

Enhancing Graphene-Based Supercapacitor with Ionic Liquid/Surfactant Electrolyte by Structural Characterization and Modification

Tianyu Liu

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Author's Declaration

The thesis consists of material all of which I authored or co-authored: see Statement of Contributions included in the thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

I understand that my thesis may be made electronically available to the public.

Statement of Contributions

The small angle X-ray and neutron scattering studies presented in this thesis were carried out in collaboration with Dr. Keenan Smith from the University of College London. I helped plan the experiments, prepared all materials, dispersion and composites with Dr. Smith carrying out the measurements at various beamlines. All data analysis was carried out by me with the guidance of Dr. Smith and under the supervision of Prof. Pope.

The heavy ion bombardment experiment was conducted with the assistance of Yossarian Liebsch. The transmission electron microscopy and nuclear magnetic resonance characterizations were performed with the assistance of Bersu Bastug Azer and Dr. Manila Ozhukil Valappil respectively. All other characterizations were carried out by me under the supervision of Prof. Pope.

Abstract

Supercapacitors are advanced energy storage devices designed to deliver frequent, short-duration energy bursts due to their distinct charge storage mechanisms. Significant research efforts have been directed toward enhancing their capacitance and energy density. Preliminary investigations have demonstrated promising outcomes through the incorporation of high-surface-area reduced graphene oxide (rGO) as the active electrode material, combined with ionic liquids (ILs) whose broad electrochemical stability window maximizes the energy density and non-ionic surfactant to bind them together while boosting the double layer capacitance. This mixture of surfactant and IL simultaneously facilitates as the electrolyte and a spacer material, preventing restacking of rGO sheets and maximizing the ion accessible surface area. However, the self-assembling process of this composite is not yet fully studied.

It is challenging to characterize the nano-scale structure of the composite specifically at the double-layer. Common characterization techniques at this resolution range, such as atomic force microscopy (AFM) and scanning electron microscopy (SEM), probe only the surface. Hence, this thesis investigates the self-assembled structures of GO, IL, and surfactant through small angle X-ray and neutron scattering (SAXS, SANS). These techniques provide bulk structural information on structures in the range of 1 – 100 nm, enabling precise determination of size, shape, and internal organization. The dispersion of each component and their mixtures was studied progressively, from simple to more complex systems, to understand their individual and collective behavior. The surfactant was found to form stable spherical micelles with a

radius of 5.9 nm when the concentration reaches 20 mg/mL. The addition of IL to the surfactant allows the formation of an amphipathic micelle by attaching to the hydrophilic tails of the surfactant while also lowering the minimum micelle formation concentration to 0.8 mg/mL due to the strong ion-dipole interaction. However, at higher concentrations, large aggregates were found in the dispersion. This is not favorable for the self-assembly of proposed lamellar structure with rGO in the composite electrode, as it would result in inhomogeneous distribution of electrolyte. The surfactant flattens GO sheets by attaching its hydrophobic segment, promoting the formation of ordered layered structures. A new model of the complete self-assembled structure is proposed based on contrast-varied SANS profiles. The GO is sandwiched by the hydrophobic layer, then the hydrophilic layer decorated by spherical IL droplets. When compressed to dense solid electrodes, these droplets spread and fill up the rGO interlayer spaces. If the electrolyte is insufficient, voids may form, reducing the ion-accessible surface area and leading to poor performance or long work-in cycles observed in previous studies.

In addition to the structural characterization, vertical ion bombardment to suppress the work-in cycles and improve rate performance was found to be selectively damaging the electrolyte rather than perforating rGO, resulting in deteriorating capacitance. However, the performance was able to partially recover from cycling. Since long-term electrochemical performance of the electrolyte along was found to negatively impacts its capacitive behavior, this recovery suggests the replenishing of fresh IL, added while assembling the device, driven by scanning potential.

