage drop can be observed in the GCD plot when the current inverts from positive to negative (Figure 1-13). Series resistance is calculated using:

$$R = \frac{V_{drop}}{\Delta I} \quad (1.12)$$

Figure 1-13 GCD curve illustrating voltage over time while applying a current. Inset shows the voltage drop observed during current inversion. Reproduced from Ref. [2].

Electrochemical Impedance Spectroscopy (EIS)

The EIS is a complex and powerful technique in analysing performance and kinetics of supercapacitors. Under a steady state, a voltage is applied to the system. A small sinusoidal voltage amplitude (few millivolts) is then applied over a range of frequencies. As excitation signal is small, current response is pseudolinear. Hence, the current response to the sinusoidal applied potential will also be sinusoidal at the same frequency, but phase shifted. Excitation signal is given by:

$$E_t = E_o \sin(\omega t) \quad (1.13)$$

Where E_t is the potential at time t , E_o is the signal amplitude and ω is the radial frequency. Current response is linear, but phase shifted (Φ):

$$I_t = I_o \sin(\omega t + \phi) \quad (1.14)$$

Figure 1-14 (a) accessing very small pores of porous electrode material depends on the size of pores and frequency applied, (b) typical Nyquist plot of activated carbon EDLC supercapacitor. Reproduced from Ref. [2].

Hence, impedance of the system can be expressed as:

$$Z = \frac{E_t}{I_t} = \frac{E_o \sin(\omega t)}{I_o \sin(\omega t + \phi)} = Z_o \frac{\sin(\omega t)}{\sin(\omega t + \phi)} \quad (1.15)$$

Using Euler's representation,

$$Z(\omega) = \frac{E}{I} = Z_o \exp(j\phi) = Z_o(\cos\phi + j\sin\phi) \quad (1.16)$$

Plotting the imaginary part of $Z(\omega)$ against the real part, we can obtain the Nyquist plot. Each point on the Nyquist plot corresponds to a different frequency. High frequencies points are on the left and bottom while low frequencies points are on the right and top. Figure 1-14b shows a typical Nyquist plot obtained from a porous activated carbon EDLC supercapacitor. The intercept of the plot at the x-axis gives the series resistance of the SC. The resistance is composed of the solution resistance as well as the electrode resistance of the SC. This is also the high frequency region of the Nyquist plot. Towards

the mid-frequencies, a slope region is observed. In a porous electrode, electrolyte reaches the outer surface of the active material first. This also include internal surfaces exposed by large pores or channels where electrolyte has no problem accessing (Figure 1-14a). During application of potential polarization, the adsorption of ions happens very quickly at the bulk surface of the material. The associated resistance is the equivalent series resistance. At high frequency, the inner surfaces inside small pores are not accessed. As frequency decreases, these surfaces become accessible to the electrolyte ions. However, this contributes to additional resistance as a larger total surface area is used, resulting in a slope on the Nyquist plot. Towards low frequencies, almost all the surfaces are accessible, and capacitance and resistance reach a maximum with no further changes with decreasing frequency. A vertical line is hence observed on the Nyquist plot. The transition frequency from the slope to vertical portion of the Nyquist plot is termed as the knee frequency. This is the boundary between full access of electrode material and the electrolyte penetration region. Above this frequency, the charge storage efficiency falls below 50% while below this frequency, the efficiency is above 50%. Hence, the higher the knee frequency, the more suited the device is for use in high power and high frequency applications.

1.1.9 Fabrication Techniques of In-plane Microsupercapacitors

There are a variety of fabrication techniques which developed over the years in the construction of in-plane MSCs. They are generally classified into ex-situ and in-situ methods. In ex-situ construction, active materials are first synthesized chemically/hydrothermally before a deposition or transfer process like injection [116-118], spraying [119, 120], printing [121-123] or electrophoretic deposition [124-126]. The planar MSCs are either pre-patterned or post-patterned through techniques like laser cutting/ scribing [109, 127] or chemical/plasma etching [117]. These methods afford

great flexibility in materials selection synthesis and routes to tune and elevate electrochemical performances of MSCs. In-situ techniques, on the other hand, active materials are directly deposited or grown on patterned electrodes. Techniques such as chemical vapour deposition (CVD) [128-133], electrodeposition [127, 134], and carbon MEMS based technologies [10, 135-137] are common in-situ techniques. Despite being more limited in materials and synthesis routes, in-situ techniques are more compatible with current foundry processes compared to ex-situ methods as they can be patterned and fabricated using standard lithography and thin film fabrication processes while carbon growth can be realised through subsequent CVD or carbonizing process [138].

Chemical Vapour Deposition (CVD)

In the CVD technique, active materials are converted from vapour phase to solid phase during the growth process. As CVD is widely used in the semiconductor fabrication process, fabrication of MSC using this technique is very much compatible with MEMS technologies. Films grown using CVD are generally uniform and adherent to underlying substrates with controllable thickness. Carbon nanostructures such as graphene and CNT can be grown using CVD and they have been extensively studied [14, 16, 139-142]. Common carbon source are gases like C_2H_2 or CH_4 with mixtures of carrier gas such as argon and hydrogen. They are transported into the reaction chamber where they are broken down into its constituents under high temperature. Substrates which have catalyst pre-deposited allow the growth of carbon species to proceed. Figure 1-15a and 1-15b show 2 examples of graphite petals and vertically aligned CNT grown using the CVD process.

Figure 1-15 (a) Top view of graphite petals grown on quartz substrate using MPCVD using CH_4 as gas source, and (b) Vertically aligned CNT grown on silicon using Fe as catalyst and C_2H_4 as gas source. Reproduced from Ref. [14] and [16]

Carbon MEMS-based Fabrication

In carbon MEMS (C-MEMS) based fabrication, the carbon active material is directly obtained from photoresist by a pyrolyzing process which reduces photoresist to carbon at a high temperature. The obvious advantage of this technique is its easy fabrication process. The lithography used to pattern the MSC interdigital electrode and the photoresist used are also standard foundries process and material. However, electrochemical performance of photoresist-derived carbon is not very high due to possibly incomplete pyrolyzation (resulting in unwanted pseudocapacitance reaction) and lower specific surface area compared to the bottom-up CVD method. Furthermore, the derived carbon is often amorphous and hence have moderate conductivity values. Figure 1-16 illustrates the fabrication process and the images of photoresist-derived carbon.

Figure 1-16 (a) Schematic representation of fabrication process of photoresist-derived carbon, (b) interdigital electrode of MSC device, (c) Top view and (d) side view of fabricated carbon. Reproduced from Ref. [10]

1.2 Motivations

On-chip microsupercapacitors are excellent candidates in providing next generation energy storage and usage solutions where electronic devices are getting smaller and more portable. Much research towards better electrochemical performing MSCs have been done in the past decade. However, the main barrier towards practical and widespread use is still cost and fabrication feasibility. In-situ methods employing various standard lithography, etching, CVD, and electrodeposition processes are currently the most foundry-compatible fabrication processes.

In this area, CVD-produced carbon species like graphene and CNTs show much promise due to their high specific surface area and excellent electrical properties resulting in good MSC performances. They are also able to serve as a conducting medium or scaffold for deposition of pseudocapacitance material to further enhance their performance. Being a 2D material, graphene or graphitic electrodes have very high volumetric capacitances as the layers are very thin which allow electrolyte ions to penetrate in between layers. However, as graphene are currently unable to be grown into thick layers, their areal capacitances are often low. Vertically-oriented or edge grown graphene/ graphite has been developed to overcome this issue, notably by Gao et al. [140] and Miller et al [139]. Such structures have very open structure with large surface area. However, the aspect ratio of such structures is still very small and areal capacitances achieved were $45 \mu\text{F cm}^{-2}$ and $175 \mu\text{F cm}^{-2}$ respectively.

On the other hand, vertically aligned CNTs (VACNT), with its near perpendicular substrate orientation and high aspect ratio, allows a relatively thick 3D structure carbon electrode to be fabricated. They have been extensively explored and have been commonly used as a scaffold to deposit other pseudocapacitive materials [16, 141-144].

However, VACNT-based MSCs suffer from high internal resistance and low cycling stability as they are only mechanically anchored to the current collector at the base [14].

In pseudocapacitors, similar problem exists for in-plane MSCs. Due to planar design, electroactive materials can only be deposited on current collectors as films in a layered configuration. This limits the energy storage capabilities as only a small amount of electroactive materials is deposited. To increase areal capacitance, deposition of thick films is not an ideal solution as it increases the electron and ion diffusion distance resulting in very poor areal power capabilities. Moreover, thick films prevent the access of electrolyte deep into the layer for faradaic charge transfer. Hence, there is a diminishing return on the areal energy density performance of MSCs with thicker and thicker deposited films. Furthermore, pseudocapacitive materials like transition metal oxides are mechanically brittle. Deposition of thick films will result in adhesion failure leading to delamination. Hence, there is a need to decouple areal energy density and power density performance such that both can be enhanced [19, 145-147].

It is apparent that 3D electrode nanostructures are needed for high volumetric and areal capacitance performance MSC for both EDLC and Pseudocapacitors. Material loading per unit area can be greatly increased while retaining its nanostructure for fast electron and ion diffusion. In this way, both high areal energy and power density can be enhanced. 3D electrode nanostructures should also have good thickness such that material loading and areal capacitance is high, while having an open structure with high surface area such that electrolyte ions can penetrate within the entire thickness of the electrode to realise high volumetric capacitance. Good mechanical adherence and cycling performance can also be achieved.

Progresses have been made in the development of 3D electrode nanostructures. Using template-assisted approach, good control of size, geometry and surface morphology can be achieved [148-150]. However, the approach is inherently more complicated due to added steps of template addition and removal in which additional processes and chemicals are required. Template-free approaches, although simpler, are limited by the controllability of geometry and morphology of nanoelectrodes. Fabrication of such 3D electrodes are also often limited to low aspect ratio/ thickness ($< 5\ \mu\text{m}$) [151-153].

Template-free hetero-electrode structures (where electroactive material are deposited on a scaffold of different material) like in-situ Si-based MSC make use of etching or CVD process to fabricate high aspect ratio vertical pillars which is highly compatible with foundry process [154-157]. However, Si is not an ideal current collector. Moreover, some designs have the pillars entrenched in Si substrate in a cavity due to the etching process, which restricts electrolyte movement between neighbouring electrode fingers. Nanoporous gold (npAu) 3D electrodes were also researched in recent years [158-164]. Gold and silver are first co-deposited as film. Subsequent chemical etching selectively removes the silver, leaving nanoporous gold as the electrode for further deposition of electroactive material. As an excellent electrical conductor, fabricated devices showed very high rate capability and power density performance due to efficient charge transport. However, for high material loading, the material cost for thick layer deposition of gold and silver will be very high. Furthermore, much of the occupied volume of gold within the electrode are “dead volume”, resulting in non-optimized cost-performance ratio.

Hence, the motivation of the thesis is to develop a cost-effective template-free 3D electrode nanostructure compatible with foundry processes to realise MSC with enhanced electrochemical performance.

Objectives

- We aim to address the issue of low areal material loading of carbon and pseudocapacitive material in the area of in-plane interdigital MSC by developing a facile template-free and cost-effective 3D electrode nanostructure that is compatible with foundry processes. The thick 3D electrode structure will act as a conductive scaffold for electroactive material deposition.
- Using developed 3D electrode structure, we aim to fabricate high performance in-plane interdigital EDLC and Pseudocapacitive MSCs that are superior in performance compared to similar in-plane MSCs. Carbon, transition metal oxides, conducting polymers and composite materials will be used to demonstrate the enhanced electrochemical performance of the 3D electrode structure MSC.
- Lastly, we aim to address the issue of low cycling stability of a conducting polymer, polypyrrole, which is popularly used in supercapacitors. The relationship between dopants and electrolytes and how they affect cycling stability and capacitance performance will be explored.

1.3 Major Contributions

- Successfully developed and optimized a template-less chemical oxidation and thermal reduction process to synthesize a 3-dimensional interconnected nanowire network (3DINN) as a current collector on a Si substrate. This is the first reported 3-dimensional interconnected nanowire network structure scaffold fabricated using a template-less approach for use in planar interdigital MSC.
- Fabricated a superior carbon-based MSC based on 3DINN using a CVD process to obtain carbon-encapsulated nanowire network as electrodes with good cycling stability. Obtained results are superior to reported 3-D carbon structures using CVD such as VACNT and edge-oriented graphene.
- Demonstrated the versatility of carbon-encapsulated 3DINN structure by successful incorporation of pseudocapacitance species such as transition metal oxides (Co(OH)_2 , Ni(OH)_2 , MnO_2) and conducting polymer (polypyrrole) through simple electrodeposition technique.
- Successfully fabricated new PPy@ MnO_2 core shell structure interdigital MSC on 3DINN structure with a widened electrochemical window of 1.1 V which exhibited outstanding energy density and power density. Obtained results are superior to most recently reported transition metal oxide based interdigital MSC.
- Developed and optimized first reported electropolymerized PPy-encapsulated 3DINN MSC which exhibited superior areal capacitance, energy density and power density compared to other 3-D and non-3-D PPy-based MSCs.

- Enhanced electrochemical cycling performance of PPy MSC through investigation of PPy dopant and aqueous anionic electrolyte relationship. Cycling stability performance of MSC showed remarkable improvement over reported PPy-based MSCs using conventional dopant, without much trade-off with electrochemical performance.

2. 3-Dimensional Interconnected Nanowire Network (3DINN) Electrode Structure for In-plane Microsupercapacitors

The fabrication processes for 3DINN structure is presented in Section 2.1. Section 2.2 presents the electrochemical performance of carbon-based in-plane EDLC MSC on fabricated 3DINN structure.

2.1 Synthesis of Cu 3DINN Electrode Structure

2.1.1 Introduction

Copper, an excellent electrical conductor, is an excellent choice as current collector in MSC. Conventionally, current collectors are deposited as thin film either below or on top of electroactive material. The current collector serves as an electrical conductor to transport electrons from the electroactive material to external circuit and vice versa. A good contact is hence necessary, especially for thick and vertically-aligned structures such as vertically aligned CNT (VACNT). As VACNTs are highly oriented perpendicular to the substrate, most of the electron transport in VACNT happens in the axial direction. Delamination from current collector substrate within VACNT array will result in inefficient electron transport to external circuit. As VACNTs are only weakly bonded to the current collector at the CNT tip, a relative lower cycling capability of VACNT MSCs [14] can result. Any 3D hetero-electrode structure (where electroactive materials are deposited on a 3D scaffold of another material) faces the challenge of efficient electron transport from electroactive material to the current collector if the scaffold is not an electrical conductor. Hence, a 3D nanostructured current collector can be constructed to meet the challenge.

Herein, we present a facile template-less method for synthesizing a novel 3-Dimensional interconnected nanowire network (3DINN) current collector nanostructure.

The Cu-3DINN current collector was obtained by chemical oxidation of sputtered Cu layer into $\text{Cu}(\text{OH})_2$ nanowires followed by a thermal reduction to Cu-3DINN (Figure 2-1). A pure Cu phase was successfully obtained. Furthermore, a thick vertical height of Cu-3DINN was obtained such that subsequent large electroactive material loading could be achieved.

$\text{Cu}(\text{OH})_2$ nanowires from bulk Cu were first reported by Zhang et al. in 2003 by oxidation of a thick Cu foil in alkaline environment in presence of Ammonium Persulfate [165]. High aspect ratio of hollow $\text{Cu}(\text{OH})_2$ single crystal nanotubes were synthesized. Subsequently, Liu et al synthesized CuO nanosheets using the same process with a higher concentration of reaction solutions. In 2015, both Xu et al. and Schlur et al synthesize $\text{Cu}(\text{OH})_2$ nanowire and nanotubes on Cu foil and Cu thin film respectively [166, 167]. The different nanostructures obtained using the same process and reactants (Table 2-1) show that optimization of synthesis parameters was needed under different conditions. Nonetheless, once $\text{Cu}(\text{OH})_2$ nanostructure was synthesized, a 3D nanostructure current collector architecture could be realised easily by a thermal reduction of $\text{Cu}(\text{OH})_2$ to Cu.

Table 2-1 Comparison of size and morphologies of synthesized Cu(OH)₂ and CuO nanostructures using similar reactants and processes.

Morphology	Size	Remarks	Reference
Nanotubes	50 – 500 nm diameter 10 µm length	Pure Cu(OH) ₂ after 15mins	[165]
Nanowire	200 – 500 nm diameter < 10 µm length	CuO sheets form with >30 mins reaction time or higher concentration of reactants	[168]
Nanowire	300nm diameter ~5 µm length	CuO nanoflower forms after 30 mins	[166]
Nanotube	500 nm diameter ~5 µm length	Low quantity Cu(OH) ₂ and large quantity of CuO nanosheets	[167]

2.1.2 Experiment Details

Figure 2-1 illustrates the schematic of the synthesis process. SiO₂ wafers were first prepared by depositing a 1 µm thick layer of SiO₂ on Si wafers using CVD. Prepared wafers were cut to size of 2 x 2 cm. Just before sputtering process, the substrates were ultrasonically washed with Acetone, Isopropyl Alcohol (IPA), and deionized (DI) water respectively for 5 mins each. They were subsequently dried under a flow of nitrogen gas. ELITE sputtering machine was used to sputter 200 nm Ti and 1 µm Cu film onto the substrates under nitrogen gas. The Ti was deposited as an adhesion interlayer between Cu and SiO₂.

Sputtered samples were used for chemical oxidation. Sodium Hydroxide and Ammonium Persulfate (APS) were procured from Sigma Aldrich and used as reactants. The oxidation step proceeded in 2 separate steps of different reactant concentrations. In the first step, 1 ml of 10 M NaOH, 0.5 ml of 1 M APS were used while in the second step, 16 ml of 10 M NaOH and 8 ml of 1 M APS were used. Deionized water was used to ensure the total volume of reactants were 60 ml. Reaction time for each step was 10 mins. Samples were taken out in the second step when the colour of the film turned deep blue.

Obtained $\text{Cu}(\text{OH})_2$ nanowires were thermally reduced to Cu nanowire network at 300°C under a constant airflow of 200 sccm argon and 50 sccm hydrogen in a quartz tube.

Direct observation of $\text{Cu}(\text{OH})_2$ nanostructure was conducted using scanning electron microscope (LEO 1550 Gemini FESEM and FEI Helios nanolab 600i DualBeam). XRD (Bruker D8 Discover) was used to identify $\text{Cu}(\text{OH})_2$ phase.

Figure 2-1 Schematic illustration on the formation of Cu nanowire network current collector. Adapted from [15].

2.1.3 Results and Discussion

Formation of Cu(OH)₂ and CuO nanostructures

Figure 2-2a presents the Cu(OH)₂ nanostructure synthesized with a one-step chemical oxidation of Cu film using 10 M NaOH and 1 M APS through the following overall reaction:

It is observed that the morphology of Cu(OH)₂ nanostructure produced were nanowires rather than nanotubes. Furthermore, in addition to Cu(OH)₂ nanowires, there were also significant amount of particles resembling nanoflowers. These nanoflowers were previously identified to be CuO [166, 168]. A magnified view of a single nanoflower in Figure 2-2b shows that it was composed of stacks of edge-oriented nanosheets perpendicular to the substrate plane. The resulting material composition and morphology ran in contrast to previously reported results. Zhang et al [165] reported only Cu(OH)₂ nanotubes without presence of CuO under similar condition while Xu et al produced nanowires and did not observed CuO particles until after 60 mins [166]. Meanwhile, Schlur et al produced very low quantity of Cu(OH)₂ nanotubes while a large number of individual large nanosheets CuO were produced instead of nanoflower [167].

It is known that Cu(OH)₂ can possibly form CuO in a suitable alkaline environment through the following reaction pathways [169]:

Figure 2-2 SEM images of (a) synthesized $\text{Cu}(\text{OH})_2$ nanowires and CuO nanoflowers and (b) magnified view of nanoflowers. The nanostructures are made up of clusters of edge oriented nanosheets.

