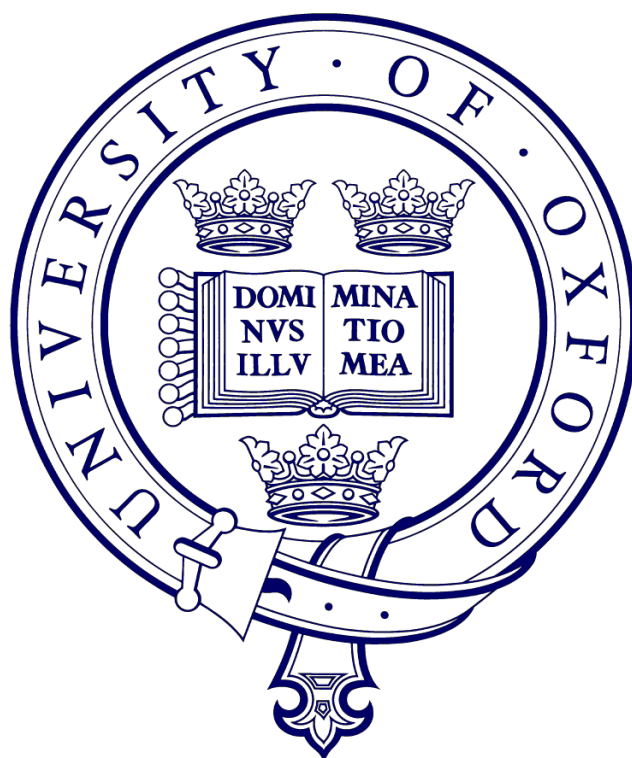


Processing and Properties of Nanostructured Thin Film Energy Storage Devices



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Abstract

A spray deposition manufacturing route has been developed for the fabrication of carbon nano-structured and micro-structured energy storage devices in a thin film format, with controlled film thickness, homogeneous film surface morphology and high electrochemical performance for both supercapacitors and lithium ion battery anodes. Three types of low cost commercially available carbon materials (graphite, activated carbon and carbon black) have been investigated, and electrodes characterised in terms of surface morphology, surface chemistry, microstructure and electrochemical properties.

By using ball milling, CO₂ activation and adding suitable carbon conductive additives, nano-graphite-based film electrodes (one meter long and $\sim 3 \mu\text{m}$ thickness) have been fabricated, with excellent ion transport and low electrical resistance ($< 1.8 \Omega$). Specific capacitance of 110 F/g at a scan rate of 100 mV/s in 1 M H₂SO₄ was achieved.

The high rate performance of activated carbon-based electrodes ($\sim 2 \mu\text{m}$ thickness) has been enhanced by reducing the contact resistance of electrode/current collector interface and building a well-interconnected and hierarchical meso/macro-porous structure. A specific capacitance of over 120 F/g at a scan rate of 600 mV/s or 20 A/g current density in 1 M H₂SO₄ was achieved.

The performance of carbon black-based electrodes ($\sim 4 \mu\text{m}$ thickness) in different electrolytes has been studied in both two- and three-electrode cells. High specific capacitances of 260 F/g at 1 A/g was achieved in 6 M KOH, together with energy and power densities of 21 kW/kg and 18 Wh/kg in 1 M Na₂SO₄.

Finally, graphite-based electrodes for rechargeable lithium-ion batteries have also been fabricated with controlled film thickness from $\sim 900 \text{ nm}$ to $\sim 40 \mu\text{m}$ and 98% capacity retention of 371 mA/g after 20 cycles.

Spray deposition has been demonstrated to have the potential for scalability in the manufacture of carbon-based thin film electrodes with competitive properties.

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Chapter 1

Introduction

1.1 Theoretical background of supercapacitors

Since the invention of electric motors in the 1870s, electrical energy has become the primary form of consumed energy. Over the past decade, the development of electrical energy storage devices have been stimulated towards more efficient energy management, higher energy density and better high-rate performance to meet the requirements from small consumer electronics, large industrial equipment, public transport and electricity distribution^[1]. Electrical energy storage is a fundamental part of all these systems, amongst which, electrochemical energy storage has become the most important.

There are two fundamentally different approaches to electrochemical energy storage: faradic reaction and electrostatic adsorption. In batteries, the charge storage process occurs in bulk electrodes through faradic reactions where electron transfer takes place in electroactive materials through redox and or inter-calation reactions^[2]. In electrochemical supercapacitors (SCs) the energy is stored by simple electrostatic charge transfer due to reversible adsorption of electrolyte ions on an electrode surface. The electrical charge is stored at an electrochemical double layer formed at the electrode/electrolyte interface^[3]. SCs that store charges only by pure electrostatic processes with no electron

transfer or chemical phase change are named electrochemical double-layer capacitors (EDLCs), and the electrode/electrolyte interface is called the electric double layer (EDL), as shown in Figure 1.1. SCs that store charge by fast and reversible faradaic processes consisting of two different mechanisms (a surface process and a bulk process) are named pseudo-capacitors.

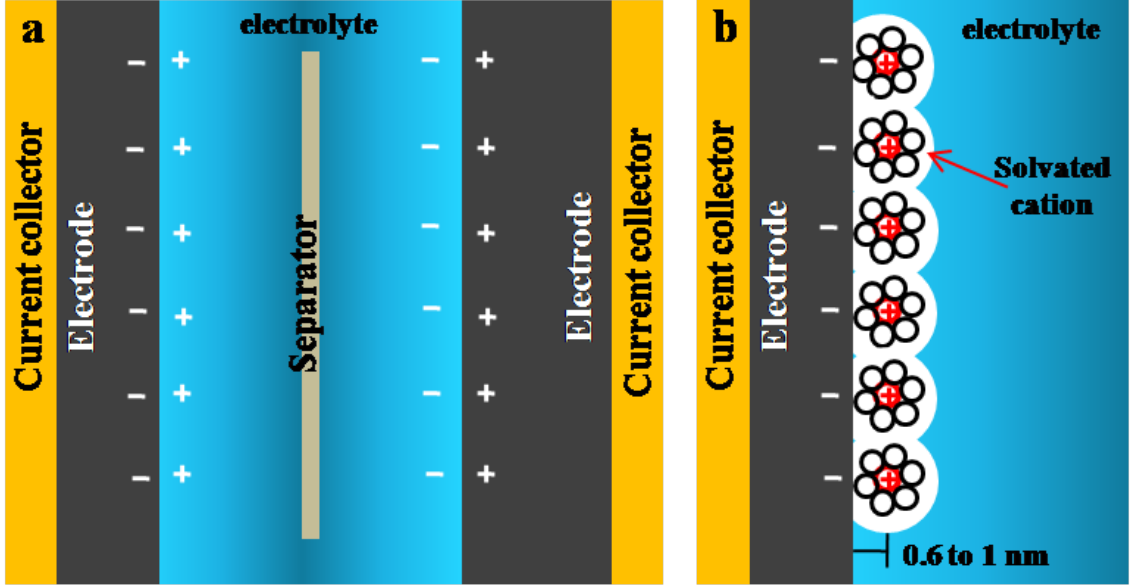


Figure 1.1: Schematic of (a) electrochemical supercapacitor: two ideally polarizable electrodes immersed in the electrolyte and physically separated by a porous membrane. Positive and negative ionic charges within the electrolyte can go through the porous membrane and accumulate separately in a thin layer formed at the electrode-electrolyte interface. (b) double-layer region under conditions where solvated cations are specifically adsorbed with a thickness around 1 nm.

The pure electrostatic ion adsorption mechanism allows the EDLCs to provide high power density (more than 10 kW/kg), long cycle-life (over 10^6 cycles), excellent reversibility, high efficiency, and low safety risks[2, 4, 5]. Thus EDLCs can be complementary to secondary batteries and fuel cells, which have a high energy density but a limited power density, to increase efficiency and system life time by providing back-up power supplies to protect against power disruptions, and to reduce the total system weight and volume[6, 7].

At the same time, the EDLCs can provide 2 - 3 orders of magnitude higher energy density than electrostatic capacitors, because a very large specific surface area (1000 - 3000 m^2/g) is deliberately engineered to enhance EDLC effects[4, 8]. Electrochemical

supercapacitors can represent an important class of electrical energy storage devices, which fill the gap between batteries and conventional solid state electrostatic and liquid electrolytic capacitors on a ‘Ragone plot’^[2, 9] in terms of their specific energy versus specific power, as illustrated in Figure 1.2.

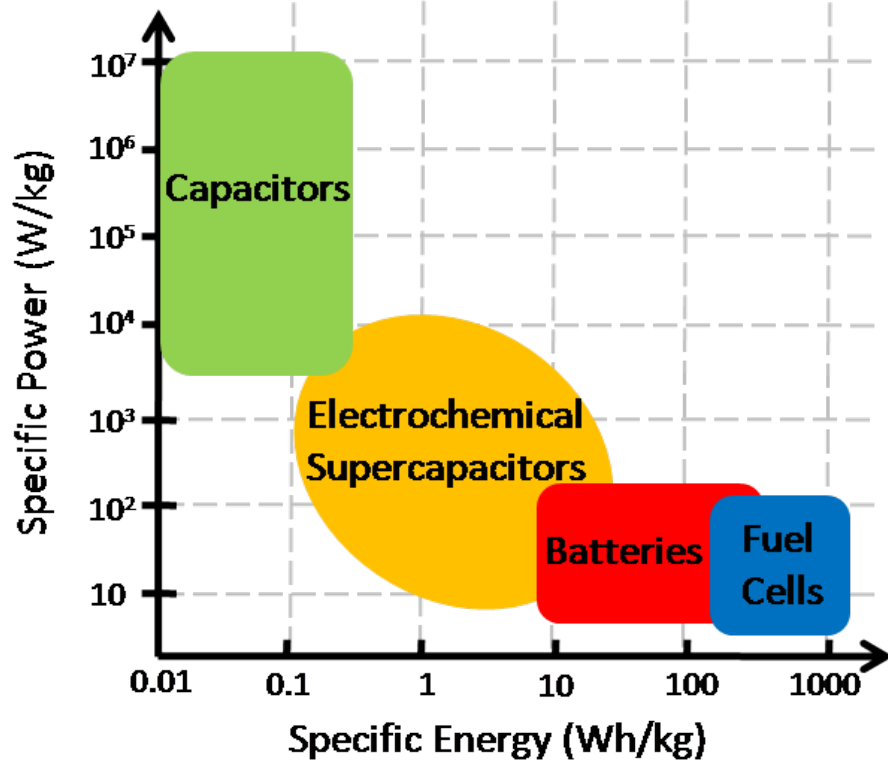


Figure 1.2: Sketch of Ragone plot for various energy storage and conversion devices.

The capacitance (C) of an EDLC is defined as^[10]:

$$C = \frac{\varepsilon_r \times \varepsilon_0 \times A}{d} \quad (1.1)$$

where ε_r is the electrolyte dielectric constant, ε_0 is the dielectric constant of a vacuum, A is the specific surface area of the electrode accessible to the electrolyte ions and d is the effective thickness of the EDL. The maximum energy density (E) stored in supercapacitors and the power density (P) are expressed by^[10]:

$$E = \frac{C_s \times V^2}{2} \quad (1.2)$$

$$P = \frac{I \times V}{2} \quad (1.3)$$

Or

$$P = \frac{V^2}{4 \times R_s} \quad (1.4)$$

where C_s is the specific capacitance of the cell (only a quarter of the single electrode specific capacitance value), V is the operating voltage of the cell which is determined by the stability window of the electrolyte, I is the applied discharge current density and R_s is the series resistance (ESR) of the cell.

Compared to other electrical energy storage devices ECs are superior for use in back-up systems (such as uninterruptible power supply (UPS)^[11], and industrial energy conservations (e.g. lift/release of cargo cranes)^[12]), high power applications (e.g. electric grids^[13, 14]), and automotive applications (e.g. electric vehicles^[15] and hybrid trains^[16]).

1.2 Development, challenge and market potential

The development of SC technology is shown in Figure 1.3. The concept of the ‘double-layer’ was first described by Hermann von Helmholtz in 1853^[17]. Almost one century later the first electrochemical supercapacitor product (a memory back-up device) was introduced into market by Nippon Electric Company (NEC). In the last two decades, with the introduction of pseudo-capacitance and the use of organic electrolytes, SCs have played an important role in complementing batteries and fuel cells in electrical energy storage applications^[17].

Notable improvements in performance of EDLCs have been achieved recently through

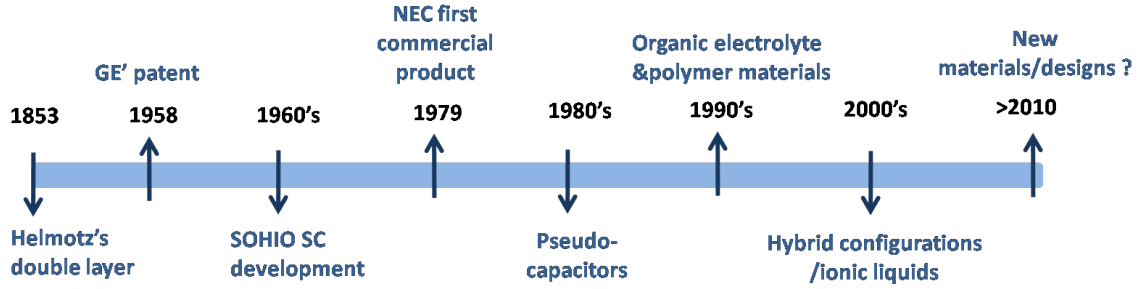


Figure 1.3: Key milestones in the development of SC technologies.

the synthesis of carbon electrode materials with designed micropores (pore size < 2 nm) and mesopores (pore size between 2 - 50 nm) nano-structure^[18--20], introducing surface functional groups^[21, 22], and enhancing the conductivity of the EDLC cells^[23]. However, the energy density of EDLCs (~ 5 Wh/kg) is low when compared with batteries (> 50 Wh/kg). Therefore, a key challenge for EDLCs in the coming decades is to bring the energy density of EDLCs closer to that of batteries without compromising the high power density by further and better understanding of the charge storage mechanisms and developing suitable nanostructures that increase the effective area of the electrode materials.

The high cost of EDLCs is the second obstacle to their commercial market development^[24]. The main cost of EDLCs arises from their electrode materials. At present, commercial products use activated carbons (ACs) materials for EDLCs electrodes which are expensive (US \$ 50 - 100/kg)^[25], not to mention the special synthesised porous carbons and other advanced carbon materials, such as carbon nanotubes, carbon fibres and graphene, which are also expensive. The goal is to reduce the cost of carbon to \$ 10 - 15 per kg^[24].

The third challenge for EDLCs manufacturers is to satisfy the well-defined configurations and various functionality applications of modern electronics. Recently, with a fast-growing market for modern portable electronics and embedded devices for health and sports^[26, 27], there has been an increasing and urgent demand for ultrathin, mechanical flexible, light-weight, wearable and low cost electrical energy storage devices in large-scale production^[28--30]. Conventional charge storage devices, such as bat-

teries and supercapacitors are bulky style with an electrode thickness of 0.15 - 0.3 mm^[31]. Although paper-like flexible batteries^[32, 33] and EDLCs^[34, 35] have been reported, these are rather thinned-down versions of conventional devices. Truly large-scale production of commercial EDLC cells with controlled film-electrode thickness (from hundred nanometers to a few microns) and designable cell shape is still required.

At present, commercial SCs are available from many countries, three Japanese companies (NEC, Elna and Panasonic) demand the greatest share of the SC market^[36]. Other SCs companies in USA (Maxwell), South Korea (NESS), Australia (Cap-XX) and Russia (ECOND, ESMA, ELIT) are beginning to secure market share^[25, 37, 38].

Although, at present only around 1% of the world market for electrical energy storage is taken by SC, an approximate 10.9% annual growth rate of SC market has been achieved since 2010^[4]. The development of new materials preparation technologies and SC manufacture are required to increase the development of the SC market. It is expected that over £877 million of worldwide sales will be generated from the SC market by 2014^[39].

1.3 Thesis objectives

The current fabrication methods for commercial supercapacitor is based on pressing/calendering a paste mixture of carbon materials (activated microporous carbon), non-activated conductive filler (carbon black to reduce equivalent series resistance) and a polymer binder (to stop electrode disintegration)^[40, 41]. This technique has many disadvantages such as only thick films ($> 80 \mu\text{m}$) can be produced, low flexibility and low material utilization efficiency (additives and binders do not contribute to the final capacitance). Nonetheless, these types of SC are comparatively cheap and used in electric vehicles, mobile electronics, emergency systems, etc. There remains considerable scope to explore new process-material combinations to provide improved specific performance without an impractical escalation in cost.

To achieve the challenges mentioned above, the objectives of this research work are:

- To develop initially a new process route for the manufacture of EDLC electrodes by spray deposition using low cost commercially available carbon materials (activated carbons, graphite and carbon black), with an emphasise on thin flexible film production;
- To characterize the microstructure and properties, through a combination of microscopy, electrochemical testing and device manufacture; and
- To explore and optimize new material-process combinations that offer a balance of attractive electrochemical properties, high conductivity, low cost and large-scale implementation.

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Chapter 2

Literature Review

This review starts with a summary description of the various carbon materials currently used for the electrodes of supercapacitors (SCs), followed by a discussion of how to optimize the performance of SC cells. Individual effects from the material resistance, pore size distribution, surface functionalization of the electrode, as well as electrolytes and current collectors are elaborated. The processing and manufacturing issues for SC applications, especially for large-scale industry production, are also discussed. Several recent manufacturing techniques which are suitable for electrochemical supercapacitors are summarized, together with a discussion on flexible thin film electrode production.

2.1 Carbon-based supercapacitors

2.1.1 Overview of carbon materials

Electrode materials for SCs can be divided into three main categories: carbon based materials, metal oxides and conductive polymers. Carbon based materials use the electric double layer for charge storage, whereas the other two are based on faradic reactions (pseudocapacitors).

For pseudocapacitors, transition metal oxides are the most widely studied, thanks to high theoretical specific capacitance, which is 10 - 100 times higher than carbon based double-layer system^[1]. The most common metal oxide pseudocapacitor is ruthenium dioxide ($\text{RuO}_2 \bullet x\text{H}_2\text{O}$), with a high specific capacitance of 760 F/g^[2]. However due to its high cost and limited supply, the application of RuO_2 in SCs is limited to defence applications. The main problems for metal oxides such as MnO_2 (the second most studied pseudocapacitor oxide) is their low electrochemical reversibility, and high equivalent series resistance (ESR) caused by the multiple redox reactions associated with their multiple oxidation states that results in a relatively low power density^[3]. Electrode integrity and long-term electrochemical stability are additional problems. Strictly, pseudo-capacitance is a surface effect only in which the charge storage magnitude varies with potential. It is distinct from battery behaviour which involves charge storage in the volume of the material, and where capacity increases over time at a constant potential. Many attempts to increase the performance of SCs using pseudo-capacitance simply result in a ‘bad battery’ -energy density is sacrificed for power density but the resulting power density is uncompetitive - where charge/discharge becomes controlled by slow diffusive processes.

Conductive polymers are another type of candidate electrode material for pseudocapacitors, where charge is stored by relatively fast and reversible oxidation and reduction processes of the π -orbital conjugations in a polymer network^[4]. Conductive polymers have some advantages, such as high theoretical capacitance performance (450 F/g for polyaniline coated on stainless steel), low cost electrochemical deposition, and ease of fabrication for thin films^[5, 6]. However, their main drawbacks are: low stability over long-term charge/discharge cycles and high equivalent series resistance^[7].

Carbons are the most studied materials for electrochemical double layer capacitors (EDLCs), with advantages of exceptionally high surface area, tailorable nanotexture, relatively high electronic conductivity, good chemical stability, acceptable cost as well as ease of processibility and compatibility in composite materials^[8--10]. In carbon-based SCs, the charge is mainly stored in the EDL, while any surface functional groups

can sometimes contribute additional pseudo-capacitance through faradic reactions^[4]. In this thesis, carbon is the material of focus and reader is directed elsewhere for reviews of other materials in SCs^[11].

The synthesis of carbon based electrodes with carbon containing highly electro-active regions created by controlling microstructure, specific surface area and pore character has been widely studied^[12, 13]. Materials include activated carbons (ACs)^[14], ordered mesoporous carbons (OMCs)^[15], carbon aerogels, and carbon nanotubes (CNTs)^[16], graphene^[17], etc. The typical capacitances of carbon materials are 50 - 200 F/g in aqueous electrolytes, 30 - 100 F/g in organic electrolytes and 20 - 70 F/g in ionic liquids^[18]. The focus of this thesis is not the development of new carbon polymorphs, but how existing materials can be combined with new processing approaches to create thinner electrodes with attractive combinations of properties.

2.1.2 Three dimensional porous carbons

2.1.2.1 Commercial activated carbons

A typical example of a 3D porous carbon material is activated carbon (AC), which has been widely used in commercial SC cells. Activated carbons are produced from the pyrolysis of natural precursors (e.g. phenolic resins, coconut shell and coal) in two steps: the carbonization of raw materials and the activation of the carbonized product. The specific surface area for ACs is usually 1000 - 3000 m²/g, depending on the carbon precursors used and activation time^[19–23]. ACs have a broad pore size distribution consisting of micropores (< 2 nm), mesopores (2 - 50 nm), and macropores (> 50 nm)^[4]. The classification is due to IUPAC and is widely used in the SC community.

However, AC can suffer from electrode kinetic problems (slow diffusion of ions) that is related to difficulties in access to tortuous internal pores in the carbon interior^[4, 19, 24]. The random uncontrollable pore connection in the interior of the carbon also leads to

poor electrical conductivity, as shown in Figure 2.1^[25]. Therefore, a large fraction of the potentially available micropores in AC may contribute little to the total capacitance due to their low accessibility for electrolyte (especially in the case of high current densities^[8]). The practical specific capacitances of activated carbon are much lower than theoretical: 75 - 200 F/g in aqueous electrolytes and 40 - 100 F/g in organic electrolytes^[18].



Figure 2.1: Schematic illustration of the inside porous structure of activated carbon particles.

To improve the performance of ACs-based electrodes and further understand the relationship between the specific capacitance and the pore size distributions, microporous carbon materials and mesoporous carbon materials in disordered and ordered formats have been synthesized and carefully investigated as EDLC electrode materials. The synthesis of microporous, mesoporous and macroporous carbons using different templates is illustrated in Figure 2.2^[26]. By using different templates followed by template removal, a range of porous carbons with designed pore size and interconnection can be synthesised, although these techniques are currently considered too slow/costly for commercial manufacture.

2.1.2.2 Microporous carbon

Microporous carbon materials can be synthesized through template methods. Microporous zeolitetemplated carbon (ZTC) can be prepared with an enormous 4000 m²/g BET surface area (Brunauer-Emmett-Teller method), constant pore size and homo-

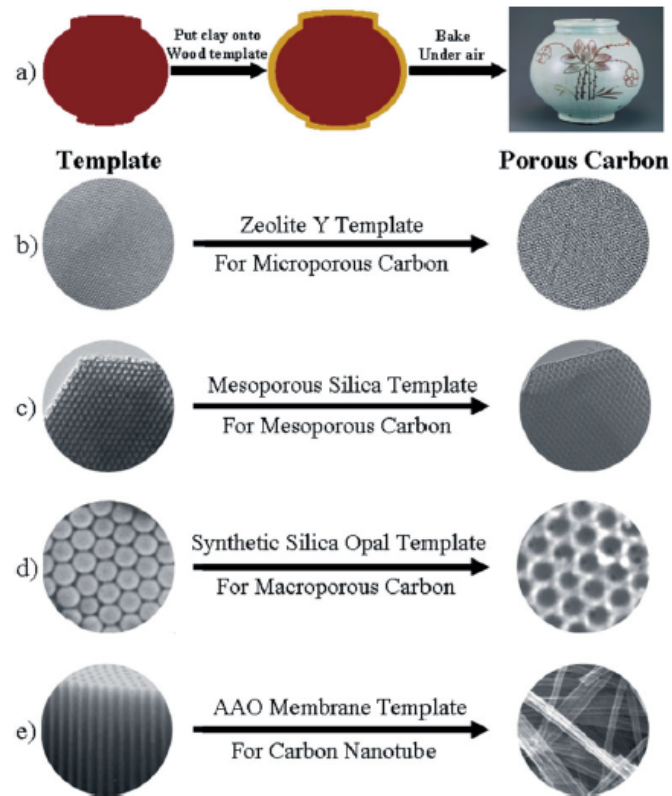


Figure 1. a) Schematic representation showing the concept of template synthesis. b) Microporous, c) mesoporous, and d) macroporous carbon materials, and e) carbon nanotubes were synthesized using zeolite, mesoporous silica, a synthetic silica opal, and an AAO membrane as templates, respectively.

Figure 2.2: (a) Schematic showing the concept of template synthesis, and synthesis of (b) microporous, (c) mesoporous, and (d) macroporous carbon materials using zeolite, mesopoeous silica, and a synthetic silica opal as templates, respectively^[26].

geneous morphology, using nano-channels of various types of zeolite as a template for carbon deposition, which is followed by subsequent template removal^[27--29], as shown in Figure 2.3.

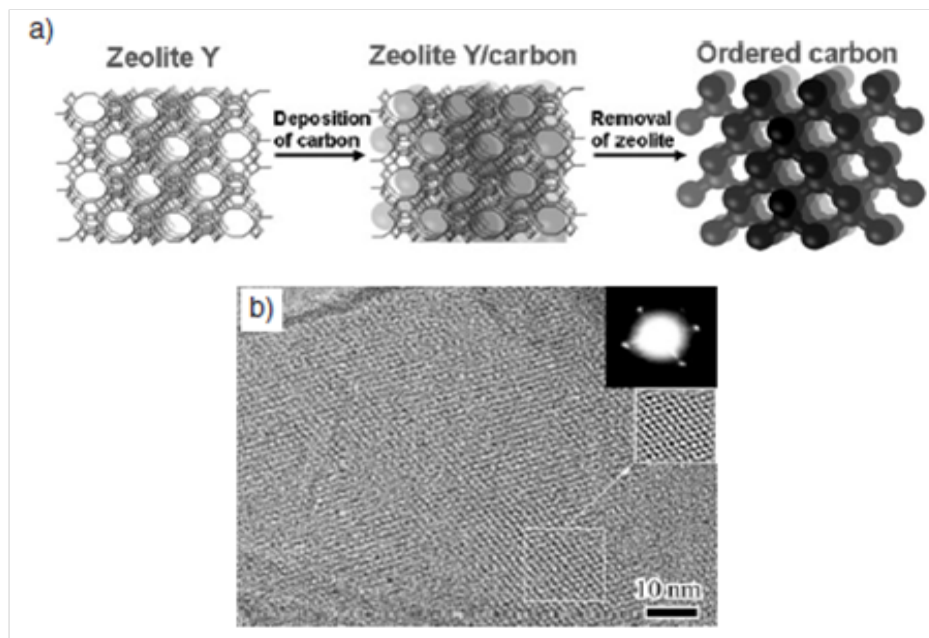


Figure 2.3: (a) Schematic of the template synthetic procedure for microporous carbon, and (b) high resolution TEM image of ordered microporous carbon^[29].

Carbide-derivation is another route to synthesize microporous carbon. Carbide-derived carbon (CDC) can be distinguished by its uniform nanoporous structure together with a narrow pore size distribution. The pore size can be closely controlled by varying the starting materials and chlorination temperature (from 400 to 1200 °C, usually below 800 °C for microporous carbon production) during the chlorination of metallic carbides (e.g. TiC, SiC and B₄C)^[30]. So far, TiC was the best CDC material for electrochemical application. High resolution transmission electron microscopy (TEM) images of TiC-CDC and ZrC-CDC synthesized at different temperatures are shown in Figure 2.4^[31]. By carefully controlling the average micropore from 0.7 to 1.1 nm, the specific capacitance of TiC could reach 130 - 190 F/g with a BET surface area in range of 1000 - 1600 m²/g^[32]. Attributed to the 3D ordered micropores in most CDCs, the ion-transfer resistance was reduced, leading to a slightly improved rate performance. For B₄C-driven carbons, 86% capacitance retention could be achieved in KOH electrolyte when the scan rate was increased from 2 to 50 mV/s^[33]. However,

due to their high cost and safety concerns about production, carbide-derived carbons are limited in commercial applications, and are mainly used for research purposes^[34].

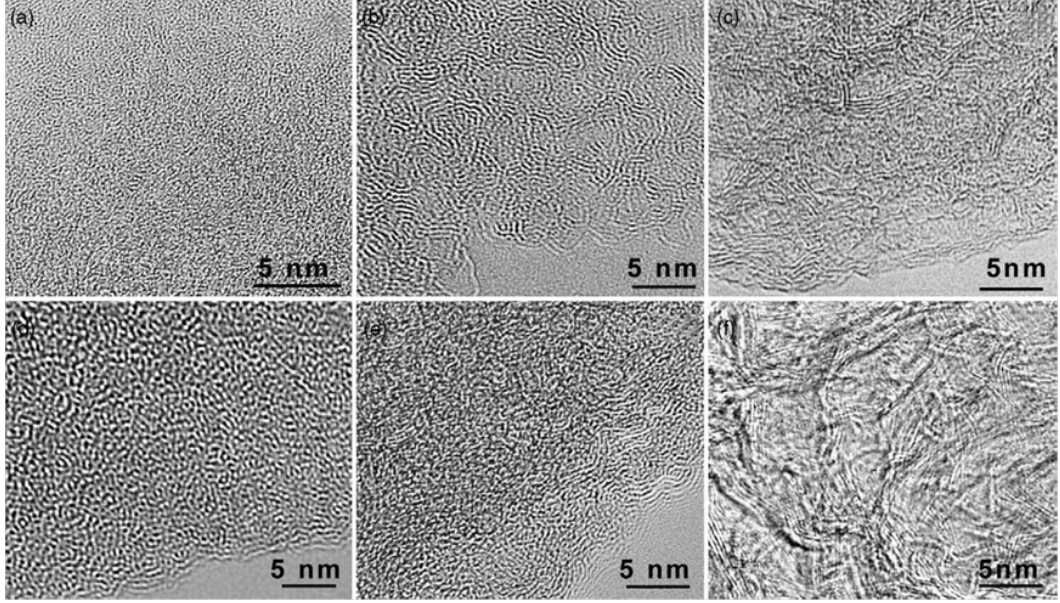


Figure 2.4: TEM images of TiC-CDC and ZrC-CDC synthesized at (a, d) 600 °C, (b, e) 800 °C and (c, f) 1200 °C^[31].

2.1.2.3 Mesoporous carbon

Mesoporous carbon materials with a highly ordered porous structure can outperform microporous carbon for high-power delivery and improved high-frequency capacitive energy storage. The larger volume of the mesopores can help make full use of the inner surface of the carbon pores and improve the electrolyte ion transportation, leading to higher rate capability and a lower reduction in capacitance ($\sim 10\%$) with increasing discharge rate^[35, 36].

Highly ordered mesoporous carbons (OMCs) (pore size 4 - 6 nm, particle size 0.5 - 1 μm) have been successfully synthesized by nano-casting approaches in which mesoporous silicas were used as the hard templates. Thanks to the uniform mesopore channels, OMCs exhibited higher surface efficiency and superior rate capability than commercially available AC (e.g. over 180 F/g at 50 mV/s compared with 73 F/g for ACs at the same scan rate, and 130 F/g at 10 mA/cm² constant current density compared with 19 F/g for ACs at the same current density^[37]), but with a lower specific capacitance

(220 F/g) due to a lower surface area (1200 - 1800 m²/g)^[38, 39]. Figure 2.5 shows a schematic of the synthesis of ordered interconnected mesoporous carbon (CMK-3 and CMK-1) using mesoporous silica templates^[40, 41]. To optimize high-rate performance in mesoporous carbon, the amount of secondary, larger pores were constructed into ‘wormhole-like’ mesoporous carbon (WMC) with a mass transport pathway designed to improve ion diffusivity, as shown in Figure 2.6^[42–44]. The main limitations of OMCs to wider spread industrial application are again their high production costs and small volumetric capacitance caused by the larger porosity^[45].

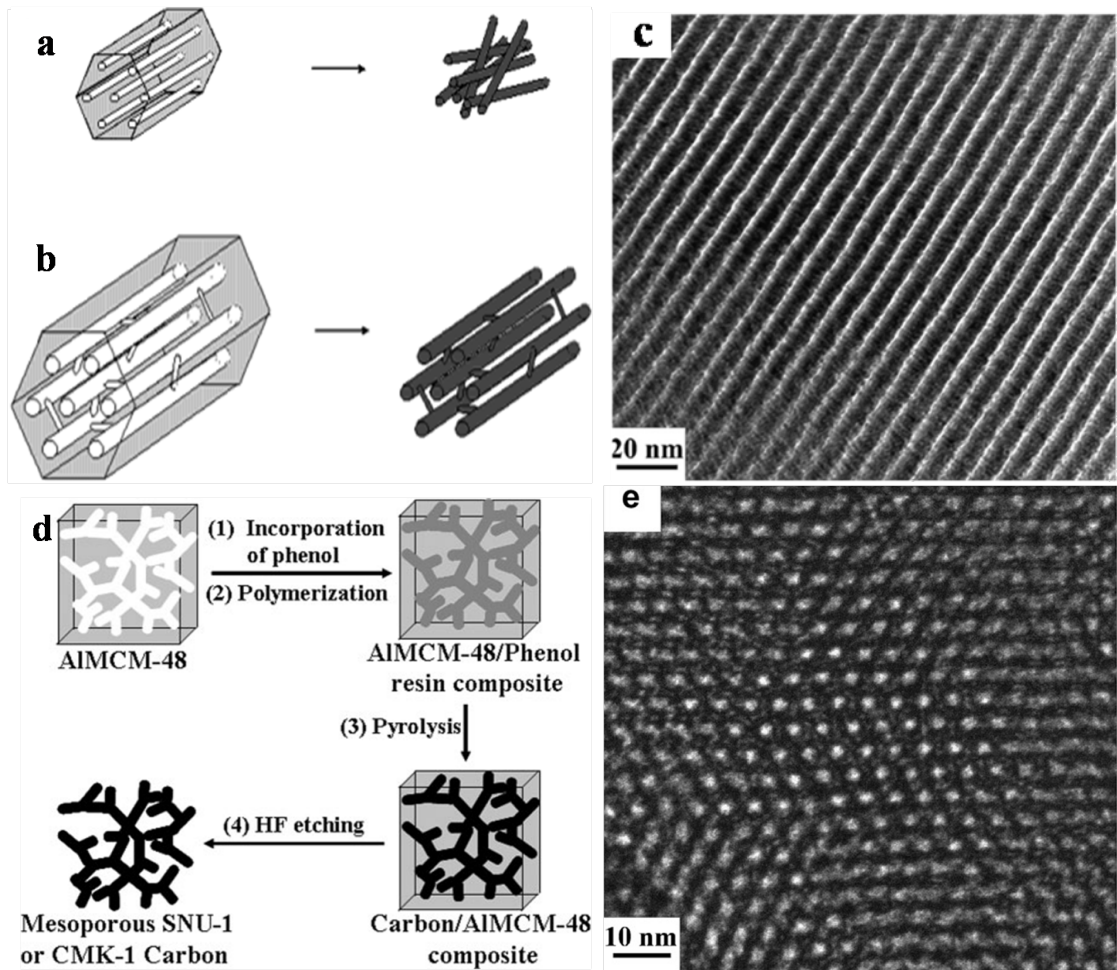


Figure 2.5: Schematic illustration of the synthetic procedure of (a) unconnected, (b) interconnected OMCs (CMK-3) with cylinder pore shape, and (d) 3D interconnected OMCs (CMK-1), (c) TEM images of CMK-3 and (e) TEM images of CMK-1^[40, 41].

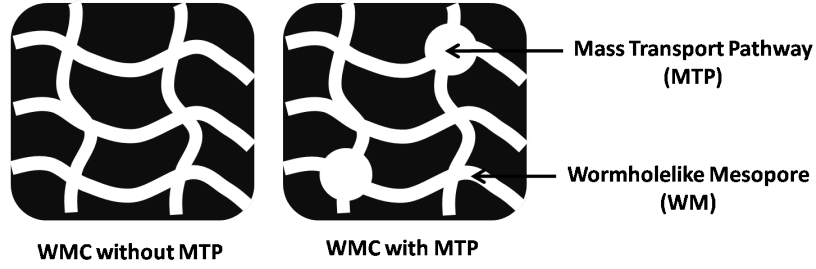


Figure 2.6: Schematic illustration of the wormholelike mesopore with and without secondary mass transport pathway.

2.1.2.4 Hierarchical carbon

The concept of a 3D hierarchical porous structure was first realized in carbon aerogels^[45]. They consist of three-dimensional mesoporous materials derived from the pyrolysis of resorcinol-formaldehyde precursors which are a poly-condensated via a sol-gel process^[46]. As carbon aerogels are an interconnected network of carbon nanoparticles (4 - 9 nm) in a chain-like structure, they have a highly interconnected porous structure with a hierarchical pore size distribution (from micro-pores to macro-pores), leading to good electrical conductivity (up to 25 - 100 S/cm), high surface area (normally 650 - 1100 m²/g, but can be increased to 2500 m²/g by an activation process^[47]), low density, and may not require additional binding materials when cast into electrodes^[48, 49].

The specific capacitance of carbon aerogels depends on the pore size distribution (150 F/g when the pore size was less than 3 nm, 171 F/g when larger micropores were introduced^[50]), and could be further improved by surface functionalization^[8, 51]. The main problem for the application of carbon aerogels in electrochemical energy storage is their low mechanical stability which always requires fibres such as polytetrafluoroethylene to be introduced for stability^[52, 53].

Recently, 3D aperiodic hierarchical porous graphitic carbon materials have been designed and synthesized for high-rate performance^[54]. They consist of macroporous cores (which serve as ion-buffering reservoirs for micropores), mesoporous walls (which provide short diffusion pathways and small resistance) and micropores (enhanced specific surface area). Furthermore, compared with other interconnected porous carbon

materials, they are differentiated by their local graphitic structure which is suggested to enhance electrical conductivity, as shown in Figure 2.7. Superior high-rate performance was achieved by a 3D aperiodic hierarchical porous graphitic carbon material (180 F/g at 1 Hz high frequency) when compared to OMCs and ACs^[55]. A novel hierarchical porous carbon (HPC) has also been synthesised with worm-like mesopores within a 3D structure (as shown in Figure 2.8), with an improvement in mass transport and enhanced power/energy density^[56].

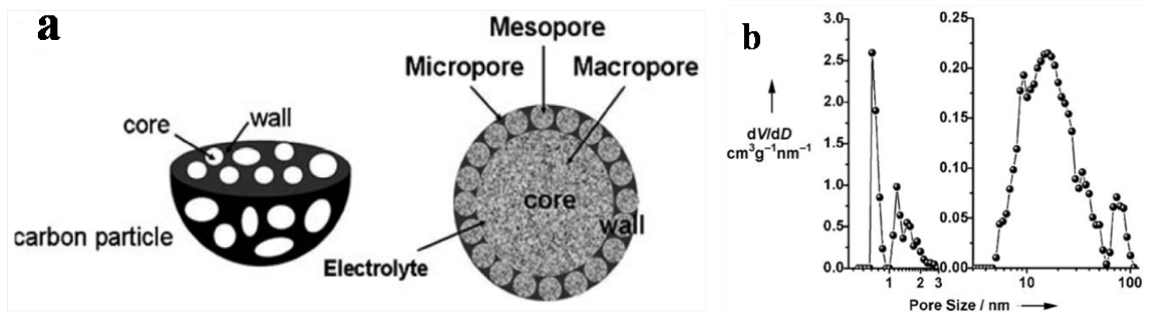


Figure 2.7: (a) Schematic illustration of the 3D hierarchical porous texture, and (b) pore size distribution of the 3D hierarchical porous carbon^[54].

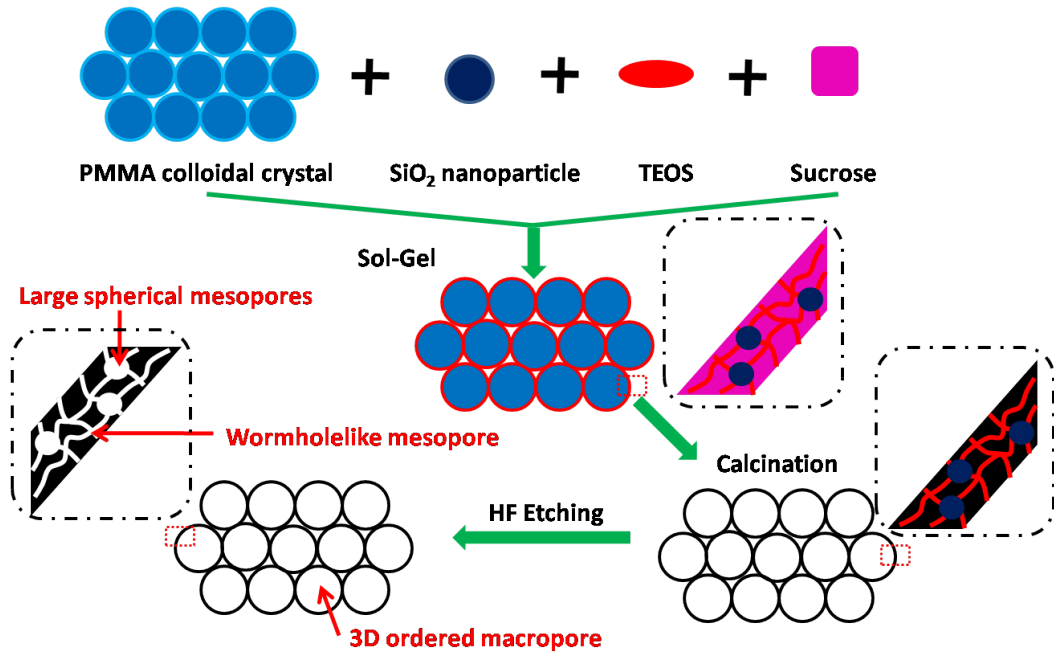


Figure 2.8: Schematic illustration of the procedure of hierarchical porous carbon and its 3D hierarchical porous texture.

2.1.3 Two dimensional carbon - graphene

Since its isolation in 2004^[57], graphene has been the focus of much research and has become another attractive carbon material for EDLC cells^[58, 59] thanks to its two-dimensional monolayer sp^2 -bonded carbon structure, which leads to exceptional properties such as high theoretical surface area (theoretical 2630 m^2/g , twice that of SWCNTs^[60]), high electrical conductivity resulting from the extensive conjugated sp^2 carbon network (64 mS/cm which is approximately 60 times greater than that of single wall carbon nanotubes (SWCNTs)^[58, 61]), fast electron transfer rate (electron transport along the graphene edge rather than its side, which is many orders of magnitude faster^[62, 63]), and two-dimensional morphology.

Different synthesis methods have been developed for graphene manufacture, including: mechanical/chemical exfoliation^[57, 64–66], epitaxial growth on metal or SiC surface via Chemical Vapour Deposition (CVD)^[67, 68], solvothermal synthesis^[69] and unzipping of carbon nanotubes^[70]. However, at present there is no single method that is optimised for the production of high-quality graphene thin films at a large scale^[71]. Mechanical cleavage of graphite could produce high quality single-layer graphene, but it is limited by its low throughput and only allows production of small area films of a few tens of micrometers^[57]. Chemical reduction of exfoliated graphite oxide layers (Figure 2.9^[66]) might satisfy mass production of the graphene thin films, but the electrical performance is reduced due to damage of graphene structure during the harsh oxidation and reduction reaction^[72]. Graphene films grown on metal (e.g. Ni as shown in Figure 2.10^[73]) or SiC substrates have problems of large area transfer without introducing cracks or tears. Furthermore, the solution reduction method can cause significant agglomerations of graphene sheets^[74].

The specific capacitance of graphene can reach 135 F/g , 99 F/g and 75 F/g in aqueous, organic and ionic electrolytes, respectively^[75, 76]. Although high performance such as 150 F/g at 0.1 A/g for 500 cycles^[77], and 205 F/g with power density 10 kW/kg at a current density of 28.5 Wh/kg ^[78] and 21 mF/cm^2 ^[79], have been reported, in general

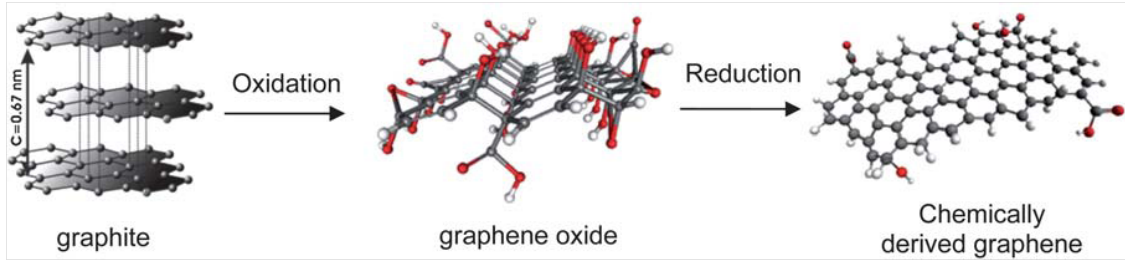


Figure 2.9: Schematic illustration of the procedure of chemically derived graphene^[66].

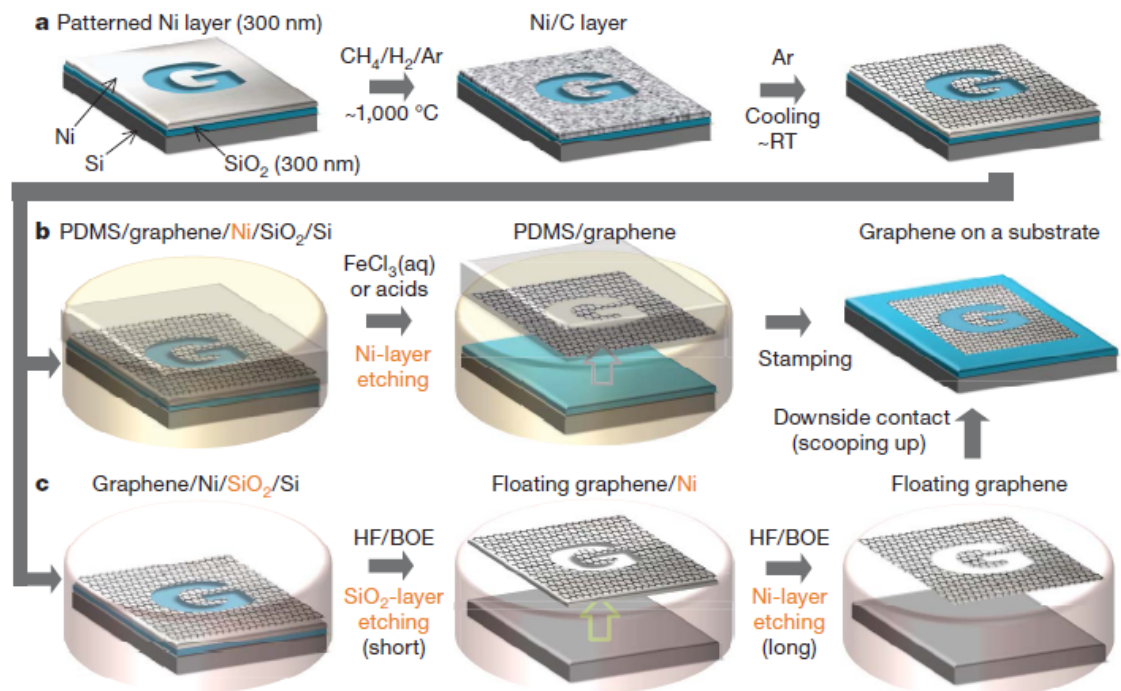


Figure 2.10: Schematic procedure of largescale graphene production: (a) synthesis graphene film on Ni layer, (b) etching Ni layer and transfer of graphene film, and (c) further etching SiO₂ layer and transfer of graphene film^[73].

the specific capacitance of graphene is not as high as expected, mainly limited by the agglomeration of graphene sheets and that the sheets are effective ion barriers. Therefore, many investigations have concentrated on graphene based composite materials, such as graphene-conducting polymer composites^[80--83] (gravimetric capacitance of 233 F/g for graphene/polyaniline composite paper^[80]). The commercial applications of graphene-based SC cells are mainly limited by the lack of large-scale high-quality graphene film production, together with toxic reducing agents employed and graphene's inherent (current) high cost^[84, 85].

2.1.4 One dimensional carbon - carbon nanotubes

Carbon nanotubes (CNTs) have been investigated as high-rate electrode materials thanks to their good electrical conductivity and high accessible surface area (from a porous network^[86--92]). However, due to their relatively low specific surface area ($\sim 500 \text{ m}^2/\text{g}$ in practice) compared with porous carbon materials, CNTs have the main disadvantage of a comparatively low energy density^[93].

For single wall carbon nanotube based SCs, the maximum specific capacitance of 180 F/g with a large power density of 20 kW/kg, and energy density around 7 Wh/kg in KOH electrolyte has been reported^[94]. For multiwall carbon nanotubes based SCs, the best specific capacitance of 113 F/g with power density of 8 kW/kg and energy density of 0.56 Wh/kg in an acidic electrolyte has been achieved^[95]. However, it is difficult to retain the good electrochemical properties of CNTs with high purity^[96]. For purified CNTs, the specific capacitance ranges from 15 to 80 F/g, with the BET surface area ranging varying between 120 and 400 m^2/g ^[97], suggesting some valuable capacity was provided by other carbonaceous materials generally mixed with CNTs in the as-received condition.

One major reason that CNT-based SCs could not meet the expected performance is the high contact resistance between the CNT electrode and the current collectors, which

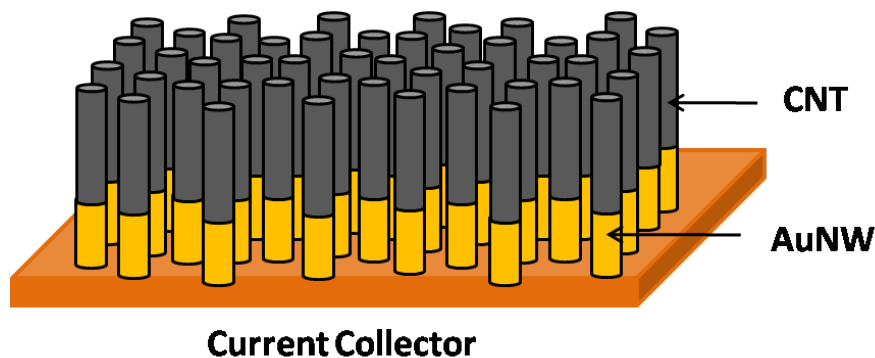


Figure 2.11: Schematic illustration of the CNT/Au nano-wire electrodes and the copper layer.

leads to a low power density^[94, 98]. The interface resistance can be reduced by the approach of growing CNTs directly on conductive substrates^[99, 100] (e.g. CNT/Au nanowire electrodes with high power density 48 kW/kg^[16], as shown in Figure 2.11). To further increase the power density, electrodes have been fabricated with aligned CNTs instead of entangled CNTs to give lower ESR and better ion transportation due to larger pore sizes and a regular pore structure^[101]. Improvements in the energy density of CNTs was achieved by increasing their specific surface area via heat treatment^[94] or chemical activation (by KOH)^[46]. Very recently, the super-high specific capacitance of 524 F/g with BET surface area of 1059 m²/g has been achieved by uniformly dispersing a carbon aerogel throughout the CNT matrix to form a CNT-aerogel composite^[91]. A 3D CNT/graphene sandwich structure was synthesized recently by CVD growth of CNT pillars between graphene layers, as shown in Figure 2.12^[102]. A high specific capacitance 385 F/g at 10 mV/s in 6 M KOH was achieved due to enhanced electrolyte ion transportation.

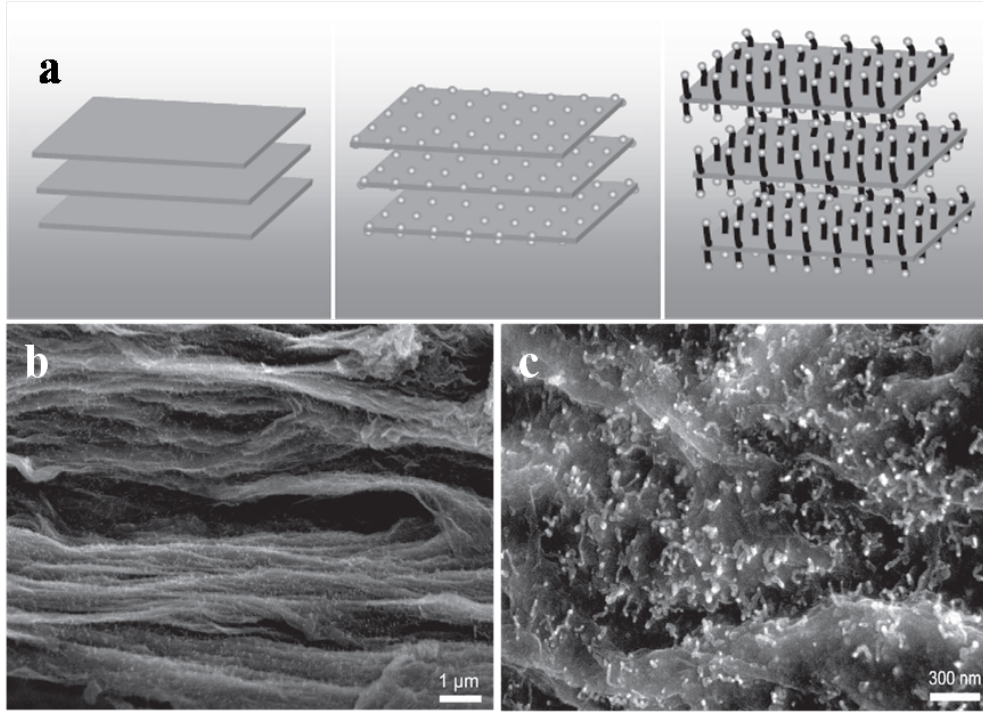


Figure 2.12: (a) Schematic procedure of CVD grown CNTs on a graphene layer, (b) and (c) TEM images of CNT/graphene sandwich structure^[102].

2.2 Optimization of the performance of electrochemical supercapacitors

2.2.1 Key parameters of cell design

To achieve good performance (such as high power density, energy density and long cycle life) a supercapacitor cell should simultaneously have large capacitance, minimum equivalent series resistance (ESR) and high operation voltage (from Equations 1.2 to 1.4). This needs an integrated consideration of the electrochemical properties of electrodes with matched electrolytes and current collectors. The structure of electrode materials, based on the electrode material's natural dimensions, surface characterization and pore size distribution, is crucial for its electrochemical properties, which in turn determines the transportation of ions and resistance of the electrode in SCs cells. The electrolyte and current collector have to be carefully chosen to provide 'matched' ion size, wettability and therefore to optimize the operating voltage window and min-

imize the ESR.

2.2.2 Resistance

The ESR value of ECs is composed of electrode material resistance, electrolyte resistance, and the resistance of the electrode material/current collector interface. The internal resistance of electrode materials can be reduced by adding conductive additives, heat treatment^[103, 104], material structure modification and surface functionalization. Conductive additives such as carbon black can improve the connection among electrode material particles; but at the same time, it also is considered to have a negative effect on energy density, power density and useful specific surface area, due to its reduction of material utilization for charge storage. Other conductive additives such as carbon nanotubes may not have these problems, but their high cost bring another limitation.

The design of 3D nanostructures is a new way to improve the conductivity of electrode materials. The key design parameters are controlling mesoporosity and the extent of crystallinity^[105]. In a traditional thick film electrode, the inactive materials in the bulk give rise to an increase in ESR. This problem could be eliminated by building a 3D metallic conductive nanotubes array structure with fast electron hoping pathways^[106]. However the high cost of these kinds of synthetic nanostructures cannot be ignored.

2.2.3 Pore size distribution and structure

The specific surface area plays an important role in EDLC energy storage, as illustrated in Equation 1.1. However, the correlation between total capacitance and specific surface area is not linear when the pore size of electrode materials is taken into account^[107] and different capacitive behaviours can be obtained for electrodes with similar surface area but different pore size distributions.

Some typical experimental data of the relationship between specific capacitance, sur-

face area (determined by gas adsorption and BET analysis) and pore diameter is shown in Figure 2.13^[108]. For any fixed pore diameter, the specific capacitance increased with the increasing BET surface area. However, for a fixed BET surface area, the specific capacitance changed with the changing of pore diameter. Higher specific capacitance was obtained at smaller pore diameter, because the solvent ions would desolvate or partially remove their solvation shells to adsorb into the pores (with a pore size very close to those of the ion size, and the removal solution shells remains somewhat controversial), this desolvation allowed a closer approach of the ion centres to the electrode surface, which led to improved capacitance^[32] (based on Equation 1.1), as shown in Figures 2.14^[109] and 2.15(b) to (d)^[32]. Therefore, simply optimising electrode area does not necessarily increase capacitance. Moreover, these inter-relationships are also dependent on the charge/discharge rate, with meso- and macro-pores becoming progressively more important.

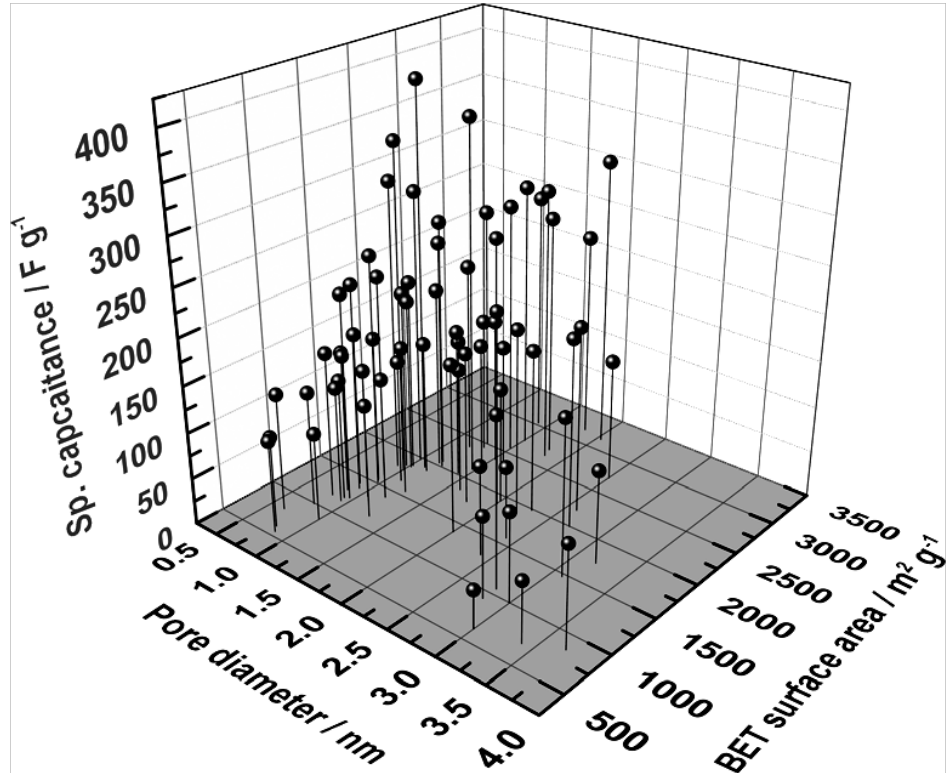


Figure 2.13: 3D graphical illustration of the typical experimental relationship between specific capacitance, BET surface area and the pore diameter^[108].

In aqueous electrolytes, the ionic dimension of cations and anions are less than 0.42 nm and 0.51 nm respectively^[110]. Thus, micropores (especially with pore sizes smaller than

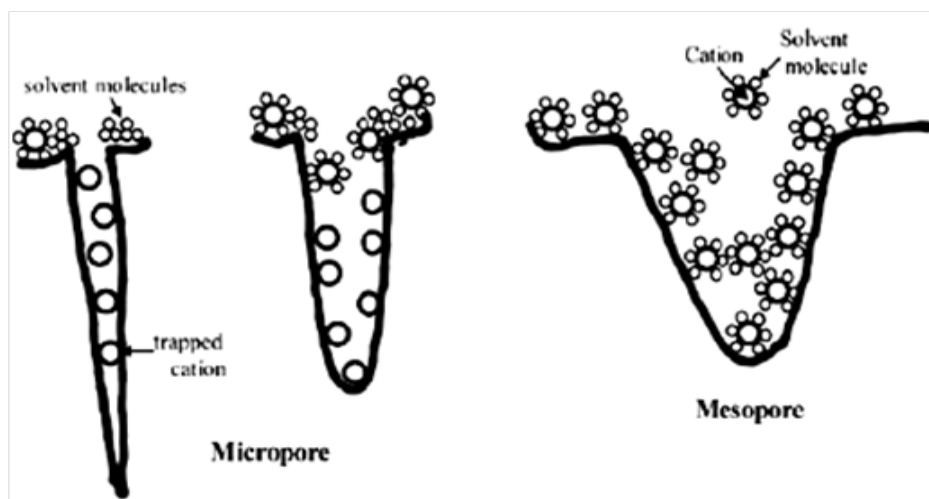


Figure 2.14: Schematic illustration of the adsorption of electrolyte ions with or without solvation to the surface of pores with different pore sizes^[109].

