Charge storage and transport mechanisms in printable supercapacitors

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NANYANG TECHNOLOGICAL UNIVERSITY

CHARGE STORAGE AND TRANSPORT MECHANISMS IN PRINTABLE SUPERCAPACITORS

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

by

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ABSTRACT

Supercapacitors (SCs) exhibiting 20 to 200 times greater capacitance and energy density (5 Wh kg^{-1} , $80\text{-}100 \text{ F g}^{-1}$) than conventional capacitors and delivering higher power density (10 kW kg^{-1}) than batteries, represent an unique class of technology with niche applications amongst other energy storage devices. While conventional SCs suffer from its bulky architecture comprising of metallic current collectors and amorphous carbon, incorporation of the carbon nanotubes (CNTs) network as a single-layer current collector and active material has been explored, which leads to a light-weight and printable charge storage device that offers a “printed power solution” that can be potentially integrated with printed electronics applications.

This thesis reports on the concept of introducing printable SCs by first exploring the use of CNTs as sole electrode materials that enables the replacement of metal current collectors. Due to the inter-tube resistance of the CNT network, the power density of this first generation of CNT-based SC is limited. To circumvent this issue, silver nanoparticles (AgNPs) with high conductivity were decorated onto the functionalized CNTs with the purpose of improving the power density of CNT electrodes. The enhancement observed with AgNP decoration is highly size-dependent and is related to the improved intertube contact resistance, electroactive surface considerations, as well as the participation of Ag in a faradaic reaction induced pseudocapacitance .

Besides power density, the energy density of the CNT-based electrodes was further improved by incorporating transition metal oxide nanostructured materials with pseudocapacitive characteristics into the CNT/carbon-based materials. The role of these nanomaterials in charge transport, electrical double layer formation, pseudocapacitive properties, charge retention, and rapid charging and discharging has been investigated through various materials and electrochemical characterization techniques such as field-

emission scanning electron microscopy, X-ray diffraction, cyclic voltammetry, galvanostatic charge-discharge, electrochemical impedance spectroscopy, and X-ray photoelectron spectroscopy. These studies provide strong support to the theory that morphology, surface area, electrode-electrolyte interfacial properties affected by process parameters, electrode and electrolyte treatment are the determining factors which impact charge storage and transport mechanisms in printable SCs.

A systematic study on the impact of electrolyte on SC performance was carried out; including correlations with electrolyte pH, and performance comparison between aqueous and organic electrolytes. In order to realize a completely printable SC, a new class of printable electrolyte, known as polyelectrolyte was also evaluated. The effect of the ionic conductivity on the polyelectrolyte film towards improved device performance, and also limiting factors which degrade device performance were investigated through frequency dependent device characteristics at different levels of relative humidity (RH).

The cycle stability of the printable SCs was examined by employing galvanostatic charge-discharge test, and the reasons for capacitance degradation after cycling were investigated. Lastly, printable SC was integrated with an energy harnessing (organic photovoltaic) device demonstrating and confirming its viability in applications ranging from printable electronics to innovative energy harnessing and storage applications.

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CHAPTER 1 INTRODUCTION

1.1 ENERGY STORAGE SYSTEMS

Progress over the past century has clearly been fueled by forms of energy that have been inexpensive, abundant, portable, and stored / recovered in a facile fashion. Energy storage has played a key role in power generation and transmission in electrical grids and in distributed energy systems; enabled us to tap into intermittent sources of energy; and has also powered the mobile electronics revolution [1]. Generally energy can be stored in various forms, such as potential energy stored in hydroelectric systems, rotational energy stored in flywheels, chemical energy stored in fuels, and electrical or electro-chemical energy as stored in batteries and various forms of capacitors.

The storage of the electrical energy can be executed in two ways: (1) indirectly in batteries as potentially available chemical energy requiring Faradaic oxidation and reduction of the electrochemically active reagents to release charges; (2) directly, in an electrostatic way, separation of negative and positive charges on the plates of a capacitor, known as non-faradaic electrical charge storage. The efficiency of these two modes of electrical energy storage is substantially larger than that of fuel combustion systems, which are limited by thermodynamic cycle considerations while electrochemical systems usually involve more reversible process with direct energy conversion. As pointed out by a recent report by the US Department of Energy [2], both supercapacitors (SCs) and batteries, have been assigned equal importance for future applications ranging from portable electronics to electrical vehicles as well as large industrial equipment. Figure 1.1 shows the energy density plotted versus power density, which is known as “Ragone plot”, for the most essential energy storage systems.

Figure 1.1 Ragone plot illustrating the energy and power density of various energy storage devices.

SCs, also known as electrochemical capacitors or ultracapacitors, exhibits capacitance which is 20 to 200 times greater than conventional capacitors with energy density about 5 Wh kg^{-1} , meanwhile also able to deliver higher power (10 kW kg^{-1}) than batteries thus arising as a new representative of technology with niche applications amongst other energy storage devices, [1, 3]. Besides bridging the gap of power density between capacitors and batteries, SCs also possess high cycle life with good stability thus they can be used to complement or replace batteries in some energy storage applications, such as for load leveling and uninterruptible power supplies. A more recent example is the utilization of SCs in emergency doors on the aero plane (Airbus A380) [4].

1.2 MOTIVATION OF THE PROJECT

New applications in renewable energy production, mobile electronics, aerospace systems and transportation, [5] bolstered further research with the motivation of improving both the energy and power densities of SC technology. Current commercial SCs electrode

architecture consists of high surface area amorphous carbon along with polymeric binder coated on a highly conductive current collector (metallic foil) which is essential owing to the rather poor conductivity of the electrode material. This leads to additional weight and a lack of flexibility for the current state-of-the art commercial SCs. Therefore, current commercial SCs can only serve the conventional transportation and consumer electronics market. However, such architecture is incompatible with the emergence of “printed electronics”: devices based on organic or other solution processable semiconductors that can be fabricated using simple printing processes and find a niche in large-area, low-cost applications. Such devices include smart cards, radio frequency identification (RFID) tags, e-paper, and wearable electronics; where light-weight, flexibility, and low-manufacturing costs are the primary drivers. In addition to the aforementioned advantages, the energy and power consumption for printed electronics are not high as compared to conventional devices. For instance, the average energy consumption of a RFID tag is only ranging in between $\sim 100\text{--}300\text{ }\mu\text{J}$ [6]; and the typical power required for operating an e-paper or smart phone display is on the order of $\sim 15\text{ to }1000\text{ mW}$ depending on the brightness requirements [7-8]. Although significant efforts have been made in the development of printed electronics, there is clearly a lack of effort addressing the compatible power supply for such circuits. To put it simply, “printed electronics needs printed power” [9].

For the realization of the aforementioned applications, the presence of metallic current collector is undesirable. New device architectures therefore need to be developed and new printable electrode materials need to be identified for replacing rigid metallic current collectors. The electrode materials chosen should be solution processable, support large-area, roll-to-roll fabrication techniques such as spraying, spin-coating, dip coating, or screen printing, and support low-cost manufacturing strategies. For this purpose,

suitable solvents have to be identified for creating fully stable dispersions that are compatible with the fabrication methods mentioned above. Another important requirement on the electrode materials is to achieve high charge storing capability (high energy density), and this can be realized through the exploration of transition metal oxide (TMO). TMO exhibit variable oxidation states, and the charge transfer between them can be exploited in reversible redox reactions. This Faradaic charge storage mechanism, so called “pseudocapacitance”, in combination with the conventional double layer charging, leads to an increased charge storage capacity of the device. Also, the kinetics for electrolyte decomposition depend strongly on the electrode material, and it has already been demonstrated that metal oxides have the potential to increase the available electrochemical window in SCs leading to an increased operating voltage and higher power and energy densities. Nanoarchitecturing of these active materials not only allows printability and the realization of thin, light-weight and flexible devices but leads potentially to a better performance due to increased surface area and chemical reactivity. Thus, the utilization of nanomaterials, either as a sole electrode component or as a nanoarchitected assembly, consisting of nanostructured metal/metal oxides, are believed to open new perspectives for the development of advanced electrodes for high-performance SCs.

In addition to the challenges presented by electrode design and fabrication, similar attention must be paid to the design and science of electrolyte to be able to meet the performance demands of the SC in printed electronic applications. The first generation of SCs typically employ liquid-based electrolytes, which is a major drawback as such liquid-based components requires additional encapsulation that hinder the flexibility and printability of the charge storage device and its potential integration with printed electronics. Another concern of liquid electrolyte-based SCs is the risk of electrolyte

leakage affecting the device reliability and safety. Solid polymer-based electrolytes need to be developed to circumvent this issue. Although the use of solid polymer electrolytes has been reported as early as in 1970s [10-11], the ionic conductivity of the polymer-based electrolyte has yet to be optimized and little attention has been paid for its limiting mechanism for the device performance. An in-depth study of the ionic conductivity of the polymer electrolyte is indeed needed for achieving higher energy and power densities for printable SCs.

Hence, this thesis will focus on the two key challenges highlighted in the introduction above: (1) development of printable electrodes and electrolytes for SCs with high electrochemical and mechanical stability (2) to gain an understanding on the impact of nanomaterials and ionic conductivity of the polymer electrolyte on the charge storage and charge transport mechanisms in SCs.

1.3 RESEARCH OBJECTIVES AND SCOPES

To address the gaps in the literature, the main objectives of this thesis may be summarized as follows:

1.3.1 Realization of a new SC device architecture compatible with printed electronics applications

One of the primary objectives of this thesis is to propose a new device architecture which is able to satisfy the stringent performance demands of the SC in printed electronic applications such as solution processability, high mechanical strength with flexibility, high energy and power densities. Such device architecture can be realized by using nanostructured materials as electrodes and polymer-based electrolytes for the fabrication of SCs on flexible substrates (carbon nanotubes/graphite paper). The thesis explores the

basic issues involved in chemical, physical, and electrochemical properties of nanostructured materials and polymer-based electrolytes to achieve high performance SCs.

1.3.2 Investigate the impact of nanomaterials based electrodes and polymer electrolytes on device performance

A critical analysis of the various factors that influence the design and science of nanomaterials and polymer electrolytes to meet the performance demands of the printed SCs will be evaluated in this thesis. For this purpose, three categories of nanostructured/nanocomposite (hybrid) electrode materials have been identified and will be the focus of this study: (1) carbon nanotubes (CNT) with and without functionalized groups (2) metal nanoparticles decorated CNT networks (3) transition metal oxide nanofibers/nanowires -CNT nanocomposites.

In order to study the effect of ionic conductivity of electrolyte on charge transport, SCs with electrolytes of various forms (liquid/solid) and pH (acid, base and organic) would be fabricated and characterized. A new class of self-ionizable proton conducting electrolyte, known as polyelectrolyte would be investigated for its application in SCs in comparison with conventional dual component (polymer + salt additives) polymer based electrolyte. An in-depth study of the ionic conductivity of these polymer electrolytes would be carried out at different levels of the relative humidity (RH) in a climate chamber, which EIS observations are expected to provide insights on the ion transport characteristic within the polymer electrolytes, while cycling test would be employed to explore fundamental mechanisms related to the impact of ionic conductivity to the device performance reliability.

1.3.3 Investigate the contributions of nanomaterials and polymer-based electrolyte towards charge storage and charge transport of the device

The complexities of charge storage and transport in nanomaterials and polymer electrolytes with the formation of electrical double layer (EDL) and redox charge transfer across the electrode/electrolyte interface are poorly understood, and constitute a challenge in the development of the devices that incorporate them. This aspect of understanding the role of nanomaterials in charge transport, electrical double layer formation, pseudocapacitive properties, charge retention, and rapid charging and discharging is of critical importance in the development of SCs and represents a focal area of this research.

A systematic study on correlations of these charge storage and transport mechanisms with morphology, surface area, and interfacial properties affected by process parameters, electrode and electrolyte treatments would be carried out through various materials and electrochemical characterization techniques. The contributions of different capacitive components towards improved device performance, and also factors that limit device performance would be investigated through frequency dependent device characteristics and equivalent circuit modeling and simulation.

1.4 THESIS ORGANIZATION

The thesis is organized as follows. Chapter 2 briefly introduces the construction and operating principles of SCs. A brief literature review of the current electrode and electrolyte materials employed as well as the issues associated with their application in SCs is presented followed by recent approaches to improve energy and power density of SCs. Chapter 3 describes the various techniques employed in this thesis including material synthesis, structural and electrochemical characterization as well as device fabrication. Chapter 4 details the experimental results followed by its discussion in Chapter 5. The discussion explores the impact of the nanomaterials as well as the ionic conductivity of the electrolyte to the device performance. Concluding remarks are presented in Chapter 6 and recommendations for future studies in Chapter 7.

CHAPTER 2 LITERATURE REVIEW

2.1 HISTORICAL OVERVIEW

In 1957, the first patent disclosing the concept of a SC, which consisted of high surface area carbon coated on metallic current collector immersed in sulphuric acid solution, was filed by Becker [12]. Nippon Electric Company (NEC) then further developed this discovery in 1971 under the energy company SOHIO's license and initiated the commercialization of the first SC in the market. Since the invention of the first SC in late 1950s, there has been no technology breakthrough in increasing the energy density of the SCs from 1960s to 1990s [5]. Only until the past couple of years, impressive performance in terms of increasing both energy and power densities of the SCs has been demonstrated due to the discovery of nanomaterials based new electrode materials. In addition, improved understanding on ion behavior in small pores, and development of new hybrid systems combining Faradaic and capacitive electrodes also contributed towards better design of SCs.

2.2 SUPERCAPACITOR CONSTRUCTION

SCs mainly consist of four major components: active material, current collector, electrolyte and separator. The combination of an active material that has high surface area coated on a good electron conducting current collector is called an "electrode". SCs are constructed with an ion permeable separator sandwiched in between two electrodes immersed in an electrolyte, as shown in Figure 2.1 [13]. In such device architecture, each electrode–electrolyte interface can be considered as a capacitor so that the complete cell construction represents two capacitors connected in series. For a capacitor in symmetrical configuration with same electrode and mass, the cell capacitance (C_{cell}), will therefore be:

$$\frac{1}{C_{cell}} = \frac{1}{C_1} + \frac{1}{C_2} \quad (2.1)$$

where C_1 and C_2 represents the capacitance of the first and second electrodes, respectively [14].

Figure 2.1 Conventional SC device structure [13].

2.2.1 Electrode/ Active Materials

The key for reaching high capacitance in a SC is the use of electrode materials with (1) high specific surface area (in the order of $1000 \text{ m}^2 \text{ g}^{-1}$) (2) good intra- and inter-particle conductivity in porous matrices; and (3) good electrolyte accessibility to intra-pore surface area [1]. To date, the most commonly used electrode material in commercial SCs is activated carbon, due to its high specific surface area, with reported specific capacitance ranging from 27.9 to 100 F g^{-1} [4, 15]. Other forms of carbonaceous materials, such as carbon black, carbon aerogels, carbon fibers, and graphite powder are also widely employed in commercial SCs. However, the main drawback of carbon is that their conductivity is strongly affected by heat treatment. Temperatures up to $\sim 700^\circ \text{C}$ was employed during carbonization to increase their conductivity by increasing the proportion of conjugated sp^2 carbon [13]. In addition, the degree of crystallographic orientation has

caused the variation of electronic resistivity in carbons [16]. Other disadvantages such as low cell voltage in both aqueous and organic electrolytes, and sensitivity to impurities limited the widespread applications of activated carbon in SC. Therefore, the performance of activated carbon needs to be improved with the purpose of increasing the energy density while maintaining the high power density and long cycling life to satisfy the stringent requirements of applications such as hybrid electric vehicles, portable electronics, or large industrial equipment. One way to address this issue is through the exploration of nanomaterials and nanocomposites SC electrodes.

2.2.1.1 Nanostructured Carbon Materials

A number of nanostructured materials based on carbon are being developed for improving the performance of SC electrodes. Some zero-, one- and two-dimensional nanocarbons are illustrated in Figure 2.2 [17].

Figure 2.2 Schematic which illustrates carbon nanostructures ranging from zero to two dimensional: a) fullerene, b) graphene, c) carbon nanotubes, and d) carbon nanofibers [17].

a) Fullerenes

The use of fullerenes as electrodes in SCs has been demonstrated by Egashira *et.al.* [18], with a reported capacitance of 58 Fg^{-1} . The fullerene electrodes exhibited comparable capacitance and higher rate stability than conventional activated carbon fiber electrodes, due to its high capacitance per unit surface area and high electronic conductivity.

However, the performance of these electrodes is limited by the homogeneity of the fullerene blend as well as the uniformity of the formed film. In order to improve the homogeneity of the blends, much effort has been invested into functionalizing the fullerene molecule for enhanced solubility and hence improved integration with the binder [19].

b) Graphene

Graphene, the representative for two-dimensional nanostructured carbon, has attracted much attention due to its high theoretical surface area of $2630 \text{ m}^2\text{g}^{-1}$, which is comparable to the Brunauer–Emmett–Teller (BET) surface area of activated carbons employed in current SCs. This has bolstered further research to incorporate graphene or graphene-related materials in SCs [20-22]. Graphene has been reported to have a specific capacitance of 117 F g^{-1} and maximum energy density of 31.9 Wh kg^{-1} in $1 \text{ M H}_2\text{SO}_4$ with a BET surface area as high as $925 \text{ m}^2\text{g}^{-1}$ and the number of graphene sheets between 3 to 16 [20]. However, the performance of graphene-like materials in SCs is not superior than activated carbon or carbon black, and additional stabilization treatment is needed for the practical usage of graphene in SCs. Optimization of graphene based electrodes is essential to further improve its performance in SCs applications.

c) Carbon Nanotubes

Graphene with a tubular structure, also known as carbon nanotubes (CNTs), have been recognized and evaluated as attractive electrode material for SCs as they offer higher conductivity per weight compared to conventional activated carbon electrodes [23-26]. Generally the CNTs are classified into multi-walled (MWNTs) and single-walled nanotubes (SWNTs). For MWNTs, capacitances of about 120 F g^{-1} at 1 Hz and 49 F g^{-1} at

100 Hz were reported, respectively [27]. Niu *et al.* [24] produced catalytically-grown MWNT network electrodes in sulfuric acid and the specific capacitance was determined to be 102 F g^{-1} (at 1 Hz). In comparison, Frackowiak *et al.* [27] reported that the specific capacitance of the MWNTs electrode was 90 F g^{-1} in alkaline media but was reduced to 65 F g^{-1} in non-aqueous media.

The main drawback of MWNTs materials for SC applications is their lower specific surface area compared to activated carbon. In contrast, SWNTs offer particular potential advantages as new carbon electrodes for SCs, because they consist of entangled- network structures with open mesopores that is not obtainable with activated carbon materials. The reported gravimetric capacitance of the SWCNT electrodes is ranging from 20 to 300 F g^{-1} [28-31]. For example, non-purified SWNTs with a specific surface area of $500 \text{ m}^2 \text{ g}^{-1}$ exhibit a specific capacitance of 40 F g^{-1} [32], whereas the specific capacitance of purified nanotubes varied between 15 and 80 F g^{-1} with surface areas that ranged from 120 to $400 \text{ m}^2 \text{ g}^{-1}$ [27, 33].

Substantial amount of work has also been done with the goal of growing vertically aligned CNTs as the SCs' electrodes, as demonstrated by Emmenegger *et al.* [23]. By growing well-aligned CNT films on aluminium substrates, volumetric capacitance of 120 F cm^{-3} with high power density have been successfully achieved. Similar approach was used by Schindall *et al.* [34], to grow aligned CNTs directly onto conducting substrates, known as the nanotube "forest" and used as SCs' electrodes. CNTs exhibit greater energy storage in SCs than activated carbon, owing to their finer dimensions and more uniform distribution. However, the high cost and complexity incurred in growing the aligned CNTs as compared to the relatively cheaper and simpler methods of producing CNTs random network are the main reasons for the uncommon usage of aligned CNTs as SCs' electrodes limiting their commercial utilization. Table 2.1 shows a comparison of physical

and electrical properties of various carbon materials with different dimensionality, and their SCs' electrode performance in aqueous and organic electrolytes.

Table 2.1 Comparison of physical and electrochemical properties of various carbon SCs' electrode materials in aqueous and organic electrolytes.

Ref	Electrode Materials	Specific surface area(m^2g^{-1})	Density (gcm^{-3})	Electrical Conductivity (Scm^{-1})	Cost	Aqueous electrolyte		Organic electrolyte	
						Fg^{-1}	Fcm^{-3}	Fg^{-1}	Fcm^{-3}
[18, 35-36]	Fullerene	1100-1400	1.72	10^{-8} - 10^{-14}	Medium	58			
[20-22, 37]	Graphene	2630	>1	10^6	High	100-205	>100-205	80-110	>80-110
[28-32, 38]	SWCNTs	120-500	0.6	10^4 - 10^5	High	20-300	<60	<60	<30
[24-27]	MWCNTs		0.6		High	49-120		<65	
[23, 34]	Aligned CNTs		0.6		High		<120		
[4, 15]	Activated carbon	1000-3500	0.4-0.7	0.1-1	Low	28-100	<80	<100	<50
[39]	Templated porous carbon	500-3000	0.5-1	0.3-10	High	120-350	<200	60-140	<100
[40]	Functionalized porous carbon	300-2200	0.5-0.9	>300	Medium	150-300	<180	100-150	<90
[40]	Activated carbon fibers	1000-3000	0.3-0.8	5-10	Medium	120-370	<150	80-200	<120
[40]	carbon aerogels	400-1000	0.5-0.7	1-10	Low	100-125	<80	<80	<40

Figure 2.3 (a) Schematic of a supercapacitor device with aligned carbon nanotubes as electrode (b) the TEM images of the nanotubes "forest" electrode [34].

2.2.1.2 Nanostructured Pseudocapacitor Materials

In spite of their superior electrical properties, carbon-based SCs do not meet the expected performance. One of the major issues is their low specific energy limited by their method of preparation and their effective surface area (*viz.* surface area that is accessible by the ions in the electrolyte). Utilization of redox-active materials such as metal oxides [41-43] and conducting polymers [44-45] in addition to high-surface-area carbons enables higher capacitance to be achieved. Fig. 2.4 represents the specific capacitance of proposed pseudocapacitor materials reported in the literature [46]. These materials are commonly known as “pseudocapacitors” in the literature and store electrochemical charge using highly reversible surface redox reactions. The charge–storage performance has increased drastically with the introduction of these fast, reversible surface processes (Fig.2.4).

Figure 2.4 The capacitive performance of carbon and pseudocapacitor materials proposed in the literature [46].

a) Electroconducting Polymers (ECPs)

Many studies have been done on ECPs such as polyaniline, polypyrrole, polythiophene, and their derivatives, which also known as synthetic metals [44-45], as they offer relatively high electrical conductivities compared to metal oxides and high doping-undoping rates during charge-discharge processes [15]. These polymers also exhibit high gravimetric and volumetric pseudocapacitance. However, the disadvantage of ECPs application as SC electrodes is related to their poor cycle-stability due to volumetric changes associated with the insertion/deinsertion of counter ions during doping/undoping process. ECP films undergo cracks, swelling, breaking or shrinkage, leading to loss of inter-particle contact that degrades their conducting properties. In addition , the electrochemical performance of the ECP is strictly governed by its operating potential range that strictly confined to an isolating state or polymer degradation caused by over-oxidation [47]. It is reported that low-cost ECPs have short cycle life when they are used as bulk materials for an electrode [48]. In contrast, electrodes made from a combination of carbon materials and polymers as active materials show improved mechanical properties [49-50].

b) Composite of nanostructured carbon with electroconducting polymers (ECPs)

Limitations in the carbon- based and ECP-based SCs have prompted further studies into the fabrication of nanocomposites ; *eg*: CNTs with ECPs [47, 51]. A composite has been successfully synthesized by incorporating pseudocapacitive active materials onto a nanotubular backbone [52]. It has been found that the charge storage process in ECPs was dependant on its synthesis conditions , oxidation state and also the solvent [53]. Such a composite realizes a large capacitance, by combining the fast charging-discharging electric double-layer capacitance of the CNTs and the large pseudocapacitance of the

ECPs. The entanglement of CNTs forms an open mesoporous network which allows easy diffusion of the ions into the conducting polymer. This reduces the equivalent series resistance and consequently leads to the increase in power density of the device. The preparation of these composites is typically done through *in-situ* chemical polymerization of a monomer which forms a homogeneous coating onto the nanotube surface. Frackowiak *et al.* have electrodeposited polypyrrole (Ppy) onto MWNTs, and specific capacitance of 180 F g^{-1} was reached due to the accumulation of charges inside the three-dimensional Ppy composite [33]. This value is higher than the corresponding capacitances obtained for pristine MWNTs or polypyrrole alone. Similarly, An *et al.* have produced SWNT-Ppy nanocomposites with specific capacitances up to 265 F g^{-1} [52]. In these nanocomposites, the Ppy functions as a conducting agent and contributes to the enhanced specific capacitance by decreasing the internal resistance of the SC. Gupta *et al.* have studied the polyaniline (PANI)/ SWNT composites, and the optimum condition was obtained by depositing 73 wt% PANI onto SWCNTs that yielded specific capacitance of 463 F g^{-1} [51]. Research efforts with ECPS for SCs applications are nowadays directed towards asymmetric configuration [54]. It has been reported that a specific capacitance of 320 F g^{-1} can be achieved for an asymmetric capacitor, with PANI/CNTs and polypyrrole/CNTs composite materials, as positive and negative electrodes, respectively.