Inhibiting growth of CuO

The pH level calculated for this reaction was 14.4. Hence, this highly alkaline environment would encourage growth of CuO particles. Since it was desired to form 3D nanowire electrode, the presence of particles is not favourable. In order for the amount of $\text{Cu}(\text{OH})_2$ to be much more than CuO , reaction 2.1 has to occur much faster than reaction 2.2 and 2.3. As such, the rate of Cu oxidation and formation into $\text{Cu}(\text{OH})_2$ has to be much faster than dissolution of $\text{Cu}(\text{OH})_2$ to form CuO . To suppress the formation of CuO particles, alkalinity of the reactant should be reduced. As such, the amount of added NaOH was reduced from 16 ml 10 M NaOH to 1 ml 10 M NaOH . Correspondingly, amount of APS was reduced from 8 ml 1 M APS to 0.5 ml 1 M APS. The calculated value of this solution was 13.2. In this manner, we ensured that the formation of $\text{Cu}(\text{OH})_2$ could proceed in an environment of low OH^- concentration, albeit slower, such that subsequent dissolution of formed $\text{Cu}(\text{OH})_2$ nanowires was kept to a minimum. However, reaction rate will be drastically reduced. As such, a two-step chemical oxidation was utilized. The first reaction step would be the formation of $\text{Cu}(\text{OH})_2$ nanowires in a diluted and less alkaline environment such that CuO formation was greatly suppressed. The second reaction step would be to use a more concentrated

reactants following the original reference concentration of reactants. The reaction parameters are summarized in Table 2-2 below. Concentration of NaOH and APS in the table was calculated over 60 ml of total reactants.

Table 2-2 Chemical oxidation process parameters of Cu to Cu(OH)₂ nanowires.

[NaOH]	[APS]	DI water	Time
<i><u>First Process</u></i>			
0.1663 M 1 ml	0.008 M 0.5 ml	58.5 ml	10 mins
<i><u>Second Process</u></i>			
2.66 M 16 ml	0.133M 8 ml	36 ml	10mins

Figure 2-3 shows the SEM images of nanostructure formed from the two-step reaction. From the low magnification image of Figure 2-3a, no CuO nanoflowers were observed. A very homogeneous nanostructure composed of Cu(OH)₂ nanowire were formed. Figure 2-3b shows a magnified view of the nanowires. No CuO nanosheets were found in between the nanowires as well. Individual widths of Cu(OH)₂ nanowires were measured to be about 150 – 200 nm, slightly smaller than other nanotubes/nanowires reported in literature. From the side profile, the layer of vertically oriented nanowires was about 10 μm tall.

XPS experiment was also done on Cu(OH)₂ samples synthesized via the 2 steps approach (Figure 2-4a) and in a single step (Figure 2-4b). In Figure 2-4a and 2-4c, the peak at 935.2 eV can be ascribed to Cu(OH)₂ while the peak at 934.2 eV can be ascribed to CuO [170]. Clearly, it can be observed that Cu(OH)₂ synthesized via the 2 steps approach successfully suppressed the growth of CuO which exists in higher proportion

Figure 2-3 SEM images showing (a) homogeneous formation and distribution of $\text{Cu}(\text{OH})_2$ nanowires from top view, (b) close-up image showing nanowire widths between 150 – 200 nm, (c) and (d) side profile images of nanowires synthesized by extending reaction time of first (45 mins) and second process (15 mins) respectively. No significant difference in nanowire height was observed.

as shown in Figure 2-4c. We could also similarly observe the difference in the O1s spectra of both the samples. The peaks at 530.8 eV and 532.3 eV can be ascribed to CuO and $\text{Cu}(\text{OH})_2$ respectively [171, 172]. Similarly, the proportion of $\text{Cu}(\text{OH})_2$ in the samples synthesized via 2 steps approach was higher (Figure 2-4b) compared the single step approach (Figure 2-4d).

Extension of growth time did not lead to a significant increase in nanowire length. Extending oxidation time of second process beyond 15 mins resulted in the formation of CuO particles while extending the oxidation time for the first process up to 45 mins does not yield any noticeable difference either (Figure 2-3c – 3d).

Figure 2-4 (a) Cu2p and (b) O1s XPS spectra of Cu(OH)₂ nanowires synthesized via a 2-step approach. (c) Cu2p and (d) O1s XPS spectra of Cu(OH)₂ synthesized in a single step.

Thermal reduction of Cu(OH)₂ to Cu nanowire network

Figure 2-5 shows the successful thermal reduction process where Cu(OH)₂ nanowires were reduced to Cu. XRD analysis conducted on synthesized samples were matched to Cu(OH)₂ phase in Figure 2-5a according to JCPDS-ICDD 01-080-0656, showing a pure phase of Cu(OH)₂ was formed. Underlying Cu and Ti substrate were also matched to the XRD spectrum. After thermal reduction, the Cu 3-DINN sample were matched to the Cu phase according to JCPDS-ICDD 04-0836 while some CuO also exist due to oxidation when exposed to the environment.

XPS analysis of the Cu(OH)₂ and Cu-3DINN after thermal reduction were also conducted as shown in Figure 2-5b. The main peaks at 932.4 and 952 eV in the XPS

spectrum in Figure 2-5b can be attributed to $\text{Cu}2p_{3/2}$ and $\text{Cu}2p_{1/2}$ respectively [173]. They can be ascribed to the Cu metal. Peaks at 935.2 eV and 934.2 eV belonging to $\text{Cu}(\text{OH})_2$ and CuO respectively which are present in the $\text{Cu}(\text{OH})_2$ sample are absent in the Cu sample. Strong satellite Cu^{2+} peaks of CuO between 946 – 957 eV were also not observed after thermal reduction. A very small broad peak between 942 – 945 eV can be attributed to a small amount of oxidation which occurred when Cu nanowires were exposed to ambient air. These findings suggest that obtained thermally reduced nanostructures are of a pure Cu phase.

There was an apparent morphology change as the nanostructure transforms from straight nanowires into an interconnected network of nanowire. $\text{Cu}(\text{OH})_2$ was first converted to CuO under heat before being reduced to Cu nanowires in a reaction with hydrogen at 300°C. A series of microstructure transformation from orthorhombic to

Figure 2-5 Thermal reduction of $\text{Cu}(\text{OH})_2$ nanowires to Cu-3DINN nanostructure shown by (a) XRD spectra and (b) XPS spectra. A pure Cu phase was obtained with some oxidation due to exposure to the ambient environment (c) Obtained Cu-3DINN nanostructure.

monoclinic and finally cubic imposed non-homogeneous strains within the material. The nanowires distorted in response forming a 3D interconnected nanowire network (3DINN). The measured resistivity of the Cu 3DINN structure was $1.7 \times 10^{-4} \Omega \text{ cm}$ or a conductivity of 5.88 kS cm^{-1} .

2.2 Fabrication of Carbon-Encapsulated 3-Dimensional Interconnected Nanowire Electrode (C-3DINN) for In-Plane Microsupercapacitor

2.2.1 Introduction

As discussed above, one motivation or objective was to fabricate high performing in-plane MSC using a novel 3D electrode approach to obtain high areal electrochemical performance. In previous section, we fabricated a Cu 3D interconnected nanowire network (Cu-3DINN) structure. In this section, we aim to deposit high quality carbon species on Cu-3DINN structure using conventional chemical vapour deposition method. The electrochemical performance of this fabricated electrode was also evaluated.

High quality and large area graphene growth using CVD techniques have been well developed in the recent decade. They are typically grown on Cu or Ni substrates at a temperature of around 1000°C [45, 174-176]. CH₄ gas was used as carbon source. At high temperature, the gas first gets adsorbed on the surface of Cu. A dehydrogenation process follows as CH₃ radicals nucleate and grow in graphene layers. A high temperature aids the growth of high-quality graphene as dehydrogenation happens more readily while carbon atoms have higher mobility during growth and nucleation. Other factors affecting the quality of grown graphene can be substrate defects, CH₄/H₂ gas mixture composition and chamber pressure [175, 177-179].

In the years following, graphene growth at temperature below 1000°C were achieved using different carbon sources [180-185]. In particular, Yang et al. deposited thin carbon films consisting of a mixture of curved graphene and amorphous carbon between 2 – 5 nm on Cu foils using C₂H₄ as carbon source at a temperature as low as 500°C [186]. The carbon thin films showed good electrical conductivity performance with increasing temperature as expected.

Low temperature CVD growth was suitable for our structure as low temperature preserves the structure of the nanowire. Although bulk Cu melts at 1080°C, temperatures above 800°C would likely melt the structure due to nanosize effect. Using C₂H₂ as carbon source, we successfully grew thin layer (~7nm) of carbon on our 3DINN structure (C-3DINN) in which Cu nanowires were encapsulated. The effect of growth temperature on the quality of the grown carbon as well as its electrochemical performance in a 3-electrode set up was investigated. It was found that carbon grown at 600 °C had the best performance. Interdigital in-plane C-3DINN MSC was also fabricated which showed an excellent areal capacitance of 1.45 mF cm⁻².

2.2.2 Experimental Details

Cu-3DINN nanowire network samples were prepared according to Section 2.1. After thermal reduction process in which Cu(OH)₂ was reduced to Cu, the samples were not removed from the furnace as CVD process can be carried out immediately after the reduction process. This was to 1) prevents the oxidation of Cu as the sample was kept in an environment of Ar and H₂ and 2) be a simple process where thermal reduction and CVD carbon growth can be done in a single sequential step.

Figure 2-6 illustrates the CVD set up using a horizontal quartz tube enclosed at both ends to enable gas flow. The quartz tube was enclosed by a furnace in the middle section in which heating profile can be controlled. After a 30 mins, 300°C thermal reduction process under a 200 sccm Ar and 50 sccm H₂ gas flow, the temperature was increased to desired temperature (between 300°C to 700°C) for a period of 30 mins. Flow rate of H₂ was reduced to 20 sccm while Ar remains at 200 sccm. Once the target temperature is obtained, a flow rate of 20 sccm C₂H₂ was introduced. After carbon

Figure 2-6 illustration of set-up for carbon growth process.

growth, C₂H₂ gas was turned off while Ar and H₂ gas remained flowing through the quartz tube till room temperature was reached.

Direct observation of the C-3DINN was conducted using scanning electron microscope (LEO 1550 Gemini FESEM and FEI Helios nanolab 600i DualBeam). Transmission Electron Microscope (TEM) images were taken using FEI Tecnai G2. Elemental identification and distribution were examined using Electron Dispersive X-ray on the TEM (Oxford X-Max 80T). Carbon structure was examined using Raman spectroscopy (Witec UHT S300).

Three-electrode electrochemical tests (Figure 2-7) using a potentiostat (Metrohm Autolab PGSTAT 101M). The prepared C-3DINN electrodes acted as the working electrode, while the counter electrode was a platinum foil. An Ag/AgCl electrode in 4 M KCl solution was used as the reference electrode. 1 M LiCl aqueous solution with pH 7 was used as the electrolyte.

For interdigitated planar micro-supercapacitor samples, a two-electrode configuration was used instead. Solid electrolyte was made with 1 g of Polyvinyl Alcohol (PVA) in 10 ml DI water heated to 80°C. The mixture melted to form a clear

liquid in which 1 M H_3PO_4 was then added. Fabricated MSC was then dipped into the mixture before pulling out slowly. To create the interdigital MSC pattern, a stainless-steel mask with laser cut MSC pattern was applied on the Si wafer substrate such that only the exposed interdigital electrode pattern was sputtered with Cu. Figure 2-8 shows the interdigital electrodes pattern and dimension. The calculated area of the pattern was 0.7158 cm^2 while the area utilized during electrochemical testing was 0.588 cm^2 .

Figure 2-7 three-electrode set up for electrochemical analysis.

Figure 2-8 Interdigital pattern electrodes for in-plane MSC

2.2.3 Results and Discussion

Physical Characterization of Electrodes

Morphology of carbon growth was observed using SEM and TEM. Figures 2-9a to 2-9d show the SEM images of carbon growth on Cu-3DINN structure at temperatures of 300, 400, 500, and 600 °C respectively. Carbon grown at 300 °C revealed that carbonaceous material grew perpendicularly in a fin-shape along a central Cu nanowire. This was supported by EDX elemental mapping shown in Figure 2-10a to 2-10d. A similar carbon structure grown on Cu nanowires at 250°C was reported by Qin et al [187]. They have found that Cu nanowires were aligned to [110] direction while the carbon sheets grew along the [100] direction. Cu nanowires still retained their crystal structures, sizes, and shapes after carbon growth, showing that the Cu nanowires did not undergo notable melting or dissolution during carbon growth. Instead, it was suggested

that C_2H_2 gas was non-dissociatively adsorbed on Cu nanowire surface due to the low processing temperature and then agglomerated and polymerized in the [100] direction of the Cu nanowire [187].

At the growth temperature of 400°C (Figure 2-9b), the fin-shaped structure disappeared. Higher magnification image (inset of Figure 2-9b) revealed that the nanowires resembled chains of small particles, suggesting that the initial Cu nanowires had partly melted but kept its structural integrity because of carbon coverage. In previous studies, Cu nanoparticles wrapped with carbon nanofibers were obtained using Cu foil as the starting material and C_2H_2 gas at 350 °C in which pyrolysis of acetylene

Figure 2-9(a) SEM images of carbon grown on copper nanowire at 300 °C shows that the nanostructure to be comprised of a single Cu nanowire in the middle while carbon species grows on opposite side of the Cu nanowire. SEM images of samples grown at (b) 400 °C with inset showing chains of small Cu particles, (c) 500 °C, (d) 600 °C with insets showing the magnified view of carbon grown at 600 °C measured to a width of about 75 nm and the side profile view of the C-3DINN with a thickness of about 8.5 μm. Adapted from [15]

gas and subsequent polymerization of carbon compounds occurred [188, 189]. This suggests that formation of Cu particles could occur even at a relative low temperature, well below its melting point. At ~ 400 °C and above, acetylene gas dissociates more completely and nucleates into graphitic layers through a surface-mediated growth process [190, 191]. In this process, C_2H_2 undergoes a more complete dissociation to C and H as this process is more energetically favourable compared to other unwanted processes such as formation of CH_4 and C_2H_4 [192]. Hence, it seems that the transition of the formation of polymeric carbon to amorphous/crystalline carbon on Cu nanowire is between 300 to 400 °C. At temperatures beyond 400 °C, formation of other carbon compounds can be further suppressed, thus maximizing the efficiency of dissociation to C and H. The difference in morphology between 400, 500 and 600 °C samples (Figure 2-9b to 2-9d) were not significant though we could expect that the quality of the carbon will be different. The widths of carbon-encapsulated nanowires for 400 – 600 °C samples measured were from 75 to 80 nm while the vertical height of C-3DINN layer was about 8.5 μm (inset of Figure 2-9d). 300 °C sample nanowire width was much larger at about 700 nm with a larger corresponding surface area. EDX elemental mapping carried out on carbon-encapsulated nanowire structure grown at 600 °C illustrates the distribution of carbon (Figure 2-10e). As shown in the red inset of the figure, carbon was observed to be homogeneously grown and distributed on the nanowire structure. Lastly, carbon growth at 700 °C was attempted but Cu nanowire structure melted and formed droplets of Cu on the surface of the substrate.

Figure 2-10 (a) Fin-shaped polymeric carbon growing perpendicular to Cu nanowires, (b) EDX elemental mapping on the nanostructure showing elemental distribution of (c) carbon and (d) Cu. Scale bar is 500 nm for (a) to (d). (e) SEM image of carbon grown on Cu nanowire at 600°C with inset illustrating homogeneous distribution of Cu in green and carbon in red.

TEM was utilized to observe a single carbon-encapsulated nanowire as shown in Figure 2-11. It is observed that a single core of Cu is encapsulated by a thin layer of carbon of about 7 nm in thickness (inset of Figure 2-11a). Figure 2-11b to Figure 2-11d show the EDX elemental mapping on a single nanowire, further illustrating the encapsulation of Cu nanowire by carbon.

Raman spectroscopy is very sensitive to the in-plane vibration mode and breathing mode of sp^2 hybridized carbon [193]. Presence of the G-band (around 1580 cm^{-1}) indicates existence of all forms of sp^2 carbon, including both aromatic and olefinic straight chain carbon while the presence of the D-band and the intensity ratio of D-band to G-band are direct indication of amorphous carbon, 6-fold aromatic rings, etc. [194, 195]. Figure 2-12 shows the Raman spectra of carbon grown from 300 to 600 °C. At 300 °C, very small D to G-band intensity ratio and a strong background suggest that amorphous and polymer carbon were the dominating carbon skeletons, indicating that C_2H_2 gas was not dissociated completely at such low temperature. At this temperature, much of the gas was adsorbed on the Cu surface and polymerized. At 400°C and above, morphology of carbon changed as growth temperature changes. The significant increase in the dissociation of C_2H_2 to C and H now allows the formation of graphitic structure. This is reflected in the Raman spectra of 400 and 500 °C carbon where the D and G band rises significantly as the formation of sp^2 carbon was largely enhanced. Further increase in growth temperature allows the nucleation and growth process to be more structurally ordered with less defects. The large overlap between the D and G band indicate that 400 and 500°C carbon are still quite disordered. In comparison to 400 °C carbon, the shoulder peak at D-band position of 500 °C carbon is slightly more pronounced, indicative of slight improvement in chain ordering with temperature. As the growth

temperature further increased to 600 °C, its characteristic G and D-band significantly deconvolute and became much more prominent. This indicates that grown carbon was of a defective graphitic structure.

Figure 2-11 TEM images of a) carbon grown on Cu nanowire at 600 °C shows the carbon encapsulated Cu nanowire with the inset image showing that the carbon layer is about 7nm thick, b) TEM-EDX image of carbon encapsulated Cu nanowire showing the elemental distribution of c) C and d) Cu. Adapted from [15]

Figure 2-12 Raman spectrum of carbon grown from 300 to 600°C. Adapted from [15].

Electrochemical Characterization of Electrodes

The performances of the C-3DINN electrodes were evaluated with cyclic-voltammetry (CV) and galvanic charge-discharge (GCD) measurements. Figure 2-13a displays the CV results at a scan rate of 200 mV s^{-1} in 1 M LiCl electrolyte solution. The CV profiles of all the electrodes were of a similar rectangular shape profile, indicating an ideal double layer capacitance. Areal capacitance, C_a (F cm^{-2}) can be calculated from the CV profile using the Equation 2.4 below.

$$C_a = \frac{1}{Av(E_2 - E_1)} \int_{E_1}^{E_2} i(E) dE \quad (2.4)$$

where E_1 and E_2 are the cut off potentials in the CV measurement and $i(E)$ is the current measured at each potential value. v is the scan rate and A is the area of the electrode participating in the measurement. Thus, the areal capacitances of the C-3DINN electrodes fabricated at 300, 400, 500 and 600 °C were 0.50, 0.89, 0.98 and 1.37 mF cm⁻², respectively.

GCD measurement was carried out in a similar potential window in 1 M LiCl solution electrolyte at a constant current of 25 μ A cm⁻² as shown in Figure 2-13b. The GCD profiles display a linear charge and discharge characteristics which further reveal that the capacitance of the electrodes was dominated by the double layer mechanism. The areal capacitance, C_a , of the electrodes can also be calculated from the linear discharge portion of the GCD measurement using Equation 2.5:

$$C_a = \frac{I_d \times \Delta t}{\Delta V \times A} \quad (2.5)$$

where I_d is the discharge current, Δt is the discharge time, ΔV is the discharge potential range and A is the area of the electrode participating in the measurement. The areal capacitance of C-3DINN electrodes at 400, 500 and 600 is 0.84 mF cm⁻², 1.09 mF cm⁻² and 1.67 mF cm⁻² respectively. C-3DINN electrode fabricated at 300 °C failed to reach neither the upper potential cut off value of 0.8 V the low current density. As observed from the inset GCD curve of 300°C sample, charging and discharging at 25 μ A cm⁻² produced a highly asymmetrical charging and discharging curve. Time taken to charge the sample from 0.2 – 0.7 V was about 1.5s while it discharged within 0.6s.

Figure 2-13 (a) CV measurements of the carbon coated electrodes fabricated at 300 - 600 °C. Inset is the enlarged CV curve for 300 °C electrode. (b) galvanic charge-discharge curve of the electrodes fabricated at 400 - 600 °C. Inset of (b) shows the GCD curve of 300 °C grown carbon. Adapted from [15].