1 nm) are more efficient than mesopores for capacitance enhancement. A study using CDCs showed that: the highest capacitance was achieved when the pore dimension was a little bit narrower than the solvent ion size (peak at 0.7 nm for aqueous electrolyte and 0.8 nm for organic electrolyte), as shown in Figure 2.15^[109, 111].

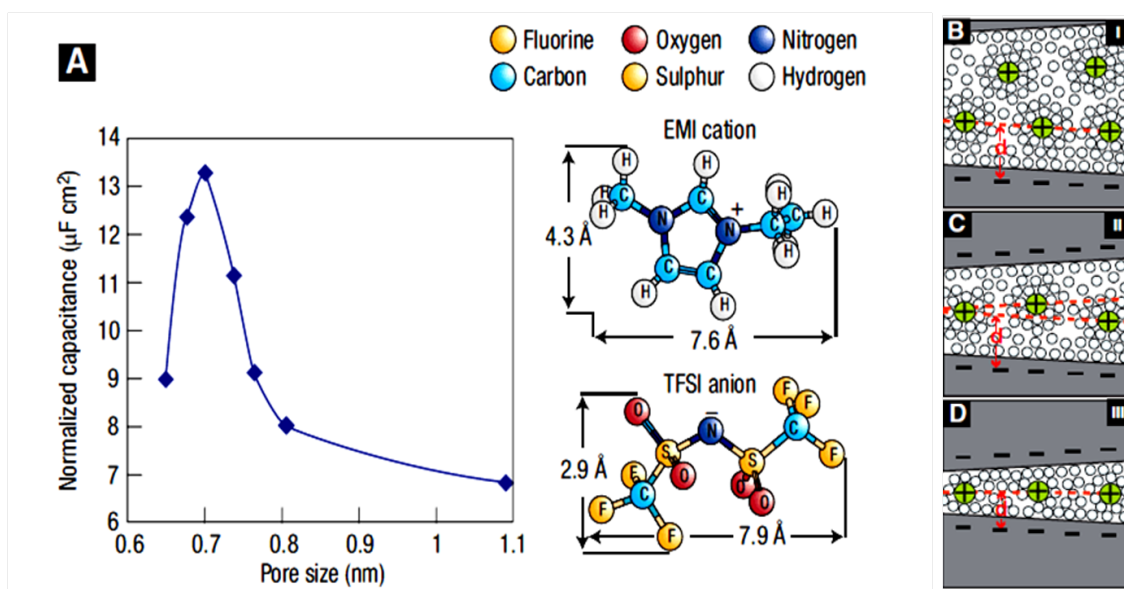


Figure 2.15: (A) The changes of capacitance as a function of the pore size of CDC samples in ionic liquid at 60 °C. Inset illustrating the structure and size of EMI and TFSI ions. (B to D) Drawings of solvated ions residing in pores with distance between adjacent walls (B) greater than 2 nm, (C) between 1 and 2 nm, and (D) less than 1 nm illustrate this behaviour schematically^[109, 111].

Although micropores have a significant contribution to specific capacitance, developing large volume micropores with surface area that is inaccessible for ions cannot improve

the capacitance. In fact inaccessible porosity has a detrimental effect, leading to poor electrical conductivity (loss of power capability) and low volumetric capacitance^[21]. Furthermore, micropores are not helpful at high current densities due to restricted ion transportation into pores smaller than 1.2 nm, and the power density is reduced. For high rate applications (> 1 Hz), mesopores provide entry for ions into the bulk of the material to access the micropores and shorter nanoscale diffusion distances (< 100 nm) are needed. Typical data for the effects of micropore and mesopore volume on specific capacitance are shown in Figure 2.16^[108]. For fixed mesopore volumes, higher capacitance was obtained at higher micropore volumes. For fixed micropore volume, capacitance increases at first with increasing mesopore volume, but deteriorated at high mesopore volumes. The maximum specific capacitance was obtained with a high micropore volume ($1.2 \text{ m}^3/\text{g}$) and a moderate mesopore volume ($0.42 \text{ m}^3/\text{g}$).

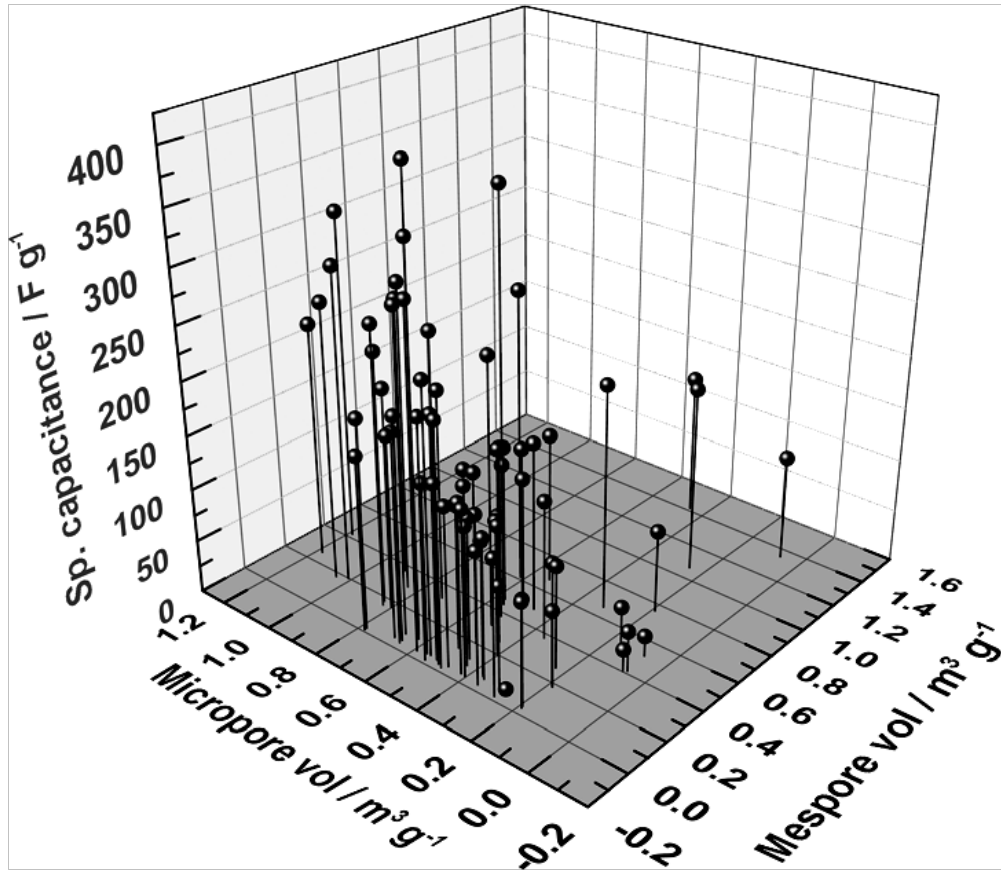


Figure 2.16: Typical data and 3D graphical illustration of the contribution of micro/mesopore volume on the specific capacitance^[108].

2.2.4 Surface treatment

Surface treatment is an important technique for increasing the charge storage in SCs through an increase in the surface area, porosity and wettability of the material, and by introducing a potentially pseudocapacitance mechanism for charge storage^[21, 46, 112]. Surface treatment can be divided into physical activation, such as with CO₂ or steam activation at high temperature, plasma/laser treatments; and chemical activations, such as surface functionalization through acidic/alkali oxidation or grafting of organic groups^[15, 20, 97, 113].

2.2.4.1 Physical activation

Physical activation is used to modify carbon electrode materials by introducing a microporous structure onto the surface and enlarging the existing pore size. Thermal activation such as gasification of carbonized carbon is generally carried out with CO₂, steam, air or any mixture of these gases at high temperature between 800 °C - 1100 °C. The extent of gasification depends on the nature of the gas employed and activation temperature. The gasification reaction with steam and CO₂ can be described as follows:



The chemisorption of produced H₂ or CO on the active centres of the carbon surface will minimize the amount of oxygen functional groups whilst increasing the surface area. Attributed to the moderate reaction speed of CO₂ with carbon materials, activation with CO₂ can achieve a more homogeneous development of porosity in the carbon than

with steam^[114].

2.2.4.2 Surface functionalization

Functionalization techniques have been used to modify carbon electrode surfaces, with the aim of improving their wettability and facilitating rapid electrolyte ion transport within the micropores by enhancing the adsorption of the ions, and introducing pseudo-capacitance which can lead to an increase (5 - 10%) in the final specific capacitance^[115]. Based on the nature of the reaction, surface functionalization can be classified into two main type.

Firstly, oxidizing the carbon surface directly by applying an oxidizing potential sufficiently high, such as using nitric acid or potassium permanganate, to form surface oxygenated functional groups(e.g. -COOH, CO, and others), which can be further used to attach covalently bonded organic groups on the surface^[116]. Carbon electrodes modified by phosphoric acid activation showed a large and stable performance^[117], with stable capacitance at voltages greater than 1.3 V in H₂SO₄ ^[118]. High electrochemical performance (energy density 10 Wh/kg, with power density 10 kW/kg) have been achieved in acidic electrolytes using an AC-based electrode, which has a high concentration of oxygen functional groups but low surface area^[21]. The cyclic voltammograms of activated carbon fibres (ACFs) rich in -COOH or -OH groups are shown in Figure 2.17^[119]. Obvious faradic reaction peaks are obtained on ACFs with -COOH, illustrating the contribution of pseudocapacitance (Figure 2.17(a)). A linear relationship between the amount of oxygen-containing groups and the capacitance C_0 was obtained on both activated carbon and activated carbon fibers (Figure 2.17(b)), thus confirming the enhancement of capacitance with oxygen-containing group functionalization.

The second approach to surface functionalization, termed electrochemical oxidation/reduction, grafts organic moieties to the carbon surface by building up C-C covalent bond between the electrode and the functional groups. Nitrogen-containing function groups

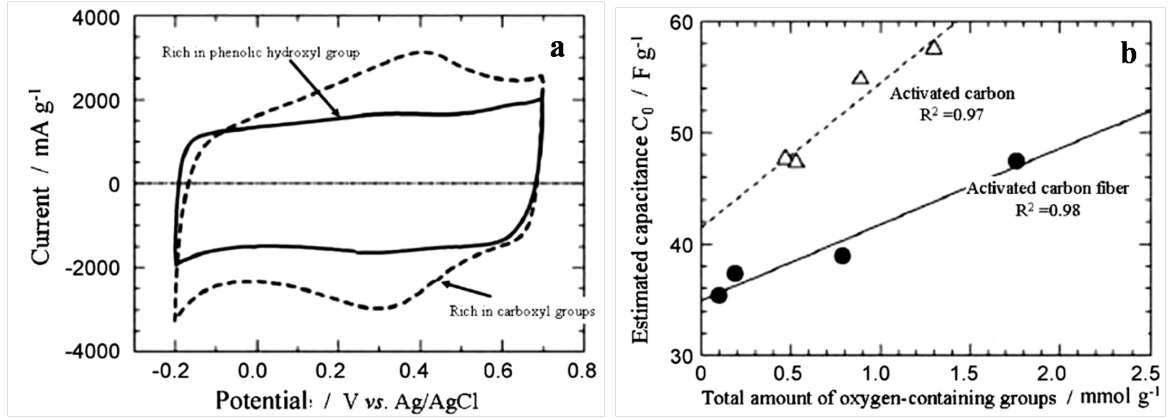


Figure 2.17: (a) Cyclic voltammograms of ACFs with -COOH or -OH groups, (b) the relationship between capacitance C_0 and total amount oxygen-containing groups^[119].

are the mostly commonly used and can increase the ratio of specific capacitance against BET surface area (C_s/S_{BET}) by more than 10 times that of most porous carbon^[120], and increase capacitance in both aqueous and organic electrolytes. The nitrogen-containing functional groups can be introduced by making carbon from carbonized melamine foam^[120], pyridine and quinoline using a mica template^[121], or using organic compounds containing nitrogen^[122--124], treated with urea or melamine^[125]. The maximum specific capacitance achieved was 200 F/g in sulphuric acid electrolyte and 159 F/g in an organic electrolyte respectively, but with characteristic non-rectangular shape, which showed enhanced capacitance in the negative potential side due to adsorption of cations, as shown in Figure 2.18^[112, 126]. Besides nitrogen-containing groups, other functional groups such as primary and secondary alcohols, and carboxylates have also been investigated^[127].

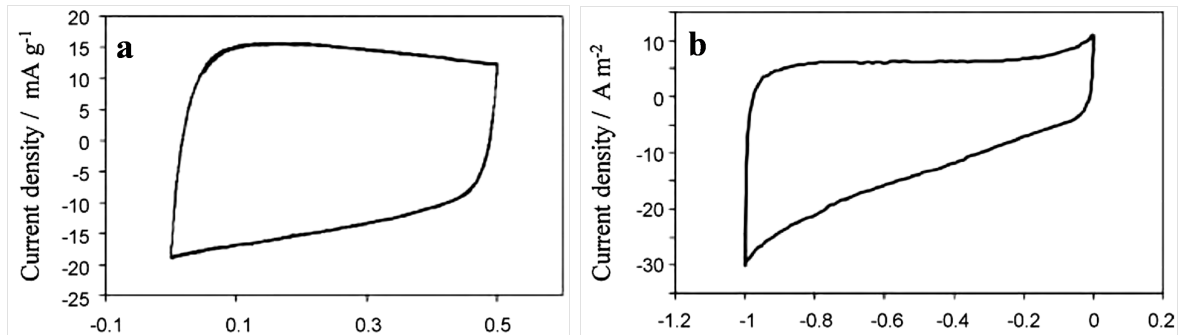


Figure 2.18: Cyclic voltammograms of carbon electrode with nitrogen containing groups in (a) 1 M H₂SO₄ aqueous electrolyte, and (b) 6 M KOH aqueous electrolyte^[112].

However, these introduced surface functional groups (especially oxygen-containing acidic

groups) can have a decomposition effect on the electrolyte, particularly in non-aqueous electrolytes^[21]. In addition, they introduce some detrimental effects on the electrodes, such as high rate self-discharge, higher ESR and leakage current^[46] and reduced electrode stability.

2.2.5 Electrolytes

Choosing the appropriate electrolyte is an important factor for a high performance supercapacitor because of its effect on charge storage speed and operating voltage, which along with its internal resistance, can finally determine the energy density of the cell^[128]. The electrolytes used in ECs are either aqueous, organic or room temperature ionic liquids.

The most commonly employed aqueous electrolytes are 1 M H_2SO_4 and 6 M KOH, and the neutral electrolytes, such as NaCl and KCl. For organic electrolytes, the materials commonly used are acetonitrile (AC), propylene carbonates (PC) and tetraethylammonium tetrafluoroborate (Et_4NBF_4).

2.2.5.1 Operating voltage

The operating voltage of an EC cell is determined by the decomposition potential of electrolyte. Due to the electrolysis of water (the electrodynamic chemical potential window is 1.23 V at 25 °C), the maximum operating voltage for most aqueous electrolyte is limited in practice to a maximum of ~ 1.2 V^[11]. Compared with this, the organic electrolytes can reach operating voltages up to 2.7 V, but are normally set to 2.5 V to prevent overcharging oxidation of electrolyte^[129]. Therefore higher energy density can be achieved and larger amounts of energy can be stored in ECs with an organic electrolyte (Equation 1.2).

However, due to their sensitivity to O_2 and water, organic electrolytes need to be

synthesized and handled in a water/oxygen-free atmosphere, which increases the manufacturing cost. An even higher voltage of up to 4.0 V has been achieved in room temperature ionic-liquid based supercapacitors^[130]. However, due to their generally poor ionic conductivity at room temperature, they are mainly confined to higher temperature applications with little improvement in the electrochemical window (3.25 V at 100 °C)^[130]. The combination of specific cations with anions to improve the conductivity of ionic electrolytes at temperatures between 30 °C to 60 °C is a research trend for the future.

2.2.5.2 Electrolyte conductivity and viscosity

Electrolyte conductivity has a significant effect on the equivalent series resistance (ESR) of ECs cell, which in turn determines the power output (Equation 1.4). Compared with aqueous electrolytes, organic electrolytes have lower conductivity and a relatively high ESR, e.g. conductivity of 6 M KOH at 25 °C is 625 mS/cm and this compares to 20 mS/cm for tetraethylammonium tetrafluoroborate in propylene carbonate (Et₄NBF₄-PC 1 M)^[5]. More than the conductivity, the low wettability caused by the high viscosity of organic electrolyte further increases the ESR. Therefore, although organic-electrolyte based supercapacitors can store a high overall energy thanks to their high operating voltage, their power density is usually lower than that of aqueous electrolyte based supercapacitors due to their much larger ESR.

However, adding salts into organic solvents can increase the transportation of mobile ions in the double layer. This method could solve the low conductivity problem of organic electrolytes to some extent^[5]. To minimize the ESR and maximize the power output, highly concentrated electrolytes are required. However, high concentrations can increase self-discharge rates displayed by EC cells.

2.2.6 Current collector

The current collector is another important component of ECs due to their influence on ESR. A suitable current collector should first ensure that the contact resistance between the electrode material and the current collector is low. It should be stable enough on both positive and negative electrodes in the potential range to prevent degradation caused by anodic oxidation. Furthermore, a suitable current collector should also be chemically compatible with the materials of both electrode and electrolyte. For carbon based electrodes, the matched current collector should not have any related faradic reactions.

To achieve an excellent electrical contact between electrode materials and the current collector, the wettability of the electrode material on the current collector should be considered first. Besides wettability, careful design of the connection can have a strong effect on the reduction of the contact resistance. For instance, carbon nanotubes directly grown on a metallic substrates^[99, 100], or deposited carbonaceous powder on aluminium foil substrate by sol-gel processing^[131].

At present, in aqueous electrolytes, stainless steel is used for sulphuric acid, nickel or copper are used for alkaline solutions, sometimes, to ensure the stability of current collector, gold was also considered^[132]. In organic electrolytes, aluminium is the most commonly used current collector with a passive nanoscale Al_2O_3 layer with negligible effect on ESR, which can protect the under-lying metal^[109]. Besides metals, ultra-porous carbon aerogels and CNT films have also served as current collectors for ECs in some reports^[118, 133].

2.3 Thin film processing techniques

Electrochemical supercapacitors could be developed further to achieve greater commercial potential. To provide higher performance SC cells with lower prices, many

manufacturing issues need to be considered alongside the chemical and physical aspects already described, such as minimisation of production cost, ensuring quality and uniformity of fabrication, minimizing packaging weight (the presence of inactive weight is a major reason for the current low energy densities of supercapacitor cells) and thickness, to ensure long cycle and shelf life by minimizing leakage currents that are commonly caused by impurities in electrodes and electrolytes.

As mentioned in Chapter 1, the current technology for preparing commercial supercapacitor electrodes is pressing a slurry mixture of carbon-based materials into a bulk or thick film ($> 80 \mu\text{m}$). Electrodes in the form of a thin and flexible film is a new and attractive tendency in the manufacture of supercapacitors to meet the requirements of functional devices, such as smart cards, displays and implantable medical devices. For fullest potential, these approaches need to be combined with thinnest Cu and Al based current collectors, which are now available in thickness $< 20 \mu\text{m}$. Several methods have been used to prepare the thin film electrodes, including vacuum filtration^[134], inkjet printing^[135], spin/dip coating^[136], using colloidal crystal templates^[137], and electrophoretic deposition (EPD)^[138]. A simple and quick air brush technique has also been used to produce CNT coatings with controlled transparency between 0% and 100%. These manufacturing routes have their own advantages and disadvantages, but most of them are difficult or too expensive to scale up for widespread commercialization, and present severe limitations in terms of film quality or production efficiency.

2.3.1 Vacuum filtration

Vacuum filtration has been used to produce CNT ‘buckypaper’^[134]: the CNT suspension is first prepared with the addition of a surfactant or chemical functionalization^[95], the CNT-based suspension is then vacuum-filtered through a filtration membrane, followed by removal of the surfactant with purified water, and finally the filtration membrane is dissolved in a solvent to produce the free-standing buckypaper.

The vacuum filtration technique enables simple assembly of a binder-free thin film carbon electrode and has been used in many cases of CNT-based thin film production^[139, 140]. However, this processing technique is associated with poor film thickness control, inhomogeneous surface morphology, weak adhesion and high resistance between the carbon electrode and current collectors when used in electrochemical devices^[140]. Another drawback of the vacuum filtration technique is that it requires the carbon films to be first formed on a filter paper, making it difficult to implement coating on a large scale.

There is therefore a need to develop a technique that allows for practical implementation of carbon coatings that is scalable, cost effective and suitable for roll-to-roll processing.

2.3.2 Inkjet printing

Inkjet printing technology has the advantage of room temperature printing. The prepared stable carbon material ink is pressured by an ink pump and directed from the ink cartridge through a microscopic nozzle, where the stream of ink is broken into small droplets by ultrasonic vibration caused by a piezo-electric actuator. The resulting small droplets are then ejected in an electrostatic field to get near-uniform diameter droplets, and these are directed (deflected) to the correct position on the substrate, as shown in Figure 2.19(a). SWCNT-based and graphene-based thin film electrodes have been fabricated by inkjet printing technology^[135, 141, 142], as shown in Figure 2.19(b). However, pre-coating was required to enhance the adhesion and electrical connection between the carbon thin film and substrates. The requirement for ink stability leads to complex procedures and low utilization of materials (half hour ultrasonic, 24 h stir and four centrifuge steps), and 20/30 times repetition of printing on each substrate for good electrical conductivity also leads to a time-consuming process^[135, 141].

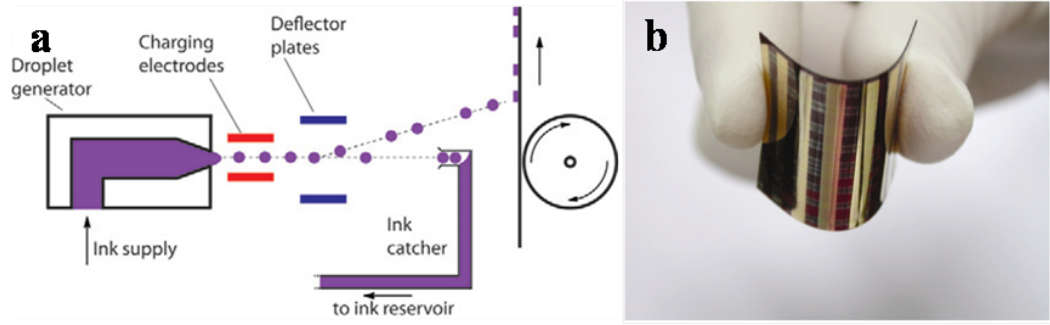


Figure 2.19: (a) Schematic of inkjet printing principle, and (b) graphene pattern inkjet printed on a polyimide substrate^[141].

2.3.3 Roll-to-roll processing and transfer

A schematic illustration of the three essential steps in roll-to-roll processing of graphene thin films is shown in Figure 2.20^[143]: (i) the polymer support is first adhered to the graphene film, which was grown on a copper foil, and passes between two rollers; (ii) then the copper layers were released by etching in 0.1 M $(\text{NH}_4)_2\text{S}_2\text{O}_8$ solution, (iii) finally, the graphene layers were released from the polymer support and transferred onto a target by heat treatment.

However, while this process has scalable potential, it is primarily designed for the production of very thin films (micron or below) for transparent/conducting applications, rather than energy storage.

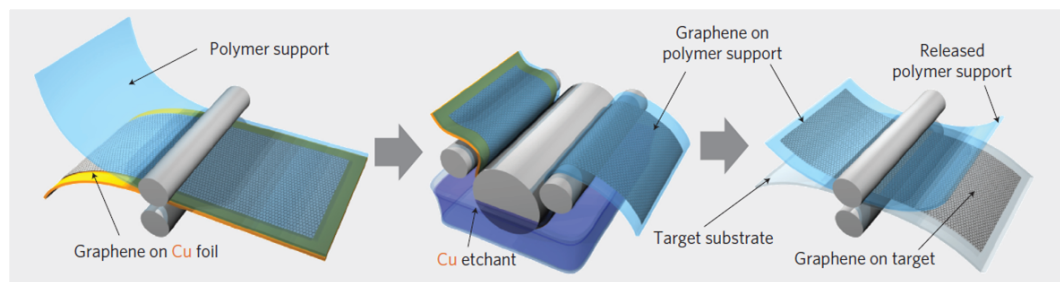


Figure 2.20: Schematic illustration of the roll-to-roll based production of graphene films^[143].

2.3.4 Dip-coating

Dip-coating is a simple process and also has some (more limited) potential for scale up. Compared with other processing techniques, dip-coating can produce carbon thin films with amongst the lowest sheet resistance^[136].

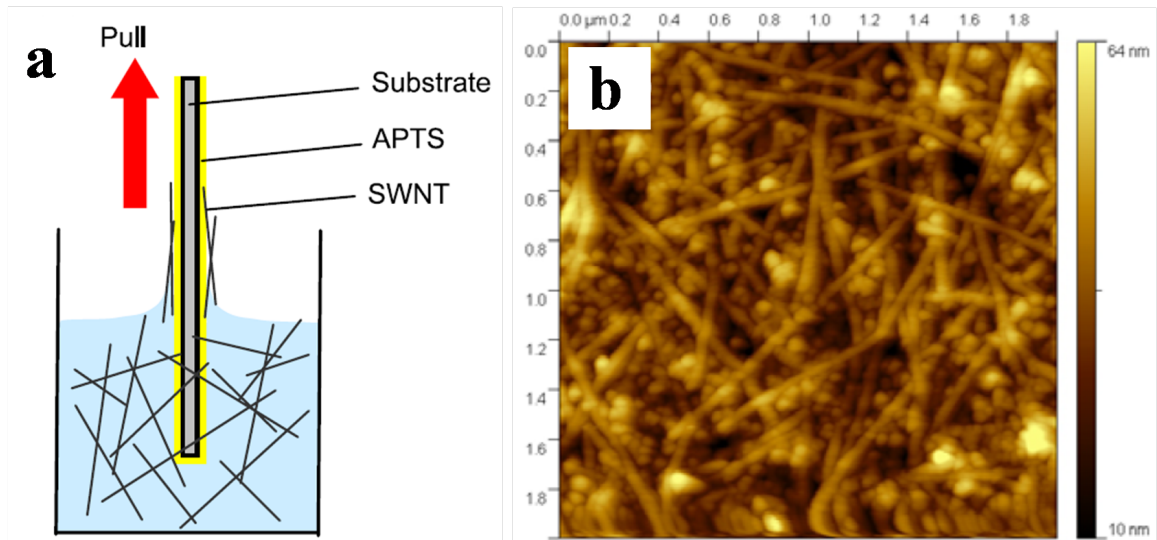


Figure 2.21: (a) Schematic graph illustrating the dip-coating technique, and (b) atomic force microscopy (AFM) image of SWCNT/APTS (3-aminopropyltriethoxysilane) thin film surface morphology^[136].

The biggest problem with dip-coating process for EDLC manufacture is that it is time-consuming. For a single coating, the substrate needs to be dipped into a carbon suspension for a few minutes to stabilize, then pulled out of the suspension at a very low speed (5 mm/min), followed by deionized (DI) water washing and finally left for dry (as shown in Figure 2.21(a))^[136]. To produce a CNT-based thin film with good conductivity, more than 10 coating layers are required. Another problem for dip-coating is that carbon materials are naturally hydrophobic, therefore, suitable surfactants and adhesion promoters such as aminopropyltriethoxysilane (APTS) must be introduced to improve deposition on hydrophilic substrates, or by introducing self assembly layer-by-layer (LBL) systems through creating negatively/positively charged CNTs via chemical functionalization, as shown in Figure 2.22^[144].

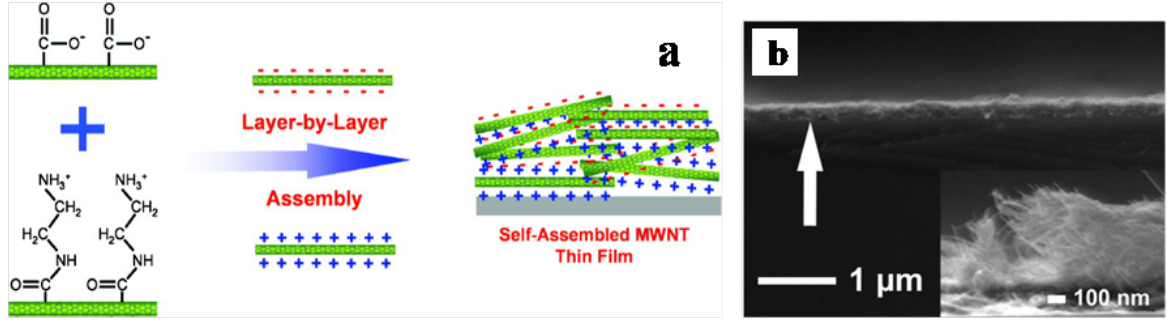


Figure 2.22: (a) Schematic illustration of self-assemble MWNT thin film using layer-by-layer (LBL) technique, and (b) SEM image of 15 bilayers of MWNTs thin film fabricated by dip-coating and LBL^[144].

2.3.5 Two-dimensional colloidal crystal templates

Using colloidal arrays as sacrificial templates has been investigated in many nanostructures. To fabricate CNT films, a 2D colloid-CNT complex crystal films was first formed on a flexible substrate, and then followed by an elimination of the crystallized colloidal particles, leaving a well ordered CNT network structure with regular pores, as showed in Figure 2.23^[137]. This technique can be used to produce continuous carbon films with good electrical properties, controlled film thickness, density and microstructures. No special equipments are required and it is time and materials efficient. The major disadvantage of this technique is that the structure between each layer is always random^[137].

2.3.6 Electrophoretic deposition

Electrophoretic deposition (EPD)^[145–147] has two essential steps: first, the suspended charged particles are forced to move towards an electrode under an applied electric field; then particles deposit on the electrode forming a homogeneous compact or film^[145], as shown in Figure 2.24^[138]. Supercapacitors produced from these electrodes have an ideally box-shaped cyclic voltammogram even at a high scan rate of 1000 mV/s, and high power density of 20 kW/kg. The electrophoretic deposited carbon films can also be used as a coating to reduce the contact resistance between other

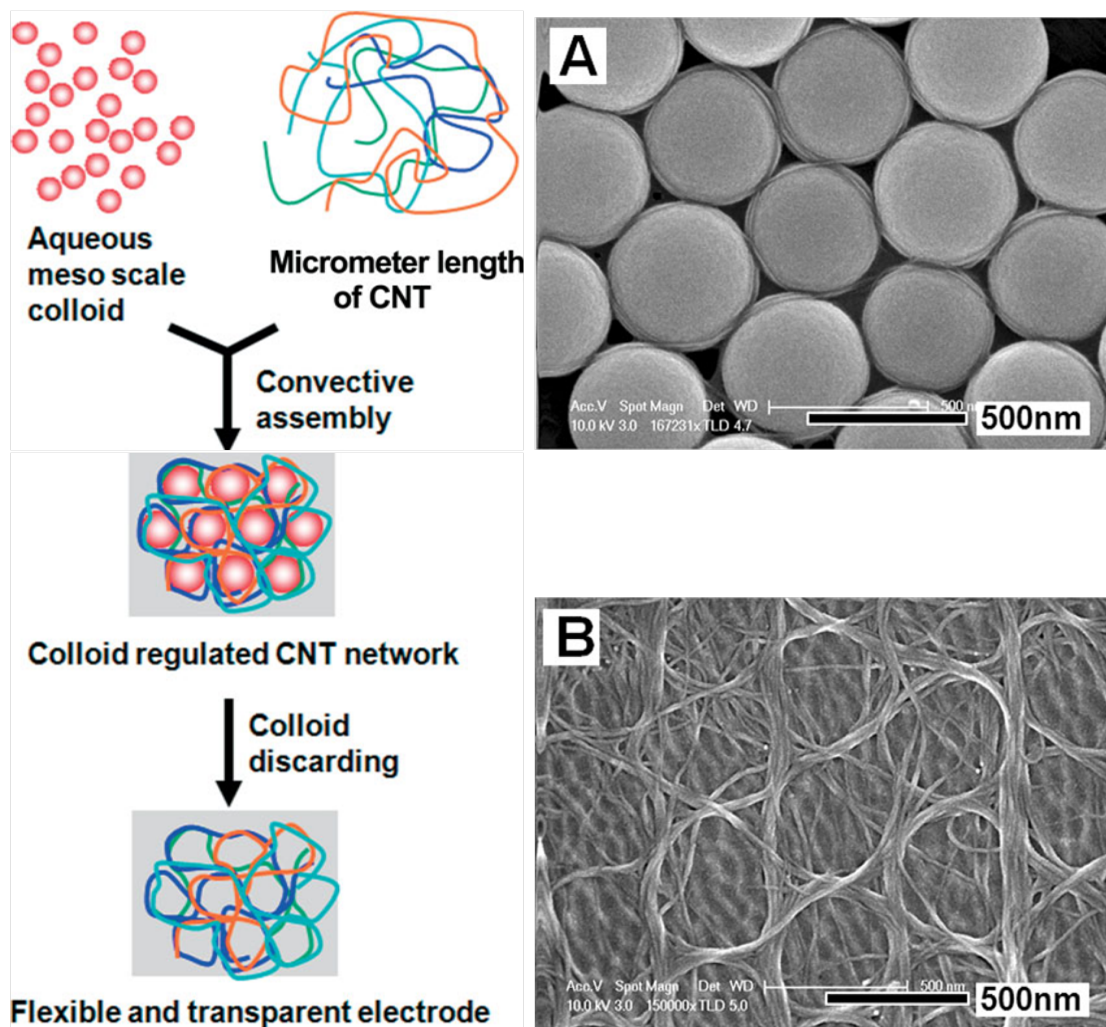


Figure 2.23: Schematic illustration of the procedure for the fabrication of CNT film with unique network structures. (A) SEM surface images of 2D silica colloid-CNT complex crystals, and (B) SEM image of the CNT network morphology after removing the colloidal particles^[137].

active materials and the current collector.

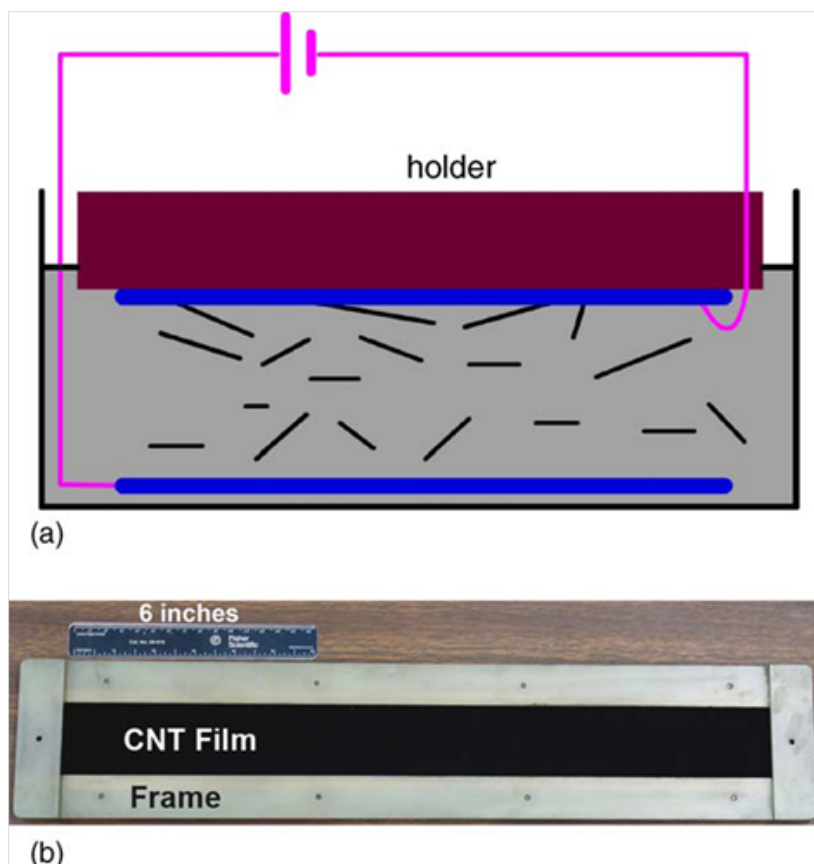


Figure 2.24: (a) Schematic illustration of the EPD principle, and (b) optical image of CNT thin film fabricated by the EPD technique^[138].

The EPD technique can be used for any solid with fine powder ($< 30 \mu\text{m}$) or colloidal suspension. It is suitable for room-temperature and large-scale thin film fabrication with good adhesion properties. The shape and size of the substrates on which the thin film is formed could be flexibly designed^[138, 148]. However, the EPD technique is still challenged by the film thickness/mass and surface uniformity control^[140].

2.3.7 Spray deposition

The electrostatic spray deposition (ESD) technique has been used for thin film metal oxide preparation for the cathode materials of a lithium battery^[146, 149]. It can also be used to produce binder-free, flexible conductive carbon layers and thin film transistors. In this technique, a carbon suspension was sprayed downwards to the substrate

under an electrostatic field, which is produced by constant voltage applied between the spray nozzle and the substrate, as shown in Figure 2.25^[127]. The CNT film electrode prepared by ESD can have a well-entangled porous structure and good adherence to the substrate, with a specific capacitance that has reached 108 F/g^[127].

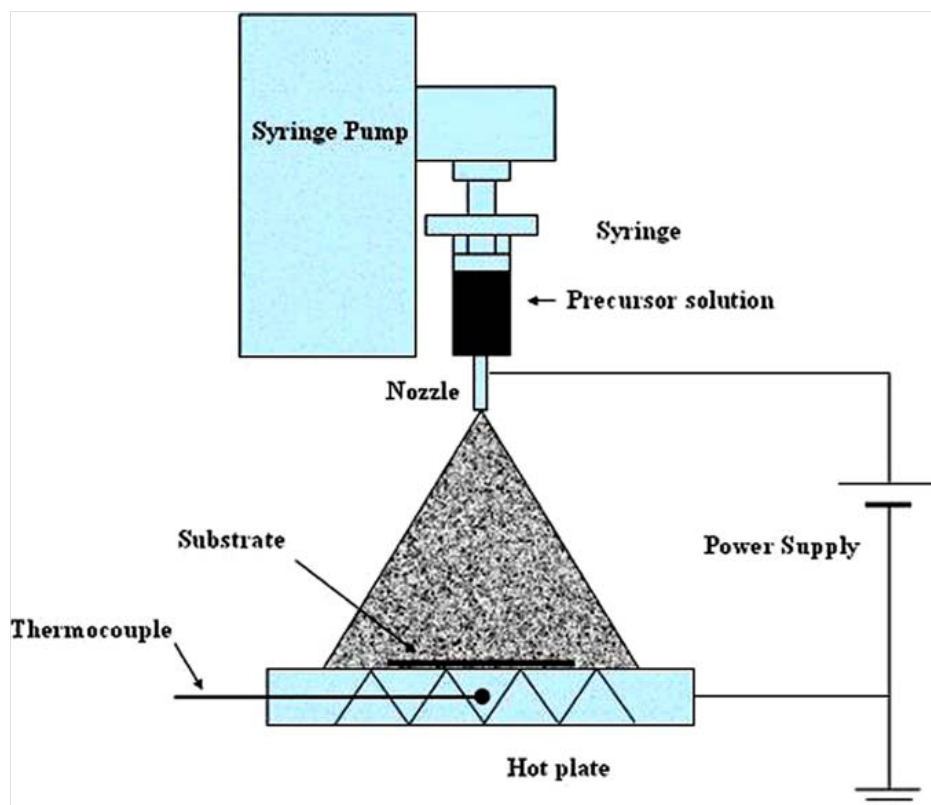


Figure 2.25: Schematic graph illustrating the electrostatic spray deposition^[127].

Spray deposition is quite similar, but forms the thin film without the need for an electrostatic field. The procedure of spray deposition is simple: a surfactant is added to the suspension (or chemically functionalized suspension) usually prepared with the help of ultra-sound. The suspension is then atomized at the tip of spray nozzle and sprayed directly onto a heated substrate with compressed air or an inert gas. The fine droplets are dried immediately at the hot substrate surface, leaving the CNTs or other materials to form an entangled network with flat film surface morphology and a homogeneous film structure^[150--154]. The spray deposited CNT network can be used as thin film electrodes without any further treatment.

With the advantages of a low cost processes, more accurate film thickness control, high uniformity in film thickness, morphology and electrochemical properties, and good

compatibility with different substrate shapes, the spray technique can replace the time consuming and costly vacuum processes, and may be suitable for large-scale production. However, the adhesion of carbon or other materials to different substrates and the dispersibility of carbon materials are serious drawbacks requiring further investigation.

In this project, a spray deposition is developed for the fabrication of carbon nano-structured and micro-structured energy storage devices in a thin film format, with controlled film thickness, homogeneous film surface morphology and high electrochemical performance for both supercapacitors, and lithium ion battery anodes.

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Chapter 3

Experimental Techniques

In this chapter, the experimental procedures used throughout the thesis for the manufacture of EDLC electrodes is described, along with the various characterisation techniques used across all electrode types. For those materials and processes that were studied more extensively on the basis of standard tests, these specific analyses and characterisation details are given later in the following Chapters.

3.1 Carbon processing

Commercial carbon materials termed synthetic graphite, activated carbon, and carbon black were all used to produce thin film EDLC electrodes. For some carbon particles, ball milling and CO₂ activation treatments were used to reduce the as-supplied particle size to make them processable using the spray deposition technique, or to tailor the particle size and/or pore size distribution in pursuit of improved performance.

3.1.1 Ball milling

Ball milling was used in many cases as the first step of processing to reduce the mean size of feedstock carbon particles towards the nanoscale. Since EDLC electrodes rely on surface area for their performance, a high specific surface area was a general requirement. At the same time, ball milling also helped to provide a more uniform particle size distribution, which was assumed to help the formation of a comparatively homogeneous and reproducible electrode microstructure. The ball milling treatment was performed at room temperature under air atmosphere in a Fritsch ‘Planetary 6’ ball mill in which the deformation forces were mostly shear, as shown schematically in Figure 3.1.

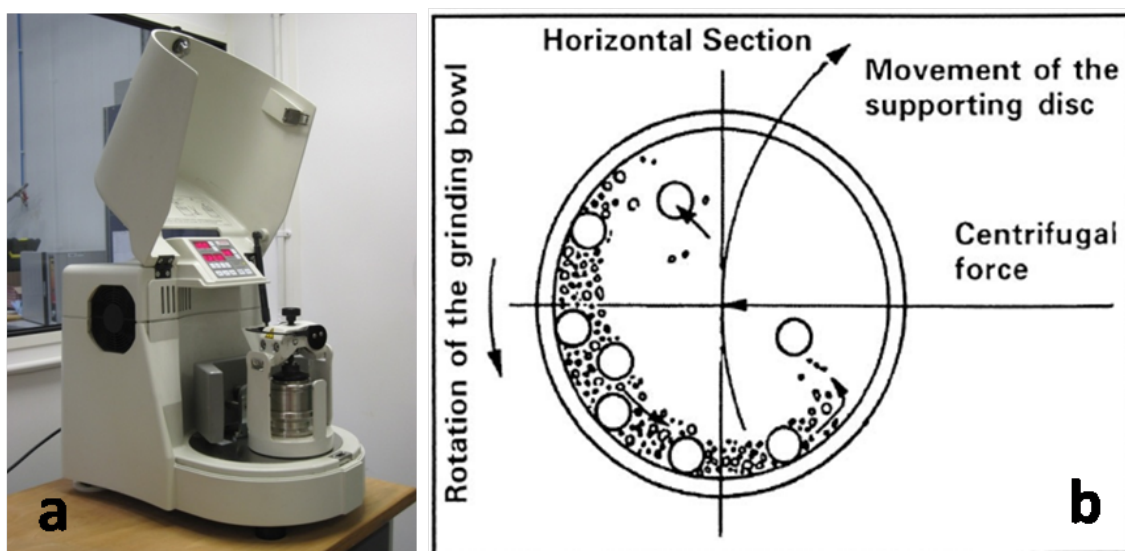


Figure 3.1: (a) Fritsch ‘Planetary 6’ one station ball mill, and (b) schematic depicting the ball motion inside the ball mill ^[1].

The feedstock carbon powders were loaded into a stainless steel jar (80 ml in volume) together with stainless steel balls (10 mm in diameter). The milling conditions varied the weight-to-ball ratio (1/15 to 1/75), rotation velocity (200 rpm to 600 rpm), and milling time (2 h to 20 h). A total ball weight of 75 g was kept constant. To avoid any large increases in temperature during the milling process, the milling treatment was interrupted by computer control every 30 min and rested for 30 min.

3.1.2 Surface treatment by CO₂ activation

In some situations, CO₂ activation treatment was subsequently applied to ball milled carbons to further increase surface area, pore volume, and tailor pore size distribution. As already described in Chapter 2, activation is used widely in commercial supercapacitors to increase surface area. The activation was carried out in a tube furnace as shown in Figure 3.2(a). A ceramic boat loaded with 0.5 g ball milled carbon powder was put in the middle of the tube. The tube furnace was heated (10 °C/min) from room temperature to the activation temperature of 800 °C in Ar atmosphere to prevent oxidation. When the activation temperature was reached, the gas stream was then switched to CO₂ and maintained with a flow rate of 200 ml/min for 5 h. The furnace was finally cooled down to room temperature under Ar protection. The activation procedure is shown schematically in Figure 3.2(b).

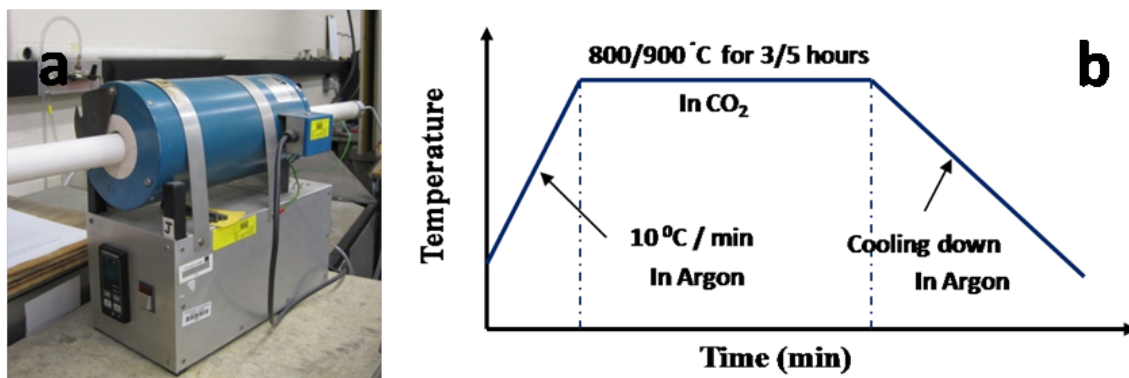


Figure 3.2: (a) Furnace used for CO₂ activation, and (b) schematic of temperature-time history for CO₂ activation of the carbon materials.

The specific surface area and pore size distribution of carbon powders were analysed by N₂ adsorption before and after ball milling, and after activation treatments, (see later).

3.2 Electrochemical double layer capacitor production

3.2.1 Suspension preparation

As the carbon electrodes for EDLCs were produced by a spray deposition approach, a homogeneous and stable suspension of carbon powders in a fugitive liquid carrier was firstly required. To disperse the carbon particles effectively, two kinds of suspension were studied: deionized water as the aqueous fugitive carrier, and n-methylpyrrolidone (NMP) as an organic alternative.

For the aqueous based suspensions, 0.1 - 5 wt.% (with respect to weight of carbon powder) of sodium carboxymethyl cellulose (CMC) was used as a surfactant to prevent agglomeration and to provide the best suspension stability. The pH value of the CMC containing suspensions was adjusted to 10.5, based on the literature^[2].

Carbon powders were then further dispersed into the CMC aqueous suspension with ultrasonication using a probe (600 W, 20 kHz) in an ice bath, to form stable suspensions (no obvious sedimentation in a few hours) with concentrations of 0.5 to 20 mg/ml.

For NMP, carbon powders were directly dispersed into the NMP in less than 10 min, again using ultrasonication (600 W, 20 kHz) in an ice bath to form stable suspensions of concentration 20 mg/ml.

3.2.2 Spray deposition of electrodes

Carbon electrodes were formed by spray deposition of the suspensions on different substrates, including stainless steel, Cu foil or Al coated polyethylene terephthalate (PET) film. Two types of spray deposition facilities were used, and the apparatus are shown schematically in Figures 3.3(b) and 3.4(b).

The key parts of both spray deposition apparatus were: an industrial spray nozzle (Lechler Ltd, details given later) which sprayed onto a heated substrate which maintained the substrate temperature at 110 °C for the aqueous based suspensions and 200 °C for the NMP based suspensions. The suspension was delivered to the nozzle by either a PUMP-NE-300-U syringe pump from New Era Pump system (2 - 5 ml/min), or a 300 series peristaltic pump from Watson-Marlow (2 - 20 ml/min), atomized continuously in the nozzle using 300 - 400 kPa compressed air with suspension flow rates of 2 - 20 ml/min. The spray was directed vertically downwards onto the substrates at a spray distance of 20 cm. Depending on the size and thickness of electrodes, the typical deposition times were in the range of 1 - 30 min.

For both configurations of equipment, spray deposition must take place in a confined, well-ventilated environment. For the long flexible electrodes formed on a drum, spraying took place in a closed cabinet (Figure 3.3(a)) maintained at a reduced relative pressure by means of a strong extraction flow to a microfilter array located on the exterior of the building; while for small flat electrodes, the entire spray apparatus was housed in a fume cupboard, as shown in Figure 3.4(a).

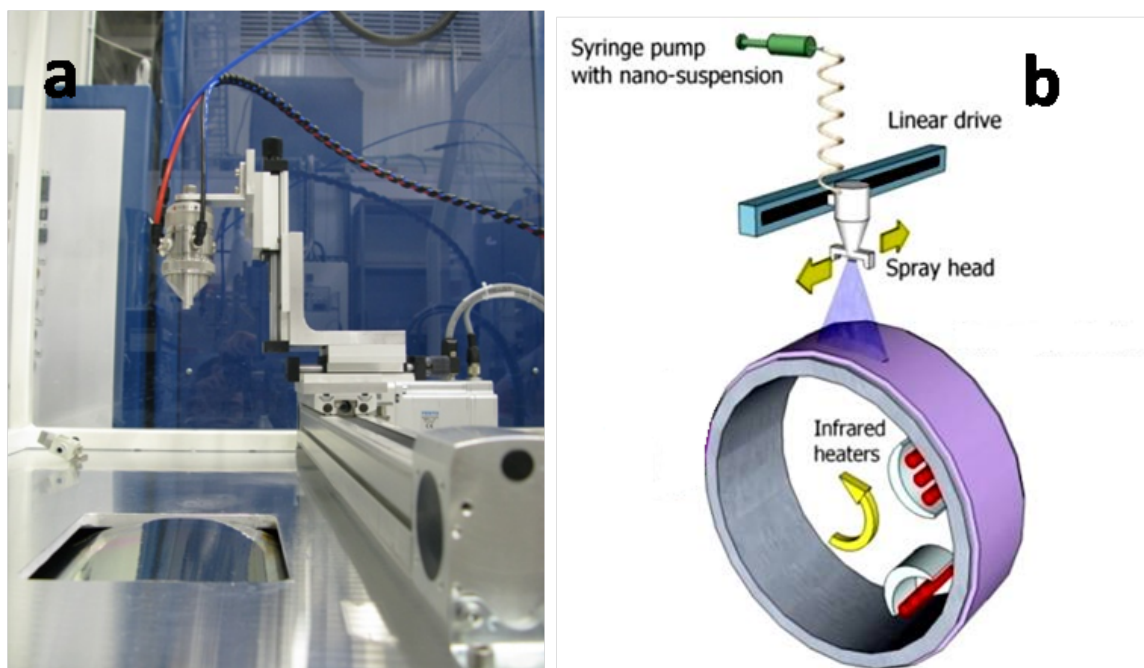


Figure 3.3: (a) Image of the spray deposition apparatus for one meter long flexible electrodes, and (b) schematic of the process for the spray deposition of one meter long electrodes.

As shown in Figure 3.3(b), to produce the long film electrodes, foil substrates were wound onto the heated drum which was rotated under a linearly reciprocating nozzle. To produce large area flat surface electrodes, substrates sat on a flat heating plate (30 cm $\times$ 30 cm, Al, Hillesheim, Germany) which was moved in a controlled x-y path plan under a fixed nozzle, as shown schematically in Figure 3.4(b). As exhibited in Figure 3.4(c), the starting point (x-y position), pitch between rasters, spray lengths and the coating speed can be controlled by the user. Typical values were 1 mm pitch, 50 mm $\times$ 50 mm spray area, 200 mm/s for small samples production and 2 mm pitch, 130 mm $\times$ 130 mm, 200 mm/s for large samples production.

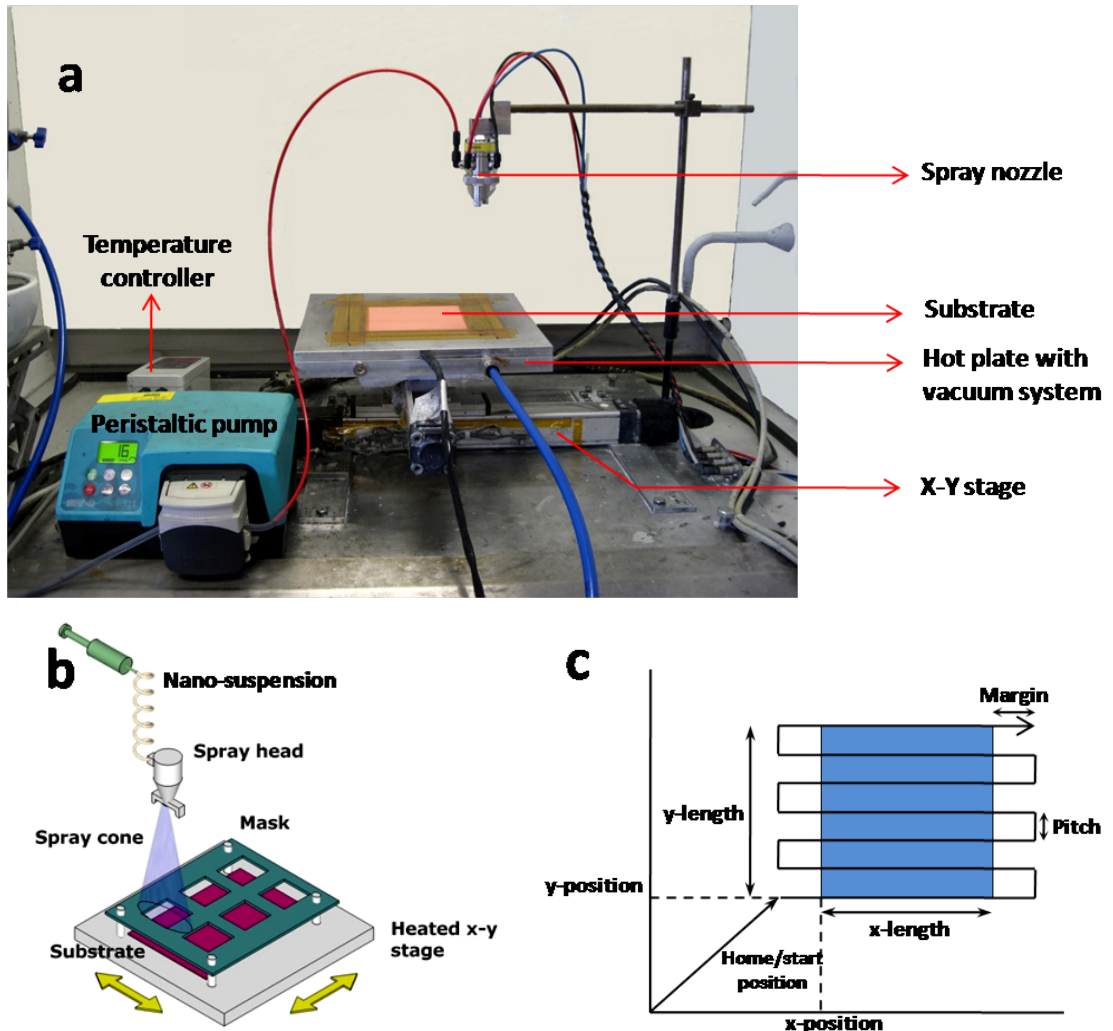


Figure 3.4: (a) Image of the spray deposition apparatus for large area flat electrodes, (b) schematic diagram of the apparatus for the spray deposition of electrodes, and (c) schematic of the substrate movement under the spray.

As shown in Figure 3.5(a), the spray nozzle consisted of five parts: spreader, fluid nozzle, main body, the needle and the body. The nozzle body had five inlet ports,

two for different liquids (suspensions), and the other three for piston air (controls the position of the needle), atomizing air and fan air (to control the spray cone shape) (Figure 3.5(b)). As shown in Figure 3.5(c), atomising air is fed around the outside of the fluid nozzle, mixing and atomizing the liquid from the fluid nozzle to form fine ($< 50 \mu\text{m}$) liquid droplets. By varying the atomizing air pressure and fan pressure, the desired droplet size and spray pattern can be achieved. The piston air is supplied to retract or extend the needle. Because the liquid and air pressure are independently controlled, different combinations of these pressures can be used to change the spray cone angle, and consequently change the spray properties.

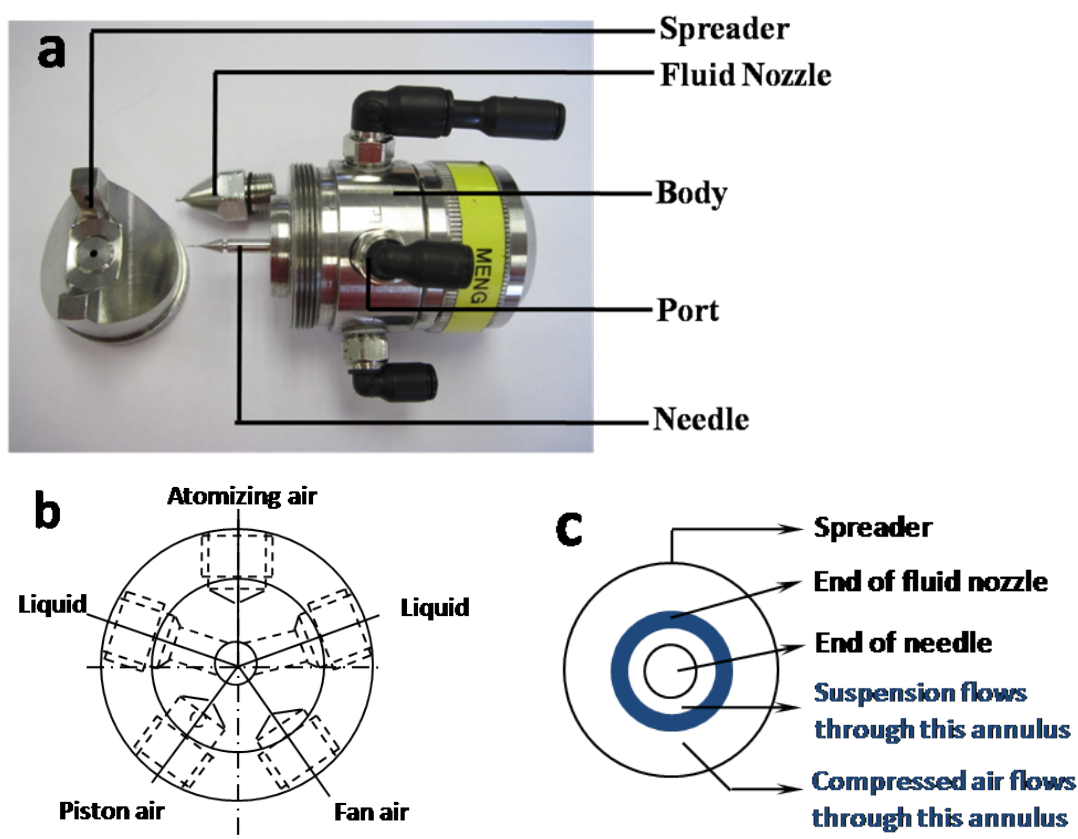


Figure 3.5: (a) Nozzle contents: spreader, fluid nozzle, main body, ports and needle, (b) schematic of five ports on the nozzle body, and (c) schematic planform of spreader.