A breakthrough for a new generation of SCs has been initiated by incorporating these composites of nanocarbons with ECPs, which combine two relatively low- cost materials to gain the high pseudocapacitance of the conducting polymers, as well as the good conductivity, transport properties and mechanical strength of nanocarbons. However, the presence of the large pore volumes might have limited the power density or volumetric energy of such porous systems. This is the main drawback of such materials especially for portable devices. It is also worth noting that the methodology for

determining the specific capacitance of conducting polymer- based electrodes is rather critical [54]. Experimental cells with three-electrode construction are useful for investigating the electrochemical behavior of only a single electrode, due to the dependence of the capacitance of conducting polymer on the investigated potential window range. Therefore the obtained specific capacitance values from both three-electrode and two-electrode cell configurations are not directly comparable. For example, PANI/CNTs composite electrode in a three-electrode cell has achieved a specific capacitance as high as 1100 Fg^{-1} , whereas for two-electrode cell set up only 360 Fg^{-1} was obtained [54]. It is worth mentioning that the two-electrode device data is more relevant to the real world SCs applications.

c) *Transition metal-based materials*

As ECPs do not exhibit a good cycle life due to their strong propensity to degradation, considerable efforts have been focused on the development of advanced inorganic electrode materials for SCs. Amongst all the inorganic materials studied to date, transition metal oxides (TMOs) have received significant attention due to their enhanced stability and their pseudocapacitive behavior, where the capacitance arose from the Faradaic reaction at the interface of the electrode and the electrolyte.

To date, the most widely investigated TMO is unequivocally hydrated ruthenium oxide due to its high conductivity and accessibility of the three distinct oxidation states within 1.2 V. In the past 30 years, the pseudocapacitive behavior of RuO_2 in acidic solutions has been widely investigated [1]. According to equation (2.2), the oxidation states of Ru can change from (II) up to (IV):

where $0 \leq x \leq 2$, and the specific capacitance of over 700 F g^{-1} has been reported [41]. However, the high cost of this metal oxide severely limits its applications in commercialized SCs. Thus, alternative cheaper materials have been investigated. In conjunction with this, recent research efforts were focused on using an electrolyte which is more environmental friendly than concentrated acid. To this end, materials such as vanadium oxide [43, 55], chromium oxide [56], manganese oxide [57], indium oxide [58], and tin oxide [59] were synthesized and tested in neutral electrolyte. MnO_2 is one of the potential candidates among these oxide materials, as low-cost replacement to RuO_2 [42]. Specific capacitance of $\sim 125\text{--}250 \text{ F g}^{-1}$ was obtained for MnO_2 micro-powders/thick films in neutral aqueous electrolytes within a potential window of less than 1 V [42, 60]. Charge storage mechanism is based on surface adsorption of electrolyte cations, M^+ (eg: K^+ , Na^+) as well as incorporation of protons according to the reaction:

As pseudocapacitive materials store charges in the first few nanometers from the surface, decreasing the particle size increases the active material utilization and also reduces the solid-state transport paths of cation insertions. Thus, much effort has been focused on nanostructuring redox-active materials to improve the capacitive performance of the SCs. One good example is demonstrated by Kumta *et al.*: a new class of SC based on nanocrystalline vanadium nitride [61] has achieved high specific capacitance of 1340 F g^{-1} at a scan rate of 2 mV s^{-1} . MnO_2 has been reported for an impressive gravimetric capacitances (~ 700 to 1380 F g^{-1}) when forming a thin film (tens to hundreds of nanometers) on planar current collectors [62–64]. With a nanoscopically thin MnO_2 film or coating in close contact to the current collector, the limitations of the poor electronic conductivity of MnO_2 ($10^{-5}\text{--}10^{-6} \text{ S cm}^{-1}$) can be overcome. This concept has been proved by Sugimoto's group, who have prepared hydrated RuO_2 nano-sheets with capacitance

exceeding 1300 F g^{-1} [65]. The RuO_2 specific capacitance also increased drastically when the film thickness was decreased.

d) Composites of nanostructured carbon with transition metal-based materials

These findings have been extrapolated to 3-dimensional electrode designs in which nanoscopic pseudocapacitive materials are incorporated onto the surface of nanostructured carbons, including carbon nanotubes [66-69], templated mesoporous carbons [70], and carbon aerogels/nanofoams [71] (Fig. 2.5). As demonstrated by Zhang *et. al.*, manganese oxide nanoflowers can be grown on vertically aligned CNT arrays for producing composite electrodes with excellent rate capability, high capacitance of 199 F g^{-1} and long cycle life [72]. Dong *et. al.* also prepared a MnO_2 composite nanostructure with templated mesoporous carbon with reported specific capacitance of $\sim 600 \text{ F g}^{-1}$ [70]. In such device architecture, nanostructured carbon substrate acts as a 3-D current collector with high-surface-area for the MnO_2 coatings, defining the internal pore structure of the electrode and facilitating efficient transport of electrolyte to the nanoscopic MnO_2 phase. Although these sophisticated nanocomposites are promising as electrode materials, their low yield and high manufacturing cost will probably limit their usage to small electronic applications.

Table 2.2 A comparison of specific capacitances and cell voltage of various carbon-containing composite materials in different electrolytes for SCs.

Ref	Composite Materials ^[a]	Specific capacitance(Fg ⁻¹)	Electrolyte	Cell Voltage(V)
[73]	PANI/Carbon	780-900	1 M H ₂ SO ₄	-0.2-0.7 vs. SCE
[74]	PANI/MWCNTs	20-240	1 M NaNO ₃	-0.2-0.8 vs. SCE
[51]	PANI/SWCNTs	360-1100	1 M H ₂ SO ₄	0-0.7
[75]	PANI/CNTAs	1000	1 M H ₂ SO ₄	-0.2-0.8 vs. SCE
[76]	PANI/CNT paper	424	1 M H ₂ SO ₄	-0.2-0.8
[33]	Ppy/MWCNTs	180	1.4 M TEABF ₄	0-2
[52]	Ppy/SWCNTs	265	7.5 M KOH	0.1-0.8
[67-68]	MnO ₂ /CNT	140-200	1 M Na ₂ SO ₄	-0.2-0.8 vs. SCE
[72]	MnO ₂ /CNTAs	200	1 M Na ₂ SO ₄	0-1
[77]	MnO ₂ /CNT paper	168	0.1 M Na ₂ SO ₄	0-0.8
	MnO ₂ / template			
[70]	carbon	20-700	2 M KCl	0-1
[78]	RuO ₂ /CNT	1170	0.5 M H ₂ SO ₄	0-1 vs. SCE
[79]	RuO ₂ /MWCNTs	133-147	1 M H ₂ SO ₄	0-1
	RuO ₂ /Carbon			
[80]	aerogel	100-270	1 M H ₂ SO ₄	0-0.8
[81]	Ni/MWCNT	210	6 M KOH	0.2-1.2 vs. SCE
[82]	NiO _x /CNT	671	1 M KOH	0.-0.5 vs. SCE
			1 M H ₂ SO ₄ /6 M	
[56]	Cr ₂ O ₃ /SWCNTs	60	KOH	0-0.8
				-1-0.8 V vs.
[83]	V ₂ O ₅ /CNT	313-440	1 M Na ₂ SO ₄	Ag/AgCl
[84]	V ₂ O ₅ /Carbon	233-295	2 M KCl	-0.2-0.7 vs. SCE
				0-0.8 vs.
[85]	SnO ₂ -V ₂ O ₅ /CNT	104-121	0.1 M KCl	Ag/AgCl
[79]	SnO ₂ /MWCNTs	93	1 M H ₂ SO ₄	0-1
[79]	TiO ₂ /MWCNTs	160	1 M H ₂ SO ₄	0-1
[86]	MnO ₂ -ppy/CNT	280	1 M Na ₂ SO ₄	0.1-0.9

[a] Abbreviations: carbon nanotubes (CNT), carbon nanotube arrays (CNTAs), multi-walled carbon nanotubes (MWCNTs), single-walled carbon nanotubes (SWCNTs), polyaniline (PANI), polypyrrole (Ppy)

Figure 2.5 Strategies that have been employed for improving both energy and power densities for SCs. (a) activated carbon grains (b) activated carbon grains decorated with pseudocapacitive materials (c) highly ordered CNTs array (d) decorating pseudo-capacitive materials onto highly ordered high-surface-area CNTs [4].

2.2.2 Current Collector

The current collector mainly acts as the conductor in the electrode facilitating the electron movement during charge and discharge process. In general, the requirements for current collectors are high conductivity and chemical stability, so that the charges can be conducted efficiently within the electrode while avoiding any undesired chemical reaction with the electrolyte. Metals such as gold [87], aluminium [88], stainless steel [89], nickel [31] and titanium [90] are the common choices of current collector materials for most SCs. The shape of the current collector can be in various forms: foil, mesh, disc, rod and so on depending on the geometry of the SC devices.

The choice of current collector needs particular attention as it will determine the interface conductivity between the active material and the current collector [31]. Surface treatment has been shown to be a key factor in decreasing ohmic drops at this interface [88], and particular attention has been paid to improve electrochemical stability at high

potentials and interface conductivity through coatings on aluminium. An *et. al.* have discovered that [17] the poor contact resistance between SWCNT and a plain Ni foil can be reduced significantly to 105 mΩ by polishing the surface of the Ni foil.

Another way to increase the contact area between current collector and active material is through the modification of current collectors with nanostructured materials. To achieve this, carbon can be synthesized in various morphologies, including porous networks and nanotube arrays that can be grown on various current collectors [91] and serve as substrates for further depositing (Figure 2.5(c) and (d)) active material. The performance of these nano-architected electrodes is more superior than the existing systems by confining a material with good pseudocapacitive properties to a high specific surface area thin film. This concept has been proved by Long's group [71], with a deposition of 20-nm layer of MnO₂ onto a porous carbon nano-foam, the area-normalized capacitance can be doubled to 1.5 F cm⁻², with an excellent volumetric capacitance of 90 F cm⁻³. Another attractive form of material for current collectors is carbon nanotube or graphene paper, which consists of high chemical stability and good flexibility. It is expected that the use of nanotube paper for fabricating flexible SCs would grow as the cost of small-diameter nanotubes required for making paper decreases.

2.2.3 Electrolyte

The choice of electrolyte in a SC is as important as the choice of electrode material, as the cell voltage attained for a SC is related to the electrolysis voltage of the electrolyte, hence the energy density which is directly proportional to the square of the voltage according to $E = \frac{1}{2}CV^2$, will be affected by the choice of the electrolyte. The power density is inversely proportional to the cell's equivalent series resistance (ESR), which is strongly dependent on the conductivity of the electrolyte. For this reason, numerous research

efforts have been focused in designing stable and highly conducting electrolytes with a wider electrochemical potential window. Currently there are two types of electrolytes used in SCs: liquid and solid electrolytes, with liquid electrolytes further classified into aqueous, organic and ionic electrolytes.

2.2.3.1 Aqueous

Most common aqueous electrolytes used in SCs are acids (e.g., H_2SO_4) and alkalis (e.g. KOH), which are cheap and easily available, and have high ionic conductivity of $\sim 1 \text{ S cm}^{-1}$. However, their limited voltage range with a relatively low electrolysis potential of $\sim 1.23 \text{ V}$ [92] has restricted their usage to SCs with operating voltage $< 1 \text{ V}$. Nevertheless, the higher dielectric constant in aqueous electrolyte has caused higher specific capacitance of high surface-area carbons in aqueous electrolytes in comparison with non-aqueous solutions [93]

2.2.3.2 Organic

The limitations of aqueous electrolytes have motivated the development of various types of organic (non-aqueous) electrolytes to enable the operation of cell voltages beyond 2.5 V [92, 94]. Organic electrolyte mixtures have been commonly used in commercial SCs, for instance quaternary alkyl ammonium salts dissolved in propylene carbonate or acetonitrile, with the target of achieving higher energy density. Propylene carbonate is more popular than acetonitrile, because of its low evaporating temperature and toxicity. However, the electrical resistivity of organic electrolytes is an order of magnitude higher than aqueous electrolytes in general. Thus, a high internal resistance would be expected for capacitors that use organic electrolytes.

2.2.3.3 Ionic Liquids

Ionic liquids based electrolytes are solvent-free low temperature melting salts that are liquid at room temperature with high electrochemical stability. Commercial devices with high voltage (3 V) and capacitance (1000 F) are readily available in the market by using ionic electrolytes with different combination of cations and anions [95]. However, low ionic conductivity of these liquids at room temperature has limited their practical usage (a few mS cm^{-1}), high temperature is indeed required for their applications. Carbide derived carbons with an $\text{EMI}^+/\text{TFSI}^-$ ionic liquid electrolyte was reported to achieve high specific capacitance of 160 F g^{-1} and $\sim 90 \text{ F cm}^{-3}$ at higher temperature of 60°C . Promising performance was also shown by hybrid activated carbon/conducting polymer devices with cell voltages as high as 3 V. In the coming years, the research on ionic liquids for SCs is expected to play an important role in improving the performance of SCs.

2.2.3.4 Solid

The use of solid polymer-based electrolytes, *eg.* polyethylene oxide-salt complexes was reported by Wright [10] and the potential use of these materials as a new class of solid electrolytes for energy storage applications was envisaged by Armand [11] in early 80's. However, the ionic conductivity of these electrolytes (in the range of $10^{-8} - 10^{-7} \text{ S cm}^{-1}$) [96-99] is too low for usage in practical devices. Salt additives, which are either basic or acidic (e.g. KOH and H_3PO_4), need to be added to improve the ionic conductivity of these polymer electrolytes [100-102]. Since then, polymeric gel electrolyte (PGE) has been introduced as a new concept and examined extensively. In these systems, the electrolytic salts dissolve in the polymer components that serve as the matrix, then dissociate into ionic species, and the resulting phase is maintained in a solid (gelled) state. Similar to

liquid electrolyte systems, PGE can be categorized into two classes, aqueous and non-aqueous.

Aqueous polymer gel electrolyte has been reported by Nohara *et al.* using both basic and acidic PGE [101-102], the former is prepared from dissolving 1M H₂SO₄ aqueous solution into poly(vinyl alcohol) (PVA) and glutaraldehyde (GA), whereas the latter is prepared from dissolving KOH aqueous solution into crosslinked potassium poly(acrylate). Frackowiak *et al.* [100] have also reported the work of using PEO (polyethylene oxide) –KOH–H₂O as polymer electrolyte in SC.

Polymeric gels which do not contain aqueous components have also been evaluated as the electrolytes of SC. They are mainly made of either polar polymer matrices immersed in organic electrolyte solutions or plasticized polymer complexes with electrolytic salts. or An all-solid SC using a non-aqueous polymeric gel electrolyte composed of poly(ethylene oxide) –modified polymethacrylate (PEO-PMA) as the polymer matrix, with propylene carbonate as the solvent and tetraethylammonium tetrafluoroborate (TEABF₄) as the ionic salt has first reported by a research group at Yamaguchi University [103-104]. Despite the ionic conductivity of these systems is relatively lower than aqueous PGE system, the operating voltage of the SC could be increase to above 1V with better thermal stability at elevated temperature as there is no free water contained in such systems [105]. The experimental results reveal that the polymer-based gel electrolytes are promising for use in practical SC systems, especially at high temperature applications.

It is worthy of note that in PGE system the concentration of conducting ions is related to the amount of salt additives in the polymer matrix. However, high salt additives concentration leads to phase separation, with separated polymer and crystalline salt domains, resulting in the brittle nature of the electrolyte [106]. To date, no solutions have

been proposed to circumvent this issue. The experimental findings also show that the electric double layer capacitance of the high surface area carbon electrode can be enhanced by polymeric component itself. Although the mechanisms of such capacitance enhancements are poorly understood, this additional capacitance in PEGs could be possibly attributed to some pseudocapacitance [101, 107] or changes in the double-layer structure [106]. On-going studies and developments on the polymer electrolytes are essentially needed for bringing breakthrough in fabricating high performance printable SC devices as well as high power batteries.

2.2.4 Separator

The role of the separator is mainly to avoid the existence of electrical contact between the two electrodes. However it is ion-permeable, and thus allowing the transfer of ionic charges to take place. Polymer or paper separators are used in organic electrolytes, whereas ceramic or glass fiber separators are more commonly used in aqueous electrolytes. The requirements for separator are high ionic conductance, high electrical resistance, and low thickness for achieving best SC performance.

2.3 OPERATING PRINCIPLES OF SUPERCAPACITORS

2.3.1 Charge Storage Mechanism

SCs combine two energy storage mechanisms simultaneously: (i) the electrochemical double layer (EDL) formation, where only pure electrostatic attractions occurs at the interface between ions of electrolytes and the charged surface of an electrode; and (ii) pseudocapacitance, which arises from quick Faradaic charge transfer reactions at the surface of the electrodes. These two mechanisms are discussed in details in the literature as summarized in the following two sections.

2.3.1.1 Electrochemical Double Layer (EDL) Capacitance

During the formation of the EDL, the separation of charges takes place at the electrode–electrolyte interface upon polarization of the electrodes, producing the double layer capacitance C , as described by Helmholtz in 1853:

$$C = \frac{\epsilon_r \epsilon_0 A}{d} \quad (2.4)$$

where ϵ_r is the electrolyte dielectric constant, ϵ_0 is the dielectric constant of the vacuum, d is the double layer thickness (charge separation distance) and A is the surface area of the electrodes. The double layer capacitance is ranging from 5 to 20 $\mu\text{F cm}^{-2}$ depending on the electrolyte used [13]. A SC electrode is different from a battery electrode as the electrochemical kinetics is not limited through a polarization resistance, and thus enabling surface storage mechanism with fast energy uptake and delivery, leading to better power performance. Without Faradic reactions, the swelling observed in the active material during charge/discharge cycling of the batteries can be eliminated. Hence, SCs using EDL charge storage mechanism can survive millions of cycles whereas batteries only able to sustain for a few thousand cycles. In addition, there is no involvement of the solvent of the electrolyte in the charge storage mechanism, which is very different from Li-ion batteries. This opens a wider choice of solvents for SCs, and electrolytes with high energy delivery performances at low temperature ($\sim -40^\circ\text{C}$) can be designed for the applications of SCs. However, the electrostatic surface charging mechanism has caused a limited energy density of these devices. A rectangular shape obtained for a cyclic voltammogram of a two-electrode SC cell indicates a pure EDLC mechanism for charge storage according to:

$$I = C \times \frac{dV}{dt} \quad (2.5)$$

where I is the current, (dV/dt) is the potential scan rate and C is the EDL capacitance.

Chmiola *et.al.* [108] have identified that one of the key issues in improving energy density and power capability of EDL capacitors applications is through fine-tuning the carbon pore size to maximize the capacitance. Depending on the pore size, different models describing the charge of the EDL were used. For mesoporous carbon, the capacitance was calculated from

$$C / A = \frac{\epsilon_r \epsilon_0}{b \ln\left(\frac{b}{b-d}\right)} \quad (2.6)$$

where ϵ_r is the electrolyte dielectric constant, ϵ_0 is the dielectric constant of the vacuum, b is the pore radius and d is the distance of the ion to approach the carbon surface. This equation agreed well with data obtained in the mesoporous range (zone III) as shown Fig. 2.6. For micropores with pore size smaller than 1 nm, an ‘electric wire in cylinder’ model was proposed with an assumption that ions line up in a cylindrical pore and the capacitance can be calculated using the following equation [109]

$$C / A = \frac{\epsilon_r \epsilon_0}{b \ln\left(\frac{b}{a_0}\right)} \quad (2.7)$$

where a_0 is the effective size of the desolvated ion. This proposed model agrees well with the change of normalized capacitance versus pore size (zone I in Fig. 2.6).

Figure 2.6 Normalized specific capacitance plotted versus average pore size for different carbon samples tested in Net4+BF_4^- in acetonitrile. Zones I and II were modelled as the electric wire-in-cylinder capacitors, zone III was considered as an electric double-cylinder capacitor, and zone IV represented the planar electric double layer capacitor for larger pores, when the curvature/size effect is negligible [109].

This work suggests that small pores with diameter less than 1 nm contribute greatly to the double layer charge storage even if the solvated ions are larger in size. This enhancement seen in the capacitance was related to the solvation shell distortion of the ion, leading the ion closer to the carbon surface and improved the capacitance. These results have pointed out that the design of the next generation of EDL capacitors should focus in fine tuning the carbon porosity, with a large volume of narrow but short pores for achieving high energy density.

2.3.1.2 Pseudocapacitance

Pseudocapacitance is defined as fast, reversible redox reactions that exist at the surface of the electrodes. The charge transfer in these reactions is dependent on the voltage, as could be seen in Fig. 2.7. A deviation from ideal rectangular cyclic voltammogram of an EDL capacitive electrode can be observed, with significant redox peaks attributable to

pseudofaradaic reactions. The observed delay of current upon the reversal of the potential sweep is due to the kinetically slow charging of the pseudocapacitance.

Figure 2.7 Typical charge/discharge voltammetry characteristics of a supercapacitor. [7].

Generally, the following modifications enable the capacitance enhancement for carbon materials by quick Faradaic reactions:

(a) Surface functionalization of carbon

A special oxidation/nitridation of carbon can be achieved through chemical [110], electrochemical [111] or plasma treatment [112]. It has been reported that the introduction of hydrophilic functional groups helps in improving the wettability of carbon materials in aqueous media; thus the overall capacitance is improved with the contribution from pseudocapacitance through redox processes [113-114]. For organic electrolytes, the wettability of the electrode can be improved by applying hydrophobic functional groups [115-116]. While functionalization of carbon significantly increases the specific capacitance with enhanced surface area, the reactions are partially reversible or irreversible after frequent cycling. Thus, their contribution to the pseudocapacitance of SCs is not longstanding. In addition to this instability, the presence of oxygenated groups may increase the internal resistance and the leakage current of the electrode [117]. All

these disadvantages can offset the capacitance enhancement from the oxygenated surface functional groups.

(b) Formation of ECP on carbon surface

As described in section 2.1.1.2 (b), polymerization of monomers *eg*: aniline, pyrrole can be deposited on the carbon surface by electro-polymerization or chemical method of polymerization.

In conducting polymers, delocalized π -electrons were delivered and stored as electrical energy. These electrons were transferred during electrochemical doping/undoping processes, as shown below:

There are three types of SCs utilizing conducting polymer electrodes: (i) SCs employing p-doping conducting polymers, such as polyaniline, polypyrrole, and polythiophene, for both positive and negative electrodes with low operating potential (< 1 V), (ii) SCs utilizing p-doping and n-doping polymers as positive and negative electrodes in an asymmetric configuration that provide higher capacity and working voltage than SCs mentioned in (i), and (iii) SCs utilizing conducting polymers which can be both n- and p-doped such as polythiophene derivatives [44] and polyacene [118], for both positive and negative electrodes. The widest operating voltage (2.5-3.0 V) and the highest energy density can be obtained for these SCs as compared to the previous two types.

(c) Insertion of transition metal oxide into carbon materials.