Electrochemical performance of C-3DINN electrodes was clearly dependent on the carbon growth temperatures. Carbon grown at 600 °C showed the highest areal capacitance while the carbon grown at 300 °C had the least. As discussed above, graphitic carbon formed at 600 °C exhibited excellent electrical conductivity. Hence, charge transfer could complete very quickly to and from the surface of the carbon to current collector. Furthermore, the large surface afforded by the carbon/Cu nanowires serve as the electric double layer, contributing to the high capacitance value. In contrast, carbon grown at lower temperatures exhibited a lower electrical conductivity due to presence of large area of amorphous/polymer carbon structures. Thus, the effective surface area utilizable in the formation of the electric double layer was much smaller, yielding lower capacitances with decreasing temperature.

Figure 2-14a shows the CV response of C-3DINN electrode grown at 600°C recorded in 1 M LiCl solution at various scan rates from 10 mV s⁻¹ to 5 V s⁻¹. Even at a high scan rate of 5 V s⁻¹, the electrode still exhibited a clear rectangular profile, suggesting excellent charge propagation in the electrodes which leads to high capacitance in the charge and discharge processes at high scan rates and current densities [196-198]. This is also further supported in the galvanic charge-discharge measurements (Figure 2-14b) at various current densities of 25 , 37 , 75 , 125 and 250 μA cm⁻². The corresponding capacitances were 1.67 , 1.59 , 1.55 , 1.52 and 1.51 mF cm⁻² respectively. A 10 times increase in the current density only caused a 9.5% decrease in areal capacitance (Figure 2-14c).

Figure 2-14 (a) CV measurements performed on 600°C sample between scan rate of 10 mV s^{-1} and 5000 mV s^{-1} in 1 M LiCl electrolyte, (b) galvanic charge-discharge plot of same sample performed at current density between 25 $\mu\text{A cm}^{-2}$ and 250 $\mu\text{A cm}^{-2}$ and (c) calculated areal capacitance vs discharge current density. Adapted from [15]

Electrochemical performance was also evaluated for C-3DINN grown at 600°C for 3 different duration- 30 mins, 45 mins, and 60 mins. Figure 2-15a illustrates the areal capacitance calculated from CV cycle of respective samples. The capacitance performance of all electrodes was very similar, with a maximum difference of 1.3% for

Figure 2-15 (a) Areal capacitance and %capacitance of carbon grown at 30, 45, 60 mins when compared to sample grown at 30 mins and (b) respective CV plots of the samples.

electrode grown for 45 mins when compared to the electrode grown at 30 mins. Hence, a longer growth time beyond 30 mins would not result in appreciable capacitance performance. Comparing the CV curves of all 3 samples from Figure 2-15b, the shape or “square-ness” are also very similar. This shows that there were also no significant changes in the quality of the carbon grown which would have affected the electrode series resistance and/ or leakage resistance. As the growth of carbon on Cu is a surface mediated process where carbon species gets adsorbed, nucleate and grow, carbon growth will stop once the surfaces are covered, leading to the formation of a relatively thin layer of graphitic carbon in a self-limiting process [45, 190, 199]. Thickness measured on TEM images also confirmed that the thickness did not show appreciable increase by extending the growth time to 45 and 60 mins. As shown in Figure 2-16a to 2-16c, the thickness of the carbon layer were 6.9 nm, 7.1 nm and 6.8 nm for growth time of 30 min, 45 min and 60 min respectively.

Figure 2-16 Carbon encapsulation thickness of (a) 30 mins, (b) 45mins and (c) 60 mins.

Interdigital In-Plane Microsupercapacitor

In-plane C-3DINN MSC with interdigital pattern was fabricated at 600 °C. The CV curves of the MSC at various scan rates from 1 mV s⁻¹ to 100 mV s⁻¹ in a solid electrolyte of H₃PO₄ in PVA from 0 V to 0.8 V are shown in Figure 2-17a. Similar to the CV curves of 3-electrode test, clear rectangular shape of the CV curves can be observed. At a scan rate of 50 mV s⁻¹ and above, the CV curves became more rounded and tapered as the ions in the solid electrolyte could not respond to the higher scan rates and hence, the capacitance was limited through ion diffusion [126, 200]. Correspondingly, the galvanic charge-discharge curves of the micro-supercapacitor at different current densities are shown in Figure 2-17b. The calculated areal capacitances from the charge-discharge curves at the current densities of 10, 20, 40, 80 and 170 $\mu\text{A cm}^{-2}$ are 1.45, 1.30, 1.16, 0.97 and 0.86 mF cm⁻² respectively (Figure 2-17c). The volumetric capacitance can be calculated from the areal capacitance by dividing the areal capacitance with the height of the nanowire electrode [107, 201, 202] i.e., 1.71, 1.52, 1.37, 1.14 and 1.01 F cm⁻³ respectively (Figure 2-17c). Maximum volumetric energy density and power density are also calculated to be 0.66 mWh cm⁻³ and 0.36 W cm⁻³, comparable to commercially available activated carbon electrochemical capacitors [203].

Figure 2-17 (a) The CV measurements performed on MSC under a scan rate from 1 mV s⁻¹ to 100 mV s⁻¹ in 1 M H₃PO₄ in PVA solid electrolyte, (b) the galvanic charge-discharge plot from 10 μA cm⁻² to 170 μA cm⁻² and (c) calculated areal and volumetric capacitance as a function of discharge current density. Adapted from [15].

A comparison between various in-situ and ex-situ carbon-based MSC devices is shown in Table 2-3. Our C-3DINN MSC showed superior performance to other CVD or ex-situ carbon-based planar MSC devices such as onion-like carbon, reduced graphene oxide, reduced graphene oxide, vertical oriented graphene, and VACNT. Even when compared to some carbon-based MSC decorated with pseudocapacitive materials like MnO₂, NiO, NiCoSe and PPy, our C-3DINN MSC showed relatively comparable capacitance performance.

Table 2-3 Areal and volumetric capacitance comparison of various carbon-based in-plane MSCs with 3D carbon-encapsulated nanowire network MSC. Adapted from [15].

Ref	Active Material	Areal Capacitance	Volumetric Capacitance	Fabrication Method
[125]	Onion-like carbon	1.1 mF cm ⁻²	-	Electrophoretic deposition (ex-situ)
[203]	Reduced Graphene Oxide	80.7 μF cm ⁻²	17.9 F cm ⁻³	Reduced from GO followed by patterning (ex-situ)
[204]	Reduced Graphite Oxide	2.40 μF cm ⁻²	6.00 mF cm ⁻³	Laser writing on GO film (ex-situ)
[205]	Reduced Graphene Oxide/ MnO ₂	1.63 mF cm ⁻²	3.60 F cm ⁻³	Electrodeposition (ex-situ)
[206]	NiCoSe@PPy@GF	-	5.21 F cm ⁻³	Chemical synthesis followed by deposition and patterning (ex-situ)
[140]	Vertical Oriented Graphene Nanosheets	45 μF cm ⁻²	-	Microwave plasma enhanced CVD (in-situ)
[144]	Vertically aligned CNT	430 μF cm ⁻²	-	CVD (in-situ)
[142]	NiO decorated VACNT	-	1.26 mF cm ⁻³	CVD (in-situ) followed by electrodeposition
This work	CVD graphitic carbon on nanostructured current collector	1.45 mF cm⁻²	1.71 F cm⁻³	CVD on 3D Cu nanowire network (in-stu)

Additionally, full cell electrochemical impedance spectroscopy (EIS) was also performed on C-3DINN MSC from 0.1 Hz to 0.1 MHz in order to understand its electron and ion transport properties. The Nyquist plot of the micro-supercapacitor is displayed in Figure 2-18a. For an ideal capacitor, the impedance response at all frequencies should

be that of a straight line parallel to the imaginary axis of the Nyquist plot. For practical capacitors, a semicircle might appear at high frequencies depending on interfacial and bulk properties of the electrode material and electrolyte, followed by a rising line from mid to low frequencies which deviates from the ideal vertical line parallel to the imaginary axis. In this case, a semicircle was not observed at the high frequency region, suggesting negligible charge transfer resistance and hence, a kinetically fast

electrochemical system, which is typical of electric double layer capacitors [203, 207, 208].

The intercept at the real axis of the plot is the bulk resistance, R_s while the extrapolation of the low frequency data to the intercept of the real axis gives the Warburg impedance, W . R_s value is a combination of carbon-Cu contact resistance, solution resistance of electrolyte and resistance of electrode material itself and our MSC displayed a good R_s value of 15.6Ω ($9.98 \Omega \text{ cm}^2$) showing efficient movement of charges in our electrodes. This compares favourably to some of the MSCs listed in table 2-3 ($16 \Omega \text{ cm}^2$ [125], 17.6Ω [203], 18.7Ω [206], $23 \Omega \text{ cm}^2$ [142]). A very low Warburg impedance of 1.96Ω indicates very low diffusion resistance as the open structure of the electrode allows fast movement of ion species in forming the electric double layer at the surface of the carbon. Towards the lower frequencies, the data plot trends towards more negative imaginary impedance values with deviation away from an ideal vertical plot. The characteristic frequency and the relaxation time constant of the micro-supercapacitor can be found from the bode plot where phase angle is plotted against the frequency (Figure 2-18b). For an ideal capacitor, the current response to a small sinusoidal potential should exhibit a -90° phase angle. The phase angle also varies with the frequency of the potential. At very high frequencies, the device behaves like a resistor while at lower frequencies, the device behaves like a capacitor [209]. Hence, the characteristic frequency (f_0) is defined. Above f_0 , the capacitor starts to behave like a resistor, and this occurs at a phase angle of -45° . It is noted that our planar supercapacitor exhibited a f_0 of 41.09 Hz. Correspondingly, the relaxation time constant ($t_0 = 1/f_0 = 24 \text{ ms}$) tells the minimum time needed to discharge all the energy from the device with an efficiency of more than 50% [210-212].

Our device showed an efficient and fast charge response kinetics with a relaxation time constant of only 24 ms. The value is comparable to other reported carbon-based micro-supercapacitors, such as activated carbon ($t_0 = 714$ ms) [211], reduced-GO ($t_0 = 33$ ms) [213], onion-like carbon ($t_0 = 26$ ms) [211], and MnO₂-carbon fiber ($t_0 = 22$ ms) [214].

Cycling performance is another important performance indicator in energy storage devices. Electric double layer capacitors have an especially long cycling life due to its electrostatic charge storage mechanism. The lack of chemical reactions minimizes irreversible damages to the carbon electrode. Ideally, MSC in embedded systems such as on-chip MSCs should have cycling life comparable or exceeding that of the device working life. Figure 2-19 illustrates the cycling performance of our MSC device. The percentage capacitance retention of the device can be found to decrease from 100% at the first cycle to 94.2% after 10000 cycles of charging and discharging with a coulombic efficiency of 99.0%, suggesting an excellent cycling capability. The high coulombic efficiency indicates that unwanted side reactions at the electrodes or electrolytes during charging and discharging are kept to a minimum [215]. Almost all the capacitance decay

Figure 2-19 %capacitance retention and Coulombic efficiency as function of cycle number. Inset: the last 10 charge-discharge cycles of the device. Adapted from [15].

comes from the first 500 cycles where capacitance retention reached 94.1%. Thereafter, capacitance retention maintained at this level for the rest of the charging-discharging cycle, ending at 94.2% retained capacitance at the end of 10000 cycles.

The capacitance retention is comparable to other carbon-based co-planar micro-supercapacitors, such as vertical oriented graphitic petals (95%, 2000 cycles) [14], photoresist-derived carbon (87%, 1000 cycles) [216], CNT stretchable micro-supercapacitor (98.5%, 1000 cycles) [217], laser-scribed graphene micro-supercapacitors (96.5%, 10000 cycles) [218], reduced-GO (70%, 10000 cycles) [219], rGO-CNT micro-supercapacitors (95%, 1000 cycles) [213], and PANI/rGO based micro-supercapacitors (90%, 1700 cycles) [220].

2.3 Conclusion

In chapter 2.1, we demonstrated a novel 3D interconnected nanowire network (3DINN) of pure Cu nanowires on SiO₂/Si substrates. Sputtered Cu film was transformed into Cu 3DINN through a template-free chemical oxidation process followed by a thermal reduction process. The chemical oxidation process was optimized by using a two-step process in which Cu was first reacted with diluted NaOH and APS followed by a more concentrated mixture of the same reactants so that pure Cu(OH)₂ nanowires without CuO particles were synthesized. Synthesized Cu nanowires were about 150 nm in width and about 10 μm in vertical height.

The ability to fabricate a 3D Cu nanostructure is crucial as it acts as a scaffold and allow subsequent electroactive materials to be deposited on the 3D electrode nanostructure. Furthermore, the synthesis process is template-free, simple and cost effective.

Next in chapter 2.2, we successfully utilized CVD technique to grow graphitic carbon on 3DINN nanostructures to obtain a carbon-encapsulated 3D nanostructured electrode for microsupercapacitors (C-3DINN). We find that a growth temperature of 600 °C gave the best electrochemical performance as the grown carbon is of graphitic structure. Growth temperature below 600 °C could produce more polymeric carbon while a temperature beyond 600 °C melted the Cu nanostructure. The electrochemical performance did not alter significantly beyond a growth time of 30 mins as the self-limiting and surface-mediated growth process of C on Cu limits the thickness of grown carbon.

We successfully fabricated an all-solid state in-plane MSC using the C-3DINN electrode. The MSC device displayed excellent areal and volumetric capacitance performance of 1.45 mF mc^{-2} and 7.43 F cm^{-3} respectively at a current density of $10 \mu\text{A cm}^{-2}$. The electrochemical performance is superior to other reported carbon-based CVD in-plane MSCs. C-3DINN MSC also showed an efficient and fast charge response kinetics with a relaxation time constant of only 24 ms. Lastly, the cycling stability was also excellent with a capacitance retention of 94.2% after 10000 cycles.

The excellent performance can be attributed to the developed 3DINN nanostructure where a vertically thick layer ($\sim 8.5 \mu\text{m}$) allowed large material loading in the vertical direction while still maintaining large area for formation of electric double layer, resulting in superior capacitance performance. Furthermore, only a thin layer of CVD carbon was deposited such that most of the carbon can be accessed efficiently and quickly. Electron transport pathway is thus short and quick, resulting in high rate capability of the MSC. 3DINN structure has been shown to be efficient in enhancing the electrochemical performance of carbon-based MSC. It also has great potential for further performance enhancement by acting as a scaffold for incorporation of other electroactive species.

3 High-Performance Pseudocapacitors Based on 3D Interconnected Nanowire Network Electrode Design

Section 3.1 shows the results of using electropolymerized PPy on the developed 3DINN structure for an in-plane PPy/PPyNT-3DINN MSC device which showed excellent performance compared to similar PPy-based MSCs. In Section 3.2, the versatility of the developed 3DINN structure is presented through the successful conformal electrodeposition of various types of pseudocapacitive materials. The electrochemical results of a composite in-plane MSC made of PPy@MnO₂-3DINN are also presented.

3.1 Electropolymerized PPy-Encapsulated Interconnected Nanowire Network as High Performance Microsupercapacitor.

3.1.1 Introduction

Conducting polymers such as polyaniline (PANI), polypyrrole (PPy) and poly(3,4-ethylenedioxythiophene) (PEDOT) are promising PC materials for planar MSCs [221-226] due to their low cost, ease of fabrication, and versatility in tuning their molecular structure and functional groups. Among the conducting polymers, polypyrrole (PPy) stands out due to its high conductivity, fast charge-discharge kinetics, low cost, high energy density, and relatively high thermal stability [227-230]. However, similar to most conducting polymers, PPy can undergo volumetric changes during charge and discharge which results in the weakening of its bulk structure, leading to poor cycling performance. In a study by Smela and Gadegaard, dry PPy first undergo a ~11% swelling its thickness when immersed in electrolyte, followed by 30 – 40% change in volume when cycled between its oxidized and reduced state [231]. Its dense growth also limits its capacitive performance in its bulk form as ions are unable to penetrate deep into the material [160, 226, 232]. To overcome the issues, strategies such

as synthesis of designed PPy nanostructure or compositing of PPy with carbon materials or metal oxides have been developed [233]. Invariably, the different approaches converge to the fact that PPy in various 3-dimensional architectures are indispensable in enhancing electrochemical performance and cycling stability through the availability of large surface area for redox reaction and improved ion and electron diffusion rate.

In the area of in-plane MSCs, a large number of nanostructured ppy-based MSCs were synthesized by compositing PPy with electroactive materials such as carbon or metal oxides such as MnO₂ nanoflakes [114, 226, 234, 235]. However, the thickness of the active materials was still relatively small (<3 μm). Wu et al. fabricated an interdigital MSC based on 5 alternating stacked layers of exfoliated graphene and PPy-Graphene of about 10 μm in thickness [115]. However, due to the 2-dimensional and planar nature of graphene, electron transfer in the vertical direction towards the current collector is not efficient. Moreover, fabrication of 5 alternating stacked layers is challenging and extremely time-consuming.

Deposition of PPy on nanostructured scaffolds allows effective loading of materials in the vertical direction. Aradilla et al. deposited PPy on thin silicon nanowires and nanotrees scaffold up to $\sim 10\ \mu\text{m}$ in height vertically which yielded relatively high capacitance and energy density performance [156]. However, silicon is not very effective for electron transport and power performance was relatively low as a result. Lastly, Beidaghi et al. deposited PPy on large vertical carbon pillars up to 140 μm in height and 50 μm in diameter [236]. However, the large size and low density of pillars (39 pillars in a single electrode finger) meant that the amount of deposited PPy was relatively low which resulted in low amount of energy stored.

PPy can be synthesized through chemical or electrochemical methods. Electropolymerization offers certain advantages over chemical synthesis. First, PPy could be directly grown on electrode substrate offering good mechanical adherence and conductivity. Secondly, morphology and intrinsic properties such as thickness, mass, electrical conductivity can be tightly controlled through optimizing electrodeposition parameters. Lastly, the process is time and cost-effective as synthesized electrodes can be directly used for application without further processing steps such as material transfer, deposition and addition of binders [233].

In this section, we attempted to meet the challenges presented above by utilizing 3D interconnected nanowire network (3DINN) nanostructure we developed in Chapter 2 and fabricated a solid-state in-plane MSC consisting of symmetric PPy-encapsulated 3DINN and PPy nanotubes (PPyNTs). Electrodeposition was employed as it is a convenient, quick and economical method to selectively deposit high quality PPy on patterned in-plane MSC interdigitated design. The PPy/PPyNT-3DINN in-plane MSC exhibited a high areal capacitance performance of 89.9 mF cm^{-2} and areal energy and power densities of $12.5 \text{ } \mu\text{Wh cm}^{-2}$ and 5.95 mW cm^{-2} respectively in 1 M H_3PO_4 -PVA. The results show that our developed 3DINN nanostructure is an excellent design in which nanostructured PPy can be easily and quickly deposited to achieve high performance PPy-based in-plane MSC.

3.1.2 Experimental Details

Carbon-encapsulated 3DINN (C-3DINN) electrode structure was prepared according to Chapter 2 on a 2 x 2 cm Si substrate. 0.1 M pyrrole and 0.1 M KCl in DI water were prepared for use as electrodeposition solution. 5 mM of Methyl Orange (MO) was also added while 1 M HNO₃ was added dropwise into the pyrrole solution until a pH level of 2 was obtained. Reddish precipitation would form in this acidic medium [237, 238]. The acidic medium allows MO to aggregate and form tubular structure in which polymerization of pyrrole occurs during the electrodeposition process to form PpyNTs.

Anodic electrodeposition process was carried out in a three-electrode chemical cell with platinum as the counter electrode and Ag/AgCl electrode as the reference electrode (Figure 3-1). A constant current of 1.5 mA cm⁻² was applied to the samples for 300s, 400s, 500s, 600s, 700s and 800s to obtain PPy/PPyNT-3DINN electrodes. After electrodeposition, samples were rinsed thoroughly with copious amount of DI water and dried under constant flow of nitrogen.

Figure 3-1 Schematic of 3-electrode setup for electrodeposition of PPy-PPyNT.

Morphology of the samples was examined by FESEM (Hitachi SU5000). Elemental distribution was obtained with Electron Dispersive Spectroscopy (EDS) using EDAX Octane Elect detector. Raman spectroscopy was carried out using Renishaw InVia instrument.