In order to produce high quality carbon film electrodes, the spray parameters such as spray air pressure, substrate temperature, heating plate moving speed, moving space and suspension flow rate were carefully studied, and were controlled using the operator panel shown in Figure 3.6. The detailed experimental parameters are given in each subsequent chapter.

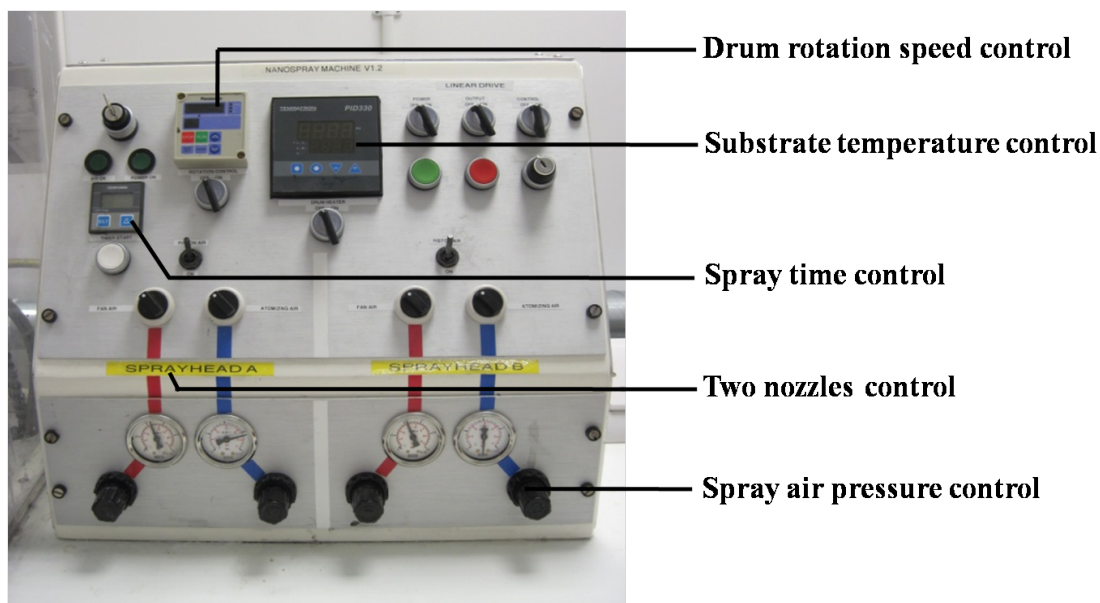


Figure 3.6: Control parameters for the spray deposition process.

To ensure good adhesion of the carbon films for subsequent electrochemical measurements, a few layers of poly(ethyleneimine) (PEI) was pre-sprayed on substrates, and has previously been shown to have no effect on electrochemical properties in electrolytes of interest in this thesis [3].

3.2.3 Preparation for electrochemical testing

For thin film battery electrode production in Chapter 7, gentle hand controlled roller pressing was used to increase the density of the film electrodes.

For the subsequent battery testing, sprayed and rolled electrodes were cut into round discs with a diameter of 12.5 mm, and sealed into a coin cell using a compact hydraulic crimping machine (at St Andrews University), as shown in Figure 3.7(a). The placing of cathode/anode, separator, spacer and spring inside the coin cell was followed according to the order shown in Figure 3.7(b). All the coin cells were assembled in an Ar-filled glove box, where the moisture content of the atmosphere was controlled < 2 ppm. The entire procedure conformed to standard practice used many hundreds of times in the laboratory of Prof. P. G. Bruce, St Andrews University, who provided training during a 1 week visit.

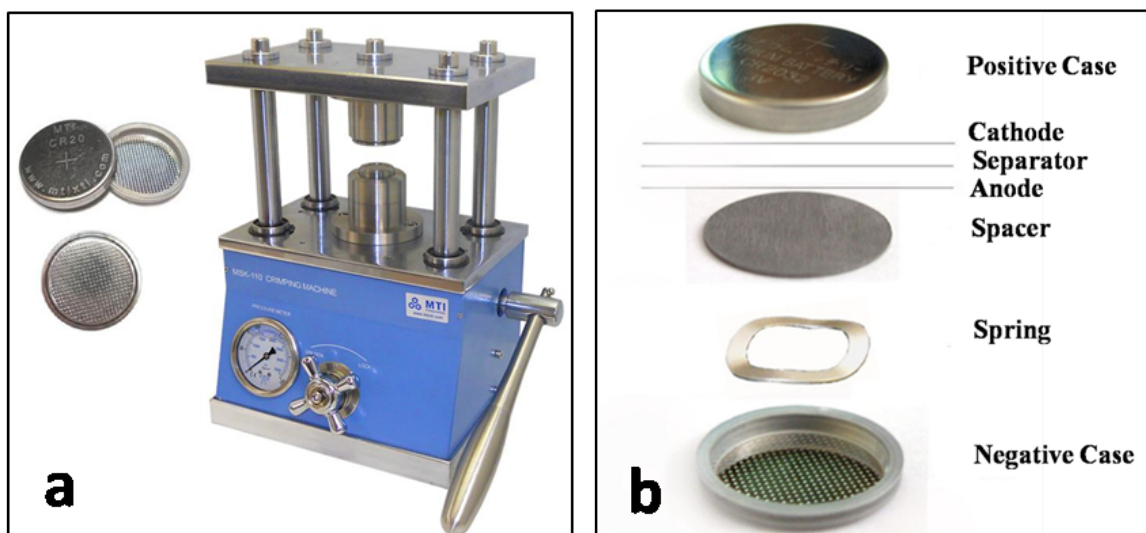


Figure 3.7: (a) Compact hydraulic crimping machine for coin cell sealing, and (b) coin cell assemblage order.

Supercapacitor electrodes were not rolled and were tested as both half-cells and full-cells, as described later.

3.3 Physical characterization

3.3.1 Particle size

The carbon particle sizes were measured using a Mastersizer 2000 Analyser (Malvern Instrument) using a laser light diffraction technique and Mie/scattering measurement principle. A laser beam was passed through a dilute suspension of carbon powders and scattered by the powder samples, as shown in Figure 3.8^[4]. The carbon powder sizes were calculated from the diffraction fringes based on the principle that the diffraction angle is inversely proportional to the particle diameter, and powders are assumed to be spherical.

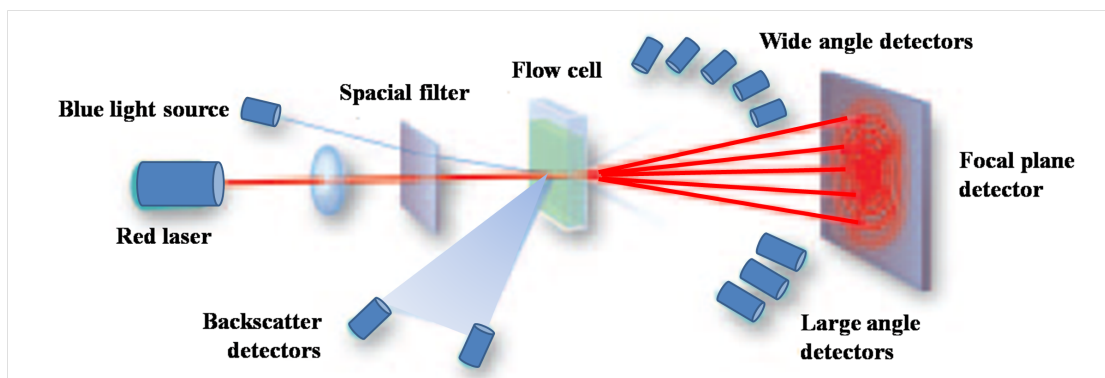


Figure 3.8: Schematic of the principle of operation of laser diffraction used in the Mastersizer 2000 particle size analyser.

3.3.2 X-ray diffraction

The crystalline structure of the ball milled carbon samples was investigated in a Siemens D500 X-ray powder diffractometer with Cu K_{α} radiation ($\lambda = 0.154$ nm) in the 2θ range from 10° to 120° . In principle, XRD can provide information on the nature of crystal phases, the presence of amorphous phases, and under some conditions, indications of particle size and residual strain.

3.3.3 Brunauer-Emmett-Teller/micropore analysis

The porosity of carbon powders were investigated using N_2 adsorption/desorption behaviour in a Micrometrics Gemini VI, as shown in Figure 3.9(a). All the samples were prepared by degassing at 200°C under nitrogen (N_2) atmosphere overnight to remove physically adsorbed molecular species before the measurements were taken. All the sample weights were measured after degassing.

The specific surface area (S_{BET}) was calculated by the BET (Brunauer-Emmett-Teller) method, which is an extension of Langmuir's kinetic theory (for monolayers only) to multilayer adsorption with the assumptions as follows [5, 6]:

1. The uppermost molecules in adsorbed stacks are in dynamic equilibrium with the vapour;

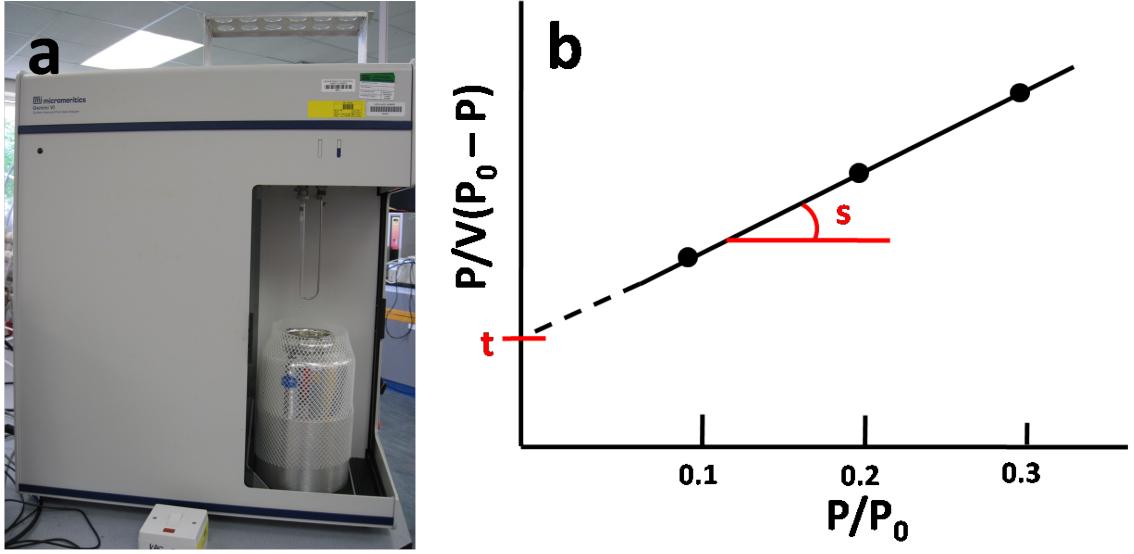


Figure 3.9: (a) Micrometrics Gemini VI instrument used for BET surface area and pore size measurements, and (b) typical BET plot.

2. The actual location of the surface sites covered by one, two or more layers may vary but the number of molecules in each layer will remain constant.

The resulting BET equation is expressed by:

$$\frac{P}{V(P_0 - P)} = \frac{1}{CV_m} + \frac{C - 1}{CV_m} \times \frac{P}{P_0} \quad (3.1)$$

where P and P_0 are the equilibrium and the saturation pressure of adsorbates at the temperature of adsorption, V and V_m are the quantities of the adsorbed gas and the monolayer adsorbed gas, and C is the BET constant. As shown in Figure 3.9(b), a straight line can be obtained when $P/V(P_0 - P)$ is plotted versus P/P_0 in the range of $0.05 \leq P/P_0 \leq 0.35$. The slope s and the intercept t of the BET plot are:

$$s = \frac{C - 1}{CV_m} \quad (3.2)$$

$$t = \frac{1}{CV_m} \quad (3.3)$$

The weight adsorbed in a monolayer can be calculated by:

$$V_m = \frac{1}{s + t} \quad (3.4)$$

The determination of specific surface areas from the BET theory is a straight forward application of Equation (3.4):

$$S_{BET} = \frac{S_t}{m} = \frac{A_m N_A V_m}{m V_0} \quad (3.5)$$

where S_t is the total surface area, m is the mass of absorbing sample, A_m is the area of the surface occupied by individual gas molecules (0.162 nm² for N₂), N_A is Avogadro's number, and V_0 is the molar volume of the gas, which is 22,414 cm³/molar for gas at atmospheric pressure.

The adsorption-desorption behaviour was measured using N₂ at 77K, in the relative pressure range from 0.001 to 0.95, and a 72-point method was used.

The specific internal surface (S_{inter} , from micropores), external surface (S_{exter} from particles and mesopores) were determined using a t-plot method as follows^[7]:

$$\bar{n} = f_c(P/P_0) \quad (3.6)$$

$$t = \bar{n} \times t_m = f_c(P/P_0) \times t_m = F_c(P/P_0) \quad (3.7)$$

where $\bar{n}$ is the number of adsorbed layers, t_m (nm) is the thickness of monolayer, t (nm) is the total thickness of adsorbed layers, f_c and F_c are functions of P/P_0 .

Because the pore volume (V) is also a function of (P/P_0), a V - t plot can be obtained

and a straight line can be obtained in the range of $0.4 \leq t \leq 0.6$. The slope and intercept of the V - t plot are A and B respectively. The S_{exter} , S_{inter} and micropore volume (V_{micro}) quantities can be obtained as follows:

$$S_{exter} = \frac{15.47}{0.975} \times A \quad (3.8)$$

$$S_{inter} = S_{BET} - S_{exter} \quad (3.9)$$

$$V_{micro} = 1.547 \times 10^{-3} \times B \quad (3.10)$$

The pore size distribution and pore volume were analyzed by using a non-local density functional theory (NLDFT), which is a molecular-based statistical thermodynamic theory^[8, 9]. At equilibrium state, a model can be developed for the adsorption isotherm for the system, because the distribution of gas molecules near the surface can be described by a function of pressure and molecular properties of the components. Compared with other approaches (e.g. Monte Carlo simulation, molecular dynamics), NLDFT was first used as the basis of a practical solution for accurately determining pore size distribution (PSD) in the range from micropore to mesopore and less computational requirements.

To characterize the PSD of porous material, the NLDFT assumes that each pore acts independently, and each pore size present then contributes to the total adsorption isotherm in proportion to the fraction of the total area of the sample that it represents. The relation can be expressed mathematically as follows:

$$Q(p) = \int dH q(p, H) f(H) \quad (3.11)$$

where $Q(p)$ is the experimental quantity adsorbed at pressure p , $q(p, H)$ is the quantity adsorbed per unit area at the same pressure p in an ideal pore of size H , and $f(H)$ is the total area of pores of size H in the sample.

For carbon materials analysis, the pore was assumed to be of slit shape. The total pore volume (V_t) was calculated at relative pressure $P/P_0 = 0.95$. All the analytical techniques applied to the adsorption/desorption data are standard in the field.

3.3.4 Electrode thickness

The sprayed electrode thickness was measured by a Veeco Dektak 6M Surface Profiler using a ‘step height’ method. Carbon film samples sat on a stage that could move in x-y precisely under a diamond-tipped stylus. The carbon film thickness was measured from the vertical displacement of the stylus between the smooth substrate and the electrode top surface, as shown in Figure 3.10. Si substrates were used as the reference to zero the profile. A 5 mN stylus force and 10,000 μm scan length were used for all measurements. The film thickness was measured in 5 different places on each sample, and an average obtained.

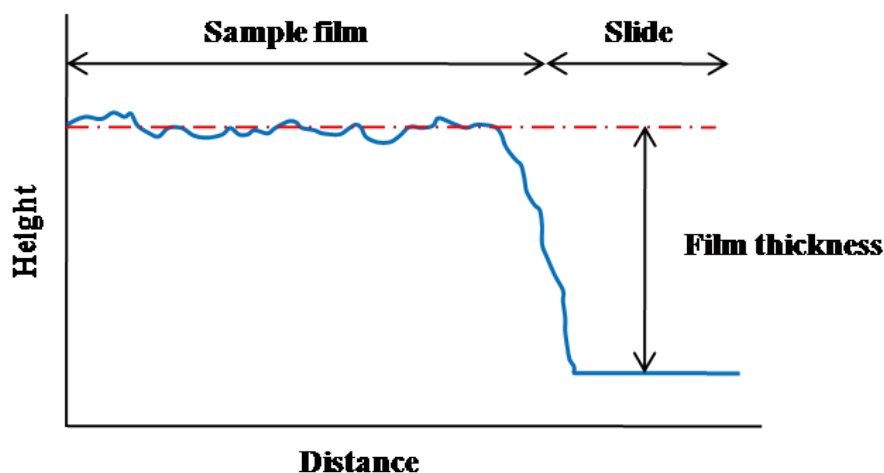


Figure 3.10: Schematic of film thickness measurement by step height method.

3.3.5 Transmission electron microscopy

The structure and morphology of ball milled carbon powder samples were investigated by high resolution transmission electron microscopy (HRTEM, JEOL 4000HR) at a voltage of 400 kV. The carbon powder samples for TEM were prepared by ultrasonic

dispersion in ethanol, pipetted and dried on a holey-carbon film-coated copper grid (300 mesh). Transmission electron microscopy image were obtained by Aleksey Shmeliov and Dr Antal Koos with the author in attendance.

3.3.6 Scanning electron microscopy

The morphology of the various carbon particles, the electrode top surface and the microstructure of the electrodes in cross-section were investigated in a field emission gun scanning electron microscope (FESEM, JEOL 840 F) at 5 kV voltage and *ca.* 8 mm working distance. To prepare the electrode samples, silver conducting paint was placed along the edge between the carbon film, the Si substrate and the mounting stub to avoid charging. The weight of deposited films was obtained using a Sartorius microbalance.

3.4 Electrochemical characterization

Electrochemical properties of carbon electrodes for EDLCs were characterized in both three-electrode and two-electrode configurations using a Gamry Reference 600 Electrochemical Analyzer. For three-electrodes cell tests, a platinum (Pt) wire and Ag/AgCl were used as the counter and reference electrodes respectively, as shown in Figure 3.11. Various aqueous electrolytes such as 1 M H_2SO_4 and 6 M KOH were used, as indicated in each results chapter. All aqueous electrolytes were bubbled with N_2 for 20 min to calibration before using.

For supercapacitor two-electrodes cells (full cell) tests, Swagelok cells were assembled with two thin film carbon electrodes facing each other, separated by a glass microfiber membrane (0.3 mm Whatman), as shown in Figure 3.12. Basic solution (KOH) and neutral aqueous solutions (Na_2SO_4 , Li_2SO_4 and NaCl) were used as electrolytes respectively. The stainless steel main parts and nylon fittings were purchased from Swagelok

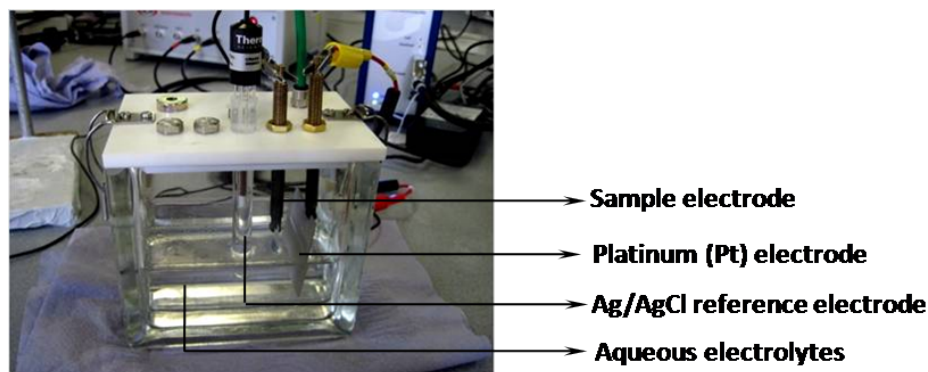


Figure 3.11: Three-electrodes cell for supercapacitor electrochemical measurements.

and subsequently machined in-house, as shown in Figure 3.12.

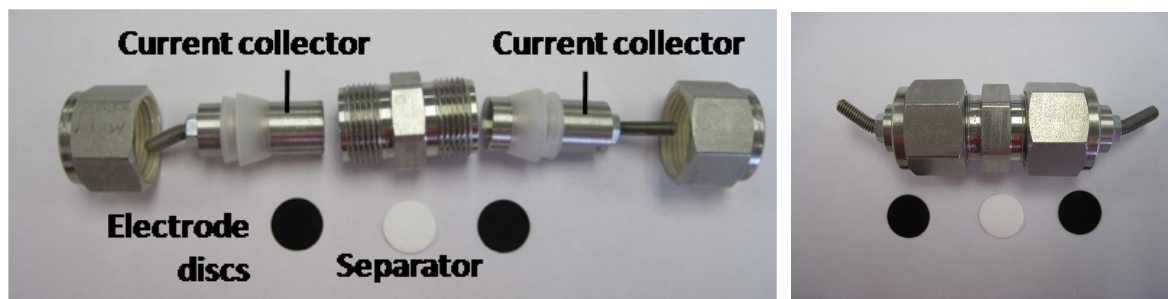


Figure 3.12: Two-electrodes cell (Swagelok cell) for supercapacitor electrochemical measurements.

As previously mentioned, electrochemical measurements for thin film battery electrodes (Chapter 7) were carried out in a coin cell. A Cu foil with a graphite powder coating prepared by spray deposition was used as the negative electrode, Li metal (ribbon, thickness $\times$ W 0.75 mm $\times$ 45 mm, 99.9% trace metals basis, Sigma-Aldrich) was used as the counter, as shown in Figure 3.13. The positive and negative shells and stainless steel current collectors for coin cell were purchased from the National Research Council, Canada. A piece of stainless steel spring and spacer parts (MTI Ltd) were used for battery coin cell test to improve the quality and reproducibility of the electrical contacts. A layer of glass microfiber membrane (0.3 mm Whatman) was again used as the separator. LP30 (1 M LiPF_6 in ethylene carbonate: dimethyl carbonate 1:1) from Merck, UK was used as the electrolyte.

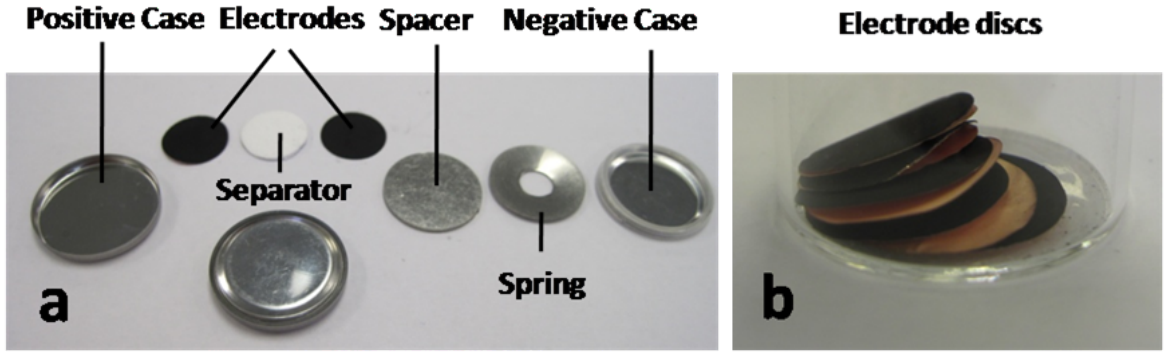


Figure 3.13: (a) Coin cell for thin film battery electrode electrochemical measurements, and (b) battery anode-graphite coated Cu foil round discs.

3.4.1 Cyclic voltammetry

The carbon-based supercapacitor electrodes were investigated by cyclic voltammetry (CV) in various aqueous electrolytes in both three-electrodes cells and two-electrodes cells at scan rate of 5 - 10000 mV/s. The specific capacitance C_s was calculated from the CV curves as follows:

$$C_s = \frac{Q}{2\Delta V} = \frac{\int Idt}{2\Delta V} = \frac{\int IdV}{2S\Delta V} \quad (3.12)$$

where Q is the quantity of charge, ΔV is the potential window, I is the current density, t is the time, V is the voltage, S is the scan rate^[10]. The value of $\int IdV$ equals the shadowed area formed by the CV curves, as shown in Figure 3.14(a).

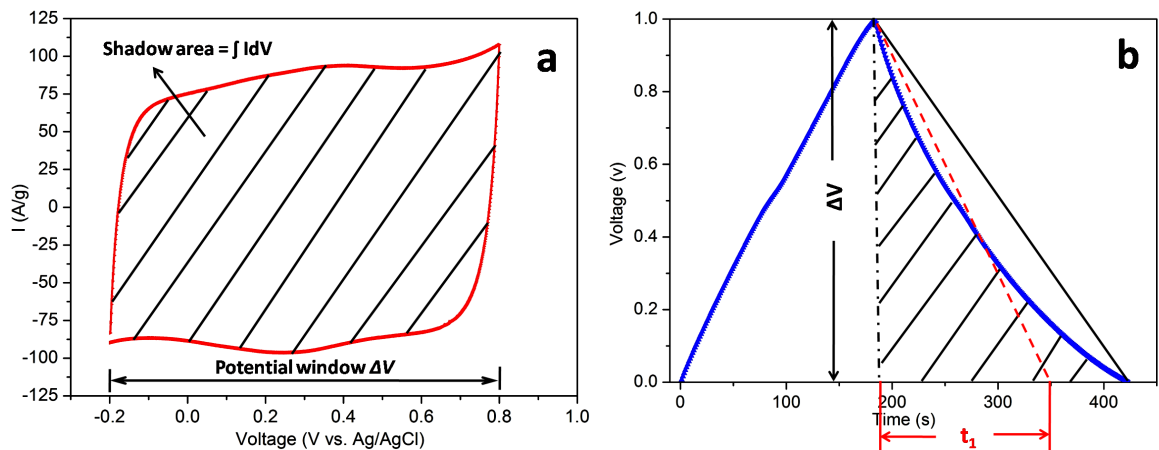


Figure 3.14: (a) Schematic explanation of how specific capacitance was calculated from a cyclic voltammetry curve, and (b) from a discharge curve.

For some carbon electrodes, pseudocapacitance arises from reversible surface faradaic processes which dependent on the electrode potential. These appear as peaks above and below the zero current line (in a mirror image) in the CV curves. The forming of peaks in the CV curves can be explained in the following way. When reaching a potential where the oxidation/reduction process begins, the current increases as in a steady-state voltammogram. The oxidation/reduction consumes electroactive species and creates a concentration gradient (diffusion layer near electrode surface). Therefore, due to the depletion of electroactive species, the current then starts to decay as the potential continues to sweep, leading to the formation of a peak. The peak current I_p can be calculated as follows^[11]:

$$I_p = 0.45 \left(\frac{nF}{RT} \right)^{1/2} nFAD^{1/2}CS^{1/2} \quad (3.13)$$

where n is the number of electrons transferred/molecule, F is the Faraday constant (96,485 C/mol), R is the gas constant, T is the temperature, A is the electrode surface area, D is the diffusion coefficient, C is the electrolyte concentration and S is the scan rate.

3.4.2 Galvanostatic charge-discharge behaviour

The carbon electrodes for EDLCs during charge/discharge was investigated at different current densities of 0.5 - 26 A/g. The maximum voltage was 1 V for KOH and H₂SO₄ electrolytes and 1.6 V for neutral electrolytes.

Specific capacitance was also determined from galvanostatic charge/discharge from:

$$C_s = \frac{I}{dV/dt} \quad (3.14)$$

where I is the applied constant current density and dV/dt is the absolute value of the

slope of the discharge curve^[10]. For a non-linear discharge curve, the value of dV/dt was approximated:

$$\frac{dV}{dt} = \frac{\Delta V}{t_1} = \frac{\Delta V}{2S/\Delta V} = \frac{\Delta V^2}{2S} \quad (3.15)$$

where ΔV is the potential window, t_1 is the corresponding discharge time for linear discharge behaviour and S is the shadowed area in Figure 3.14(b).

3.4.3 Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) was employed to study various electrodes using a sinusoidal voltage signal with a 0 V mean voltage and 10 mV amplitude over a frequency range of 10000 - 0.01 Hz at room temperature. The equivalent series resistance (ESR) was measured by extrapolation of a best-fit line to capacitive behaviour to the real impedance axis, or could be measured at 1 kHz. More details are given in subsequent chapters.

3.4.4 Cycling behaviour

For the EDLC electrodes, 500 - 10000 cycles of galvanostatic charge/discharge were performed at constant current densities of 1 A/g between 0 - V_{max} in aqueous electrolytes. For battery coin cells, 20 cycles of galvanostatic charge/discharge were performed at constant current density of 20 mAhr/g between 0 - 2 V in a LP30 electrolyte.

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Chapter 4

Thin Film Carbon Electrodes Based on Synthetic Graphite

4.1 Introduction

As reviewed in Chapter 2, many different types of carbon materials such as ordered mesoporous carbon (OMC), 3D hierarchical porous graphitic carbon (3D HPGC), carbon nanotubes (CNTs), carbon fibres and graphene have been investigated as potential materials for supercapacitor electrodes^[1–9]. However, these carbon materials have had only limited impact on commercial applications because in terms of economic performance, the unit cost of the carbon in relation to its specific capacitance is the key issue for the commercial application^[10]. Biomass derived carbon and its activation currently provides the most attractive cost-performance balance.

Synthetic graphite is a manufactured product made by the high-temperature treatment of highly graphitizable forms of carbon and has been widely studied as an anode material in Li-ion batteries and as a minority additive conductive agent in ECs (5 - 10 wt.%)^[11], and is a promising candidate for the primary constituent in EDLCs^[12] due to its relatively good conductivity (graphitic structure, with a resistivity of 2.5 -

$5.0 \times 10^{-6} \text{ } \Omega\text{m}$) and relatively low cost (\$ 4,000 - 6,000/tonne)^[13]. Furthermore, the comparatively high density of synthetic graphite may help to contribute to high volumetric capacitance.

For all types of carbon, the particle size can be reduced by ball milling^[14--16]. Graphite with a mean particle size in the nanometer range and with a high specific surface area of $600 \text{ m}^2/\text{g}$ can be achieved^[17]. Phase transformations and properties of graphite under different milling conditions have also been investigated (a mixture of amorphous phases and nanocrystalline graphite with about 2 nm crystallite size could be produced after 8 h of ball milling)^[18--21]. Ball milling often takes place under a controlled atmosphere, such as O_2 , Ar and H_2 in order to tailor the surface functional groups on ball milled graphite particles or to prevent the agglomeration of particles^[22--24].

To date however, few studies of nano-graphite after activation in supercapacitors have been conducted^[16, 25, 26]. In this chapter, nano-graphite was prepared by high energy ball milling followed by CO_2 activation, and the electrochemical performance as EDLC electrodes then examined. The nano-graphite based electrodes were in the form of thin and flexible films with a usually homogeneous surface manufactured by spray deposition. Electrodes showed a stable charge/discharge performance during extended cycling process, and provided comparatively high gravimetric volumetric capacitances of up to 110 F/g at 100 mV/s .

4.2 Materials and methods

4.2.1 Materials

As shown in Figures 4.1(a) and (b), synthetic graphite with a typical flake morphology, average particle size of approximately $10 \text{ } \mu\text{m}$ and BET surface area *ca.* $13.5 \text{ m}^2/\text{g}$

were provided by Sigma-Aldrich (UK), and designated as ‘original graphite’ (OG). Carbon black powder ($> 99.9\%$), with a BET surface area *ca.* $39 \text{ m}^2/\text{g}$, as shown in Figure 4.1(c), was provided by Alfa-Aesar (UK). CVD-grown multi-wall nanotubes (MWNTs) were provided by Professor Nicole Grobert’s group at Oxford University (Figure 4.1(d)).

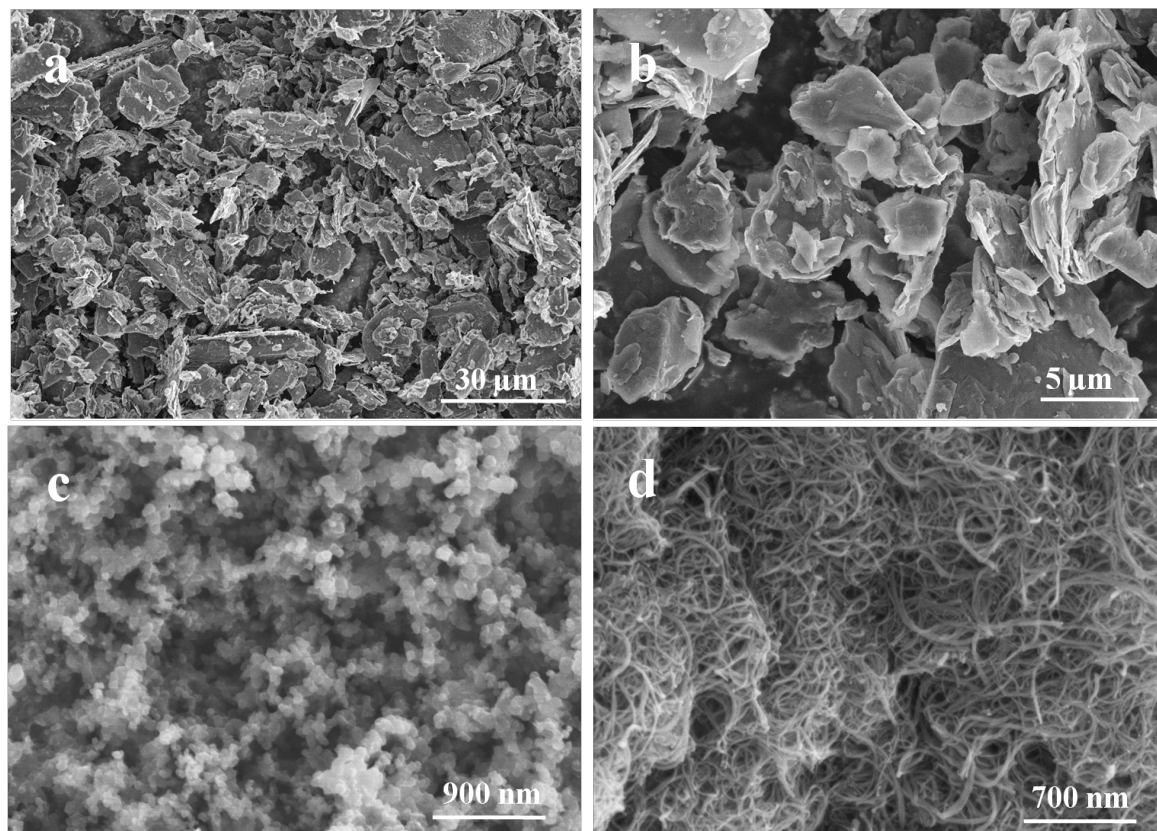


Figure 4.1: SEM images of (a) and (b) original graphite particles from Sigma-Aldrich, (c) commercial carbon black from Alfa-Aesar, and (d) MWNTs from Prof. Nicole Grobert’s group.

4.2.2 Preparation of nano-graphite particles

Ball milling treatment was used to reduce the mean size of feedstock graphite particles towards the nanoscale, in order to produce thin film electrodes, and to aid in suspension of the particles required for spraying. Ball milling was performed at room temperature under ambient atmosphere using a Fritsch ‘Planetary 6’ planetary mill. Various charge weight-to-ball ratios (1/15, 1/25, 1/50, 1/75), rotation velocities (400/600 rpm), and milling times (2 - 20 h) were used. Ball milling in aqueous medium (water) with

1/15 weight-to-ball ratio, 400 rpm rotation speed for 83 h was also investigated for comparison.

Activation of the graphite surface was subsequently carried out on the ball-milled graphite particles to increase the surface area and pore volume. The activation procedure was previously described in Chapter 3.

4.2.3 Preparation of nano-graphite based thin film electrodes

To prepare electrodes, a mixture of ball milled graphite (BG) or activated and ball milled graphite (ABG) with 5 wt.% carbon black or 2 wt.% MWNTs as a conductivity enhancing material was dispersed in de-ionised water using high shear mixing. The suspension was then ultrasonicated for 20 min to form a stable suspension with a concentration of BG or ABG of 0.5 mg/ml. To give the best suspension stability, 5 wt.% (with respect to graphite weight) CMC was used as surfactant, and the pH of suspension was adjusted to 10.5, as described in Chapter 3. The details of the various material/process abbreviations are given in Table 4.1.

Table 4.1: A summary of abbreviations used to describe the different C-based materials.

Name	OG	BG	BG+5CB	BG+2MWNT	ABG	ABG+5CB
Ball milling	No	Yes	Yes	Yes	Yes	Yes
Activation	No	No	No	No	Yes	Yes
Additives	No	No	5 wt.% carbon black	2 wt.% MWNTs	No	5 wt.% carbon black

A one meter long thin film carbon electrode (20 μm thick) was then prepared by spray deposition of suspensions on Al coated polyethylene terephthalate (PET) film with the spray nozzle linearly reciprocating at a speed of 500 mm/s. Small area thin film carbon electrodes (with 800 nm to 10 μm film thickness) were also prepared by spray deposition of suspensions on stainless steel substrates. In both situations, a total syringe pump flow rate of 2 ml/min and an atomising pressure of 300 kPa compressed air were

provided. The temperature of substrates were maintained at 110 °C, as previously described in Chapter 3.

A few layers of PEI were pre-coated on the substrates to improve the adhesion. The thickness of carbon film electrodes ranged from 800 nm to 20 μm , depending on the spraying time, which was typically in the range 5 to 30 min. Faster production could be achieved by increasing the concentration of spray suspension but which required *in-situ* ultrasonication of the suspension reservoir during extended spraying times, or by increasing the number of nozzles.

4.2.4 Electrochemical performance

Electrochemical properties of the electrodes were investigated by CV, EIS, and galvanostatic charge/discharge cycles using a three-electrode configuration in 1 M H_2SO_4 aqueous electrolyte. CV curves were measured in the potential range -0.2 to 0.8 V (vs. Ag/AgCl) at a scan rate of 2 - 500 mV/s. EIS was measured using a AC voltage of 10 mV amplitude over a frequency range of 10000 - 0.01 Hz at room temperature. Galvanostatic charge/discharge cycles were performed at constant current density of 1 A/g between 0 to 0.8 V in 1 M H_2SO_4 .

4.3 Results and discussion

4.3.1 Scanning electron microscopy

4.3.1.1 Wet ball milling

Ball milling in liquid media can provide a more homogeneous particle size with less agglomeration and high retention of graphitic crystallized structure compared with dry ball milling^[27]. This is because the liquid media can act as lubricant and moderates the

violence of impacts during the milling process. However, the high retention of dense, crystalline graphite after wet ball milling provided only a moderate increase in surface area (S_{inter} is the surface area which comes from the micropores ‘inside’ the carbon particles, as described in Chapter 3) compared with when the graphite has increasing amorphous character due to the accumulation of more significant milling damage^[27]. Figure 4.2 shows the evolution of graphite particle size under wet ball milling with 1/15 weight-to-ball ratio, 400 rpm rotation speed and milling time from 1 to 83 h. As shown in Figure 4.2(f), after 83 h of ball milling in water, which was initially explored, most of the graphite particles were still significantly larger than 1 μm . Further, wet ball milled graphite is generally more readily contaminated by the material of the milling balls when water is used^[27]. Thus this approach was discontinued.

4.3.1.2 Dry ball milling

Ball milling without liquid was an effective way to reduce the graphite particles towards the nanoscale. Besides the choice of ball milling media, other conditions such as rotation speed, weight-to-ball ratio and milling time had effects on the final graphite particle size and morphology. As shown in Figure 4.3(a), many graphite particles were still approximately 5 μm when a low weight-to-ball ratio (1/75) was used that gave comparatively inefficient milling of the graphite, with most of the milling energy expended between the milling balls themselves. Longest ball milling times (20 hrs) produced an apparently more homogeneous and smaller particle size, but ‘over-milling’ caused particle agglomeration due to the very high surface area created, as shown in Figure 4.3(b).

After many combinations of parameters (a detailed comparison will be given later), the optimized ball milled graphite particles are shown in Figure 4.3(c) and were obtained when the large feedstock graphite flakes were crushed into approximately spherical particles with a diameter ~ 200 nm, but without excessive agglomeration, after 4 h of ball milling and a weight-to-ball ratio of 1/15. Figure 4.3(d) shows the same particles

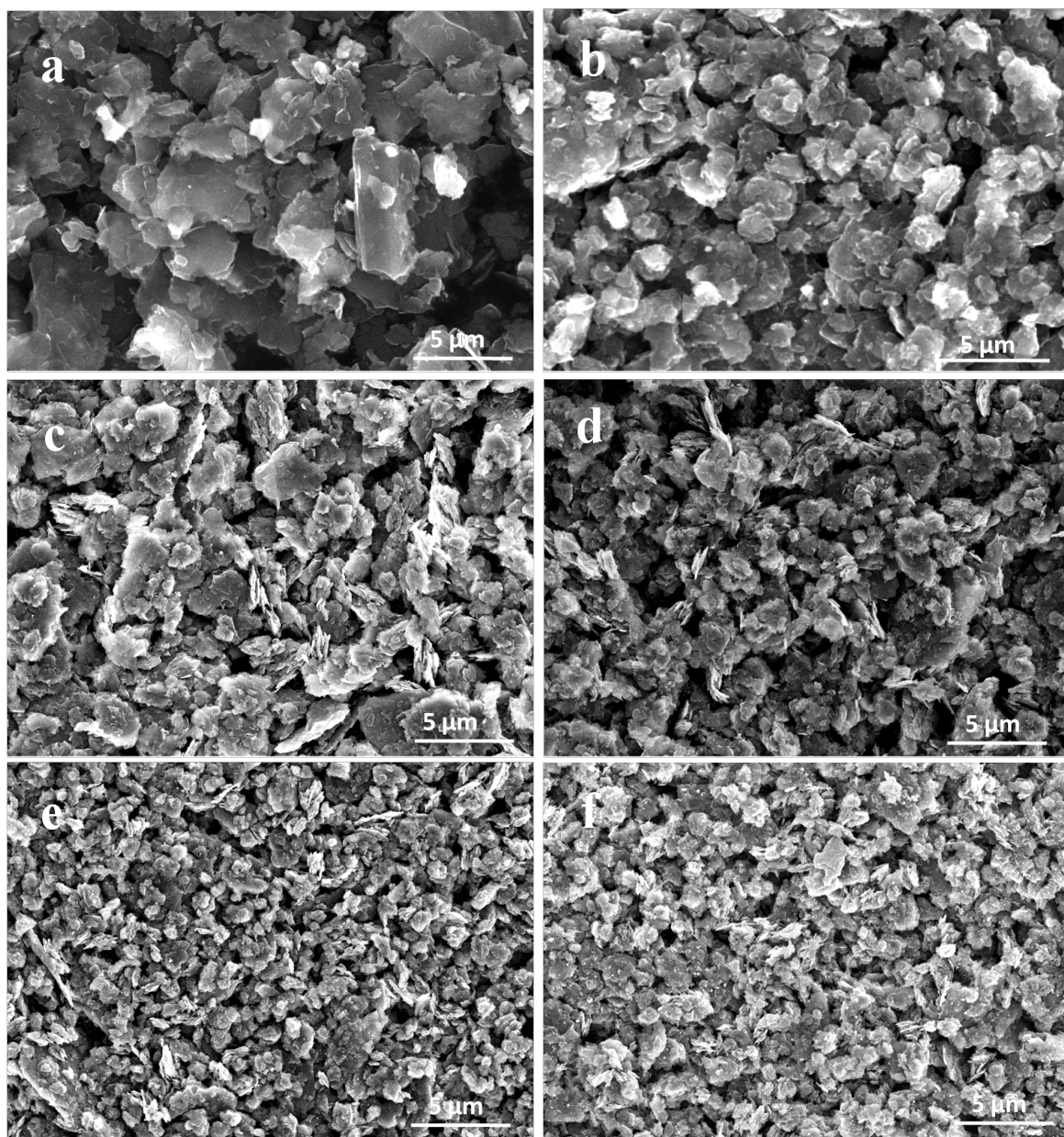


Figure 4.2: SEM images of the evolution of graphite particle size under wet ball milling with 1/15 weight-to-ball ratio, 400 rpm rotation speed for (a) 1 h, (b) 10 h, (c) 24 h, (d) 47 h, (e) 62 h and (f) 83 h.

following activation. There was a tendency for a ‘rounding’ of particles after activation at this magnification, presumably driven by a reduction in surface energy and increased carbon mobility at high temperature.

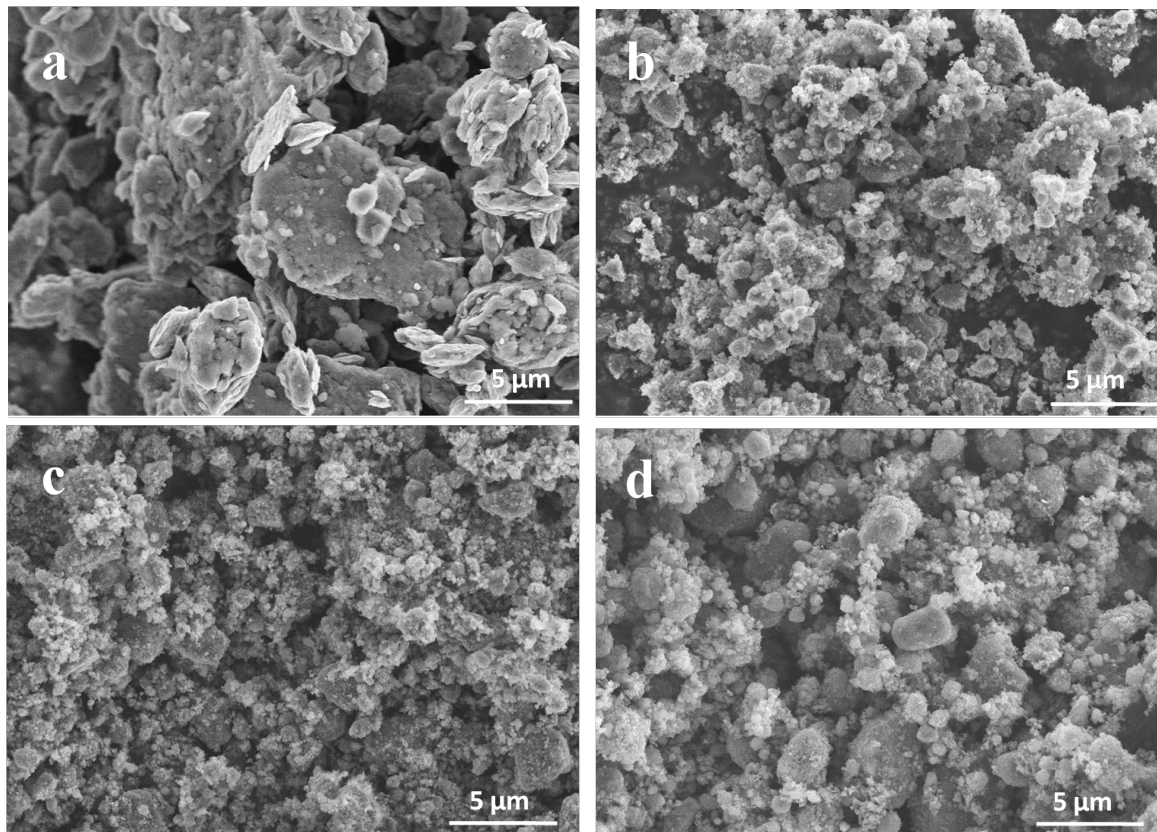


Figure 4.3: SEM images of (a) ball milled graphite particles at a weight-to-ball ratio of 1/75, 600 rpm rotation speed for 4 hrs, (b) 1/15, 600 rpm for 20 hrs ball milled graphite particles, (c) optimised ball milled graphite particles (1/15, 600 rpm for 4 hrs), and (d) optimised ball milled graphite particles after CO₂ activation treatment.

4.3.1.3 Sprayed electrodes

A one meter-long spray deposited nano-graphite film electrode manufactured according to the procedure given in Chapter 3 and using the ‘optimum’ ball milled graphite is shown in Figure 4.4(a). The suspended ball milled graphite was readily spray deposited onto the flexible Al coated PET film substrate. A SEM image of the electrode surface is shown in Figure 4.4(b), which exhibited a high internal porosity and suggesting generally good homogeneity of graphite particle size and dispersion. By adding 2 wt.% MWNTs, the ball milled graphite particles became embedded in the interconnected MWNT network, which together comprised a highly interconnected but macro-porous

structure (Figure 4.4(c)).

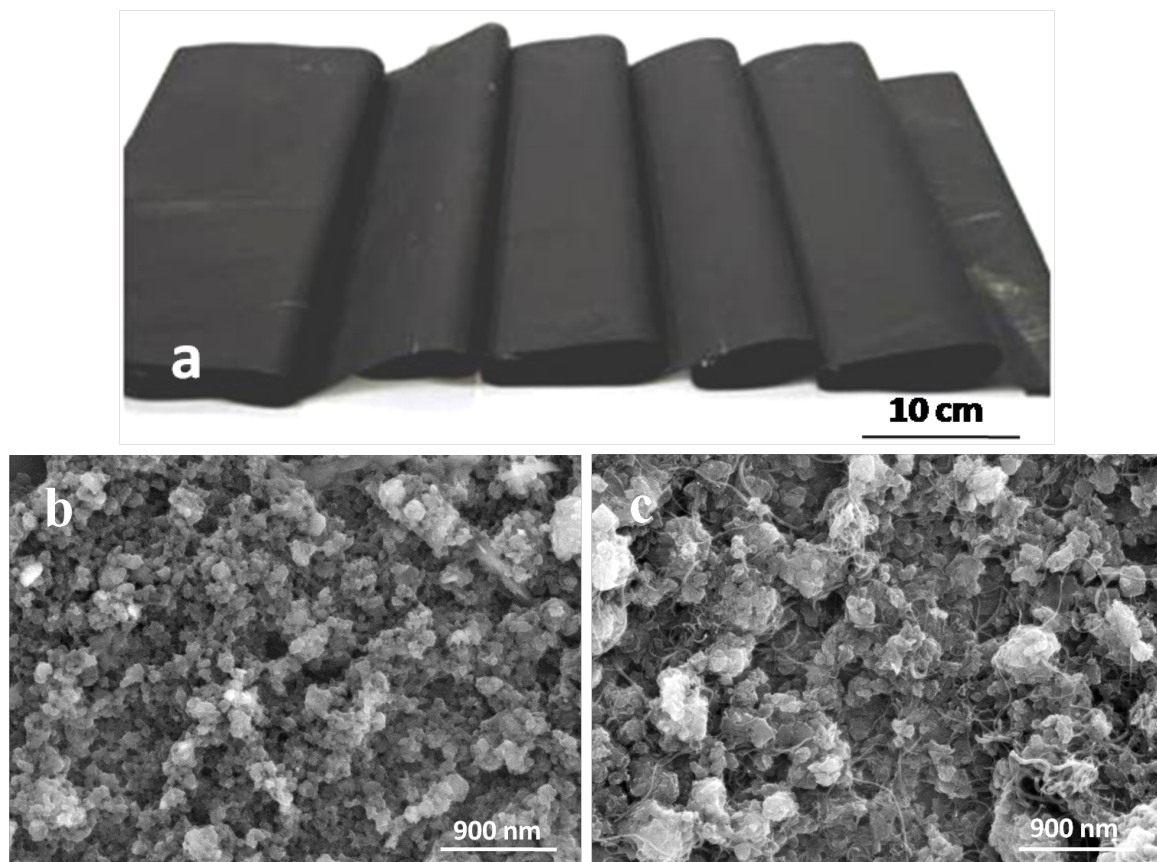


Figure 4.4: (a) A one meter long flexible nano-graphite based electrode sprayed on Al coated PET film, (b) the spray deposited film surface of ball milled graphite, and (c) the spray deposited film surface of ball milled graphite particles with 2 wt.% MWNTs.

4.3.2 X-ray diffraction

The effect of ball milling time on the as-supplied graphite structure was investigated using X-ray diffraction (XRD), as shown in Figure 4.5(a). The intensity of the diffraction peak at 26° corresponding to the graphite (002) reflection in the feedstock graphite decreased sharply and became asymmetric after 2 h ball milling. The asymmetric (002) reflection peak after 2 hours ball milling could be divided into two components corresponding to different crystallographic spacing: one from comparatively ‘ordered’ or pristine graphite associated with the original graphite, and another from lattice ‘damaged’ regions that are associated with buckling of basal planes or half Frank loop introduction^[18, 28]. The (002) and (100) reflection peaks (at 26° and 43° respectively

on XRD pattern) also became broadened when the milling time was increased from 2 to 20 hours, indicating that at this stage probably most of the crystalline graphite fraction had been broken down and sufficiently defective to more closely resemble an amorphous phase with few nano-crystallites remaining^[29], indicating that the typical hexagonal crystalline structure was increasingly defective and disrupted into basal planes during the mechanical milling. At the same time, some Fe contamination (iron carbide, iron fcc and bcc) from the milling balls and milling pot were also introduced into the graphite particles.

In Figure 4.5(b), the (002) peak did not become broader as expected after activation, because the disorder introduced by milling may to some extent be annealed by the high temperature of activation (i.e. partial graphitization). The new peaks at $2\theta = 30^\circ, 35^\circ, 37^\circ, 43^\circ, 54^\circ, 57^\circ$ and 63° were related to magnetite ($\text{Fe}^{+2}\text{Fe}^{+3}\text{O}_4$) peaks, suggesting that the prior iron contamination from milling balls became oxidized during the CO_2 activation treatment. The oxidation of these minority iron contaminants may be related to some minor leaking problems in the apparatus at some stage of the activation process.

4.3.3 Transmission electron microscopy

Figure 4.6 shows a selection of TEM images of the OG, BG and ABG particles and were obtained by Antal Koos with the author in attendance. Figure 4.6(a) shows an original graphite particle with $\sim 3 \mu\text{m}$ diameter, clearly comprised of many crystalline sub-domains, many with a high aspect ratio, plate-like morphology. Figure 4.6(b) shows a higher magnification view of an edge plane, showing it comprised many layers with sub-structure, and which were ascribed to be stacks of graphite sheets. Figure 4.6(c) shows the effect of milling for 4 hrs at 1/15 weight-to-ball ratio and 600 rpm rotation speed. The planar graphite morphology was substantially disrupted, with much finer (10 - 80 nm) turbostratic regions, along with regions that were essentially amorphous at this magnification.

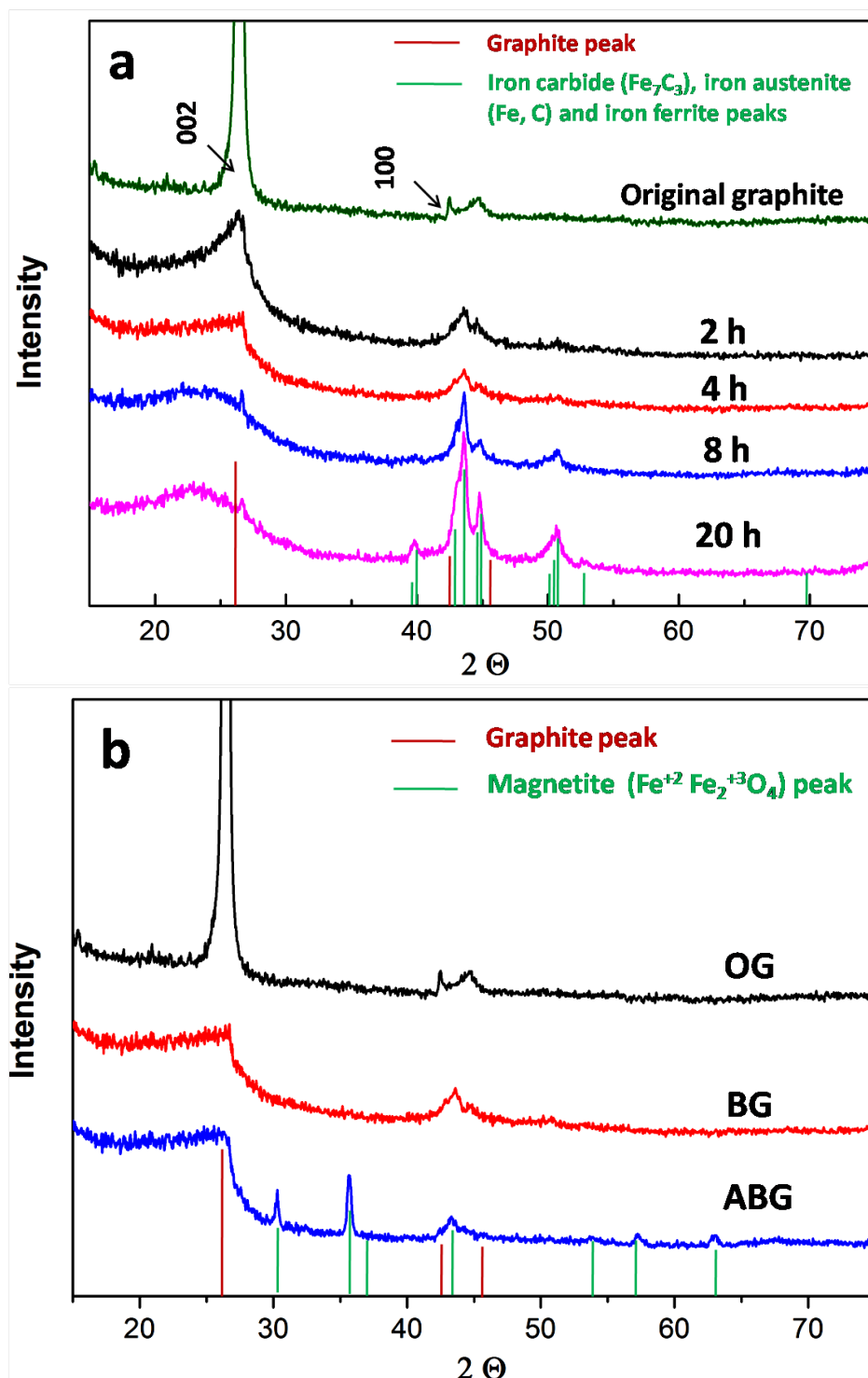


Figure 4.5: (a) XRD patterns of graphite particles as a function of ball milling time, other ball milling conditions were constant (1/15, 600 rpm), (b) XRD patterns of original, ball milled (1/15, 600 rpm for 4 hrs) and activated ball milled graphite particles.

The amorphization of graphite is associated with the break-up of multi-graphene layers and the accumulation of defects produced during the milling process^[29]. Figure 4.6(d) at higher magnification supports the break-up of the original comparatively ordered crystalline structure into a progressively disordered amorphous microtexture with the disordered basic structure units (BSU)^[14], approximately containing 3 - 5 stacked 2 nm long graphene sheets. As shown in Figure 4.6(c), particles with size 20 - 80 nm were composed of these BSUs and amorphous carbon. These particles were further agglomerated into larger particles of several hundred nanometers in size. The formation of nanoporous structure is associated with disorientation of BSU and plastic deformation of the (002) planes, as illustrated in Figure 4.6(g). Figures 4.6(e) and (f) exhibited the graphite-based structure after further CO₂ activation. As shown in Figure 4.6(e), during the CO₂ activation process, most nano-sized amorphous graphite particles were consumed in the reaction. Therefore the remaining graphite is mainly of turbostratic structure, which was characterized by nano-sized carbon ribbons of 5 nm width with parallel fringes, as marked in Figures 4.6(e) and (f)^[15, 19]. Any micropores (< 2 nm) formed during activation could not be observed convincingly in the TEM images.