Capacitance enhancement of carbon materials can be realized by utilizing transition metal oxide *eg*: RuO_2 , MnO_2 , TiO_2 , *etc.* as described earlier in section 2.1.1.2(d). Among all these TMO materials, the underlying charge storage mechanism of MnO_2 has been

studied extensively in order to gain more understanding on the controlling factors of the charge-storage mechanism and to ultimately develop materials with demonstration of improved electrochemical performance. The initial study of Lee and Goodenough [42] has shown that the chemisorption of cations in the electrolyte (Li^+ , Na^+ , K^+) on the oxide surface and the hydrated cations were important contributing parameters to the pseudocapacitive behavior of the materials. This observation has lead to a surface adsorption mechanism of electrolyte cations (C^+) on MnO_2 , which can be described by:

where $\text{C}^+ = \text{Na}^+, \text{K}^+, \text{Li}^+$.

However in another study, Pang and Anderson [62] proposed that the intercalation/deintercalation of the protons , electrons and metal alkaline cations can take place within the oxide lattice during the redox process :

The contradiction between Lee' s and Pang's early investigations, which the former suggested that the charge storage of MnO_2 is a mechanism based on surface adsorption, whereas the latter suggested that the pseudocapacitance of MnO_2 involves intercalate/deintercalate of ions into the bulk oxide lattice, have not been conclusively resolved although spectroscopic tools were applied to such systems.

A recent study has been carried out by Toupin *et al.* [63] to determine the invariance of the manganese oxidation states for the composite electrodes using X-ray photoelectron spectroscopy . The results suggest that only a thin layer of MnO_2 is involved in the pseudocapacitance process. However in another study [119], a reversible expansion and shrinkage of the oxide lattice spacing was observed during charge transfer at Mn sites upon reduction/oxidation of MnO_2 as revealed by *in-situ* synchrotron X-ray

diffraction. This indicates that the intercalation or insertion of cations into the bulk of the oxide structure is contributing to the pseudocapacitance of MnO_2 and is not limited to only the surface in contact with the electrolyte.

2.3.2 Charge Transport Mechanism

2.3.2.1 Effects of temperature

The charge transport mechanism in a solid-state SC is connected with the ionic conductivity of the electrolyte. Kumar *et.al.* [120] have studied the effect of temperature on the ionic conductivity of the polymer electrolyte using electrochemical impedance spectroscopy (EIS) in the temperature range of 298- 434 K. In that study, the bulk ionic conductivity of the solid polymer electrolyte was determined from the complex impedance spectra using the equation:

$$\sigma = \frac{L}{RA} \quad (2.15)$$

where L , A and R are the thickness, area and bulk resistance of the solid polymer electrolyte respectively. The high frequency intercept on the real impedance axis of the Nyquist plot was used for the calculation of the bulk resistance [121]. The experimental results point out that the ionic conductivity increases as temperature increases, which is expected as the degree of salt dissociation increases at higher temperature and resulting in the increase of free ions or charges. The mobility of the ions also increases with higher temperature, since less activation energy is needed as calculated using Arrhenius equation given by:

$$\sigma = \sigma_0 \exp \frac{-E_A}{kT} \quad (2.16)$$

where σ is specific conductivity of the film, σ_0 is the pre-exponential factor, E_A is activation energy, k is Boltzmann constant and T is absolute temperature. On the other hand, the conductivity of ions changes to Grotthus- type at low temperature in which a proton moves rapidly from H_3O^+ to a hydrogen bonded water molecule. With an rearrangement of hydrogen bonds, it is then transferred further along a series of hydrogen-bonded water molecules [122].

2.3.2.2 Effects of polarization at various frequency

In another study carried out by Larsson *et.al.* [123], the charge transport mechanism of a thin, proton-conducting polyelectrolyte film at a frequency ranged from 100 Hz to 1 MHz was investigated using EIS. Three different charge transport characteristics were identified at three different frequency regions as illustrated in Fig. 2.8.

Figure 2.8 The effective capacitance normalized by area and the phase angle plotted as a function of frequency at 10% RH for a capacitor with titanium electrodes and PSS:H electrolyte. Three frequency regions were identified from the graph : (i) dipolar relaxation , (ii) ionic relaxation , and (iii) electric double layer formation [123].

Region (i) with high frequency ($f > 120$ kHz) exhibits capacitive behavior where the effective capacitance gradually increases as the frequency decreases, which is associated

with dipolar relaxation of the materials. At intermediate frequencies ranging from 80 to 120 Hz, there is a rapid increase in effective capacitance as frequency decreases, exhibiting a resistive behavior which originates from a phenomenon known as ionic relaxation. At frequency lower than 800 Hz, the effective capacitance saturates at $\sim 20 \mu\text{F cm}^{-2}$, which is attributed to the formation of EDL at the interfaces between two polyelectrolyte and metal electrode.

2.3.2.3 Effects of humidity

In the same study, it was found that the timescale of the various polarization mechanisms may be modified by the presence of water molecules in the polyelectrolyte. The impact of the humidity on the ionic conductivity of the polyelectrolyte was studied at various relative humidity (RH) levels ranging from 10% to 80% RH. The three different frequency regimes: (i) dipolar relaxation (ii) ionic relaxation, and (iii) EDL formation, all shifted towards higher frequencies as the RH increases. The fitted experimental data to the impedance model revealed that the proton conductivity was related to the quantity of absorbed water, which would affect both the amount and mobility of free protons. The mobility was strongly dependent on the water content [124] and it evolved in two steps as the humidity increased. First, the formation of hydronium ions (H_3O^+) has increased the proton mobility as a function of the hydration level, as they screen the electrostatic interaction between the protons and the anions and has thus decreased the activation energy for proton transport [125]. Second, the proton mobility reached a maximum as the humidity level further increased, to a high hydration level. This phenomenon is known as Grotthuss mechanism or structure diffusion, which the percolation paths are formed by the large amount of absorbed water, enabling proton transport occurs via hopping between absorbed water molecules [122].

2.3.3 Equivalent Series Resistance (ESR)

Internal resistance is another important evaluation parameter for the performance of SC, as it is one of the limiting factors for power density besides the applied voltage. In SCs, a number of factors contribute to the device internal resistance, and are commonly termed as the equivalent series resistance, or ESR [126]. These sources mainly originated from:

- electrode resistance
- electrolyte resistance
- interfacial resistance between the electrode and the current collector
- ionic resistance diffusing in small pores of the porous electrode
- ionic resistance moving across the electrolyte and through the separator
- external lead contact resistance

2.3.4 Energy Density and Power Density

Energy density indicates how much charges can be stored in the SC, whereas power density indicates how fast the stored charges can be released upon discharging. Both energy (E) and power ($P_{\max}$) of SCs are calculated according to:

$$E = \frac{1}{2} CV^2 \quad (2.17)$$

$$P_{\max} = \frac{V^2}{4R} \quad (2.18)$$

where C is the dc capacitance obtained in Farads, V is the nominal voltage, and R is the equivalent series resistance (ESR) in ohms [13, 126].

2.4 APPLICATIONS AND FUTURE CHALLENGES OF SCs

2.4.1 Applications of SCs

The applications of SCs are generally divided into two categories of totally different performance requirements: i) low power and low operating voltage applications such as memory back up in portable electronic devices. ii) high power and high operating voltage applications such as load leveling in electrical vehicles.

For the low power and low voltage applications, SCs are more commonly used as memory backup and standby power to bridge short power interruptions rather than operate as a main battery, where electrical energy is stored during low-load power and released quickly during peak-power. Such energy “bursts” gives supplement power from the source and smooths out the voltage fluctuations. CAP-XX, one of the SC manufacturers, have found the application of their products typically in boosting the power delivered from the mobile phone to support new functionality and extend their battery life time [127], which SCs are used as power architecture that provides light emitting diode (LED) flash camera phones with sufficient light for producing high-resolution images. In addition, cordless tools utilizing SCs as the power sources, such as screwdrivers and electric cutters are found available on the market [5].

Another potential use in future years for SCs is in the storage of electrical energy generated from solar photovoltaic systems [1]. Each unit of a photovoltaic device is essentially a low-voltage system, which would therefore be compatible with aqueous SC units. Hence, bank of low-voltage SCs could be charged photovoltaically in parallel and be discharged in series, to maximize the voltage availability. The utilization of SCs as energy storage for storing off-peak electricity from the utility grid during night time to support day-time usage have also been proposed, since electricity is more abundant and low cost at night as compared to day time. A successful implementation of this concept

could provide ~ 20% of the energy needed during day time from the energy stored in the previous evening, and it is found that asymmetric SCs with lead acid and activated carbon, as positive and negative electrodes, respectively, are suitable for this application [5].

As for high power and high voltage applications, SCs have found a ready market for a combination with batteries to enhance peak-load performance, for electric-powered vehicles [1, 34]. When high current is needed for the car's electric motor within a short time, the SCs are able to provide sufficient current through their rapid discharging processes. After the demand eases, the SCs then recharge from the batteries. Because of their ability to rapidly charge/discharge within ten seconds, SCs are used to accelerate the engine and recover braking energy for automotive applications. Benefiting from their rapid charge/discharge capability and outstanding cycle life, SCs have also clearly identified for their usage in tramway/metro segment, to supply power for the operation of trains across short distances in big cities, where electric cables are undesired for aesthetic reasons [4]. Another recent example is the use of SCs as emergency doors on an aeroplane (Airbus A380). The modules with an assembly of 100 F, 2.7 V cells are directly integrated into the doors in series/parallel to restrict the usage of heavy copper cables [4]. This application had demonstrated that SC technology is progressing towards a more mature state in terms of performance, reliability and safety for a niche market.

2.4.2 Future Challenges

Despite all the proposed or realized applications as mentioned above, the relatively high cost of SCs is currently the main reason for limiting their wide usage in energy storage technology. The limited number of suppliers has primarily causes the high cost of porous carbon used for SC rather than their intrinsic cost, and thus reducing the price of carbon materials for SCs would help in removing the main obstacle for their wider usage [128].

The costs of SCs can also be reduced effectively through improving the energy density, which would mean less packaging, separators, and electrolyte would be used as more energy is stored for the similar amount of electrode materials. With a higher cell voltage, less cells in series are required for achieving a specified system voltage, both the burden of the external voltage-balance circuits and the cost could be reduced simultaneously. For heavy hybrid vehicles applications, the main challenges for any energy storage units are the long cycling life required and the efficiency in dissipating the generated heat due to charge/discharge loss. Hence, the invention of SCs with high cycling efficiency and good thermal management is needed for better utilizing them in heavy hybrid vehicle applications.

Increasing energy density, lowering cost and implementing thermal management have thus become the primary challenges currently faced by the SC developers. While trying to tackle these issues, the SC research community has to keep in mind that all the solutions must be executed without sacrificing the high cycle-stability and high power density that distinguish SCs from batteries.

CHAPTER 3 EXPERIMENTAL PROCEDURES

This chapter contains a summary of experimental procedures employed in the synthesis and fabrication of nanostructured printable electrode materials for SC applications. In addition, the methodology of fabricating printable polymer electrolyte at room temperature via solvent casting is described in detail. SC fabrication and its electrochemical characterization including galvanostatic charge/discharge (GCD), cyclic voltammetry (CV), and electrochemical impedance spectroscopy (EIS) is also presented. Material characterization techniques including Field-emission Scanning Electron Microscopy (FESEM), X-ray diffraction (XRD), transmission electron microscopy (TEM) and X-ray Photoelectron Spectroscopy (XPS) were also used extensively for this project.

3.1 ELECTRODE PREPARATION

3.1.1 Chemical Synthesis

a) Ag nanoparticles decorated carbon nanotubes (Ag-CNT)

Silver decorated single walled carbon nanotubes (Ag-CNTs) were prepared by first dispersing 0.8 g of SWCNT in 15 mL of deionized water followed by 20 min ultrasonication (120 kW). The SWCNTs used here were P3-SWNT (Carbon Solution Inc.), which have been purified using nitric acid, resulting in highly functionalized nanotubes (1.5–3 atom % carboxylic acid). Typically, this is done by refluxing CNTs in concentrated nitric acid (2–3 M) for 45 h. Silver nanoparticles (AgNPs) were deposited on the SWCNTs using a facile room temperature deposition precipitation method. The size of the AgNPs was controlled through pH adjustment ($4 < \text{pH} < 7$) using 0.1 M NaOH (99%, Merck) that was added to 100 mL aliquots of AgNO_3 (99.99%, Aldrich, 0.05–0.15 M). The SWCNT suspension was mixed with the pH adjusted AgNO_3 solution and stirred

vigorously for various times ranging from 15 to 120 minutes, yielding different AgNP sizes. The Ag-CNTs were separated by centrifugation (15,000 rpm, 10 min), and excess Na ion and nitrate were removed by multiple washing steps with deionized water. The final product was then re-dispersed in deionized water before use.

b) MnO₂ nanostructured materials

MnSO₄ (0.2 g) and KMnO₄ (0.5 g) powder were mixed in 25 ml de-ionized (DI) water and transferred to a Teflon-lined stainless steel autoclave. The autoclave was heated in an oven at 140 °C for a dwell time varied from 1 to 18 hours in order to modify the surface morphology of the samples. After heating, the autoclave was cooled to room temperature. The final product was filtered and washed with DI water to remove all the impurities, then dried at 100 °C in air before use.

3.1.2 Electrospinning

An electrospinning set up consists of a metering syringe pump (KD Scientific), metallic needle, high voltage power supply (Gamma High Voltage Research) and a metal collector plate is shown in Fig 3.1.

Figure 3.1 Schematic diagram of an electrospinning set up.

V₂O₅ nanofibers (VNF)

Poly(vinylpyrrolidone) (PVP, 0.2 g ml⁻¹) of molecular weight 360,000 (Fluka) and 0.08 g ml⁻¹ vanadyl acetylacetonate (VO (acac)₃, 98%, Sigma-aldrich) were dissolved in a mixture (1 : 4 volume ratios) of acetic acid (Tedia Company Inc.) and ethanol (>99.8%, Fluka) by stirring for 24 h to obtain a homogenous precursor solution. All chemical reagents were used as received. This sol-gel precursor solution was loaded into a 10 ml glass syringe of the electrospinning set-up with a 200 mm diameter needle made of stainless steel, and ejected with a flow rate of 2 ml h⁻¹. A positive potential of 10 kV was applied between the needle tip and an aluminium foil collector placed at a distance of 10 cm. In the electric field, the ejected polymer jet is accelerated toward the collector, and V₂O₅ fibers were formed on the aluminium foil after solvent evaporation. These electrospun fibers were then heated in the furnace with a heating and cooling rate of 2 °C min⁻¹ and annealed at three different temperatures of 300, 400 and 500 °C for 15 min.

3.1.3 Electrode Fabrication

a) CNT-based electrodes

SWCNT or Ag-CNT suspension was prepared by dispersing 40 mg of as- prepared SWCNT (P3-CNT, Carbon Solution Inc.) or Ag-CNT in 200 ml deionized water, and sonicated for 30 minutes using a bath sonicator. The MnO₂-CNT composite was prepared by adding various weight percentages of MnO₂ nanoflowers or nanowires to the CNT suspension and stirred for 24 hours to obtain homogenous solution. The suspension was then filtered through a filter membrane (Whatman, 20 nm pore size, 47 mm diameter) using a filter flask and vacuum pump. The CNTs (pristine, Ag decorated or mixed with MnO₂ nanomaterials) are trapped on the surface of the filter, forming an interconnected network, as shown in Fig. 3.2. After drying, the CNT or Ag-CNT network can be peeled off from the filter as a freestanding thin film with a thickness of approximately 20 μm,

and is ready to be used as the electrode without using any binder or attaching it to any metallic current collector.

Figure 3.2 The filtration process of a CNT suspension which leads to the formation of a freestanding CNT network.

For preparing electrodes with thinner CNT network, spraying was used instead of filtration method. As-prepared or purified CNT materials (single-walled, multi-walled or double-walled CNTs) were suspended (3 mg ml^{-1}) into water with the aid of tip sonicator (Sonics Vibra-cell) for 40 minutes. The stable suspension was sprayed onto polyethylene-terephthalate (PET) substrates placed on a hot plate with an air brush pistol (Figure 3.3). During spraying, the water evaporated and the CNTs formed an entangled network on the PET. Subsequently, the CNT-sprayed PET substrates were employed as thin film electrodes. The mass of the CNTs sprayed on each substrate was evaluated by weighing the PET before and after the deposition.

Figure 3.3 (a) Spraying of the CNT solution on the PET substrate. (b) Sprayed CNT thin network on PET.

b) MnO₂ and VNF-based electrodes

MnO₂ nanoflowers, MnO₂ nanowires and VNF-based electrodes were prepared by dispersing annealed MnO₂ nanoflowers/MnO₂ nanowires/electrospun VNF with carbon black conducting additive (super P, 99%, Alfa Aesar) and poly(vinylidene fluoride) binder (PVDF, Sigma-Aldrich) in N-methylpyrrolidinone (NMP, Sigma-Aldrich) with a weight ratio of 75 : 15 : 10, respectively, as shown in Fig. 3.4. The resulting slurry was coated onto a 1 cm² area of graphite paper, and dried in the oven at 60 °C for 24 hours.

Figure 3.4 Preparation procedures for VNF-based electrodes.

3.2 POLYMER ELECTROLYTE PREPARATION

3.2.1 Polymer electrolyte with acid additives

The polymer electrolyte with acid additives was prepared by heating 5 g of poly(vinyl alcohol) (PVA) (Alfa Aesar, 98-99%, medium/high molecular weight) in 50 ml of deionized water at 90 °C to obtain a clear gel-like solution to which 3 ml of H₃PO₄ (Sigma-Aldrich, 85%) was added, resulting in a concentration of 1 M under continuous stirring. Air bubbles and excess water in the gel-like solution were removed using a vacuum desiccator, and dried at 60 °C for 4 hours to obtain a polymer electrolyte film with ~0.5 mm thickness.

3.2.2 Polyelectrolyte

The polyelectrolyte solution was prepared by adding 2 g of poly(styrenesulfonic acid) (PSS:H) powder (Sigma-Aldrich) to 10 ml of deionized water at room temperature followed by sonication (30 min) to obtain a clear solution. A solid-state PSS:H film was created by annealing the solution in a vacuum oven at 60 °C for 6 hours, resulting in a film with a thickness of ~0.5 mm, as shown in Fig. 3.5.

Figure 3.5 The chemical structure of a) poly(styrenesulfonic acid) (PSS:H) and b) poly(vinyl alcohol) (PVA). c) Schematic illustration of the preparation procedures of PSS:H as electrolyte of SCs.

3.3 SC DEVICE FABRICATION

3.3.1 SCs with liquid electrolyte

The SC devices were constructed by fixing two strips of CNT network with the dimensions of 0.5 cm X 2 cm with double-sided scotch tape on a PET plastic substrate. These two electrodes were sandwiched together with a nitrocellulose membrane

(Millipore Membrane Filters, pore size of 2 μm) which acts as a separator. The top part was remained open to fill in the electrolyte (1 M H_2SO_4). The plastic functions both as a support for the CNT network and encapsulation for the electrolyte. Electrical contacts were added using silver paste. A sketch of the CNT SC and a typical image of the device are presented in Fig. 3.6.

Figure 3.6 The left image is schematic and right image shows the real picture of the SC utilizing CNT networks as both the current collector and the electrode. The CNT network (black) and the separator (white strip) are encapsulated in a PET container filled with 1 M H_2SO_4 .

3.3.2 All solid- state SC

The solid electrolyte was stacked in between two strips of CNT or Ag-decorated CNT network with the dimensions of approximately 0.5 cm X 2 cm, which had been fixed separately to a PET substrate using double-sided scotch tape. In this case, the solid electrolyte also acts as the separator which avoids the electrical contact between the two electrodes, but allowing ionic charges transfer to take place. A sketch of an all solid-state SC and a typical image of the device are presented in Fig. 3.7.

3.3.3 Sealing of the device

The sealing of the devices was done by heat pressing the SCs in-between two pieces of polymer-coated Aluminum foil (Charlston Technologies, D-EL40H) at 400 $^{\circ}\text{C}$. The CNT

electrode strips were acted as the electrical connectors, which were directly connected to the external wire connection of the measurement equipment.

Figure 3.7 a) Schematic illustration and b) Photograph of the SC device structure, two carbon nanotube (CNT) networks sandwiching a 0.5 mm thick electrolyte film and encapsulated in PET c) A device which was laminated using polymer-coated aluminum foil.

3.3.4 Integration of printable SC with organic photovoltaic (OPV)

To integrate a SC on top of the OPV, CNT solution (3 mg ml^{-1} in isopropanol) is drop-cast on top of the Al cathodes of an OPV at room temperature to create a CNT network which acts as the integration platform as well as the electrode of the SC, as shown in Fig. 3.8(a). This is then followed by the stacking of a free-standing polymer electrolyte, made up of polyvinyl alcohol with 1 M acid phosphoric acid dopant (PVA- H_3PO_4) on top of the CNT network, and the device is completed by stacking a free-standing CNT network on top of the polymer electrolyte such that the PVA- H_3PO_4 polymer electrolyte is sandwiched between two CNT networks. The configuration of the integrated device, which is known as photo-supercapacitor (PSC) is illustrated in Fig. 3.8 (b).

Figure 3.8 (a) The formation of CNT network by drop casting the CNT solution on the OPV device. (b) A schematic representation of a PSC fabricated using layer-by-layer approach, with the thickness indicated for each layer of components.

3.4 CHARACTERIZATION TECHNIQUES

3.4.1 Material properties characterizations

- **Field-emission Scanning Electron Microscopy (FESEM)**

The surface morphology of the nanostructured electrode materials was characterized using a field-emission scanning electron microscope (JSM 6340 F). Samples were prepared by pasting the thin-film like structure networks onto the copper holder using carbon tapes. Scanning of the images was done at an accelerating voltage of 5 kV with the magnification range of 5000 to 60,000. All samples were coated with ~10-15 nm platinum using a coater (JEOL JFC-1600) before scanning.

- **X-ray Diffraction (XRD)**

Powder X-ray diffraction (XRD) was performed using a Shimadzu diffractometer (Cu-K α) with step scanning (0.02°, 0.6 s dwell time) over 10 to 140° 2 θ range. The patterns were analyzed applying the Rietveld method using the fundamental parameters approach contained within the software TOPAS V3 (Bruker-AXS).

- **Transmission Electron Microscopy**

The high resolution TEM (HRTEM) images were performed at 200kV by using a JEOL JEM-2100F transmission electron microscope equipped with high contrast objective aperture (20 μ m in diameter) equivalent to a point to point resolution of 1.7Å.

- **Brunauer-Emmet- Teller (BET) surface area measurement**

The BET surface area of the samples was determined by N₂ adsorption-desorption isotherms using a Micromeritics ASAP 2020 system at 77 K. Prior to the measurement, the samples were degassed at 373 K under nitrogen flow for 20 h.

- **X- ray Photoelectron Spectroscopy**

X-ray photoelectron spectroscopy (XPS) spectra were recorded using a Kratos AXIS Ultra spectrometer with the monochromatic Al K α X-ray radiation. Deconvolution and peak fitting were performed with computer assisted surface analysis XPS software using a Voigt function with 30% Lorentzian character and a Shirley background.

- **Thermo gravimetric Analysis (TGA)**

The experiment was carried out with a heating rate of 2 or 10 °C /min from room temperature to 900 °C using the TGA Q500 Series from TA, with 40% air as sample gas and 60% nitrogen as balance gas.

- **Fourier Transform Infrared Spectroscopy (FT-IR)**

The infrared spectra data of the CNTs were obtained by dropping the CNT solution onto the KBr disc and repeatedly scanned four times over the range of 4000 – 400 cm⁻¹ using Perkin-Elmer Spectrum GX FTIR.

- **Contact angle measurement**

The test was done using sessile drop method in air with the FTA 200 Dynamic Contact Angle Analyzer (First Ten Ångstroms).

- **Four-point probe resistivity analyzer**

The sheet resistivity of the CNT-based electrodes was obtained by taking 8 measurements on the same sample using a four-point probe resistivity analyzer (CMT-SR 2000N).

- **Surface profiler**

The thickness of the CNT films was measured using a surface profiler (ASTQ 7082955). By measuring the height difference between the edge of CNT film and PET substrate, the thickness of the sprayed CNT network or bucky paper could be estimated.

3.4.2 Electrochemical Characterization

- **Cyclic Voltammetry (CV)**

For CNT-based electrodes, the CV measurements were carried out in a symmetrical two electrode configuration using a computer controlled bipotentiostat (Pine Instrument, AFBP1) in the potential range of 0–1 V with a scan rate of 20 mV s^{-1} . The electrochemical behavior of the electrospun VNF was investigated using a three-electrode cell set-up, which consisted of a working electrode, platinum foil as the counter electrode and Ag/AgCl as the reference electrode. CV measurements were carried out in aqueous (2M KCl, 2M KOH, 1M H_2SO_4) and organic (1M LiClO_4 , (battery grade, Sigma-Aldrich) in propylene carbonate (anhydrous, 99.7%, Sigma-Aldrich)) electrolyte at room temperature using a computer controlled potentiostat (Solartron 1470E) in the potential range of 0–0.9 V for aqueous electrolyte and 0–3 V for organic electrolyte (scan rates from $1\text{--}50 \text{ mV s}^{-1}$).