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Table of Contents

Author's Declaration.....	ii
Statement of Contributions	iii
Abstract	iv
Acknowledgements.....	vi
List of Figures	ix
List of Tables	xiii
Chapter 1 Introduction	1
Chapter 2 Background	5
2.1 Supercapacitors	5
2.1.1 Electric Double Layer Capacitor	5
2.1.2 Pseudocapacitor	8
2.2 Performance Evaluation of EDLC	9
2.3 Electrolyte	10
2.3.1 Ionic Liquids.....	11
2.3.2 Ionic Liquid Double Layer	12
2.4 Electrode Material	14
2.4.1 Activated Carbon	14
2.4.2 Graphene and Graphene-Based Materials	15
2.4.3 Review of Graphene Based Electrode	17
2.4.4 Self-assembly among EMImTFSI/Pluronic P123/Graphene	21
2.5 Motivation and Thesis Objectives.....	22
2.6 Thesis Layout	24
Chapter 3 Evaluating Graphene-Based Supercapacitor Composite Electrode Fabrication Using Ionic liquid/Non-ionic Surfactant Electrolyte as Spacer Material .	26
3.1 Introduction	26
3.2 Materials and Method.....	26
3.3 Results and Discussion.....	29
Chapter 4 Small Angle X-ray and Neutron Scattering Study in Aqueous Assemblies of Graphene Oxide with Pluronic Surfactant and Hydrophobic Ionic Liquid	32

4.1 Introduction	32
4.2 Materials and Method.....	33
4.3 Results and Discussion.....	36
4.4 Conclusion.....	64
Chapter 5 Long Term Electrochemical Performance of Ionic Liquid/Non-Ionic Surfactant Electrolyte and Ion Bombarded Graphene-Based Electrode.....	66
5.1 Introduction	66
5.2 Materials and Methods	67
5.3 Results and Discussion.....	69
5.4 Conclusion and Future Work	75
Chapter 6 Conclusions and Future Works	77
Letter(s) of Copyright Permission	79
References.....	85

List of Figures

Figure 1-1. Ragone plot showing the power vs. energy density of energy storage devices. Reproduced with permission from [3]	2
Figure 2-1. Schematic of a supercapacitor. Reproduced with permission from [7]	6
Figure 2-2. Graphical representation of the double layer model by Helmholtz(left), Gouy and Chapman (middle), and Stern (right). Reproduced with permission from [9]	8
Figure 2-3. Three common types of pseudo-capacitive electrode. Reproduced with permission from [10].....	9
Figure 2-4. Common cations (top) and anions (bottom) in ILs and their ionic sizes. Reproduced with permission from [13]	11
Figure 2-5. Schematic of IL at polarized electrode surface. Reproduced with permission from [15].....	13
Figure 2-6. Differential capacitance of alkylimidazolium bis(trifluoromethanesulfonyl)imide at graphite surface as a function of electrode potential. Reproduced with permission from [16]	13
Figure 2-7. Schematic of the fabrication process for IL-mediated rGO electrode used by She et al. Reproduced with permission from [33]	19
Figure 2-8. Schematic comparison of ion transport between (a) stacked and (b) vertically aligned graphene electrode when charged. Reproduced with permission from [39]	21
Figure 2-9. Possible interaction between EMImTFSI and Pluronic P123	22
Figure 2-10. Pluronic surfactant attached to graphene surface. Reproduced with permission from [40].....	22
Figure 2-11. Cross-sectional SEM (left) and cycle stability test (right) of the composite electrode fabricated by Lashkari et al. Reproduced with permission from [6].....	23
Figure 3-1. Schematic diagram of the preparation of rGO/P123/EMImTFSI electrode material	28