4.3.4 Nitrogen adsorption

4.3.4.1 Investigation of the optimum ball milling condition

As the specific capacitance of carbon-based supercapacitor electrodes strongly depends on the specific surface area of the electrode materials, different ball milling conditions were compared in order to optimise the specific surface area of the ball milled graphite particles. The measured S_{BET} , S_{inter} , S_{exter} (defined in Chapter 3) as a function of ball milling time are illustrated in Figure 4.7(a), under the milling condition of 1/15 weight-to-ball ratio and 600 rpm rotation speed. S_{BET} increased rapidly during the first 4 h from an original 13.5 m²/g to a maximum of 543 m²/g, 30% of which was estimated to be contributed by the S_{inter} . The increase in S_{exter} with time was due

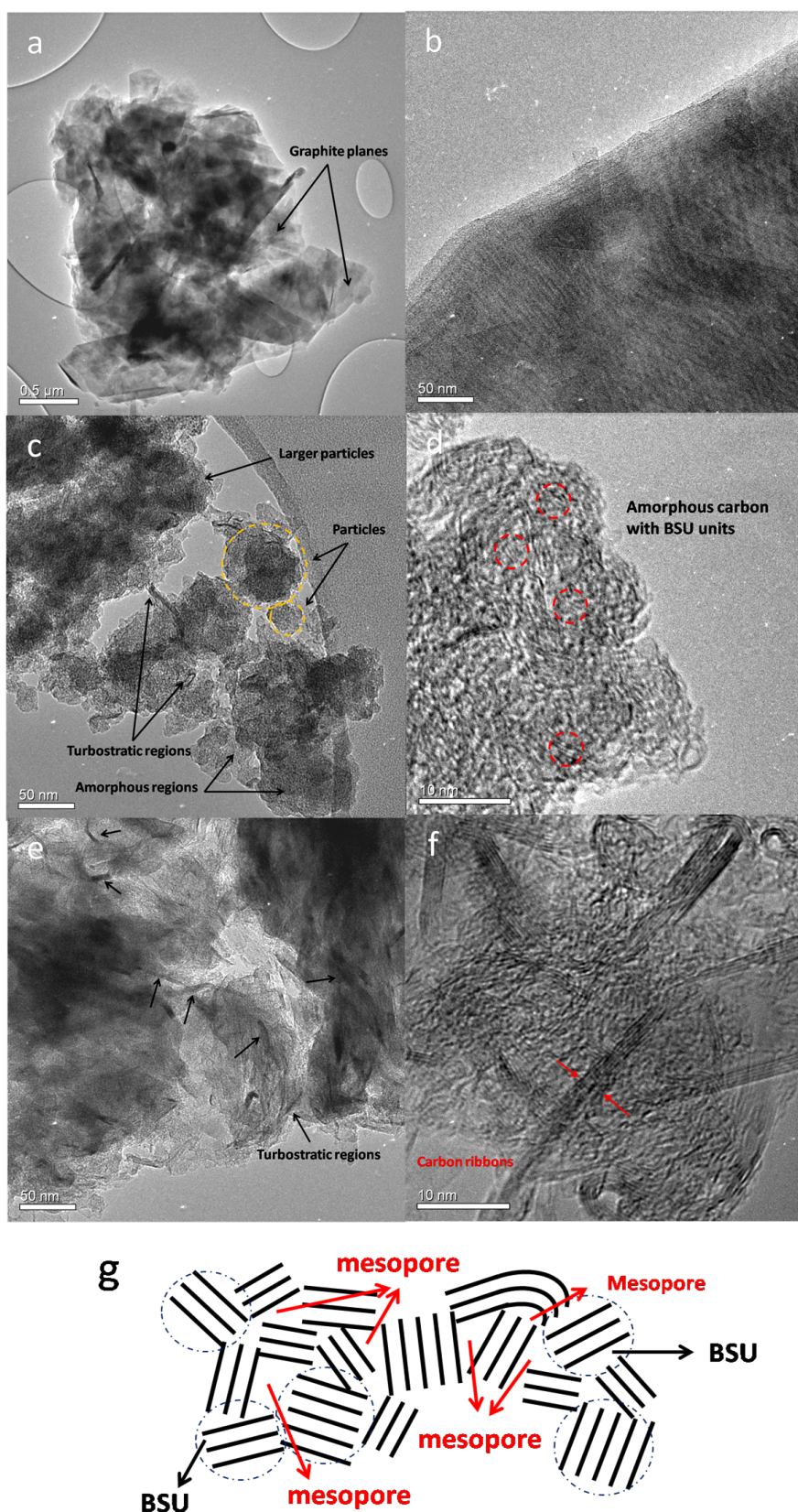


Figure 4.6: TEM images of graphite particles (a, b) original graphite particles, (c, d) after 4 hrs ball milling (1/15 ball-to-weight ratio and 600 rpm), (e, f) after ball milling and CO₂ activation, obtained by Antal Koos with the author in attendance, and (g) schematic of the nanoporous structure in ball milled graphite particles formed by the disorientation of BSU and plastic deformation of the (002) planes.

to fracturing of the graphite particles and exfoliation of graphene layers; the increase in S_{inter} was attributed to the increased density of lattice defects (previous showed by XRD and TEM) and the associated increased fraction of basal edge planes.

Extending the milling time might be supposed to facilitate even smaller and more homogeneous graphite remnants with very high specific surface area, but S_{inter} and S_{exter} both reduced at milling time > 4 hrs. The reduction in S_{exter} was related to agglomeration, because increasing fine fragments had high specific surface energy which eventually became dominant over the de-agglomerating effects of mechanical impact, as shown in Figure 4.3(b). The slight reduction of S_{inter} might be explained by the increasing amorphization, although more lattice defects were also introduced in the remaining crystal fraction. The trend of specific surface area as a function of milling time was similar to previously reported: division→fracture→agglomeration^[30]. Although long-time ball milling can lead to an amorphous structure which by definition is increasingly homogenous, the agglomeration and iron contamination effects become progressively problematical; furthermore, the high fraction of amorphous structure will also increase the intrinsic resistance^[30].

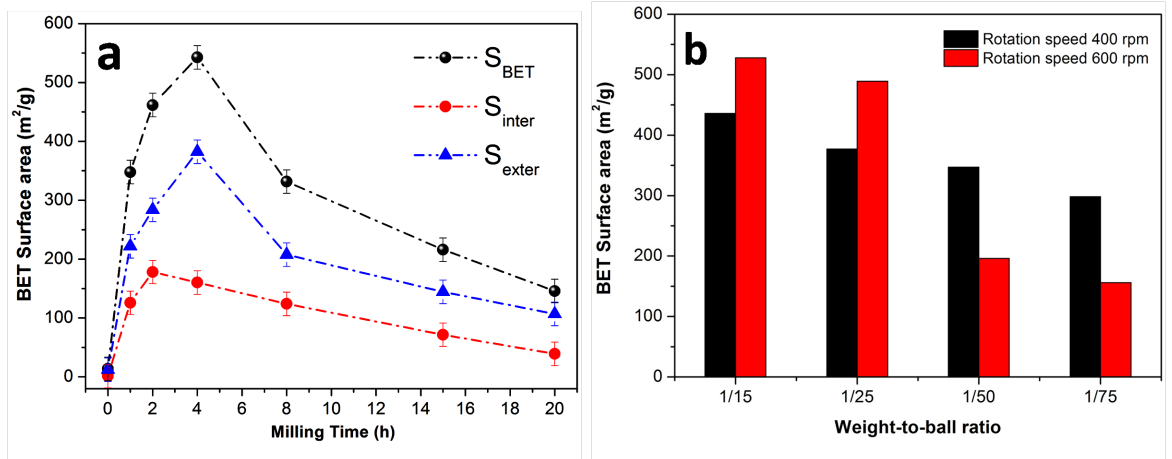


Figure 4.7: (a) BET (S_{BET}), internal(S_{inter}), external(S_{exter}) surface area of graphite particles as a function of milling time, (b) BET surface area obtained under different ball milling conditions.

The effects of other ball milling conditions (weight-to-ball ratio and rotation speed) on S_{BET} were also studied and further data is given in Figure 4.7(b). When the weight-to-ball ratio was comparatively high (1/15, 1/25), a high rotation speed (600 rpm) was

more effective in promoting high specific surface area whereas at a low weight-to-ball ratio (1/50, 1/75), a high rotation speed imparted too much energy of impact to the particles, and agglomeration was accelerated. As previously flagged, the overall surface area reduced as the weight-to-ball ratio reduced because more energy was expended between the milling balls rather than to the graphite. The maximum specific surface area was achieved at a condition of 1/15 weight-to-ball ratio, 600 rpm rotation speed and 4 h milling.

The relationship between specific capacitance (calculated from CV curves at 10 mV/s scan rate) and BET surface area of the ball milled graphite is shown in Figure 4.8(a). The specific capacitance shows an approximately linear dependence on S_{BET} consistent with Equation 1.1, although some deviation should be expected^[31--33], because the proportion of micropore and mesopores, the pore shape, and pore surface chemistry will all affect the ion adsorption process, which in turn will influence the EDLC behaviour and overall capacitance. The dependence of specific capacitance on micropore and mesopore volume is illustrated in Figure 4.8(b). The maximum specific capacitance was not obtained with the highest micropore volume but with a moderate micropore volume (0.08 cm³/g) combined with very high mesopore volume (0.45 cm³/g), indicating that mesopore volume was more effective under these conditions and with this particular electrolyte. The optimum volume ratio between micropore and mesopore for different types of electrolytes together with pore shape are under investigation by other groups, e.g.^[34].

4.3.4.2 Effects of ball milling and CO₂ activation

The N₂ adsorption-desorption isotherms that underpin the area data and the corresponding pore size distributions for original graphite, ball milled graphite (1/15, 600 rpm and 4 hrs) and activated graphite are shown in Figure 4.9. The pore volume and specific surface for these three graphite samples are summarized in Table 2.

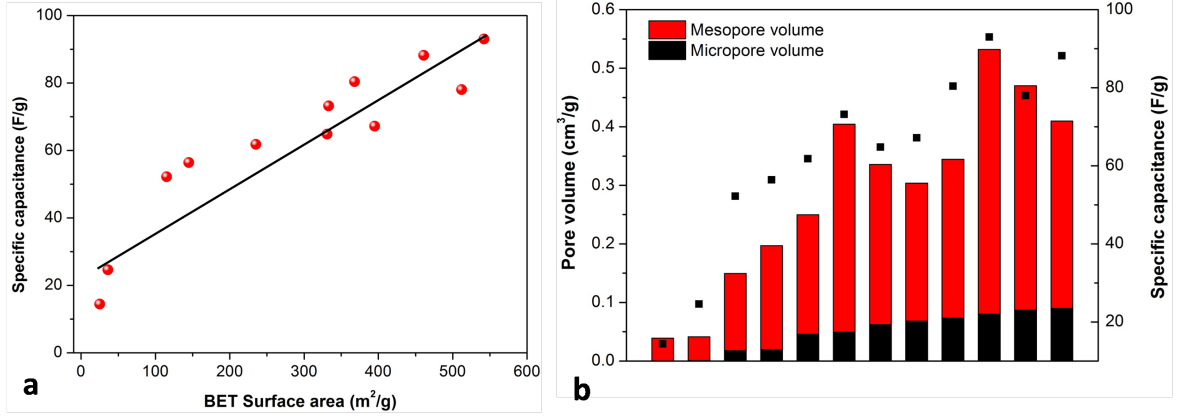


Figure 4.8: (a) Specific capacitance versus BET surface area for ball milled graphite electrodes, and (b) specific capacitance corresponding to different mesopore and micropore volumes.

Table 4.2: Results of adsorption measurements of different graphite samples.

Sample	S_{BET} (m²/g)	S_{inter} (m²/g)	S_{exter} (m²/g)	V_{mi} (cm³/g)	V_{ex} (cm³/g)	V_t (cm³/g)
OG	14	1.4	12	0.0007	0.02	0.02
BG	542	160	382	0.08	0.45	0.53
ABG	1207	389	818	0.2	0.8	1.00

S_{BET} - BET specific surface area, S_{inter} - micropore surface area, S_{exter} - surface area of mesopore and macropore ($S_{exter} = S_{BET} - S_{inter}$), V_t - total pore volume, V_{mi} - micropore volume, V_{ex} - pore volume of mesopore and macropore.

The flat N_2 adsorption-desorption isotherms in Figure 4.9(a) for the original graphite were suggestive of a relatively low micropore and mesopore volume, as shown in Table 4.2. After ball milling, there was an increase in N_2 adsorption at all relative pressures suggesting that a large fraction of micropores were introduced into the graphite, which might be associated with the BSU formation (Figure 4.6(d)), and a reduction in the effective structural unit of the graphite, as well as simply an reduction in particle size. Meanwhile, based on the IUPAC classification^[35], a typical H4 hysteresis loop developed at higher relative pressures ($P/P_0 > 0.45$), indicating that mesopores with a ‘slit’ morphology were generated. The increase in associated pore volume for micropores (< 2 nm) and external pore (mesopore and macropore, > 2 nm) can also be seen in Table 4.2, increasing from $0.0007 \text{ cm}^3/\text{g}$ and $0.02 \text{ cm}^3/\text{g}$ to $0.08 \text{ cm}^3/\text{g}$ and $0.45 \text{ cm}^3/\text{g}$ respectively.

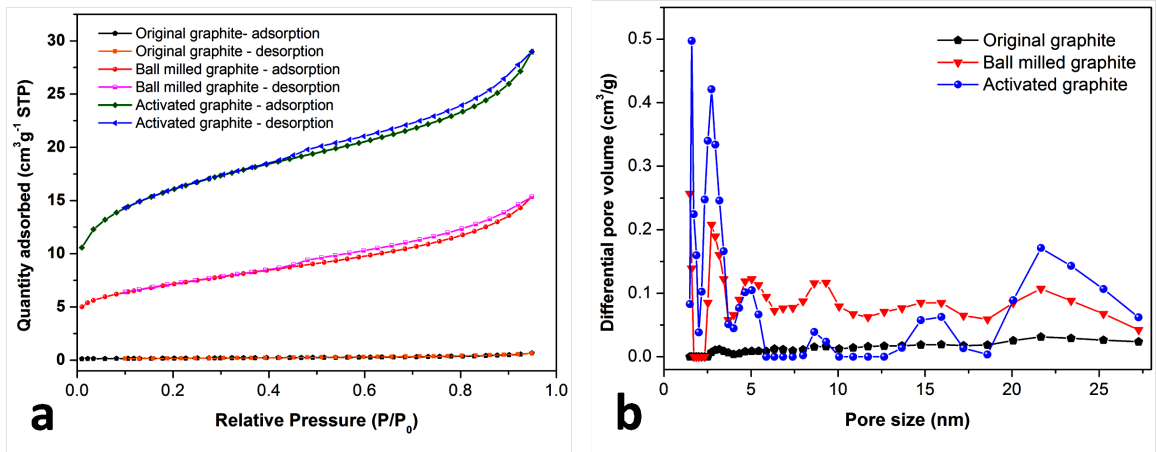


Figure 4.9: (a) N_2 adsorption/desorption isotherms of original, ball milled and activated graphite and (b) the corresponding pore size distribution curves using NLDFT methods and assuming a slit pore shape.

The activation process had a more complicated effect on pore size distribution. On one hand, CO_2 activation introduced more micropore volume, perhaps associated with defects in the graphite lattices, and widened the diameter of the pre-existing micropores, with the micropore volume and external pore volume increased from 0.08 to $0.19 \text{ cm}^3/\text{g}$ and from 0.45 to $0.81 \text{ cm}^3/\text{g}$ respectively, and shown in the pore-size distribution in Figure 4.9(b). The population of pores in the micropore region (~ 1.2 nm) and sub-mesopore region (~ 3.4 nm) became more evident after the CO_2 treatment. This suggests larger micropore and mesopore volume, which led to a very overall high S_{BET}

surface area of 1207.3 m²/g. On the other hand, it may be expected that the CO₂ etched small, nanosized domains, leaving less easily etched turbostratic structures and the long ‘carbon ribbons’ remarked in the TEM after the activation process, as shown in Figures 4.6(e) and (f). Overall, the contribution of mid-sized mesopores with pores between 6 - 20 nm reduced after activation to less than 0.05 cm³/g, as shown in Figure 4.9(b).

4.3.5 Electrochemical performance

4.3.5.1 Cyclic voltammetry

Typical cyclic voltammograms (CV) for the spray deposited graphite films at a scan rate of 2 - 500 mV/s between -0.2 V and 0.8 V (vs. Ag/AgCl) in 1 M H₂SO₄ aqueous solution are presented in Figure 4.10. All the films were typically 3 μm in thickness. As shown in Figures 4.10(a) and (b), at a low scan rate (5 mV/s), the CV curves of ball milled graphite and graphite with carbon black showed a generally rectangular shape without obvious redox reaction peaks at discrete potentials, indicating largely double-layer capacitance only behaviour. By contrast, there were symmetric redox peaks at *ca.* 0.3 V vs. Ag/AgCl for activated graphite and graphite with MWNTs, which was associated with quinoidal functional groups^[36, 37] suggesting the introduction of surface groups (such as carbonyl groups) during the CO₂ activation process, or associated with the introduction of the MWNTs^[37].

In the case of ball milled graphite in Figure 4.10(c), the CV curves were noticeably possibly distorted above a scan rate of 200 mV/s, deviating from idealized capacitive behaviour, indicating an increasing effect of internal resistance and which may be ascribed to the increased fraction of amorphous material. After CO₂ activation, as shown in Figure 4.10(d), the CV curves exhibited again a more rectangular shape but with residual distortion, suggesting that the turbostratic structure/‘carbon ribbons’ provided improved electronic transport associated with a higher fraction of graphitic

character.

As shown in Figures 4.10(e) and (f) respectively, the presence of 5 wt.% carbon black or especially 2 wt.% MWNTs within the bulk ball milled graphite particles also significantly improved the capacitive performance at high scan rate, presumably by enhancing the electrical conductivity of the electrodes. As previously described for Figure 4.4(c), the graphite nano-particles were better connected or ‘wired up’ by the MWNTs.

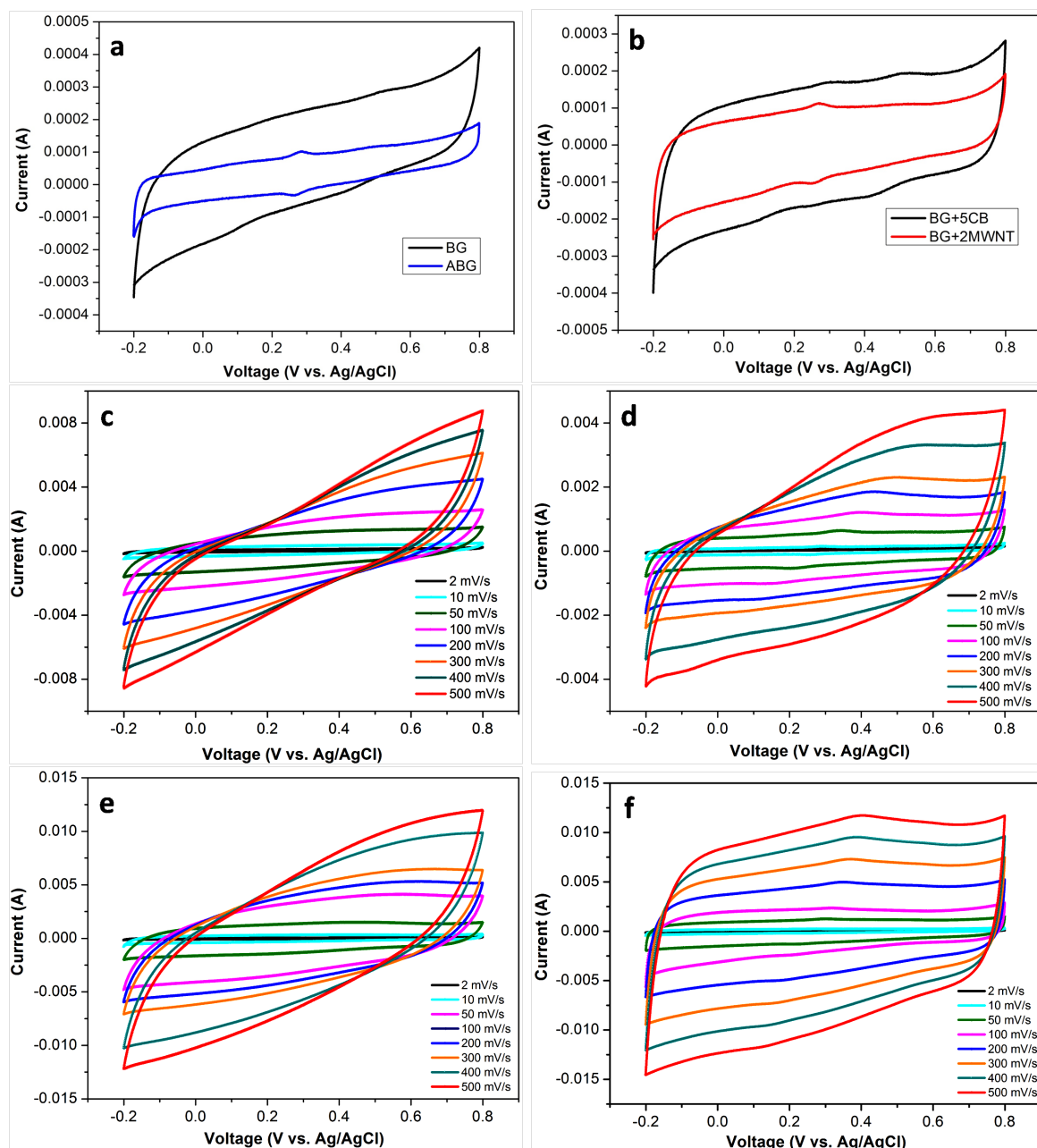


Figure 4.10: Cyclic voltammograms of graphite films on PEI coated stainless steel substrates: (a) BG and ABG films at 5 mV/s scan rate, (b) BG+5CB and BG+2MWNTs films at 5 mV/s scan rate, (c) BG film, (d) ABG film, (e) BG+5CB film, (f) BG+2MWNT film at different scan rates.

The specific capacitance of graphite films as a function of the scan rate is exhibited in Figure 4.11. For all the nano-graphite based film electrodes, the specific capacitance decreased with increasing scan rate due to the progressively less efficient infiltration of ions into the porous structures at faster potential sweeps. Compared with the BG electrode, the specific capacitance of the ABG electrode decreased from ~ 109 F/g to ~ 71 F/g at a low scan rate of 5 mV/s after CO₂ activation treatment, due to the lower utilization of micropore surface area of ABG, caused by the reduced mid-range mesopore volume (6 - 20 nm). However, with the help of long ‘carbon ribbons’ and larger external pore volume, the activated and ball milled graphite electrode significantly improved the ion/electronic transport, showing higher capacitance retention. The reduction of specific capacitance for the ABG electrode was only 31% to 49 F/g when the scan rate increased from 5 mV/s to 100 mV/s, and smaller than a 49% reduction for an equivalent BG electrode film.

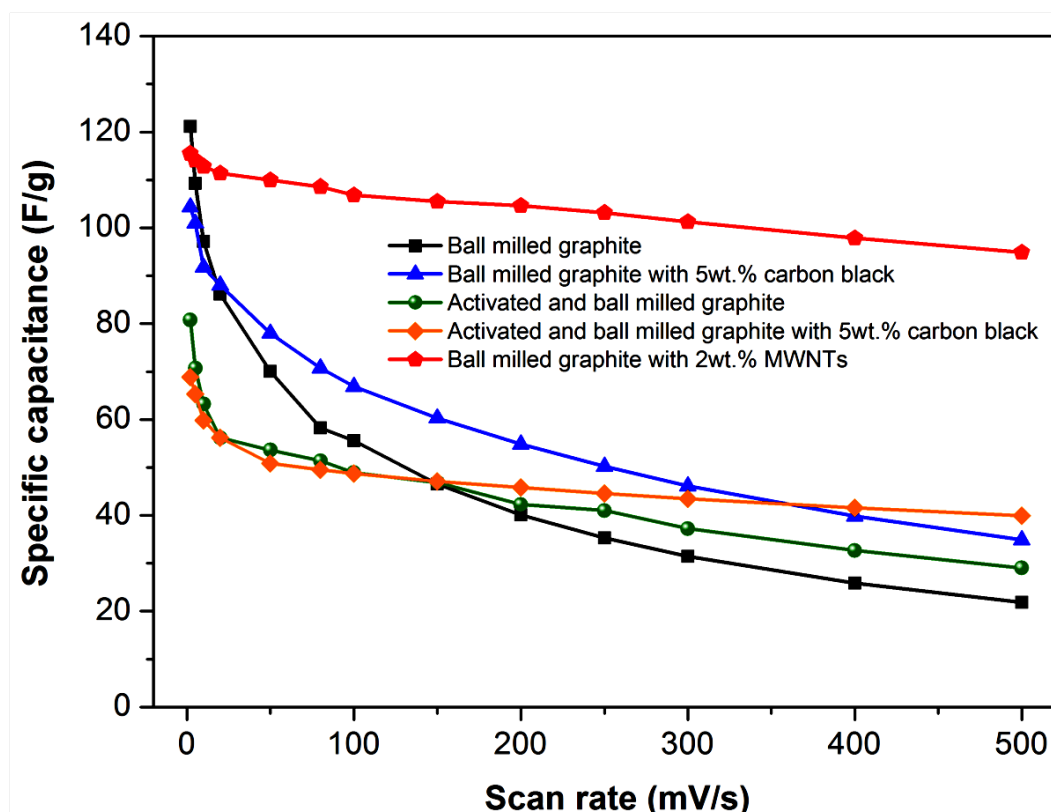


Figure 4.11: The dependence of specific capacitance of graphite films on voltage scan rate.

The addition of conductive materials such as carbon black and MWNTs enhanced the electrochemical performance of the nano-graphite based electrodes (increasing the spe-

cific capacitance retention ratio from 51% to 94% at 100 mV/s with 2 wt.% MWNTs), providing performance superior to some reported ordered mesoporous carbon electrodes (their capacitance retention was only 87% when scan rate increased from 5 to 50 mV/s)^[38]. The error in the capacitance value - a compound of manufacturing reproducibility and measurement reproducibility/accuracy - was estimated at typically 5%.

4.3.5.2 Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy data was used to construct Nyquist plots and these are presented in Figure 4.12. The Nyquist plots for each of the nano-graphite based electrodes were characterized by a single semi-circle in the high frequency region and a straight line in the low frequency region. The semi-circle is indicative of an electrochemical process which was associated with pseudo-transfer reaction and the porous structure of carbon electrodes^[31]. The diameter of the semi-circle is widely interpreted to represent the sum of pseudo-transfer resistance (R_{ps}) at the electrode-electrolyte interface and the resistance of porous electrode^[31, 39].

The intercept of the best fit line to the Nyquist plot on the Z' axis in the high frequency region is also widely interpreted as the internal resistance (R_s), which is the sum of the resistance of the aqueous electrolyte and the contact resistance between electrode and the current collector^[40]. R_s is also known as the equivalent series resistance (ESR), which is an important factor for supercapacitor power density^[31].

The 45° portion of the Nyquist curve between the semi-circle and straight line represents the Warburg resistance (Z_w) which is related to the frequency dependency of ion penetration in the thickness of the porous structure of the electrode^[41].

The best-fit straight line in the low frequency region demonstrated the electrolyte ion diffusion properties in the electrode micro-structure. In other words, it represents the capacitive performance^[41]. Ideal capacitance behaviour will show as a vertical line.

Any deviation from this ideal 90° angle may be related to an ‘unsuitable’ pore size distribution or long ion-transport pathway.

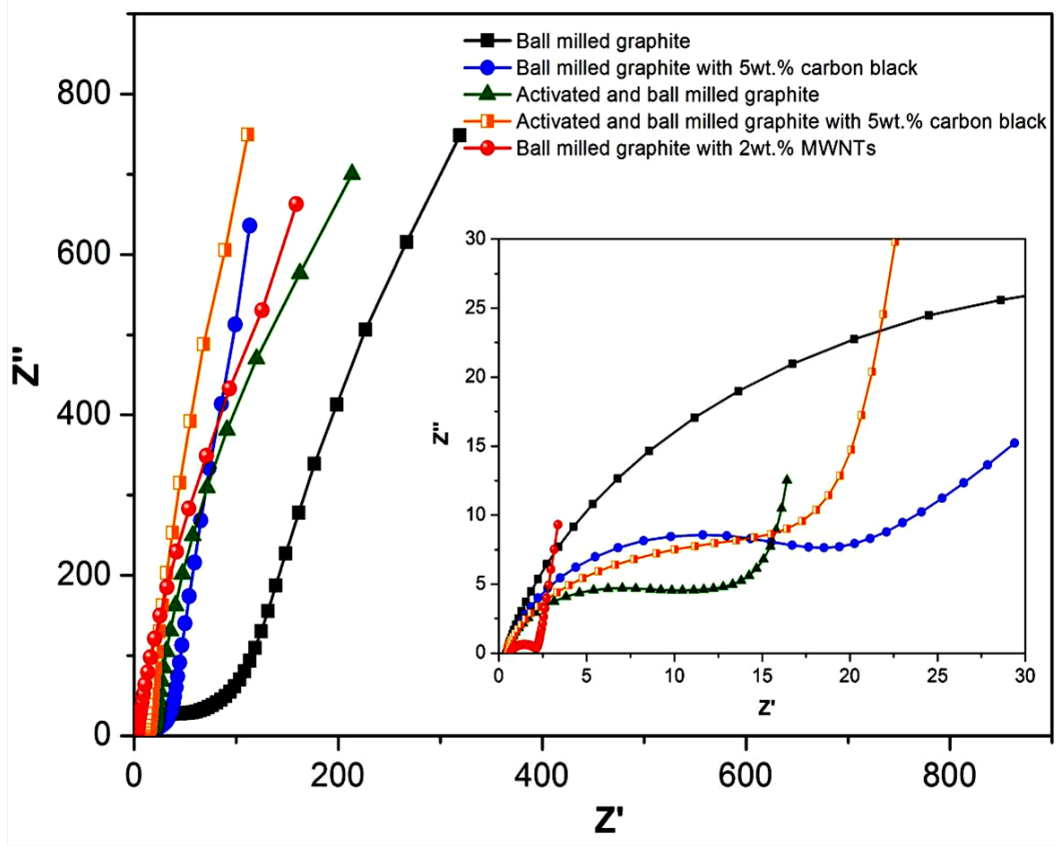


Figure 4.12: Nyquist plot of graphite films in the frequency range of 10 kHz to 0.01 Hz after 10 cycles (the inset shows the expanded high frequency region of the plot).

In order to derive a more physical understanding of the impedance plots, a model equivalent circuit can be used, as shown in Figure 4.13^[31, 39], where R_e is the electrolyte resistance, C_f and R_f are the capacitance and contact resistance associated with the electrode/current collector interface, C_{dl} is a constant phase element representing the capacitance of the double-layer, R_{ct} is the charge-transfer resistance, which is the sum of the pseudo-transfer resistance (R_{ps}) and the resistance of porous electrode, and Z_w is the Warburg impedance. By fitting data to this circuit, or assuming that the electrochemical system contains these characteristic elements, impedance plots can be interpreted to provide values of each element.

All the nano-graphite based thin film electrodes showed comparatively small ESR of approximately 0.5Ω , which were much lower than the resistance reported for ordered mesopore electrodes (e.g. 5Ω)^[42]. The enhanced ionic/electronic transport

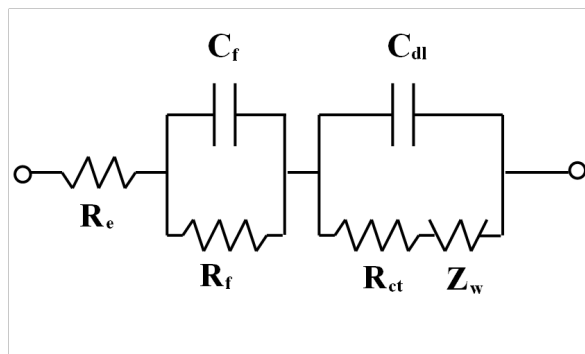


Figure 4.13: Equivalent circuit model to describe the response of the nano-graphite based electrode during charge/discharge.

contributed by the incorporation of CO₂ activation process and the addition of conductive materials was also evident from the impedance analysis. As shown in Figure 4.12, more graphitic structure in the activated graphite particles gave better electronic transport, and the larger external pore volume also reduced the ion-transport resistance, contributing to the decrease of charge-transfer resistance (R_{ct}) from more than 60 Ω to around 12 Ω . Furthermore, the carbon black or MWNT additives reduced the interfacial contact resistance between the graphite particles inside the film electrode, and therefore improved the conductivity, leading to a lower R_{ct} of 1.8 Ω .

4.3.5.3 Charge/discharge and current density

The galvanostatic charge/discharge curves of graphite films are presented in Figure 4.14(a). All the curves had typical triangular shapes between 0 - 0.8 V (vs. Ag/AgCl), which indicated EDLC behaviour. The BG+2MWNT sample had the lowest IR drop (a sharp drop in voltage) as the current switches, again attributed to its reduced charge-transfer resistance provided by the MWNTs.

As shown in Figure 4.14(b), the improvement in the high-rate performance provided by the activation process and the MWNT addition was also evident in the high capacitance retention (58% and 77% respectively) of the nano-graphite based electrodes when the current density increased to 10 A/g. Moreover, the improvement in ionic/electronic transport also increased the stability of capacity retention during long electrochemical

cycling. As exhibited in Figure 4.14(c), the charge-discharge curve for ABG+5CB thin film electrode maintained a near symmetric shape over 5,000 charge/discharge measurements.

Both ABG+5CB and BG+2MWNT thin film electrodes presented stable behaviours over the long consecutive charge/discharge cycles, as shown in Figure 4.14(d), with less than 5% capacitance loss for BG+2MWNT and 3% specific capacitance change for ABG+5CB thin films.

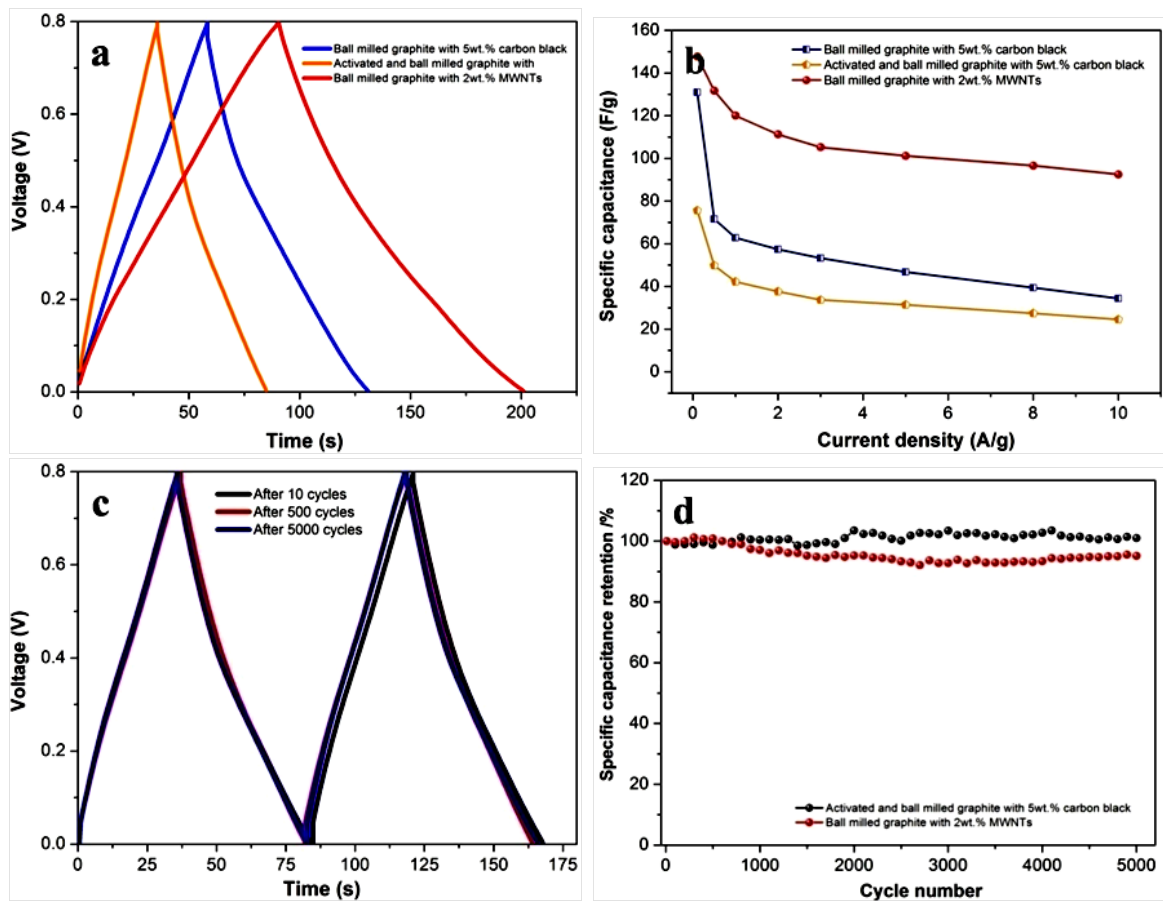


Figure 4.14: (a) Galvanostatic charge/discharge behaviour of nano-graphite based thin film electrodes at 1 A/g current density, (b) specific capacitance as a function of current density for nano-graphite based thin film electrodes, (c) galvanostatic charge/discharge behaviour of ABG+5CB film electrode after 10, 500, 5000 cycles at 1 A/g current density, and (d) capacitance retention of ABG+5CB and BG+2MWNT thin films during 5000 cycles at 1 A/g current density.

4.4 Conclusions

Nano-graphite based thin film electrodes have been fabricated on one meter long flexible webs using the spray deposition technique, with homogeneous film surface morphology, controllable film thickness and good film adhesion.

The nano-graphite based thin film electrodes with microporous structure comprising ball milled graphite followed by CO₂ activation exhibited high electrochemical performance in a 1 M H₂SO₄ electrolyte, attributed to the large fraction of lattice defects, high specific surface area and well balanced ionic/electronic transport. A high specific capacitance of 110 F/g at 100 mV/s, low equivalent series resistance and charge-transfer resistance (less than 0.5 Ω and 1.8 Ω respectively) and stable cycles behaviour at 1 A/g current density with only 3% variation of capacitance has been achieved. The performance was broadly similar or superior to conventional slurry cast electrodes of similar materials.

The spray deposition technique has therefore demonstrated the potential for scalability and processability necessary to process nano-graphite based thin film electrodes with competitive properties.

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Chapter 5

High-rate Performance

Improvement of Activated Carbon Based Supercapacitors

5.1 Introduction

In the previous chapter, commercial graphite-based thin film electrodes were fabricated successfully by spray deposition and showed encouraging electrochemical performance. However, due to the relatively low specific surface area of $\sim 540 \text{ m}^2/\text{g}$ of the ball milled nano-graphite materials, they were relatively limited in terms of high-capacitance applications. In comparison, commercial activated carbons (ACs) have a higher specific surface area that can be in the range $1000 - 3000 \text{ m}^2/\text{g}$, are relatively cheap and already widely used in super capacitors. However, they have generally not been considered for thin film supercapacitor applications, primarily due to a lack of a suitable process route.

Although high surface area is usually considered to be the main requirement for high capacity EDLCs, the performance of AC-based and other electrodes has already been

shown and described to depend on other factors, such as the nature of the porous structure, electrical conductivity, interfacial resistance and surface chemistry (wetting) of the materials^[1--6]. For example, although there is a well-known correlations between the specific capacitance per unit weight (C_s) and specific surface area when measured in Brunauer-Emmett-Teller (BET) apparatus (S_{BET})^[7--9], with C_s approximately linearly increasing with increasing S_{BET} , the efficiency per surface area reduces beyond a surface area of $\sim 1500 \text{ m}^2/\text{g}$ ^[10], because of space constriction for charge accommodation inside the pore walls^[11], and overall, the pore size distribution and related electrical conductivity are as important to optimise as the surface area^[12--14].

As illustrated in Chapter 2, due to the generally random pore structure, commercial ACs can suffer from both poor electrical conductivity and restricted ion mobility (long ion diffusion pathways and high ion transfer resistances). The internal micropores suggested by BET-based or other measurements of surface area cannot always be effectively accessed by the electrolyte ions in practice, leading to a capacitance of normally 75 - 200 F/g in aqueous electrolytes^[15], which suggests that perhaps only 10 - 20% of the theoretical area is effectively utilised at high current density or high scan rate^[16, 17]. Consequently, much effort has been expended to control better the mesopore volume and inter-connected nature of porous structure, such as by using templated carbons, but which are expensive^[18--20].

In addition to the porous structure, the surface chemical properties of the pore walls are important^[7, 21--24]. The surface function can be manipulated to improve the carbon wettability and/or increase the total specific capacitance by inducing faradic related pseudo-capacitance^[2, 22, 24--27] (but not all the functional groups have the same contribution to pseudo-capacitance^[10, 28]).

In summary, the electrochemical performance of AC-based electrodes is highly attractive and already exploited, and derives from a complex combination of properties. Nonetheless, in all cases where overall electrode areas beyond a few cm^2 are required, slurry casting is the process of choice, which produces the traditional ‘thick’ electrode

structure with compromised (but often acceptable) performance.

In this chapter, three types of commercial ACs were investigated for their suitability as thin film electrodes, fabricated by spray deposition. In order to improve performance in supercapacitor applications, methods to improve the physio-chemical properties of the AC-based electrodes were explored, such as: reducing the contact resistance of the electrode/current collector interface by modifying the pre-coated layers, improving the electrode microstructure by choosing suitable solvents, and re-organizing the electrode porous structure of the feedstock followed by surface chemical features by mechanical grinding and secondary activation.

5.2 Materials and methods

5.2.1 Preparation of activated carbon particles

Three types of commercial activated carbons were studied: Darco_60 (Sigma-Aldrich, UK), MAST (Mast Carbon International Ltd, UK) and YP_50 (Kuraray Chemical Co, Ltd, Japan) and further details are given later. Sodium carboxymethyl cellulose (CMC), acetylene black, MWNTs, and poly(ethyleneimine) (PEI) were again also added in various proportions used in electrode fabrication, as already described in Chapter 4.

For some of the AC samples, a ball milling treatment was used in an attempt to reduce the particle size for higher specific surface area, and to likely re-organize the porous structure. Ball milling was performed at room temperature under ambient atmosphere in a Fritsch ‘Planetary 6’ planetary mill. Various weight-to-ball ratios (1/15, 1/25), rotation velocities (200/400/600 rpm), and milling times (2 - 20 h) were used.

For some AC samples, secondary activation was subsequently carried out on ball milled AC particles in an attempt to restore or further increase the surface area and pore

volume. This was required because ball milling can destroy the porous carbon surface structure from primary activation treatments. This secondary activation procedure was the same as described in Chapter 3.

For convenience, a shortened form for the Feedstock/Ball milled/secondary Activated powders is used in this chapter: Darco_60, MAST and YP_50 are: (FD, BD, AD), (FM, BM, AM) and (FY, BY, AY).

5.2.2 Preparation of activated carbon based thin film electrodes

To prepare the electrodes, the AC powders (feedstock or ball milled or secondary activated) were dispersed in suitable solvents (deionised water or n- methylpyrrolidone (NMP)) with ultrasonication for 10 min to form stable suspensions with a solid concentration of 5 mg/ml. To give the best stability for aqueous suspensions, 1 wt.% (with respect to AC weight) CMC was used as a surfactant, and the pH value of suspension was adjusted to 10.5. No surfactant was required in the NMP suspensions.

Thin film AC-based electrodes were fabricated by spray deposition of the suspensions onto heated stainless steel substrates using 400 kPa compressed air, and a suspension flow rate of 2 ml/min. During the spray, the stainless steel substrates sat on a heated plate with temperature maintained at 110 °C/200 °C for aqueous and NMP suspensions respectively. In each case, a few layers of PEI/conductive carbon (such as MWNT, carbon black, AC) mixture were pre-coated on the substrates to pursue a lower contact/interfacial resistance. Substrates with a few layers of PEI only pre-coatings were also prepared for comparison. The concentration of the conductive carbon/PEI suspension was 1 mg/ml. The pre-coating was 2 layers in each case and estimated at a few 10's of nanometer thickness (~ 0.02 mg conductive carbon and ~ 0.04 mg PEI). The film thickness for all the sprayed electrodes was $\sim 2 \mu\text{m}$.

5.2.3 Characterization

5.2.3.1 Surface morphology and structure characterization

The approaches for characterising the surface morphology and structure have already been described in Chapter 3, and very similar approaches were used here, based primarily on microscopy and XPS. The XPS spectra were analyzed and fitted using Casa XPS software, with the C_{1s} (sp^2) binding energy (284.9 eV) used as the reference for the XPS spectra calibration.

5.2.3.2 Electrochemical determination

Electrochemical properties were characterized by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and galvanostatic charge/discharge cycles using a three-electrode configuration in a 1 M H_2SO_4 aqueous electrolyte. Note the AC electrodes in commercial supercapacitors utilise an organic electrolyte (such as acetonitrile, propylene carbonates and tetraethylammonium tetrafluoroborate) that operate in an electrochemical stability window of typically 2.5 - 3 V. These were not studied here (although similar electrolytes are used in Chapter 7), because the emphasis in the present work is to focus on low cost systems for scale-up where aqueous systems offer safety and simplicity. Further, the ability of thinner, sprayed electrodes to offer high performance in a less compromised configuration than thick slurry cast materials, and thus make aqueous systems more comparable and competitive, was of particular interest.

As is standard in the literature for these materials, CV curves were measured in the potential range of -0.2 to 0.8 V (vs. Ag/AgCl) at a scan rate of 5 - 600 mV/s. Electrochemical impedance spectroscopy (EIS) used a AC voltage at 10 mV amplitude over a frequency range of 10000 - 0.01 Hz at room temperature. Galvanostatic charge/discharge cycles were performed at constant current density of 1 A/g between

0 - 1 V in 1 M H₂SO₄.

5.3 Results and discussion

5.3.1 Morphology and structure

The morphology and texture of feedstock Darco_60, MAST and YP_50 powders are presented in Figures 5.1, 5.2 and 5.3 respectively. According to the manufacturers of Darco_60 (Norit/Cabot USA), it is a steam activated carbon produced from a proprietary raw material^[29, 30]. As shown in Figure 5.1(a), the feedstock Darco_60 particles had a blocky, ribbed shape with a wide range of particle sizes from 30 to 50 μm . Because it was strongly non-spherical, size quantification by laser diffraction was not pursued. As shown in Figure 5.1(b), the ‘ribs’ on the larger blocks appeared friable, in some views, the ribs appeared as agglomerations of smaller particles, or containing agglomerations between the ribs: structures were highly variable. The ribs had a diameter of *ca.* 5 μm , length of *ca.* 50 μm , and wall thickness of *ca.* 1 μm . Figure 5.1(c) shows the complicated ribs structure end-on. Small ($< 1 \mu\text{m}$) spherical powders, possibly amorphous in nature, filled/covered the axial ribs. Nonetheless, the powder also contained a high fraction of ‘free’ blocky particles, that may be remnants of the broken down rib-type agglomerates, as shown in Figure 5.1(d).

The MAST carbon was produced by solution polymerisation of a phenolic resin, followed by carbonisation and activation^[31]. Figure 5.2(a) shows the feedstock MAST carbon powders that were spherical with a wide diameter range from 10 to 200 μm , consistent with reports from MAST Carbon International Ltd^[31]. As exhibited in the TEM image in Figure 5.2(b), the MAST powders comprised two parts: loose, large mesoporous carbon particles and comparatively dense, apparently substantially amorphous fragments. Figure 5.2(c) shows a higher magnification view of the mesoporous structure: the large mesopores were bounded by a graphitic carbon framework, with

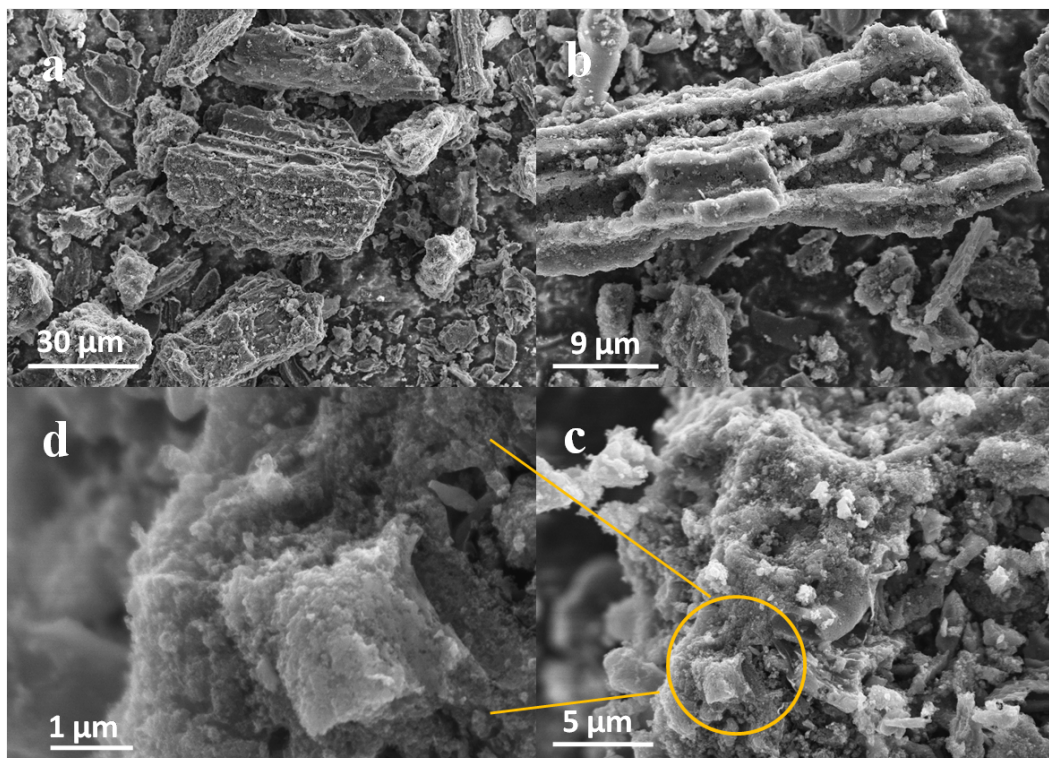


Figure 5.1: SEM image of (a) Darco_60 feedstock (FD) powder, (b) an axially ribbed FD particle, (c) a ribbed FD particle, end-on, and (d) high resolution of the FD end-on surface.

typically a 2 nm pore wall thickness and 10 - 50 nm pore diameter. As described in Chapter 2, these large mesopores can provide short ion diffusion pathways during ion adsorption/desorption to increase the capacitive response at high rates. Meanwhile, Figure 5.2(d) shows a high magnification view of the amorphous-like structure. As discussed in Chapter 4, a defective, amorphous-like structure can provide relatively large fractions of micropores. Previous studies of phenolic resin based porous carbon from MAST Ltd also showed a similar micropore/mesopore structure, with micropore volumes varying between 0.29 and 0.66 cm³/g [32].

YP_50 is coconut shell-based carbon, activated with water vapour in the temperature range 950 to 1150 °C, and is promoted by the manufacturer to be specifically tailored for the supercapacitor market (with high surface area and purity)^[33]. Figure 5.3(a) shows that the average particle size of the YP_50 feedstock particles was $\sim 5 \mu\text{m}$, consistent with Kuraray Chemical Co data^[34], and the particle size distribution was noticeably narrower than that of the feedstock Darco_60 and MAST carbon par-

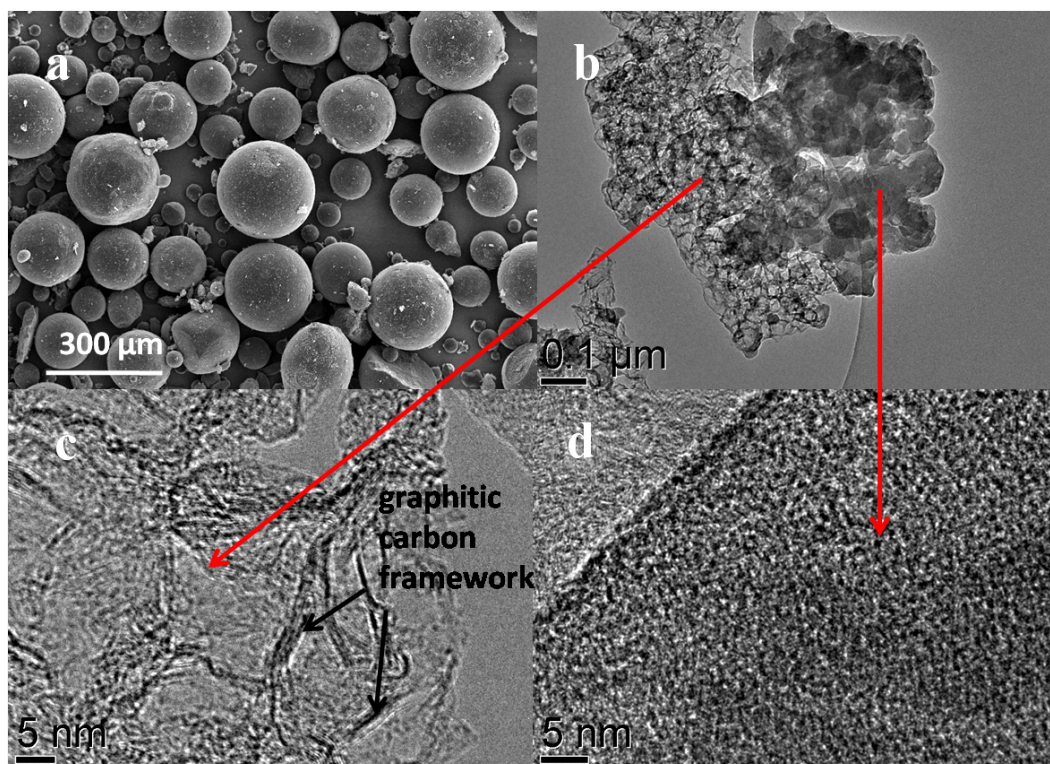


Figure 5.2: (a) SEM image of feedstock MAST powders, (b) TEM image of FM powder (interconnected mesoporous structure and amorphous piece), (c) high resolution TEM image of mesoporous structure, and (d) high resolution TEM image from an amorphous fragment.

ticles. The FY particles were comparatively faceted, with distinct edges and relatively ‘smooth’ surfaces, as shown in Figure 5.3(b). At higher magnification in Figure 5.3(c), the edges showed extremely fine-scale roughness at the nanometer scale. The HRTEM image in Figure 5.3(d) was typical for the powder and indicated that FY particles contained both amorphous and graphitic regions.

The N_2 adsorption-desorption isotherms of feedstock Darco_60, MAST and YP_50 are shown in Figure 5.4(a). All materials showed a typical mesopore response, characteristic of type IV adsorption isotherms with obvious H4 hysteresis loops at high relative pressure ($P/P_0 > 0.45$), which can be attributed to the capillary condensation of N_2 in mesopores or macropores^[35]. Feedstock Darco_60 (FD) and MAST carbons (FM) had similar adsorption behaviour: N_2 adsorption increased at relative pressures from 0.1 to 0.8, and dramatically increased from 0.8 to 0.95 P/P_0 , indicating their relatively broad mesopore size distribution and high mesopore volume and/or potential macropores. Compared with FD and FM, the adsorption behaviour of feedstock YP_50 (FY) was

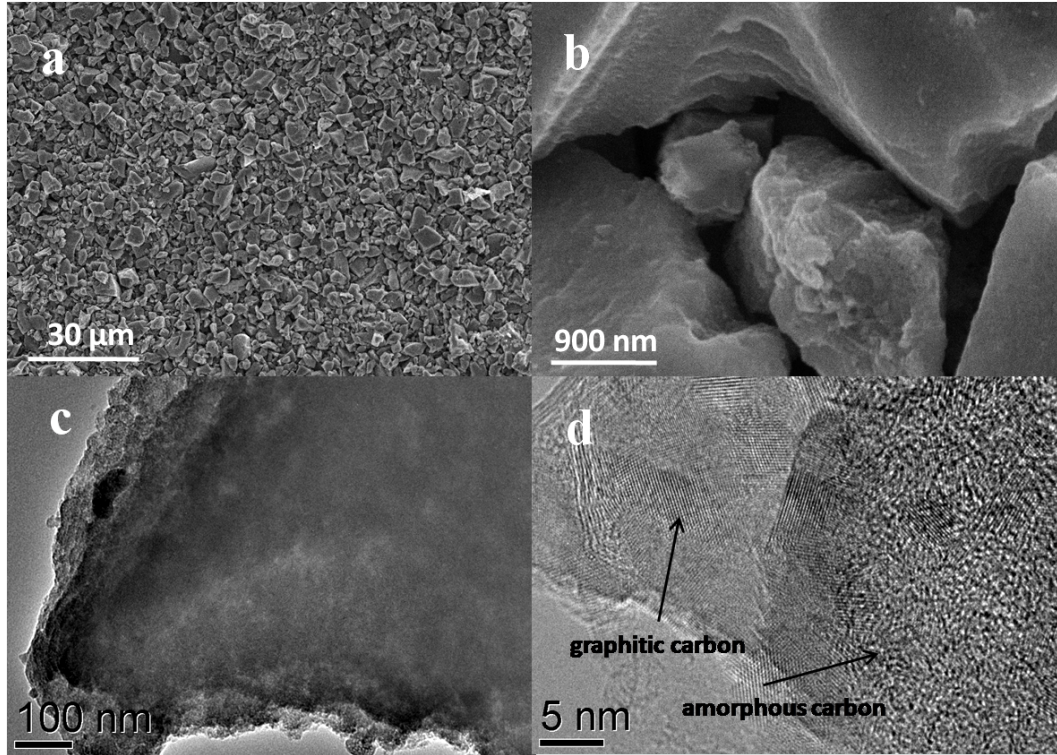


Figure 5.3: (a) SEM images of FY particles, (b) SEM images of FY particles at higher magnification, (c) TEM image of a corner of a FY particle, and (d) high resolution TEM image, showing a combination of amorphous and graphitic structures.

characterized by the rapid increase of N_2 adsorption at P/P_0 below 0.1 and relatively flat curve from 0.1 to 0.95 P/P_0 , indicating a relatively large micropore volume and smaller meso/macropore volume.

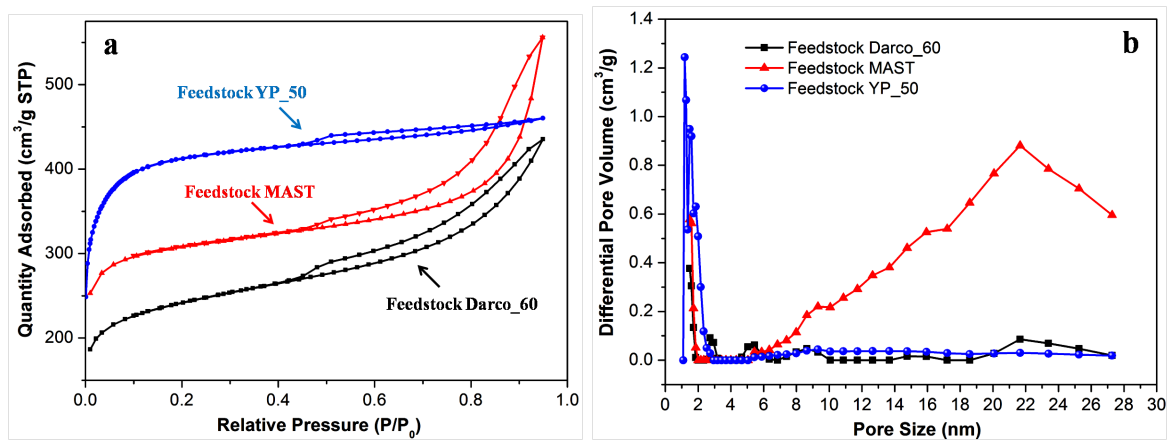


Figure 5.4: (a) N_2 adsorption/desorption isotherms (77K) for FD, FM and FY, and (b) their relative pore size distribution determined by the NLDFIT model.

Assuming pore behaviour can be approximated to the NLDFIT model^[36, 37], then the corresponding pore size distribution (PSD) curves of the three activated carbons are shown in Figure 5.4(b). Compared with FM and FY, Darco_60 particles had the lowest

fraction of micropores < 2 nm and mesopores (2 nm - 50 nm), although the difference between Darco_60 and YP_50 in the mesopore region was not particularly marked. There were two peaks present in the PSD curve of FM: at ~ 1 nm and 23 nm, which is suggested to correspond to contributions from the smaller amorphous fragments and the larger mesoporous carbon frameworks respectively (Figure 5.2(c)). The peaks in the PSD curve of FY were mainly in micropore and sub-mesopores (slightly larger than 2 nm) regions, consistent with the TEM images that suggested both amorphous and crystalline fractions could be expected to present different micropore populations (Figure 5.3(d)). However the lack of larger mesopores and macropores might inhibit ion mobility. The detail of pore volumes and specific surface area of three materials are summarized in Table 5.1 for completeness, but recognising the assumptions required to convert adsorption/desorption ‘raw data’ into these quantities, they should be used only to suggest trends rather than relied upon absolutely, and Figure 5.4(b) likely gives the most helpful indications of similarities/differences.