For the fabrication of solid state PPy/PPyNT-3DINN MSC, a stainless-steel mask with interdigitated design was clamped on a 2 x 2 cm SiO₂/Si substrate before the deposition of 100 nm Ti and 1000 nm Cu film using sputtering process. C-DINN was prepared according to steps described in Chapter 2. Thereafter, the PPy/PPyNT-3DINN electrodeposition on C-3DINN process was same as described in above paragraphs. Solid electrolyte was made with 1 g of Polyvinyl Alcohol (PVA) in 10 ml DI water heated to 80°C. The mixture melted to form a clear liquid in which 1 M KCl was then added. Fabricated MSC was then dipped into the mixture and held for 30 mins before pulling out slowly. The interdigital MSC was allowed to dry in ambient condition overnight.

Electrochemical measurements were carried out in a three-electrode configuration using a computerized potentiostat (Metrohm Autolab PGSTAT 101M) with Platinum as the counter electrode and Ag/AgCl as the reference electrode. 3 M KCl solution was used as the electrolyte. For interdigitated planar MSC, a two-electrode configuration was used instead, with a symmetric PPy-PPyNT electrodes as the working and counter electrodes. Cyclic Voltammetry (CV), Galvanostatic charge/discharge (GCD) and electrochemical impedance spectroscopy were conducted.

3.1.3 Results and Discussion

Physical Characterization of PPy/PPyNT-3DINN

The successful electropolymerization of pyrrole is supported by SEM images in Figures 3-2a to 3-2f. It can be observed that PPy grew conformally and encapsulated the

Figure 3-2 SEM images of PPy-PPyNTs deposition on 3D carbon nanowire network at different deposition times of a) 300s, b) 400s, c) 500s, d) 600s, e) 700s and f) 800s. PPyNTs are pointed out in red. All images are of same magnification. g) Side profile view of the layer at about 7.5 μm . h) C-DINN structure without PPy/PPyNT electrodeposition.

C-3DINN nanowires. The uniformity in PPy deposition is due to uniform adsorption of pyrrole monomer and excellent conductivity of the underlying interconnected carbon nanowire network. As deposition time was increased from 300s to 800s, the thickness and diameter of nanowire network also increased. At 800s, many neighbouring nanowires in proximity clumped together, forming large clusters of PPy (Figure 3-3).

To further illustrate uniformity of PPy and PPyNTs deposition, elemental mapping was carried out using energy dispersive X-ray spectroscopy (EDX) shown in Figure 3-4. It can be clearly observed that the PPy-containing elements such as C and N are homogeneously and conformally deposited on the 3D nanowire network.

PPyNT was also observed to be successfully deposited. In synthesis of PPyNT, the Methyl Orange in the deposition solution, under acidic condition, served as the tubular scaffold on which PPy was polymerized, forming PPyNTs. At shorter deposition times of 300s and 400s, the PPyNTs are shown to be in contact with the nanowire network (Figure 3-2a and 3-2b). At longer deposition times from 500s onwards however, the PPyNTs are integrated into the nanowire network as the polymerization process had fused them together (Figure 3-2c to 3-2f). Figure 3-2g shows the side profile of the structure with a total vertical height of about 7.5 μm .

Lastly, Raman analysis was used to further confirm and characterize the electrodeposited PPy/PPyNT material. In the Raman spectrum shown in Figure 3-5a, the main peak at 1574 cm^{-1} could be attributed to the benzoic band of C=C, while 1410 cm^{-2} and 1325 cm^{-1} peaks were caused by the C-N and C-C vibration respectively. The peaks at 1044 cm^{-2} , 975 cm^{-1} were due to C-H in-plane bending and ring bending mode respectively while peak at 931 cm^{-1} was due to the presence of polaron [239-242]. Figure 3-5b shows the reference Raman spectrum of C-3DINN in which electrochemical

polymerization was carried out on. Both the G-band at 1599 cm^{-1} and D-band at 1328 cm^{-1} attributed to the benzoic band of C=C and C-C vibration from the graphitic carbon are clearly present. In this case, the characteristic peaks belonging to vibration modes of C-N, C-H and polaron from PPy are not present.

Figure 3-3 SEM image of PPy-PPyNT deposited for 800s. Clusters of fused nanowires can be clearly observed which are boxed in red.

The observations from SEM images, EDX elemental mapping, and Raman spectroscopy confirm the successful electrochemical polymerization and deposition of PPy and PPyNT on 3DINN nanostructure

Figure 3-4 (a) SEM image of PPy, (b) elemental map overlay, (c) and (d) elemental map of C and N respectively of PPy. (e) SEM image of PPyNT, (f) elemental map overlay, (g) and (h) elemental map of C and N respectively of PPyNT.

Figure 3-5 Raman spectra of a) PPy/PPyNT-3DINN illustrating successful electrochemical polymerization and deposition on nanowire network and b) C-3DINN before electrochemical polymerization for reference.

Electrochemical Characterization

To evaluate the electrochemical performance of PPy/PPyNT-3DINN electrodes, electrochemical measurements were done using a 3-electrode chemical cell setup consisting of a platinum counter electrode, an Ag/AgCl reference electrode, a working electrode, and 3 M KCl electrolyte. Figure 3-6 provides a CV performance comparison between electrodeposited PPy film on Ti, PPy/3DINN, and PPy/PPyNT-3DINN

network. The electrodeposition processes were carried out using a constant current of 1.5 mA cm^{-2} for 400s. Clearly, comparing the CV curves of PPy-3DINN and PPy-Ti, the 3D electrode architecture provided a much larger total surface area for the faradaic process between the interface of PPy and the electrolyte, thereby increasing the capacitance. Furthermore, by incorporating additional active material in the form of PPyNTs, a small but appreciable increase in capacitance was also observed. The shape of the CV curve of PPy/PPyNT-3DINN slightly differs from that of the other two. There are two possible origins of the hump and valley feature of the CV curve for PPy/PPyNT-3DINN. Firstly, with increasing material deposition of PPyNT, the flow of ions into the 3DINN structure may be slightly impeded. In the initial potential increase, there could be a rapid increase in surface anion concentration from the electrolyte. This corresponds to the quick rise in current response, where it reached maximum at the crest of the hump

at 0.1 V. Beyond 0.1 V, the anion surface concentration asymptotically reached its maximum value. The rate of surface ion accumulation slows down beyond 0.1 V which in turn results in a drop in current density where the valley occurs [243, 244].

Secondly, the incorporation of PPyNT involved the use of methyl orange (MO) where it acts as the scaffold which PPy is deposited on. As such, MO might have contributed partially to the increase in capacitance in the form of faradaic reaction, resulting in a reaction peak near 0.1 V [244, 245].

Figure 3-7a shows the CV measurements of PPy/PPyNT-3DINN electrodes with different deposition times from 300s (sample PN300) to 800s (sample PN800) at a scan rate of 20 mV s^{-1} respectively. Clearly, as deposition time was increased, the peak current and enclosed area of CV curve also increased. As the enclosed area of the CV

Figure 3-6 CV performance comparison between PPy film polymerized on Ti substrate, PPy polymerized on nanowire network, and PPy-PPyNT polymerized on nanowire network. Scan rate for CV was 20 mV s^{-1} .

curve is directly proportional to the capacitance, the findings suggest that the longer the deposition time was, the larger the capacitance obtained. This was corroborated by the galvanic charge/discharge (GCD) results illustrated in Figure 3-7b. A constant current of 0.5 mA cm^{-2} was applied on the electrodes between a potential window of $-0.1 \text{ V} - 0.7 \text{ V}$. Under a fix constant current in a given potential window, time needed to charge and discharge PN800 was the longest while PN300 was the shortest. Calculated areal capacitances of the samples from GCD measurement are shown in Figure 3-7c. PN800 showed the highest areal capacitance of 207.7 mF cm^{-2} while PN300 showed the lowest areal capacitance of 82.2 mF cm^{-2} .

From Figure 3-7c, it can be observed that capacitance increased linearly from PN300 to PN600. Above deposition time of 600s, the rate of increase in the capacitance reduced and nearly plateaued at PN800. In fact, PN700 had only a slightly lower capacitance value of 198.6 mF cm^{-2} . This can be explained that as deposition time increases, more nanowires are bound together by deposition of PPy. As a result, the total

Figure 3-7 (a) CV curves and (b) GCD curves of PPy-PPyNT samples deposited for different amount of time. (c) Areal capacitance of respective PPy-PPyNT samples. CV curves obtained at scan rate of 100 mV s^{-1} for (d) PN300 and (e) PN800 electrodes. (f) Areal capacitance performance of PN700 at various charge-discharge current density.

surface area exposed to the electrolyte does not increase in proportion to the amount of electrodeposited PPy-PPyNTs.

Furthermore, with extended deposition time, it was observed that the CV curves started to deviate from the ideal CV characteristics of a rectangular shape. At a scan rate of 100 mV s^{-1} , PN300 exhibits a rectangular CV curve, indicative of fast response and high rate capability of the deposited PPy-PPyNTs (Figure 3-7d). PN800, on the other hand, showed a CV curve that had greatly tapered off into a ‘fisheye’ shaped, indicative of poor response time and small rate capability (Figure 3-7e). The small rate capability may result from increased diffusion of electrolyte into the bulk volume of PPy for redox reaction. With a thinner deposited layer, a larger proportion of redox-active sites are near the interface between the material and electrolyte whereas for a thicker deposited layer, a larger proportion of redox-active sites are deeper in the bulk of PPy. Hence, the response and rate capability for a thicker deposit was slower although the total capacitance was larger.

Considering the small difference in capacitance between PN700 and PN800, and the poorer rate capability of PN800, PN700 was shown to have the most optimized performance among the different electrodeposition time. Calculated areal capacitances of PN700 from GCD curves at various current densities is shown in Figure 3-7f. The highest capacitance of 198.6 mF cm^{-2} obtained at a current density of 0.2 mA cm^{-2} and 109.1 mF cm^{-2} at a current density of 10 mA cm^{-2} . The CV curves of PN700 in Figure 3-8a show that even at a scan rate of 100 mV s^{-1} , PN700 still maintained a relatively good response and high rate capability performance. Figure 3-8b illustrates the GCD curves of PN700 at various current densities.

Figure 3-8 (a) CV and (b) GCD curves of PN700 electrode at various scan rate and current densities.

Solid-State In-Plane Microsupercapacitor

Based on electrochemical results on the optimized deposition time, a symmetric PPy/PPyNT-3DINN all solid-state planar MSC device was fabricated. Electrochemical performance of the device was similarly evaluated. The CV plots of the MSC device cycled from a scan rate of 2 to 70 mV s^{-1} within a potential window of 1 V in a solid electrolyte composed of 1 M KCl-PVA are shown in Figure 3-9a. Similar to the three-electrode CV curves, clear rectangular-shaped CV curves are also observed here. Limited by ion diffusion, the solid electrolyte could not respond as the scan rate increased [126, 200]. Consequently, this was reflected in the CV plot as the curves' edges became more rounded while the slope became tapered. The GCD curves at various current densities from 0.5 to 15 mA cm^{-2} are illustrated in Figure 3-9b. The corresponding calculated areal capacitances of the PPy/PPyNT-3DINN MSC device are shown in Figure 3-9c. The device obtained a maximum areal capacitance of 66.6 mF cm^{-2} at a current density of 0.5 mA cm^{-2} and a minimum areal capacitance of 13.7 mF cm^{-2} at a current density of 15 mA cm^{-2} . Calculated areal energy density and power density values at different current densities are illustrated in Figure 3-9e

Full cell Electrochemical Impedance Spectroscopy (EIS) was also performed on the MSC in the frequency range from 0.1 MHz to 0.1 Hz to understand its ion transport properties. In practice, a capacitor may display a semicircle in the high frequency region, followed by a 45° Warburg resistance in the mid-frequencies, and a vertical line parallel to the imaginary axis at the low frequencies in a Nyquist plot. The semicircle high frequency region is a combination of the charge transfer resistance (R_{ct}) as well as the double layer capacitance (CPE_{DL}). R_{ct} is related to the redox reaction occurring at the interface between PPy and electrolyte. The value of R_{ct} corresponds to the diameter of

the semicircle. CPE_{DL} is the double layer capacitance occurring also at the electrode-electrolyte interface due to ionic/electronic charge separation [246, 247].

In the equivalent circuit, the double layer capacitance is modelled as a constant phase element instead of a capacitor to account for the distortion of the semicircle [248]. The series resistance (R_s) can also be obtained from the intercept of the Nyquist plot at

Figure 3-9 (a) CV curves and (b) GCD curves of PPy/PPyNT-3DINN symmetric planar MSC at different scan rates and current densities respectively, (c) Calculated Areal capacitance of MSC device at different current densities and (d) Nyquist plot of MSC device with inset showing enlarged view of plot and equivalent circuit used for fitting of plot. (e) Calculated areal energy density and power density of PPy/PPyNT-3DINN MSC. Inset of (c) shows the image of fabricated PPy/PPyNT-3DINN MSC.

the real axis in the high frequency region. R_s is the combination resistance of electrode material, electrolyte, current collector and contact resistance [249].

Obtained Nyquist plot in Figure 3-9d was fitted to an equivalent circuit (inset). At the high frequencies region, obtained (R_s) of the device was $34.9\ \Omega$, showing efficient movement of charges within the PPy electrode. The main contributor to the (R_s) was the solid electrolyte. Towards the mid-frequencies, a distorted semicircle was observed and a charge transfer resistance of $8.19\ \Omega$ was obtained. The low charge transfer resistance shows excellent charge transfer performance occurring between the electrode and the electrolyte. This can be attributed to the excellent conducting properties of PPy-PPyNT and the short conduction pathway due to the relatively thin layer of PPy. Furthermore, the open 3D electrode nanostructure allows electrolyte ions access to its large surface area where redox reaction can proceed quickly.

Long term electrochemical cycling performance of the MSC was also evaluated in Figure 3-10. 10000 GCD cycles between 0 and 1 V were performed at a current density of $5\ \text{mA cm}^{-2}$. An excellent capacitance retention of 80.1% was recorded, illustrating the benefit of depositing thin layer of PPy on 3DINN which could reduce mechanical strain in electrolyte insertion and extraction during charging and discharging.

Lastly, energy and power density were calculated based on obtained charge-discharge duration, potential window and capacitance. The planar PPy/PPyNT-3DINN MSC device achieved a maximum areal energy density of $9.25\ \mu\text{Wh cm}^{-2}$ and a maximum areal power density of $5.95\ \text{mW cm}^{-2}$. Volumetric energy density and power density were also calculated to be $12.2\ \text{mWh cm}^{-3}$ and $7.93\ \text{W cm}^{-3}$ respectively. Comparing to other planar PPy-based MSC devices (Table 3-1), our device based on the 3DINN nanostructure did admirably well.

Figure 3-10 Electrochemical cycling performance of PPy/PPyNT-3DINN MSC device over 10000 cycles. Inset shows the GCD curves of the last 10 cycles.

Table 3-1 : Comparison of capacitance, energy density and power density of PPy-PPyNT MSC device with similar PPy-based MSC devices.

Materials	Specific Capacitance	Energy Density	Power Density	Ref
PPy-G, alternate stacking	37.8 mF cm ⁻² -	- 10.1 mW h cm ⁻³	- 1.7 W cm ⁻³	[115]
Graphite-PPy	6 mF cm ⁻² -	0.697 μWh cm ⁻² -	0.05 mW cm ⁻² -	[114]
PPy- 3DrGO/npAu	29.21 mF cm ⁻² -	11.72 μWh cm ⁻² -	2.36 mW cm ⁻² -	[160]
PPy/C-MEMS	78.35 mF cm ⁻² -	0.696 μWh cm ⁻² -	0.63 mW cm ⁻²	[236]
MnO ₂ - PPy//V ₂ O ₅ - PANI	6.37 mF cm ⁻² -	- 19.8 mWh cm ⁻³	- 2.57 W cm ⁻³	[234]
MnO ₂ @PPy@ MWCNT	21.8 mF cm ⁻² -	7.9 μWh cm ⁻² -	1.77 mW cm ⁻² -	[235]
PPyNW	8.15 mF cm ⁻² -	- 15.25 mWh cm ⁻³	- 10 W cm ⁻³	[113]
rGO/PPy	9.40 mF cm ⁻² -	-	-	[226]
Silicon nanotrees/ PPy	14 mF cm ⁻² -	7.9 μWh cm ⁻² -	0.80 mW cm ⁻² -	[156]

PPy/PPyNT- 3DINN	66.6 mF cm⁻² 88.0 F cm⁻³	9.0 μWh cm⁻² 12.2 mWh cm⁻³	5.95 mW cm⁻² 7.93 W cm⁻³	This Work
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3.2 Pseudocapacitance Characteristics and PPy@MnO₂-3DINN Composite Microsupercapacitor

3.2.1 Introduction

In Chapter 3.1, we successfully incorporated a conducting polymer, polypyrrole, onto our 3DINN nanostructure and achieved a high performing in-plane MSC superior to many similar PPy-based MSCs. In this section we further demonstrate the flexibility of our 3DINN structure by incorporating metal oxides and even polymer-metal oxide composite.

In the case of some transition metals such as Ni, Co and Mn, their oxides and hydroxides compounds can undergo faradaic charge storage processes through valence state changes during redox reactions [250]. Conducting polymers undergo similar process in which electrons are removed/ added into polymer chains which attract doping and de-doping species from the electrolyte in order to achieve energy storage.

Amongst metal oxides, layered metal hydroxides are popular pseudocapacitance materials due to their lamellar structures [251]. The structures allow quick intercalation of electrolyte species between the layers to achieve high capacitance and energy density. Ni(OH)₂ and Co(OH)₂ are two typical layered metal hydroxides with specific capacitances comparable to that of RuO₂ [251]. The specific redox reactions associated with Ni(OH)₂ and Co(OH)₂ are:

From above reaction processes, an alkaline-based electrolyte like KOH or NaOH is preferable when hydroxides are used. Both Ni(OH)₂ and Co(OH)₂ also form clusters of nanosheets either chemically through chemical pot synthesis or electrochemical methods. This high surface area morphology is also beneficial for good electrochemical performance. The hydroxides are often composited with carbon structures to provide synergistic improvement to the electrochemical and cycling performance of MSCs [252-256].

Another metal oxide which is very popularly used as a pseudocapacitive material is MnO₂. Similar to Ni(OH)₂ and Co(OH)₂, MnO₂ can be synthesized into a lamellar structure (specifically δ -MnO₂) which allows fast and deep penetration into its interlayer for charge storage [257]. Its energy density performance is only second to RuO₂ amongst metal oxide materials. Unlike the hydroxides, MnO₂ can undergo redox reaction in a neutral electrolyte below without a phase change [258]:

where M⁺ are H⁺, Li⁺, Na⁺, K⁺. MnO₂ is also often composited with carbon materials to provide performance enhancement to capacitance [259-261].

Polypyrrole (PPy) is a very common conducting polymer (CP) used as a pseudocapacitance species as discussed in previous section. Compared to oxides and hydroxides, conducting polymers offer mechanical advantages as they are more mechanically flexible. As such, they can be mass-loaded without causing delamination or brittle failure. Conductivities of CPs are also generally higher than oxides and hydroxides. PPy has one of the highest specific capacitances amongst CPs which makes them a very popular choice in constructing MSCs. PPy is a p-doped polymer which charges and discharges according to:

Pseudocapacitance materials are often composited with carbon to enhance performance of MSC. Incorporation of these materials greatly improves carbon-based MSCs while still allowing reasonably excellent cycling performances. Similar to electric double layer MSCs, a large amount of surface area is critical to the good performance of pseudocapacitors. Nanostructures of pseudocapacitive materials are synthesized either through chemical or electrodeposited processes. In the electrodeposition process, a nanostructured template or scaffold is normally first synthesized such that electrodeposited materials are also nanostructured. In this work, we compare the capacitance performance of pseudocapacitance materials using a facile electrodeposition process to incorporate them onto our 3DINN electrodes.

The results show that our 3DINN structure is an excellent scaffold in which pseudocapacitance species can be easily electrodeposited to obtain nanostructured electrode design. Amongst the 4 pseudocapacitance species, Ni(OH)₂-3DINN achieved the highest areal capacitance of 139.5 mF cm⁻² while Co(OH)₂-3DINN yielded the highest energy density value at 8.38 μWh cm⁻² in a three-electrode electrochemical test.