- **Galvanostatic charge-discharge (GCD)**

This test was carried out for all the SCs in a two-electrode configuration. The GCD measurements of CNT-based electrodes were conducted using the bipotentiostat (Pine Instrument, AFBP1) between cell voltages of 0–1 V at the constant current density of 1 mA cm^{-2} . As for VNF-based electrodes, this test was done using a computer controlled potentiostat (Solartron, 1470E) in the potential range of 0–1 V for aqueous and 0–3 V for organic electrolyte at current density of $0.1, 0.5$ and 1 A g^{-1} , respectively.

- **Electrochemical Impedance Spectroscopy(EIS)**

Alternating current(AC) impedance for all the SC devices was measured using an impedance spectrum analyzer (Solatron, SI 1255B Impedance/gain-phase analyzer; computer software ZView) with an AC amplitude of 10 mV, from 55 kHz to 20 mHz at open circuit potential (OCP).

- **Self-discharge**

Self-discharge behavior of a SC was determined by charging the device to certain voltage for certain time (i.e., 1 V for 1 hour), then followed by discharge at open circuit. The self-discharge test can be done in two electrode configuration using computer controlled potentiostat (Pine Instrument, AFBP1 or Solartron 1470E).

- **Climate chamber**

To artificially control the ionic conductivity of the solid-state polymer films, the measurements on the SCs were conducted at different levels of the RH, keeping the temperature constant (20 °C), in a Challenge 160 environmental chamber (Angelantoni Industries). The level of the RH was varied from 80% to 10% RH.

CHAPTER 4 RESULTS

This chapter details the results of various experiments undertaken in this thesis. Firstly, the use of CNTs with high surface area and conductivity as both active electrode material and the current collector for printable SC applications was explored. Due to the power density limitation attributed to the internal resistance of the CNT electrodes, metal nanoparticles which are highly conducting had been incorporated into the CNT network with the purpose of improving the power density of CNT electrodes. Thus, the feasibility of room temperature decorated Ag nanoparticles (AgNPs) on functionalized CNTs by deposition-precipitation process was investigated. The pseudocapacitance contribution observed in Ag- decorated CNT devices had inspired the study of transition metal oxide (TMO) nanomaterials, which possess promising pseudocapacitive properties as electrodes in printable SCs. MnO_2 nanostructured materials was incorporated into CNT network for an in-depth investigation due to its high specific capacitance reported [57], environmental benign nature, and cost effectiveness. It's worth noting that even though the performance of these CNT-based materials were at most comparable but not better than conventional activated carbon electrodes as outlined clearly from the literature survey (Table 2.1), the results obtained in these studies have served the purpose of setting up baseline values and also developing protocol for realizing printable SCs.

To continue the effort of increasing the energy density of printable electrodes, another potential TMO material, V_2O_5 nanofibers (VNF) were chosen for further investigation due to their multiple valencies allowing surface/bulk redox reactions, and have shown good capacitive behavior in both lithium ion batteries and SCs [55, 129]. Electrospinning, a simple, one-step, cost effective method which is much more ascendant than the other processes in synthesizing nanofibers with diameters ranging from tens of nanometers to several micrometers was employed to synthesize the VNFs. A correlation

of the charge storage and transport mechanism of SCs with morphology, surface area, and interfacial properties affected by process parameters, electrode and electrolyte treatments had been carried out through various materials and electrochemical characterization techniques.

Besides printable electrodes, a new class of printable electrolyte, known as polyelectrolyte was also developed in order to realize a completely printable SC. Furthermore, a study on the effect of humidity to the ionic conductivity of this polyelectrolyte was carried out. Lastly, the integration of a printable SC with an energy harnessing device, organic photovoltaic was demonstrated at the end of this chapter.

4.1 CNTs - BASED SUPERCAPACITORS

4.1.1 Electronic properties of CNTs

CNT was chosen as the first generation of electrode materials for printable SCs mainly due to its conductivity ($\sim 10^4 \text{ Scm}^{-1}$) which is much higher than activated carbon ($0.1\text{-}1 \text{ Scm}^{-1}$) used in conventional SCs, and thus enables CNTs to be used as sole electrode materials that combines both functions of current collector and electrode active material. Therefore, examining the electronic properties of different CNTs is of critical importance for selecting the best electrode materials for SC applications. In general, the conductivity of the CNTs can be affected by the amount of impurities, functional groups and the number of wall layers [130]. Table 4.1 summarizes the electrical conductivity measured for various types of sprayed CNT thin networks on polyethylene tetraphthalate (PET) flexible substrates using 4- point probe resistivity measurements.

Table 4.1 Electrical conductivity measured on different types of sprayed CNTs film on PET substrate.

Types of CNT	Conductivity(S) [S/cm]	4-probe resistance(R) [Ω]	Thickness (t)[μm]
AP SWNT ^a	196.078	15	3.4
P2 SWNT ^b	29.762	70	4.8
P3 SWNT ^c	267.38	11	3.4
DWNT ^d	33.333	100	3
MWNT ^e	26.709	104	3.6

^a as-prepared single-walled CNTs ^b purified non-functionalized single-walled CNTs

^c purified –COOH groups functionalized single-walled CNTs ^d double-walled CNTs

^e multi-walled CNTs

The conductivity is calculated employing the following equation:

$$S = \frac{1}{t \times R} \quad (4.1)$$

where S is conductivity, t is CNT film thickness and R is 4-probe resistance (also known as sheet resistance)

It is observed that single-walled CNTs are more conducting than multi-walled and double-walled CNTs, and COOH-functionalized single-walled CNTs (P3 CNT) have the highest conductivity among all the CNTs. The investigation on thermal stability and surface properties of P3 CNTs is carried out to further verify its compatibility as printable electrode materials in SCs.

4.1.2 Surface properties of functionalized and non-functionalized CNTs

The presence of functional groups on the surface of CNTs can be detected using two characterization techniques: (1) thermo gravimetric analysis (TGA) and (2) fourier transform infrared spectroscopy (FTIR). For TGA, the experiment was carried out in air atmosphere with a heating rate of 10 °C /min from room temperature to 900 °C. Under this condition, the thermal behavior of both functionalized (denoted as P3 CNT) and non-functionalized (denoted as P2 CNT) CNTs is presented in Fig. 4.1.

Figure 4.1 Thermal gravimetric analysis of P2 and P3 CNTs.

There is a gradual weight loss observed for P3 CNT at lower temperature (~ 100 °C) as compared to P2 CNT, which the weight percentage only started to decrease rapidly at ~ 500 °C. The lower thermal stability exhibited by P3 CNT as compared to P2 CNT is an evidence of the presence of functional groups [131]. As temperature rises beyond 750 °C, the CNTs is burned completely, and the final residual weights of 8.9 and 8.1 wt% were obtained for P2 and P3 CNT respectively, revealing a purity of $>90\%$ for both CNTs. The impurities are mainly constitute of metal catalyst used during the growth process of CNTs, as stated on the product description from Carbon-Solutions® [132].

Figure 4.2 Infrared transmittance spectrum of P3 CNTs.

Infrared spectroscopy has been employed to analyze the type of functional groups present in P3 CNTs. The absorbance peak located in the range of $3100\text{--}3600\text{cm}^{-1}$ corresponds to the stretching vibrations of hydroxyl (--OH) groups, which might be due to the physisorbed free water trapped within porous CNT surface. The small peak located at about 1750 cm^{-1} is identified as C=O stretching vibration, suggesting the presence of carboxylic acid group (--COOH , IR frequency $\nu_{\text{C=O}} = 1719\text{ cm}^{-1}$) rather than carboxylate groups (--COO-- , $\nu_{\text{C=O}} = 1620\text{ cm}^{-1}$) [133]. In the range of $1550\text{ to }1580\text{ cm}^{-1}$, a distinct peak was observed possibly attributed to carboxylate anion stretch [134]. The presence of C=C bonds in P3 CNT is confirmed by the slight absorbance peak at 1500 cm^{-1} which is related to the aromatic carbon-carbon bond stretch mode [134].

Figure 4.3 FESEM images with the inset show water angle measurements which reveal (a) hydrophilic surface of P3 CNT and (b) hydrophobic surface of P2 CNT.

As wetting capability and surface morphology of the CNT electrode are the important aspects affecting the electrochemical interaction between electrolyte and electrode, water contact angle and SEM characterization were done on both P2 and P3 CNT. A hydrophilic surface with high wettability was observed for P3 CNT surface with water contact angle of $\sim 8 \pm 5^\circ$. Besides, FESEM image reveals an entangled-network like structure with CNT bundles' diameter in the range of $\sim 20\text{-}30\text{ nm}$. On the other hand, the surface of P2 CNT is hydrophobic, as indicated by a larger water contact angle of $\sim 140 \pm 5^\circ$. The diameter of the P2 CNT bundles is twice as large as P3 CNT bundles ($\sim 50\text{-}60\text{ nm}$), indicating a smaller surface area than the latter.

4.1.3 Electrochemical characteristics of functionalized CNT electrodes

Based on the evaluations of the above conductivity and surface properties measurements, functionalized CNTs (P3 CNT) with higher conductivity and better surface wettability, are more advantageous than non-functionalized CNTs (P2 CNT) as an electrode for SC applications. Hence, the electrochemical behavior of P3 CNT were tested in $1\text{ M H}_2\text{SO}_4$ liquid electrolyte (the device structure as shown in Fig. 3.4) with a typical CV curve as presented in Fig. 4.4(a). The peak observed at 0.35 V can be attributed to

oxygenated functional groups contributing as Faradaic capacitance to the overall capacitance [135]. In general, the deviation from an ideal box-shape CV curve of a SC without internal resistance (dotted line) can be explained by the presence of functional groups, impurities, and a decreased conductivity due to the absence of a dedicated current collector. From the CV measurement, the specific capacitance, C_m of the electrode can be calculated using the following equation:

$$C_m = \frac{2I}{\left(\frac{dV}{dt}\right) \cdot m} \quad (4.1)$$

where dV/dt is the voltage scan rate (20 mVs^{-1}), I is the current corresponding to the applied voltage, and m is the mass per electrode. The specific capacitance of the device is found to be 44 F g^{-1} , which is in agreement with the reported results in literature [26, 29, 32, 136], despite the fact that these studies were being carried out using metallic current collectors or mixed CNTs with amorphous carbon.

Besides CV measurements, galvanostatic charge/discharge (GCD) tests are another device characterization that can be employed to evaluate the specific capacitance and internal resistance of a SC device. Fig. 4.4 (b) shows GCD curves of the same device measured at a constant current of 1 mA.

Figure 4.4 (a) Cyclic voltammogram and (b) GCD curves of a P3 CNT network device with 1 M H_2SO_4 liquid electrolyte [137].

Each branch of the entire curve starts with a voltage drop (V_{drop}), and thus the internal resistance (R) of the device can be calculated according to

$$R = \frac{V_{drop}}{2I} \quad (4.2)$$

where I is the constant current applied. The slope of the discharge curve is used to determine the specific capacitance C_m of the electrode using

$$C = \frac{2I}{S \cdot m} \quad (4.3)$$

where I is the current applied, and S is the discharge rate obtained from the slope of the discharge curve ($S = dV/dt$) and m is the mass per electrode. For the device shown, the specific capacitance was 33 F g^{-1} as obtained from the CV. With the right choice of parameters such as the treatment of the CNT material, the types of raw CNT materials, and the combination of CNT material and electrolyte, the minimization of the internal resistance and the maximization of the device performance can be expected. Based on the above results P3-SWNT was chosen for further studies.

4.2 METAL NANOPARTICLES DECORATED CNT BASED SUPERCAPACITORS

The previous section has established a new printable SC device architecture by capitalizing on CNT networks, which allow the combination of both current collector and active material in one single layer. This has led to lightweight and flexible SC devices which can be fabricated using roll-to roll or inkjet printing processes, the essentials of “printed power” which is fully compatible with printed electronics applications. However, the proposed CNT device architecture needs improvement in terms of energy and power density. These shortcomings are attributed to (1) inherently low specific capacitance of CNT-based materials [46], and (2) inter-tube (CNT-CNT) contact resistance that limits the power density and charge-discharge capability of SCs [138]. To overcome these

problems, metal nanoparticles with high conductivity are potential candidates that can be incorporated into CNT networks with the purpose of improving the charge transport within the electrode. Among all the metal nanoparticles, silver nanoparticles (AgNPs) were chosen as they are more conducting than CNTs [139-140], and a capacitance enhancement of 300% was achieved by incorporating Ag particles into activated carbon cloth electrodes of SCs as reported by Tanahashi [141]. For this reason, a simple approach has been employed to synthesize silver nanoparticles decorated CNTs (Ag-CNTs) by a facile room-temperature deposition-precipitation process with the aim of reducing device internal resistance and concurrently enhancing the device energy density.

4.2.1 The effects of pH and aging time on the size of silver nanoparticles (AgNPs)

The experimental results show that pH and aging time are the two main parameters controlling the dispersion and size of AgNPs on CNTs. After introduction of P3 CNTs to 0.15 M AgNO₃ solution, the pH decreases from 5.6 to 3.4 as shown in Table 4.2 due to the presence of the acidic carboxyl groups. Subsequently, the absorption of AgNO₃ at these groups on the CNTs forms COO-Ag groups as presented in Fig. 4.5(a). The addition of NaOH solution is a critical step in controlling pH to ensure that the quantity of hydroxyl ions is sufficient for the progressively reduction of Ag^I to Ag⁰. Table 4.2 shows the variation of AgNP size as a function of pH and aging time. At pH 4.3, the AgNP size was the largest with diameter ≈ 15nm. As the pH increases to 6.3, the AgNP size dramatically decreases to 6 nm for the same aging time. This phenomenon might be due to the reaction between excess hydroxyl ions and the COO-Ag groups at higher pH, which promotes the reformation of carboxyl groups on SWNTs with concomitant release of Ag-OH as shown in Fig. 4.5(b). Consequently, the number of available nucleation sites and the growth of AgNPs decreases. By reducing the reaction time from 120 to 15 minutes with the same pH condition, the size of the AgNP has been decreased from 6 to 3

nm. This indicates that longer aging time actually yielded larger AgNPs through the crystal growth and aggregation after nucleation.

Table 4.2 Different size of AgNPs decorated on CNTs as a function of pH and aging time

sample	AgNO ₃ conc. (M)	pHs ^a	pHsc ^b	pHn ^c	rxn. time (min)	average Ag crystal size ^d (nm)
Ag-CNT(12-15 nm)	0.15	5.6	3.4	4.3	120	13
Ag-CNT(6-8 nm)	0.15	5.6	3.4	6.3	120	4
Ag-CNT(3-5 nm)	0.15	5.6	3.4	6.3	15	7
Ag-CNT(1-2 nm)	0.05	5.6	3.4	6.3	15	1

^a pH of AgNO₃ solution. ^b pH of AgNO₃ after added SWNTs. ^c pH of suspension after added NaOH. ^d Determined by TEM

Figure 4.5 Proposed reaction mechanisms for (a) the deposition of AgNPs at carboxyl-functionalized CNTs and (b) the resolution of silver hydroxide from CNTs surfaces at high pH.

TEM images of the uniformly high dispersion of faceted and multiple-twinned AgNPs with the sizes varying from 1- 13 nm formed on SWCNTs are shown in Figure 4.6. From the images shown in Figure 4.6 (d), it can clearly be seen that the AgNPs decorated on the SWCNT are elliptical rather than spherical in shape.

Figure 4.6 TEM images for (a) 13 ± 1 nm Ag-CNT (b) 6 ± 1 nm Ag-CNT (c) 4 ± 1 nm Ag-CNT (d) 1nm Ag-CNT

Presence of AgNP on the SWCNT was further analyzed by powder X-ray diffraction which showed diffraction peaks at $2\theta = 38, 45, 64, 78,$ and 82° in addition to CNT[142-143] confirming the formation of cubic Ag^0 nanoparticles on CNT (Fig.4.7). The amount of AgNP loading on the SWCNT was constant as verified by Rietveld phase analysis of powder X-ray diffraction patterns, and the crystalline diffraction peaks revealed AgNP amount as 2wt% for all the samples.

Figure 4.7 Representative Rietveld phase analysis plot of Ag-CNT showing metallic silver reflections and the weight percentage of AgNP on SWCNT.

4.2.2 Device characteristics of Ag-CNTs based SCs

SC devices were fabricated by stacking a polyvinyl alcohol acidic polymer electrolyte film (PVA/H₃PO₄) (Fig. 3.5(a)) in between two electrode strips of pristine or Ag-decorated CNT. Cyclic voltammograms for SCs with P3 CNT and Ag-CNT electrodes of various AgNP sizes (denoted as 1 to 13nm Ag-CNT) are presented in Fig. 4.8 (a). The specific capacitance of a conventional activated carbon electrode with PVA/H₃PO₄ electrolyte is <10 F g⁻¹, whereas the specific capacitance of a dense CNT network is 46 F g⁻¹ showing good agreement with literature values [32] and its CV curve shows the peak at 0.1 V, which can be attributed to oxygen containing functional groups [135]. Surfactants and impurities contributed by the CNT synthesis are thought to lead to the deviations from the box-shaped CV characteristics of an ideal SC. These box-shaped CV curve deviations are also observed for 1 and 4 nm Ag-CNT, which exhibit significantly larger specific capacitances of 106 F g⁻¹ and 68 F g⁻¹ respectively as compared to P3 CNT.

Figure 4.8 (a) Cyclic voltammograms for CNT, 13 nm Ag-CNT, 7 nm Ag-CNT, 4 nm Ag-CNT, and 1 nm Ag-CNT devices measured at 20 mVs^{-1} . (b) GCD curves for the same devices mentioned in (a) measured at $\sim 1 \text{ mAcm}^{-2}$.

The specific capacitance decreases with increasing Ag particle size with 7 and 13 nm Ag-CNT devices yielding values of 43, and 23 Fg^{-1} respectively. Similar observations were also obtained from the measurement of specific capacitance using GCD method. The capacitance normalized by area of the electrode (F cm^{-2}) has been evaluated for all devices, with the values showing similar trend as specific capacitance (F g^{-1}) as shown in Table 4.3.

Table 4.3 Specific capacitance, internal resistance and sheet resistance measured in PVA/H₃PO₄ electrolyte for P3 CNT and Ag-CNT based SCs using both CV and GCD methods.

Sample	Area per electrode (cm ²)	Mass per electrode (mg)	C(F cm ⁻²)		C(F g ⁻¹)		Internal resistance (Ω)	Sheet Resistance (Ω □ ⁻¹)
			CV	Galv	CV	Galv		
P3CNT	0.6	1.10	0.09	0.08	46.5	41.9	83.2	15.7
13nm-AgCNT	0.6	1.20	0.05	0.03	22.8	16.5	159.9	10.3
7 nm-AgCNT	0.7	1.40	0.09	0.06	43.4	28.3	72.8	5.9
4 nm-AgCNT	0.5	1.23	0.15	0.10	67.5	44.8	65.5	6.3
1 nm-AgCNT	0.5	1.22	0.24	0.21	105.8	89.4	83.0	10.2

From the voltage drop at the beginning of the discharge curve, the internal resistance (IR) of the CNT electrode was found to be 83.2 Ω. Incorporation of AgNP into the CNT network yields an internal resistance of 65 Ω for 4 nm Ag-CNT; however, the 13 nm Ag-CNT device displays a high internal resistance of 160 Ω. The electrode resistance, or CNT/Ag-CNT network sheet resistance, as measured at several points on the network using a probe station, decreases from 15.7 Ω □⁻¹ for the reference CNT device to lower values with a minimum sheet resistance of 5.9 Ω □⁻¹ observed at a AgNP size of 7 nm. The result of both internal resistance and sheet resistance of the electrode is shown in Table 4.3 for giving a clearer overview on the correlation between AgNP sizes and both the internal resistance and sheet resistance of the devices.

Figure 4.9 (a) Nyquist impedance plots, inset showing the high frequency, low impedance region. (b) Equivalent circuit model for CNT, 13 nm Ag-CNT, and 7 nm Ag-CNT devices. (c) Equivalent circuit model for 4 nm Ag-CNT and 1 nm Ag-CNT devices.

The effect of AgNP on SC performance and the electrochemical behavior of Ag-CNT electrodes were further investigated with electrochemical impedance spectroscopy (EIS) as shown in Fig 4.9(a). The occurrence of an intersection was observed at the real axis in the high frequency region, followed by a non-vertical slope in low frequency region. This observation can be well-explained by two reasons: (1) an interface exists between the electrode and the electrolyte, and (2) a double-layer capacitance connects in parallel with a resistance and leads to the formation of a RC loop [81]. The transformation of the plot to a vertical line takes place at low frequency, mainly ascribed to the capacitive response of porous carbons. The presence of the non-vertical slope at low frequency region of the impedance plot may be associated with different pore size distribution of the carbons, and low ionic mobility within the electrodes [81]. An equivalent circuit simulating Ag-CNT electrodes would involve the following circuit elements: the bulk solution resistance, R_s ; the double layer capacitance, C_{dl} ; the interfacial

charge transfer resistance, R_{ct} , and the Warburg impedance due to distributed resistance within the mesopores, W_s . Since both active material and current collector have been combined into a single component in the devices, C_b and R_b correspond to the capacitance and resistance within the electrode. The combination of the circuit elements are proposed and shown in Fig. 4.9(b) and 4.9(c) respectively.

4.3 TRANSITION METAL OXIDE (TMO) BASED SUPERCAPACITORS

To further enhance the energy density of printable SC electrodes, TMO nanomaterials, which are expected to show higher specific capacitance (Fig 2.4) than conventional carbon materials and better electrochemical stability than conducting polymer have been explored. The following sections mainly focus on the utilization of two TMO nanomaterials as printable SC electrodes: V_2O_5 and MnO_2 . Detailed investigations on the effects of annealing condition on the morphology and electrochemical characteristics of both materials have been studied. The effect of different TMO weight percentage in TMO-CNT hybrid electrodes has been explored to optimize the energy and power density of SCs.

4.3.1 The effect of annealing condition on the surface morphology of TMO nanomaterials

a) V_2O_5 nanofibers(VNF)

Following the electrospinning of the VNF precursor, the fibers were annealed by heat treatment as described in section 3.1.1(c). The optimized annealing temperature range of electrospun fibers was first estimated through thermal gravimetric analysis (TGA), as shown in Fig. 4.10(a).

Figure 4.10 (a) Thermal gravimetric analysis of as-spun VNF before calcination. SEM images for (b) as-synthesized electrospun vanadium oxide nanofibers. Electrospun vanadium oxide nanofibers after annealed at (c) 300 °C (d) 400 °C, the inset shows the TEM image of the fibers with crystal size ~ 100 nm and (e) 500 °C.

As seen from TGA curve, there is a slight drop initially at ~80-90 °C, mainly due to the evaporation of water trapped in the as synthesized VNF. The weight percentage of

the VNF continues to decrease gradually in the temperature range of ~ 100 - 350 $^{\circ}\text{C}$, and dropped rapidly at ~ 400 $^{\circ}\text{C}$. The TGA data has shown that the PVP is fully decomposed at the temperature of 400 $^{\circ}\text{C}$, thus suggesting that the optimized temperature to obtain fiber-like V_2O_5 after calcinations might fall in the range of ~ 300 - 500 $^{\circ}\text{C}$. Therefore, these electrospun fibers were annealed in the furnace at three different temperatures of 300 , 400 and 500 $^{\circ}\text{C}$, for a constant period of 15 min.