5.3.2 Surface chemical analysis

The XPS spectra of the three activated carbons all presented two distinct peaks for carbon and oxygen. The peaks were as graphitic carbon at 284.7 eV, carbonyl groups at 287.1 eV, and carboxyl groups at 289.5 eV^[38]. The carbonyl group belongs to CO-type surface functionalities and the carboxyl group belongs to CO₂-type, because CO and CO₂ is produced during the high temperature activation^[39–42]. The approximate concentration of C and O in the feedstock, and secondary activated AC particles, are shown in Table 5.2. Note that only the YP_50 powder showed a significant change on secondary activation, with a reduction in residual O concentrations to the mid-range of those of the other materials. The higher feedstock concentrations may be associated with its highest initial surface area (Table 5.1) or the nature of the steam (as opposed to CO₂) activation.

Table 5.1: A summary of estimated pore characteristics of the three activated carbon particles, based on N₂ adsorption/desorption isotherms.

Sample	Darco_60 (FD)	MAST (FM)	YP_50 (FY)
S_{BET} (m ² /g)	626	942	1313
S_{inter} (m ² /g)	365	716	1029
S_{exter} (m ² /g)	261	226	284
V_t (cm ³ /g)	0.5	0.8	0.7
V_{mi} (cm ³ /g)	0.2	0.4	0.5
V_{ex} (cm ³ /g)	0.3	0.4	0.2
D_{aver} (nm)	3.0	3.7	2.2
% <i>micro</i>	48	44	72

S_{BET} - BET specific surface area, S_{inter} - micropore surface area, S_{exter} - surface area of mesopore and macropore ($S_{exter} = S_{BET} - S_{inter}$), V_t - total pore volume, V_{mi} - micropore volume, V_{ex} - pore volume of mesopore and macropore, D_{aver} - average pore width, % *micro* - micro-porosity percentage.

Table 5.2: Composition of activated carbons derived from XPS analysis.

Sample	FD	AD	FM	AM	FY	AY
C (atom %)	94.2	94.8	96.7	97.3	91.2	95.1
O (atom %)	5.8	5.2	3.3	2.7	8.8	4.9

5.3.3 Capacitive and electrical conductive improvements

In order to design high performing capacitive and electrical conductive properties of the AC-based electrodes, 4 methods were explored: electrode/current collector interface control, suitable suspension type, mechanical grinding and secondary activation. The optimisation targets are: increasing capacitive behaviour increasing area and tailoring pore sizes), minimising the equivalent series resistance (ESR) and minimising the charge-transfer resistance (R_{ct}). Electrochemical impedance spectroscopy (EIS) was used as the main tool to analyse the effects of any changes.

5.3.3.1 Reduction of contact resistance at the electrode/substrate interface

To improve the adhesion of the electrode on the current collector, a few layers of PEI are usually pre-coated on the stainless steel current collectors (the same in Chapter 4), to create a hydrophilic surface. Although used successfully in previous work^[43], further improvement may be possible. Therefore, carbon based conductive additives (MWNTs or carbon black or the electrode AC) were mixed with PEI and then this carbon/PEI mixture was pre-coated on the current collectors with ~ 30 nm film thickness (2 layers). The cyclic voltammograms and electrochemical impedance of the resulting AC-based electrodes (Darco_60, MAST, YP_50) with different pre-coatings in 1 M H_2SO_4 aqueous electrolyte at scan rate between 50 - 500 mV/s are shown in Figures 5.5, 5.6 and 5.7 respectively.

Similar trends were obtained for all three electrodes, and therefore Figure 5.5 is used for the basis of the description of the behaviour. The CV curves of carbon electrodes with a PEI only pre-coating had a parallelogram shape as expected, but with non-vertical edges when the direction of voltage sweep was reversed, which was indicative of a significant resistance somewhere in the half-cell arrangement. This was most evident when the scan rate increased to 500 mV/s, as shown in Figure 5.5(a). This resistive charac-

ter was slightly reduced when a ‘electrode materials/PEI mixture’ (Figure 5.5(b)) or ‘MWNTs/PEI mixture’ (Figure 5.5(c)) was used, implying that the electrode/substrate interface properties had been improved with the aid of carbon polymorphs known to have comparatively high electrical conductivity. The most well-defined rectangular shapes characteristic of lowest resistance and ‘pure’ EDLC behaviour were obtained in electrodes with ‘carbon black/PEI mixture’ pre-coating layers (Figure 5.5(d)).

The suggested mechanism for the reduction of interfacial resistance by adding carbon conductive materials into PEI coatings is illustrated schematically in Figure 5.8. PEI is needed to provide adhesion and wetting across the interface, and the added carbon then electrically connects the electrode particles to the current collector directly, through the PEI layers, via an electrically percolating network. The best enhancement was achieved by the PEI/carbon black mixture because the nano-scale carbon black provided many contact points, compared with the other carbons. While MWNTs also have high intrinsic conductivity, it may be speculated that their effect was less marked because (i) they were bundled rather than disperse in PEI, and (ii) they tended to lie in the plane of the coating and their contribution to through-plane conductivity was limited.

The improvements in contact resistance were also evident when the carbon electrodes were analysed by electrochemical impedance spectroscopy. In the Nyquist plots in Figure 5.5(e), the contact resistance (R_f) in the high frequency region were dramatically reduced when using the ‘conductive carbon/PEI mixture’ rather than the ‘pure PEI’ pre-coating. For the AC electrodes with ‘carbon black/PEI mixture’ pre-coating, the smallest equivalent series resistance (ESR) was achieved: $0.3\ \Omega$ for Darco_60 (Figure 5.5(f)), $0.5\ \Omega$ for MAST (Figure 5.6(f)), $0.6\ \Omega$ for YP_50 (Figure 5.7(f)) respectively. These improved contact resistances were competitive or better than those reported for surface treated Al current collectors ($ESR = 0.5\ \Omega$)^[44], and CNT/Au(nano wire) segments ($ESR = 0.48\ \Omega$)^[45]. Furthermore, compared with the complex etching/sol-gel surface treatment procedure for Al^[44] or the two step synthesis of CNT/Au nano wire interfaces^[45], the approach of pre-coating using a carbon black/PEI mixture was much easier, more scaleable and likely to be much cheaper.

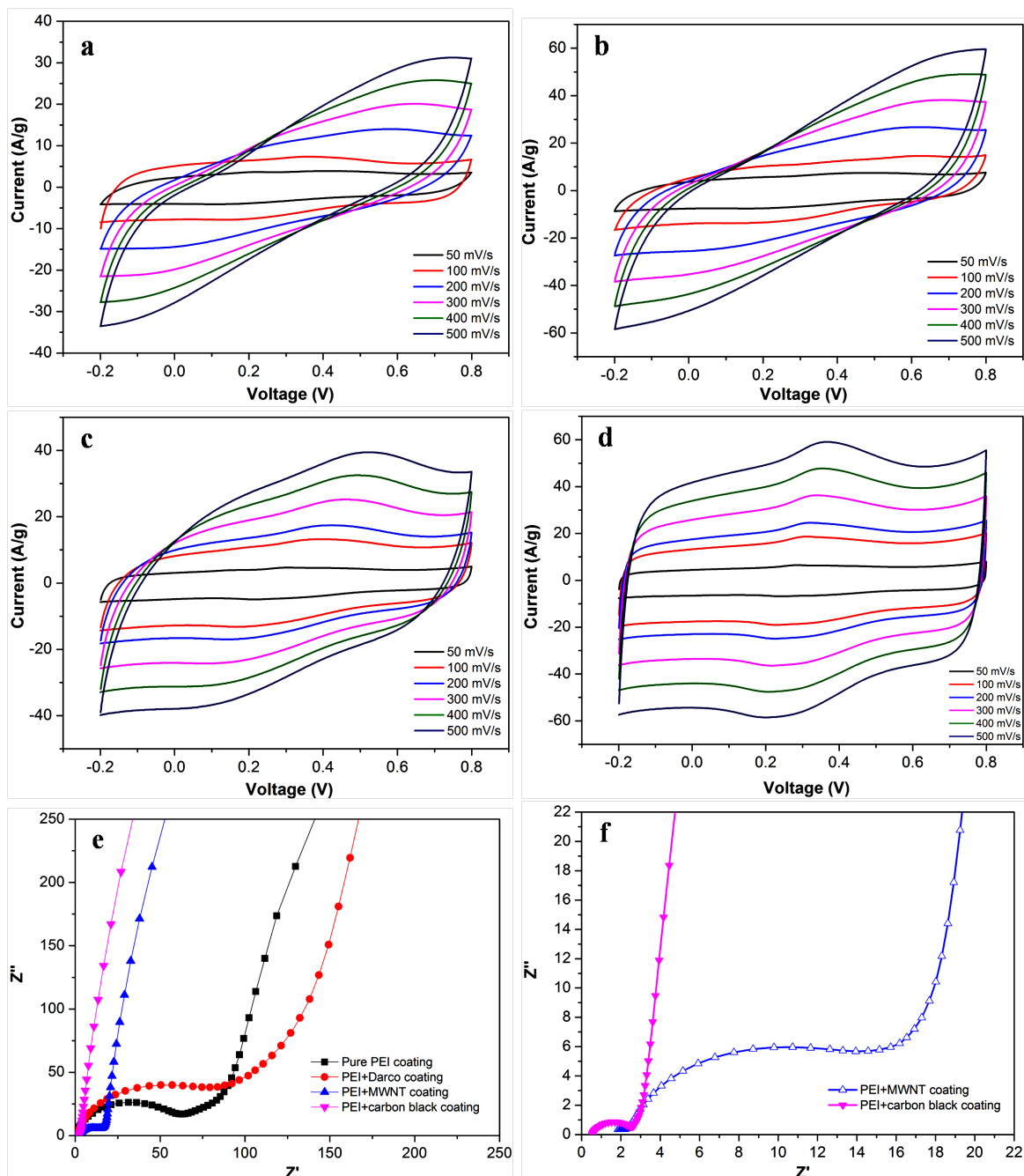


Figure 5.5: Cyclic voltammograms of Darco_60 thin film electrodes in 1 M H₂SO₄ aqueous electrolyte with substrates pre-coated by (a) pure PEI, (b) Darco_60/PEI mixture, (c) MWNTs/PEI mixture, and (d) carbon black/PEI mixture. (e) and (f) are Nyquist plots of Darco_60 thin film electrodes with the different pre-coating layers.

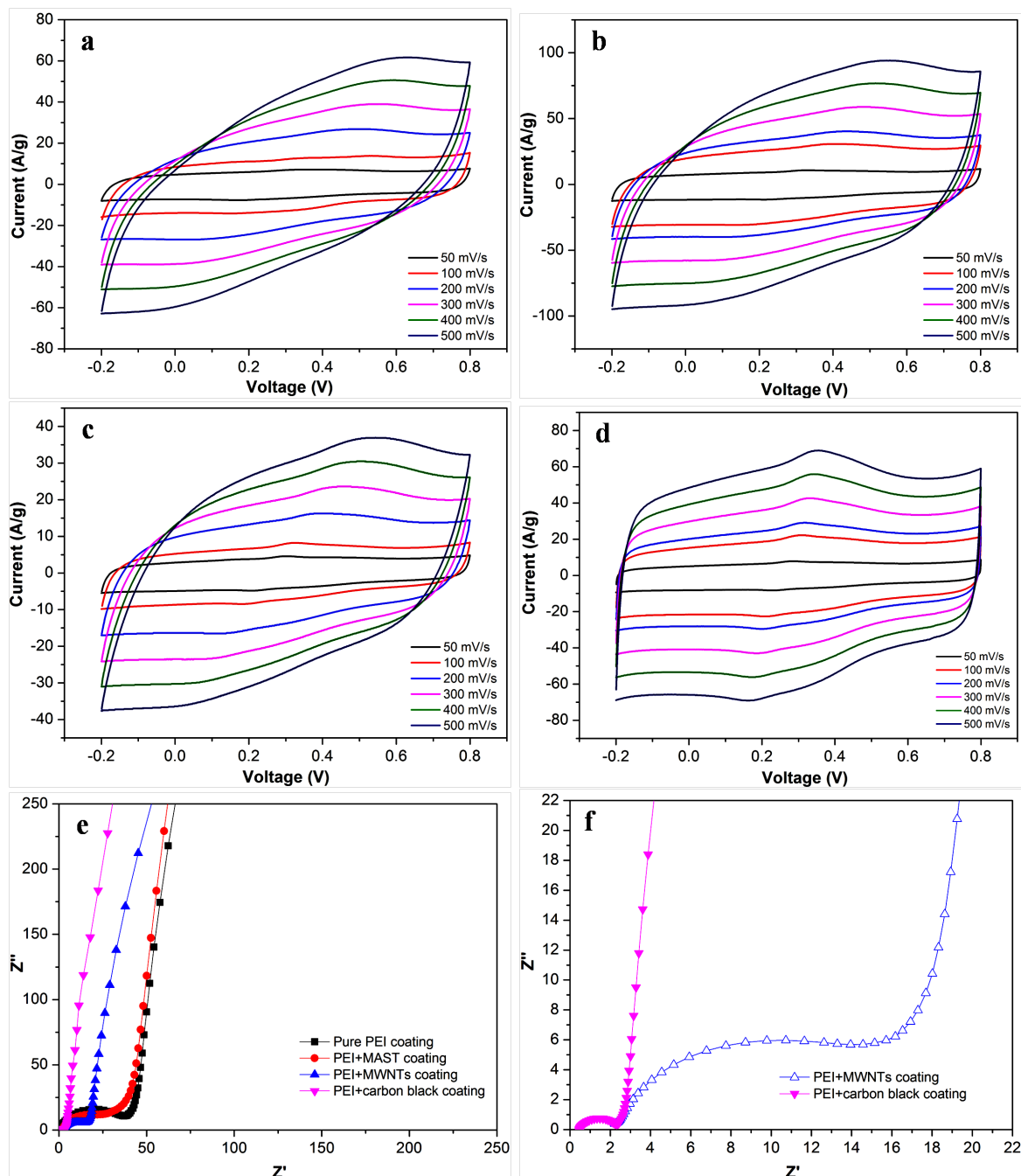


Figure 5.6: Cyclic voltammograms of MAST thin film electrodes in 1 M H₂SO₄ aqueous electrolyte with substrates pre-coated by (a) PEI, (b) MAST/PEI mixture, (c) MWNTs/PEI mixture, and (d) carbon black/PEI mixture. (e) and (f) are Nyquist plots of MAST thin film electrodes with the different pre-coating layers.

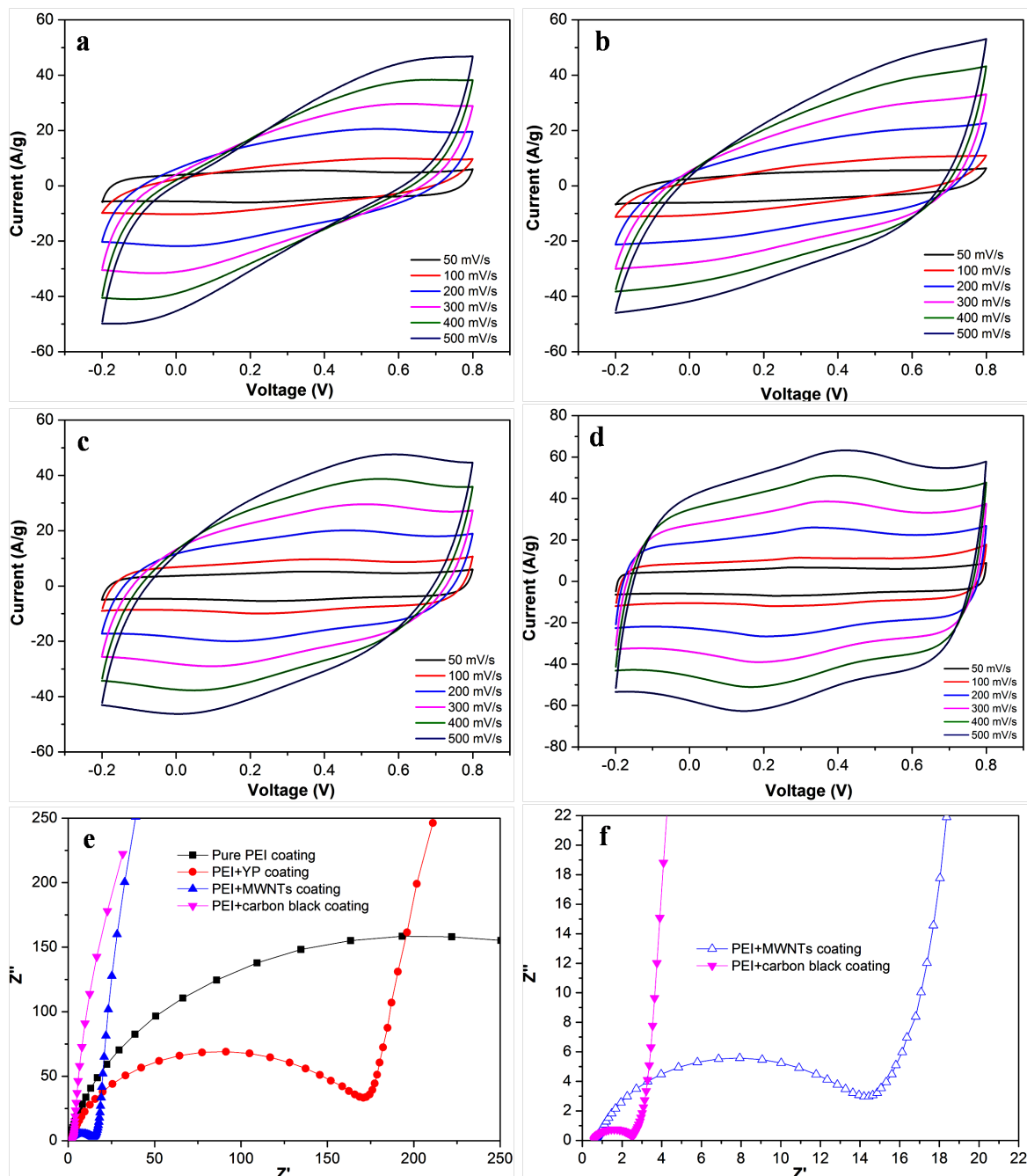


Figure 5.7: Cyclic voltammograms of YP_50 thin film electrodes in 1 M H₂SO₄ aqueous electrolyte with substrates pre-coated by (a) PEI, (b) YP_50/PEI mixture, (c) MWNTs/PEI mixture, and (d) carbon black/PEI mixture. (e) and (f) are Nyquist plots of YP_50 thin film electrodes with the different pre-coating layers.

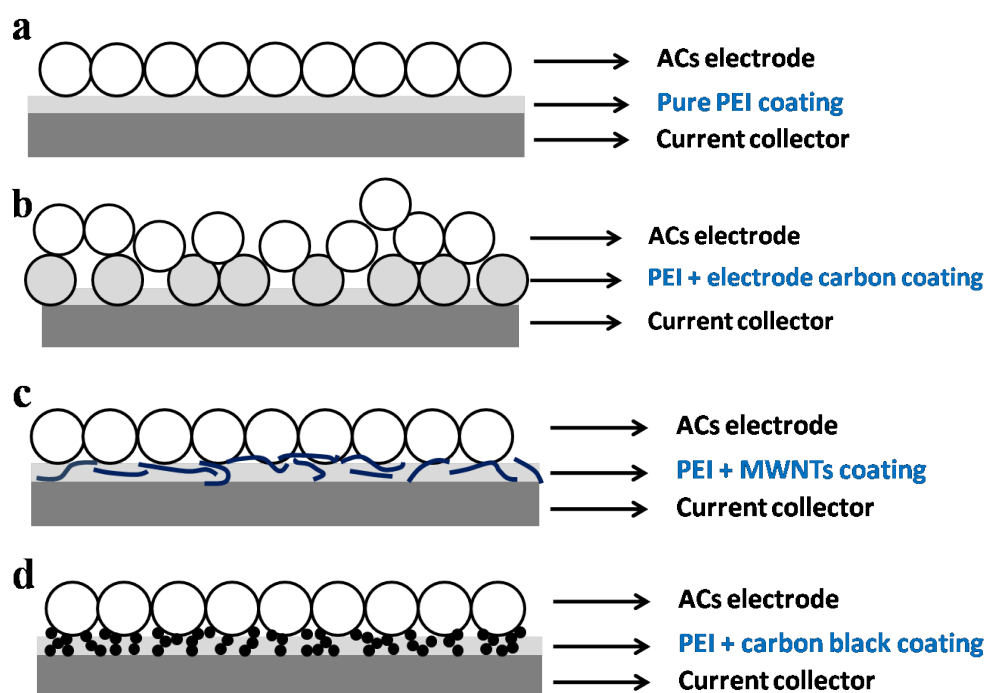


Figure 5.8: Schematic illustration of interfacial conductivity enhancement by different pre-coated layers: (a) Pure PEI, (b) electrode carbon/PEI mixture, (c) MWNTs/PEI mixture, and (d) carbon black/PEI mixture.

5.3.3.2 Improvement of microstructure by using suitable suspensions

As previously discussed several times, the microstructure of the electrodes can influence the capacitive behaviour (the resistance behaviour), especially of high-rate performance where limiting aspects of the microstructure tend to be revealed^[46]. Preferred microstructures will have good particle contact and relatively open channels for electrolyte ions to go through the electrode layer, both of which will enhance the capacitive behaviour (reduce the resistance behaviour) in high-rate performance for EDLCs. By contrast, electrodes with excessive agglomeration will have limited performance due to increased ion diffusion resistance.

To provide electrodes with a consistent microstructure, AC particles should be well dispersed by choosing suitable liquids for the suspensions. In this chapter, deionised water and NMP were used to disperse the Darco.60, MAST carbon and YP.50. Surfactant sodium carboxymethyl cellulose (CMC) was not used when using organic NMP as the dispersant. The electrochemical impedance behaviour of resulting electrodes and

the cyclic voltammograms (at scan rates between 50 - 500 mV/s) are shown in Figures 5.9 and 5.10 respectively.

As shown in the Nyquist plots in Figure 5.9(a), the Darco_60 electrode with suspension prepared in NMP had a higher gradient and more linear response at high frequency than that prepared in water, indicating a lower resistive character when NMP suspensions were used. The enhancement of capacitive behaviour can also be observed in cyclic voltammograms: comparison of Figures 5.10(a) and (b) shows that NMP suspensions produced CVs with more rectangular shape and larger capacity than aqueous suspensions, with a capacity in each case of 84 and 117 F/g. The reason for the enhanced capacitive behaviour (reduced resistive behaviour) was the improved electrode microstructure formed by better dispersion. The Darco_60 had better dispersion in NMP was because compared with water, which has a low affinity for pure carbon, the organic NMP is non-polar with a good affinity towards the hydrophobic AC particles, making it easier to disperse^[47] (no surfactant needed). Because in the case of NMP, the CMC surfactant was not needed for suspension stability, this may also have improved capacitive response since more of the AC surface may be available for charge storage.

However, as shown in Figure 5.9(b), compared to using water as the suspension vehicle dispersant, relatively large semi-circle diameters (related to higher pseudo-transfer resistance R_{ps} , as described in Chapter 4) in Nyquist curves at high frequency region were obtained for the NMP suspension. As shown in Figure 5.10(b), more obvious peaks in the CV curves were introduced when using NMP. The increased R_{ps} and introduced peaks were related to the introduction of faradic reactions, which were attributed to the introduction of oxygen surface groups formed by interactions between NMP and the carbons.

The MAST carbon electrodes for suspensions prepared in water and NMP had similar capacitive behaviours: both had straight tails in Nyquist plots in the low frequency region (Figure 5.9(c)) and similar rectangular CV shape (Figure 5.10(c) and (d)),

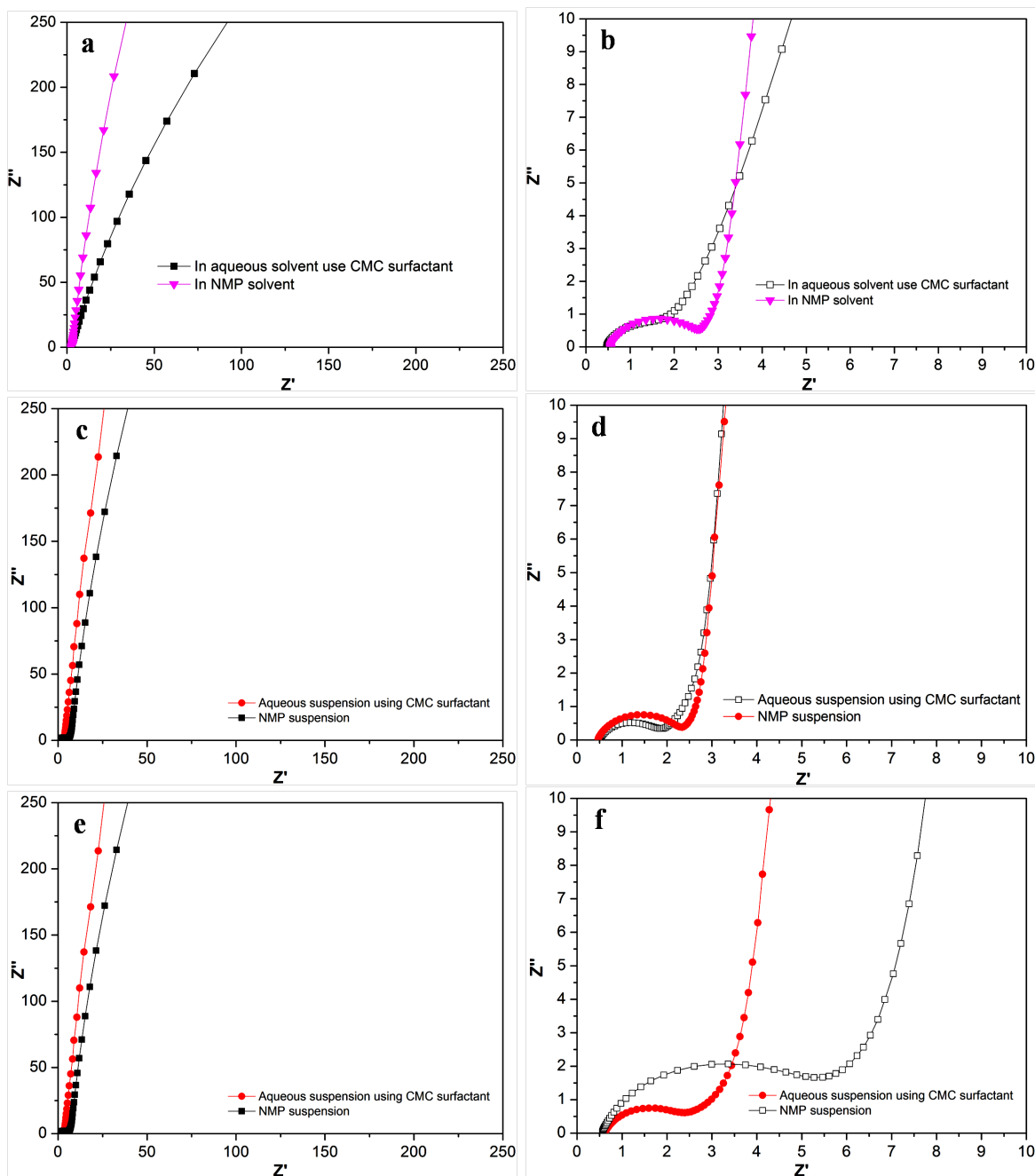


Figure 5.9: Nyquist plots in AC-based electrodes in a 1 M H_2SO_4 aqueous electrolyte with suspension prepared in water or NMP: (a) and (b) Darco_60, (c) and (d) MAST carbon, (e) and (f) YP_50.

but the capacity of the MAST carbon electrode prepared using NMP suspension was slightly higher than that prepared in water, attributed to better dispersion in NMP, which leads to less agglomeration and therefore higher particle surface utilisation. As shown in Figure 5.9(d), and unlike FD, the increase in R_{ps} for FM when using NMP was almost negligible, which was likely due to its lower starting oxygen content (3.3 atom% in MAST compared with 5.5 atom% of Darco_60).

Like MAST carbon, the YP_50 electrode had similar capacitive behaviour with suspension prepared in water and NMP, as shown in Figure 5.9(e). However, in contrast, a higher capacity of YP_50 electrode was obtained when using water for dispersion (as shown in Figure 5.10(e) and (f)), this may arise because of its high oxygen-containing surface groups (8.8 atom%, previous XPS result) which provided more compatible interaction with water molecules to facilitate dispersion^[48]. As exhibited in Figure 5.9(f), compared with Darco_60 and MAST carbon, the YP_50 electrode had the most obvious increase on R_{ps} when using NMP for dispersion, similarly due to the comparatively high starting oxygen concentration.

5.3.3.3 Improvement of electrochemical performance by ball milling

Following the improvement of capacitance for the graphite-based electrodes in Chapter 4, a ball milling pre-treatment was also investigated for some of AC-based electrodes, with the intention that smaller particle sizes might increase specific capacitance via increased surface area.

The N_2 adsorption-desorption isotherms and relative pore size distributions of Darco_60, MAST and YP_50 in three different conditions (as feedstock, after ball milling, and after secondary activation) are shown in Figure 5.11. The changes in pore volume and specific surface area for these AC particles after ball milling and secondary activation treatment are summarized in Table 5.3. Results regarding any secondary activation treatment are discussed later in the next section.

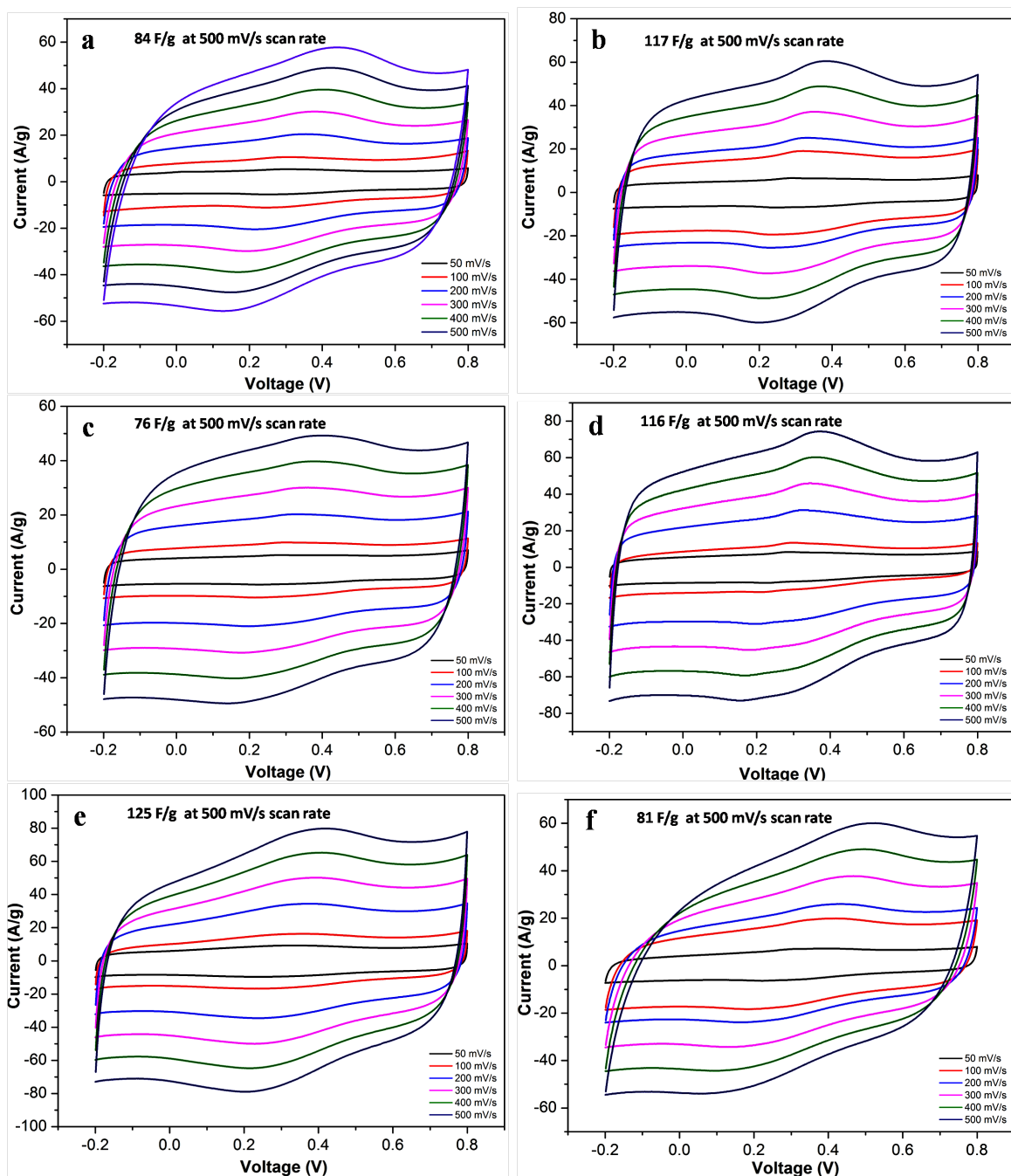


Figure 5.10: Cyclic voltammograms measured in 1 M H_2SO_4 aqueous electrolyte for (a) Darco_60 electrodes with suspension prepared in water, (b) Darco_60 electrodes with suspension prepared in NMP, (c) MAST carbon electrodes with suspension prepared in water, (d) MAST carbon electrodes with suspension prepared in NMP, (e) YP_50 electrodes with suspension prepared in water, and (f) YP_50 electrodes with suspension prepared in NMP.

Figure 5.11(a) exhibited that for Darco_60, after ball milling, the N_2 adsorption fraction at $P/P_0 \sim 0.1$ increased, indicating an increase in micropore volume. As shown in the pore size distribution plots in Figure 5.11(b), the mesopore volumes of Darco_60 were also enhanced, with the mesopore fraction increasing from $0.05 \text{ cm}^3/\text{g}$ to $0.15 \text{ cm}^3/\text{g}$ (at 9 nm), and from $0.02 \text{ cm}^3/\text{g}$ to $0.13 \text{ cm}^3/\text{g}$ (at 16 nm). As previously discussed in Chapter 2, a large fraction of mesopores can make full use of the inner surface of the material and can improve the electrolyte ion transportation, leading to higher rate capability. The increase in pore volume after ball milling is also shown in Table 5.3: the V_{mi} and V_{ex} increased from 0.2 to $0.3 \text{ cm}^3/\text{g}$ and from 0.3 to $0.4 \text{ cm}^3/\text{g}$ respectively.

As shown in Figures 5.11(c) and (d) for MAST carbon, the ball milling effect was mainly on mesopore and macropore volume enhancement (V_{ex} increased from 0.4 to $0.5 \text{ cm}^3/\text{g}$, as shown in Table 5.3). Conversely for YP_50, the ball milling effect was mainly on micropore volume enhancement, as shown in Figure 5.11(e) where V_{mi} increased from 0.5 to $0.6 \text{ cm}^3/\text{g}$, as shown in Table 5.3. As discussed in Chapter 4, the micropore volume tends to increase for amorphous structures, therefore the enhancement of V_{mi} for YP_50 was due to the break-up of feedstock particles, which allowed more of the inner micropores (with an amorphous structure as shown in Figure 5.3) to be accessible. Overall, ball milling had the greatest effect on pore size distributions for Darco_60 and the least effect on YP_50.

Ball milling conditions (weight-to-ball ratio, rotation speed, and milling time) were also studied with the aim to optimize capacitance and conductivity. The effects of ball milling time on surface area quantities S_{BET} , S_{inter} , S_{exter} (see Chapter 3 for details) for Darco_60 under different weight-to-ball ratios (1/15, 1/25) and rotation speeds (400, 600 rpm) are presented in Figure 5.12.

In contrast to its effect on graphite particles, ball milling had a more limited effect on specific surface area for AC particles, due to their already high starting micropore and mesopore volume, as also shown in Table 5.1. The same overall tendency was shown at all milling conditions: both S_{inter} and S_{exter} showed an initial, relatively modest increase

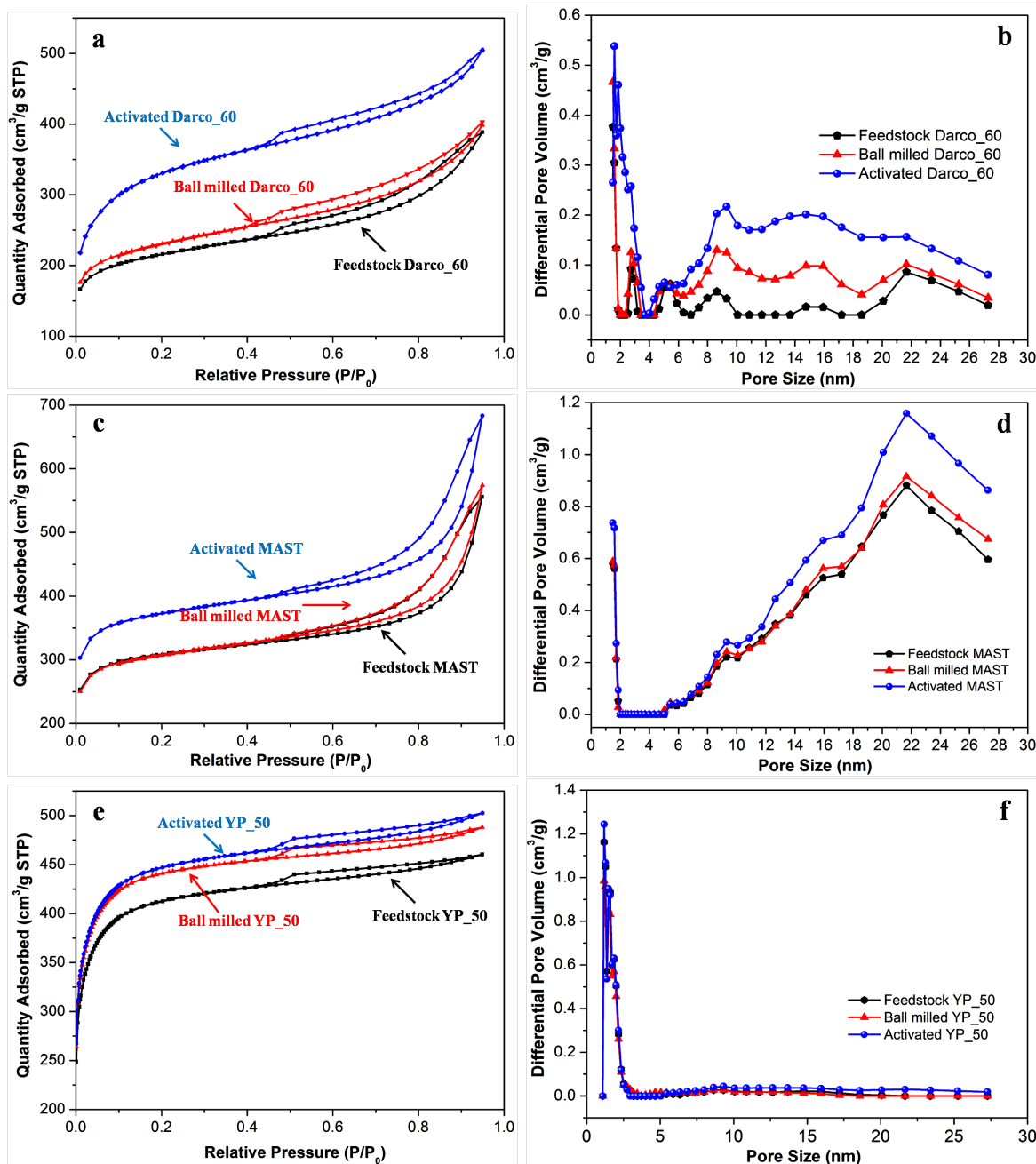


Figure 5.11: N₂ adsorption-desorption isotherms at 77K for (a) Darco_60, (c) MAST, (e) YP_50, and their relative pore size distribution determined by the NLDFT model of (b) Darco_60, (d) MAST, and (f) YP_50.

Table 5.3: Pore characteristics of investigated activated carbons in three conditions.

Sample	FD	BD	AD	FM	BM	AM	FY	BY	AY
S_{BET} (m ² /g)	626	846	979	942	988	1144	1313	1402	1424
S_{inter} (m ² /g)	365	472	554	716	733	852	1029	1117	1111
S_{exter} (m ² /g)	261	374	425	226	255	292	284	285	313
V_t (cm ³ /g)	0.5	0.7	0.8	0.8	0.9	1.0	0.7	0.8	0.8
V_{mi} (cm ³ /g)	0.2	0.3	0.3	0.4	0.4	0.4	0.5	0.6	0.6
V_{ex} (cm ³ /g)	0.3	0.4	0.5	0.4	0.5	0.6	0.2	0.2	0.2
D_{aver} (nm)	3.0	3.0	3.1	3.6	3.7	3.7	2.1	2.1	2.2
% $micro$	48	39	38	44	42	40	72	75	75

up to 2 hours ball milling, and thereafter longer milling times led to a reduction in both S_{inter} and S_{exter} , most likely due to initial break-up of larger particles, followed by progressive destruction of the porous, etched structure of the activated carbon surface.

The maximum S_{BET} was obtained in the condition of 1/15 weight-to-ball ratio, 400 rpm rotation speed and 2 hours milling time, at 879 m²/g as shown in Figure 5.12(c). To further increase the S_{inter} of activated carbon particles, long time ball milling is likely required (more than 50 hours^[49]) by which point crystalline regions are so defective that they appear with increasing amorphous character. Such long milling times are likely not viable for industrial production and can be expected to increase intrinsic resistance.

As illustrated in section 5.3.1, the morphology and porous structure of the feedstock MAST (FM) and YP_50 (FY) powders were different to that of Darco_60 (FD). FM and FY had a higher initial micropore volume, and were thus more sensitive to the destructive effects of milling. The maximum S_{BET} for MAST and YP_50 were both obtained at a lower rotation speed (200 rpm) than Darco_60, at: 987 m²/g for MAST

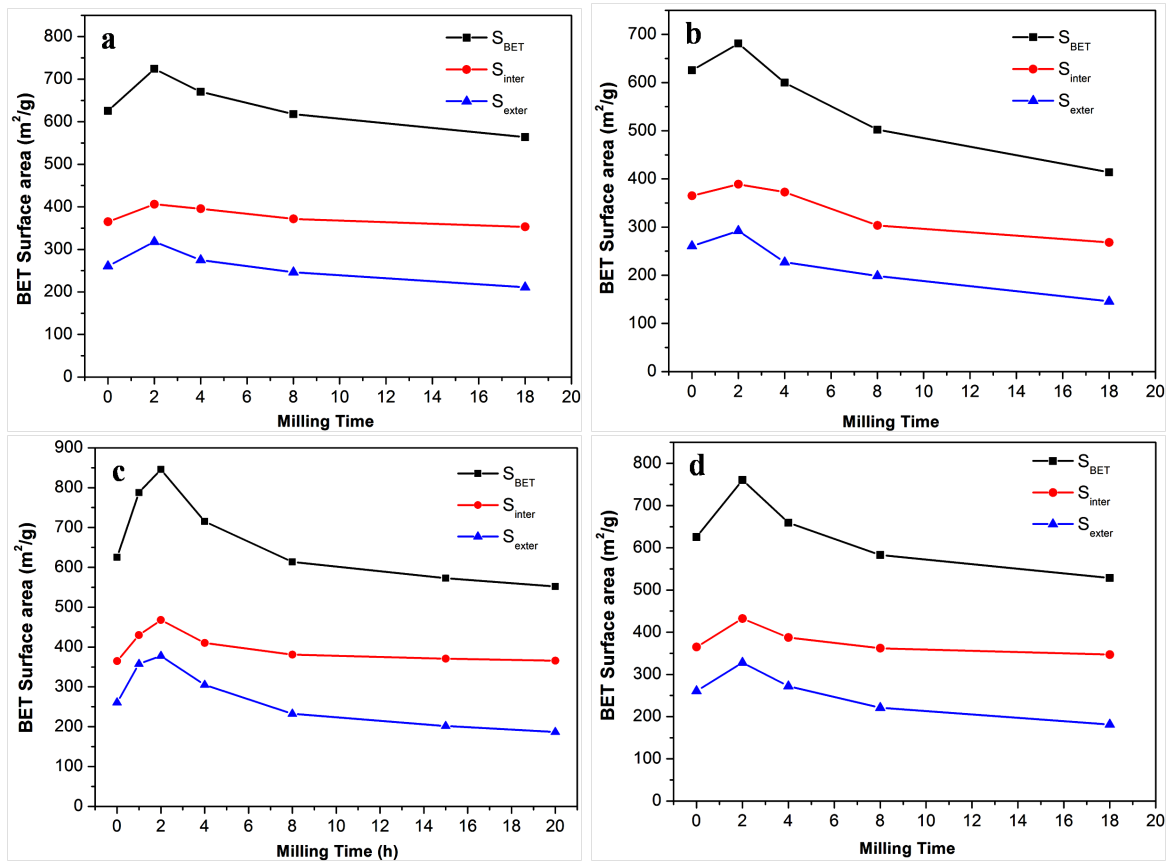


Figure 5.12: BET, internal and external surface area of Darco_60 particles as a function of milling time under milling conditions of (a) 1/25, 400 rpm, (b) 1/25, 600 rpm, (c) 1/15, 400 rpm, and (d) 1/15, 600 rpm.

AC and 1402 m²/g for YP_50 AC, although the YP_50 required a longer milling time of 8 h compared with MAST of 2 h to reach this maximum.

The surface morphology of the ball milled electrodes (BD, BM and BY) are shown in Figure 5.13. All three types of electrode had an acceptably uniform surface at low magnification (Figures 5.13(a), (c) and (e)), with obvious meso-porosity implying access for electrolyte ions. Compared with the large bulky FD, FM and FY particles, most of the BD, BM and BY particles were generally sub-micron and large agglomerations were nonetheless avoided, as shown in the high magnification images (Figures 5.13(b), (d) and (f)), although some agglomeration in the dried electrode must be expected (and required for in-plane electron transfer).

To further study the effects of different ball milling conditions on the AC-based electrodes, especially on their electrochemical behaviour, cyclic voltammograms and electrochemical impedance spectra are compared in Figures 5.14 to 5.16. Based on the previous studies, all the substrates were pre-coated with 2 layers carbon black/PEI mixture. The Darco_60 and MAST carbon suspension were prepared in NMP, the YP_50 suspension was prepared in water. The capacity behaviour will be discussed systemically later in Figure 5.17.

Comparing Figures 5.14(a) to (d), the charge transfer resistance (R_{ct} , the diameter of the semi-circle) of feedstock Darco_60 was dramatically reduced from $\sim 10 \Omega$ to $\sim 2.5 \Omega$ at a low weight-to-ball ratio (1/25). As described in Chapter 4, the R_{ct} was associated with a porous structure and the conductivity of carbon electrodes. Therefore, the reduction of R_{ct} by ball milling indicated that the micro-structure of the Darco_60 had been improved for quicker ion-transfer and charge conduction. However, as shown in Figure 5.14(a), the equivalent series resistance (ESR) and charge transfer resistance (R_{ct}) stayed approximately the same at $\sim 0.5 \Omega$ and $\sim 2.9 \Omega$ respectively, when the milling time increased from 2 to 8 hours, indicating that the micro-structure of the Darco_60 electrode did not change dramatically with increased the milling time at the low weight-to-ball ratio (1/25).

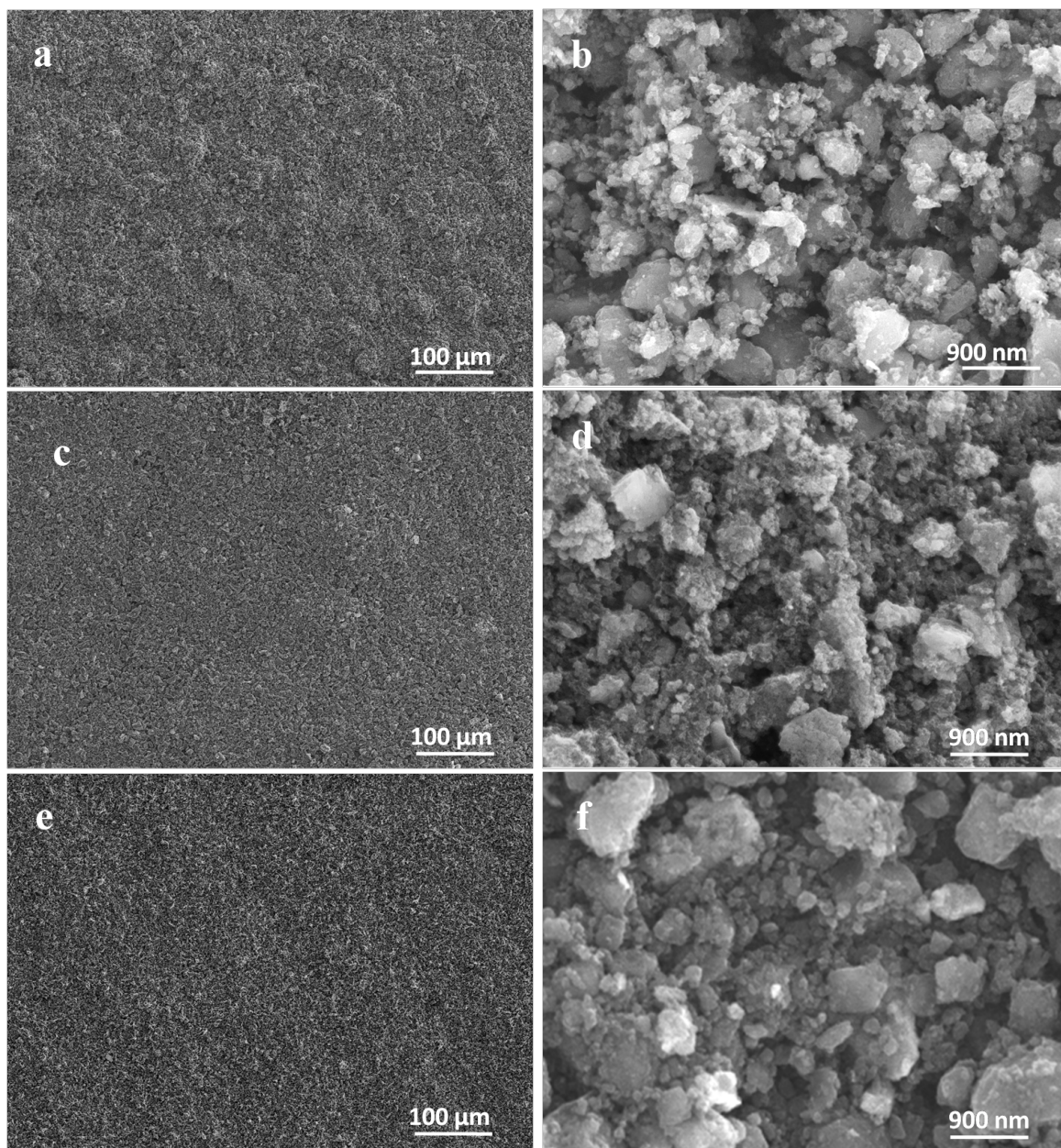


Figure 5.13: SEM images of the spray deposited electrode film surface of (a) ball milled Darco_60 at low magnification, (b) ball milled Darco_60 at high magnification (c) ball milled MAST carbon at low magnification, (d) ball milled MAST carbon at high magnification, and (e) ball milled YP_50 at low magnification, (f) ball milled YP_50 at high magnification.

As shown in Figures 5.14(b) and (c), at a higher weight-to-ball ratio (1/15), the micro-structure of the Darco_60 was more strongly affected by the milling conditions: both ESR and R_{ct} increased as the milling time increased, indicating the negative effect of longer milling times. Increased resistance may be related to a more defective structure and higher ion transport resistance or clogging of mesoporous channels between particles with particle fragments from milling. However, all the Darco_60 electrodes at a weight-to-ball ratio (1/15) had smaller a R_{ct} and straighter capacitive tail than feedstock Darco_60.

Figure 5.14(d) illustrates that compared with the feedstock Darco_60 electrode, the ball milled Darco_60 electrode (under the optimised condition of 1/15, 400 rpm, 2 h) had straighter tail in the Nyquist plot in the low frequency region (indicating its improved capacitive behaviour) and a reduced best-fit semi-circle diameter (indicating smaller charge-transfer resistance), both of which would support high-rate performance. The reduction in resistive character by ball milling was attributed to the increased mesopore/macropore volumes (as shown in Table 5.3), and reduced ion-diffusion pathway (nano-sized particles). The enhancements on electrical conductivity and reduction on charge-transfer resistance could also be observed in the cyclic voltammograms, as shown in Figures 5.14(e) and (f), in which more rectangular CV curves with a steeper slope at the sweep switch point were obtained for the ball milled Darco_60 electrode.

Reduction in charge-transfer resistance by ball milling treatment was also obtained for MAST and YP_50 electrodes in Figures 5.15 and 5.16. The MAST carbon density was relatively low due to a high fraction of macro-pores (as shown in the TEM images of Figures 5.1 and 5.2), so that the optimum weight-to-ball ratio (1/15) for Darco_60 was not suitable for MAST carbons. Therefore, as shown in Figure 5.15(b), for MAST carbon with a weight-to-ball ratio of 1/15, the capacitive behaviour was significantly improved (straighter tail in low frequency region) only after 8 hours ball milling, due to inefficient grinding. By contrast, as shown in Figure 5.15(d), with a 1/25 weight-to-ball ratio, an enhancement in capacitive behaviour was obvious after only 2 h. Longer milling times, as shown in Figure 5.15(d), tended to increase intrinsic resistance (ESR increase from

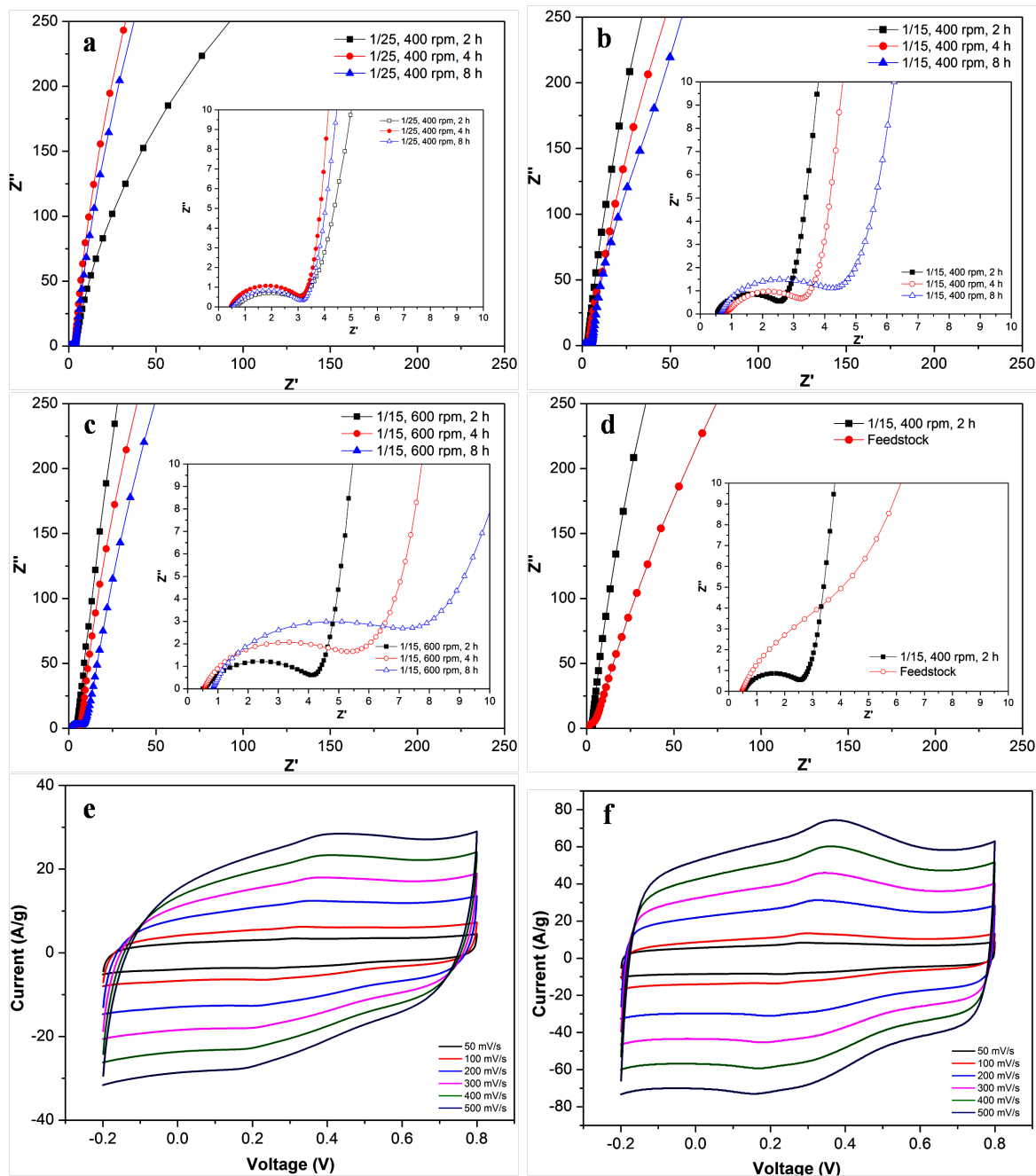


Figure 5.14: Nyquist plots from Darco_60 electrode under different ball milling conditions (a) 1/25, 400 rpm and 2 to 8 h, (b) 1/15, 400 rpm and 2 to 8 h, (c) 1/15, 600 rpm and 2 to 8 h, (d) comparison of feedstock Darco_60 electrode with ball milled Darco_60 electrodes. Cyclic voltammograms of (e) a feedstock Darco_60 electrode, (f) 1/15, 400 rpm, 2 h ball milled Darco_60 electrode, in a 1 M H_2SO_4 aqueous electrolyte at scan rates between 50 - 500 mV/s.

0.47 Ω to 2.24 Ω at 200 rpm and from 0.98 Ω to 2.54 Ω at 400 rpm). As shown in Figure 5.15(f), the R_{ct} of feedstock MAST carbon was reduced from $\sim 10 \Omega$ to $\sim 2 \Omega$ after ball milling, with a straighter tail in the low frequency region. The reduction in charge-transfer resistance could also be observed from the cyclic voltammograms, as shown in Figures 5.15(a), (c) and (e), in which more rectangular CV curves were provided by the ball milled MAST carbon electrode (Figures 5.15(a) and (c)).

For YP_50, as exhibited in Figure 5.16(d), the best enhancements of capacitive behaviour (straighter tail) and faradic reaction (more obvious semi-circle) for YP_50 was achieved at a 1/25 weight-to-ball ratio. The ball milled YP_50 electrode exhibited a more rectangular CV shape in Figures 5.16(b) and (c) than feedstock YP_50, in Figure 5.16(a).