The downside of using transition metal oxides as pseudocapacitor materials are their low conductivities. For example, the electrical conductivity of MnO₂ can be a few orders of magnitude lower than that of conducting polymer (10⁻⁵ – 10⁻⁶ S cm⁻¹ compared to 10 – 100 S cm⁻¹). Secondly, transition metal oxides are brittle and thus not suitable to be grown thickly [262, 263]. Hence, increasing the material loading of transition metal oxides on MSCs may lead to a slow rate capability and poor mechanical properties. Consequently, despite the good theoretical capacitance value of MnO₂, it remains

challenging to construct MnO₂ MSC with high rate capability and high energy density [264].

We constructed a solid state symmetric MSC based on PPy@MnO₂-3DINN core shell structure by a sequential electrodeposition of PPy and MnO₂ on a 3DINN structure in order to increase the mass loading of the electroactive material. Taking advantage of the high conductivity and capacitance characteristics of PPy, an enlarged potential window of 1.1 V was achieved. Excellent areal capacitance and energy density values of 92.3 mF cm⁻² and 15.5 μWh cm⁻² were obtained as a result. These values are superior to many current transition oxide/hydroxide based interdigital planar MSCs, demonstrating the effectiveness of our 3D nanostructure in contributing to good areal electrochemical performance through high material loading with a large surface area.

3.2.2 Experimental Details

Carbon-encapsulated C-3DINN electrodes were prepared according Chapter 2 on 2 x 2 cm Si substrates. Prepared samples were used as the working electrode for either cathodic or anodic reaction for electrodeposition of Ni(OH)₂, Co(OH)₂, MnO₂, and PPy in a three-electrode set up. 0.2 M of Ni(NO₃)₂, Co(NO₃)₂, Mn(NO₃)₂ and Pyrrole from Sigma Aldrich were used as the precursor solution. 0.2 M of Na(NO₃)₂ and KCl were added into Mn(NO₃)₂ and pyrrole precursor solution as a supporting electrolyte respectively. Cathodic deposition was carried out for electrodeposition of Ni(OH)₂ and Co(OH)₂ while anodic deposition was carried out for polypyrrole and MnO₂. All electrodeposition processes were carried out for 500s at 2 mA cm⁻² (1 C cm⁻²). The samples are named as Ni(OH)₂-3DINN, Co(OH)₂-3DINN, MnO₂-3DINN, and PPy-3DINN. PPy@MnO₂-3DINN interdigital MSC was prepared by the sequential electrodeposition of PPy and MnO₂.

Direct observation of deposited samples was conducted using scanning electron microscope (Hitachi SU5000). Elemental identification and distribution were examined using Electron Dispersive X-ray Spectroscopy (EDAX Octane Elect) on the SEM.

Electrochemical tests were carried out in a three-electrode electrochemical cell using a computerized potentiostat (Metrohm Autolab PGSTAT 101M). The prepared electrodes acted as the working electrode, while the counter electrode was a platinum foil. An Ag/AgCl electrode in 4 M KCl solution was used as the reference electrode. 3 M KOH aqueous solution was used as the electrolyte for 3-electrodes tests while 1 M KCl-PVA solid electrolyte was used for PPy@MnO₂-3DINN interdigital MSC.

3.2.3 Results and Discussion

Physical Characterization of the Electrode

SEM imaging was used to observe the morphology of electrodeposited materials. Figures 3-11a and 3-11b show the successful homogeneous deposition of Ni(OH)₂ nanosheets on the nanowires at different magnifications. The nanosheet structure is clearly visible in Figure 3-11b. Average thickness of deposited nanowire was about 286 nm. During electrodeposition process, nitrate ions from Ni(NO₃)₂ precursor could first be reduced to OH⁻ ions at the surface cathode (nanowire) with the supply of electrons. At the localized high concentration of OH⁻, Ni(OH)₂ precipitates to form Ni(OH)₂ instantaneously on the surface of the electrode grew as follows [265].

This desirable nanostructure provides large surface area and short diffusion path for both electrons and ions which contributes to a large specific capacitance performance.

Figures 3-11c and 3-11d show the morphology of electrodeposited Co(OH)₂. Co(OH)₂ was also similarly grown into a nanosheet structure following the same reaction pathway as Ni(OH)₂. The individual nanosheets were noticeably larger in size. However, the thickness of the nanowires grown were thinner at 204 nm. Since the deposition conditions and the reduction of nitrate ions are the same in both cases, it meant that the precipitation and growth rate from Co²⁺ to Co(OH)₂ was slower compared to Ni²⁺ to Ni(OH)₂.

Figures 3-11e and 3-11f show the morphology of deposited MnO_2 nanowires. Its morphology were identical to that of Ni(OH)_2 . However, it was larger in size measured at 459 nm.

Lastly, Figures 3-11g and 3-11h show the morphology of PPy under an anodic deposition condition instead of cathodic. Morphology of deposited PPy was distinctly different compared to the hydroxides and MnO_2 . The thickness of the nanowires was evidently smaller at about 117 nm. Instead of randomly oriented nanosheets, PPy was observed to be growing in layers stacked along the axial direction of the nanowires (Figure 3-11h and inset). In the deposition of PPy, pyrrole monomer was first oxidized, and then formed conjugated polymer chains with other monomers or polymer chains. Anionic dopants from the supporting electrolyte (Cl^- in this case) were incorporated into the polymer as a charge balance during electropolymerization [266, 267].

Successful homogeneous electrodeposition of transition metal oxides and conducting polymer illustrates the versatility of our 3DINN structure in incorporating a variety of electroactive materials. The 3DINN structure acted as a nanostructured scaffold and allowed in-situ deposited materials to be nanostructured, hence providing a facile fabrication pathway for MSC electrodes.

Figure 3-11 SEM images showing electrodeposited (a) – (b) Ni(OH)_2 , (c) – (d) Co(OH)_2 , (e) – (f) MnO_2 , and (g) – (h) PPy.

Electrochemical Measurements

Figures 3-12a to 3-12d illustrate the CV response plots of $\text{Co}(\text{OH})_2$ -3DINN, $\text{Ni}(\text{OH})_2$ -3DINN, MnO_2 -3DINN, and PPy-3DINN electrodes respectively. CV tests were conducted from a scan rate of 2 mV s^{-2} to 100 mV s^{-1} in 3 M KOH. The operating voltage of each pseudocapacitor system was selected to ensure that the range of potential in which faradaic process happened are covered. As redox reactions require time to proceed, rising scan rate restricts the ability of the redox reaction to keep up with the fast change in potential. Hence, the CV curves tapered towards an oblong shape. Redox peaks, if any, would also be smoothed out. This phenomenon was observed in the CV curves for all 4 electrode samples. The inset of respective samples' CV plot are the CV curves measured at a slower 10 mV s^{-1} scan rate so that a defined characteristic shape can be observed. The apparent difference among the CV curves of the 4 electrodes is

Figure 3-12 CV curves of (a) $\text{Co}(\text{OH})_2$ -3DINN (b) $\text{Ni}(\text{OH})_2$ -3DINN, (c) MnO_2 -3DINN, and (d) PPy-3DINN electrode samples.

that both $\text{Co(OH)}_2\text{-3DINN}$ and $\text{Ni(OH)}_2\text{-3DINN}$ possess very obvious redox peaks, suggesting that the redox reactions discussed above in Equation 3.1 to 3.3 occurred.

In the inset of Figure 3-12a, the anodic peak at 0.06 V corresponds to the oxidation of Co^{2+} to Co^{3+} while the cathodic peak at 0.12 V corresponds to the reduction reaction from Co^{3+} to Co^{2+} . We can also observe that the difference between the potential of the anodic and cathodic peak increases with scan rate. In the case of $\text{Co(OH)}_2\text{-3DINN}$ in Figure 3-12a, the peak anodic current potential occurred at 0.06 V while the peak cathodic current potential occurred at 0.12 V at a scan rate of 2 mV s^{-1} . At a high scan rate of 100 mV s^{-1} , the peak anodic and cathodic current potential occurred at -0.18 V and 0.39 V (0.57 V difference) respectively. At low scan rates, electrolyte ions and Co(OH)_2 had sufficient time to diffuse and react with one another, which increased the probability of occurrence of redox reactions, hence producing sharp and well defined potential peaks. At high scan rates, the residence time of ions was decreased, restricting the reaction, resulting in reactions occurring at “spread out” and shifted range of potentials [267, 268]. Hence, a broadened peak current potential peak could be observed. Furthermore, the redox peaks are symmetric, which shows high reversibility of the Co(OH)_2 reaction [171].

The CV curves of $\text{Ni(OH)}_2\text{-3DINN}$ in Figure 3-12b also show 2 distinctive redox peaks as the electrode underwent very similar redox reactions to Co(OH)_2 . At a scan rate of 2 mV s^{-1} as shown in the inset, the anodic peak current at 0.22 V corresponds to the oxidation of Ni^{2+} to Ni^{3+} while the cathodic peak current at 0.38 V corresponds to the reduction of Ni^{3+} to Ni^{2+} . However, the difference between the anodic and cathodic peak current potential was smaller compared to Co(OH)_2 . At 100 mV s^{-1} the peak anodic current potential was 0.19 V while the peak cathodic current potential was 0.51 V (0.32 V difference). Although the redox peaks show symmetrical characteristics, it is less

symmetrical compared to the CV curves for $\text{Co(OH)}_2\text{-3DINN}$, suggesting that the reaction might be less reversible compared to Co(OH)_2 . Lastly, the working potential window (0.6 V) was narrower compared to $\text{Co(OH)}_2\text{-3DINN}$ (0.9 V).

CV curves of $\text{MnO}_2\text{-3DINN}$ electrodes are presented in Figure 3-12c. The redox peaks are not observed. In contrast to redox reactions of hydroxides, redox reaction of MnO_2 does not depend on OH^- ions from the electrolyte. Instead, as reported by previous studies, the positive cation, K^+ in this case, participates in the intercalation of MnO_2 , forming MnO_2K^+ during the oxidation process from Mn(II) to Mn(III) without any phase changes as shown in Equation 3.4 [269, 270]. The reaction could occur quickly across a range of potential, instead of a fixed potential, resulting in a current response curve very similar to that of an EDLC supercapacitor. In a strict sense, this is a “true” pseudocapacitor material as the electrochemical behaviour mirrors that of an EDLC capacitor while the hydroxide electrodes’ behaviour is more “battery-like” [271, 272]. The working potential window of MnO_2 was also 0.6 V.

Lastly, the CV response of PPy-3DINN electrode is presented in Figure 3-12d, which seems to be in between that of $\text{MnO}_2\text{-3DINN}$ and the hydroxides samples. Redox peaks are clearly present in the CV curves, but they exist as broad peaks which are not well-defined like the hydroxides’ electrodes even at slow scan rates. Redox reaction of PPy occurred with the insertion of the anions from the electrolyte (Equation 3.5) occurring across the range of working potential. The presence of broad redox peaks here suggests the possibility that redox reaction with OH^- anions may occur with a slightly higher probability at a certain potential. The working potential window of PPy-3DINN electrode was 0.8 V.

GCD plots of the 4 electrodes are shown in Figures 3-13a to 3-13d. GCD was carried out at different current densities from 0.2 mA cm^{-2} to 2 mA cm^{-2} . Compared to EDLC capacitors, the shape of the GCD curves here deviates from a linear response, especially for Co(OH)_2 -3DINN and Ni(OH)_2 -3DINN. This is typical of layered hydroxides in which a battery-like behaviour contributes to the capacitance of the

Figure 3-13 GCD curves of 3DINN electrodes deposited with (a) Co(OH)_2 , (b) Ni(OH)_2 , (c), MnO_2 , and (d), PPy. (e) Nyquist plot comparison of the 4 electrodes

devices [273]. Battery-like behaviour during charge and discharge processes involve a material phase change, which is reflected as a flat plateau in the GCD curves as a function of potential. However, as the layered hydroxide thickness decreases/ size becomes smaller, the flat plateau region in the GCD curves progressively becomes smaller, approaching that of a linear slope akin to EDLC capacitance [274, 275]. This is explained by the hypothesis that layered hydroxides undergo phase transformation during charge-discharge at a certain potential while at the same time solid-state diffusion occurs in the bulk of the material. Hence, phase transformation occurs sequentially from the interface into the bulk, thereby resulting in a horizontal flat plateau in a GCD curve. In a nanostructured form, a significant proportion of the active site for phase transformation occurs at or near the surface of the material. This results in a shortening or even elimination of this battery-like behaviour [276]. As such, layered hydroxides in their nanostructure form has a higher rate capability than in their bulk form [273]. This phenomenon can be observed in the GCD curves of $\text{Co(OH)}_2\text{-3DINN}_2$ in Figure 3-13a and $\text{Ni(OH)}_2\text{-3DINN}$ in Figure 3-13b, $\text{Co(OH)}_2\text{-3DINN}$ clearly exhibited a more pseudocapacitive behaviour with a proportionately shorter plateau. In contrast, almost all the charging and discharging time of $\text{Ni(OH)}_2\text{-3DINN}$ was involved in a bulk solid-state diffusion phase transformation, resulting in a long plateau GCD curves. Since it was observed above in the morphology that electrodeposition of hydroxides resulted in a thicker deposit for $\text{Ni(OH)}_2\text{-3DINN}$ than $\text{Co(OH)}_2\text{-3DINN}$, it is most likely that the thicker deposit of Ni(OH)_2 resulted in this dominant battery-like behaviour for $\text{Ni(OH)}_2\text{-3DINN}$, rather than for $\text{Co(OH)}_2\text{-3DINN}$.

Figures 3-13c and 3-13d show the GCD curves of $\text{MnO}_2\text{-3DINN}$ and PPy-3DINN electrode respectively. Compared to the hydroxide electrodes, both $\text{MnO}_2\text{-3DINN}$ and PPy-3DINN electrodes exhibited a near linear-shaped GCD curves. This is

consistent with the fact that they do not undergo a phase transformation during the charging and discharging process. As such, they can be considered to be intrinsic pseudocapacitor materials as they exhibit such behaviour at almost all sizes/morphology [273].

Lastly, the Nyquist plot from electrochemical impedance spectroscopy for the 4 electrodes are shown in Figure 3-13e. As the intercept of the Nyquist plot on the real impedance axis represents the series resistance of the electrodes, it is seen that PPy displayed the least series resistance, while MnO₂-3DINN has the highest. As a conducting polymer, PPy has a much higher conductivity compared to MnO₂ and the hydroxides (PPy: $\sim 10 - 50 \text{ S cm}^{-1}$, MnO₂: $10^{-7} - 10^{-3} \text{ S cm}^{-1}$, Co(OH)₂/ Ni(OH)₂: $\sim 10^{-4} \text{ S cm}^{-1}$) [99, 277, 278], which is in agreement with the values of the series resistance obtained from the Nyquist plot.

As described in section 1.1.8, charge transfer resistance is characterized by the semicircle of the Nyquist plot at high frequencies. Different morphology of active material and electrode design may result in variation of the semi-circle shape. In the case of MnO₂-3DINN and the hydroxides, the charge transfer resistance manifested as heavily distorted semi-circles close to that of horizontal straight lines in the high frequency region. In contrast, there was negligible charge transfer resistance in the PPy-3DINN electrode. This further illustrates the fast-redox reaction and high conductivity characteristic of PPy-3DINN electrode where charges can transport quickly and efficiently.

A long 45° diagonal line characteristic of Warburg resistance was observed for PPy-3DINN electrode in the mid frequency region. This corresponds to the diffusion resistance of the ions within the PPy material. As observed from the morphology of the

PPy-3DINN electrode, PPy grew in a layered stack-disc morphology along the axial direction of the nanowires. The outer circumference surface is relatively smoother compared to the rougher perpendicularly-grown nanosheet morphology of MnO_2 and the hydroxides. This resulted in relatively higher diffusion resistance of the PPy-3DINN electrode. The Nyquist plot of MnO_2 -3DINN shows a smaller diffusion resistance before angling upwards towards the low frequency.

CV and GCD Comparison between the 4 electrodes are illustrated in Figure 3-14a and 3-14b respectively. Since the capacitance is proportional to the enclosed area of CV curves, $\text{Ni}(\text{OH})_2$ -3DINN is observed to have the highest capacitance among the 4 electrodes. Calculated capacitance in Table 3-2 below using the CV plots based on Equation 1-10 at a scan rate of 5 mV s^{-1} do show that $\text{Ni}(\text{OH})_2$ -3DINN has the highest areal capacitance value of 139.4 mF cm^{-2} . However, as energy density is proportional to the square of potential window, $\text{Co}(\text{OH})_2$ -3DINN, in fact, stored the largest amount of energy at $8.38 \text{ } \mu\text{Wh cm}^{-2}$.

Figure 3-14 (a) CV comparison of the 4 electrodes. Y-axis scale is fixed. (b) GCD comparison of the 4 electrodes.

Table 3-2 Potential window and areal capacitance of electrodes.

Electrode	Potential Window (V)	Areal Capacitance (mF cm⁻²)	Energy Density (μWh cm⁻²)
Co(OH) ₂ -3DINN	0.9	74.5	8.38
Ni(OH) ₂ -3DINN	0.6	139.4	6.97
MnO ₂ -3DINN	0.6	53.6	2.68
PPy-3DINN	0.7	30.7	2.09

Solid state in-plane MSC based on PPy@MnO₂-3DINN nanostructure

In this section, we fabricated a high performance symmetric in-plane MSC by a facile sequential electrodeposition of PPy followed by MnO₂ on our 3DINN electrode to obtain a PPy@MnO₂-3DINN core shell nanostructure. Electrodeposition was carried out for a total of 1 C cm⁻². PPy was deposited for 250s followed by MnO₂ for 250s at a constant current of 2 mA cm⁻². 1 M KCl in PVA was used as the solid electrolyte.

Figures 3-15a and 3-15b show the SEM images of PPy@MnO₂ nanowires. The stacked-disc layers of PPy grown along the axial direction of the nanowires is clearly visible. The homogeneous deposit of MnO₂ nanosheets morphology on PPy surfaces is also clearly apparent. EDX elemental maps shown in Figure 3-15c show the significant presence of N (3.2 wt%) belonging to the PPy and Mn (30.0 wt%) and O (55.7 wt%) belonging to MnO₂.

Figures 3-16a and 3-16b show the CV and GCD curves of the MSC respectively. Redox peaks are not present which show that the redox reactions occurring with the materials using KCl electrolyte induced no phase transformation. This is also well corroborated in the GCD curves where charge and discharge profiles are linear. Inset of GCD curves in Figure 3-16b shows the calculated areal capacitance of the MSC from a current density of 0.2 mA cm⁻² to 5 mA cm⁻². The device showed an excellent capacitance performance with the highest obtained capacitance at 0.2 mA cm⁻² 92.3 mF cm⁻² and the lowest value of 22.8 mF cm⁻² at 5 mA cm⁻². As the scan rate or charge-discharge current density increased, the diffusion of electrolyte ion into PPy@MnO₂ structure and pores became more difficult (diffusion limited). Hence, the ineffective interaction between electrolyte and PPy@MnO₂ occurred, resulting in an expected decline in capacitance [147, 279]. This is commonly observed in pseudocapacitance

Figure 3-15 (a) SEM image of PPY@MnO₂ electrodeposited on nanowire network, (b) magnified view of PPY@MnO₂. (c) EDX elemental maps show homogeneous electrodeposition of PPY and MnO₂ on nanowire network.

material as faradaic process can be comparatively slow at high scan rate [147]. The working potential of the PPy@MnO₂ MSC was also at a relatively large value of 1.1 V, compared to 0.6 V for MnO₂ and 0.7 V for PPy electrode in 3 M KOH electrolyte, as shown in Figures 3-16c and 3-16d. This is likely due to the well-separated individual working potential of MnO₂ and PPy such that when they are composited together in an

Figure 3-16 (a-b) CV and GCD curves of PPy@MnO₂-3DINN MSC respectively. Inset of (b) shows the calculated areal capacitance. (c-d) CV and GCD comparison of PPy@MnO₂-3DINN MSC with MnO₂ and PPy only electrodes respectively. (e) Energy and power density of PPy@MnO₂-3DINN MSC at various current densities from 0.2 mA cm⁻² to 5 mA cm⁻². (f) Corresponding Nyquist plot of MSC.

electrode, the working potential widened as faradaic reactions can occur across an even large range of potentials [280]. This improves the energy density performance as it is proportional to the square of the operating potential. Furthermore, the better conductivity of PPy facilitates better electron transport from the outer MnO₂ layer compared to a thicker unitary MnO₂-3DINN system thus enhancing capacitance performance [256, 281]. Lastly, it was reported that by reducing the deposition time, MnO₂ exhibited less clumping or aggregation in its nanostructure during electrodeposition and hence maintained relatively higher utilizable surface area compared to nanostructures deposited for longer time. This had possibly played a part in improving capacitance performance as well [281]. The device also showed impressive energy and power density performance with a maximum energy density of 15.5 $\mu\text{Wh cm}^{-2}$ at 0.2 mA cm^{-2} and a maximum power density of 2.6 mW cm^{-2} at 5 mA cm^{-2} (Figure 3-16e). Figure 3-16f shows the Nyquist plot of the MSC. The charge transfer obtained from the plot is 15.3 Ω , indicating good efficiency and electrical conductivity of PPy@MnO₂ material.