The SEM image of as-synthesized fibers in Fig. 4.10(b) shows that the fibers have smooth, uniform surfaces and uniform diameters ranging from 500 to 600 nm. After being heated in the furnace at an annealing temperature of 300 $^{\circ}\text{C}$ for 15 minutes, the fibrous morphology is still maintained with an increased diameter of ~ 1 μm as shown in Fig. 4.10(c), which might be due to the expansion of the polymer during heat treatment, and the crystallization of the fibers has yet to be initiated at this temperature. The fibers obtained after annealing at 400 $^{\circ}\text{C}$ exhibit a spiral like structure and the diameter of the fibers shrinks to 300 - 500 nm as illustrated in Fig. 4.10(d), mainly due to the decomposition of the PVP component and the initiation of fiber crystallization. The TEM image (inset of Fig. 4.10(d)) further confirms the shrinkage of the fibers, which also exhibits partial crystallinity with crystal size ~ 100 nm. As the temperature was increased to 500 $^{\circ}\text{C}$, the fibrous morphology collapsed and turned into flaky-like structures with rough surfaces (Fig. 4.10(e)). These images show that optimization of the annealing temperature is critical for obtaining a fibrous morphology as annealing beyond 400 $^{\circ}\text{C}$ may lead to the disintegration of PVP which acts as the template for fiber microstructure. Also, rapid V_2O_5 crystal growth at temperatures greater than 400 $^{\circ}\text{C}$ contributes to the collapse of nanofiber architecture.

Figure 4.11 (a) XRD patterns collected for VNF 300, VNF 400, VNF 500 and V_2O_5 powder (as reference) over 10° to 60° 2θ range. (b) Rietveld phase analysis plot of VNF 400 showing 100% crystallized V_2O_5 with orthorhombic Shcherbinaite phase structure.

In order to monitor the crystal structure formation with respect to annealing temperature XRD patterns have been collected for V_2O_5 powder ($> 98\%$, Fluka), and electrospun vanadium oxide fibers (VNF) annealed at 300, 400 and 500 $^\circ\text{C}$ (denoted as

VNF 300, VNF 400 and VNF 500) respectively as shown in Fig. 4.11. The lack of any discernable diffraction peaks indicates that VNF 300 has an amorphous structure, whereas the presence of [001] and [110] peaks for VNF 400, VNF 500 and V_2O_5 powder confirms the high crystallinity of these samples. Rietveld phase analysis conducted on powder X-ray diffraction patterns, further confirms that the VNF 400 and VNF 500 have orthorhombic Shcherbinaite phase structure (Pmn21) with lattice parameter $a=11.513(2)$ Å, $b=4.377(2)$ Å and $c=3.566(3)$ Å. Crystal size obtained from Rietveld analysis indicated V_2O_5 crystal growth from VNF 400 (48.7 nm) to VNF 500 (66.3 nm).

Figure 4.12 N_2 adsorption-desorption isotherms for VNF 300, VNF 400 and VNF 500

Brunauer-Emmett-Teller (BET) surface area of $6 \text{ m}^2 \text{ g}^{-1}$ was observed for VNF 500 compared to VNF 400 ($10 \text{ m}^2 \text{ g}^{-1}$) as revealed by the N_2 adsorption-desorption isotherms in Fig. 4.12. VNF 300 has the lowest surface area of $3 \text{ m}^2 \text{ g}^{-1}$ amongst all the samples. The narrow hysteresis loops that appeared at different relative pressure are characteristic of hierarchical pore, and it is worth noting that the charge stored per gram of VNF (specific capacitance) does not necessarily correlate with N_2 accessible surface area but rather more related to the pore volume of the VNF [144-145].

(b) MnO_2 nanoflowers (MnNF) and nanowires (MnNW)

MnO_2 nanostructured materials were prepared using the hydrothermal method as described in section 3.1.1. From FESEM characterization, a strong correlation between annealing time and surface morphology of nanostructured MnO_2 can be observed, as evidently shown in Figure 4.13.

figure 4.13 FESEM images of nanostructured MnO_2 prepared at different hydrothermal annealing time of (a) 1 hour (b) 6 hours (c) 18 hours. The inset shows the enlarged image for each corresponding MnO_2 formed.

By heating the well mixed solution of MnSO_4 and KMnO_4 to 140°C for 1 hour, porous flowerlike nanowhiskers of MnO_2 were obtained, with a diameter of $\sim 0.45\ \mu\text{m}$ and pore size of $\sim 100\ \text{nm}$. As the annealing time was increased to 6 hours at same annealing temperature, some of the nanoflowers had started to grow into wire-like structures, which led to the formation of both nanoflowers and nanowires simultaneously as shown in Figure 4.13(b). Further increasing the annealing time to 18 hours resulted in the complete conversion to nanowires, with a width of $\sim 100\ \text{nm}$ and a length of more than $1\ \mu\text{m}$. The observations detailed through FESEM characterizations have thus suggested that the morphological manipulation MnO_2 is possible by controlling the annealing time of hydrothermal process.

Figure 4.14 XRD patterns collected for MnNF and MnNW over 10° to 70° 2θ range.

Table 4.4 Crystal structure, lattice parameters, cell volume and density of MnNF and MnNW obtained from Rietveld refinement.

Sample	Crystal Structure	Lattice Parameters(Å)			Cell Volume(Å ³)	Density(g/cm ³)
		a	b	c		
MnNF	Orthorhombic	9.119	5.721	7.431	387.66	2.708
MnNW	Tetragonal	9.7847	-	2.863	274.1	4.21

The phase purity and crystal structure of both MnNF and MnNW have been examined by XRD. As shown in Fig. 4.14, the diffraction pattern of MnNF shows broad peak features, indicating a unique textural combination of both amorphous and crystalline structures. From Rietveld phase analysis, the crystal structure of MnNF is identified as orthorhombic with lattice constant of $a = 0.9119$ nm, $b = 0.57208$ nm and $c = 0.7431$ nm (JCPDS 44-0268). An increase in crystallinity is observed for MnNW which were annealed for longer times, as evidenced by the appearance of sharper peaks on its diffraction patterns. All the peaks can be exclusively indexed as the tetragonal α - MnO_2 with lattice constant of $a = 0.97847$ nm and $c = 0.2863$ nm (JCPDS 44-0141). The findings

from XRD and EDX characterizations have suggested that longer annealing time is indeed needed for complete transformation of nanostructured MnO_2 with higher crystallinity.

From the N_2 adsorption-desorption isotherms in Fig. 4.15, BET surface area obtained for MnNF ($\sim 44 \text{ m}^2\text{g}^{-1}$) is four times higher than MnNW ($11 \text{ m}^2\text{g}^{-1}$). This is within expectation as could be seen from Fig. 4.13, MnNFs have a more porous structure which contributes to higher surface area than MnNWs.

Figure 4.15 N_2 adsorption-desorption isotherms for MnNF and MnNW.

4.3.2 Electrochemical characteristics of TMO and TMO-CNT based SCs

(a) VNF based SCs

Cyclic voltammograms for SCs with VNF annealed at various temperatures are presented in Fig. 4.16(a), showing a near-ideal rectangular shape at scan rate of 5 mVs^{-1} for all devices, indicating a small equivalent series resistance (ESR) [146].

Figure 4.16 (a) Cyclic voltammograms for VNF 300, VNF 400 and VNF 500 measured at 5 mVs^{-1} in 2 M KCl in two-electrode configuration. (b) Galvanostatic charge-discharge curves for the same devices mentioned in (a) measured at 0.1 Ag^{-1} .

Specific capacitance of 25 F g^{-1} was obtained for electrospun nanofibers annealed at 300°C (VNF 300), and this value reached a maximum of 190 F g^{-1} as the annealing temperature was increased to 400°C , which is in agreement with the reported literature values [55]. As annealing temperature was further increased to 500°C , the specific capacitance was found to decrease from 190 to 86 F g^{-1} . GCD measurements (Fig. 4.16(b)) yield capacitances of 21, 176 and 87 F g^{-1} respectively for SCs with VNF 300, 400 and 500 measured at a constant current density of 0.1 Ag^{-1} , further corroborating observations from CV measurements. From the voltage drop of each discharge curve, the device resistance of the SC with the VNF 300 as electrode is calculated to be 14Ω , which is higher than both VNF 400 and 500 with device resistance of 6 and 5.5Ω respectively, indicating that the presence of PVP polymer in the electrospun fibers has reduced the electrical conductivity of the electrode as well.

The electrochemical performance of VNF electrodes was further explored using EIS. The Nyquist plots recorded for all devices are shown in Fig. 4.17(a).

Figure 4.17 (a) Nyquist impedance plots for devices with VNF 300, VNF 400 and VNF 500 in 2 M KCl, inset showing the high frequency, low impedance region. (b) Equivalent circuit model for same devices mentioned in (a).

An equivalent circuit simulating VNF electrodes with various annealing temperatures in 2 M KCl electrolyte would involve the following circuit elements: the electrolyte resistance, R_e ; the double layer capacitance, C_{dl} ; the pseudocapacitance, C_p ; the interfacial charge transfer resistance, R_{ct} ; and the Warburg impedance (W_s) due to distributed resistance within the pores of VNF [81]. The experimental data was fitted well with the proposed model as shown in Fig. 4.17(b).

b) MnNF and MnNW based SCs

Typical cyclic voltammograms recorded at a scan rate of 5 mV s^{-1} in 1 M Na_2SO_4 liquid electrolyte for both MnNF and MnNW based SCs are shown in Fig. 4.18. MnNF displayed a larger CV curve as compared to the MnNW, indicating a higher specific capacitance of the former (153.1 Fg^{-1}) than the latter (51.9 Fg^{-1}). This significant difference in specific capacitance might be attributed to higher surface area and regular pore size of the MnNF, as observed from both SEM and BET characterizations. The

correlation between surface morphology and specific capacitance will be further discussed in section 5.1.2.

Figure 4.18 Cyclic voltammograms of MnNF and MnNW recorded at 5 mV s^{-1} in $1 \text{ M Na}_2\text{SO}_4$ liquid electrolyte.

c) *MnO₂-CNT composite based SCs*

The main drawback of the MnO_2 based electrodes is their poor electrical conductivity (10^{-5} - $10^{-6} \text{ S cm}^{-1}$), which limits their power-delivery capability. To design a better SC with both high energy and power density, strategy pursued would include the incorporation of CNTs into MnNW and MnNF (denoted as MnNW-CNT and MnNF-CNT, respectively). The CNT would function as a backbone structure that not only ensures electrical contact within MnO_2 active material, but also ensures an open entangled network forming a porous electrode. Consequently, the charge transport in between the active material within the electrode would be more efficient and the energy density could be maximized. Figure 4.19 shows the cyclic voltammograms recorded at a scan rate of 20 mV s^{-1} in $1 \text{ M H}_2\text{SO}_4$ liquid electrolyte for MnNW-CNT and MnNF-CNT composite based SCs

Figure 4.19 Cyclic voltammograms of (a) MnNF -CNT and (b) MnNW-CNT measured at a scan rate of 20 mVs^{-1} in $1 \text{ M H}_2\text{SO}_4$ liquid electrolyte.

The area of the CV curves is used to calculate C , the capacitance of the SCs according to:

$$C = \frac{Q}{V} = \frac{I \times V}{\frac{V}{t}} \times \frac{1}{V} = \frac{A}{sV}$$

(4.4)

where Q is amount of charges stored in the SCs, V is the voltage range, s is the scan rate and A is the area under the discharge curves of the CV. The variation of specific capacitance with respect to the different weight percentage of MnNF/ MnNW added into the CNT is presented as a bar chart in Fig.4.20.

Figure 4.20 Comparison of specific capacitance for MnNF-CNT and MnNW-CNT at various MnO₂ weight percentages ranging from 0-70 wt%.

For MnNF-CNT, an increase of capacitance was observed from 89.9 F g⁻¹ for pure CNT electrodes, to 167.4 F g⁻¹ after adding 3 wt% of MnO₂. This value was further increased to a maximum capacitance of ~ 200 F g⁻¹ which was achieved when 6 wt% of MnO₂ were being added into the CNT composite electrodes. However, the specific capacitance started to decrease when there were more than 6 wt% of MnO₂ in the composite electrode, and it could decrease to a value which was even lower than pure CNT electrode, 53.6 F g⁻¹, after adding 70wt% of MnO₂. A similar trend was observed for MnNW-CNT, indicating that 6 wt% was the optimum amount of MnO₂ that can be added into MnO₂-CNT composite electrodes. With the same added weight percentage, MnNF-CNT show slightly higher capacitance as compared to MnNW-CNT, suggesting that the former has higher surface area than the latter, which is more favorable for the formation of electrical double layer, and thus helping in improving the charge storage capability of the electrodes.

The electrochemical performance of electrodes based on MnNFs and MnNWs, and MnO₂-CNT composite electrodes with 6 wt% of MnNFs and MnNWs (denoted as

6wt% MnNF-CNT and 6wt% MnNW-CNT, respectively), was further explored using EIS. The Nyquist plots recorded for all devices are shown in Fig. 4.21(a).

Figure 4.21 (a) Nyquist impedance plots for devices with MnNF, MnNW, CNT+6wt% MnNF and CNT+6wt% MnNW in 1 M H_2SO_4 , inset showing the high frequency, low impedance region. (b) Equivalent circuit model for same devices mentioned in (a).

An equivalent circuit simulating MnO_2 and MnO_2 -CNT based electrodes in 1 M H_2SO_4 electrolyte would involve the same circuit elements as VNF based electrodes: the electrolyte resistance, R_e ; the double layer capacitance, C_{dl} ; the pseudocapacitance, C_p ; the interfacial charge transfer resistance, R_{ct} ; and the Warburg impedance due to distributed resistance within the pores of CNT and MnO_2 nanostructured materials. The proposed model with combination of the circuit elements which was well-fitted with the experimental data is shown in Fig. 4.21 (b).

4.4 PRINTABLE ELECTROLYTE FOR SUPERCAPACITORS

Apart from the electrodes, there is an ongoing quest for printable solid electrolyte materials that do not compromise the device performance while providing advantages of compactness and reliability without the leakage of liquid components. Polymer-based

electrolytes have been widely studied to circumvent this issue [147-148], however these types of electrolytes are suffering from low ionic conductivity, therefore salt additives that are either acidic or basic need to be added to improve their ionic conductivity. Generally, the higher the acid/base content is, the higher the ionic conductivity of solid electrolyte. However, excessively high acid/base concentration leads to phase separation, with separated polymer matrix and crystalline salt domains, resulting in a brittle nature of the electrolyte [106]. Thus, in this section, the use of a new class of polymer electrolyte, called “polyelectrolytes”, has been investigated for SC applications. Unlike conventional polymer electrolytes, the self-ionization characteristics of polyelectrolytes in polar solvents have eliminated the need of adding conducting salts into the electrolyte, and also provide higher mechanical strength and flexibility, while maintaining a very high capacitance value. The comparison in terms of the specific capacitance, internal and ionic resistances of SCs based on a polyelectrolyte, poly(styrenesulfonic acid) (PSS:H, see chemical structure in Fig. 4.22(a)), and a conventional polymer with acid additives, poly(vinyl alcohol) (PVA, see Fig. 4.22(b)) with 1 M of H_3PO_4 (PVA/ H_3PO_4), respectively, were characterized using EIS, CV, and GCD techniques. In addition, the effect of the ionic conductivity on the electrochemical performance of the solid-state PSS:H-based SCs was studied. The ionic conductivity of the PSS:H film was artificially controlled by conducting all experiments of the SCs at different levels of the relative humidity (RH) in a climate chamber.

4.4.1 Comparison between polymer and polyelectrolyte-based SCs

SCs were fabricated by sandwiching a 0.5 mm thick solid-state PSS:H film, or PVA/ H_3PO_4 film between two ~ 20 μm thick electrodes of carbon nanotube (CNT) networks as shown in Fig. 4.22 (c).

Figure 4.22 The chemical structure of a) poly(styrenesulfonic acid) (PSS:H) and b) poly(vinyl alcohol) (PVA). c) Schematic illustration of the SC device structure, two carbon nanotube (CNT) networks sandwiching a 0.5 mm thick electrolyte film.

When a voltage is applied to such SCs, electric double layers are formed at the interfaces between the electrolyte and the CNT-based electrodes. In the case of the polymer electrolyte (PVA/H₃PO₄), the positive and negative ions migrate towards the oppositely charged electrode forming the electric double layers. In contrast, for a polyelectrolyte only one type of ion is mobile in the solid state, while the oppositely charged ions are covalently attached to the polymer chains. More specifically, in PSS:H-based SCs mobile protons migrate towards the negatively charged electrode while the immobile polyanions remain close to the positively charged electrode forming the electric double layers.

Figure 4.23 (a) The effective capacitance per area and the phase angle versus the frequency for SCs with PVA/ H_3PO_4 (open symbols) and PSS:H (solid symbols) as the electrolyte. The measurements were conducted at 50% RH and 20 °C. (b) Cyclic voltammogram (CV) curves for SCs with PSS:H, and PVA with and without 1 M H_3PO_4 measured at 20 mV s⁻¹. The inset shows the enlarged view of the CV curve for the SC with pristine PVA.

Experimental ac impedance data ($C_{\text{Eff}}(f)$ and $\phi(f)$) in the frequency range between 2×10^{-2} Hz and 2×10^4 Hz with an amplitude of 100 mV are given in Fig. 4.23(a) for PVA/ H_3PO_4 and PSS:H-based SCs, with the same thickness of the electrolyte, at 50% RH and 20 °C. The total complex impedance of the SCs ($Z_{\text{Tot}}(f)$) is described in terms of the effective capacitance per area ($C_{\text{Eff}}(f)$), where the area represents the surface area of the electrodes disregarding their porosity, the phase angle ($\phi(f)$) and the real part of the impedance ($Z_{\text{Re}}(f)$) as functions of the frequency (f). The effective capacitance exhibits an increasing trend as the frequency decreases, and reaches very high values at low frequencies ($\sim 50\text{ mF cm}^{-2}$ at 2×10^{-2} Hz, Fig. 4.23(a)) compared to capacitance values typical for ordinary electric double layer capacitors with non-porous metal electrodes ($1\text{--}10\ \mu\text{F cm}^{-2}$) [149]. The high capacitance of electric double layer capacitors in general is attributed to the very short-distanced charge separation of the ions and the oppositely charged electrode, confining the electric field to the electric double layers. In combination with the extremely high effective surface area of the CNT electrode networks ($\sim 120\text{--}430$

$\text{m}^2 \text{g}^{-1}$) [15, 27, 33], this results in an extraordinary high effective capacitance for the SCs [13, 150].

Typical CV characteristics are given in Fig.4.23 (b) for CNT-based SCs composed of various polymeric electrolytes; PSS:H and PVA, with (1 M) and without H_3PO_4 , respectively, at 50% RH. The specific capacitance of an electrode measured in a device configuration was calculated from equation 4.1. In order to limit the contribution from the electrolysis of water, the SCs were charged below 1 V. As expected, the device with pure PVA (i.e. without H_3PO_4), did not work as a SC (inset in Fig. 4.23(b)). Instead its resistive behavior translates a leakage current. PVA cannot be considered as an electrolyte because of its lack of dissociated protons (the $\text{p}K_a$ of the alcohol OH group is high, estimated between 15 and 17) [151]. The addition of a high concentration of inorganic acid, 1 M H_3PO_4 into the PVA results in an enormous increase of the area of the CV curve, i.e. the specific capacitance of the device, as shown in Fig. 4.23 (b) and gives rise to a specific capacitance of 25 F g^{-1} . The $\text{p}K_a$ values for the three acid groups, i.e. $\text{p}K_a = 2, 7$ and 12 [151], of H_3PO_4 implies a large amount of mobile protons available in the film, which leads to a high capacitance of the device. In comparison, SCs which employ PSS:H as electrolyte exhibited a near-ideal rectangular shape of the CV curve, indicating a small ESR [146] and yielded a capacitance value of 46 F g^{-1} , which is twice that of the PVA/ H_3PO_4 film. This is attributed to the efficient dissociation of the polyelectrolyte chains into polyanions and protons in the presence of water ($\text{p}K_a = 1$) [151]. The mobile protons then contribute to the formation of the electric double layers upon the application of an electric field, which is supported by these EIS observations.

4.4.2 Ionic Conductivity study of polyelectrolyte at various humidity levels

The effect of the ionic conductivity on the SC characteristics was investigated. It has been reported that the proton conductivity in PSS:H increases from $7 \times 10^{-7} \text{ S cm}^{-1}$ at

10% RH to $4 \times 10^{-4} \text{ S cm}^{-1}$ at 80% RH [123]. Thus, the ionic conductivity of the electrolyte in the SCs can be controlled by varying the RH, which can be monitored by characterizing the impedance characteristics of the SCs while placed in a climate chamber. The effective capacitance per area, the phase angle and the real part of the impedance versus the frequency are all given in Fig. 4.24 for SCs with a solid-state PSS:H film at various RH levels (10-80% RH) and also with a water-based solution of PSS:H (1 M), respectively.

Figure 4.24 a) The effective capacitance per area, b) the phase angle and c) the real part of the total impedance versus the frequency for a solid film PSS:H-based SC (an 0.5 mm thick PSS:H layer sandwiched between two CNT electrodes) at different levels of the RH (10% to 80% RH) and for a SC with the CNT electrodes dipped into a 1 M PSS:H water solution (w.s. in the graphs) at 20 °C. The dashed lines represent data at 80% RH reached after the RH was cycled from 80% to 10% RH.

For the different humidity levels the overall trend of the effective capacitance is the same; it increases with decreasing frequency (Fig. 4.24(a)). However, the evolution of $C_{\text{eff}}(f)$ is shifted towards higher capacitance values for higher RH levels. The phase angle of the SC based on a solid PSS:H film is $\geq -45^\circ$ at all humidity levels, indicating that the SC is still under the process of storing charges even at $2 \times 10^{-2} \text{ Hz}$ (Fig. 4.24(b)). The fact

that the value of the effective capacitance increases with RH, as well as that the phase angle is more negative at low frequencies, is attributed to the increased proton conductivity (the number of dissociated protons and the proton mobility are both expected to increase) with increased RH. In order to compare the impedance characteristics with a SC including an electrolyte that possesses an even higher proton conductivity than a PSS:H-based SC at 80% RH, a SC was fabricated in which the CNT electrodes were dipped into a 1 M PSS:H water solution. As expected from the trend obtained when increasing the RH level, i.e. increasing the ionic conductivity, the effective capacitance of the SC based on the PSS:H water solution is further increased as compared to the SC based on the solid PSS:H film, and saturates at low frequencies (Fig. 4.24(a)). Simultaneously, the phase angle approaches and even reaches below $\varphi(f) = -45^\circ$ at low frequencies (Fig. 4.24(b)). This gives the SC now a dominant capacitive behavior at these frequencies, rather than a resistive character like with the solid PSS:H film. Looking at the real part of the impedance (Fig. 4.24(c)), which is related to the ionic resistance of the PSS:H, only a weak frequency-dependence is observed for the SC based on the solid-state PSS:H film (10-80% RH). The real part of the impedance increases only slightly with decreasing frequency at the low frequency region. In the case of the SC based on the PSS:H water solution the resistive part of the impedance is close to independent versus the frequency. As expected, it is found that the real part of the impedance decreases, throughout the entire frequency region studied, when the ionic conductivity (monitored as the RH) increases.

Figure 4.25 a) CV curves and (b) GCD curves for SCs based on a PSS:H film tested at different humidity levels ranging from 10-80% RH and a PSS:H water solution (w.s.). The inset of (a) shows the enlarged view of the CV curves tested at 10% and 30% RH, whereas inset of (b) shows the enlarged view of the GCD curve tested at 10% RH.

Fig. 4.25(a) shows CV curves for a SC with PSS:H at various humidity levels, ranging from 10% to 80% RH. At low humidity levels, the amount of stored charges, as indicated by the area under the CV curve, is small and gives rise to a specific capacitance of 2 F g⁻¹ at 10% RH. As the RH is increased to 30%, a slight increment in the specific capacitance (7 F g⁻¹) is observed, whereas this value further increases to 36 F g⁻¹ as the humidity increases to 50% RH. The maximum specific capacitance of the PSS:H film-based capacitors (69 F g⁻¹) was achieved as the humidity level reaches 80% RH. In comparison, the specific capacitance of the SC with the 1 M PSS:H water solution is as high as 77 F g⁻¹. Together, these observations reveal the hygroscopic nature of PSS:H and again illustrate the importance of the ionic conductivity in the overall performance of the device.