The specific capacitance as a function of scan rate for the three AC-based electrodes is shown in Figure 5.17. As previously described, high surface area is usually considered to be the main requirement for high capacity EDLCs, however the performance of AC-based electrodes depends also on other factors, such as the nature of the porous structure, electrical resistance, interfacial resistance and surface chemistry (wetting) of the materials. Although the specific surface area of Darco_60, MAST carbon and YP_50 was reduced under some ball milling conditions, their micro-structures were all improved for better ion transfer and reduced resistive character. Therefore, the specific capacitance was increased at all scan rates after ball milling. The extent of the increase depended on the specific milling conditions. Maximum specific capacitance was achieved for electrodes which has both the highest specific surface area and the lowest resistance (straightest tail and smallest semi-circle diameter in Nyquist plots). For Darco_60, as shown in Figure 5.17(a), the maximum specific capacitance of 173 F/g at 5 mV/s and 131 F/g at 100 mV/s was obtained at 1/15, 400 rpm and 2 h ball milling. For the MAST carbon, as exhibited in Figure 5.17(b), the maximum specific capacitance of 163 F/g at 5 mV/s and 131 F/g at 100 mV/s was obtained at 1/25, 200 rpm, 2 h ball milling condition. For YP_50, although its specific surface area was almost twice of that of Darco_60 (as shown in Table 5.3), its low mesopore

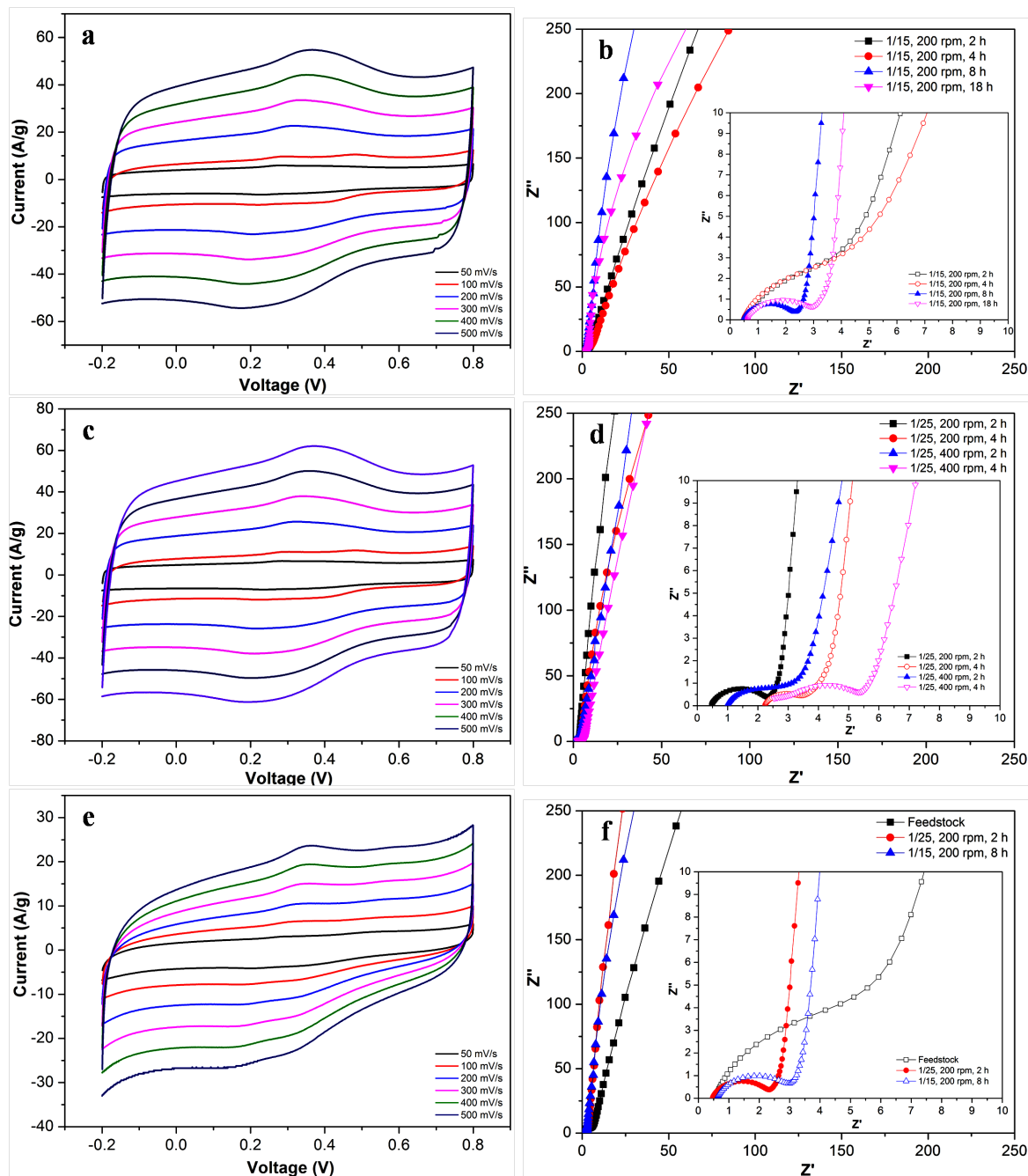


Figure 5.15: Cyclic voltammograms of (a) 1/15, 200 rpm, 8 h ball milled MAST carbon (BM) electrode, (c) 1/25, 200 rpm, 2 h BM electrode, (e) feedstock MAST carbon (FM) electrode in 1 M H_2SO_4 aqueous electrolyte at scan rates between 50 - 500 mV/s. Nyquist plots of MAST electrode under different ball milling conditions (b) 1/15, 200 rpm and 2 - 18 h, (d) 1/25, 200/400 rpm and 2 to 4 h, (f) FM electrodes with BM electrodes.

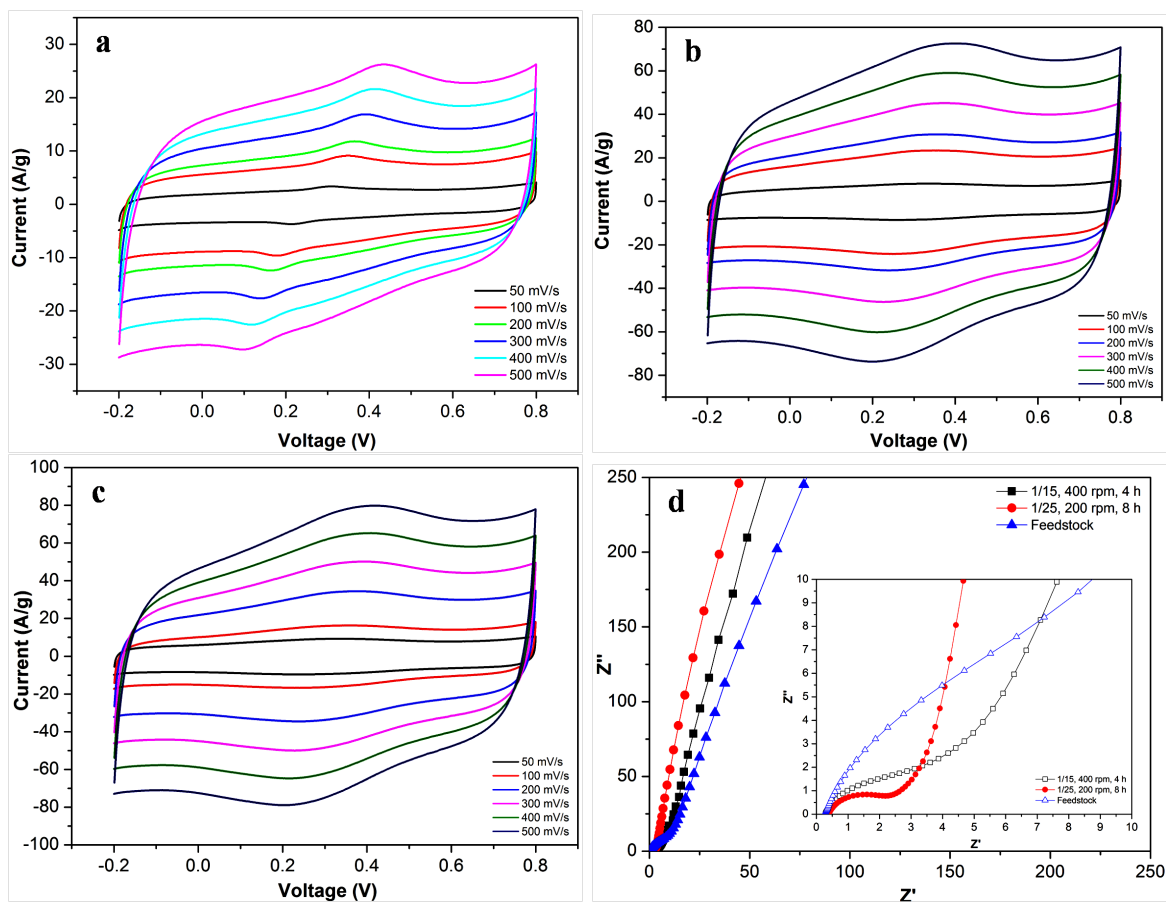


Figure 5.16: Cyclic voltammograms of (a) feedstock YP_50 electrode, (b) 1/15, 400 rpm, 4 h ball milled YP_50 electrode, (c) 1/25, 200 rpm, 8 h ball milled YP_50 electrode, in 1 M H_2SO_4 aqueous electrolyte at scan rates between 50 - 500 mV/s. (d) Nyquist plots of feedstock YP_50 electrodes with ball milled YP_50 electrodes.

and macropore volume (only $0.2 \text{ cm}^3/\text{g}$ for both FY and BY) limited its capacity. Therefore, as shown in Figure 5.17(c), the maximum specific capacitance for YP_50 of 166 F/g at 5 mV/s and 147 F/g at 100 mV/s was obtained under 1/25, 200 rpm, 8 h ball milling condition.

5.3.3.4 Improvement of low-frequency resistance by secondary CO_2 activation

Figure 5.11(a) for Darco_60 showed that the CO_2 activation treatment could increase N_2 adsorption at $P/P_0 \sim 0.1$ because of an increased fraction of micropores and sub-mesopores. As shown in the pore size distribution plots in Figure 5.11(b), the mesopore volumes of Darco_60 were also enhanced by the secondary activation. The mesopore fraction increased from $0.15 \text{ cm}^3/\text{g}$ to $0.25 \text{ cm}^3/\text{g}$ (at 9 nm), and from $0.13 \text{ cm}^3/\text{g}$ to $0.2 \text{ cm}^3/\text{g}$ (at 16 nm).

As shown in Figure 5.11(c), similar strong enhancement of micropore volume by secondary CO_2 activation treatment was also obtained in MAST carbon. For YP_50, the secondary activation treatment however, as shown in both Figures 5.11(e) and (f), had no obvious effect on pore volume changes, with the curves after CO_2 treatment almost overlapping those for ball milling only. The negligible effect of secondary activation treatment on YP_50 will be explained later.

To further understand the influence of secondary CO_2 activation treatment on the electrochemical behaviour of AC-based electrodes, especially on their capacitive behaviour, Nyquist plots and capacitance-frequency dependence plots are presented in Figure 5.18. The capacitance-frequency dependence plots can reflect the penetration effect of the alternating current on ion mobility in the electrode pores by showing how many solvated ions have reached the pore surfaces at a specific frequency. The capacitance can be separated into two parts: the real and imaginary capacitance, according to Equation 5.1^[50]. The variation of the real part of capacitance (C) with frequency

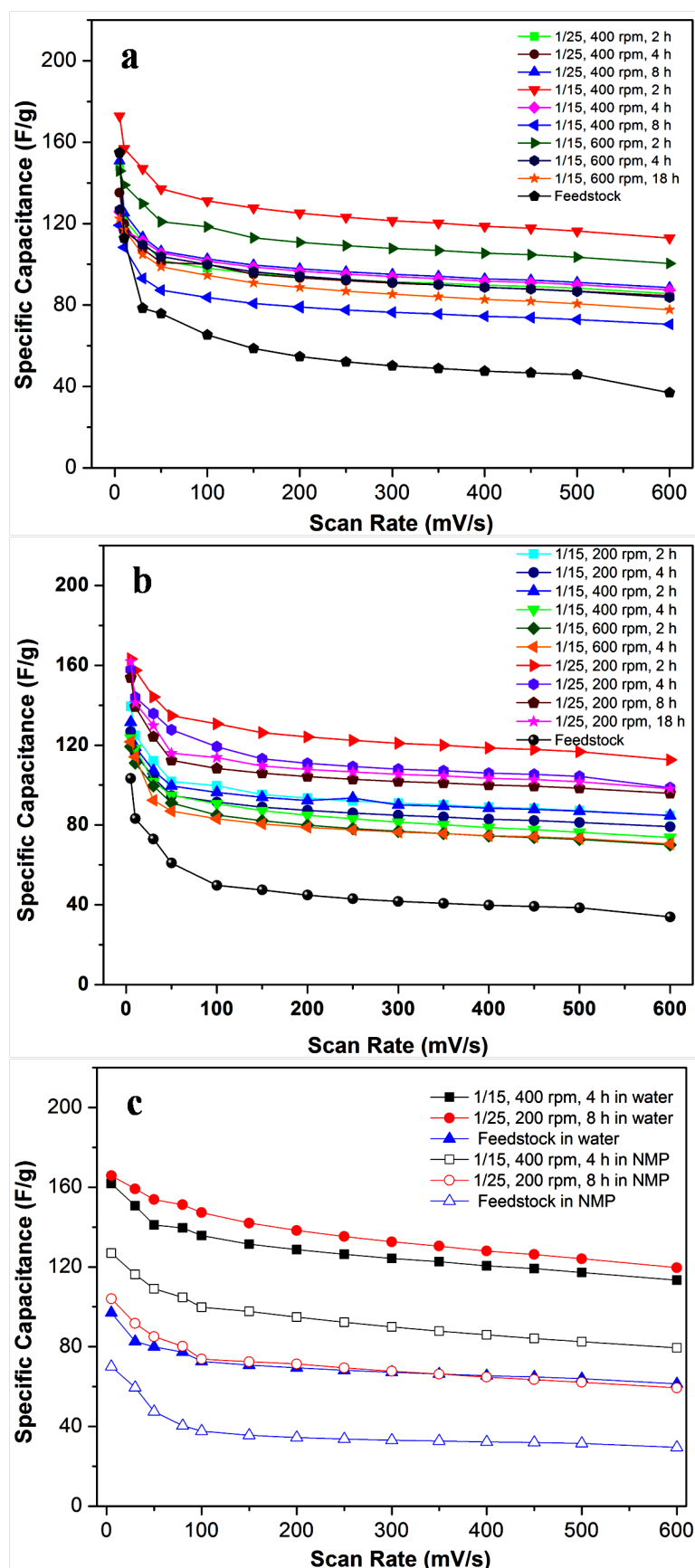


Figure 5.17: The dependence of specific capacitance on voltage scan rate for (a) feedstock and ball milled Darco_60 electrodes, (b) feedstock and ball milled MAST carbon electrodes and (c) feedstock and ball milled YP_50 electrodes in 1 M H₂SO₄ aqueous electrolyte.

range from 0.01 to 1000 Hz can be calculated as follows:

$$C = C' - jC'' \quad (5.1)$$

$$C' = \frac{1}{2\pi f Z''} \quad (5.2)$$

where C' is the real part of the capacitance, C'' is the imaginary capacitance related to the losses in the charge storage process leading to an energy dissipation^[44], f is the applied frequency and Z'' is the imaginary part of impedance. Generally, the capacitance calculated from the impedance measurement is slightly lower than that calculated from cyclic voltammetry, due to the more hindrance of the alternating current penetrating into the electrode bulk^[51].

In the capacitance-frequency dependence plots (e.g. Figure 5.18(b)), the performance of electrodes transformed from capacitive behaviour to resistive behaviour with increasing frequency. Generally, micropores can only be accessed by ions effectively at lower frequencies, while mesopores and macropores are easier to access at high frequencies, but contribute less to overall capacity. In general, electrodes with high capacitive character (and low resistive character) will be less frequency dependent, which is manifest by an increase in the frequency at which capacitive behaviour fades and resistive behaviour dominates.

As shown in Figures 5.18(a) and (c), compared with ball milled equivalents, the electrodes of secondary activated Darco_60 and MAST carbon showed higher gradient Nyquist plots in the high frequency region, illustrating that the capacitive behaviour of was improved by secondary activation. The enhancement of capacitive behaviour was due to the increased mesopore and macropore volumes (as shown in Table 5.3), which favoured electrolyte ion access at higher frequencies. As shown in Figures 5.18(b) and (d), capacitive behaviour improvements were also shown in the capacitance-frequency

dependence plots, where after the secondary activation treatment the capacitance transition frequency (electrode nearly approached saturation below the capacitance transition frequency) increased from ~ 1.5 Hz to ~ 7 Hz and from ~ 1.5 Hz to ~ 4 Hz for Darco_60 and MAST, respectively. The capacitance transition frequency was estimated by eye.

For YP_50, as exhibited in Figure 5.18(e) however, secondary activation had no obvious effect on capacitive behaviour: AY and BY had over-lapped Nyquist plots at high frequency and the same approximate capacitance transition frequency of 0.6 Hz in Figure 5.18(f). The negligible difference between AY and BY was due to the limited increases in mesopore and macropore volume after secondary activation (as illustrated in Table 5.3).

As shown in Figures 5.19(a) and (b), the capacitative character of secondary activated Darco_60 and MAST carbons was also shown in the cyclic voltammograms by the near vertical plots on reversal of the potential sweep direction, even at 500 mV/s. However, YP_50 was less affected by secondary activation with more resistive character at all scan rates.

The capacitance of ball milled Darco_60, MAST and YP_50 electrodes started to saturate above 1 Hz, implying that ion adsorption reached equilibrium within 1 s, which is much faster than commercial devices of 10 - 100 s^[52] based on non-aqueous electrolytes with lower ion mobilities, and even better than that of microporous carbons, ordered mesoporous and hierarchically porous carbons^[53, 54], no doubt in part due to the relatively thin electrodes. The saturated capacitances of the three ball milled activated carbon electrodes at 1 Hz was at or above 100 F/g, which is competitive with commercial supercapacitor performance.

As shown in Figures 5.18(b), (d) and (f) and Table 5.3, although the activated electrodes (AD, AM and AY) had higher total pore volume and specific surface area, their specific capacitances were lower than that of the ball milled electrodes (BD, BM and

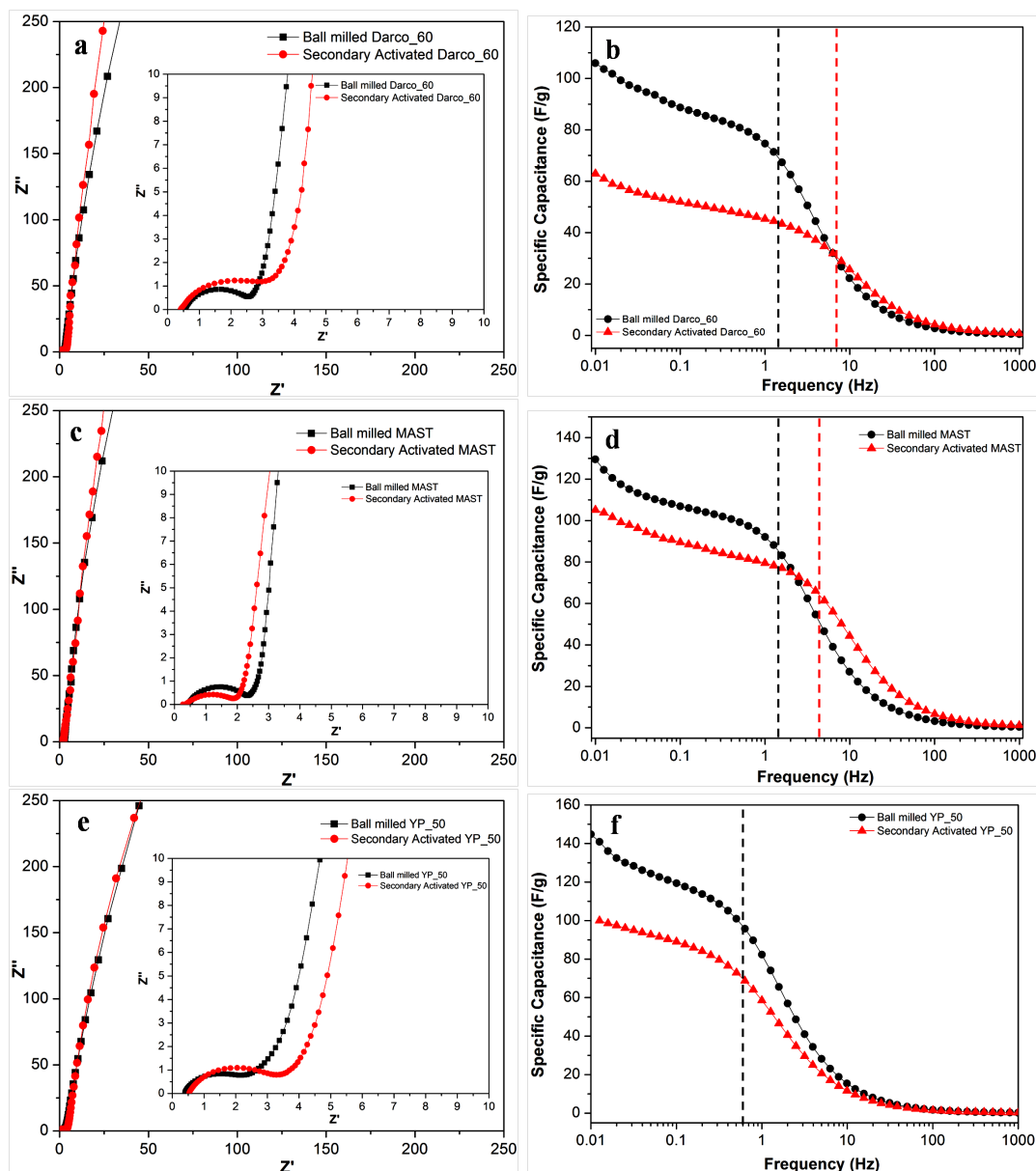


Figure 5.18: Nyquist plots for (a) secondary activated Darco_60 (AD) and ball milled Darco_60 (BD) electrodes, (c) secondary activated MAST carbon (AM) and ball milled MAST carbon (BM) electrodes, (e) secondary activated YP_50 (AY) and ball milled YP_50 (BY) electrodes. Capacitance-frequency dependence plots of (b) AD and BD electrodes, (d) AM and BM electrodes, (f) AY and BY electrodes.

BY) at low frequencies. The reason for the capacitance decrease after secondary activation treatment despite advantageous increases in pore volumes and lowered resistive character, is ascribed to the modification of the electrode surface functionality. As illustrated in the XPS results in Table 5.2, the surface oxygen concentration reduced after secondary activation, mainly corresponded to the transformation of CO-type groups to CO₂-type groups. Unlike the CO-type groups, which can enhance capacitance by introducing pseudo-capacitance^[25, 55–58], the CO₂-type groups have no or very limited contribution to capacitance^[59], and therefore the total specific capacitance reduced. As illustrated in Figures 5.19(b), (d) and (f), the reduction of the pseudo-capacitance contribution after secondary activation treatment was shown in the cyclic voltammograms, in which the faradic reaction related peaks at potentials of ~ 0.3 and ~ 0.25 V on forward and reverse sweeps on activated electrodes were significantly smaller than those on ball milled only electrodes.

The specific capacitance as a function of scan rate for ball milled and secondary activated electrodes is presented in Figure 5.20. BY had the highest capacitance at lowest scan rate of 168 F/g, capacitance faded with increasing scan rate to 127 F/g at 500 mV/s, corresponding to its highest specific surface area and lowest mesopore/macropore volume. Although the secondary activated electrodes had lower specific capacitance across the scan rate range compared with ball milled electrodes, they exhibited better stability with scan rate. The error in the capacitance value - a compound of manufacturing reproducibility and measurement reproducibility/accuracy - was estimated at typically 5%.

5.3.3.5 Charge/discharge behaviour

To further evaluate the performance of the ball milled electrodes and the secondary activated electrodes, galvanostatic charge/discharge behaviour was investigated in 1 M H₂SO₄ aqueous electrolyte at current densities from 0.5 to 10 A/g, as shown in Figure 5.21.

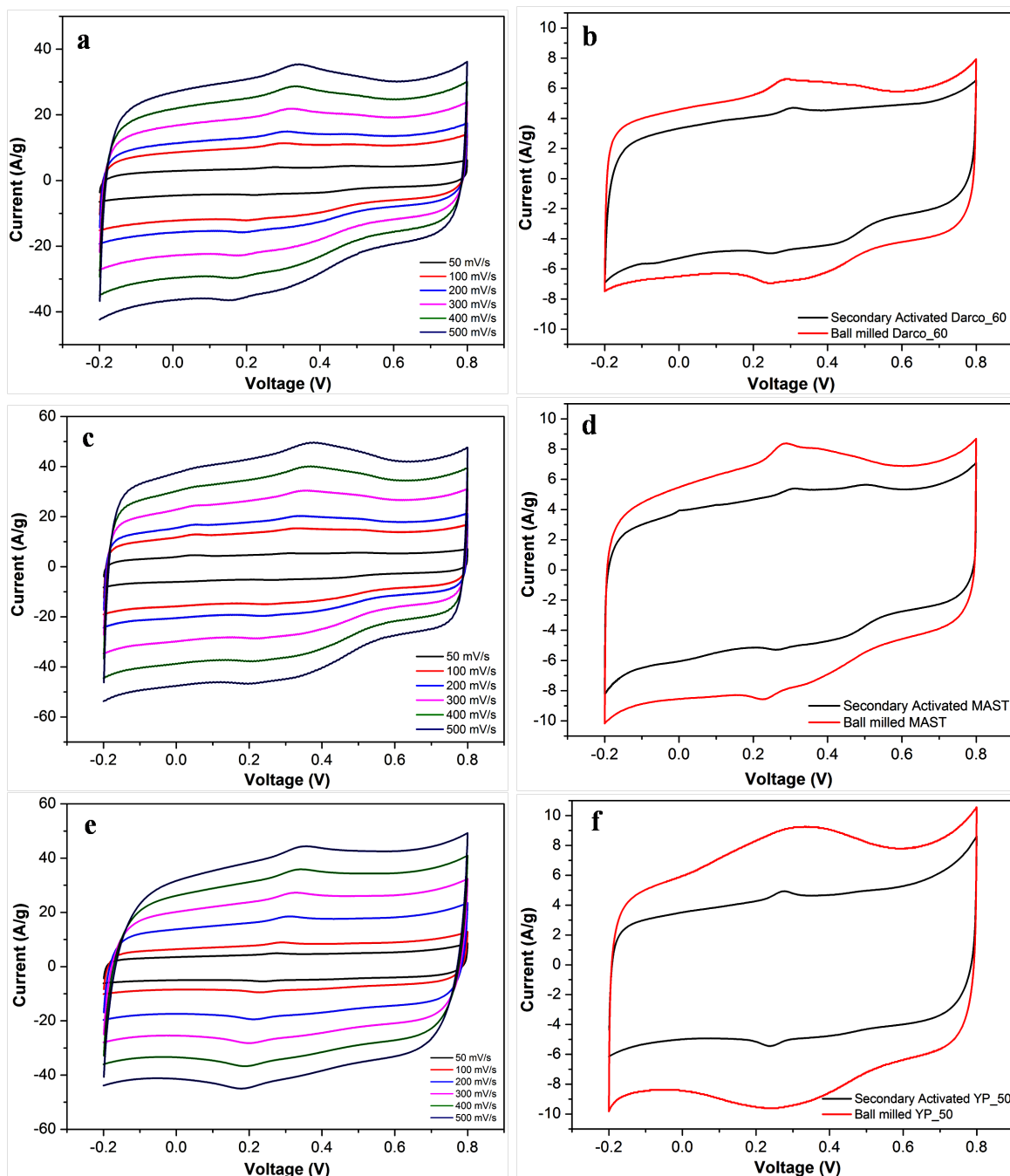


Figure 5.19: Cyclic voltammograms for secondary activated (a) Darco_60, (c) MAST carbon, (e) YP_50 at scan rate from 50 to 500 mV/s. Comparison of cyclic voltammograms for (b) secondary activated Darco_60 with ball milled Darco_60, (d) secondary activated MAST carbon with ball milled MAST carbon, and (f) secondary activated YP_50 with ball milled YP_50, at scan rate 50 mV/s.

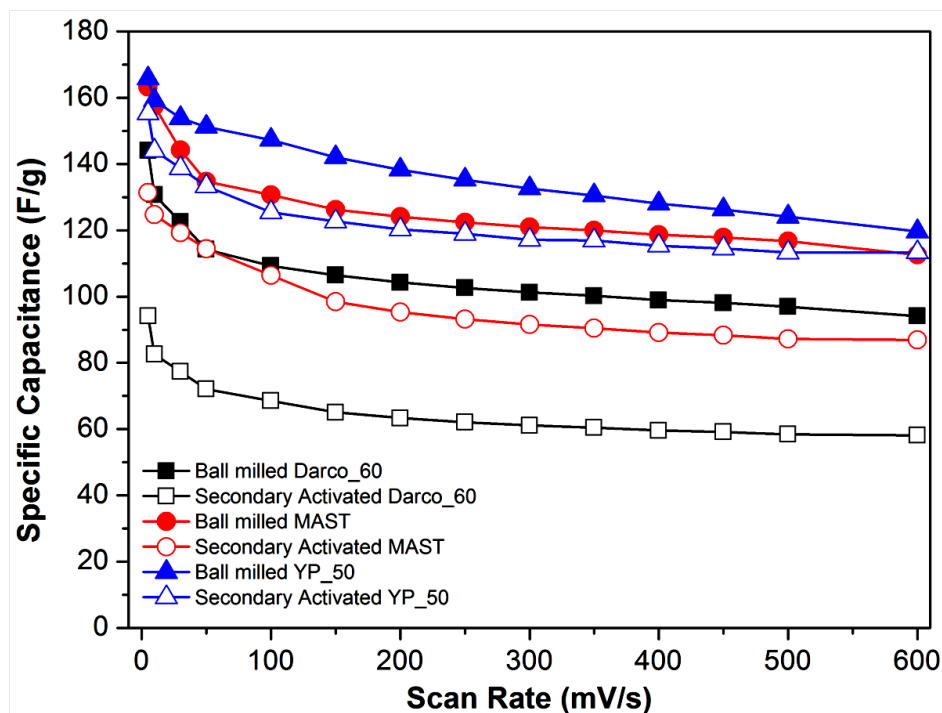


Figure 5.20: Specific capacitance as function of scan rate for ball milled and ball milled and activated Darco_60, MAST and YP_50, obtained from CV curves.

Compared with the secondary activated electrodes, the ball milled electrodes exhibited more linear and symmetrical charge/discharge curves at different current densities, indicative of limited pseudocapacitance contributions and relatively low ESR. The slightly more non-linear charge/discharge shapes and larger ‘IR drop’ on reversal of charging for the secondary activated electrodes was because electron delocalization was weakened by the strong electro withdrawing groups on the electrode materials (such as the CO₂-type groups), leading to a slight increase in resistive character of the electrode^[60]. This increased resistive nature after secondary activation was in agreement with the EIS data in Figures 5.18(a), (c) and (e): the larger semi-circle diameter in the Nyquist plots, indicated an increased charge-transfer resistance. Similar insights that CO₂-type groups had a negative effect on capacitance and electrical conductivity have been previously reported^[22, 56, 58]. However, the detailed identification and role of CO₂-type or other groups in various process conditions and effects on capacity requires further detailed electrochemical and surface analysis study.

The charging curve at low current density (0.5 A/g) tended to show a flattening at approximately 0.9 V for YP_50 based electrodes and may be due to some irreversible

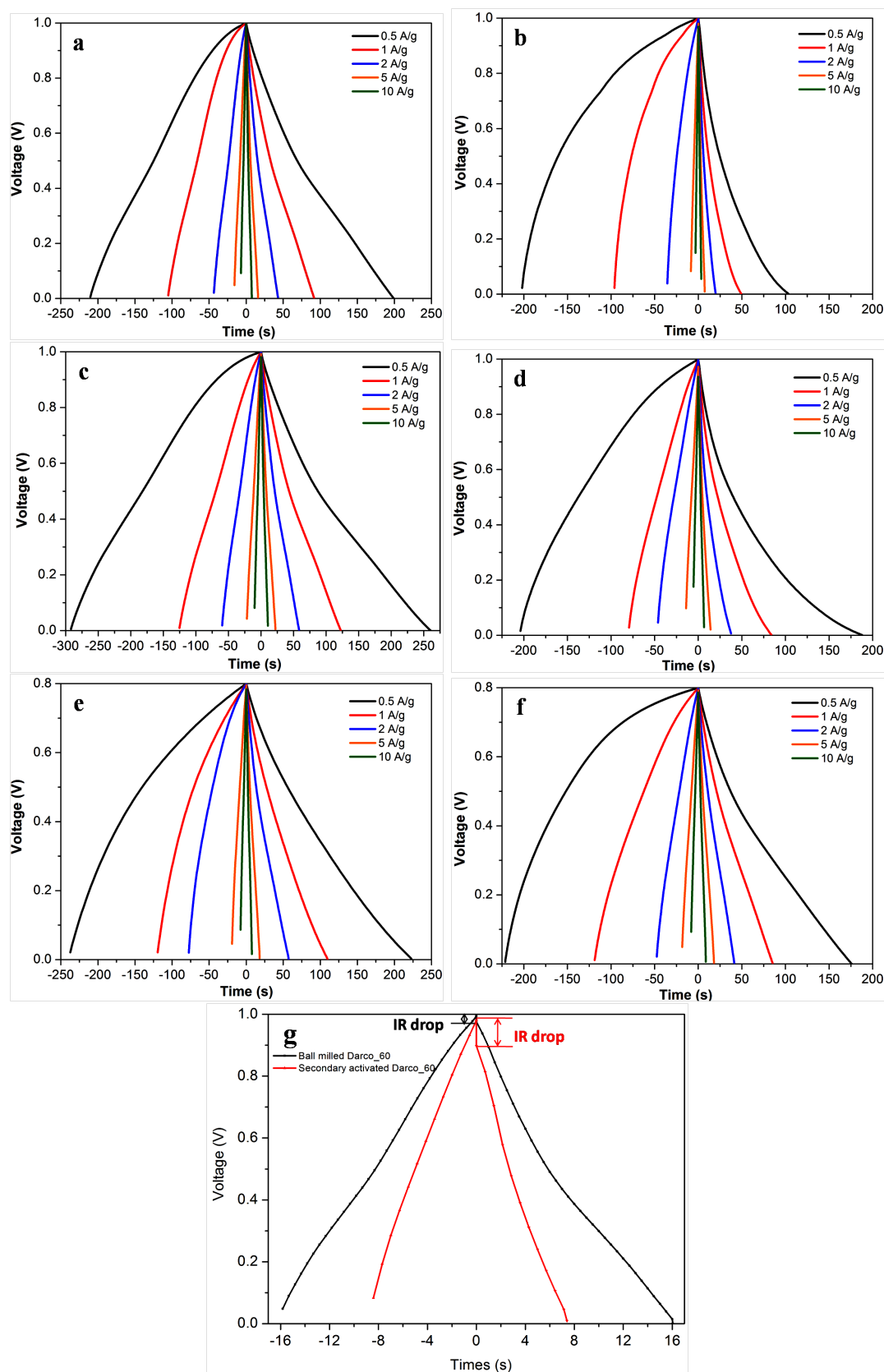


Figure 5.21: Galvanostatic charging/discharging behaviour of (a) ball milled Darco_60, (b) secondary activated Darco_60, (c) ball milled MAST carbon, (d) secondary activated MAST carbon, (e) ball milled YP_50, and (f) secondary activated YP_50 based thin film electrodes at different current densities (0.5, 1, 2, 5 and 10 A/g) in 1 M H_2SO_4 aqueous electrolyte, (g) IR drop on ball milled Darco_60 and secondary activated Darco_60 at 5 A/g current density.

oxidation, impurity effect or even self-discharge^[61]. Therefore, 0.8 V was the maximum voltage for YP_50 based electrodes to have an approximately linear and symmetrical charge/discharge behaviour. The possible reason for any irreversible oxidation behaviour for the YP_50 based electrodes at higher initial voltage maybe due to their comparatively high oxygen concentrations: almost 1.5 times and 2.7 times of that in Darco_60 and MAST respectively, as illustrated in the XPS results in Table 5.2.

On the other hand, higher surface oxygen concentration contributed pseudo-capacitance to the YP_50 based electrodes. Therefore, combining the highest oxygen content with high specific surface area, the ball milled YP_50 electrode overall exhibited the highest capacitance over the current density range, as shown in Figure 5.22. All the secondary activated electrodes exhibited a better capacitance stability than that of ball milled electrodes when the current density increased from 0.5 A/g to 20 A/g. However, improvements in capacitance stability were limited. The overall trends of capacitance with current density from charge/discharge behaviour was similar to that with scan rate obtained from the CV curves and previously shown in Figure 5.20. Once again, error was estimated at 5%. The CV data typically gave slightly higher capacitances, which is typical for the field.

Long term charge/discharge cycling (5,000 cycles) behaviour with a current density of 1 A/g was investigated for the ball milled electrodes, as shown in Figure 5.23. The working voltage for the Darco_60 and MAST carbons was 1 V, and 0.8 V for YP_50. The three electrodes maintained stable capacitance up to 5,000 cycles.

5.4 Conclusions

Three types of commercial activated carbons with different porous structure and surface chemical properties were chosen as the electrode materials for EDLCs. By using the spray deposition technique, $\sim 2 \mu\text{m}$ thick film electrodes with a generally acceptable smooth film surface and homogeneous microstructure were fabricated. To

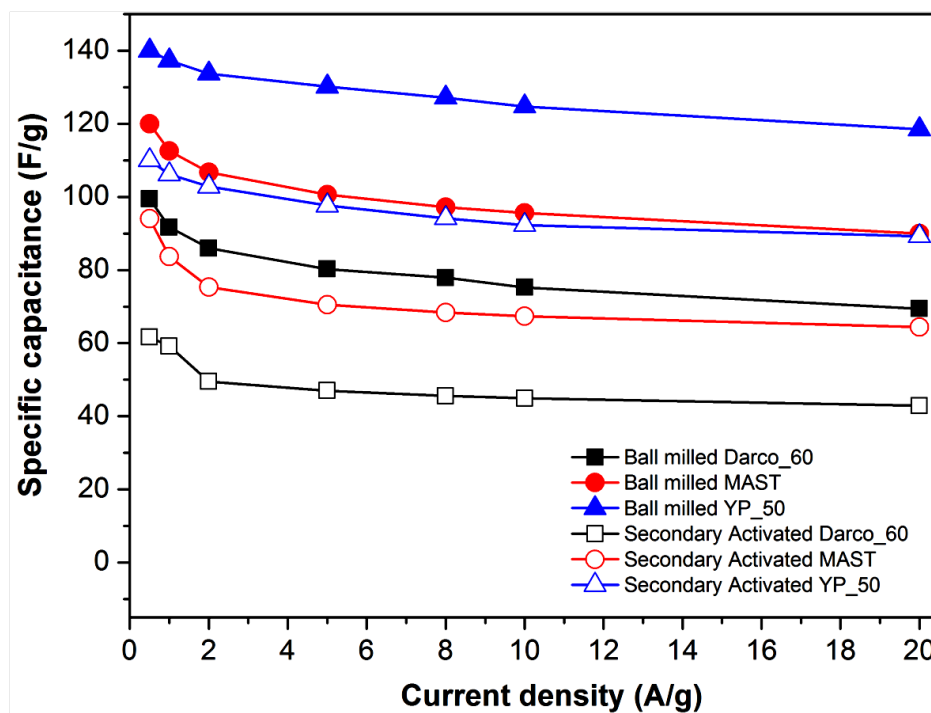


Figure 5.22: Variation of specific capacitance with current density of AC-based electrodes in 1 M H_2SO_4 aqueous electrolytes, obtained from charge/discharge experiments.

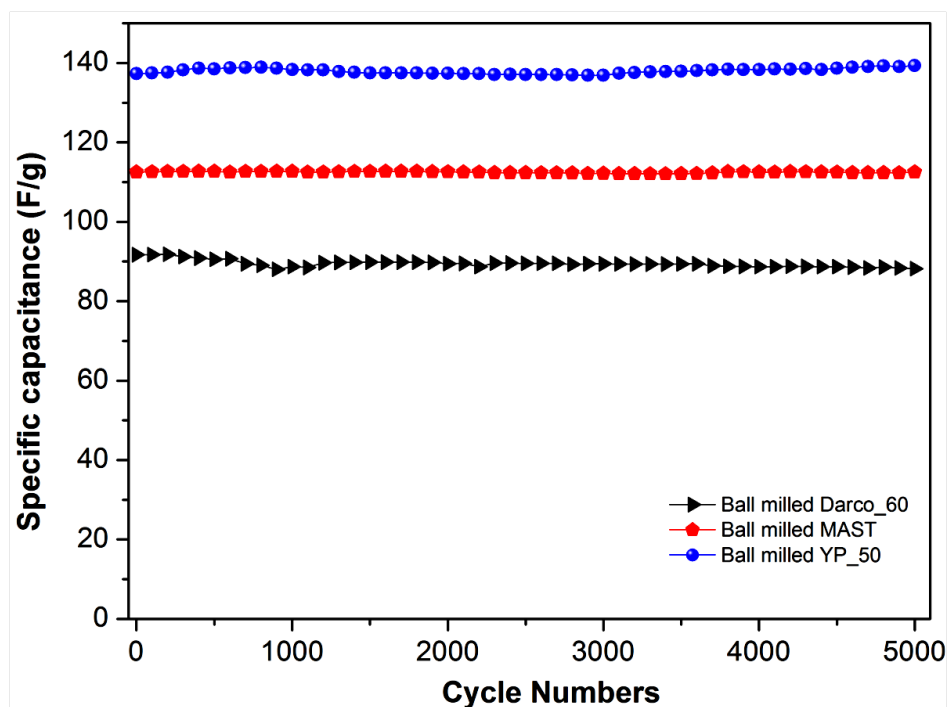


Figure 5.23: Long term charge/discharge cycling performance of ball milled Darco_60, MAST carbon and YP_50 thin film electrodes in 1 M H_2SO_4 at a 1 A/g current density.

enhance the performance of the AC-based electrodes, four approaches were investigated to improve their capacitive behaviour. Firstly, to reduce the electrode/substrate interface contact resistance, a few layers of carbon black/PEI mixture were pre-coated on the substrates, and the ESR and R_{ct} were reduced to only 0.3 Ω and 2.3 Ω for Darco_60, 0.5 Ω and 2.0 Ω for MAST, 0.6 Ω and 2.1 Ω for YP_50, respectively. Secondly, by using suitable suspensions based on NMP, the capacitive behaviour of two of the AC-based electrodes was improved, due to the formation of more homogeneous and interconnected porous microstructure. Thirdly, ball milling treatment not only efficiently increased the specific capacitance by increasing the specific surface area, but also improved the capacitance behaviour and reduced the charge-transfer resistance. A secondary CO₂ activation treatment had a complex influence on the electrochemical performance: on one hand, it improved the capacitive behaviour by increasing the mesopore and macropore volume, but on the other hand, the displacing of CO-type surface groups by CO₂-type functionalities reduced pseudo-capacitance and increased charge-transfer resistance. Combining these improvements, the three types of AC-based electrodes maintained high capacitance at a scan rate of 600 mV/s and current density of 20 A/g, and maintained stable capacitance up to 5,000 charge/discharge cycles. Overall the electrodes offered an attractive balance of properties in an aqueous electrolyte.

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Chapter 6

High Performance Carbon Black Based Thin Film Electrodes in Different Aqueous Electrolytes

6.1 Introduction

A supercapacitor is required to have high-rate performance (high capacity at high current density) since this is a key characteristic of supercapacity. As long as sufficient electrical transport is made available by the use of conducting additives, high rate performance is then primarily determined by the ion mobility in the electrolyte. Although ordered mesoporous carbons (OMCs) have enhanced the carbon surface utilization by improving the ion transport inside the particles, and therefore provided specific capacitances of up to 223 F/g^[1], they cannot fulfil high-rate (< 2 s) EC applications^[2], due to the lack of larger mesopores (> 10 nm, OMCs normally have narrow pore size distribution between 3 - 7 nm^[3]) and lack of nanometer-scale diffusion distances (< 100 nm)^[2]. Carbon nanotube (CNT) based supercapacitors have relatively low surface area (~ 500 m²/g) but much higher electrical conductivity (4×10^9 A/cm² in

theory)^[4, 5]. However, in some samples, CNT-based electrodes had a relatively high contact resistance (e.g. 3.4Ω) at the electrode/current collector interface, which limited performance^[6, 7]. Reducing contact resistance by directly growing CNTs on the current collector has been studied, however this technique is expensive and cannot be used in large-scale manufacturing^[6]. Graphene^[8] and 3D HPGC as supercapacitor electrodes have been studied in recent years, however they both present problems for commercial supercapacitor manufacturing (e.g. difficulty in large-scale transfer and high quality control for graphene^[9], or high price and complicated synthetic procedure for 3D HPGC^[1]).

In this chapter, two types of high surface area commercial carbon blacks were studied as potential electrode materials for high performance thin film supercapacitors. These were termed SC2 and SC3 carbon black (see later), had a porous structure, with a specific surface area comparable with activated carbon (ACs) but a much broader pore size distribution and a higher relative volume of mesopores and macropores, which provided shorter ion diffusion pathways, leading to comparatively efficient utilization of micropore surface area. Moreover, SC2 and SC3 had much higher graphitic character (organized graphene layers) compared with the largely amorphous structure of AC^[10]. This graphitic character can provide better electrical conductivity than that of amorphous structures^[11], and in effect, the hierarchical porous and localized graphitic structures of SC2 and SC3 may combine the advantages of ACs (high specific area and high ion mobility) and graphite (high electrical conductivity). Compared with graphene, CNTs, carbon fibres and synthetic 3D HPGC, industrial carbon black materials were easy and cheap to obtain.

Moreover, as previously described in Chapter 1, the maximum energy density (E) stored in supercapacitors was proportional to square of the cell operate voltage (V^2). Therefore, organic electrolytes are usually preferred in industrial applications to provide relatively high energy due to the higher cell operate voltage ($\sim 2.7 \text{ V}$) facilitated when compared with aqueous electrolytes ($\sim 1 \text{ V}$)^[12]. However, aqueous electrolytes have the advantages of lower cost, safe, low solvent resistance and easy to handle and may

still be attractive for commercial SCs applications^[13, 14], especially when the highest ion mobilities for ultra-high power is required.

Aqueous electrolytes, such as acids (e.g. H_2SO_4) and alkalis (e.g. KOH) have the advantage of high ionic conductivity (up to $\sim 1 \text{ S/cm}$), low cost and wide acceptance^[15]. The operating voltage of aqueous electrolyte can be increased, for example to 1.6 V by utilizing asymmetric cells with carbon for the negative electrode and MnO_2 for the positive one^[16, 17], or by using two different carbons with different stability potential windows^[18]. A symmetric AC/AC cell with an operating voltage of up to 1.6 V in a neutral aqueous electrolyte has also been reported, which was ascribed to the effect of carbon surface functional groups on modifying the over-potentials of hydrogen evolution and carbon oxidation^[19]. Therefore, in order to enhance the amount of energy storage in carbon black based electrodes (SC3 and SC2), not only the traditional H_2SO_4 and KOH electrolytes were studied, but also neutral electrolytes (e.g. Na_2SO_4 , Li_2SO_4 and NaCl) under a 1.6 V working voltage were also carefully investigated. Outstanding electrochemical properties were obtained that suggest potential use in high-rate applications.

6.2 Materials and methods

6.2.1 Preparation of carbon black thin film electrodes

Two kinds of high surface area commercial carbon black materials SC2 and SC3 (Cabot Corporation) were chosen as the electrode materials, and some details are summarized in Table 6.1. The principle difference between SC2 and SC3 was that SC3 had much higher external pore volume (V_{ex} , volume of mesopore and macropore), resulting in much higher S_{exter} and S_{BET} areas. Ball milled carbon black samples were prepared for comparison. The milling condition was 1/15 weight-to-ball ratio, 400 rpm rotation speed and 2 h milling time. The abbreviations for ‘original’ as-supplied carbon black

are OSC3 and OSC2, for ball milled carbon black are BSC3 and BSC2, respectively.

Table 6.1: Characteristic pore properties of the as-supplied carbon black particles.

Sample	S_{BET} (m ² /g)	S_{inter} (m ² /g)	S_{exter} (m ² /g)	V_t (cm ³ /g)	V_{mi} (cm ³ /g)	V_{ex} (cm ³ /g)
OSC3	3068	434	2634	1.9	0.3	1.6
OSC2	1300	689	612	1.0	0.4	0.6

S_{BET} - BET specific surface area, S_{inter} - micropore surface area, S_{exter} - surface area of mesopore and macropore ($S_{exter} = S_{BET} - S_{inter}$), V_t - total pore volume, V_{mi} - micropore volume, V_{ex} - pore volume of mesopore and macropore.

To prepare the electrodes, the as-supplied or ball milled carbon black powders with 5 wt.% polytetrafluoroethylene (PTFE) were dispersed in n-methylpyrrolidone (NMP) solvent under ultrasonication (600 W, 20 kHz) in ice bath for 10 min with a concentration of carbon black in suspension of 5 mg/ml. The PTFE was required in order to bind the fine powder together.

One meter long carbon black based electrodes ($\sim 10 \mu\text{m}$ thickness) were then prepared by spray deposition of suspensions on Al coated polyethylene terephthalate (PET) film with the spray nozzle linearly reciprocating at a speed of 500 mm/s. The suspension was prepared in NMP. Small area carbon black based electrodes (1 cm $\times$ 2 cm on stainless steel or 10 cm $\times$ 10 cm on Cu foil, both with 4 μm electrode film thickness) were also prepared by spray deposition of suspensions on heated substrates (200 °C). The pitch between rasters was 1 mm, the coating speed was 200 mm/s and the coating areas were 50 mm $\times$ 50 mm for stainless steel substrates and 130 mm $\times$ 130 mm for Cu foil, as previously described in Chapter 3.

In both long film and small area situations, a total syringe pump flow rate of 2 ml/min and an atomising pressure of 400 kPa compressed air were provided. The temperature of the substrates were maintained at 200 °C, as previously described in Chapter 3.

6.2.2 Characterization

6.2.2.1 Surface morphology and microstructure

The morphology and microstructure of carbon black powders and thin film samples were characterized in a FESEM JEOL 840 F and JEOL 3000F HRTEM. The specific surface area and pore volumes were measured in a Gemini VI adsorption/desorption instrument, with further details already given in Chapters 3, 4 and 5. The XPS spectra were analyzed and fitted using Casa XPS software as previously described in Chapter 5.

6.2.2.2 Electrochemical characterisation

A Gamry Reference 600 Electrochemical Analyzer was used for electrochemical properties characterization. For experiments carried out in a three-electrodes cell, a platinum (Pt) wire was used as the counter electrode, and Ag/AgCl and Hydroflex-reference were used as the reference electrodes for H_2SO_4 and KOH respectively. All symmetric carbon black two-electrodes full cells were formed using Swagelok cells with carbon black sprayed onto Cu foil ($\sim 15 \mu\text{m}$ thickness) as the current collector and using a 0.3 mm thick glassy fibre membrane (Whatman) as the separator. Cyclic voltammetry was performed at scan rates of 5 - 10000 mV/s, while galvanostatic charge/discharge behaviour was investigated at current densities in the range of 0.65 - 26 A/g, with an operating window 1.0 V for 6 M KOH and 1 M H_2SO_4 , and 1.6 V for neutral electrolytes, as previously described in Chapter 3. EIS was performed using an AC voltage with 10 mV amplitude at 0 V over a frequency range of 10000 - 0.01 Hz at room temperature.

6.3 Results and discussion

6.3.1 Morphology and structure

As shown in Figure 6.1(a), one meter long carbon black based electrodes were successfully spray deposited onto the Al coated PET web. Carbon black based electrodes on other substrates, such as 1 cm $\times$ 2 cm stainless steel and 10 cm $\times$ 10 cm Cu foil were also achieved according to the previous procedure using the as-supplied carbon black particles, as shown in Figures 6.1(b) and (c), respectively. The as-supplied carbon black particles (OSC3 and OSC2) had nano-scale particle size, in the range of 10 - 15 nm, as presented in Figure 6.1(d). Figure 6.1(e) at higher magnification exhibited more detail of the OSC2 particles: they were agglomerations of nano-scale units, which had ‘onion shape’ graphitic microstructure of 10 - 15 nm in diameter. OSC3 particles had similar ‘onion shape’ graphitic units, as shown in Figure 6.1(f). Figures 6.1(g) and (h) show the surface morphology of the as-supplied carbon black based electrodes at different magnifications. A relatively homogenous and well-connected porous structure was obtained.

6.3.2 Characterization of porosity

The N₂ adsorption-desorption isotherms and pore size distribution for OSC3, OSC2, BSC3, and BSC2 are shown in Figure 6.2. The data assuming the BET method for specific surface area, and the DFTNL method for pore volume, of the carbon black samples are summarized in Table 6.2.

OSC2 and OSC3 exhibited typical type IV adsorption isotherm characteristics with obvious H2 hysteresis loops (based on the IUPAC classification^[20]) at a relative pressure of $P/P_0 = 0.7 - 0.95$ (Figure 6.2(a)), indicating a comparatively large external pore volume of 1.64 cm³/g for OSC3 and 0.65 cm³/g for OSC2, and a relatively broad

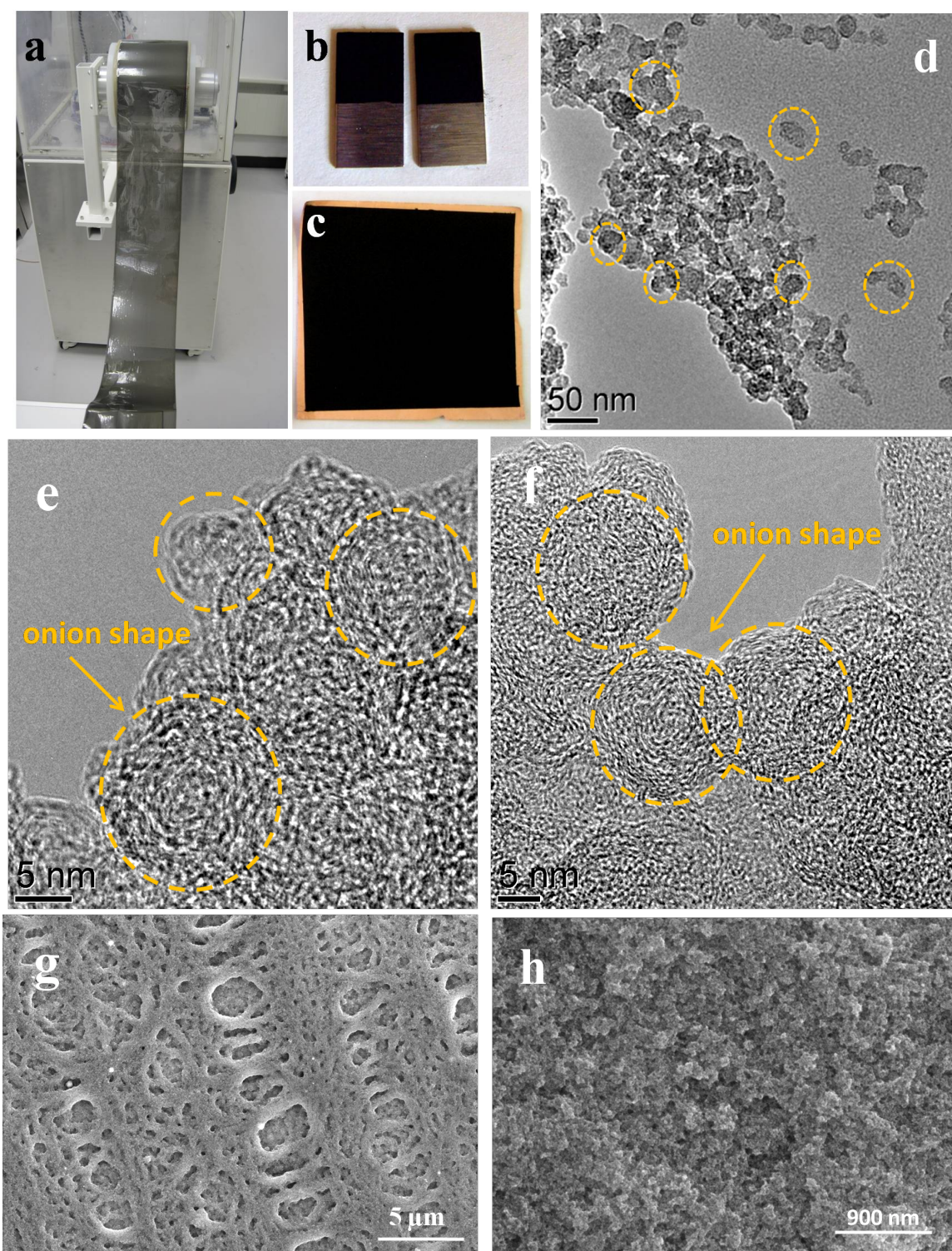


Figure 6.1: Optical images of the spray deposited carbon black film electrodes, spray deposited on (a) a $0.15\text{ m} \times 1\text{ m}$ flexible Al coated PET web, (b) $1\text{ cm} \times 2\text{ cm}$ stainless steel sheets, (c) $10\text{ cm} \times 10\text{ cm}$ copper foil, and (d) TEM image of OSC2 particles, (e) higher resolution TEM image of the ‘onion shape’ graphitic microstructure in OSC2 particles, (f) higher resolution TEM image of the ‘onion shape’ graphitic microstructure in OSC3 particles, (g) SEM image of surface morphology of the spray deposited carbon black electrode, and (h) a higher magnification SEM image of the porous structure of the spray deposited carbon black.

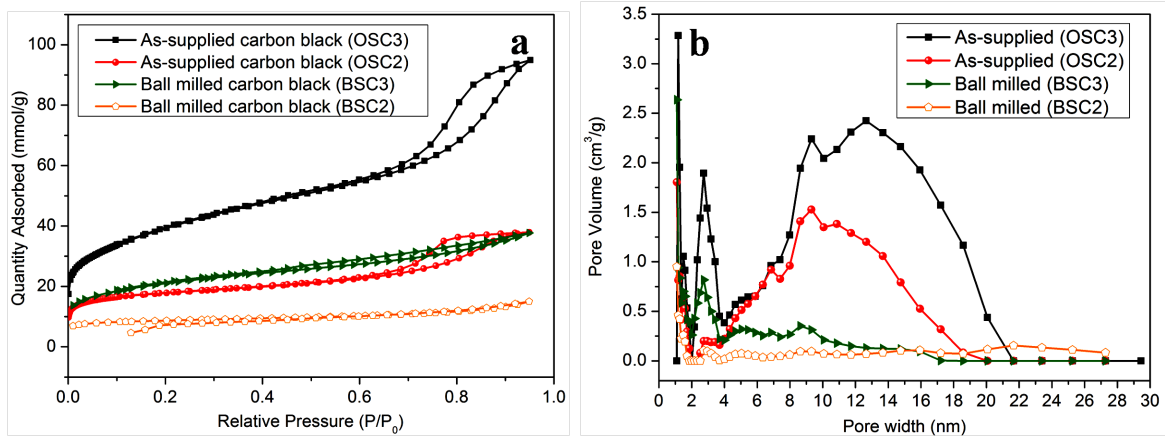


Figure 6.2: (a) N₂ adsorption-desorption isotherm (77 K) of as-supplied carbon black particles (OSC3, OSC2) and ball milled carbon black particles (BSC3, BSC2), and (b) the corresponding pore size distribution curves determined using the NLDFT model and assuming a slit pore shape.

mesopore size distribution. Meanwhile, the gradient of the N₂ adsorption isotherm at P/P_0 below 0.1 for the SC3 and SC2 powder indicated a micropore volume of 0.22 cm³/g for OSC3 and 0.35 cm³/g for OSC2. The micropore and mesopore size distribution for OSC3 and OSC2 are shown in Figure 6.2(b), which is obtained from Figure 6.2(a) by applying the NLDFT method, the key assumptions of which were given in Chapter 3. The pore size distribution of OSC2 showed a bimodal shape with a narrow micropore peak at 1.2 nm and a broad mesopore peak at approximately 10 nm, and an average pore width of 6.2 nm. Compared with OSC2, OSC3 showed a possible additional sub-mesopore peak at 3 nm (although this data relied on only 1 or 2 points taken at the limits of the machine/method), and a broader mesopore peak around 13 nm, which correlated to its steeper isotherm and wider hysteresis loop in Figure 6.2(a). Compared with OSC2, the high pore volume in OSC3 was anticipated to provide higher specific capacitance (due to the higher specific surface area which was attributed to higher sub-mesopore volume) and better high-rate capacitance performance (due to the better ion transportation which was enhance by the broader mesopore size).

After ball milling, the specific surface area of SC3 and SC2 decreased dramatically from 3069 m²/g to 1573 m²/g and from 1300 m²/g to 679 m²/g respectively, due to the mechanical destruction of the original surface porous structure. The micropore volume of SC3 decreased from 0.3 cm³/g to 0.2 cm³/g, and the overall external pore volume

reduced from 1.6 cm³/g to 0.5 cm³/g, correlated to the smaller adsorption quality below 0.1 P/P_0 , and the flatter and smaller hysteresis loop in Figure 6.2(a). Similar trends were also shown by the SC2 powders after ball milling, as shown in Table 6.2.

Based on the microstructure, N₂ adsorption/desorption isotherms and NLDFT analysis results, the commercial carbon black materials had porous structures that can be considered comparable with those 3D HPGC^[1] in that when sprayed into a porous film they show a 3D macroporous network between particles that will aid ion diffusion, they have a relatively large mesopore volume to increase the BET surface area, and a high graphite content to maintain intrinsic electrical conductivity.

Table 6.2: Characteristic pore properties of the ball milled carbon black particles.