Clearly, utilization of 3D nanostructure in the form of 3DINN as a scaffold for depositing polymer-metal oxide composite pseudocapacitive material with a high surface area results in excellent energy and power density performance. Furthermore, the combination of PPy and MnO₂ in a PPy@MnO₂-3DINN core shell structure allows a relatively wide operating potential window of 1.1 V which further benefited the energy density performance of the MSC.

The performance of PPy@MnO₂-3DINN MSC device is compared with other similar interdigital planar MSC devices based on transition metal oxides or hydroxides in Table 3-3. Evidently, our MSC device based on a 3D architecture allows high material

loading with a large exposed surface area resulting in superior capacitance and energy density performance.

Table 3-3 Electrochemical performance of various in-plane interdigital MSC based on transition metal oxides/ hydroxides.

Material	Structure	Electrochemical Performance	Ref
SiNW@MnO ₂ Core shell	Randomly oriented collapsed nanowire	2.1 mF cm ⁻²	[282]
Graphene/NiOOH/Ni(OH) ₂	Thin film of graphene flakes and NiOOH/Ni(OH) ₂ nanoflakes	0.75 mF cm ⁻² 0.3 μWh cm ⁻² 0.59 mW cm ⁻²	[283]
MnO ₂ /MoO ₂	Electrodeposited thin film with microstructure	0.25 mF cm ⁻² 51 μWh cm ⁻² 30 mW cm ⁻²	[284]
Au/RuO ₂	Laser irradiated RuO ₂ film on Au	27 mF cm ⁻² 3.1 μWh cm ⁻²	[285]
NiNW@MnO ₂ core shell	MnO ₂ electrodeposited on vertically oriented NiNW	12.76 mF cm ⁻² 4.17 μWh cm ⁻² 0.31 mW cm ⁻²	[286]
rGO@Co(OH) ₆ -Mn(OH) ₆ layered double hydroxide	Electrodeposited layered double hydroxide vertical oriented nanoflakes on rGO film substrate	36.28 mF cm ⁻² 6.82 μWh cm ⁻² 0.10 mW cm ⁻²	[287]

Ni/Mn ₃ O ₄	Electron beam evaporated Mn ₃ O ₄ on vertical porous Ni film	~19 mF cm ⁻²	[288]
NiCoP@NiOOH//ZIF- Carbon	Electrodeposited NiOOH on NiCoP layer nanosphere structure	54.7 mF cm ⁻² 13.9 μWh cm ⁻² 0.27 mW cm ⁻²	[289]
MnO ₂ @PPy	Chemical formation of MnO ₂ and PPy film on carbon cloth substrate	25.9 mF cm ⁻² 3.5 μWh cm ⁻² 7.2 mW cm ⁻²	[264]
PPy@MnO₂-3DINN	Electrodeposited PPy@MnO₂ on 3D interconnected nanowire network (3DINN)	92.3 mF cm⁻² 15.5 μWh cm⁻² 2.6 mW cm⁻²	This Work

3.3 Conclusion

In chapter 3.1, we successfully fabricated a symmetric PPy/PPyNT-3DINN in-plane MSC based on our developed 3DINN structure. PPy/PPyNT was directly electropolymerized on C-3DINN to obtain a large surface area with high material loading for redox reaction which resulted in excellent energy and power density performance of the MSC. A maximum capacitance of 66.6 mF cm^{-2} at 0.5 mA cm^{-2} current density was achieved. The energy and power density of the MSC were $9.0 \mu\text{Wh cm}^{-2}$ and 5.95 mW cm^{-2} respectively. The performance was much better compared to similar PPy-C based microsupercapacitors reported recently. We attribute this excellent performance to the 3D nanostructure of the electrodes as:

- 1) 3DINN afforded large surface area between PPy and electrolyte
- 2) 3DINN layer was vertically thick ($\sim 7.5 \mu\text{m}$) such that a relatively high material loading was achieved, resulting in high areal capacitance performance
- 3) Electropolymerized PPy was thin and in an intimate and robust contact with the nanowire substrate leading to efficient charge transfer and transport which resulted in a high rate and power capability with a long cycling lifetime.

Evidently, the developed 3DINN electrode structure is highly versatile in acting as a scaffold for facile electropolymerization of nanostructured PPy. The same process can be applied to other species of conducting polymer to obtain desired MSC properties and performances.

In chapter 3.2, with the novel 3D nanostructure which we developed and described in the previous chapter, we successfully electrodeposited a few popular metal oxide and polymer pseudocapacitive materials such as Co(OH)_2 , Ni(OH)_2 , MnO_2 , and PPy to achieve high performance MSCs. Deposited materials homogeneously covered the

entire 3DINN nanostructure. Three-electrode electrochemical analyses showed that they greatly enhanced the capacitance performance of the carbon-based electric double layer MSC from the Chapter 1. Furthermore, a full cell PPy@MnO₂-3DINN core shell structure MSC was fabricated by a sequential electrodeposition of PPy followed by MnO₂. The combination of PPy and MnO₂ allows a widened working potential window of 1.1 V while the nanostructured electrode provides a large surface area for redox reaction resulting in high capacitance and energy density. The nanostructured electrode allowed very short electron conduction pathways, yielding a high power density performance of 2.6 mW cm⁻² at current density of 5 mA cm⁻². The highest obtained areal capacitance and energy density were 92.3 mF cm⁻² and 15.5 μWh cm⁻² at a current density of 0.2 mA cm⁻² respectively. This compares very favourably to other transition metal oxide/ hydroxide based in-plane interdigital MSCs. There is a great potential in utilization of the novel electrode to realise high energy and power density performances of MSCs.

4 Enhanced Cycling Performance of Microsupercapacitor

In Chapter 4, the cycling performance of PPy-3DINN in-plane MSC is enhanced through the optimization of dopant used during electrodeposition process and electrolyte used during electrochemical cycling. The decay of cycling performance is shown to be strongly related to dopant loss using a combination of characterization techniques. This was in turn shown to be related to the relative ion size ratio between dopant and electrolyte ions.

4.1 High Cycling Performance of PPy Microsupercapacitor Based on Dopant and Electrolyte Optimization

4.1.1 Introduction

Good cycling stability is one advantage supercapacitors have over other energy storage solutions such as batteries. Commercial supercapacitors have life cycles of over a million while batteries range in a few thousands [2]. In the area of micro-energy storage devices, the highest cycling performance of thin-film lithium batteries (LMBs) was reported to be about 90% capacity retention after 1000 cycles whereas for EDLC microsupercapacitor the value could be nearly 100% capacitance retention after 100 000 cycles [290, 291]. In the area of pseudocapacitive microsupercapacitors, a cycling performance of about 10 000 cycles has been obtained [127, 292]. For PPy-based microsupercapacitors, the typical cycling performance is between 85 - 95% capacitance retention after 5000 - 10000 cycles [115, 160, 234, 293, 294].

The main cause of cycling instability for conducting polymers in general can be attributed to mechanical effects such as structural pulverization and chemical effects such as counterion drain effect [222, 295-297]. During oxidation, polarons are generated on the PPy in which the anions from the electrolyte will diffuse into the PPy bulk to

balance the charges. This results in the swelling of PPy. During discharging, electrons are injected back into PPy. The electrolyte anions will hence diffuse back into the bulk electrolyte. The repeated ion insertion and extraction of electrolyte anions hence result in a cyclical swelling and shrinking of PPy. This leads to a structural pulverization of PPy so that loss of material and hence, degradation of capacitance occur. Secondly, the conductivity of PPy is proportional to the number of polarons it can generate during the oxidation process. Generation of polarons is highly dependent on the defects (in which majority are dopant anions from synthesis process) of PPy as the defects trap the charges locally. During the discharge of PPy, some dopants will irreversibly be diffused into the electrolyte, leading to a loss of site for formation of polarons in the next charging cycle. This too leads to a loss of capacitance of PPy.

One method to mitigate the above problems is to make use of nanostructures through deposition of PPy on nanostructured substrates such as reduced graphene oxide or CNT [298-301]. Opposed to a thick film, depositing thinner layers of PPy on nanostructures allow PPy to swell and shrink without generating as much internal strain, thereby suppressing structural pulverization effect. In the application of in-plane MSC, nanostructuring of active material to generate high surface area is already a well-used strategy.

Another method to enhance structural integrity of PPy is to deposit another very thin (~ nm) layer of harder materials such as SiO₂ or carbon to “lock” and mechanically stabilize the PPy in order to reduce the swelling and shrinking effect [206, 222].

Lastly, chemical method such as anionic doping of PPy has also been explored. Large anionic species such as Tiron, sulfanilic acid azochromotrop, β -naphthalene sulfonate and p-toluenesulfonate doped into PPy during synthesis were thought to

enhance cycling performance through 1) formation of covalent bonds with the current collector resulting in increased adhesion [302, 303], 2) reduction of dopant ions during charge and discharge cycles as they are large and immobile [304, 305], and 3) formation of compact and ordered PPy structure with increased crystallinity through preferential ordering of large dopant ionic chains which leads to better mechanical properties of PPy macroscopically [306, 307].

Despite the numerous studies in exploring the synthesis conditions of PPy for cycling and capacitance enhancement, few has been done on the combined effects of electrolytes and PPy dopants on cycling and capacitance performance. In this chapter, we aim to systematically study the effects of several different commonly used electrolyte on 235 μm thick PPy synthesized with different doping ions. Their interactions and effects on the cycling performance were analysed. We discovered that the anionic size ratio of PPy dopants and electrolyte plays a crucial role in the cycling stability. Specifically, a ratio of much lesser than 1 result in a steep drop in capacitance retention performance. Furthermore, using analytical techniques such as Raman spectroscopy, ToF-SIMS, XPS and nano-indentation, we could correlate dopant loss with capacitance retention performance and that electrodes with a dopant to electrolyte anion size ratio of much lesser than 1 suffered the most severe dopant loss.

Lastly, we fabricated a solid-state symmetric PPy MSCs based on our developed 3DINN nanostructure using Sodium Dodecyl Sulfate (SDS) as the dopant and K_3PO_4 and KCl as electrolyte. The MSCs showed remarkable cycling stability performance with a capacitance retention value of over 80% after 20000 cycles. The performance is much better than most reported PPy-based MSC. Furthermore, the cycling stability enhancement did not come at a hefty cost of electrochemical performance.

4.1.2 Experimental Details

PPy films were electropolymerized on as-received 1.5 x 0.5 cm Ti foils (Sigma Aldrich) using a 3-electrode set up using a computerized potentiostat (Metrohm Autolab PGSTAT 101M). Platinum was used as the counter electrode while an Ag/AgCl reference electrode was used. All electropolymerization processes were carried out galvanostatically at 2 mA cm⁻² for 400s (total 0.8 C cm⁻²). After electropolymerization, the PPy electrodes were washed with copious amount of deionized water.

Prepared electrodes were then CV cycled for up to 2000 cycles at 50 mV s⁻¹ in different electrolyte solutions in a 3-electrode configuration similar to above for electropolymerization.

Electropolymerization solutions were composed of 0.2 M of pyrrole monomer and 0.1 M of dopants. Dopants used in this study were KCl (Sinopharm Chemical Reagent Pte. Ltd.), KNO₃ (Sigma Aldrich), K₃PO₄ (Sigma Aldrich), and Sodium n-dodecyl Sulfate (Calbiochem).

Electrolyte solutions used for cycling of doped PPy were 3 M KCl (Sinopharm Chemical Reagent Pte. Ltd.), KNO₃ (Sigma Aldrich), and K₃PO₄ (Sigma Aldrich).

Raman Spectroscopy (Renishaw InVia) was used to characterize PPy polymer structure, XPS (Phi Quantera II) was used to characterize for polaron losses and ToF-SIMS (IONTOF TOF.SIMS 5) was used to characterize for loss of dopant species. Nano-indentation (Talysurf PGI 2540) was used to characterize PPy film hardness. SEM (Hitachi SU5000) was used to observe morphology of electropolymerized PPy on 3DINN and EDS (EDAX Ocatane Elect) was used for element identification.

The doped-PPy electrodes cycled in different electrolyte solutions are denoted below in Table 4-1 following a *dopant-P/electrolyte* labelling convention.

Table 4-1. Denoted PPy electrodes polymerized with different dopants and cycled in different aqueous electrolyte.

	KCl electrolyte	K₃PO₄ electrolyte	KNO₃ electrolyte
Cl⁻ doping	Cl-P/Cl	Cl-P/PO	Cl-P/NO
PO₄³⁻ doping	PO-P/Cl	PO-P/PO	PO-P/NO
NO₃⁻ doping	NO-P/Cl	NO-P/PO	NO-P/NO
DS⁻ doping	SD-P/Cl	SD-P/PO	SD-P/NO

Two symmetric solid state PPy-3DINN MSCs were also fabricated. PPy was electrodeposited on C-3DINN which were synthesized according to steps outlined in Chapter 2. The MSCs were fabricated using 0.1 M Pyrrole monomer and 0.1 M Sodium Dodecyl Sulfate as dopant. Solid electrolyte was made with 1 g of Polyvinyl Alcohol (PVA) in 10 ml DI water heated to 80°C. The mixture melted to form a clear liquid in which 1 M K₃PO₄ or KCl was then added. Fabricated MSCs were then dipped into the mixture and held for 30 mins before pulling out slowly. The interdigital MSC was allowed to dry in ambient condition overnight. The two MSCs were named SD-PPy/PO and SD-PPy/Cl to indicate the use of PO₄⁻ and Cl⁻ ions as electrolyte respectively.

4.1.3 Results and Discussion

Film Morphology

Morphology of electropolymerized PPy film is shown in Figure 4-1. Films from all 4 different dopants exhibited a globular “cauliflower”-liked structure typical of electrodeposited PPy film [308, 309]. It is suggested that the film forms through the simultaneous growth of many nucleating sites, eventually converging or overlapping to form a continuous film [308, 309]. It can be observed that for Cl-PPy and NO-PPy (Figure 4-1a and 4-1b, respectively), the individual globules are large, while that of PO-PPy and SD-PPy (Figure 4-1c and 4-1d, respectively) are noticeably smaller. It is possible that smaller dopant ions allow higher mobility and freedom of movement of the polymer chains such that they can agglomerate and form larger globules during nucleation. On the other hand, larger dopants provide more hindrance to movement and as such, less agglomeration happens during the growth of nuclei.

Figure 4-1 Electrodeposited PPy films for (a) Cl-PPy, (b) NO-PPy, (c) PO-PPy and (d) SD-PPy. Insets of respective images are the magnified view of the film. Scale for all images are similar and shown in (d).

Capacitance Performance

Areal capacitance (C_a) of doped-PPy electrodes in various electrolytes are also compared here in Table 4-2. C_a was calculated based on galvanic charge-discharge process in which supplied current density was 1 mA cm^{-2} over a potential window of 0.8 V on fresh doped-PPy electrodes.

By comparing between KCl and K_3PO_4 electrolytes, we observed that there was not much difference in capacitance performance between KCl and K_3PO_4 with an average areal capacitance of 52.1 mF cm^{-2} and 52.3 mF cm^{-2} across the four doped-PPy respectively. In contrast, KNO_3 consistently yielded the lowest areal capacitance value among the three doped-PPy.

Between the various doped-PPy, the capacitance performance of Cl-PPy and NO-PPy were comparable, with an average of 52.0 mF cm^{-2} and 52.4 mF cm^{-2} across three electrolytes respectively. PO-PPy showed the highest capacitance performance with an average C_a of 57.9 mF cm^{-2} while SD-PPy had an average capacitance of 43.3 mF cm^{-2} .

Table 4-2 Areal capacitances of doped-PPy electrodes in various electrolytes. Unit of areal capacitance value in the table is mF cm^{-2} .

	Cl-PPy	NO-PPy	PO-PPy	SD-PPy
KCl	51.15 ± 0.31	55.00 ± 0.33	59.50 ± 0.36	42.13 ± 0.25
K_3PO_4	55.38 ± 0.33	51.25 ± 0.31	58.00 ± 0.35	44.63 ± 0.27
KNO_3	49.00 ± 0.29	50.88 ± 0.31	56.13 ± 0.34	43.25 ± 0.26

As discussed in the previous section, Cl^- and NO_3^- are similar in their ion size (184 pm and 179 pm respectively) and charge (one negative unit charge). Hence, doping

them into PPy could yield a similar electrochemical performance. In contrast, PO_4^{3-} ions are larger in ionic size at 238 pm than both Cl^- and NO_3^- . As such, channel spaces in which anions from electrolyte can insert and extract are larger. Hence, more active sites are also available in which charge transfer can occur, resulting in a better capacitance performance. However, this does not apply in the case of SD-PPy. SD-PPy showed the lowest areal capacitance despite having the largest dopant size. We believe the size and shape of DS^- ion fundamentally changed the mechanical properties of grown PPy. In this case, the large linear dopant induced an orientation preference during PPy growth such that grown film was denser and more closed-pack. This was shown earlier with the hardness test that SD-PPy was the hardest film among all the doped-PPy samples. Hence, this restricts the penetration of electrolyte anions into PPy which resulted in lower capacitance performance.

Electrochemical Cycling Performance

Figure 4-2 shows the capacitance retention of doped-PPy electrodes after 2000 CV cycles in different electrolytes. The results are summarized in table 4-3.

The electrodes cycled in KCl obtained the highest capacitance retention followed by in KNO_3 and lastly, in K_3PO_4 . This phenomenon holds true for all four doped-PPy electrodes. Capacitance retention performances across all doped-PPy are very close when cycled in KCl and KNO_3 electrolyte. In the case of PO-PPy and SD-PPy, the

different in capacitance retention between cycling in KCl and KNO₃ is only 0.1% and

Figure 4-2 (a) – (d) Capacitance retention of different doped-PPy cycled in different electrolyte after 2000 CV cycles. (e) – (h) GCD curves obtained from the different doped-PPy cycled in different electrolyte at the 1st and 2000th cycle.

0.6% respectively. In contrast, cycling using smaller dopant size PPy like Cl-PPy and NO-PPy results in larger difference in capacitance retention at 0.9% and 1.8% respectively. Capacitance retention performance for K₃PO₄ electrolyte is noticeably the worst across all doped-PPy. However, the performance improved as the PPy dopant size increased. Capacitance retention increased from about 75% for Cl-PPy and NO-PPy to 80.2% for PO-PPy. In SD-PPy, capacitance retention further increased to 89.0%, near

Table 4-3 Capacitance retention of different doped-PPy cycled in different electrolyte after 2000 CV cycles.

	Cl-PPy	NO-PPy	PO-PPy	SD-PPy
KCl	84.1%	84.9%	83.8%	90.2%
K₃PO₄	74.8%	75.6%	80.2%	89.0%
KNO₃	83.2%	83.1%	83.7%	89.6%

to the performance level of KCl and KNO₃ electrolyte at 89.6% and 90.2% respectively. It is observed that the same electrolyte cycled with different doped-PPy resulted in different capacitance retention performance. Similarly, the same doped-PPy electrode obtained different capacitance retention performance when cycled in different electrolyte. Therefore, there is surely a dependency of capacitance retention performance on the combination of PPy dopants and electrolytes.