GCD measurements, given in Fig. 4.25(b), were performed to study the influence of the ionic conductivity (the RH level) on the performance of the constant-current charge and discharge characteristics of the SCs. All devices were measured at a constant charge and discharge current density of 1 mA cm⁻², which is a low current density as compared to commercial SCs but comparable to SC measurements reported by other research groups in

the literature [100-102]. The specific discharge capacitance of a single electrode (C) of the SCs was calculated according to equation 4.3. The galvanostatic measurements for the SC with the PSS:H film yielded capacitance values of 0.3 F g^{-1} at 10% RH, 3.3 F g^{-1} at 30% RH, 22.7 F g^{-1} at 50% RH and 85 F g^{-1} at 80% RH, respectively. When operating the SC in a humid environment, the specific capacitance is relatively higher, further supporting the observations from the EIS and CV measurements. The SC with liquid PSS:H yielded the highest capacitance (104 F g^{-1}). Note that although a higher effective capacitance per area and a lower ionic resistance are observed for the SC with the PSS:H water solution as compared to the SC with a solid PSS:H film at 80% RH, the difference is not overwhelming. In one experiment, after the humidity level reached 10% RH, the humidity level was immediately changed back to 80% RH again (dashed lines in Fig. 4.24(a)). These “recovered curves” are almost indistinguishable from the curves first measured at 80% RH. Similar observations were obtained in the CV measurements (dashed lines in Fig. 4.25(a)).

4.5 INTEGRATION OF PRINTABLE SC AND ORGANIC PHOTOVOLTAIC (OPV)

To demonstrate the feasibility of printable SC in real life applications, a printable SC was integrated with an energy harnessing device, organic photovoltaic (OPV). Such a hybrid module is termed as “photo-supercapacitor (PSC)”, which can be realized through fabrication steps as detailed in section 3.3.4.

The device configuration of a PSC is shown in Fig. 3.6(b). Before measuring the performance of the PSC, the individual device performances of OPV and SC were first tested. Fig. 4.26 (a) shows both dark and light J - V curves of the OPV. The dark J - V profile shows an ideal behavior of a diode, whereas from the light J - V profile, a short-circuit current density (J_{SC}) as high as 10.37 mA cm^{-2} can be obtained by the OPV when

no bias was applied. The device yields an open circuit voltage (V_{OC}) of ~ 0.6 V, which is the highest voltage achievable for an OPV in charging the SC in the hybrid device. Analysis of the shunt resistance of the device gives a low value of $12 \Omega \text{ cm}^2$ which correlates with its relatively high fill factor (FF) of 55% and power conversion efficiency (η) of 3.39%.

Figure 4.26 (a) J - V curves in dark and under AM 1.5G illumination (100 mW cm^{-2}) of the P3HT:PCBM-based OPV device (b) CV curves for SC with CNT electrode and PVA- H_3PO_4 polymer electrolyte measured at 20 mV s^{-1} .

CV curves of the SC device are shown in Fig. 4.26(b), where the near-rectangular shape of the CV curves indicates good capacitive characteristics of the device[15], with specific capacitance of 84.5 F g^{-1} . Similar observations were obtained from the measurement of specific capacitance using GCD method with constant current of 0.2 mA , yielded a specific capacitance of 86 F g^{-1} mirroring the CV results. By increasing the thickness of the CNT network which is proportional to its mass (by assuming same network areas), the charge capacity increases accordingly as indicated by a larger current-voltage curve shown in Fig. 4.26(b). This implies that during productization, the form factor and device architecture can be readily optimized – that is, the SC can match the OPV through variation in area or the SC may only partially match the OPV areal coverage, with the thickness variation to account for any mismatch between the energy generated by the OPV and the charge storage capacity of the SC. Potentiostatic measurements yield a

power density of 0.15 kW kg^{-1} and energy density of 2.96 Wh kg^{-1} for the SC device, which compare favorably with reported ranges ($0.01\text{-}10 \text{ kW kg}^{-1}$) of commercial SCs and are similar to the reported flexible devices [76, 152].

Figure 4.27 (a) Schematic and circuit illustration of a PSC during (a) charging process (b) galvanostatic discharge. The voltage and current profiles plotted versus time for (c) charging and (d) discharging process of a PSC.

Fig. 4.27(a) shows the schematic and circuit illustration of PSC charging, in which ITO and another free-standing CNT electrode of the SC were connected in series (denoted as terminal 1); whereas both OPV and SC were integrated in parallel with common interface consisting of the drop-casted CNT network on the Al cathode of the OPV (denoted as terminal 2). After charging the PSC for 70 s under an illumination of 100 mW cm^{-2} , the light source was switched off and the discharge was performed by connecting a $1 \text{ k}\Omega$ resistor in parallel to terminal 1 and 2 of the PSC (Fig. 4.27(b)), which acts as a load drawing a maximum current of 0.6 mA from the SC. The charge and discharge curves of the PSC were plotted as a function of voltage and current versus time as shown in Fig. 4.27(c) and 4.27(d), and yielded a capacitance of 28 F g^{-1} . This lower specific capacitance

of the PSC as compared to individual SC is mainly due to the V_{OC} limitation of 0.6 V from the OPV, which is insufficient to charge the SC up to its maximum capacity. Thus, this has reflected the need of increasing the charging voltage, by connecting a few OPVs in series or with tandem solar cell architectures [153-154]. The main challenges of coupling the two OPVs in series lie in two aspects: (i) the patterning of ITO region on the same substrate as illustrated in Fig. 4.28(a), and (ii) the deposition of the silver paint has to be carefully restraint within a small region to avoid electrical contact with the Al cathodes of another OPV as shown in the following figure.

Figure 4.28 (a) Schematic and circuit illustration of a PSC showing the SC connected in parallel with two OPVs in series during charging process. The charge-discharge curves of the PSC plotted as a function (b) voltage and (c) current versus time.

The doubling of the charging voltage had been achieved by connecting two OPVs in series, and the voltage and current profiles of GCD curves plotted as a function of time are shown in Fig. 4.28(b) and (c), respectively. The increase of the V_{oc} to ~ 1.1 V and I_{sc} to ~ 1 mA by connecting two OPVs in series as could be seen as charging voltage and current in Fig. 4.28 (b) and (c) has proven to be critical in charging the SC to its

maximum storage capability, yielding a specific capacitance of 79.8 F g^{-1} , which is nearly three times higher as compared to SC integrated with single OPV.

Chapter 5 DISCUSSION

This chapter is divided into three sections. The first section focuses mainly on the impact of utilizing nanomaterials as electrodes in order to enhance the SC performance, extensively discussing the effects of decorated particle size, surface morphology, crystallinity and weight percentage of nanomaterials on the performance of SCs. Pseudocapacitance contributions of all these nanomaterials on the enhanced SC performance were studied using various techniques including CV scan rate analysis, XPS and EIS. The acquired data will be presented and discussed. The second section examines the impact of various electrolytes on the SC performance, which includes the effect of electrolyte pH, comparison of SC performance using aqueous and organic electrolytes as well as polymer-based electrolytes, and lastly the influence of ionic conductivity of polymer-based electrolytes on printable SC performance. The third section will focus on assessing data on the cyclestability and reliability of the SCs and PSCs, which can be correlated to incorporation of pseudocapacitive materials and device sealing.

5.1 THE IMPACT OF NANOMATERIALS ON ENHANCED SC PERFORMANCE

5.1.1 The effect of decorated particle size

The experimental data obtained from both CV and GCD measurements on AgNP decorated CNT as shown in section 4.2 has prompted an investigation of the AgNP size effect on the performance of the device. The energy density of SCs, which is directly proportional to the specific capacitance of the device (refer to equation 2.17) decreases with increasing particle size, resulting in 4, 7 and 13 nm Ag-CNT devices, yielding values of 1.9, 1.2 and 0.7 Wh kg⁻¹, respectively, as shown in Fig 5.1. Similar observations were obtained from the measurement of specific capacitance using GCD method, with the capacitance values (Table 4.3) mirroring the CV results.

Figure 5.1 Ragone plot of SCs consisting of Ag-CNT electrodes with PVA/H₃PO₄ electrolyte.

The decrease in the specific capacitance of the devices using larger AgNPs (e.g. 7 and 13 nm Ag-CNT devices) may be attributed to pore blockage of the CNT network by larger AgNP, resulting in a reduction of the effective surface area and thus reducing the electrical double layer capacitance. On the other hand, smaller AgNP (with diameter < 5 nm) are less likely to block the pores of the CNT network and may additionally increase the effective surface area as the cluster of Ag atoms create small protrusions on the CNT surface. A 1 nm AgNP is estimated to consist of only ~31 Ag atoms, which may result in an increased effective surface area (Fig. 5.2(b)) that contributes to enhanced capacitances observed for the 1 and 4 nm Ag-CNT devices.

The particle size effect of AgNPs contributing to the enhanced capacitance of SCs was further investigated by studying devices in which the electrode was prepared by physically mixing 2 wt% of Ag particles into the CNT, denoted as 2%Ag+CNT device. The recorded capacitance, 39 F/g, was higher than 13 and 7 nm Ag-CNT devices (>5 nm AgNP), but lower than the 4 and 1 nm Ag-CNT devices (<5 nm AgNP). Lower capacitance of devices with > 5 nm AgNPs compared with the 2%Ag+CNT device

comprising Ag particle size of 2- 3.5 μm , suggest that these micrometer-sized Ag particles did not block the nm-sized CNT network pores. On the other hand, the higher capacitance of the < 5 nm AgNP devices suggest that the CNT pores were not blocked by Ag, and furthermore, the nanostructured Ag contributed to increased capacitance. The observations detailed in the preceding paragraphs may thus be explained as follows: specific capacitance in Ag-CNT SCs comprises of contributions from the electrical double layer capacitance and from pseudocapacitance; with the former governed primarily by surface area whereas the latter is influenced strongly by the size of the AgNPs. Smaller AgNPs do not decrease the overall surface area (indeed, as shown in Fig. 5.2(b) it may even slightly increase the surface area) whereas they enhance the pseudocapacitance thus resulting in a specific capacitance and energy density enhancement (106 F g^{-1} and 3.3 Wh kg^{-1}) for 1 nm Ag-CNT, which is twice as high as the reference CNT device.

Low internal resistance (IR) is of critical importance in SCs, since it is one of the limiting factors for power density (refer to equation 2.18). In SCs, a number of sources including sheet resistance of the electrode, interfacial resistance between the electrode and the electrolyte, ionic resistance of the electrolyte, and the external lead contact resistance contribute to the IR and are collectively measured and referred to as the ESR [10]. The result of both IR and sheet resistance measurements of the electrodes are represented by the bar chart (Fig. 5.2(a)) for giving a clearer overview on the correlation between AgNP sizes and both the internal resistance and sheet resistance of the devices.

Figure 5.2 (a) Bar chart which shows the internal resistance and sheet resistance measured for all Ag-CNT devices.(b) An illustration of an AgNP decorated CNT, and corresponding energy diagrams illustrating the potential barrier within the tube (intra-tube resistance), which is deeper for larger AgNP (>20nm AgNP, dotted line) decorated CNT as compared to smaller AgNP (<5 nm, solid line). (c) Energy diagram of a metallic and semiconducting CNT junction leading to formation of a Schottky barrier; and an AgNP mediated reduction in the barrier height leading to improved charge transport (lower inter-tube resistance) between the metallic and semiconducting nanotubes.

As seen in Fig 5.2(a), the sheet resistance decreases from $15.7 \Omega \square^{-1}$ for the reference CNT device to lower values with a minimum sheet resistance of $5.9 \Omega \square^{-1}$ observed at a AgNP size of 7 nm. Since the CNT electrodes are well above the percolation threshold for nanotubes, the charge transport can be expected to be dominated by metallic conduction paths and thus these results can be explained by two collaborating mechanisms. On the one hand, addition of the AgNPs increases the percentage of metallic material (AgNP plus metallic CNT) as opposed to the pure CNT where a ratio of metallic CNT to semiconducting CNT of 1:2 is expected). This leads to an increased number of metallic conduction paths and thus to a lower resistance due to the law of inverse addition of parallel resistances. Additionally, nanostructured silver possesses a lower resistivity than

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metallic CNT [139-140], which results in conduction paths that are partially or fully made up from silver having a smaller resistance. The sheet resistance for 2%Ag + CNT device is the lowest at $5 \Omega \square^{-1}$, arguably due to large silver clusters and possible percolation paths within the 2-5 μm silver particles.

To understand the observed behavior of the IR, the effect of Ag on the intra-tube as well as the inter-tube resistances of semiconducting CNTs needs to be discussed. Whenever a contact is formed between a metal and a semiconductor, Fermi level alignment is expected to occur resulting in charge redistribution and the formation of a depletion layer surrounding the metal. Thus, such phenomenon contribute to the intra-tube resistance of the Ag-CNTs which creates a localized depletion region, acting as a charge scattering site and creating a potential barrier within the nanotube, leading to a decrease in mobility and intra-tube conductivity (Fig. 5.2(b)). However it may be argued that the depth of the depletion region (and potential barrier) increases with the number of atoms in the nanocluster, reaching a maximum value somewhere in the 5-20 nm range, beyond which this depth may remain constant [155]. The significant inter-tube contact resistance between semiconducting and metallic CNTs has been attributed to the creation of a Schottky barrier [156]. The semiconducting-metallic CNT junction mediated with Ag nanoparticles can lead to a reduction in the Schottky barrier height (Fig. 5.2(c)) thus reducing the inter-tube contact resistance, because of the smaller difference between the valence band maximum (majority carrier in p-type semiconductor) and metal Fermi level of Ag as compared to metallic CNT. The superposition of these two effects could explain the observed size dependent variation of the internal resistance. In this study, the intra-tube resistance with 13 nm AgNP is probably higher than 4nm Ag-CNT and reference CNT devices, which explains the high internal resistance of the former device.

5.1.2 The effect of surface morphology

The surface morphology plays a vital role in the characteristics of the SC devices, and in particular the ability to store charges is critically determined by the surface area of the electrode, directly affecting the energy density of the SCs. Table 5.1 summarizes the measured device characteristics of SCs with different electrode surface morphologies.

Table 5.1 The device characteristics of SCs with different electrode surface morphologies.

Sample	Crystal Structure	Cell Volume ($\text{\AA}^3$)	Density (g cm^{-3})	BET surface area (m^2g^{-1})	Specific Capacitance (Fg^{-1})	Energy density (Wh kg^{-1})	Power density (W kg^{-1})
VNF 300	amorphous	-	-	3	25	0.7	1266.9
VNF 400	Orthorhombic	179.67	3.27	10	190	5.2	3333.3
VNF 500	Orthorhombic	180.62	3.25	6	86	2.4	3852.1
MnNF	Orthorhombic	387.66	2.71	44	153	5.3	1993.6
MnNW	Tetragonal	274.1	4.21	11	52	1.8	2882.7

Noticeably, it was observed that materials with high BET surface area consistently showed impressive device characteristics, regardless of the different crystal structure, thus suggesting the importance of this parameter for obtaining high specific capacitance. The relatively low specific capacitance of VNF 300 might be due to the remaining PVP in the electrospun nanofiber as evident from SEM images, XRD and BET data (Fig. 4.10, 4.11 and 4.12), in which the amorphous microstructure with low surface area has less active sites to be involved in the charge storage mechanism. On the other hand, the increase in specific capacitance observed for VNF 400 may be attributed to the fact that annealing VNF at 400 °C finely crystallizes the electrospun nanofibers while maintaining its fibrous morphology, the participation of resulting V_2O_5 in a Faradaic reversible redox reaction leading to pseudocapacitive contribution in addition to the electrical double layer capacitance. The pseudocapacitive characteristics of VNF 400 are discussed further in subsequent sections. However, the decrease of the capacitance observed for VNF 500 as annealing temperature increases to 500 °C, can possibly be attributed to the crystal growth

which reduces electroactive surface for forming electrical double layer with the electrolyte. Even though BET surface area is often considered as an important parameter of electrode materials, it is important to highlight that the specific capacitance does not necessarily correlate with N_2 accessible surface area, but rather more related to the pore volume of the VNF [137-138]. This explains why VNF 300, 400 and 500 though does not show significant difference in BET surface area, differ significantly in term of specific capacitance. In another study of comparing the device performance of MnNF and MnNW, the higher specific capacitance obtained for MnNF could be readily related to the flower-like structures with regular pore size of 100-nm, thus having much higher BET surface area which leads to higher specific capacitance as compared to MnNW, confirming the surface area effect.

In general, the energy density of the electrodes was improved more effectively with nanoflower as compared to nanowire or nanofiber morphologies. This proves that the unique architecture of nanoflower increases the specific surface of MnO_2 exposed to the electrolyte, leading to a high electrical double layer formation and better electrochemical utilization of the MnO_2 active sites for higher pseudocapacitance. The combination of both of these effects has enhanced the energy density of the SCs, On the other hand, the nanowire/nanofiber structures creates porous entangled network, which is more effective in facilitating electron transport, and thus improve the power density of the electrodes. The aforementioned explanation is in agreement with the experimental values obtained as shown in Table 5.1.

5.1.3 The effect of different weight percentage of CNTs

As the charge storage capability of CNT based electrodes is mainly limited by double layer formation, which has lower specific capacitance than pseudocapacitors, therefore incorporating MnNFs/MnNWs as pseudocapacitive materials into CNT network

has been explored. MnNFs/MnNWs have a high theoretical value of 1100 Fg^{-1} [157-158], but lower electrical conductivity (10^{-5} - 10^{-6} Scm^{-1}) than CNTs (10^3 - 10^5 Scm^{-1}), thus these composites were created with the purpose of combining the high conductivity of CNTs and high capacitance of MnO_2 . The ratio of CNTs and MnO_2 in the composite plays a critical role in the electrochemical performance of the electrode, as displayed in Fig. 4.20.

Jiang *et. al* [159] has reported that the specific surface area of the CNT- MnO_2 composite only started to increase when the CNT content is higher than 50 wt%. With CNT content less than 50 wt%, CNTs are buried among MnO_2 nanostructured materials that were less conducting and reduced the charge transport paths within the electrode, consequently causing a decrease of the specific capacitance as observed in Fig.4.20. As CNT content further increases, the MnNFs/MnNWs are surrounded in entangled network of CNTs, which improves the connectivity of MnO_2 nanostructured material and thus the conductivity, and leads to the observed enhancement in specific capacitance. For CNT- MnO_2 composite, CNTs act as both the conductive agent and the electrochemical active material. The electrochemical performance of the composite electrode is unsatisfying when the content of the CNTs is either too low or too high, which is because of the high polarization resistance and low specific capacitance, respectively. The optimum content of CNTs is $\sim 94 \text{ wt\%}$, at which point the maximum capacitance of 200 Fg^{-1} is achieved. The enhancement of capacitance might be due to (i) the increase of effective surface area and enhancement of material utilization by incorporating MnNFs/MnNWs into CNT matrix, which is mainly governed by the surface properties of both materials (ii) the pseudocapacitive characteristics of MnO_2 , which is influenced by crystallinity and bulk properties of MnO_2 .

5.2 CHARGE STORAGE MECHANISM

The charge storage mechanism of SCs comprises of contributions from the (i) electrical double layer capacitance (EDLC) and from (ii) pseudocapacitance; with the former governed primarily by pure electrostatic attractions between ions and the charged surface of an electrode whereas the latter is arises from quick Faradaic charge transfer reactions at the surface/bulk of the electrodes. Various factors influence these two mechanisms are discussed in the following sections.

5.2.1 Effect of various scan rates

In order to elucidate the mechanism of pseudocapacitance, CV curves at various scan rates were collected for both pristine CNT and 1nm-AgCNT. As seen from Fig. 5.3 (b), obvious oxidation peaks were observed for 1nm-AgCNT at lower scan rates (<20 mVs^{-1}), which are absent in the CV curves of pristine CNT (Fig. 5.3 (a)).

Figure 5.3 Cyclic voltammograms curves for (a) pristine CNT and (b) 1nm- AgCNT electrode with PVA/H₃PO₄ polymer electrolyte measured at different scan rate from 1 to 20 mVs^{-1} .

As reversible redox reactions are diffusion-limited processes, measurements at low scan rates allow enough time for charges to diffuse to the inner and less accessible active surface as compared to high scan rate which limits the accessibility of charges only to the outer active surface of the electrode [158, 160-161]. Thus, the oxidation peaks which can only be observed at lower scan rates for small AgNP decorated CNT is a strong indication

of the presence of pseudocapacitance, as compared to pristine CNTs which only contribute to the electrical double layer capacitance. At higher scan rates, the response from Faradaic reactions is reduced, hence revealing that some diffusion and resistance limitation takes place. CVs at various scan rates reveal that the peak potential shifts towards higher values at higher scan rates and the peak is disappearing at high scan rates, which indicates that the exact mechanism of pseudocapacitive behavior of silver is different from that of oxides.

As described previously in section 4.3.2, V_2O_5 nanofibers annealed at 400 °C (VNF 400) and 6 wt% MnO_2 nanoflowers- CNT composites (6wt% MnF-CNT) were identified as the optimum metal oxide/metal oxide-CNT composite electrodes in SCs. To further elucidate the charge storage mechanism in these two materials, pseudocapacitance behavior of VNF 400 and 6wt% MnF-CNT were characterized by varying the scan rate of CV measurements in a three-electrode cell set up. Fig. 5.4 shows the typical CV measured at scan rates from 1 to 50 mVs^{-1} for VNF 400 and 6wt% MnF-CNT in 2 M KCl and 1 M H_2SO_4 , respectively.

Figure 5.4 Cyclic voltammograms for (a) VNF 400 in 2 M KCl and (b) 6 wt% MnNF-CNT measured in 1 M H_2SO_4 at difference scan rate from 1 to 50 mVs^{-1} in three-electrode configuration with Pt foil as counter electrode and Ag/AgCl as reference electrode. The inset of (b) shows the enlarge view of CV curve measured at 1 mVs^{-1} .

At low scan rate (1 mVs^{-1}), the CV curve of 6 wt% MnNF-CNT exhibits a pair of cathodic and anodic peaks at -0.1 V and + 0.05 V vs Ag/AgCl, respectively. These two

peaks were ascribed to the responsive redox reaction of the $\text{Mn}^{3+}/\text{Mn}^{4+}$ couple, which require a finite amount of time as the insertion and deinsertion of ions are diffusion controlled [64]. A pair of oxidation peaks are clearly observed for VNF 400 at potentials of + 0.15 and + 0.5 V vs Ag/AgCl, coupled with corresponding reduction peaks at potentials of + 0.4 V and - 0.15 V vs Ag/AgCl, mirroring the observation which has been reported in the literature [162]. Accordingly, both VNF 400 and 6 wt% MnNF-CNT exhibit pseudocapacitive characteristics with promising potential in SC applications. The specific capacitance was found to decrease with increasing scan rate for both VNF 400 and 6 wt% MnNF-CNT, and this phenomenon can be understood by the slow diffusion of protons into the pores of electrode materials [56, [163]. As mentioned previously, diffusion limits the movement of protons at high scan rates due to time constraints and only the outer active surface is utilized for the charge storage, whereas at low scan rates all the active surface area can be utilized for charge storage and thus leads to higher specific capacitance.

To further understand the effect of scan rates on the electrochemical utilization of nanomaterials based electrodes, the voltammetric charge densities q have been investigated as a function of scan rates (ν) for pristine CNT, 1 nm Ag-CNT, MnO_2 -CNT composite (6wt% MnF-CNT) and V_2O_5 nanofibers (VNF 400). The dependency of q on $\nu^{-1/2}$ and q^{-1} on $\nu^{1/2}$ for all the various nanostructure electrodes are shown in Fig. 5.5.

Figure 5.5 Variation of charge density (q) with respect to scan rates (v): (a) Extrapolation of q to $v = \infty$ (the y-intercept of the q vs. $v^{-1/2}$ plot) given the outer charge for CNT electrodes. (b) Extrapolation of q to $v = 0$ (the y-intercept of the q^{-1} vs. $v^{1/2}$ plot) given the total charge for CNT electrodes. Extrapolation as mentioned in (a) for (c) 1 nm Ag-CNT (e) 6 wt% MnNF-CNT and (g) VNF 400. Extrapolation as mentioned in (b) for (d) 1 nm Ag-CNT (f) 6 wt% MnNF-CNT and (h) VNF 400.