Sample	S_{BET} (m ² /g)	S_{inter} (m ² /g)	S_{exter} (m ² /g)	V_t (cm ³ /g)	V_{mi} (cm ³ /g)	V_{ex} (cm ³ /g)
OSC3	3068	434	2634	1.9	0.3	1.6
OSC2	1300	689	612	1.0	0.4	0.6
BSC3	1573	419	1155	0.7	0.2	0.5
BSC2	679	370	400	0.3	0.2	0.1

S_{BET} - BET specific surface area, S_{inter} - micropore surface area, S_{exter} - surface area of mesopore and macropore ($S_{exter} = S_{BET} - S_{inter}$), V_t - total pore volume, V_{mi} - micropore volume, V_{ex} - pore volume of mesopore and macropore.

6.3.2.1 X-ray photoelectron spectroscopy (XPS)

The XPS data revealed that some oxygen and nitrogen were present in both OSC3 (O = 3.83 at.%, no nitrogen) and OSC2 (O = 5 at.%, N = 0.6 at.%). Therefore, oxygen related functional groups on the surface of carbon black particles, such as quinine, ketone, phenol (C-OR) and carboxylic (-O-C=O)^[19], may facilitate some weak pseudo capacitance, and wetting with aqueous electrolytes.

6.3.3 Electrochemical properties: half-cell performance

6.3.3.1 Cyclic voltammetry

The cyclic voltammogram (CV) curves for the carbon black based thin film electrodes in 1 M H₂SO₄ and 6 M KOH aqueous electrolytes at various scan rates are presented in Figures 6.3 and 6.4 respectively. In this case, all the electrodes had the same thickness of approximately 4 μm . The density of the SC3 and SC2 based film electrodes was estimated as $\sim 0.38 \text{ g/cm}^3$ and $\sim 0.48 \text{ g/cm}^3$ respectively.

As shown in Figures 6.3(a) and (b), in 1 M H₂SO₄ aqueous electrolyte, both the OSC3 and OSC2 curves exhibited nearly perfect rectangular shapes, indicating good ion mobility within the electrodes and low internal and contact resistance. Close to rectangular shapes were retained even at scan rate up to 600 mV/s. A set of anodic and cathodic peaks centering on 0.3 V were related to the reversible hydroquinone/quinone reactions^[21, 22], which will be explained later. The CV curves for BSC3 electrodes in Figure 6.3(c) had a similar rectangular shape at low scan rates, but became progressively distorted at higher scan rates, suggesting progressive restrictions in ion mobility or increased resistance. Besides the reversible quinone/hydroquinone transformation at $\sim 0.3 \text{ V}$, there was new peak at $\sim 0.1 \text{ V}$ on the forward sweep, suggesting that the ball milling process had introduced some additional functionality onto the carbon surface, probably due to Fe related contamination from the stainless steel milling balls and milling pot. As shown in Figure 6.3(d), the position of this peak was largely insensitive to the sweep rate in the range studied. Electrodes of BSC2 were more resistive, showing a pronounced superimposed tilt at all scan rates, indicating that resistive elements became increasingly important.

The more resistive nature of BSC2 than BSC3 was difficult to rationalise but probably related to the overall coherency of the electrode-recognising that it is comprised extremely small particles with a tendency to agglomerate and reduced interfacial adhesion. Nonetheless, it should be noted that within the context of the behaviour of

the other carbon materials in Chapters 4 and 5, all the carbon black electrodes showed the least resistive nature, in both as-supplied and ball milled conditions. Furthermore, their capacitive behaviour at high scan rates (close to rectangular shape was retained up to 600 mV/s) exceeded that OMC-based electrodes, which had obviously distorted CV curves from 25 mV/s^[23].

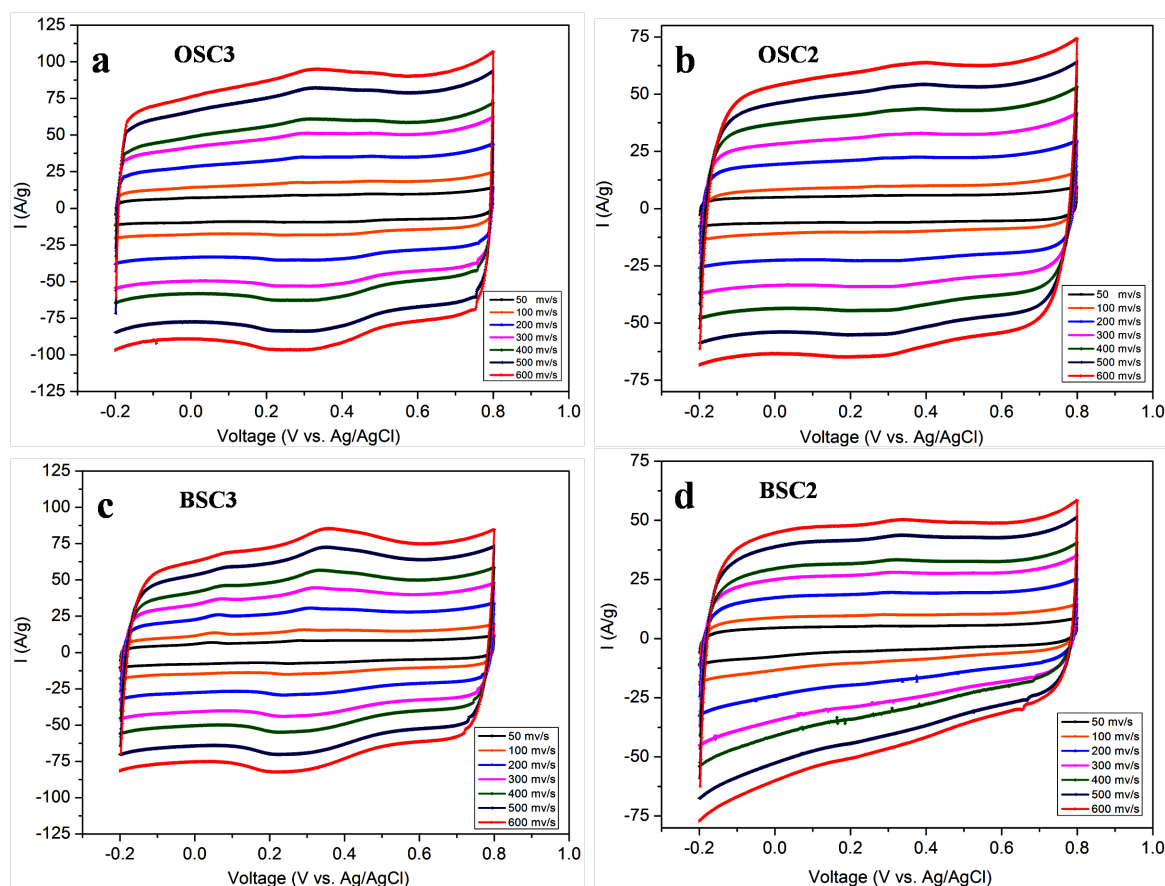


Figure 6.3: Cyclic voltammetry curves for carbon black based thin film electrodes recorded at room temperature at scan rates of 50, 100, 200, 300, 400, 500, 600 mV/s in 1 M H₂SO₄ aqueous solution: (a) OSC3, (b) OSC2, (c) BSC3 and (d) BSC2.

Figures 6.4(a) to (d) show the same electrode behaviour in 6 M KOH, which is also a commonly studied electrolyte for carbon materials, attributed to its chemical stability and non-corrosive behaviour with metallic components of a supercapacitor (e.g., current collectors, connections, can, etc)^[19]. In this case, the CV curves showed less idealised electric double layer behaviour, with some resistive character in all cases. Once again there was the suggestion of weak electrochemical activity at ~ 0.5 V, and once again the ball milled versions in Figures 6.4(c) and (d) showed a slight increase in resistive character. The measured currents for all the electrodes in 6 M KOH were broadly

similar to those measured for 1 M H_2SO_4 .

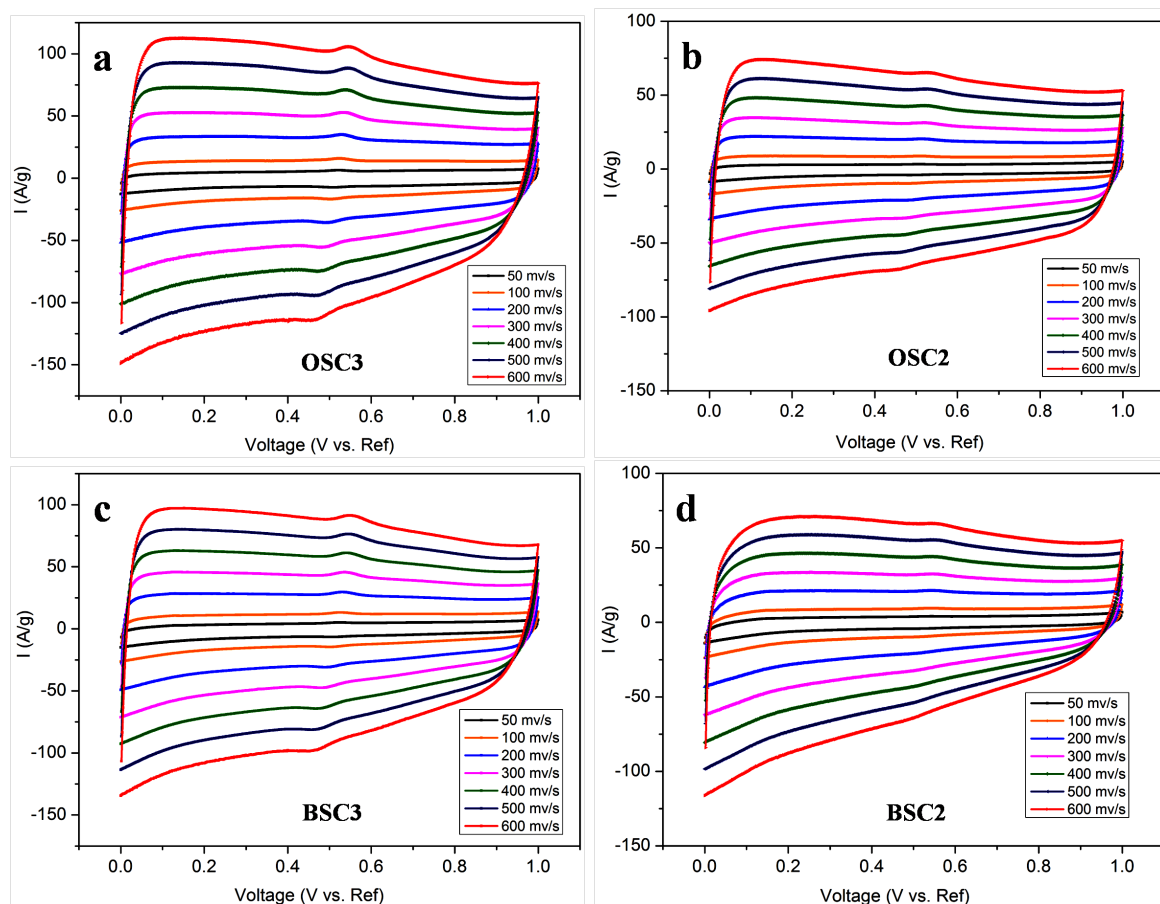


Figure 6.4: Cyclic voltammetry curves of carbon black film electrodes recorded at room temperature with scan rates of 50, 100, 200, 300, 400, 500, 600 mV/s in 6 M KOH aqueous solution: (a) OSC3, (b) OSC2, (c) BSC3 and (d) BSC2.

The small pseudocapacitance peaks (at approximate 0.3 V vs. Ag/AgCl) that appeared in all the carbon black film samples in 1 M H_2SO_4 were attributed to the reversible quinine/hydroquinone transformation from the oxygen functional groups^[21, 22] (as confirmed in XPS results), which had two main contributions: improving the electrode/electrolyte wettability and introducing weak reversible redox reactions^[24, 25], both of which can enhance supercapacitor behaviour. The cathodic/anodic peaks (at 0.5 V vs. hydroflex-reference) in 6 M KOH were also related to the reduction/oxidation of oxygen functional groups. Although the quinine group related redox reaction is depressed when the pH of the electrolyte increases, some other groups such as those which are pyrone-like can be active in 6 M KOH^[26].

The specific capacitances derived from cyclic voltammetry curves of these carbon black

electrodes were calculated from Equation (3.12), as previously described in Chapter 3, and specific capacitance as a function of scan rate in 1 M H_2SO_4 and 6 M KOH aqueous electrolytes is plotted in Figure 6.5, and are summarized in Table 6.3.

For all the carbon black based thin film electrodes, the specific capacitance decreased with increasing scan rate because of progressive difficulties of ion transport and adsorption of ions into the porous structures at faster potential sweeps, as shown in Figure 6.5. OSC3 exhibited the highest specific capacitance across the whole scan rate range in both acidic and alkaline electrolytes, attributed to its highest BET specific surface area and broad mesopore size (2 - 23 nm, Figure 6.2(b)), which facilitated electrolyte ion transportation and efficient utilization of micropore surface area. Meanwhile, in 1 M H_2SO_4 , more than 84% specific capacitance retention was achieved for the OSC3 based electrode as the scan rate increased from 30 mV/s to 600 mV/s, compared with a 83%, 81% and 69% capacitance retention for OSC2, BSC3 and BSC2 respectively, as shown in Table 6.3. Overall, specific capacitances at the high scan rates were at the upper range of those reported for carbon materials, in these, or any electrolyte.

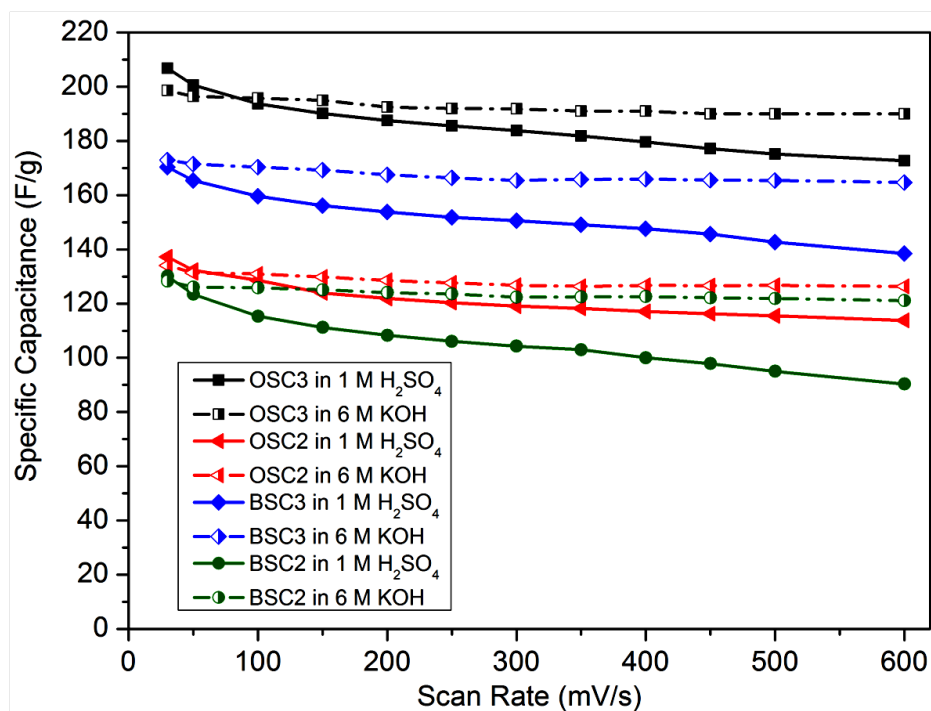


Figure 6.5: Variation of specific capacitance with scan rate for various spray deposited carbon black based electrodes in 1 M H_2SO_4 and 6 M KOH. Voltage window = 1.0 V.

In general, the electrodes showed slightly smaller specific capacitances in 6 M KOH

than that in 1 M H₂SO₄ at scan rate below 30 mV/s, but had higher and more stable capacitance above ~ 30 mV/s. Differences in ion transport stability could be explained by the smaller size of OH[−] ions (0.22 nm)^[27] in KOH than the size of SO₄^{2−} ions (0.46 nm) in H₂SO₄, which allowed faster transport in the porous structure at high scan rates. The specific capacitance of OSC3 and OSC2 decreased from 208 and 136 F/g at 30 mV/s to 189 and 126 F/g at 600 mV/s respectively, representing a 96% and 94% capacitance retention respectively. BSC3 and BSC2 electrodes also had similar capacitance retention.

Table 6.3: Specific capacitance of carbon black based thin film electrodes at 30 and 600 mV/s scan rate in different electrolytes.

Electrode	Capacitance in 1 M H ₂ SO ₄		Capacitance in 6 M KOH	
	(F/g) at 30	Retention at 600	(F/g) at 30	Retention at 600
	mV/s	mV/s	mV/s	mV/s
OSC3	207	84%	200	96%
OSC2	137	83%	134	94%
BSC3	170	81%	173	95%
BSC2	130	70%	128	94%

Both in 1 M H₂SO₄ and 6 M KOH aqueous solutions, the OSC3 electrode exhibited the highest specific capacitance and ion-transport stability, while BSC2 had the poorest performance, which was consistent with the pore size distribution and BET surface analysis. The high capacitance retention (84%) of OSC3 based film electrode in 1 M H₂SO₄ electrolyte was comparable to some reported value of graphene-based electrodes (85%), and higher than some reported SWNTs based electrodes (77%)^[28], due to the large mesopore and macropore volume (which decreases the ion transport resistance and ion diffusion pathways) and good wettability.

6.3.3.2 Charge/discharge behaviour

To further evaluate the rate performance of carbon black electrodes, galvanostatic charge/discharge cycles were measured again in 1 M H_2SO_4 and 6 M KOH aqueous solutions with current densities in the range 1 - 10 A/g, as presented in Figures 6.6 and 6.7 respectively.

As shown in Figure 6.6, in 1 M H_2SO_4 , nearly linear charge/discharge behaviour and symmetrical shapes with negligible IR drop were obtained for all the carbon black film electrodes under high current density (e.g. 10 A/g, 5 A/g). However, as current density reduced from 10 A/g to 1 A/g, the deviation from linearity increased, especially after ball milling, consistent with CV behaviour shown earlier, and most noticeable in Figures 6.6(c) and (d) at 1 A/g. The ‘plateau’ formed at 0.8 V in 1 M H_2SO_4 at low current density (1 A/g) is related to the faradaic pseudocapacitive reaction of the acidic groups on carbon black surface^[10], which is in agreement with the redox-type peaks in the CV curves.

In 6 M KOH, as shown in Figure 6.7, the galvanostatic charge/discharge curves of all the carbon black film samples exhibited nearly linear charge/discharge behaviour and symmetrical shapes at all current densities. The IR drop on reversal charge/discharge was negligible, indicating relatively low internal resistance.

The galvanostatic specific capacitances (calculated from Equation 3.14) as a function of current density for all the electrodes are plotted in Figure 6.8, and is an analogue to Figure 6.5, which plotted similar data, but in that case obtained from the CV curves. In this case under this method, the specific capacitance in the two electrolytes were more similar and decreased with increasing current density, as it became harder to use efficiently all the available area, and resistive effects (both on electron and ion mobility) become more significant.

OSC3 had the highest specific capacitance of the four carbon black electrodes in the

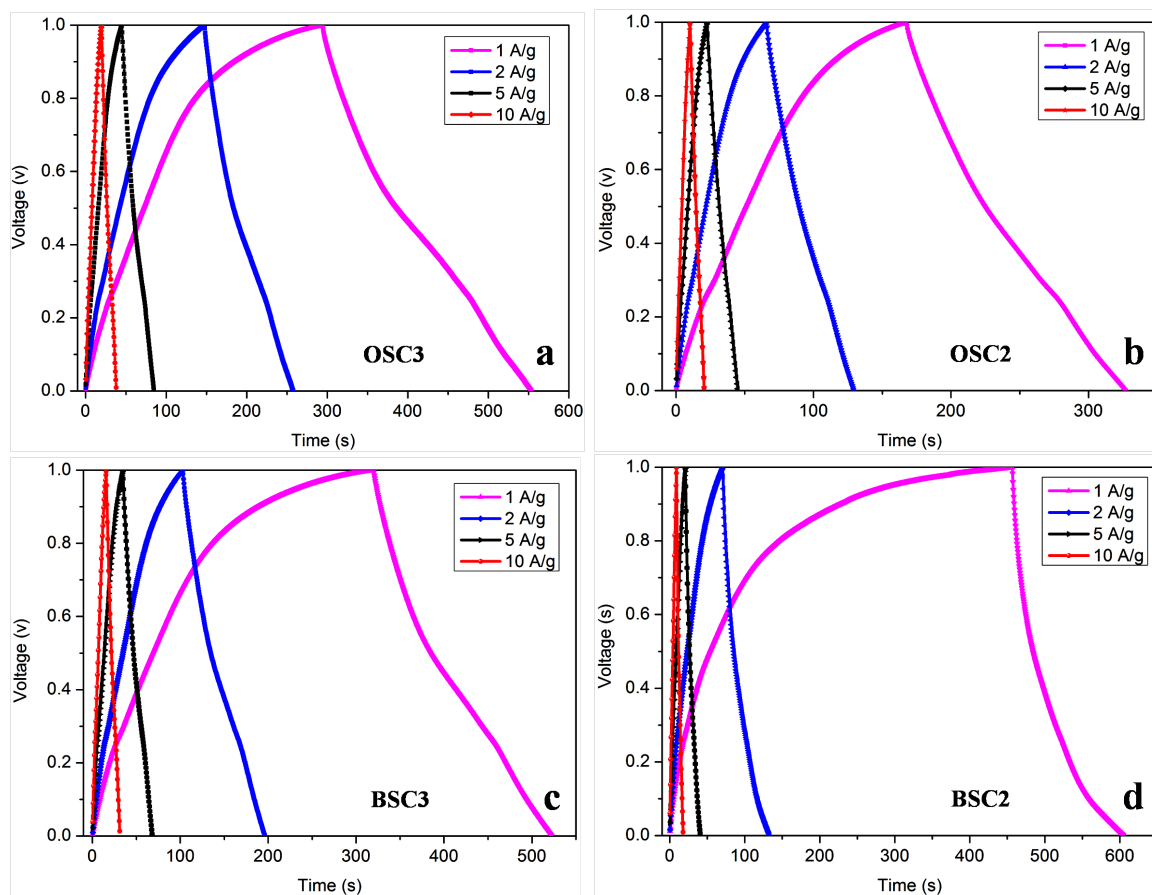


Figure 6.6: Galvanostatic charging/discharging behaviour of carbon black based thin film electrodes at different current densities (1, 2, 5, 10 A/g) in 1 M H₂SO₄: (a) OSC3, (b) OSC2, (c) BSC3, and (d) BSC2.

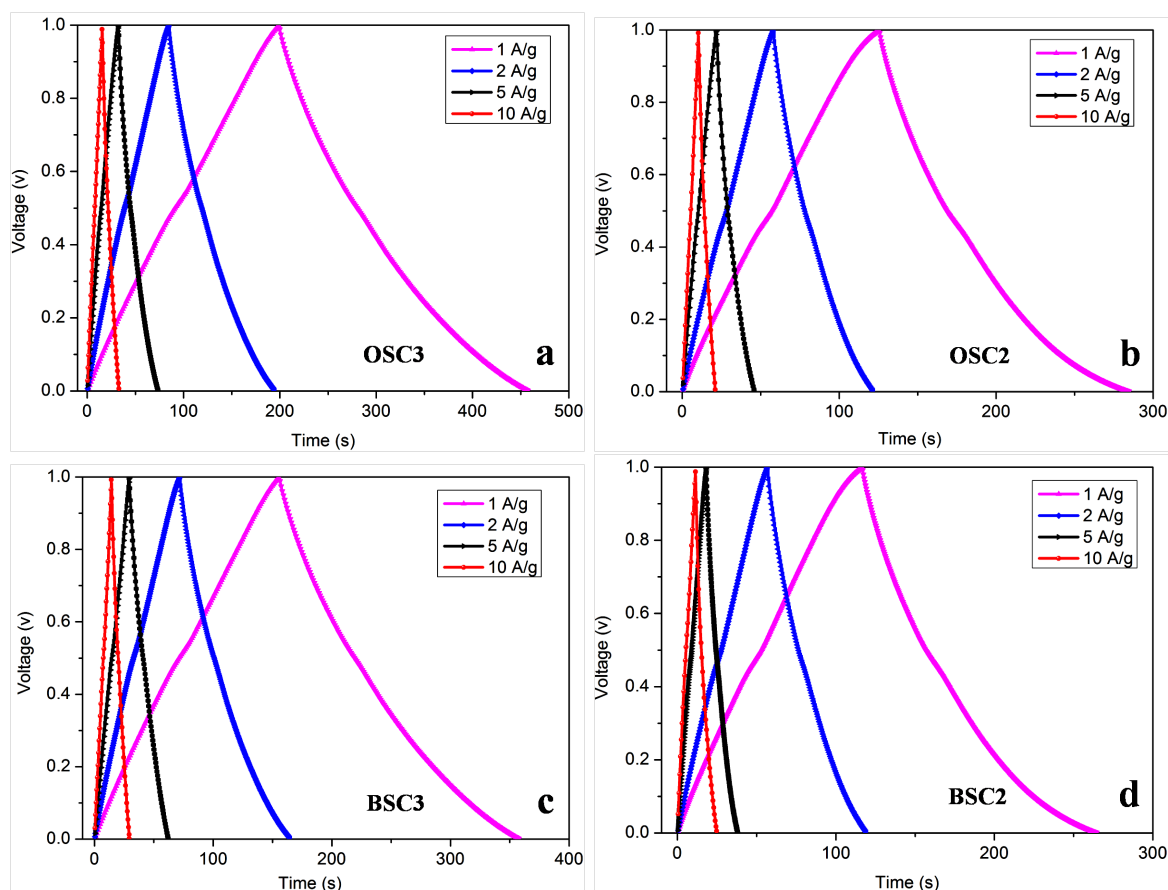


Figure 6.7: Galvanostatic charging/discharging behaviour of carbon black based thin film electrodes at different current densities (1, 2, 5, 10 A/g) in 6 M KOH: (a) OSC3, (b) OSC2, (c) BSC3, and (d) BSC2.

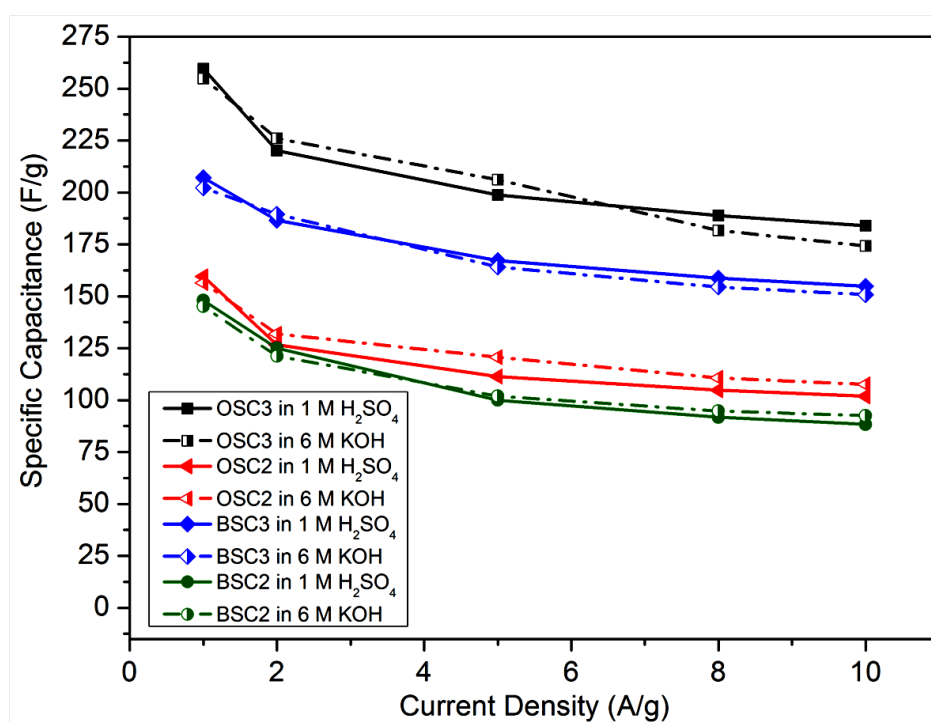


Figure 6.8: Variation of specific capacitance with current density in 1 M H₂SO₄ and 6 M KOH. Voltage window = 1.0 V.

current density range 1 - 10 A/g, with 260 F/g at 1 A/g and 184 F/g at 10 A/g (71% retention). The specific capacitance at 1 A/g of 260 F/g for OSC3 was approximately twice that of some reported CNT-based electrodes^[29–31].

6.3.3.3 Electrochemical impedance spectroscopy (EIS)

To further study ion transport and other properties of the carbon black electrodes, electrochemical impedance spectroscopy (EIS) was performed on electrodes in the higher performing 6 M KOH, as shown in Figure 6.9.

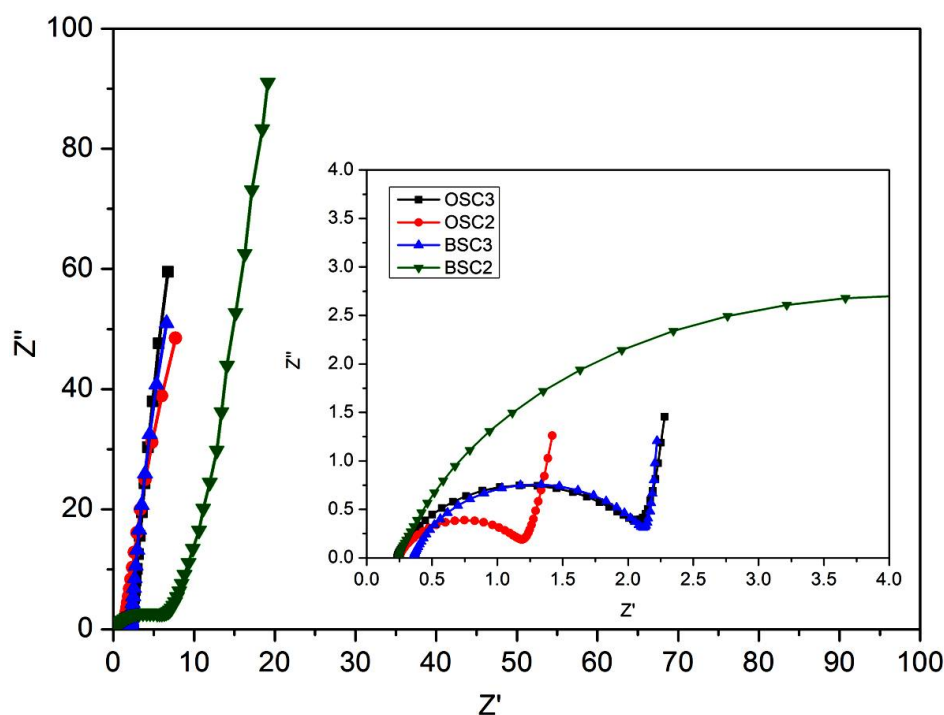


Figure 6.9: Nyquist impedance spectra of the carbon black based thin film electrodes obtained in 6 M KOH.

Figure 6.9 shows a Nyquist plot for all four electrodes, giving similar and a low equivalent series resistance of approximately $0.2 \, \Omega$, a negligible Warburg 45° portion, and then a steep gradient capacitive region, illustrating low intrinsic resistance and strong character of ideal capacitive behaviour, as previously seen in the rectangular shape of the CV curves.

As previously described in Chapter 4, the semi-circle is characteristic of an electrochem-

ical process that is associated with porous structure, pseudo-transfer reactions^[32], and conductivity of both the electrode materials and the current collectors^[33]. The diameter of the semi-circle estimates the charge transfer resistance (R_{ct}) at the electrode-electrolyte interface^[32, 33]. Therefore, the larger R_{ct} of BSC2 (8 Ω) compared with that of OSC2 (1 Ω , much lower than that of some reported ordered mesopore carbon materials^[34]), may be ascribed to a higher particle contact resistance after ball milling, which is also represented in the generally more inclined CV curves (Figure 6.3(d)) and slightly more pronounced plateaux in charge/discharge curves (Figure 6.6(d)).

6.3.3.4 Cycling behaviour

Long cycle life is essential for supercapacitor applications^[35, 36] and one of their primary advantages. The investigation of OSC3 and OSC2 based thin film electrodes in 1 M H_2SO_4 after 5,000 cycles under 1 A/g charge/discharge current density is shown in Figure 6.10. Both electrodes showed a slight increase in specific capacitance on cycling, and was suggested to arise because of progressive, slightly enhanced pseudo-capacitive reactions of surface functional groups during the cycling test although conclusive evidence could not be collected. Assuming this is the case, the OSC2 based film electrode exhibited a more obvious increase in specific capacitance, because its higher contents of oxygen and nitrogen related surface functional groups. Good cycling stability was provided by OSC3 and OSC2, with only a 7% variation of specific capacitance over 5,000 cycles.

6.3.4 Electrochemical properties: full cell performance

6.3.4.1 Cyclic voltammetry

The previous studies showed that overall ball milling treatment did not have a positive on the electrochemical properties of carbon black based electrodes. Therefore, only the

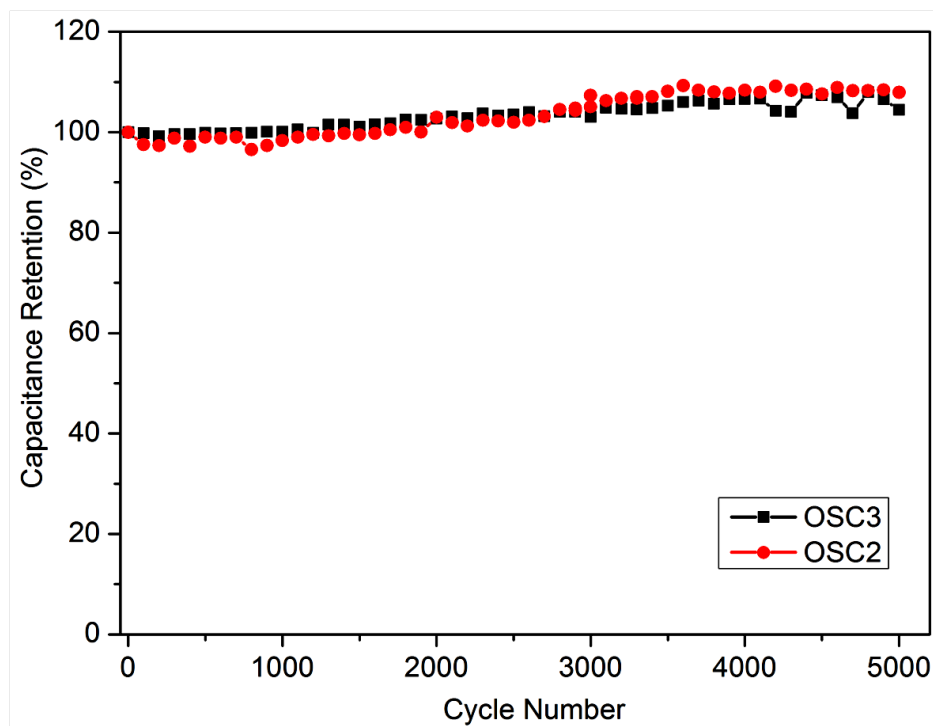


Figure 6.10: Long term charge/discharge cycling performance of carbon black-based thin film electrodes in 1 M H_2SO_4 at 1 A/g current density.

as-supplied carbon blacks (OSC3 and OSC2) were chosen for full cell (two-electrode cell) investigations. In order to explore the performance of OSC3 and OSC2 based electrodes under higher operating voltages, three types of neutral electrolytes (Na_2SO_4 , Li_2SO_4 and NaCl) of differing concentration were studied; the previously used 6 M KOH electrolyte was also studied for comparison. Cu foil as the current collector was preferred for full cell fabrication as it offered more reliable electrical contact over stainless steel and therefore H_2SO_4 was not considered because of its corrosive reaction on Cu.

The cyclic voltammogram (CV) characterization of carbon black (OSC3) in neutral and basic aqueous electrolytes at various scan rates in two-electrodes cells are presented in Figure 6.11. As shown in Figure 6.11(f), the OSC3 based electrode displayed much better rectangular CVs in 6 M KOH than in the other neutral aqueous electrolytes (Li_2SO_4 , Na_2SO_4 and NaCl) at the same scan rate. The better capacitive behaviour and larger capacitance obtained in 6 M KOH aqueous electrolyte was attributed to the high electrolyte concentration which can provide more mobile electrolyte ion species, and to

the smaller OH^- ion size compared to other anions, which facilitates ion transportation and relatively efficient micropore utilization in all parts of the electrode. However, the stable working window of the OSC3 based electrode in KOH electrolyte was less than 1 V, being limited by the oxygen evolution potential^[12]. By contrast, as shown in Figure 6.11(a), the stable potential window of OSC3 based electrodes in neutral electrolytes 1 M Li_2SO_4 could be extended to 1.6 V.

The extension of operating voltage windows was the result of three aspects: first was the overpotential caused by the low concentration of H^+ and OH^- [37]. The gas evolution reaction is related to the decomposition of H_2O (the OH^- oxidation and H^+ reduction), and these reactions are affected by the pH of the electrolyte. At a high concentration of H^+ (in acid electrolyte), H_2 gas evolution readily occurs, which limits the operating working window. Similarly, the high concentration of OH^- (in basic electrolyte) can activate the O_2 gas evolution reaction at lower potential, which also limits the operating working window. In neutral electrolytes, attributed to the very low concentration of both H^+ and OH^- ions, the H_2/O_2 gas evolutions were obtained at lower/higher potentials respectively, resulting in a tendency to extend the operating voltage window^[37]. The second reason for the overpotential was that the nascent hydrogen was stored in the carbon black electrodes below the thermodynamic potential for water decomposition [13]. Thirdly and probably most significantly the maximum working potential was not only dependent on the electrolyte pH, but also on the surface functional groups of the electrode materials. A higher oxygen content on the carbon electrode surface facilitated a higher overpotential for dihydrogen evolution and carbon oxidation, protecting the electrode from uncontrollable reduction/oxidation^[38]. The oxygen surface functional groups on the carbon black surface enhanced the wide operating window in neutral electrolyte, compared with that previously reported glassy carbon^[39].

The current remained approximately stable when the cell voltage increased from 1 V to 1.6 V, indicating the good reversibility of the charge storage process. When the potential window was further extended up to a 2 V, the currents increased sharply during

the scan, suggesting that 2 V potential window was higher than the thermodynamic limit for the carbon oxidation and hydrogen evolution^[40, 41].

As shown in Figure 6.11(b), the OSC3 based film electrode was also able to operate reversibly in a 1.6 V working window in 1 M Na₂SO₄ electrolyte. Moreover, the OSC3 electrode had a more rectangular shape in 1 M Na₂SO₄ than in 1 M Li₂SO₄ at 1000 mV/s scan rate, indicating a better high-rate performance. Similar results for improved double-layer capacitive rate behaviour in Na₂SO₄ have also been reported in the literature, due to two reasons: (1) Na₂SO₄ contributes less to equivalent series resistance than Li₂SO₄, and (2) the hydrated Na⁺ ion had a higher migration speed than the hydrated Li⁺ ion in the bulk electrolyte and in the inner pores of carbon electrodes^[42, 43].

The effect of electrolyte ion concentration on OSC3 based electrode is shown in Figures 6.11(c) and (d): as the concentration of Na₂SO₄ decreased from 1 M to 0.5 M and further to 0.1 M, the shape of CV curves were distorted gradually from rectangular shape at the same scan rate, suggesting that more limited ion transportation and availability occurred at lower ion concentrations.

The CV performance in 1 M NaCl electrolyte is shown in Figure 6.11(e). Obvious redox peaks are displayed for the OSC3 based electrode, which could be associated with the evolution of Cl⁻ itself during the scan, or related to the accelerated dissolution of the Cu foil in the NaCl electrolyte. Although a NaCl neutral electrolyte can provide a larger electrochemical stability window (2 V), the strong oxidation/reduction peaks suggest it was not a good choice for carbon black-based EDLC cells.

The OSC2 based electrode had a similar performance to the OSC3 based electrode in basic and neutral electrolytes. Their specific capacitances, derived from the CV curves as a functions of scan rates for single OSC3 or OSC2 based electrodes in different electrolytes are presented in Figure 6.12. The carbon black electrodes had similar behaviour in basic and neutral electrolytes: the specific capacitance of carbon black

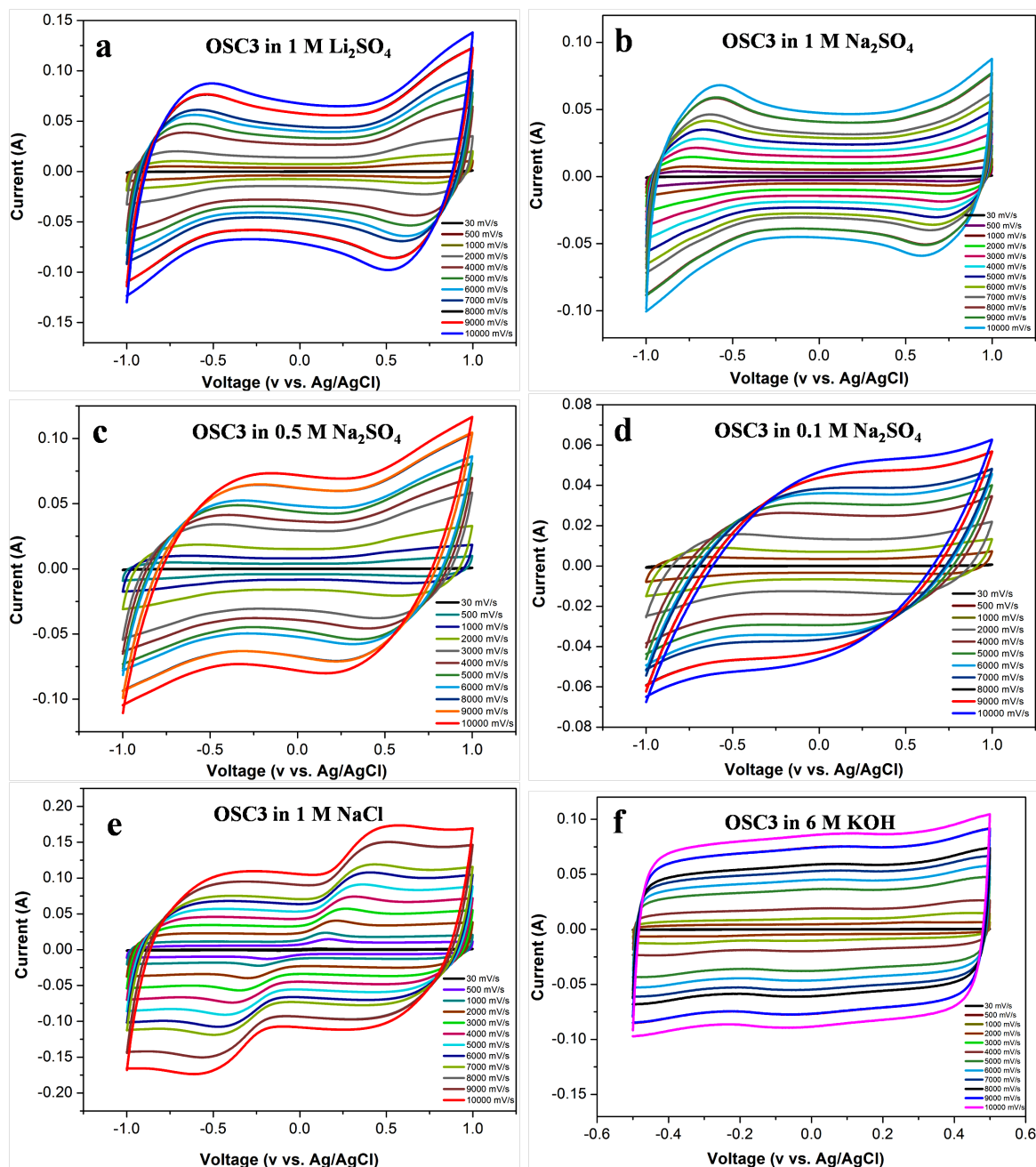


Figure 6.11: Cyclic voltammetry curves of OSC3 based thin film electrodes recorded at room temperature with scan rates of 30 to 10000 mV/s in (a) 1 M Li_2SO_4 , (b) 1 M Na_2SO_4 , (c) 0.5 M Na_2SO_4 , (d) 0.1 M Na_2SO_4 , (e) 1 M NaCl , and (f) 6 M KOH electrolytes.

decreased as the scan rate increased, due to the inefficient utilisation of the electrode surface area at high scan rate. However, the specific capacitance of OSC3 electrodes were still approximately 200 F/g in both 6 M KOH and 1 M Na₂SO₄ electrolyte when the scan rate was increased up to 10,000 mV/s, indicating that the electrolyte ions in both KOH and Na₂SO₄ electrolytes had high diffusivity. The concentration of the electrolyte was also a critical factor for supercapacitor performance. For the Na₂SO₄ electrolyte, low concentration 0.1 M Na₂SO₄ displayed the lowest specific capacitance across the whole scan rate range, especially at high scan rate, due to insufficient ion supply. The performance of OSC3 based electrodes in 1 M Na₂SO₄ and 1 M Li₂SO₄ were comparable at low scan rate, but higher capacitances were obtained in 1 M Na₂SO₄ when the scan rate was higher than 2,000 mV/s, attributed to the smaller equivalent series resistance and higher migration speed of Na⁺ than Li⁺. OSC2 based film electrodes had similar performance in 6 M KOH and 1 M Na₂SO₄ electrolytes, but showed lower specific capacitance (*ca.* 125 F/g at 10,000 mV/s) than OSC3 at the same scan rate, due to their lower specific surface area.

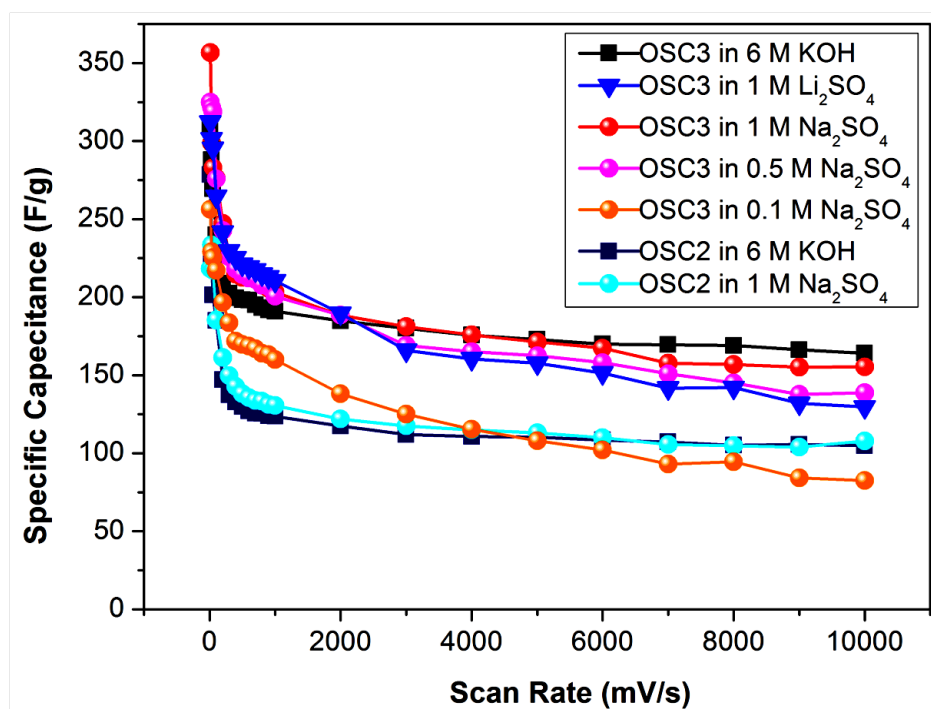


Figure 6.12: Specific capacitance of single OSC3 or OSC2 based film electrodes with scan rates in basic and neutral aqueous electrolytes, over their maximum electrochemical stability windows.

6.3.4.2 Charge/discharge behaviour

To further assess the maximum working voltage and evaluate the cell capacitances, galvanostatic charge/discharge investigations of OSC3 base film electrodes in two-electrode cells were performed in different electrolytes with current densities of 0.65 - 26 A/g, as presented in Figure 6.13. Due to the dissolution of copper foil in NaCl electrolyte, only Na₂SO₄ and Li₂SO₄ were used as the neutral electrolytes for further investigation.

As shown in Figures 6.13(a) and (b), both OSC3 and OSC2 exhibited nearly linear and symmetrical shapes with negligible IR drops at different current densities under a 0.9 V working cell voltage in 6 M KOH. As shown in Figures 6.13(d) to (f), in 1 M, 0.5 M and 0.1 M Na₂SO₄, almost linear charge/discharge curves were obtained as the operating voltage increased up to 1.6 V. A plateau will form in the charge curve at low current density (0.5 A/g) when the cell voltage was over 1.6 V, due to the irreversible oxidation of carbon black. Therefore, the maximum cell voltage for carbon black based film electrodes in Na₂SO₄ neutral electrolyte is 1.6 V. Similar behaviour was obtained in 1 M Li₂SO₄ electrolyte as in 1 M Na₂SO₄, as shown in Figure 6.13(c), indicating their generally comparable performance.

The galvanostatic specific capacitance as a function of current density for single OSC3 or OSC2 based film electrodes in different electrolytes are plotted in Figure 6.14. For all carbon black based film electrodes, their specific capacitances decreased as the current density increased, due to the inefficient utilisation of the electrode surface area at high current density. For OSC3 based electrodes, the specific capacitance remained at ~ 200 F/g in both 6 M KOH and 1 M Na₂SO₄ electrolyte when the current density increased up to 26 A/g. Once again, the reduction of electrolyte ion concentration had a negative effect on electrochemical performance, due to insufficient ion supply. And once again, under the same ion concentration, Na₂SO₄ exhibited better high rate performance than Li₂SO₄.

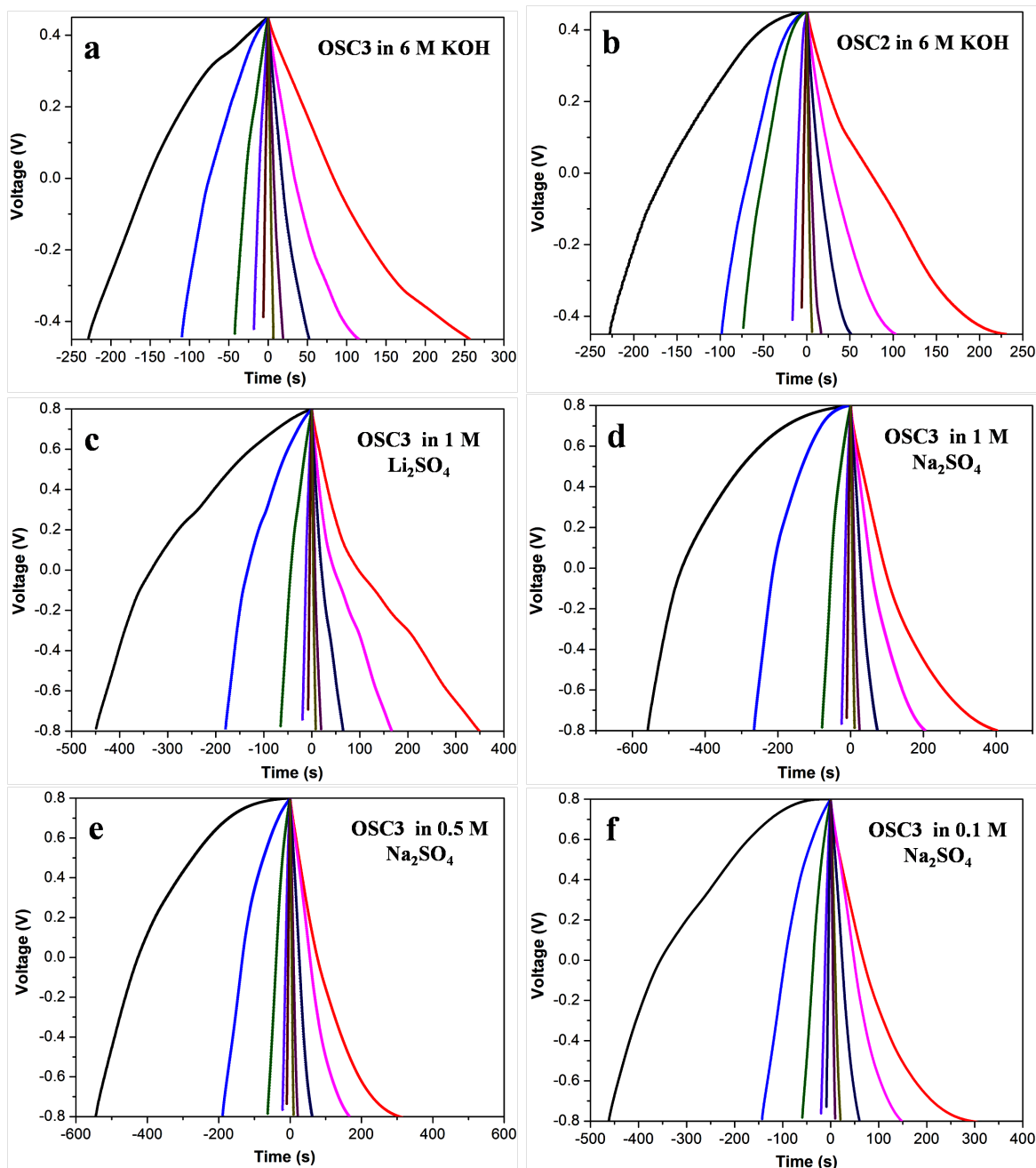


Figure 6.13: Galvanostatic charging/discharging behaviour of single as-supplied carbon black-based thin film electrodes at different current density (0.65, 1.3, 2.6, 5.3 and 13 A/g) in different aqueous electrolytes. (a) OSC3 in 6 M KOH, (b) OSC2 in 6 M KOH, (c) OSC3 in 1 M Li_2SO_4 , (d) OSC3 in 1 M Na_2SO_4 , (e) OSC3 in 0.5 M Na_2SO_4 , and (f) OSC3 in 0.1 M Na_2SO_4 .

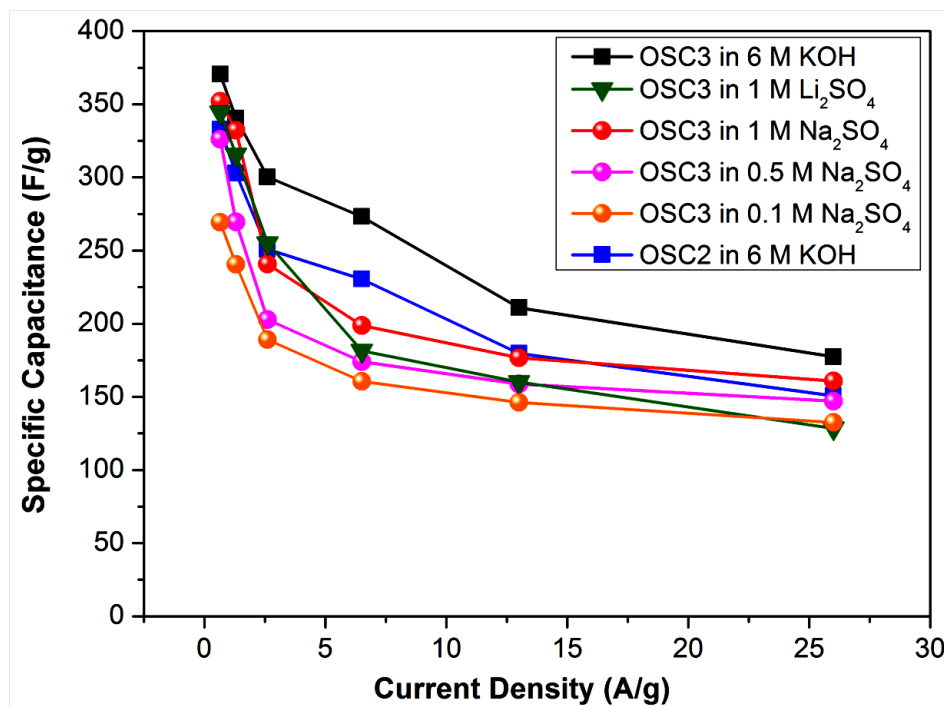


Figure 6.14: Specific capacitance of OSC3 and OSC2 based film electrodes with current density in basic and neutral aqueous electrolytes. Voltage window is 0.9 V for 6 M KOH, 1.6 V for Na₂SO₄ and Li₂SO₄.

According to Equations 1.2 and 1.3 previously described in Chapter 1, the high working voltage in neutral electrolytes can improve both the energy density (E) and power density (P) of the cell. The Ragone plot of performance of OSC3 or OSC2 based electrodes in two-electrode cells in 6 M KOH and 1 M Na₂SO₄ electrolytes is showed in Figure 6.15, with a cell-voltage window of 0.9 V for KOH and 1.6 V for Na₂SO₄, and current density varied between 0.65 and 26 A/g. In 1 M Na₂SO₄ at a power density of ~ 21 kW/kg, the energy density was higher than 18 Wh/kg, and much higher than reported for 3D HPGC^[2]. Even in 6 M KOH, the power density was ~ 12 kW/kg, the energy density was ~ 5.2 Wh/kg which was higher than graphene-based supercapacitors^[44] and symmetric AC/AC capacitors^[13]. Although the OSC3 or OSC2 based electrodes had lower capacitance in 1 M Na₂SO₄ than in 6 M KOH (as shown in Figure 6.14), they both show higher energy density and power density in 1 M Na₂SO₄, attributed to the 1.6 V high cell-voltage window in 1 M Na₂SO₄, which was almost twice of the 0.9 V cell-voltage in 6 M KOH. Because the energy density was proportional to square of the cell operate voltage, the enhancement of E in 1 M Na₂SO₄ was more obvious.

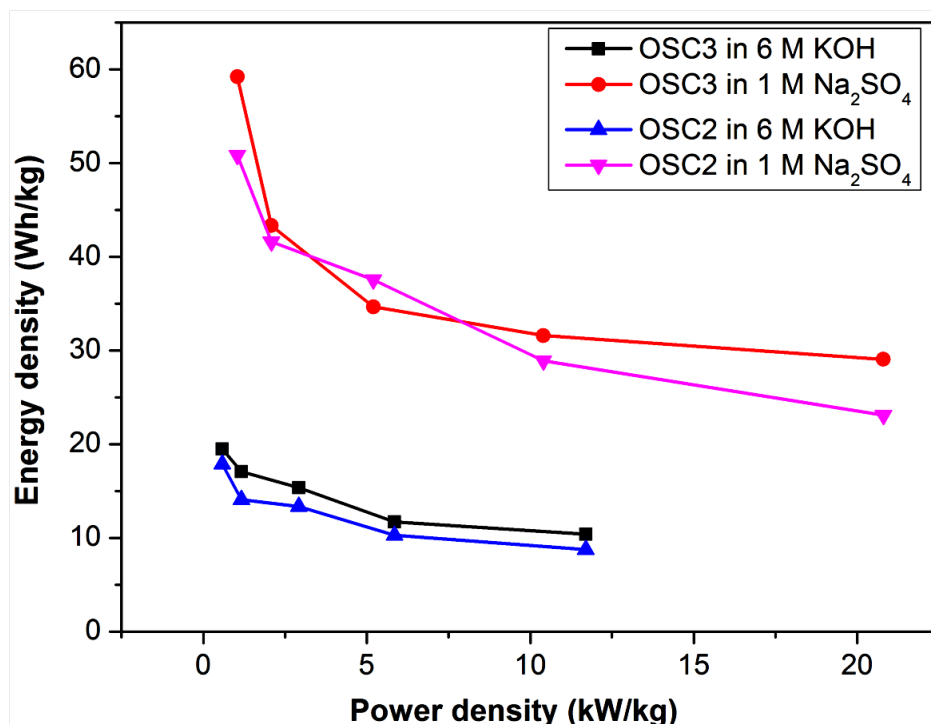


Figure 6.15: Ragone plot of the performance of OSC3 and OSC2 based two-electrodes cells in 6 M KOH and 1 M Na₂SO₄ electrolytes over a potential window of 0.9 V and 1.6 V respectively.