The capacitance retention figures are reflected in a scatter plot of capacitance retention performance against the ratio of dopant anion size and electrolyte anion size (Figure 4-3). Note that the sizes of Cl⁻, NO₃⁻, PO₄³⁻ and DS⁻ ions are 184 pm, 179 pm, 238 pm and 1070 pm respectively [310-312]. A sharp drop in capacitance retention was observed when the ratio was lesser than 1 (the dopant size was smaller than electrolyte anion size). Conversely, capacitance retention was improved when dopant size increased with respect to electrolyte anion size. It is possible that larger dopant ions resulted in a

Figure 4-3 Scatter plot of capacitance retention vs dopant/electrolyte anion size.

more expanded PPy polymer structure which contained larger channel spaces in which anions from the electrolyte can freely insert and extract, resulting in less swelling and hence, better cycling stability [313]. In the case of decreasing dopant size and increasing electrolyte anion size, swelling effect increased as large electrolyte anions were forced through the reduced channel spaces, resulting in a poorer cycling stability.

In a further analysis to observe for changes in the kinetics of charging and discharging over 2000 cycles, electrochemical impedance spectroscopy was performed. Figures 4-4a to 4-4c show the Nyquist plots of Cl-PPy while Figure 4-4d to 4-4f show the Nyquist plots of SD-PPy cycled in the different electrolytes.

Since the intercept of the Nyquist plot at $Z'' = 0$ represents the series resistance of the electrode, Cl-PPy/Cl (Figure 4-4a) showed the least resistance at 3.28Ω before cycling. The resistance decreased slightly to 3.17Ω after 2000 cycles. Cl-PPy/PO (Figure 4-4b) showed a series resistance of 7.38Ω before cycling and 8.14Ω after 2000

Figure 4-4 Nyquist plot of Cl-PPy cycled in (a) KCl, (b) K₃PO₄, and (c) KNO₃. Nyquist plot of SD-PPy cycled in (d) KCl, (e) K₃PO₄, and (f) KNO₃.

cycles while Cl-PPy/NO (Figure 4-4c) showed a series resistance of 5.54 Ω before cycling and 5.20 Ω after 2000 cycles. The observed series resistance was well consistent with the ionic conductivity of 1 M of KCl at about 143 mS cm^{-1} , KNO₃ at 87.3 mS cm^{-1} and K₃PO₄ at 40.3 mS cm^{-1} [314-316]. Charge transfer resistances (R_{ct}) of Cl-PPy/Cl and Cl-PPy/NO were at 1.44 Ω and 1.3 Ω respectively. R_{ct} of Cl-PPy/PO was higher at 1.9 Ω . Lastly, the diffusion resistances (R_d) of Cl-PPy/Cl and Cl-PPy/NO were 2.7 Ω and 3.67 Ω respectively while R_d of Cl-PPy/PO was noticeably higher at 6.2 Ω . In the

case of SD-PPy (Figure 4-4d to 4-4f), charge transfer resistance was almost negligible for all electrolytes at the high frequency region of the Nyquist plots. This shows SD-PPy has better electrical properties than Cl-PPy. On the other hand, diffusion resistance of SD-PPy cycled in the different electrolytes were higher than Cl-PPy (26.3 Ω , 37.2 Ω and 40 Ω for Cl-PPy/Cl, Cl-PPy/NO and Cl-PPy/PO respectively). In this case, diffusion of electrolyte anions through SD-PPy was less efficient compared to Cl-PPy.

Raman analysis

Figure 4-5 compares the Raman spectra of the various doped-PPy while the deconvoluted peaks for the respective spectrum are shown in Figure 4-6. Obtained information such as relevant peak intensities, peak widths and peak ratios are further shown in table 4-4 and 4-5 respectively. In Figure 4-5a, the Raman spectrum of fresh Cl-PPy was compared against Cl-PPy/Cl and Cl-PPy/PO after 2000 cycles. The main peak around 1580 cm^{-1} corresponds to the symmetric stretching of the C=C bonds of the PPy. This peak can be deconvoluted into 2 constituent peaks at around 1580 and 1630 cm^{-1} . They correspond to the reduction (benzoid structure) and oxidation state (quinoid) of the PPy [239, 317]. In transformation from the benzoid to quinoid structure upon oxidation, the dopants are incorporated into the polymer chain. Hence, presence of doped/oxidized PPy are inferred from the vibrational peaks from the quinoid structure [318]. The same can be said for the pair of peaks at 985 and 924 cm^{-1} . Presence of a mixture of benzoid and quinoid polaron structure produces the peak at 985 cm^{-1} while the presence of the bipolaron quinoid structure produces the peak at 985 cm^{-1} [239, 319]. Next, the double peak at around 1410 and 1337 cm^{-1} corresponds to the ring stretching mode of the PPy for the oxidized and reduced states of PPy respectively [320, 321]. Lastly, the pair of peaks at 1082 and 1044 cm^{-1} arise from the C-H in-plane bending mode of the PPy which is also caused by the oxidized state and reduced state of the PPy respectively [322, 323]. Peak at 1255 cm^{-1} is ascribed to the N-H in-plane deformation mode. Similar peak had been observed in other studies in which PPy with higher proportion of oxidation states show more prominence. However, explicit study of this peak assignment was not studied [323-325].

Figure 4-5 Raman spectrum comparison of (a) fresh Cl-PPy and Cl-PPy cycled in K_3PO_4 and KCl for 2000 cycles, (b) fresh SD-PPy and SD-PPy cycled in K_3PO_4 for 2000 cycles, and (c) fresh SD-PPy and Cl-PPy.

Figure 4-6 Fitted Raman spectra of (a) Cl-PPy 0 cycle, (b) Cl-PPy/Cl 2000 cycles, (c) Cl-PPy/PO 2000 cycles, (d) SD-PPy 0 cycle, and (e) SD-PPy/PO 2000 cycles electrodes. Inset of (d) and (e) are the magnified and deconvoluted Raman spectra at 1580 cm^{-1} .

S

In Figure 4-5a, the 1580 cm^{-1} C=C peak ascribed to the benzoid structure of PPy from fresh Cl-PPy was much more prominent than cycled Cl-PPy/Cl and Cl-PPy/PO samples. Calculated FWHM of this peak was 69.2 for fresh Cl-PPy while the FWHM of this peak for cycled Cl-PPy/Cl was 79.4. This peak broadening effect was most

significant in the case of Cl-PPy/PO with a FWHM of 103.1. This suggests that Cl-PPy/PO after electrochemical cycling has a larger distribution of polymer conjugation length [324, 326]. This larger distribution of polymer conjugation length further shows that cycled Cl-PPy/PO has more inhomogeneity and disorder compared to fresh Cl-PPy and cycled Cl-PPy/Cl [323]. Hence, we can see that the electrochemical cycling of Cl-PPy in a larger anionic electrolyte such as K_3PO_4 induces larger structural disorder in the PPy. We also compare the oxidized state at 1630 cm^{-1} to that of reduced state at 1580 cm^{-1} ascribed to the C=C bond of PPy. The I_{1630}/I_{1580} ratio decreases slightly from fresh Cl-PPy (0.19) to cycled Cl-PPy/Cl (0.16). The oxidized peak was not present in the case of cycled Cl-PPy/PO.

Next, we compared the pair of peaks associated with the oxidized ($\sim 1410\text{ cm}^{-1}$) and reduced state ($\sim 1337\text{ cm}^{-1}$) of PPy. This pair of peaks corresponds to the quinoid and benzoid ring stretching mode respectively [320, 321]. Here, we clearly see the decrease in oxidized state was most significant for Cl-PPy/PO where I_{1410}/I_{1337} ratio decreased from 1.61 for fresh Cl-PPy to 0.58. Cl-PPy/Cl showed less decline from 1.61 to 0.81. We are able to similarly see the same trend when we observe another pair of peaks associated with the oxidized and reduced state of PPy ascribed to the C-H in-plane bending mode (1082 cm^{-1} and 1044 cm^{-1} respectively). I_{1082}/I_{1044} ratio decreases from 0.97 (fresh Cl-PPy) to 0.83 (Cl-PPy/Cl) and 0.36 (Cl-PPy/PO). Again, the largest decline in oxidized state was found to be the cycling of Cl-PPy in K_3PO_4 . Lastly, the bipolaron and polaron peaks ratio at 985 and 924 cm^{-1} also showed the most reduction in the case of Cl-PPy/PO from 0.94 (fresh Cl-PPy) to 0.72. Cl-PPy/Cl shows lesser decline with a ratio of 0.85.

Hence, we see that cycling of Cl-PPy in a larger anionic solution such as K_3PO_4 results in a larger decrease of oxidized state which implies larger amount of dopant loss.

Dopant loss also decreases the conductivity and reduces charge transfer sites during charging and discharging. Thus, it explains why electrochemical cycling of Cl-PPy in K_3PO_4 resulted in the largest drop in capacitance from a structural point of view.

In Figure 4-5b, the Raman spectra of fresh SD-PPy, SD-PPy/PO are compared. Cl-PPy/PO spectrum from Figure 4-5a was also added for reference. The C=C stretching mode at 1580 cm^{-1} also showed obvious peak broadening with an increase of FWHM value of 48.2 to 82.1, indicating higher disorder and inhomogeneity of the PPy polymer after cycling. However, the broadening in this case was not as significant compared to Cl-PPy/PO's FWHM at 103.1. The peak intensity ratio associated with the oxidized and reduced state of the ring stretching mode at 1410 cm^{-1} and 1337 cm^{-1} also showed a decrease from 2.25 to 0.8. Similarly, the ratio is the lowest for Cl-PPy/PO at 0.58. The peak intensity ratio associated with the oxidized and reduced state of the C-H in plane bending mode at 1082 cm^{-1} and 1044 cm^{-1} showed a decrease from 1.22 to 0.63. The ratio is the lowest again for Cl-PPy/PO at 0.36. Lastly, the bipolaron to polaron ratio decreases from 1.01 to 0.92. This value was 0.72 for Cl-PPy/Cl. Hence, it is apparent that SD-PPy showed more structural resilience compared to Cl-PPy when cycled in the same K_3PO_4 electrolyte.

In Figure 4-5c, a comparison between fresh Cl-PPy and SD-PPy is shown. SD-PPy showed a significantly sharper C=C stretching mode peak at 1580 cm^{-1} (FWHM 48.2) when compared to fresh Cl-PPy (FWHM 69.2). This implies that structurally, SD-PPy was less disordered and more crystalline than Cl-PPy [323]. The ratios of oxidized to reduced state of the various vibrational modes of SD-PPy are also higher compared to Cl-PPy (2.25 compared to 1.61, 1.22 compared to 0.97, and 1.01 compared to 0.94 for ring stretching, C-H in plane bending and bipolaron/polaron respectively). This shows that fresh SD-PPy has better electrochemical properties than Cl-PPy given that it possessed higher proportion of oxidized state associated with PPy conductivity and

charge transfer process. This hence explains the negligible charge transfer resistance of SD-PPy electrodes compared to Cl-PPy electrodes measured by EIS in Figure 4-4.

Table 4-4 Peak intensities and peak widths of various deconvoluted peaks associated with reduced, oxidized, bipolarons and polarons states of the different PPy electrodes

	C=C stretching due to reduced and oxidized state			Ring stretching of PPy		C-H in plane bending due to reduced and oxidized state				Ring deformation of PPy due to bipolaron and polaron			
	~1580 (reduced) & 1630 cm ⁻¹ (oxidized)			~1337 & 1410 cm ⁻¹		~1044 (reduced) & 1082 cm ⁻¹ (oxidized)				~924 (bipolaron) & 985 cm ⁻¹ (polaron)			
	I ₁₅₈₀	I ₁₆₃₀	FWHM ₁₅₈₀	I ₁₃₃₇	I ₁₄₁₀	I ₁₀₄₄	I ₁₀₈₂	FWHM ₁₀₄₄	FWHM ₁₀₈₂	I ₉₂₄	I ₉₈₅	FWHM ₉₂₄	FWHM ₉₈₅
Cl-P 0 cycle	23691.28	4599.60	69.2	7487.3	12067.06	4480.05	4332.91	24.89	53.54	6208.97	6622.81	35.28	31.44
Cl-P/Cl 2k cycles	22793.71	3696.94	79.4	9792.02	7924.24	3730.9	3094.23	25.39	62.48	4243.97	4966.55	38.28	33.82
Cl-P/PO 2k cycles	19856.39	0	103.1	10098.33	5872.94	4090.97	1476.3	26.18	68.93	2153.37	2978.21	46.79	31.15
SD-P 0 cycle	18991.23	1116.58	48.2	2826.83	6370.97	3329.09	4064.8	23.83	35.6	4977.36	4906.62	44.85	23.22
SD-P/PO 2k cycles	17597.62	3656.48	82.1	7425.01	5939.45	4384.14	2756.08	21.46	50.57	4291.17	4659.03	46.27	28.51

Table 4-5 Relative peak intensities of various deconvoluted peaks associated with reduced, oxidized, bipolarons and polarons states of the different PPy electrodes.

	C=C stretching due to reduced and oxidized state	Ring stretching of PPy	C-H in plane bending due to reduced and oxidized state	Ring deformation of PPy due to bipolaron and polaron	
	~1580 (reduced) & 1630 cm ⁻¹ (oxidized)	~1337 (reduced) & 1410 cm ⁻¹ (oxidized)	~1044 (reduced) & 1082 cm ⁻¹ (oxidized)	~924 (bipolaron) & 985 cm ⁻¹ (polaron)	
	I ₁₆₃₀ /I ₁₅₈₀	I ₁₁₄₀ /I ₁₃₃₇	I ₁₀₈₂ /I ₁₀₄₄	I ₉₂₄ /I ₉₈₅	I ₉₈₅ /I ₁₀₄₄
Cl-P 0 cycle	0.19	1.61	0.97	0.94	1.48
Cl-P/Cl 2k cycles	0.16	0.81	0.83	0.85	1.28
Cl-P/PO 2k cycles	0	0.58	0.36	0.72	0.73
SD-P 0 cycle	7.72	2.25	1.22	1.01	1.47
SD-P/PO 2k cycles	8.90	0.80	0.63	0.92	1.06

Nano-indentation

Nano-indentation was performed on the four doped-PPy samples to measure their hardness. A diamond indenter (Berkovich indenter) was impressed onto the PPy films to a fixed depth of 500 nm. The load responses were recorded to generate load vs depth curves. Hardness is calculated by taking the ratio of maximum load and residual indentation area. Figure 4-7 shows the bar chart comparison of the average hardness of 4 doped-PPy samples. SD-PPy had the highest hardness value at 0.573 GPa. Cl-PPy, PO-PPy and NO-PPy showed similar hardness values at 0.357, 0.40 and 0.313 GPa respectively. With the hardness measurement in Figure 4-6 and the Raman spectrum in figure 4-4c which implied a higher crystallinity of SD-PPy than Cl-PPy, we believe that large DS⁻ dopants promote a preferred orientation of pyrrole rings parallel to the substrate surface. Mitchel et al. and Pruneanu et al. showed that PPy doped with aromatic dopants produced structurally-anisotropic films while smaller spherical dopants produced more isotropic films [307, 327, 328]. Although DS⁻ ions are not an aromatic compound, we believe the very long and linear hydrocarbon chains induce a similar effect here in which the SD-PPy anisotropic film produced a more aligned and compact polymer layer, resulting in higher crystallinity and mechanical. Consequently, the more compact and crystalline SD-PPy material resulted in a higher resistance for electrolyte anions diffusing in the bulk of the material which resulted in a higher diffusion resistance measured with EIS in Figure 4-4.

Figure 4-7 Hardness value of doped-PPy based on nano-indentation. Inset shows an example of force load vs indentation depth curves of 3 measurements of SD-PPy.

XPS analysis

XPS experiments are useful in determining polaron structures in conducting polymer. Since dopants contribute to a significant portion of polarons and bipolarons in PPy, it would be useful to observe the changes in polaron ratio in cycled doped-PPy to infer and relate dopant loss to capacitance retention performance. In PPy, polarons are observed by the deconvolution of N1s core level spectrum. Binding energy above 400 eV are ascribed to polarons ($-N^+=$ and $-N^+H-$ cations) [295, 299, 329].

Figure 4-8 shows the XPS spectra of fresh and cycled CI-PPy and SD-PPy electrodes while Table 4-6 shows the binding energy and peak area ascribed to the respective bonding. Polaron ratio was calculated by taking the areal ratio of polaron signal over total nitrogen signal. Polaron ratio dropped from 28.6% to 13.3% and 14.3% for CI-PPy/Cl and CI-PPy/NO respectively as shown in Figure 4-8a to 4-8d. The biggest

drop in polaron ratio happened for Cl-PPy/PO electrode from 28.6% to 10.2%. This is consistent with the capacitance retention results where Cl-PPy/PO had the least capacitance retention while Cl-PPy/Cl and Cl-PPy/NO had similar capacitance retention performance. In contrast, Figures 4-8e to 4-8h show that the decrease in polaron ratio for SD-PPy is much lesser from a value of 31.3% down to 20.1%, 20.2% and 24.7% for SD-PPy/Cl, SD-PPy/NO and SD-PPy/PO respectively. Evidently, the decrease in polarons in SD-PPy is less severe than Cl-PPy, suggesting the better capacitance retention performance of SD-PPy. The biggest improvement in polaron reduction occurred for doped-PPy cycled in K_3PO_4 . Polarons for Cl-PPy/PO (dopant to electrolyte anion size ratio = 0.77) reduced from 28.6% to 10.2% while SD-PPy/PO (dopant to electrolyte anion size ratio = 4.50) reduced from 31.3% to 24.7%. The improvement in polaron reduction was less significant in other four doped-PPy electrodes where dopant to electrolyte anion ratio were larger than 0.97.

Taken together, XPS supports the hypothesis clearly that polaron reduction causes a decrease in capacitance retention of doped-PPy electrodes due to the de-doping of dopants. More importantly, the effect is most significant for systems with dopant to electrolyte anion size ratio much lesser than 1.

Figure 4-8 show the XPS spectra of (a) fresh Cl-PPy cycled in (b) KCl, (c) KNO_3 and (d) K_3PO_4 . (e) shows the XPS spectrum of fresh SD-PPy. XPS spectra of SD-PPy cycled in (f) KCl, (g) KNO_3 and (h) K_3PO_4 are also shown. Calculated polaron intensity are also indicated

Table 4-6 Binding energy and peak area% of respective polaron peaks. Polaron ratio is the sum of respective polaron peak area%.

Sample	N+H		N+=		Polaron ratio
	BE	Area%	BE	Area%	Total Area%
Fresh Cl-PPy	401.22	21.25	402.54	7.34	28.59
Cl-PPy/Cl 2000 cycles	401.39	9.54	402.66	3.73	13.27
Cl-PPy/NO 2000 cycles	401.19	11.4	402.37	2.89	14.29
Cl-PPy/PO 2000 cycles	401.22	8.02	402.65	2.21	10.21
Fresh SD-PPy	400.63	22.27	402.1	8.79	31.06
SD-PPy/Cl 2000 Cycles	400.96	14.44	402.31	5.69	20.14
SD-PPy/NO 2000 Cycles	400.95	16.22	402.28	3.95	20.17
SD-PPy/PO 2000 Cycles	401.38	18.16	402.77	6.55	24.71

ToF-SIMS analysis

XPS requires a deconvolution process of detected N1s core energy level signal to separate the binding energy peaks in order to identify polarons which are used to compare the degradation state between different cycled doped-PPy. However, accurate deconvolution requires accurate assignment and knowledge of required binding energy

which can vary to different extent depending on analysis and material conditions. This leads to uncertainty of obtained deconvoluted results. Given that Time-of-Flight Secondary Ion Mass Spectroscopy (ToF-SIMS) has a very high detection limit from ppm to ppb level ($10^{-4} \% - 10^{-7} \%$) and does not require extensive signal processing, accurate comparison of polymer degradation state can be achieved by a direct comparison of detected amount of dopants among different electrodes.

ToF-SIMS is a surface sensitive analysis in which an ion beam of either Cesium or Oxygen is used to remove materials from surface of target material. Fragmented materials are either positively charged or negatively charged depending on the ion beam. The charged fragments are accelerated into a flight path to a detector in which their mass is determined by the flight time. The high accuracy and high detection limit of the ToF-SIMS technique allow unambiguous physical identification of atoms and molecules using the fragments mass value (m/z), which is very useful for identification and distinguishing of polymers [330]. In this work, negative ion ToF-SIMS was used to analyze for Cl^- and DS^- dopant species of fresh and cycled doped-PPy samples.