According to Ardizzone *et. al.* [164], the extrapolation of q to $\nu = \infty$, the y-intercept of the q vs. $\nu^{-1/2}$ plot (Fig. 5.5 (a),(c), (e) & (g)) gives the outer charge q_s , which is related to the outer and more accessible surface, given by the following equation:

$$q = q_s + \text{const} \left(\frac{1}{\sqrt{\nu}} \right) \quad (5.1)$$

At a low scan rates, protons have enough time to diffuse to the inner and less accessible active surface. Thus, the extrapolation of q to $\nu = 0$, the y-intercept of the q^{-1} vs. $\nu^{1/2}$ plot (Fig. 5.5 (b) ,(d), (f)&(h)) gives the total charge, q_T , which is related to the whole active surface including the outer and inner active surface, given by the following equation:

$$\frac{1}{q} = \frac{1}{q_T} + \text{const} (\sqrt{\nu}) \quad (5.2)$$

One can then easily calculate the charge related to the inner (less accessible) sites, q_i , by

$$q_i = q_T - q_s \quad (5.3)$$

The charge density at very low and very high scan rates for various nanomaterials based electrodes has been evaluated as described above and is presented in Table 5.2.

Table 5.2 The estimated charge density at very low and very high scan rates, and the percentage of surface charge utilization for various nanomaterials based electrodes.

Samples	q_s (Cg ⁻¹) *	q_T (Cg ⁻¹) *	q_i/q_T (%)	q_s/q_T (%)
CNT	30.56	166	81.59	18.41
1 nm Ag-CNT	34.49	178	80.62	19.38
6wt% MnNF-CNT	95.41	256	62.73	37.27
6wt% MnNW-CNT	87.83	250	64.87	35.13
VNF 400	14.73	333	95.58	4.42

The ratio of q_i/q_T and q_s/q_T indicates the percentage of electrical charge density due to the inner and outer active sites, respectively. From Table 5.2, it can be seen that the total charge density of pristine CNT increases from 166 C g⁻¹ to 178 C g⁻¹ with decoration of CNT with Ag nanoparticles. Incorporation of TMO nanoparticles such as MnNFs and

MnNWs into the CNT electrodes increased the total charge density further to $\sim 256 \text{ Cg}^{-1}$. The incorporation of these pseudocapacitive materials also enhances the contribution of surface capacitive reaction to the charge storage mechanism, as indicated by the increased value of q_s/q_T ratio. It is worth noting that the total charge density estimated for both 6wt% MnNF-CNT and MnNW-CNT is almost the same, but the percentage of surface charge utilization (q_s/q_T) of MnNF-CNT is higher than MnNW-CNT, indicating higher electrochemical utilization of MnNFs in the charge storage mechanism. This observation is consistent with the observation using SEM and BET characterizations, which show a higher surface area for MnNFs as compared to MnNWs and MnO_2 powders, facilitating better transport of the electrolyte ions and increases the electrochemical utilization of MnO_2 .

On the other hand, the total charge density of VNF evaluated at very slow scan rate is the highest (333 Cg^{-1}) among all these nanostructured electrode materials. However at very high scan rates, the outer charge of VNF only reached 14.7 Cg^{-1} , indicating that only $\sim 4\%$ of the VNF surface atoms participate in the charge storing process. This phenomenon is in accordance with the observation of the low surface area of VNF ($10 \text{ m}^2\text{g}^{-1}$) as evaluated from the BET measurement (Fig.4.12), meaning there is a lack of active sites for storing charges on the outer surface of the VNF. In contrast, a high value of q_i/q_T ratio was observed for VNF electrodes, suggesting that the inner surface/bulk of the VNF provide more active sites for charge storage. Thus, the primary charge storage mechanism, for VNF is mainly governed by the intercalation of cations into the VNF structure rather than the surface-driven EDLC or redox reactions.

5.2.2 X-ray Photoelectron Spectroscopy(XPS) Study

Pseudocapacitance based charge storage mechanism involves surface redox reaction resulting in oxidation states changes in the transition metals of the TMO

involved. In order to elucidate the mechanism of pseudocapacitance, XPS measurement have been carried out on Ag decorated CNT (1nm Ag-CNT), MnNF and VNF before and after charging.

Figure 5.6 High resolution curve fitted Ag 3d X-ray photoelectron spectroscopic scan of 1nm-Ag-CNT a) before b) after charging to 1V.

XPS curves of the 1nm Ag-CNT electrode before charging (Fig. 5.6(a)) show the presence of silver in the Ag⁰ oxidation state in the sample as indicated by the binding energy (BE) of Ag3d_{5/2} (367.03 eV) spin-orbit split peak. After charging, in addition to these, additional peaks were observed at higher BE (369.26 eV) which may be attributed to silver oxides (Ag₂O) (Fig. 5.6(b)). Appearance of these additional peaks after charging suggests that during charging of the electrode some of the silver (Ag⁰) takes part in a reversible pseudocapacitive surface redox process getting converted to oxide, as expressed by the following equations [156]:

The investigation of the change of oxidation state of Mn2p in MnNF after charging and cycling for 100 cycles were also carried out through XPS analysis, data as shown in Fig. 5.7.

Figure 5.7 a) High resolution curve fitted Mn 2p X-ray photoelectron spectroscopic scan of MnNF before charging, after charging to 1V, and after cycling for 100 cycles. b) O1s spectrum and curve fitting for MnNF after charging to 1V.

Figure 5.7(a) displays the XPS spectra of MnNF electrodes before and after charging, and after cycling for 100 cycles. Before charging, it is observed that the Mn 2p_{3/2} peak is located at 642.34 eV and the Mn 2p_{1/2} peak at 653.90 eV, indicating the existence of element Mn in the state of Mn⁴⁺ [165]. The difference between binding energy values of the Mn 2p_{3/2} and Mn 2p_{1/2} levels is 11.7 eV, mirroring with the reported spin-orbit splitting of Mn 2p_{3/2} (642.40 eV) and Mn 2p_{1/2} (654.00 eV) in MnO₂ [166], further confirming that the MnNFs before charging consist of MnO₂. After charging to 1 V, the detected peaks shifted to lower binding energies of 641.32 and 653.12 eV corresponding to Mn 2p_{3/2} and Mn 2p_{1/2}, respectively, which indicates the change of MnNF from MnO₂ to Mn₃O₄ [167]. However such changes were only observed during the charging process, as the XPS peaks for MnNF after cycling for 100 cycles appeared at the same binding energy (654.01 eV for Mn 2p_{1/2}, 642.5 eV for Mn 2p_{3/2}) as compared to MnNF before charging. These results have demonstrated that during charging of the MnNF electrode some of the

MnO₂ takes part in a pseudocapacitative surface redox process getting converted to Mn₃O₄, and this process is reversible as Mn₃O₄ can be converted back to MnO₂ after having undergone a complete CV cycle. The O1s spectrum of layered MnNF electrodes after charging was analyzed by curve fitting as shown in Fig. 5.7(b). The three components fitted to the spectrum are corresponding to Mn-OH bond (530.23 eV) for hydrated trivalent oxide, H-O-H bond (532.14 eV) for residual water and Mn-O-Mn bond (528.86 eV) for the tetravalent oxide [168], indicating that the manganese oxide was hydrated, after charging. It had been reported that only the hydrated MnO₂ lattice sites are taking part in the charge storage mechanism [169], therefore higher hydration in the structure is desirable for excellent supercapacitive properties, as more active sites are contributing to the overall capacitance of the electrodes.

Similarly, the XPS spectra of VNF electrodes before charging, after charging to 0.9 V and cycling for 100 cycles were collected, as shown in Fig. 5.8. The spin-orbit splitting obtained for V 2p_{3/2} and V 2p_{1/2} for all the three samples is 7.38-7.41 eV, corresponding to the existence of V₂O₅ [170]. As the difference of binding energy for all the three samples are almost insignificant (< 0.03 eV), the change of oxidation states of VNF during charging and cycling process which is an indication of the pseudocapacitative surface redox process was not strongly evidenced by XPS analysis. However, additional peaks of K 2s, K 2p_{3/2} and K 2p_{2/3} were detected in the survey scan of VNF after charging and after cycling, as shown in Fig. 5.8 (b) and (c), which suggest the intercalation of K⁺ ions into the oxide lattice of V₂O₅ has contributed mainly to the charge storage mechanism of VNF rather than pseudocapacitative surface redox processes, in agreement with the observations seen in CV scan rate analysis of VNF electrodes as discussed in section 5.2.1.

In the previous studies done by Lee *et. al.* and Pang *et.al.* [42, 62], it was not conclusively resolved whether the pseudocapacitance is a mechanism based on surface adsorption, or involves intercalate/deintercalate of ions into the bulk oxide lattice. The original findings from the current study through XPS characterizations of various samples may thus be summarized as follows: (i) Detection of the changing oxidation states after charging Ag-CNT and MnNF electrodes has clearly shown that the pseudocapacitance mechanism of these materials is mainly dominating by reversible surface redox process (ii) Insignificant change of oxidation states of VNF, in addition to the presence of K element peaks in the XPS spectra of VNF electrodes after charging and cycling has indicated that the intercalation of K^+ ions into the oxide lattice of V_2O_5 is the main contributing factor to the pseudocapacitance of VNF rather than surface redox processes.

Figure 5.8 XPS survey spectra with the inset shows the magnification of the V 2p region of the (a) VNF before charging (b) VNF after cycling and (c) VNF after charging to 0.9 V

5.2.3 Electrochemical Impedance Spectroscopy (EIS) Study

EIS is recognized as an important technique to resolve the charge storage components resulting from different mechanism such as EDL or pseudocapacitance; as well as different resistance components such as electrolyte resistance, electrode resistance and interfacial electrode-electrolyte resistance. For Ag decorated CNT, the combination of circuit elements for impedance data shown in Fig. 4.9 (a) is proposed in Fig. 4.9 (b) and (c), respectively. Accordingly, the overall impedance Z , of the equivalent circuit for all Ag-CNT devices without the presence of pseudocapacitance is given by:

$$Z = R_s + \frac{R_b}{j\omega R_b C_b + 1} + \frac{R_{ct}}{j\omega R_{ct} C_{dl} + 1} + W_s \quad (5.5)$$

Equation (5.4) was applied for obtaining the best-fit EIS curves of CNT, 13 and 7nm Ag-CNT devices. However for 1 and 4 nm Ag-CNT particularly, an additional element of C_p , corresponding to pseudocapacitance was required in the equivalent circuit for the best-fitting EIS curves. The equation of the impedance with an additional element of pseudocapacitance, Z is expressed as:

$$Z = R_s + \frac{R_b}{j\omega R_b C_b + 1} + \frac{1}{j\omega C_{dl} + \frac{j\omega C_p}{j\omega R_{ct} C_p + 1}} + W_s \quad (5.6)$$

By fitting equation (5.5) or (5.6) to the respective impedance data (Fig. 4.9(a)), the values shown in Table 5.3 have been evaluated.

Table 5.3 Components of the equivalent circuit fitted for the impedance spectra of all Ag-CNT devices.

Sample	$R_b(\Omega)$	$R_{ct}(\Omega)$	$C_b(\mu F cm^{-2})$	$C_{dl}(F cm^{-2})$	$C_{dl} + C_p(F cm^{-2})$
CNT	1.511	28.13	18.252	0.03	-
13 nm Ag-CNT	0.84	87.24	46.883	0.017	-
7 nm Ag-CNT	2.301	47.8	13.611	0.01	-
4 nm Ag-CNT	0.945	3.773	18.699	-	0.054
1 nm Ag-CNT	0.467	1.38	50.409	-	0.117

The electrolyte resistance was approximately 65 Ω for all Ag-CNT devices, this relatively higher value as compared to the liquid electrolyte (<10 Ω) [81] is mainly due to the lower mobility of ions within the polymer electrolyte. The R_{ct} value for each Ag-CNT electrode is dominating over the R_b value. The charge transfer resistance, R_{ct} , decreases as the AgNP sizes become smaller, and a significant decrease is observed for 4 and 1 nm Ag-CNT devices, with R_{ct} in the range of 1-4 Ω (Table 5.3). This observation indicates that AgNP in the size range of 1-5 nm effectively reduce the resistance between the CNT electrode and the electrolyte; whereas, larger AgNPs (>7 nm) possibly reduce the electrochemical redox kinetics by blocking the pores on the CNT network surfaces, yielding R_{ct} values of 87 Ω for 13 nm Ag-CNT device; significantly higher even than the reference CNT device ($\sim 28 \Omega$).

The double layer capacitance, C_{dl} , obtained from impedance analysis increases as AgNP reduces from 7 to 1 nm, which is in agreement with the observation from CV measurement. The pseudocapacitance, C_p , for 4 and 1 nm Ag-CNT devices contributed to the overall capacitance as $C_{dl} + C_p$. Again, 1 nm Ag-CNT has the highest capacitance among all the devices, further supporting the findings from CV measurements, which indicates that pseudocapacitance is an important contributor to the enhancement of capacitance for the <5nm AgNP devices. The values of R_b and C_b (contribution from the electrodes) were negligibly small compared to the overall resistances and capacitances.

For TMO (MnNFs, MnNWs and VNFs) and TMO-CNT composite (MnNF-CNT and MnNW-CNT) based electrodes, the combination of the circuit elements proposed in Fig. 4.17(b) and 4.21 (b) has contributed to the overall overall impedance, Z , of the equivalent circuit for all devices as given by:

$$Z = R_e + \frac{1}{j\omega C_{dl} + \frac{j\omega C_p}{j\omega R_{ct} C_p + 1}} + W_s \quad (5.7)$$

Equation (5.7) together with the impedance data in Fig. 4.17(a) and 4.21 (a) was employed to estimate the value of the equivalent circuit in Fig. 4.17(b) and 4.21(b). These calculated values using Z-View computer software are summarized in Table 5.4.

Table 5.4 Components of the equivalent circuit fitted for the impedance spectra of devices with VNF annealed at three different temperature: 300,400 and 500°C (denoted as VNF 300,400 and 500, respectively) in 2 M KCl; MnO₂ and MnO₂-CNT composite electrodes(denoted as MnNF, MnNW, 6wt% MnNF-CNT and 6wt% MnNW-CNT, respectively) in 1 M H₂SO₄.

Sample	$R_e(\Omega)$	$R_{ct}(\Omega)$	$W_s(\Omega)$	$C_{dl}(\text{Fcm}^{-2})$	$C_p(\text{Fcm}^{-2})$
VNF 300	2.65	22.98	123.50	0.040	0.060
VNF 400	1.66	2.53	39.58	0.040	0.170
VNF 500	2.22	0.09	5.56	0.003	0.220
MnNF	4.42	1.47	264.6	0.023	0.004
MnNW	5.71	1.47	51.77	0.012	0.026
6wt% MnNF-CNT	4.90	1.94	253.3	0.033	0.050
6wt% MnNW-CNT	5.10	1.71	238.1	0.033	0.074

The above equation can be evaluated in two extreme cases: low and high frequency regions. At sufficiently high frequencies, intersection with the real axis provides the value of the electrolyte resistance and charge transfer resistance [171]. The electrolyte resistance for VNF based electrodes was found to be small ($\sim 1.7 - 2.7 \Omega$) and showed little variation for all devices. Here, we notice that the charge transfer resistance R_{ct} , decreases as the annealing temperature increases from 300 to 500 °C, indicating the microstructure of VNF 500 with less hierarchical porosities is easier to be accessed by the electrolyte ions as compared to VNF 300 and 400. The same trend was observed for

distributed resistance within the electrode W_s , further confirming the less porous structure of VNF 500.

The impedance in the low-frequency region suggests the pure capacitive behavior, where the overall capacitance, which is a combined contribution of both electrical double layer capacitance (C_{dl}) and Faradaic pseudocapacitance (C_p) of VNF electrode can be estimated. It is worth noting that VNF 300 and VNF 400 have similar double layer capacitance (C_{dl}) values, which is mainly governed by fibrous morphology of both fibers which provide the electroactive surfaces needed for the charge transfer reaction and cation diffusion. However, VNF 300 has the lowest pseudocapacitance, as could be expected due to the incomplete phase transformation into crystalline V_2O_5 , and therefore its lack of facile sites for Faradaic redox reaction. The overall capacitance of VNF 400 is higher than VNF 300 owing to the fact that VNF 400 with higher crystallinity enabled higher pseudocapacitance, which is analogous to what was observed from CV and GCD measurements. On the other hand, VNF 500 has the lowest C_{dl} as compared to VNF 300 and 400 due to the lack of fibrous morphology, but highest C_p because of its high crystallinity as revealed in SEM and XRD previously. The overall capacitance of both VNF 400 and VNF 500 was found to be comparable from impedance analysis. However considering previous findings from material characterization (SEM, XRD and BET measurements) and device testing (CV and GCD measurements), VNF 400 shows more promising result than VNF 500 and VNF 300 as it consists of both fibrous morphology and crystallinity, which are essential for the achievement of higher specific capacitance.

For MnO_2 and MnO_2 -CNT composite based electrodes, the electrolyte resistance of 1 M H_2SO_4 was found to be slightly higher than VNF based electrodes (in the range of 4-6 Ω), which use 2 M KCl as electrolyte. The charge transfer resistance R_{ct} , appeared to be similar for both MnNF and MnNW, and both of these values increased slightly when

added into the CNT network. This indicates that the presence of porous CNTs has induced higher resistance to the electrolyte ions in accessing the electrode surfaces. It was observed that MnNFs exhibited the highest Warburg impedance value among all the MnO₂ based samples, owing to distribution of the various pore sizes within the porous matrix of the MnNFs. As expected, MnNFs have higher C_{dl} than MnNWs, with its higher surface area as revealed by SEM and BET characterizations. Upon incorporating CNTs with 6 wt% of MnNFs and MnNWs, the C_{dl} of both these samples (6wt% MnNF-CNT and 6wt% MnNW-CNT in Table 5.4) has increased to almost the same value of 0.033 F cm⁻², which is mainly governed by the network-like and porous nature of CNTs.

In addition, it was also observed that the C_p of MnNWs is higher than MnNFs, which is mainly caused by higher crystallinity of the former, as evident by the XRD results shown in Fig. 4.14. The pseudocapacitance is further increases to 0.05 and 0.07 Fcm⁻² after having incorporated 6 wt% of MnNF and MnNW, respectively into CNT network. This phenomenon is attributable to the presence of oxygen containing functional groups contributing as pseudocapacitance to the overall capacitance [131]. The difference of overall capacitance ($C_{dl}+C_p$) between both 6wt% MnNF-CNT and 6wt% MnNW-CNT is insignificant, in agreement with the device characterization using CV technique as shown in Fig. 4.19 and 4.20.

5.3 THE IMPACT OF ELECTROLYTE ON ENHANCED SC PERFORMANCE

The enhancement seen in the SC performance is believed not only to depend on the improvement of electrodes, but also to be related to the choice and improvement of electrolytes. Effects such as pH value, the choice of aqueous or organic solution for liquid electrolyte may be considered as contributing factors to the observed improved device characteristics, as presented in section 5.2.1 and 5.2.2. Apart from that, the effect of the

ionic conductivity of printable electrolyte in solid state has been studied extensively and discussed in section 5.2.3.

5.3.1 The effect of electrolyte pH

(a) CNT-based electrodes

According to Conway *et. al.* [114], the redox reaction of the surface groups of a functionalized carbon requires protons to proceed, and thus would strongly dependent on the pH of the solution. The authors have studied and compared the electrochemical charging behavior of the woven C-cloth electrode in solutions of various pHs, and to date there is still a lack of such systematic study for CNT-based SCs. To further explore the effect of electrolyte pH to CNT-based SC performance, the specific capacitances of P3-CNT electrodes in solutions of various pHs are measured and presented in the following bar chart (Fig. 5.9(a)), and CV curves of the same electrode in acidic (1 M H₂SO₄), neutral (2 M KCl) and basic (2 M KOH) liquid electrolyte are shown in Fig. 5.9(b).

Figure 5.9(a) Bar chart which shows specific capacitances of P3 CNT electrodes in 1 M aqueous electrolyte with different pH, and organic electrolyte. **(b)** The CV curves of the same electrode measured at 20 mVs⁻¹ in aqueous electrolyte with different pH (1 M H₂SO₄, KCl and KOH) in two electrode configuration.

From Fig. 5.9(a), it can be clearly observed that P3 CNTs show higher charge storage capability in aqueous electrolyte as compared to organic electrolyte, owing to the higher ionic conductivity of the former [10]. Acidic aqueous electrolytes in general are

more favorable than neutral and basic electrolytes, for P3 CNTs to obtain higher specific capacitance. As could be seen in Fig. 5.9(b), a larger CV curve area is observed for P3 CNT in H₂SO₄, as compared to KOH and KCl, with an obvious peak observed. Based on literature[172-173], it is suggested that the peak seen in the CV responses of carbonaceous materials in all acids can be arise from the electrochemical reactivity of surface groups, such as quinone functionalities (Q) adsorbed on the edge sites of graphitic planes of the carbon. The redox activity of these Q species via the reaction: $\text{QH}_2 \leftrightarrow \text{Q} + 2\text{H}^+ + 2\text{e}^-$, might be responsible for the additional capacitance observed. However, the extend of this Faradaic capacitance only lies in the range 1 to 5% of the total capacitance, and only measurable at low frequencies [1]. The absence of the peaks of the CVs in the basic and neutral electrolyte is likely due to the limited amount of protons in the electrolyte. Without the presence of H⁺, the oxidation/reduction of the quinone species would be prevented and thus leads to lower specific capacitance [114].

(b) *TMO-based electrodes*

The electrochemical performance of TMO based electrodes is further explored by immersing V₂O₅ nanofibers (VNF 400) electrodes in (i) aqueous electrolyte with various pH values; viz. 1 M H₂SO₄ (pH~ 0), 2 M KCl (pH~ 6) and 2 M KOH(pH~14) and organic electrolyte; 1 M LiClO₄ in propylene carbonate. Similarly, the specific capacitance and device resistance were evaluated by employing CV (two-electrode configuration) and GCD measurements.

Figure 5.10 (a) Bar chart which shows specific capacitances of VNF 400 electrodes in aqueous electrolyte with various pH (1 M H₂SO₄, 2 M KCl and 2 M KOH), and organic electrolyte (1 M LiClO₄ in PC). (b) The CV curves of the same electrode/electrolyte combinations mentioned in (a) measured at 5 mVs⁻¹ in two electrode configuration.

The highest specific capacitance in aqueous electrolyte was obtained in 2 M KCl (190 Fg⁻¹) as compared to 1 M H₂SO₄ (106 Fg⁻¹) and 2 M KOH (8 Fg⁻¹) as seen from the bar chart in Fig. 5.10(a), whereas SC tested in organic electrolyte, 1 M LiClO₄ has a wider potential range of 3 V as compared to 0.9 V of aqueous electrolyte, and yielded a specific capacitance as high as 250 F g⁻¹ (Fig. 5.10(a) and (b)). Similarly to CNT-based electrodes, obvious redox peaks are observed for VNF electrodes in acidic solution as compared to basic and neutral solutions, suggesting that a redox reaction occurred between the surface functional groups and the electrolyte ions. In addition, a deviation from an ideal rectangular shape was observed in Fig. 5.10(b) for the CV curve of VNF electrodes in 1 M H₂SO₄, which is an indication of large resistance occurring at the interface of electrode-electrolyte, possibly attributable to the unmatched size of solvated cations/anions in the electrolyte to the pore size of the electrode that might have prohibited the mobility of these ionic species. For this reason, pore size distribution curve of the VNF 400 electrode was plotted (Fig 5.11 (a)), based on the N₂ adsorption-desorption isotherms.

Figure 5.11 (a) Pore size distribution curve for VNF 400 determined by N_2 adsorption-desorption isotherms. Schematics illustrating the hydrated (b) K^+ ions and (c) H^+ ions accomodating the pores of VNF electrodes

As displayed in the curve in Fig. 5.11(a), the pores formed by the VNF 400 electrode have distributed sizes ranging from sub-50 nm to ~ 200 nm. However, most of these pores show a narrower distribution which centered between 7 and 10 nm. Hence , the better electrochemical performance of VNF 400 in KCl may be associated with the small ionic radius of hydrated K^+ ions (~ 0.3 nm), which are three times smaller as compared to hydrated H^+ ions (~ 0.9 nm)[174]. While smaller ion size ensuring easier penetration of K^+ ions into the pores of VNF electrodes, it also enables more hydrated K^+ ions accomodating the pore volume as compared to hydrated H^+ ions, as illustrated in Fig. 5.11(b) and (c), and thus contributed to a higher electrical double layer capacitance . In addition, a small ionic radius also enhances mobility and insertion/deinsertion ability of hydrated K^+ ions into the V_2O_5 oxide lattice as reported [55, 175], and leads to higher pseudocapacitance. The enhancement seen in both electrical double layer capacitance and pseudocapacitance has thus explained the superior electrochemical performance of KCl which has risen as the most suitable aqueous electrolyte for VNF electrodes.