6.3.4.3 Electrochemical impedance spectroscopy

The electrochemical impedance behaviour of OSC3 or OSC2 based film electrodes in two-electrode cells using different electrolytes is shown in Figure 6.16. In the high frequency region, as exhibited in Figure 6.16(a), both OSC3 and OSC2 based thin film electrodes exhibited more linear behaviour in 6 M KOH electrolyte compared with Na₂SO₄ and Li₂SO₄ neutral electrolytes, confirming more idealised capacitive behaviour in KOH.

As previously described in Chapter 4, the internal resistance (R_s) relates to the resistance of the aqueous electrolyte, the contact resistance between electrode and the current collector, and the intrinsic resistance of the synthetic graphite materials^[3]. As shown in Figure 6.16(b), the R_s of OSC3 in 6 M KOH was approximately 0.1 Ω , much smaller than in 1 M Na₂SO₄ (0.8 Ω), suggesting that the basic electrolyte had a lower intrinsic resistance. For Na₂SO₄, the resistance depended on the electrolyte concentration: when the concentration reduced from 1 M to 0.1 M, the R_s increased dramatically

from 0.8Ω to more than 5Ω . The electrolyte ion concentration also had a significant effect on the charge transfer resistance (R_{ct}). As shown in Figure 6.16(b), R_{ct} increased from almost zero to around 1.5Ω when the concentration of Na_2SO_4 reduced from 1 M to 0.1 M, indicating the lower ion-transfer at the electrode and current collector interface, which had a negative effect on the overall capacitive behaviour.

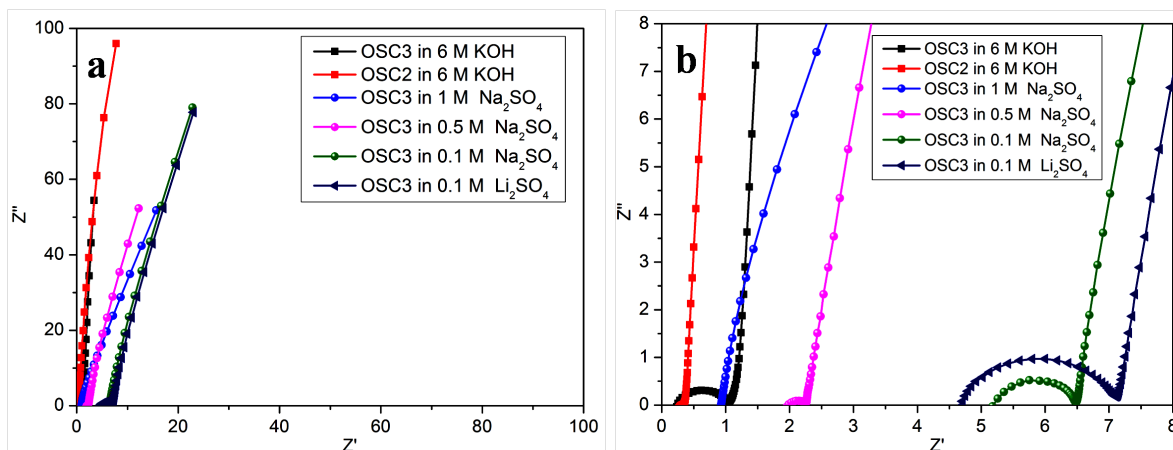


Figure 6.16: Nyquist plots of OSC3 and OSC2 based film electrodes in basic and neutral aqueous electrolytes in the frequency range of 10 kHz to 0.01 Hz after 10 cycles.

6.3.4.4 Cycling behaviour

The electrochemical cycling stability of OSC3 and OSC2 based electrodes in a two-electrode cell was evaluated in 6 M KOH (working voltage 0.9 V) and 1 M Na_2SO_4 (working voltage 1.6 V) for 5,000 cycles at a 1.3 A/g constant current density, as shown in Figure 6.17. In 6 M KOH, the OSC3 electrode maintained a stable capacitance up to 5,000 cycles, confirming that KOH was a good aqueous electrolyte for these carbon black based supercapacitors. The OSC3 electrode also showed a stable capacitance in 1 M Na_2SO_4 over 5,000 cycles, without any additional pseudo-faradic capacitance, because the discharge curve remained linear after 5,000 cycles, as shown in Figure 6.18. Consequently, considering the higher energy density and power density achieved in the large 1.6 V working voltage, and less corrosive environment compared with KOH and H_2SO_4 , Na_2SO_4 neutral aqueous electrolyte is suggested as a potentially competitive electrolyte for carbon black based supercapacitors.

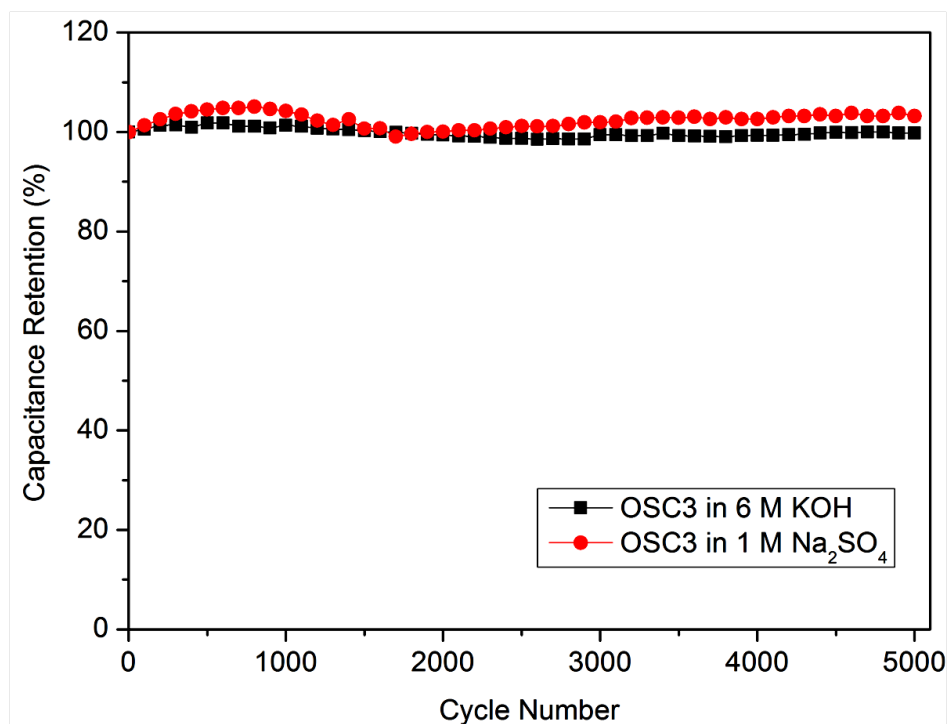


Figure 6.17: Long term charge/discharge cycling performance of OSC3 based thin film electrodes in two-electrode cell using 6 M KOH and 1 M Na₂SO₄ at 1.3 A/g current density.

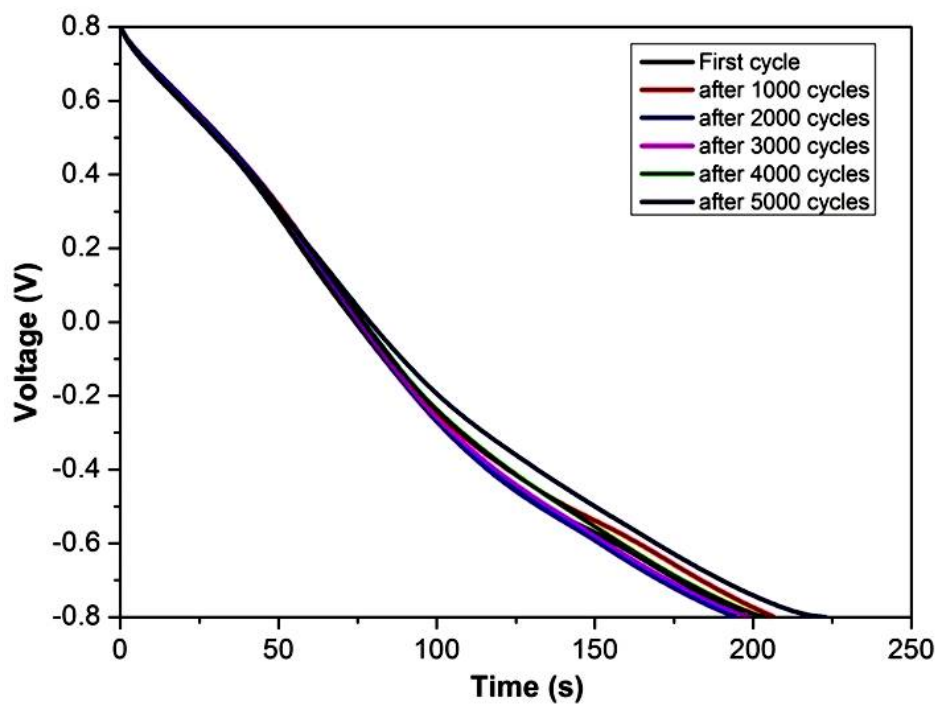


Figure 6.18: Discharge behaviour of OSC3 in 1 M Na₂SO₄ at 1.3 A/g current density during the 5000 long cycles.

6.4 Conclusions

In this chapter, carbon black based 4 - 10 μm thick electrodes with a relatively flat, homogeneous surface and 3D hierarchical porous structures were fabricated using spray deposition. A high electrochemical performance in a half cell configuration was achieved (260 F/g specific capacitance at 1 A/g, excellent high-rate performance with ideal rectangular CV behaviour at 600 mV/s high scan rate, 0.2 Ω ESR and less than 7% capacitance variation during 5000 long charge/discharge cycles), attributed to their high mesopore volume (reducing the ion transport resistance and increasing the surface area utilization), high macropore volume (reducing the ion diffusion pathways), good wettability, and high graphitic degree (improving electron conductivity).

Carbon black based thin film electrodes were also characterized electrochemically in two-electrodes cells (a symmetric carbon black/carbon black cell) using alkaline and neutral electrolytes. Although the highest specific capacitance (375 F/g) and lowest ESR (0.1 Ω) were obtained in 6 M KOH, the highest energy and power densities (18 Wh/kg) were achieved in 1 M Na_2SO_4 electrolyte, which was attributed to the higher 1.6 V cell operating voltage. The ability to operate reversibility over this comparatively wide voltage window was due to a high oxygen content on the carbon electrode surface, which facilitated a higher overpotential for dihydrogen evolution and carbon oxidation, protecting the electrode from uncontrollable reduction/oxidation. Therefore, besides the standard KOH and H_2SO_4 studied previously, the neutral Na_2SO_4 is also an attractive aqueous electrolyte for high-rate performance and environmentally friendly supercapacitor system.

The carbon black based thin film electrodes had comparable or even better electrochemical properties than those reported for graphene, CNTs and 3D HPGC based electrodes, and are much cheaper and easier to produce. By adopting a spray deposition technique, ideally suited to processing the smaller carbon black particles, large-scale flexible and thin film electrodes for commercial high performance supercapacitors

can be conceived.

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Chapter 7

Thin Film Lithium-ion Battery Electrodes and their Electrochemical Performance

7.1 Introduction

Rechargeable lithium-ion batteries (LIBs) are used to power many portable electronic devices on account of their excellent energy to weight ratio, which is typically 160 Wh/kg^[1], reasonable power density (300 - 1500 W/kg)^[2] and absence of ‘memory effect’ (an effect observed in nickel cadmium rechargeable batteries that causes them to hold progressively less charge)^[3]. Similarly to supercapacitors, the LIB has a three layer structure: a positive electrode (also called the cathode, e.g. lithium cobalt oxide LiCoO_2), a negative electrode (also called the anode, e.g. graphite) and a porous separator layer, all of which are then immersed in a Li^+ containing electrolyte (e.g. 1 M LiPF_6 in ethylene carbonate: dimethyl carbonate 1:1). The working principle of a LIB is presented in Figure 7.1.

During charging, lithium ions are extracted from the layered intercalation host (the

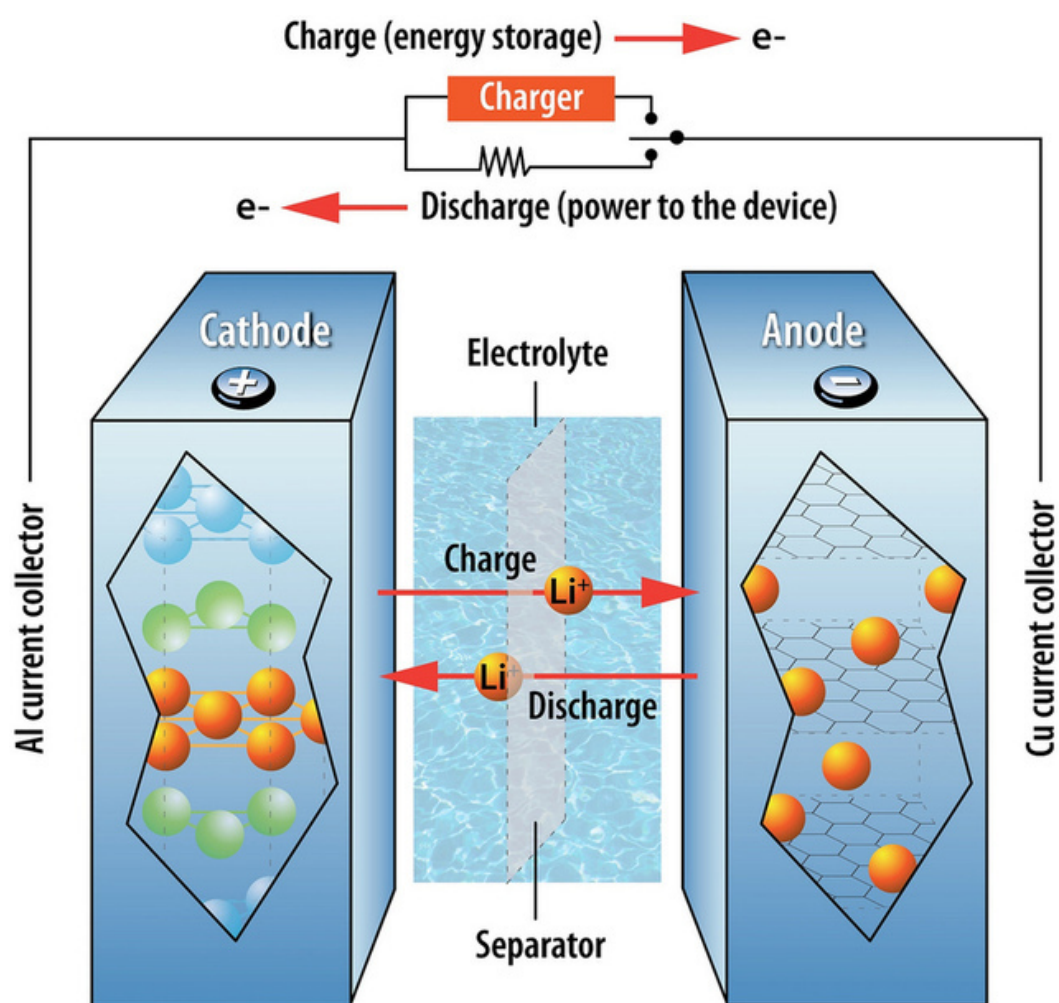
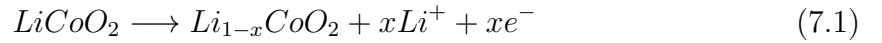


Figure 7.1: Schematic illustration of rechargeable LIBs with a graphite anode and $LiCoO_2$ cathode in $LiPF_6$ ethylene carbonate/dimethyl carbonate electrolyte^[4].

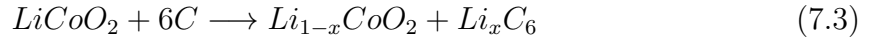
cathode), diffuse through the electrolyte and are then inserted in between the graphitic layers in the graphite (the anode) by a process known as intercalation. The electrons migrate to the anode during the charging process. On discharge, the reverse processes occurs, with the flow of electrons around the external surface providing the electric current. The overall reaction that takes place in a LIB during charging is as follow: The positive electrode half-reaction:



The negative electrode half-reaction:



The overall reaction:



Although many carbonaceous materials have been investigated as the anode materials for LIBs^[5--8], graphite is still the most commonly used choice, attributed to its high theoretical capacity (372 mAh/g for LiC_6)^[9--11], low potential (~ 0.1 V vs. Li/Li^+ , allowing larger E_{cell} , as $E_{cell} = E_{cathod} - E_{anode}$)^[12], flat negative potential (allowing the device to provide stable power for extended periods^[1]), relatively low cost and natural abundance^[11]. However in terms of rate capability, graphite is less powerful than other carbonaceous materials due to the relatively slow, diffusion controlled intercalation of Li^+ ion process^[13, 14]. The intercalation/de-intercalation process leads to very high strains in anode and cathode, which ‘pulverises’ the electrodes and leads to battery ‘fading’.

Commercial LIBs are tightly rolled cylindrical or planar multilayer devices with posi-

tive and negative electrode materials tape cast onto Al and Cu foils respectively^[15, 16]. The thickness of the coated film electrode is normally more than 100 μm , which is a convenient thickness to cast at high throughput, although not all of the resulting structure is necessarily utilised efficiently, especially when short charge/discharge times are required. Furthermore, to satisfy the market demands of next-generation electronic systems (bendable, ultrathin, implantable, etc.) the fabrication of thin, flexible LIBs in large-scale is required^[17]. Although many thin film battery electrodes have been reported, their manufacturing techniques are either complicated (e.g. deposition by evaporation under vacuum)^[18], suitable for small area production only (vertically aligned Au nanorods grown in a template on a current collector)^[17, 19], or have difficulty in film thickness and microstructure control when thinner ($< 50 \mu\text{m}$) electrodes are required (blade coating)^[20, 21], which has limited their industrial application.

Recently, a sprayed or ‘painted’ battery has successfully sequentially deposited anodes, separator and cathode to give a integrated design although the thickness was in the conventional range (more than 150 μm), the electrode microstructure was inhomogeneous, and the resulting to limited discharge capacity was restricted to only 120 mAh/g^[22]. Nonetheless, this work points the way to a method and potential benefits for a thin film battery electrode with accurate controlled film thickness, homogeneous thickness and structure, and fast fabrication at large scale.

In this chapter, the fabrication of flexible thin film graphite electrodes for LIB anodes using spray deposition with potential for both fast speed and large scale production is described. The effect of particle size on processability, microstructure and final performance is described. The spray process is shown to be an excellent route for the manufacture of electrodes of differing thickness that offer equivalent or superior performance to their industrially supplied, slurry cast equivalent using exactly the same materials. The advantages and disadvantages of using finer graphite particle sizes was also revealed. This work represents a relatively short feasibility study conducted at the end of the period of study, intended to ascertain if there is any promise for the spray deposition route for LIB anodes, and what might be the critical areas requiring

further study.

7.2 Materials and methods

7.2.1 Materials

Natural graphite particles were obtained from Pleiades Battery Manufacturing Co., Ltd, China, with a mean particle size of 10 μm . This material is used in production by various LIB mass producers for the automotive market. In order to disperse these commercial powders, CMC dispersant was again required (see earlier chapters), and in accordance with commercial practice, PTFE binder was again employed.

7.2.2 Preparation of graphite particles

The graphite particles were relatively large and there was concern regarding the ability to contrive stable suspensions. Therefore, graphite particles were also ball milled to aid their suspension. The ball milling conditions were 1/15 weight-to-ball ratio, 400 rpm rotation speed, for either 30 min or 2 hours milling time.

7.2.3 Preparation of thin film graphite electrodes

To prepare the thin film anodes, the graphite particles (as-supplied or ball milled) were first dispersed in an aqueous mixture (90% deionised water + 10% ethanol) with ultrasonication for 10 min to form a suspension of relatively high concentration of 40 mg/ml. High concentrations were sought in order to accelerate deposition times, and to understand if the spray route offered potential for competitive production rates. To improve the electrode robustness and coherence, and suspension stability, 10 wt.% PTFE and 5 wt.% CMC (with respect to graphite weight) were again used in all

cases^[23].

The well-mixed suspensions (graphite with PTFE and CMC) were then spray deposited onto heated Cu foil ($\sim 15\ \mu\text{m}$) using 400 kPa compressed air, with a suspension flow rate of 10 ml/min (0.4 g/min). A schematic illustration of the spray deposition apparatus has been given in Figure 3.4(a) in Chapter 3. Due to the relatively high graphite concentration, the feedstock suspension was constantly ultrasonicated (600 W, 20 kHz in an ice bath) during the spray process. Rather than a syringe pump, a peristaltic pump was used to provide the higher flow rate and an uninterrupted suspension supply. Because the Cu foil was very thin and soft, a vacuum chuck combined with a heating plate were used to ensure good and reproducible contact of the Cu foil to the heating plate. The temperature of the heating plate was maintained at 110 °C during the spray deposition process. The resulting electrodes could be used as one layer of a the compact commercial LIB device (as shown in Figure 7.2). Because of the ability to produce dramatically reduced electrode thicknesses (down to only a few micrometers, as will be explained later), the total thickness of a compact commercial LIB devices might be significantly reduced, or provide much faster changing times (higher power) and more homogeneous state of charge (and therefore homogeneity of electrode swelling) to extend battery life.

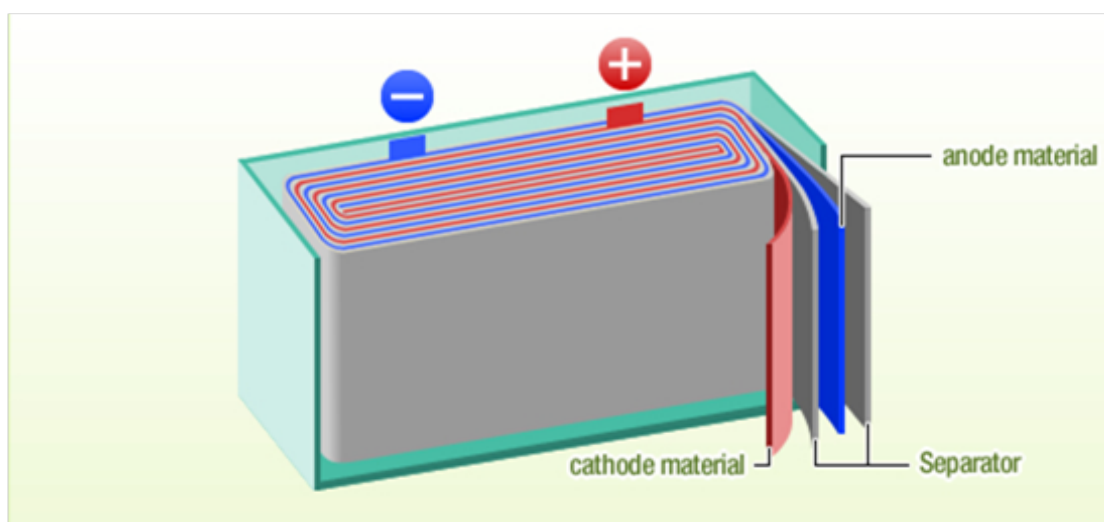


Figure 7.2: Schematic illustration of the structure of a typical rechargeable LIBs^[24].

The spray deposited anodes were then rolled gently by hand using a polished Al cylinder

to increase density. As-sprayed thicknesses were typically 1 - 45 μm (depending on the spray time), and rolling reduced thickness by typically 20%. As a comparison, electrodes fabricated by Pleiades, China using slurry casting and calendering of as-supplied graphite particles on Cu foil were also studied. In this case, the electrode thickness was in the standard industrial range of 70 - 80 μm .

7.2.4 Characterization

The surface morphology and cross-sectioned microstructure of the sprayed and cast graphite anodes were studied in a JEOL FESEM 840F under different magnifications, and the as-supplied and ball milled graphite particle sizes were measured in a Mastersizer 2000 Analyser (details given in Chapter 3).

The charge/discharge performance of the spray deposited thin film graphite electrodes were evaluated in coin cells. Lithium metal foil was used as counter electrode, the spray deposited graphite thin film was used as working electrode, and a layer of glass microfiber membrane (Whatman, 0.3 mm thickness) was used as the separator. LP30 (1 M LiPF_6 in ethylene carbonate: dimethyl carbonate 1:1) was used as the electrolyte. The details of the coin cell assembly procedure have been described in Chapter 3. The cells were cycled galvanostatically at 20 mA/g current density (*ca.* 0.05 C), as in the published protocol by Flandrois *et al*^[25], between 0.01 - 2 V for 20 cycles.

7.3 Results and discussion

7.3.1 Morphology and structure

The morphology and structure of the spray deposited thin film graphite electrodes prior to encapsulation and cell testing are presented in Figure 7.3. The 15 cm $\times$ 15 cm sprayed electrodes were flexible and could be bent by hand into any angle without

cracking.

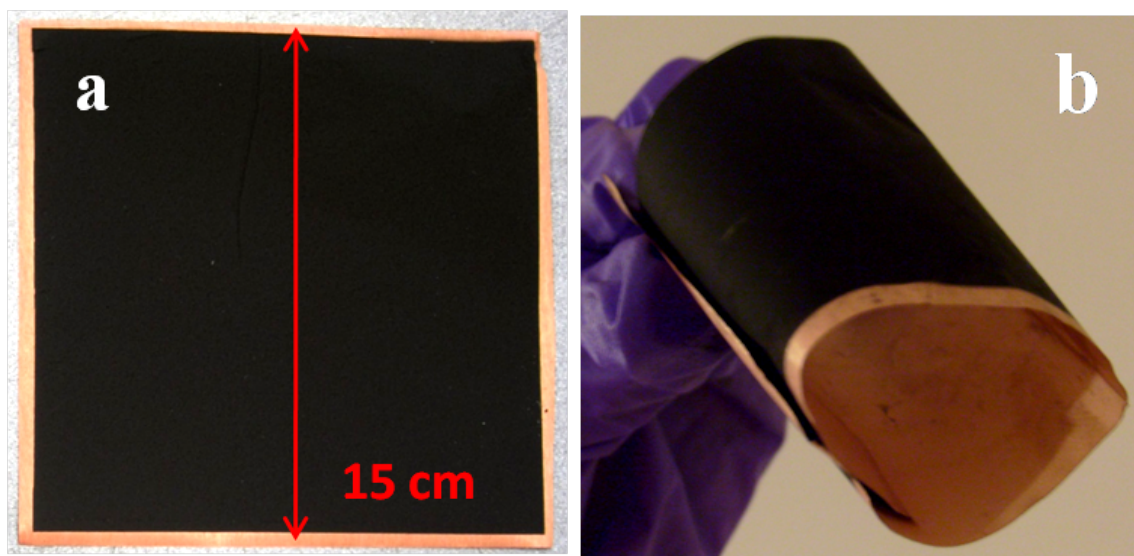


Figure 7.3: Images of sprayed graphite electrodes before cutting into round discs and encapsulation for measurement: (a) in the size of 15 cm $\times$ 15 cm, and (b) could be bent by hand into any angle without cracking.

The surface morphology of both as-supplied slurry cast electrodes and spray deposited thin film graphite electrodes (after rolling) are presented in Figure 7.4. As shown in Figures 7.4(a) and (b), the cast electrodes had a comparatively smooth surface with a mean particle size of 10 μm and void spaces between the graphite particles. In Figures 7.4(c) and (d), the spray deposited electrodes with as-supplied graphite particles appeared to have a more dense surface arrangement. The electrode densities were estimated at 0.32 g/cm³ and 0.36 g/cm³ for cast and sprayed respectively (by knowing the area, thickness and deposited mass). As shown in Figures 7.4(e) to (h), when the ball milling time was increased progressively from 0 to 2 h, the surface morphology of spray deposited film electrodes became progressively more dense and progressively smoother in appearance after rolling, attributed to the reduced graphite particle size from 10 μm (as-supplied) to $\sim$ 3 μm (after 30 min ball milling) and to $\sim$ 500 nm (after 2 h ball milling) respectively. An overly dense electrode structure will inhibit ion mobility and limit the tolerance to volume changes during the charge/discharge cycling, due to insufficient free space between graphite particles^[21, 26, 27].

Cross-section SEM images of the electrodes are presented in Figure 7.5. All the elec-

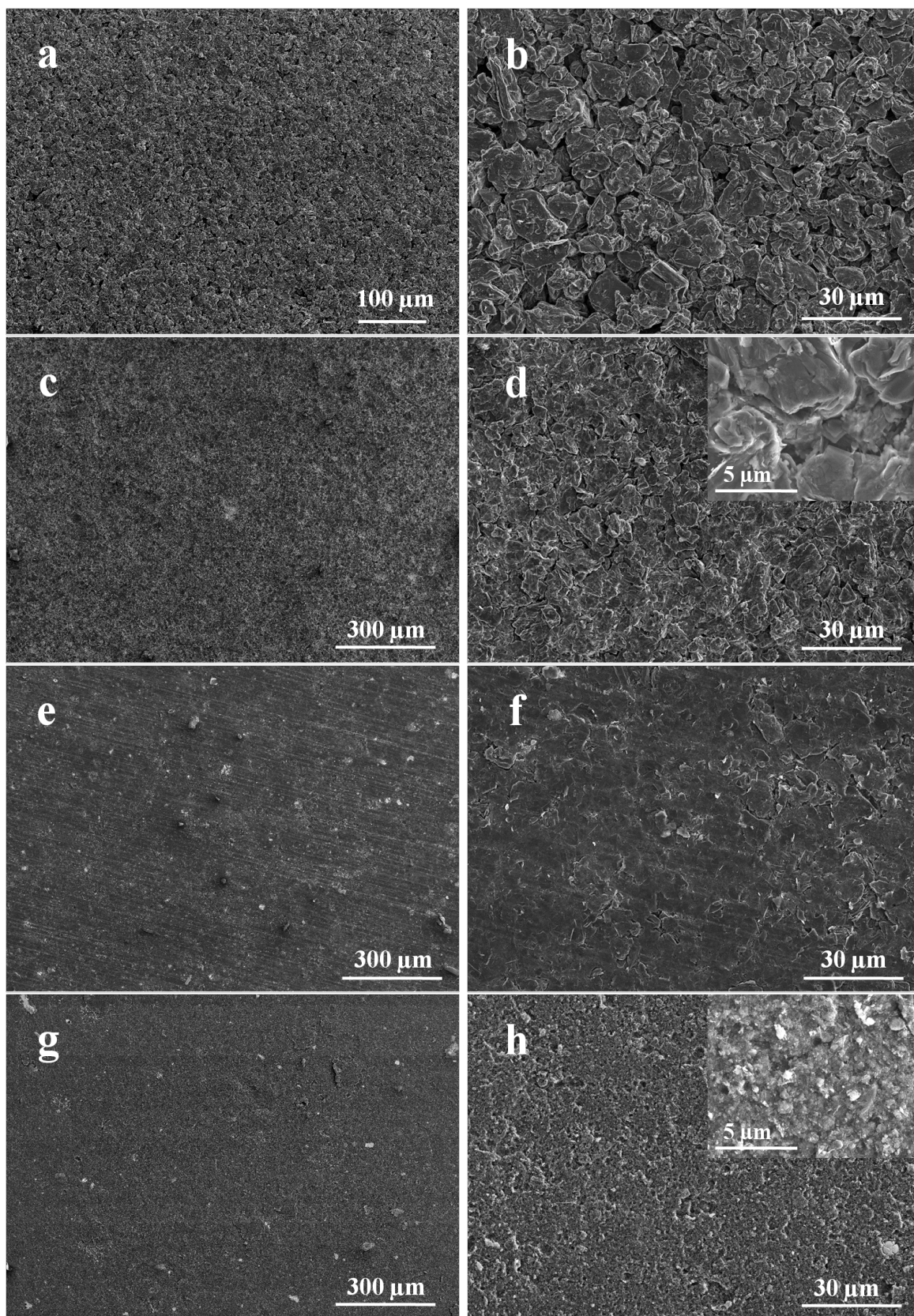


Figure 7.4: SEM images of electrode surface morphology at different magnifications: (a) and (b) as-supplied slurry cast electrode, (c) and (d) sprayed electrodes with as-supplied graphite particles after rolling, (e) and (f) sprayed electrodes with ball milled graphite particles (1/15 weight-to-ball ratio, 400 rpm for 30 min) after rolling, (g) and (h) sprayed electrodes with ball milled graphite particles (1/15 weight-to-ball ratio, 400 rpm for 2 h) after rolling.

trodes comprised a packed coating of generally uniform thickness. As shown in Figure 7.5(a), the cast electrodes had a graphite particle coating on both sides of the Cu foil, with film thickness of *ca.* 70 μm on each side. By contrast, as shown in Figures 7.5(b) to (d), the spray deposited electrodes were fabricated with a range of thicknesses: from hundreds of nanometers to a few micrometers. All the sprayed electrodes suggested good physical contact with the Cu foil after rolling, and as for the slurry cast electrode, with the graphite particles embedding into the soft Cu.

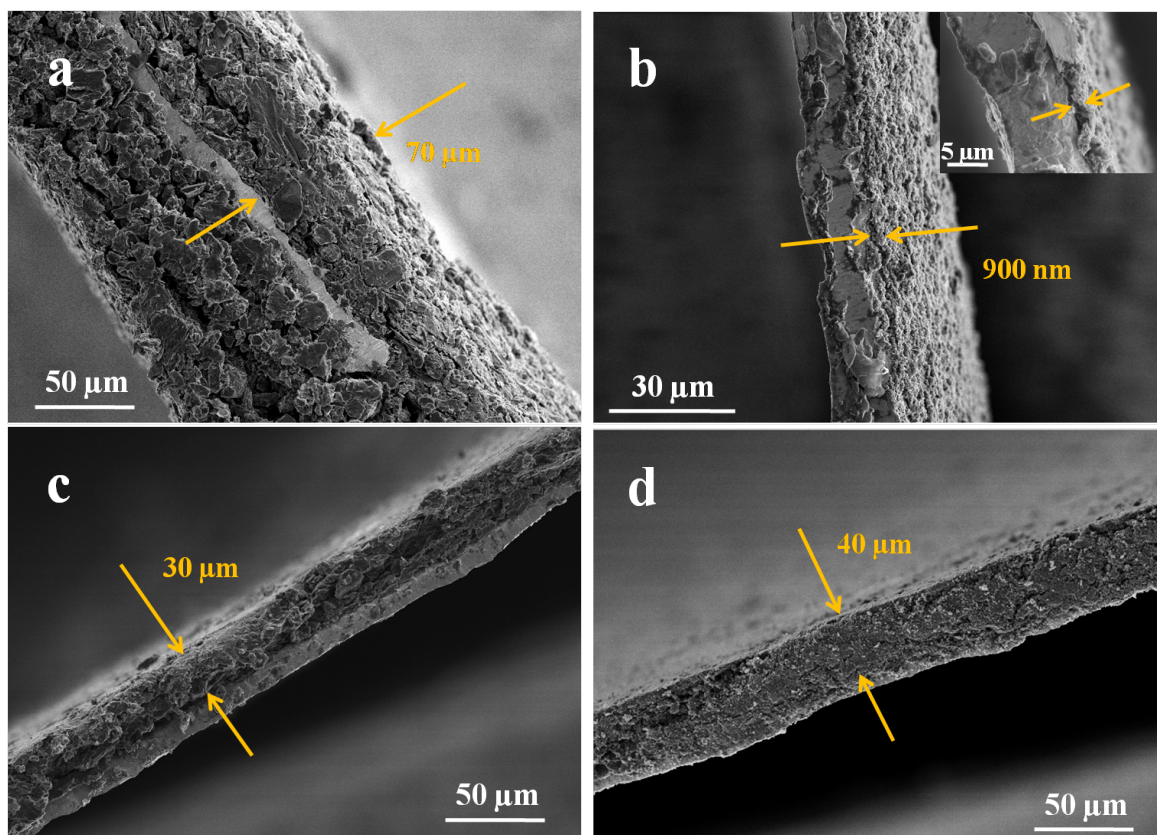


Figure 7.5: SEM images of the cross-section of (a) the as-supplied slurry cast electrode, (b) sprayed thin film graphite electrode of ~ 900 nm thickness, (c) sprayed graphite electrode of ~ 30 μm thickness, and (d) sprayed graphite electrode ~ 40 μm thickness.

7.3.2 Electrochemical performance

To investigate the electrochemical performance of various electrodes, galvanostatic charge/discharge behaviour at a current density of 20 mA/g was used, and the resulting voltage versus capacity curves are presented in Figure 7.6. In this case, all the

spray deposited electrodes had a thickness of $30\ \mu\text{m} \pm 5\ \mu\text{m}$, and only a single side of cast electrodes were used, with a thickness of $\sim 70\ \mu\text{m}$. The lithium reversible intercalation into the graphite layers, the faradaic losses during the first charge/discharge cycle and the overall voltage profile were shown to all depend on the electrode structure.

As shown in Figure 7.6(a), the cast electrodes showed a plateau of potential between 0.8 - 0.9 V versus Li/Li⁺ in the first discharge step, which corresponded to the well-known formation of a solid electrolyte interface (SEI) layer on the surface of graphite particles. The SEI formation was related to the decomposition of the electrolyte^[28--30]. This irreversible reaction consumes available graphite and ions in batteries, and although unavoidable in electrolytes of practical use, it should always be minimized^[25]. The SEI layer is mainly composed of lithium carbonate and is electronically insulating, and only permeable to Li⁺ ions^[29, 31--33]. The irreversible capacity of the slurry cast electrode was 7 mAh/g.

The irreversible capacity due to the SEI was strongly dependent on the electrode available area: a larger exchange surface area would be expected to result in a higher irreversible capacity. The relation between this faradic loss and exchange surface area has been carefully investigated^[28], and explains that, as shown in Figures 7.6(c) and (d), how the increased surface area of graphite particles after ball milling treatment, leads to the much more obvious irreversible capacity loss on the first cycle. The irreversible capacities for sprayed electrodes with 30 min ball milled particles and 2 h ball milled particles was approximately 281 and 1119 mAh/g, respectively.

As shown in Figure 7.6(b), even when the particle size was unchanged, the sprayed electrode with as-supplied graphite particles had a higher irreversible capacity of 77 mAh/g than the cast electrode. The higher irreversible capacity of sprayed pristine graphite film is tentatively ascribed to exfoliation of the graphite due to a process known as cointercalated solvent reduction^[25], which is evidenced by a second weak plateau at 0.5 V versus Li/Li⁺ in the first discharge step. This exfoliation of the graphite was caused by the constantly high power ultrasonication (600 W, 20 kHz) during the spray

process. During the ultrasonication, some of the hexagonal Bernal structure (with carbon layers arranged in ...ABABAB...) was changed into rhombohedral structure, which had stacking sequence of ...ABCABC... (C layers are shifted with respect to the B layer)^[25]. This exfoliation of the graphite particles led to an increase in effective surface area of the electrode and a loss of electrical integrity, both of which contributed to the increased irreversible capacity^[25]. The fraction of rhombohedral structure will increase with increasing ultrasonication time or mechanical grinding time. When the content of the rhombohedral structure is higher than 40%, the solvent reduction process can be restrained^[25]. Therefore, as shown in Figures 7.6(c) and (d), the second weak plateaux at 0.5 V versus Li/Li⁺ in the first discharge step did not occur for the two spray deposited film electrodes with ball milled graphite particles. More details of the ball milling effect will be discussed later, in Figures 7.7 and 7.8.

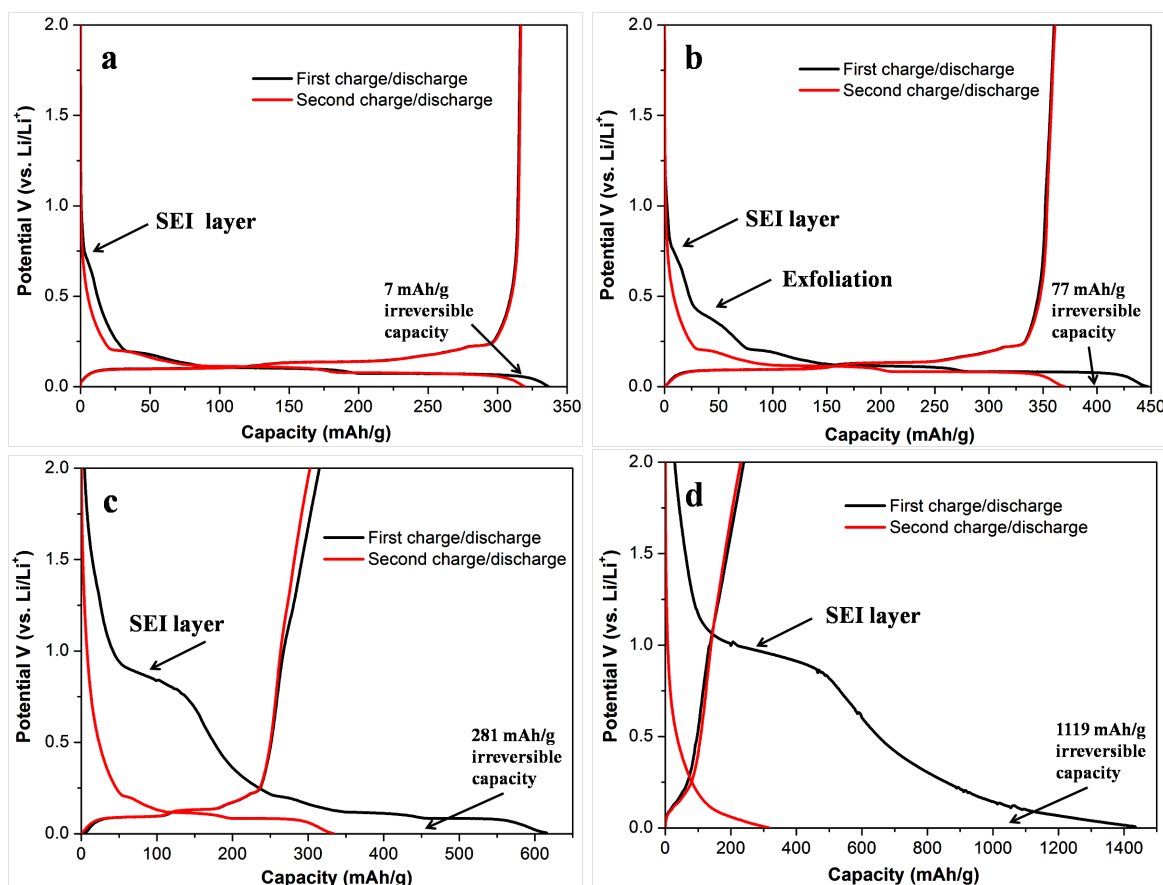


Figure 7.6: First and second charge/discharge behaviour of (a) slurry cast electrode, (b) sprayed electrode with as-supplied graphite particles, (c) sprayed electrode with 30 min ball milled graphite particles, and (d) sprayed electrode with 2 h ball milled graphite particles.

The second galvanostatic discharge curves are shown together in Figure 7.7. The cast

electrode and the sprayed electrode with the same graphite particles had a typical long flat voltage plateaux at 0.1 - 0.2 V, corresponding to the intercalation/de-intercalation of Li ions into the graphite particles. By contrast, the spray deposited electrodes with 30 min and 2 h ball milled graphite particles displayed a slanted voltage profile, which is generally quite typical of high surface carbon materials (e.g. activated carbons), due to combined adsorption/de-sorption and intercalation/de-intercalation of Li ions processes^[12]. The negative gradient of the voltage profile was decreased with increased milling time, presumably due to the more disordered structure of the milled materials, as previously discussed in Chapter 4.

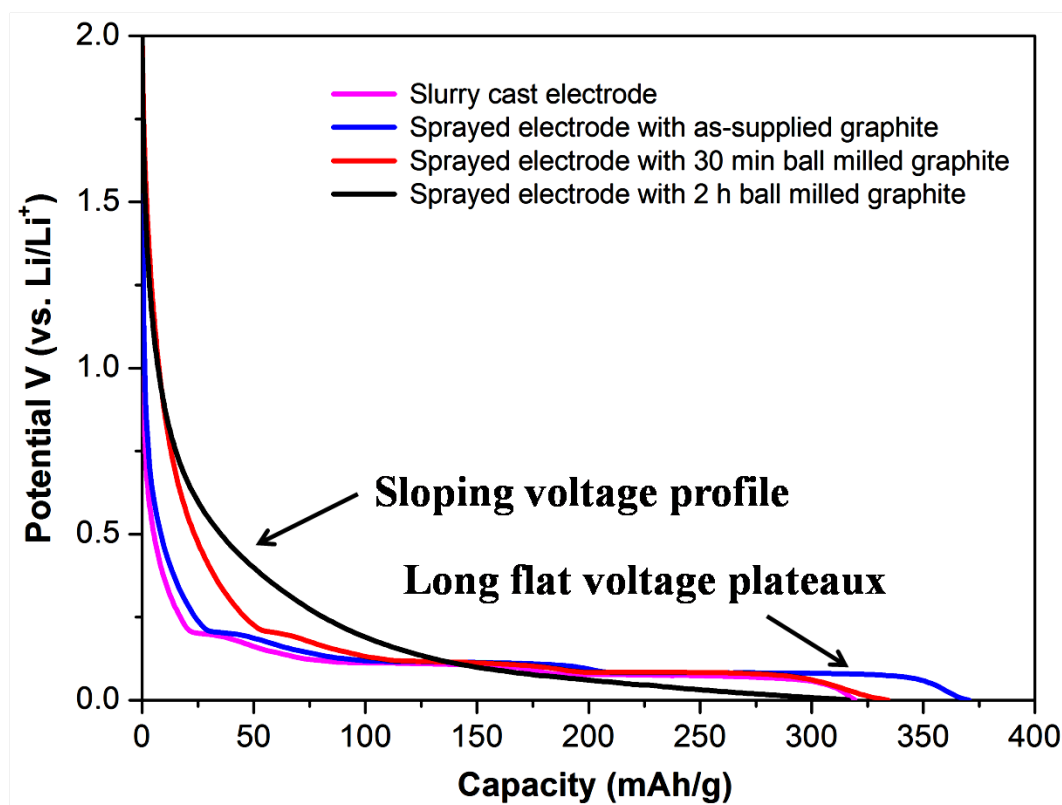


Figure 7.7: Second discharge behaviour of slurry cast electrode and other sprayed graphite electrodes.

Moreover, as shown in Figure 7.8, the potential hysteresis was more obvious for the electrodes with ball milled graphite particles than that with as-supplied graphite particles. The potential hysteresis was likely caused by Li ion insertion that induced bonding changes between the interstitial carbon or the carbon in the aromatic plane^[34]. Ball milling can introduce metastable carbon phases, therefore, the longer milling time led to more obvious hysteresis. The potential hysteresis might also be caused by the

formation of SEI, which consumed Li^+ ions, and therefore reduced the discharge efficiency. The large hysteresis is one of the main features of high surface area carbon materials^[30, 35].

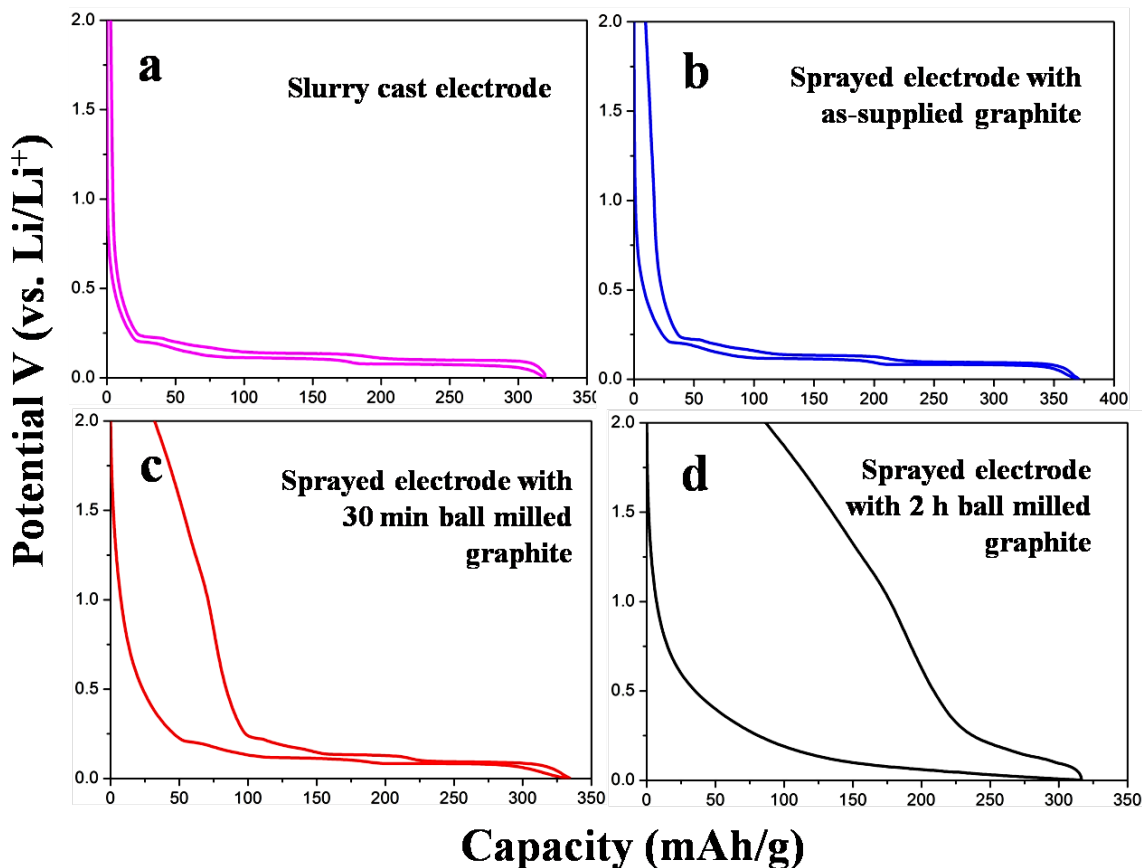


Figure 7.8: Potential profiles of (a) slurry cast electrode, (b) sprayed electrode with as-supplied graphite particles, (c) sprayed electrode with 30 min ball milled graphite particles, and (d) sprayed electrode with 2 h ball milled graphite particles.

The cycling performance of the graphite electrodes at 20 mA/g current density between 0.01 - 2 V (vs. Li/Li^+) are shown in Figure 7.9. Opposite to the increasing of irreversible capacity after ball milling treatment, the reversible capacity decreased from 371 mAh/g for the sprayed electrode with as-supplied graphite to 334 and 317 mAh/g for electrodes with 30 min and 2 h ball milled graphite respectively. One reason for the slight reduction of the reversible capacity of electrodes with ball milled graphite was probably due to their excessive SEI formation and more densely packed microstructure (as shown in Figure 7.5(d)), which resulted in a lower material utilization. Another reason for the reduction in reversible capacity was their combined charge storage mechanisms which had both Li ion intercalation and Li ion adsorption processes^[12] at high

graphite surface area, as opposed to the largely intercalation only process generally required for batteries (as opposed to supercapacitors)^[30].

Therefore, although the surface area of graphite particles increased after ball milling treatment, the correspondingly increased surface adsorption capacity was unable to compensate for the reduced intercalation capacity, leading to an overall decrease in total capacity with increasing the ball milling time^[12]. A more common conclusion in the literature^[12, 34] is that ball milling can increase the reversible capacity, but is normally concluded under a comparatively high charge rate where the intercalation capacity is much more constrained by ion mobility but the adsorption capacity is not so strongly influenced by the high charge rate^[30, 36--38].

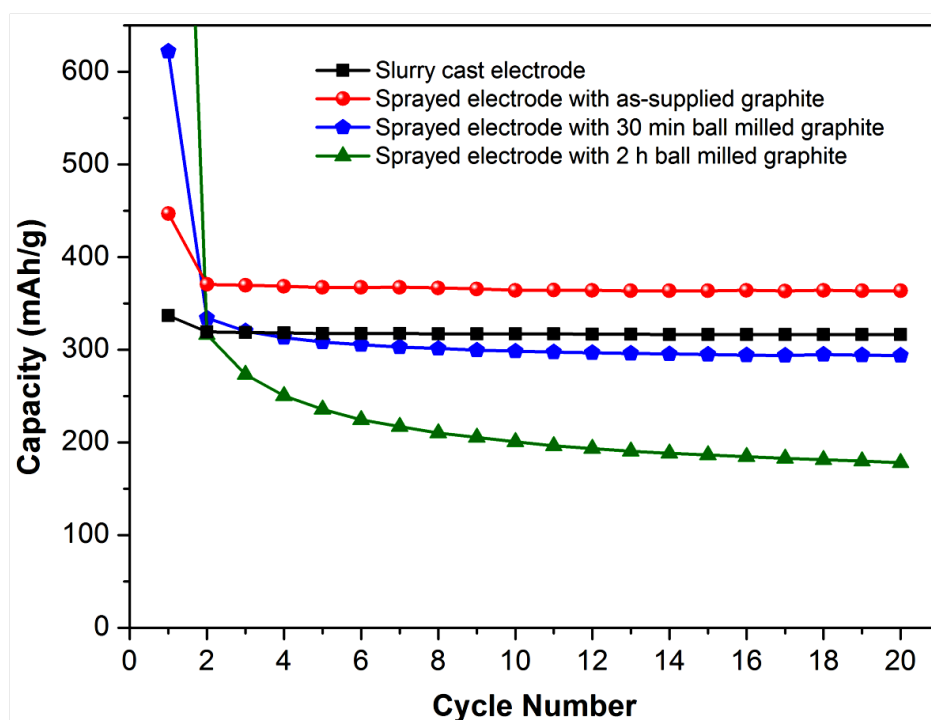


Figure 7.9: The charge/discharge cycling performance of as-supplied slurry cast electrodes and similar sprayed graphite electrodes.

As shown in Figure 7.9, all the spray deposited electrodes achieved good initial reversible discharge capacities (all above 300 mAh/g). The spray deposited electrode with as-supplied graphite had a capacity of 371 mAh/g and was effectively the theoretical capacity (372 mAh/g for LiC_6 stoichiometry)^[12], and retained 98% capacity after 20 cycles at 20 mA/g current density, suggesting that the graphite particles were working efficiently in the thin film format, without degradation or delamination. How-

ever, the capacities of spray deposited electrodes with ball milled graphite reduced to 294 mAh/g (after 30 min ball milling) and 178 mAh/g (after 2 h ball milling) respectively after 20 cycles, which corresponded to only 88% and 56% of their initial reversible discharge capacities. However, it should be noted that the rates used here were relatively slow, and allowed the thinner, spray deposited electrodes to be - on the basis of theoretical capacity - to be fully intercalated (allowing for an error of typically 10% in capacity assessment).

7.4 Conclusions

Spray deposited thin film graphite electrodes were fabricated for rechargeable lithium-ion batteries with thicknesses unachievable in commercial slurry cast electrodes. Electrode thickness could be accurately controlled from hundreds nanometer to a few micrometers, providing a large design space for different electronic device applications. Attributed to the dramatically reduced film thickness, the materials utilization of spray deposited graphite electrode was much increased, leading to a higher capacity (371 mAh/g) than slurry cast electrodes. Furthermore, the spray deposited thin film electrode with as-supplied graphite particles exhibited a outstanding cycle stability: more than 98% capacity retention after 20 charge/discharge cycles, attributed to its the uniform structure produced by spray deposition and associated homogeneity of electrode swelling likely provided in the thin film format, especially under low rate charge/discharge conditions. The better performance (both capacity and cycle stability) provided by the sprayed electrode with as-supplied graphite rather than ball milled graphite was attributed to an excessively high surface area of ball milled graphite that led to excessive SEI formation and a greater fraction of surface adsorption rather than intercalation behaviour. The spray deposition manufacturing route was comparatively flexible, and when combined with a peristaltic pump and ultrasonication, showed much faster fabrication times than previous sprayed supercapacitor electrode studies. However considerable further optimisation is required to build on this feasibility study,

including how to minimise ultrasonication damage, how might as sprayed porosity be better controlled, and choosing the optimum particle sizes as a function of electrode thickness and required charge/discharge rates.

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Chapter 8

Conclusions and Future Work

8.1 Conclusions

This thesis has focused on developing a new process route for the manufacturing of nanostructured thin film energy storage devices. A scalable spray deposition technique has been used to fabricate various carbon-based electrodes, with emphasis on low cost and comparatively thin electrodes. Three types of commercially available carbon materials have been investigated: graphite (synthetic/natural), activated carbons (Darco_60, MAST and YP_50), and carbon black. The sprayed carbon-based electrodes had a generally homogeneous film surface morphology, uniform internal structure, large film area (from 1 cm² to 1500 cm²), controlled film thickness (from 900 nm to 40 μ m), and usually high electrochemical performance.

The nano-graphite-based thin film electrodes ($\sim 3 \mu$ m) exhibited a high specific capacitance of 110 F/g at 100 mV/s, low equivalent series resistance ($< 0.5 \Omega$), small charge-transfer resistance ($< 1.8 \Omega$) and only 3% variation of capacitance during long-term cycling, attributed to their comparatively large fraction of lattice defects, high specific surface area, and enhanced ionic/electronic transport after ball milling and CO₂ activation.

The activated carbon-based electrodes ($\sim 2 \mu\text{m}$) maintained high capacitances ($\sim 80, 100$ and 120 F/g for Darco_60, MAST and YP_50 respectively) at a 600 mV/s high scan rate and 20 A/g current density. The high rate performance of these AC-based electrodes was enhanced by reducing the contact resistance at the interface of the electrode and current collector using a pre-coating, building well-interconnected and more homogeneous microstructure using an organic carrier, increasing the specific surface area by ball milling and improving the charge-transfer behaviour by secondary activation.

Carbon black-based electrodes ($\sim 4 \mu\text{m}$) exhibited the highest specific capacitance (260 F/g at 1 A/g), 0.2Ω ESR and less than 7% capacitance variation in the long term charge/discharge cycles in both half and full cells, attributed to their short ion diffusion pathway (high macropore volume), small ion transport resistance (large mesopore volume) and improved electronic conductivity (graphitic texture). Moreover, high energy and power densities ($\sim 21 \text{ kW/kg}$ and 18 Wh/kg) were achieved in $1 \text{ M Na}_2\text{SO}_4$ neutral aqueous electrolyte, attributed to a comparatively wide 1.6 V cell operating voltage.

Graphite-based electrodes for rechargeable lithium-ion batteries were also fabricated by spray deposition. The film thickness of sprayed electrodes ($900 \text{ nm} - 40 \mu\text{m}$) was thinner and more controllable than commercial slurry cast electrodes ($\sim 70 \mu\text{m}$). High capacity (371 mA/g) with outstanding cycle stability (more than 98% capacity retention after 20 cycles) was achieved in a sprayed graphite electrode, attributed to a high materials utilization, and homogeneous state of charge, enabled primarily by the reduced film thickness and low charge rates. The spray deposition manufacturing route may allow different designs of thin film electrodes, and has potential for further investigation and optimisation for thin film battery manufacture.

8.2 Suggestions for future work

Future work in this area may consider the following:

- A more detailed study on how the various spray parameters (such as spray distance, spray air pressure, suspension flow rate, substrate movement under the spray along with the particle size) affect the film surface morphology and film micro-structure. A model should be developed to describe the relationship between the spray parameters and the final film micro-structure. This model could be used to guide experimental process optimisation.
- Compared with graphite, silicon has much higher theoretical capacitance (4200 mAh/g). However, due to the volumetric change problem caused by repeated alloying and dealloying during charge and discharge, pure silicon based electrodes for LIBs always have extremely poor cyclability. Future work could consider building C+Si composite based electrodes for LIBs by incorporating two spray nozzles, each of which supplies a different suspension. As silicon particles will be well dispersed in the carbon fiber matrix (or in the gap between carbon particles), the volume changes problem of Si particles might be managed, therefore leading to higher cyclability; meanwhile, the conductivity of electrode can be improved to a certain extent, attributed to a better carbon particle contact with the Si particles produced by the spray processing method.
- To further extend the limits of aqueous electrolytes for higher energy density, future work should consider asymmetric/ hybrid electrochemical capacitors. Using carbon black as the negative electrode, but transition metal oxides as the positive electrode, will open further the electrochemical stability voltage window for higher energy and power density.
- An integrated design might be achieved if all the components of a supercapacitor or battery (such as current collector, electrodes, separator and solid electrolyte) are applied sequentially by spray deposition. To produce the integrated superca-

pacitor or battery, a large isolated ‘clean cupboard’ needs to be set up to enable safe spraying of some organic solvents or/and electrochemically active LIB cathode materials.

- Considering the demand of the market for lighter, foldable and stretchable electronics, new substrates (current collector) should be considered: such as textiles, highly conductive polymers (plastic) and graphene coated elastomeric substrates.
- To further achieve industry scale thin film energy storage devices manufacturing, the current spray technique should be upgraded to software controlled roll-to-roll spray deposition, along with automatic cutting and encapsulation processes.