Figures 4-9a to 4-9d show the enlarge ToF-SIMS mass spectra of the dopants from the samples. Chlorine related anions such as $^{37}\text{Cl}^-$ and Cl_2^- in Figures 4-9a and 4-9b, and Sulfur related anions such as S^- and SO_4^- in Figure 4-9c and 4-9d could be clearly observed at their respective mass numbers. The relative intensities of dopant species were the highest in fresh Cl-PPy and SD-PPy while reduced intensities were observed in samples that have been electrochemically cycled. Figures 4-9a and 4-9b show the reduction was most significant for Cl-PPy/PO (dopant to electrolyte anion size ratio = 0.75) where peak intensities drop by about 75% for $^{37}\text{Cl}^-$ and Cl_2^- . In contrast, the peak intensity dropped by about 50% when electrochemical cycling was carried out in KCl and KNO_3 (dopant to electrolyte anion size ratio = 1.00 and 0.97 respectively). As shown

Figure 4-9 Enlarged ToF-SIMS mass spectra centred around mass values of (a) ³⁷Cl⁻, (b) Cl₂⁻ for Cl-PPy and (c) S⁻, (d) SO₄⁻ for SD-PPy compares the amount of dopant between fresh doped-PPy and cycled doped-PPy in various electrolytes.

previously, Cl-PPy/PO had the least capacitance retention of 74.8% after 2000 cycles compared to 84.1% and 83.2% for Cl-PPy/Cl and Cl-PPy/NO. Evidently, the larger loss in capacitance performance after electrochemically cycling can be attributed to the bigger loss of dopants in doped-PPy where dopant to electrolyte anion size ratio is much lesser than 1.

Figures 4-9c and 4-9d show the mass spectra of S⁻ and SO₄⁻ ions related to DS⁻ anion. Compared to Cl⁻ dopant, the dopant loss for SD-PPy was clearly less severe. The intensity drop is only about 13% for S⁻ ion and about 29% for SO₄⁻ ion. Furthermore, the intensity drop is consistent with all 3 SD-PPy samples cycled in different electrolytes. This is also in line with obtained capacitance retention results where all SD-PPy electrodes had better retention values of 89.0% - 90.2% compared to Cl-PPy. Like the

XPS, the most significant improvement in dopant loss occurred for doped-PPy cycled in K_3PO_4 where the dopant to electrolyte anion size ratio for SD-PPy electrodes were also large (4.50 to 5.98).

Hence, through the ToF-SIMS analysis, we can unequivocally relate the loss in capacitance performance of doped-PPy to the direct loss of dopants after electrochemical cycling. This effect was also observed to be most significant with the dopant to electrolyte anion size ratio of much lesser than 1.

Enhanced Electrochemical Cycling Performance of Solid-state In-plane Microsupercapacitor Using DS⁻ as Anionic Dopant

Based on findings described above, two PPy-encapsulated nanowire network microsupercapacitors (PPy-3DINN) MSCs were fabricated. SDS was used as dopant (SD-PPy) to maximize the cycling performance while K₃PO₄ and KCl in PVA were used as solid electrolytes for superior capacitance performance. To illustrate the differences between the two MSCs, PPy-3DINN made from DS⁻ anion dopant and cycled in KCl electrolyte is labelled SD-PPy/Cl while the sample cycled in K₃PO₄ is labelled as SD-PPy/PO. Figures 4-10a and 4-10b show the electropolymerized PPy-3DINN nanostructure. The morphology was similar to the PPy-encapsulated nanowire network in Section 3.1 which was Cl-doped instead. Sheet-like growth was stacked along the axial direction of the nanowires. The inset of Figure 4-10b shows the elemental composition of the nanowire network analysed with Electron Dispersive Spectroscopy (EDS). Nitrogen and sulfur elements which are unique to PPy and SDS respectively are evidently observed, indicating the successful doping of DS⁻ anion into PPy.

Figure 4-10 (a) SEM image of electropolymerized SD-PPy on carbon-encapsulated interconnected nanowire network. And (b) magnified view of SD-PPy with inset illustrating elemental composition obtained from EDX.

Figure 4-11 shows the electrochemical performance of SD-PPy solid-state in-plane MSCs using 1 M K_3PO_4 (SD-PPy/PO) and 1 M KCl (SD-PPy/Cl) in PVA as solid electrolytes. The electrochemical performance of PPy/PPyNT-3DINN MSC in 1 M KCl-PVA solid state electrolyte from Section 3.1 is also included for comparison from

Figure 4-11c to 4-11f. It is labelled as Cl-PPy/Cl to show the dopant and electrolyte ions used.

Obtained CV curves of SD-PPy/PO shown in Figure 4-11a from a scan rate of 2 mV s⁻¹ to 100 mV s⁻¹ were highly rectangular-shaped suggesting that the MSC device is low in the internal resistance and high in the leak resistance [6]. This can be attributed to the superior electrical properties of SD-PPy discussed in previous section where charge transfer and transport could happen quickly possibly due to the strong presence of polaron and bipolaron structures. Thus, even at a high scan rate of 100 mV s⁻¹, the current response was still very quick, resulting in a highly rectangular-shaped CV plot. This is further corroborated by the Nyquist plot in Figure 4-11e where charge transfer resistance of SD-PPy/PO through equivalent circuit fitting was obtained to be only 0.16 Ω . Charge transfer resistance of SD-PPy/Cl was also very similar at 0.14 Ω . On the other hand, charge transfer resistance obtained from solid-state in-plane MSC using Cl-PPy discussed in Chapter 3.1 was 8.19 Ω instead. Diffusion resistance of SD-PPy/PO obtained from Warburg component in the equivalent circuit fitting was also very low at 1.57 Ω . SD-PPy polymerized on nanowire structure was only about 300 nm thick, as opposed to film SD-PPy electrode of about 235 μ m thick discussed in the earlier section. Hence, electrolyte could quickly diffuse into almost the entirety of SD-PPy which resulted in the low diffusion resistance value of the MSC device. Inset of Figure 4-9e shows the close up of the Nyquist plot of SD-PPy/PO and SD-PPy/Cl near the region where $Z'' = 0$. The difference between cycling SD-PPy in 2 different electrolytes was observed to be very small. Figure 4-11b shows the obtained GCD results from the SD-PPy/PO MSC from a current density of 0.2 mA cm⁻² to 15 mA cm⁻². Linear charge and

discharge curve can be clearly observed, highlighting the pseudocapacitance characteristics of SD-PPy.

Calculated areal capacitance values from GCD test of the SD-PPy MSCs and Cl-PPy/Cl MSC from Chapter 3.1 are shown in Figure 4-11c. SD-PPy/PO MSC showed

Figure 4-11 (a) CV and (b) GCD curves of SD-PPy/PO MSC . (c) Areal capacitance and (d) Energy and power density comparison between SD-PPy/PO, SD-PPy/Cl and Cl-PPy/Cl at different current densities. (e) Nyquist plot comparison between SD-PPy/PO, SD-PPy/Cl and Cl-PPy/Cl and (f) Electrochemical cycling performance of SD-PPy/PO, SD-PPy/Cl and Cl-PPy/Cl. Inset illustrates the last 10 GCD cycles of SD-PPy/PO MSC.

excellent capacitance performance with a maximum value of 57.8 mF cm^{-2} at current density 0.2 mA cm^{-2} . SD/PPy/Cl MSC showed slightly lower capacitance of 54.8 mF cm^{-2} . Although maximum areal capacitance obtained from both MSC was lower than that of Cl-PPy MSC (66.6 mF cm^{-2} at 0.2 mA cm^{-2}), the decrease in capacitance at higher discharge current was lower. At a high discharge current of 15 mA cm^{-2} , the areal capacitance of SD-PPy/PO and SD-PPy/Cl MSC were higher at 21.8 mF cm^{-2} and 20.8 mF cm^{-2} respectively, compared to 13.7 mF cm^{-2} for Cl-PPy MSC. This illustrates the superior electrical characteristics of SD-PPy where a combination of low internal resistance and high leakage resistance allows faradaic reaction to proceed quickly and efficiently even at a high discharge rate. At slow discharge rates where areal capacitances are lower than Cl-PPy MSC, the result was also consistent with observations from the previous section where obtained areal capacitance of SD-PPy film electrode was the lowest among other doped-PPy electrodes due its mechanically more compact and denser polymer structure which resulted in lesser active sites for electrochemical activity.

The calculated energy density and power density of SD-PPy MSCs and Cl-PPy MSC are illustrated in Figure 4-11d. In terms of energy density, the performance comparison is similar to areal capacitance performance discussed above as the operating window among the 3 MSCs are very similar at 1 V nominally. The power performances of the MSCs were comparable at low discharge current densities, while they diverged at higher current densities.

Lastly, the cycling performance is compared in Figure 4-11f. SD-PPy/Cl MSC showed the best cycling performance with a capacitance retention of 86.7% after 20,000 cycles followed by SD-PPy/PO MSC with a capacitance retention of 84.6%. The slightly better cycling performance of SD-PPy/Cl than SD-PPy/PO MSC is also in agreement

with previous results in which film SD-PPy/Cl electrode retained the most capacitance compared to SD-PPy/PO electrode due to the smaller ionic size of Cl^- which resulted in lesser swelling. In contrast, Cl-PPy MSC showed a capacitance retention of 80.1 % after 10,000 cycles. Table 4-7 compares the electrochemical cycling performance of various PPy-based MSC devices. Compared to the MSCs reported, our devices showed one of the best values achieved for cycling stability while preserving the excellent electrochemical performance.

Table 4-7 Performance comparison of reported PPy-based MSC devices. Some values are not recorded here as they were reported in volumetric units.

Materials	Dopant/EL anions	Electrochemical Performance	Cycling Performance	Ref
Ag@PPy	CH ₃ COO ⁻ / PO ₄ ³⁻	47.5 mF cm ⁻² 4.3 μWh cm ⁻² 0.6 mW cm ⁻²	82.6%, 10000 cycles	[331]
PPy film	ClO ⁻ /PO ₄ ³⁻	47.4 mF cm ⁻² 4.0 μWh cm ⁻² 0.185 mW cm ⁻²	85%, 16000 cycles	[106]
MnO ₂ - PPy//V ₂ O ₅ - PANI	ClO ⁻ /PO ₄ ³⁻	12.5 mF cm ⁻² - -	92%, 7000 cycles	[234]
PPy- 3DrGO/npAu	Cl ⁻ /ClO ⁻	39.21 mF cm ⁻² -	85.9%, 10000 cycles	[160]
SiNWs/PEDO T@PPy	Cl ⁻ / R ₁₃ TFSI Ionic Liquid	46.5 mF cm ⁻² 14.6 μWh cm ⁻² 0.38 mW cm ⁻²	73.4%, 5000 cycles	[332]
PPy-CNT	Cl ⁻ /PO ₄ ³⁻	27.8 mF cm ⁻² - -	65.6%, 10000 cycles	[235]
PPy/PPyNT- 3DINN	Cl⁻/Cl⁻	66.6 mF cm⁻² 9.00 μWh cm⁻² 5.95 mW cm⁻²	80.1%, 10000 cycles	This work (Chapter 3.1)
PPy-3DINN	DS⁻/Cl⁻	54.8 mF cm⁻² 7.42 μWh cm⁻² 5.62 mW cm⁻²	86.7%, 20000 cycles	This work
PPy-3DINN	DS⁻/ PO₄³⁻	57.8 mF cm⁻² 8.02 μWh cm⁻² 5.34 mW cm⁻²	84.6%, 20000 cycles	This work

4.2 Conclusion

In this chapter, we successfully demonstrated that both dopant and electrolyte anion species are crucial contributors to the electrochemical cycling performance of PPy-based pseudocapacitors. We found that a dopant to electrolyte anion size ratio of lesser than 1 resulted in a steep drop in capacitance retention performance of doped-PPy electrodes after 2000 CV cycles, while a large ratio value led to superior capacitance retention. We suggest that small electrolyte anion species are favourable for efficient ionic insertion and extraction during charging and discharging as they reduce swelling effect, structural degradation of the polymer and de-doping of dopants, thus enhancing the cycling lifetime, while large PPy dopant species are beneficial in forming a more “expanded” polymer structure where larger channel spaces allow electrolyte anions to move with less impediment during ionic insertion and extraction without severe damage to the polymer structure.

We also showed that using very large linear anionic dopant such as DS^- during electropolymerization of PPy could cause a mechanically hard PPy to be formed, as evident from the nano-indentation test. Consequently, we suggest that SD-PPy is much more mechanically resilient to damage caused by ion insertion and extraction process, resulting in superior electrochemical cycling performance. De-doping effect is also much suppressed due to the very large and immobile dopant. Hence, large dopants are very effective in prolonging the cycling lifetime of MSCs. However, a compact and dense polymer structure also reduces the number of electroactive sites where charge transfer can happen, leading to a reduction of its capacitance and energy density performance.

Furthermore, the suggestions are further supported by a combination of analysis techniques such as Raman, nano-indentation, XPS and ToF-SIMS which were used to understand the changes to PPy cycled under different combination of dopants and electrolytes. The Raman and XPS analysis showed that structural degradation, particularly polaron structures associated with conductivity of polymer in which dopants also play a part in, was most extensive in electrodes with worst electrochemical cycling performance. We demonstrated that ToF-SIMS was able to reliably characterize and directly detect for dopant species in doped-PPy which conclusively determined that dopant loss was more extensive in doped-PPy electrodes which performed poorer in cycling performance.

Lastly, we fabricated all solid-state in-plane MSCs using SD-PPy with K_3PO_4 and KCl in PVA as solid electrolytes. The MSCs performed exceptionally well in electrochemical cycling test with a capacitance retention of 86.7% and 84.6% for KCl and K_3PO_4 electrolyte respectively after 20,000 GCD cycles. This is almost twice longer than a conventional small spherical anion-doped PPy (Cl-PPy in KCl electrolyte, 80.1% after 10,000 cycles) while retaining the excellent electrochemical performance.

5 Conclusion and Recommendation

5.1 Conclusion

This thesis focuses on the enhancement of electrochemical performance of in-plane microsupercapacitors including electric double layer capacitor (EDLC) and pseudocapacitors through a novel 3-D electrode nanostructure on which electroactive materials are deposited on through CVD and electrodeposition.

We have successfully developed and fabricated a Cu 3D interconnected nanowire network (3DINN) nanostructure through a template-less chemical oxidation and thermal reduction process from an initial sputtered Cu thin film. We optimized the chemical oxidation process of Cu to $\text{Cu}(\text{OH})_2$ using a 2-step oxidation process of differing concentration. This process is robust and repeatable in obtaining pure $\text{Cu}(\text{OH})_2$ nanowires.

Solid-state in-plane EDLC microsupercapacitors were fabricated by a carbon growth process using CVD on the Cu 3DINN nanostructure (C-3DINN). Carbon growth process was optimized at a growth temperature of 600 °C for 30 mins. Obtained solid-state C-3DINN microsupercapacitors have a better capacitance performance than that for graphene or CNT based EDLC microsupercapacitors.

We also utilized the mentioned 3DINN nanostructure to fabricate pseudocapacitor electrodes. Transition metal oxides such as $\text{Co}(\text{OH})_2$, $\text{Ni}(\text{OH})_2$, MnO_2 and conducting polymer such as PPy were successfully electrodeposited on the nanostructure. PPy@ MnO_2 -3DINN solid-state in-plane MSCs with a wide operating window of 1.1 V were fabricated and showed outstanding capacitance and energy density performance compared to other transition metal oxides-based MSCs. Furthermore, a symmetric PPy/PPyNT-3DINN in-plane MSC was also fabricated. By optimizing the

polymerization time, the MSC performed outstandingly with higher capacitance, energy and power density performance than many PPy-based MSCs.

Lastly, cycling performance of PPy-based MSCs are improved through the study of anionic dopant and electrolyte effects. We discovered that a dopant to electrolyte anion size ratio of less than 1 resulted in a steep drop in the capacitance retention performance. A larger anionic dopant and smaller electrolyte anion is beneficial to the electrochemical cycling performance as a larger space channel is available for smaller anions from the electrolyte to freely insert and extract into the PPy polymer chain. For very large anionic polymer dopant such as dodecyl sulfate, mechanical hardness of PPy significantly increases due to preferred orientation of polymer chain during polymerization. The high mechanical strength and low mobility of dopant prevents de-doping and swelling of PPy during charge and discharge. Using dodecyl sulfate as dopant and PO_3^{4-} as electrolyte, we synthesized a PPy-based MSC with excellent electrochemical performance and exceptional cycling performance.

In this thesis, we demonstrated that through our novel 3DINN electrode structure design, excellent electrochemical performance of in-plane MSC can be achieved. Both EDLC and pseudocapacitive types of MSCs performed admirably well in comparison with many reported MSCs. The excellent performance can be attributed to 1) the high surface area afforded by the nanowire network such that a large amount of electrochemical active sites are available, 2) intimate contact of current collector to active materials such that charge transfer is efficient and mechanical strength is high, and 3) thick vertical height of nanowire network of $\sim 10\ \mu\text{m}$ allows high material loading leading to high areal capacitance and high energy and power density performance.

Furthermore, the synthesis process is template-less, simple, cost effective. It is highly applicable to any electroactive materials (carbon, polymers, metal oxides, etc.) without the need for customized synthesis process.

5.2 Recommendation

Although an excellent electrochemical performance of MSCs was achieved through a novel design of the electrode nanostructures, further improvements could be made to enhance the electrochemical performance. Firstly, the 3DINN nanostructure was about 10 μm in vertical height. If it can be further increased to 15 or 20 μm , the capacitance and energy density performance could theoretically be improved by 50 to 100%. However, as shown in Chapter 2.1, extension of nanowire synthesis time did not increase the nanowire length. Instead, a large number of unwanted particles could be produced through increasing the concentration of reactants. As such, other transition metals such as Ni and Sn may undergo the same chemical oxidation process as Cu with the reactants which may yield nanowires of different morphology and length, beneficial to electrochemical performance.

Graphene and graphite have been extensively used as the material for EDLC MSCs. Our 3D electrode allows them to be effectively used for MSC with enhanced capacitance performance through increased electroactive material loading in the vertical direction. By extension, our novel electrode can also be applied to other 2D materials such as selected metal sulfites and metal nitrides which have shown high theoretical capacitance. For example, edge-oriented MoS_2 nanosheets has been shown to be successfully grown using CVD on carbon substrates at a temperature of 550°C [333]. The morphology is very similar to that of edge-oriented graphene produced using CVD as well. A recent report of 1T MoS_2 in-plane

microsupercapacitor fabricated using femtosecond laser direct writing showed an excellent areal capacitance performance of 36 mF cm^{-2} [334]. Hence, it may be worthwhile to explore the electrochemical performance of CVD MoS_2 on our developed 3DINN electrode nanostructure.

Our in-plane MSCs are symmetric in which both electrodes are composed of the same material. It is possible to utilize our electrode design and electrodeposit different materials on each electrode such that an asymmetric in-plane MSCs could be achieved. This could yield a wide operating potential window which would greatly improve energy density performance. Since the energy stored in a supercapacitor, E , is proportional to V^2 , two times increase in voltage operating window (e.g. 1 V to 2 V), could theoretically increase the energy density of the supercapacitor by up to 4 times.

Publications

Enhanced Performance of an Electric Double Layer Microsupercapacitor Based on Novel Carbon-Encapsulated Cu Nanowire Network Structure As the Electrode

Jingyuan Wang, Xinghui Wang, Seok Woo Lee, and Qing Zhang

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Direct Current Triboelectric Cell by Sliding an n-type Semiconductor On a p-type Semiconductor

Ran Xu, Qing Zhang, Jingyuan Wang, Di Liu, Kie Wang, Zhong Lin Wang

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In-situ Functionalization of Metal Electrodes for Advanced Asymmetric Supercapacitors

Leimeng Sun, Xinghui Wang, Yurong Wang, Dongyang Xiao, Weifan Cai, Jingyuan Wang, Yanrong Wang, Fangjing Hu, Qing Zhang

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A Hierarchical Copper Oxide–Germanium Hybrid Film for High Areal Capacity Lithium Ion Batteries

Liyang Deng, Wangyang Li, Hongnan Li, Weifan Cai, Jingyuan Wang, Hong Zhang, Hongjie Jia, Xinghui Wang, Shuying Cheng

Frontiers in Chemistry 2020 7, 869

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