5.3.2 Comparison between aqueous and organic electrolyte

It is known that decomposition voltage of aqueous solvent limits the SC cell voltage to ~ 1 V due to the presence of water with an electrochemical window of 1.23 V [15]. This limitation can be circumvented by employing organic electrolyte which allows higher operating voltage (2-3 V). The comparison of SC performance for various electrodes based on CNT, hybrid CNT and TMO materials in both aqueous and organic electrolyte has been investigated, and their capacitance are presented in the form of bar chart shown in Fig. 5.12(a). The corresponding energy density at various power densities were calculated and plotted as a Ragone plot in Fig. 5.12(b).

[Abbreviations]: as prepared single walled carbon nanotubes(AP SWNT), purified non-functionalized carbon nanotubes (P2 SWNT), purified -COOH groups functionalized single-walled CNTs (P3 SWNT), double-walled CNTs(DWNT), multi-walled carbon nanotubes(MWNT), silver decorated single walled carbon nanotubes(Ag-CNT), V₂O₅ nanofibers(VNF)

Figure 5.12 Bar chart showing a comparison of specific capacitance of various electrodes in aqueous (1 M H₂SO₄) and organic electrolytes (1 M LiClO₄ in PC or 1 M LiPF₆ in EC:DC). (b) The Ragone plot showing energy and power densities for devices in (a).

In general, electrodes tested in organic electrolyte exhibit lower specific capacitance as compared to aqueous electrolyte and the CV curves normally deviate from ideal rectangular shape, mainly attributed to two reasons: 1) the electrical resistivity of non-aqueous electrolyte, which is at least an order of magnitude higher than that of aqueous electrolytes [13]. 2) the intercalation and deintercalation of Li⁺ ions into the oxide lattice, as indicated by the two broad peaks observed as shown in the CV curve of

VNF in Fig. 5.10(b) during anodic and cathodic sweep [176]. However, organic electrolyte allows a wider potential range of 3 V as compared to ~ 1 V of aqueous electrolyte, and thus yields much higher energy and maximum power densities since both of these parameters are proportional to the square of the operating voltage, as evident from the Ragone plot in Fig. 5.12(b). Among all the electrodes, VNF shows the highest energy density in the range of 50-70 Wh kg⁻¹ in 1 M LiClO₄ in PC, whereas CNT electrodes exhibit highest power density ranging from 10-50 kW kg⁻¹ in 1 M LiPF₆ in EC:DC [177], rendering both of these electrodes in organic electrolyte promising and attracting candidates for SC applications with different purposes.

5.3.3 The influence of ionic conductivity on charge transport mechanisms

The phase angle of an ideal capacitor is -90° while it is 0° for an ideal resistor. Based on the value of the phase angle, polarization mechanisms in polyelectrolyte-based capacitors can be divided into two different categories; a dominant resistive ($\varphi(f) > -45^\circ$) category where the behavior is more resistive than capacitive, and a dominant capacitive ($\varphi(f) < -45^\circ$) category in which the behavior is more capacitive than resistive [123]. The recorded phase angle of the PSS:H-based SCs of this study are $> -45^\circ$ over the entire frequency interval studied (Fig. 4.23(a) and 4.24(b)). Thus, the SCs are classified having a dominant resistive behavior, which is attributed to protons migrating along the polymer chains in the oscillating electric field (ionic relaxation). In other words, the protons oscillate and they do not have enough time to fully penetrate the CNT network. At high frequencies the phase angle is close to 0° , indicating a close to ideal resistive behavior, while the phase angle starts to decrease at lower frequencies. This decrease in phase angle towards $\varphi(f) = -45^\circ$ indicates a transition towards a more capacitive character of the total impedance typically observed upon the formation of electric double layers. However, note that the

phase angle never becomes dominant capacitive, i.e. $\phi(f) < -45^\circ$, to its nature as one could expect for a capacitor. Hence, ionic relaxation is the dominating polarization mechanism and the electric double layers are never fully formed, not even at very low frequencies. This indicates that the contact area between the CNT network and the polyelectrolyte [177] and/or the ionic conductivity of the solid polyelectrolyte might be the limiting factors for this type of SC. In order to distinguish between these two mechanisms limiting the performance of the device, an additional experiment was performed in which the CNT electrodes were coated with PSS:H solution before sandwiching the solid polyelectrolyte film, with the aim to improve the contact characteristics between the electrodes and the polyelectrolyte. In this way, the contact area between the CNT electrodes and the polyelectrolyte is ensured to be optimized.

Figure 5.13 The effective capacitance per area and the real part of the impedance versus the frequency for a SC with CNT electrodes sandwiching a solid PSS:H film at 30% (solid symbols) and 50% RH (open symbols) and for a SC with its CNT electrodes coated with a 1 M PSS:H water solution before sandwiching the solid PSS:H film (measured at 40% RH, dashed lines).

The dashed lines represent data obtained at 40% RH when the CNT electrodes were coated with the PSS:H water solution prior to sandwiching the solid polyelectrolyte film. These data appear to be very close to the results obtained at 30% and 50% RH for the SC fabricated by directly laminating the PSS:H film between the CNT electrodes. This similarity in behavior shows that the interface between the CNT electrodes and the PSS:H

film was already optimized for the SCs formed simply by sandwiching a single PSS:H film between naked CNT electrodes. This is likely due to (i) the hygroscopic nature of the polymer film, which is still partially wet at its surface when the mechanical contact is established with the CNT electrodes; and (ii) the hydrophilic nature of the CNTs that previously have been chemically functionalized with polar carboxylic acid groups. Hence, the limiting factor for the SCs is therefore attributed to the ionic conductivity of the polyelectrolyte and the polymer electrolyte.

The ionic conductivity of the PSS:H film (σ_e) at various RH levels and the PSS:H water solution can be estimated according to:

$$\sigma_e = \frac{L}{R_e A} \quad (5.8)$$

where L is the PSS:H film thickness or separating distance between the two electrodes in the case of the PSS:H water solution, A is the contact area between the PSS:H film and the CNT electrodes, whereas R_e is the polyelectrolyte resistance, which can be estimated from the real part of the impedance at high frequency (20 kHz) from data in Fig. 4.24 (c). The overall device conductivity σ_{dev} , is also calculated using equation (5.7) by employing the same parameters of L and A , but R is estimated from the voltage (IR) drop of the galvanostatic discharge curve as shown in Fig. 4.25(b). Both σ_e and σ_{dev} of the PSS:H film at various RH levels and the PSS:H water solution are plotted versus the specific capacitance in Fig. 5.14.

Figure 5.14 Ionic conductivity (σ_e , open symbols) and device conductivity (σ_{dev} , solid symbols) of SCs with a PSS:H film at various RH levels and a PSS:H water solution, respectively, plotted versus the specific capacitance.

From this plot, we find that both σ_e and σ_{dev} of the PSS:H film starts from low values of 0.9 and 5.6 $\mu\text{S cm}^{-1}$, respectively, at 10% RH. As the RH level increases beyond 50%, both σ_e and σ_{dev} increase several orders of magnitude and reach maximum values of 1.5 and 1.2 mS cm^{-1} , respectively, at 80% RH. This further confirms the hypothesis that the enhanced performance of the SC with increasing RH level originates from the high ionic conductivity of the humid polyelectrolyte solid film.

5.4 Cyclestability study and application for printable SCs

5.4.1 Cyclestability

The reliability of printable SC in real life application necessitates an investigation on the cycle stability for various electrodes in liquid or solid electrolytes, which evaluate the reversibility of charge-discharge capability of these devices. Such evaluation was carried out for pristine CNT (P3 CNT) and 1 nm Ag-CNT with PVA/H₃PO₄ solid electrolyte, by running galvanostatic charge-discharge (GCD) test at a current density of 1 mA cm^{-2} for 8000 cycles, as shown in Fig. 5.15 (a).

Figure 5.15 Cycle stability of (a) a pristine CNT and a 1 nm Ag-CNT electrode with a PVA/H₃PO₄ polymer electrolyte with a charge-discharge current density of 1 mA cm⁻² (b) V₂O₅ nanofibers in 2 M KCl liquid solution.

A slight degradation of ~ 10% from initial specific capacitance was observed for CNT device after 8000 GCD cycles. As the CNT used in this study is chemically functionalized with polar carboxylic acid groups, the functional surface groups may initiate chemical side reactions with the electrolyte ions as shown below[15]:

However, this type of reaction is quasi-reversible, and therefore a gradual decrease of capacitance was observed at the beginning of cycling test and then stabilized at ~ 40 Fg⁻¹ for the subsequent cycles. The specific capacitance of 1nm Ag-CNT device was ~ 84% of its initial capacitance (106 Fg⁻¹), and this larger degradation as compared to pristine CNT is mainly attributed to the accompanying Faradaic pseudocapacitance process associated with decorated AgNPs, as verified from XPS, EIS and CV scan rate analysis (section 5.2.1-5.2.3).

The cycle stability of pseudocapacitive materials was further investigated by employing GCD test for VNF electrodes in 2 M KCl, at a current density of 0.1 A g⁻¹ over 3000 cycles. From Fig. 5.16(b), the specific capacitance of the VNF remained stable at 190 Fg⁻¹ for the first 100 cycles. This observation is in good agreement with the

experimental work by Lee *et. al.* [43, 178]. As the cycling test goes beyond 100 cycles, the specific capacitance started to degrade rapidly and finally stabilized at $\sim 40 \text{ F g}^{-1}$ after 2000 cycles. Reddy *et. al.* [55] reported that this degradation after cycling is due to the insertion/de-insertion of the ions into the V_2O_5 lattice which might have destroyed the structure, reduced the number of active sites for storing charges and thus lead to the drop in capacitance. To further confirm the phenomenon, FESEM characterization was done for VNF before and after CV cycling test, and the images are as shown in Fig. 5.16.

Figure 5.16 FESEM images for VNF electrodes (a) before and (b) after CV cycling for 3000 cycles.

After the cyclic test, the fibrous structure of the VNF collapsed, as observed in Fig. 5.16 (b). These observations suggest that the relatively poor cycling life of VNF as compared to CNT-based SCs is mainly due to the loss of fibrous structure after multiple insertion/deinsertion of the ionic species.

Another factor which was found to have impact on the cycle stability performance of the printable SC is the water content of the polymeric electrolyte. To investigate this phenomenon, a GCD test was conducted for CNT devices with PSS:H polyelectrolyte for 7000 cycles using a current density of 0.9 A g^{-1} in ambient environment with an estimated humidity range of 70-80% RH. An initial rapid decrease in capacitance was observed in the graph showing the change of the specific capacitance versus the number of cycles as

given in Fig. 5.17, which is attributed to the quasi-reversible chemical side reactions initiated by functionalized surface groups of the CNT as mentioned previously. The specific capacitance of the device degrades 43% after 7000 cycles. This degradation is mainly due to the loss of water content of the PSS:H after being exposed to the ambient environment for an extended period of time. To further improve the cycling performance, the device was laminated using a polymer-coated aluminum foil as shown in the inset of Fig. 5.17. The lamination of the device has proven to be an effective way for preventing the loss of water content of the PSS:H, and the degradation of the specific capacitance has reduced to only 33% in sealed condition.

Figure 5.17 Cycle stability of SCs, with CNT electrodes and PSS:H as the electrolyte, with and without sealing using a constant charge-discharge current density of 0.9 A g^{-1} in ambient environment with an estimated humidity range of 70-80% RH. The inset shows the device which is laminated using polymer-coated aluminum foil.

5.4.2 Charge transport and cycle stability of photo-supercapacitors (PSCs)

Figure 5.18 Band diagram and charge transport of a PSC device.

The band diagram in Fig. 5.18 illustrates the electron and hole transfers within the PSC. During the charging process, photons ($h\nu$) are absorbed by P3HT and the generated excitons dissociate to produce free charges, with holes and electrons transported by the bi-continuous P3HT and PCBM phases. The work function difference between the electrodes drives the holes along the highest occupied molecular orbitals (HOMOs) of P3HT, PEDOT: PSS, to the ITO anode. On the other hand, electrons from the lowest unoccupied molecular orbital (LUMO) of PCBM are transported towards the Al cathode. Upon reaching the anode and cathode of the OPV, both electrons and holes are further transferred into the CNT electrodes and subsequently charging the adjoining SC

Figure 5.19 Charge-discharge cycle-stability of a PSC, and the inset shows the self-discharge curves of a PSC and SC plotted as a function of time.

The cycle-stability of the PSC was also investigated by employing the charge-discharge process as described previously for 10 cycles, and the discharge capacity of the device was able to retain up to $\sim 47\%$ of the initial capacity (17.5 Cg^{-1}), as demonstrated in Fig. 5.19. The self-discharge of a SC with and without coupling with OPV are as shown in the inset of Fig. 5.19, after charging for 30 minutes with 1V in ambient environment. The shorter self-discharge life span of the PSC ($\sim 64 \text{ s}$) as compared to SC ($\sim 60 \text{ minutes}$) may be attributed to the degraded energy conversion capability of OPV in ambient condition, which can be further improved by proper sealing of the device. The self discharge of the PSC could also be improved by the addition of a diode to prevent the possible charge backflow into the OPV.

Chapter 6 CONCLUSIONS

This thesis presents an in-depth investigation of the charge storage and charge transport mechanisms in printable supercapacitors (SCs) based on nanomaterials and polymer electrolytes. The first original contribution generated from this thesis was the realization of a new SC device architecture compatible with printed electronics applications. Printable SCs were realized with the use of carboxylated single-walled carbon nanotube (CNT) networks, which have high conductivity and high surface area, that allow the combination of both metallic current collector and active material into a single-layer structure. Cyclic voltammetry (CV) and galvanostatic charge-discharge measurements revealed a specific capacitance of 44 F g^{-1} for this bi-functional CNT network, which is comparable to those conventional SCs with metallic current collectors and amorphous carbon as electrodes.

Although the device performance of this first generation CNT-based SCs is promising, challenges of improving energy and power densities, attributable to the inherent low specific capacitance and inter-tube resistance of the CNTs, were identified. CNTs decorated with silver nanoparticles (AgNPs) (1 to 13 nm) improved the power density of the device through improved *inter* and *intra*-tube resistances of the CNT networks. The capacitance and energy density of the device were doubled with AgNPs of $\sim 1\text{nm}$, which do not block the CNT network and complement the double layer capacitance by a Faradaic reaction induced pseudocapacitance. The size effects of the AgNPs to the capacitance behavior of the devices were investigated and the observations revealed that the specific capacitance in Ag-CNT SCs comprised of contributions from the (i) non Faradaic electrical double layer capacitance and (ii) pseudocapacitance; with

the former governed primarily by surface area whereas the latter influenced strongly by the size of AgNPs.

The pseudocapacitance contribution observed in Ag-CNT devices was further investigated by incorporating transition metal oxide (TMO) nanomaterials into CNT electrodes, surface morphology effects and TMO contribution by weight were studied. MnO₂ nanoflowers (MnNFs) displayed higher specific capacitance (153 F g⁻¹ compared with 52 F g⁻¹ of nanowires) attributable to higher surface area and regular pore sizes, thus affirming a strong correlation between capacitance and surface morphology. An optimum MnO₂ weight percentage was found by incorporating 6 wt% of MnNFs/MnNWs into CNT network, yielding a specific capacitance of 200 F g⁻¹, where the capacitance is influenced by both the effective surface area and the conductivity of the composite materials.

Another pseudocapacitive material, V₂O₅ electrospun nanofibers (VNF) has been demonstrated to be a potential electrode material for SC applications. The annealing temperature for the electrospun nanofibers had been optimized to 400 °C, which was required to transform the fibers into crystalline V₂O₅ orthorhombic, as well as maintaining its fibrous morphology for enhancing both the pseudocapacitance and electrical double layer capacitance. VNF yielded a maximum capacitance of 190 F g⁻¹ in 2 M KCl and energy density of 5 Wh kg⁻¹, and this capacitance can be further improved to 250 F g⁻¹ in Li ion containing organic electrolyte LiClO₄, with energy density as high as 78 Wh kg⁻¹.

Pseudocapacitance contributions of all these nanomaterials on enhanced SC performance, had been studied systematically using various techniques including CV scan rate analysis, X-ray photoelectron spectroscopy (XPS) and electrochemical impedance spectroscopy (EIS). It was found that the charge storage mechanism of Ag-CNT and

MnO₂-CNT was mainly originated from the changes of oxidation state of Ag and MnO₂ in a reversible pseudocapacitive surface redox process. The XPS analysis also provided further insight into the charge storage mechanism of VNF electrodes, which mainly attributed to the intercalation/deintercalation of K⁺ ions into the bulk oxide lattice of V₂O₅.

Investigations of the impact of liquid electrolytes on device performance showed that acidic aqueous solutions yielded higher specific capacitance with CNT-based electrodes (including CNT composite), as compared to neutral or basic electrolytes. This is possibly due to the presence of H⁺ that helps in the oxidation/reduction of quinone functionalities on the carbon surface, resulting in additional charge storage through a surface redox reaction. The same study also revealed that KCl was the most suitable electrolyte for VNF, owing to the smaller hydrated K⁺ ion that favors its insertion/deinsertion of ions into the VNF pores and the V₂O₅ oxide lattice, resulting in the observed enhancement in both electrical double layer capacitance and pseudocapacitance. The relatively poorer cycle stability of VNF as compared to CNT-based electrodes resulted from the loss of its fibrous structure after multiple insertion/deinsertion of the ionic species into the pores of the electrodes.

A new class of self-ionizable proton conducting electrolyte, polyelectrolyte (PSS:H), which combined advantages of the high ionic conductivity of electrolytes and the mechanical properties of polymers had been identified and demonstrated as a new alternative for replacing conventional dual component (polymer + salt additives) polymer based electrolyte in SC applications, with specific capacitance as high as 85 F g⁻¹. Ionic conductivity of the PSS:H were found to increase with increasing humidity level and yielded a value of 1.5 mS cm⁻¹ at 80% RH.

Lastly, the application of a printable SC was demonstrated by integrating it with an organic photovoltaic device using a layer-by-layer device fabrication approach,

utilizing single-walled CNT network as a common integration platform. This hybrid device in which photogenerated charges are stored at the electric double layer was constructed by assembling supercapacitor electrode and polymer electrolyte on top of multilayered organic photovoltaic.

In summary, the main contributions of this thesis include introduction of an original printable architecture for supercapacitors including the bi-functional active materials and current collector, in combination with printable polymer electrolytes. Performance enhancement of the devices was demonstrated through the use of nanomaterials/nanocomposites with pseudocapacitive properties, as well as through electrolyte materials modifications. A thorough understanding of the contribution of nanomaterials and polymer electrolytes towards charge storage and charge transport mechanism was demonstrated. Finally the applicability of these devices towards printed electronics and integrated energy harvesting and storage devices was also demonstrated.

Chapter 7 RECOMMENDATIONS FOR FUTURE WORK

Stemming from this thesis study, the following possibilities for future work are recommended to further develop and understand the charge storage and transport mechanisms of the printable SCs.

7.1 Printable Hybrid Electrochemical Capacitors (HECS)

While SCs benefit from the long cycle life and high power density ($5\text{--}10\text{ kWkg}^{-1}$), they suffer from a moderate energy density ($<100\text{ Wh kg}^{-1}$). On the other hand, lithium-ion-batteries provide the high energy density ($150\text{--}200\text{ Wh kg}^{-1}$), but at the expense of a shorter cycle life than SCs ($<10^3$ cycles) [179-180]. The solution to overcome these limitations thus lies in the development of a new device architecture, which employs asymmetric electrode configuration that integrating both the advantages of SCs and batteries, where high energy density, long cycle life and fast power capability can be established. This asymmetric type of device is known as hybrid electrochemical capacitors (HECS), with a non-Faradaic capacitive cathode and coupled with a Faradaic ion-intercalation anode, as illustrated in Figure 6.1. The combined effects provide enhancement to both the energy and power densities, while maintaining a comparable cycle life with respect to SCs. To date, there is still lack of detail investigation on printability of HECS, which forms a promising subject for future research in the field of energy storage.

Figure 7.1 Illustration of a printable HEC architecture with a non-Faradaic capacitive cathode coupled with a Faradaic ion-intercalation anode.

7.2 Investigation of the charge storage/transfer mechanism of printable SCs using *in-situ* characterizations

Investigation of oxidation states changes in nanostructured transition metal oxides is important to provide additional information to understand the enhanced device capacitance and comprehend the charge storage/transport which takes place at the electrode-electrolyte interface. Most of the investigations done till now is based on the observation of *ex-situ* characterizations such as XPS and XRD, which are done after charging or cycling the electrodes, where there are possibilities that the surface properties of the electrodes might have changed after being exposed to the environment. Therefore it is suggested that *in-situ* XPS or XRD characterizations to be used for future investigation, that would give direct real-time evidence valence state variation, as well as the intercalation/deintercalation of cation into the bulk of the transition metal oxide electrodes.

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Appendix A- LIST OF ABBREVIATION

AC	activated carbon
Ag-CNT	silver decorated CNT
AgNP	silver nanoparticle
CNT	carbon nanotube
CV	cyclic voltammetry
EDL	electrical double layer
EIS	electrochemical impedance spectroscopy
FESEM	field-emission scanning electron microscope (microscopy)
FTIR	Fourier transform infrared spectroscopy
GCD	galvanostatic charge-discharge
HOMO	highest occupied molecular orbital
ITO	indium tin oxide
J-V	current density versus voltage
LUMO	lowest unoccupied molecular orbital
MnNF	MnO ₂ nanoflowers
MnNW	MnO ₂ nanowires
nm	nanometer
PCBM	[6,6]-phenyl-C ₆₁ -butyric acid methyl ester
PET	Polyethylene terephthalate
P3HT	poly(3-hexylthiophene)
PSC	photo-supercapacitor
PSS:H	poly(styrene) sulphonic acid
PVA	polyvinyl alcohol
RH	relative humidity
SC	supercapacitor
TEM	transmission electron microscope (microscopy)
VNF	V ₂ O ₅ nanofibers
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction

Appendix B- AUTHOR'S PUBLICATION LIST

Journal articles

1. Printable photo-supercapacitor using single walled carbon nanotubes
G. Wee, T. Salim, Y. M. Lam, S. G. Mhaisalkar, M. Srinivasan, Energy and Environmental Science, 2011, 4, 413-416.
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6. Silver nanoparticle-decorated carbon nanotubes as bifunctional gas-diffusion electrodes for zinc-air batteries
W. Ting, M. Kaempgen, N. Phonthammachai, G. Wee, S. G. Mhaisalkar, M. Srinivasan, J. Power Sources (195) 2010, 4350-4355.
7. Particle Size Effect of Silver Nanoparticles decorated Single Walled Carbon Nanotube Electrode for Supercapacitors
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8. Bi-functional carbon nanotubes networks for Supercapacitors
M. Kaempgen, G. Wee, J. Ma, S. G. Mhaisalkar, G. Gruner, Appl. Physics Letters, 2007, 90, 264104.

Manuscript in preparation

1. Synthesis and electrochemical properties of MnO₂-CNT composite electrodes for supercapacitors

Patents

1. **G. Wee**, W.F. Mak, N. Phonthammachai, M. Srinivasan, S.G. Mhaisalkar, F. Boey, “Nanoparticles Decorated Nanostructured Material as Electrode Material and Method for Obtaining the Same,” US Provisional Application No.61/095,090 filed 8 September 2008. PCT Application No. PCT/SG2009/000318 filed 7 September 2009
2. **G. Wee**, W.F. Mak, Martti Kempgen, M Srinivasan, S.G. Mhaisalkar, F. Boey,” Energy Charge Storage Device Using a Printable Polyelectrolyte as Electrolyte Material,” PCT International Application No. PCT/SG2009/000236 filed 26 June 2009
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Conference Presentations:

1. Silver decorated carbon nanotubes for energy storage applications
G. Wee, W.F. Mak, M. Kaempgen, M. Srinivasan, G. Gruner and S.G. Mhaisalkar
Nanotech Europe Conference, Berlin, 2009.
2. Hybrid nanostructured materials for improved performance of energy storage applications
G. Wee, M. Srinivasan, and S.G. Mhaisalkar
Asia-Oceania Top University League on Engineering (AOTULE), Taipei, 2009.
3. Printable photo-supercapacitor using single walled carbon nanotubes
G. Wee, T. Salim, Y. M. Lam, S. G. Mhaisalkar, M. Srinivasan
International Conference on Materials for Advanced Technologies (ICMAT), Singapore, 2011.