Figure 3-2. XRD spectra of rGO and 20% P(2) composite (containing 20 wt% P123 relative to rGO, with IL at twice the weight of P123). The peaks correspond to the (002) plane of graphite.....	29
Figure 3-3. Rate performance of 20 % P(2) composite electrode evaluated by CV. CVs measured at 5 mV s ⁻¹ and 100 mV s ⁻¹ and rate performance summary up to 1000 mV s ⁻¹	30
Figure 3-4. Impact of work-in cycles on the electrode electrochemical performance. CV expansion from 1st cycle to 10th cycle (left) and EIS comparison before and after rate testing with an offset of 500 Ω on the x-axis (right).....	31
Figure 4-1. Schematic of contrast variation in SANS.....	33
Figure 4-2. Sample 1D (left) and 2D (right) scattering intensity plot of a sample fully orientated dispersion of cylinders [50]	35
Figure 4-3. Sample Guinier-Porod model fits to the SANS data from 0.5% P85/D2O at various temperatures: (a) unimers (b) sphere (c) cylinder (d) lamellar. Reproduced with permission from [51]	38
Figure 4-4. SAXS data of P123 at 5, 20, 50, and 100 mg/mL in water	40
Figure 4-5. Spherical fit to 100 mg/mL P123 in water	41
Figure 4-6. Core-shell model fitting for 100 mg/mL P123 in water.....	43
Figure 4-7. Core-shell plus Guinier-Porod fits for 20 mg/mL and 5 mg/mL P123 in H ₂ O	44
Figure 4-8. SANS data of GO in H ₂ O/D ₂ O mixture with SLD = 0.3 $\times$ 10 ⁻⁶ , 1.6 $\times$ 10 ⁻⁶ , 5.0 $\times$ 10 ⁻⁶ Å ⁻² with linear fit in the low q region.....	46
Figure 4-9. Schematic of the cylindrical (disk) core shell model used to model GO [50].....	47
Figure 4-10. Cylindrical core shell fits on 2.4 mg/mL GO in water/D ₂ O dispersion. Inset text is the fitting result that best fits all three measurements	47
Figure 4-11. SAXS data of P123 and EMImTFSI in water. Left and right figures show two distinct scattering patterns. The red line in the left figure is a sample fit of a sphere. The numbers after P and I in the sample abbreviations denote for the concentration of P123 in mg/mL and EMImTFSI to P123 ratio respectively	48
Figure 4-12. Schematic of EMImTFSI/P123 micelle in water	49

Figure 4-13. The fixed ratio fit compared to spherical fit on P10I2. Arrow denotes where the fit deviates outside the error bar	51
Figure 4-14. Fits from more concentrated samples with summation of power law and core multi shell model.....	52
Figure 4-15. Impact of IL and P123 concentrations on IL droplet sizes.....	53
Figure 4-16. DLS measurements on P20I1, P20I2, and P20I3 micelle sizes	54
Figure 4-17. The fixed ratio fits to SANS data at solvent SLD = $5.0 \times 10^{-6} \text{ \AA}^{-2}$ from dilute IL/P123 samples. The ratios in legend correspond to IL/P123 ratio. The total concentration is 2.4 mg/mL, or 4.8 mg/mL if labeled 2x	56
Figure 4-18. SANS data collected at $5.0 \times 10^{-6} \text{ \AA}^{-2}$ of GO/P123 particles.....	58
Figure 4-19. SANS data GO/P123/IL composite dispersed in H ₂ O/D ₂ O mixture with solvent SLD = 0.3×10^{-6} , 1.6×10^{-6} , $5.0 \times 10^{-6} \text{ \AA}^{-2}$	60
Figure 4-20. Proposed structure of GO/P123/EMImTFSI composite particle dispersion in water.	60
Figure 4-21. SANS profiles of solid composite electrodes (left) and corresponding Kratky (q vs. $q^2 I(q)$) plots (right).....	61
Figure 4-22. Guinier-Porod plus Gaussian fit to 20% P(2) and fractal fit to 20% P(12) solid composite SANS profiles.....	63
Figure 4-23. Effect of electrode preparation (compression) on composite structure ..	64
Figure 4-24. Summary of the self-assembly process among (r)GO/P123/IL and their solid composite structures.....	65
Figure 5-1. Sample holder for ion bombardment chamber.	68
Figure 5-2. Comparison of CVs for pure EMImTFSI (black) and EMImTFSI/P123 composite (red) electrolyte within their electrochemical voltage window. Solid and dashed lines represent the 0th and 1000th cycle respectively.....	70
Figure 5-3. Nyquist impedance (left) and admittance (right) plot of P123/EMImTFSI electrolyte.....	71
Figure 5-4. Comparison of EIS spectra at selected potential before (left) and after (right) cycling.....	72
Figure 5-5. Effect of cycling on the physical appearance (left) and NMR spectra of P123/EMImTFSI electrolytes	73

Figure 5-6. CVs of bombarded samples measured at 5 mV/s.....	74
Figure 5-7. Approximated R_{ct} of samples at different fluxes from EIS spectra at OCV	74
Figure 5-8. TEM image of bombarded sample (10^{11} ions cm^{-2}) (left) and Raman spectra of all bombarded samples compared to as prepared sample (right)	75

List of Tables

Table 2-1. Examples of physical spacers and their energy storage performance for graphene-based composite supercapacitor electrode	17
Table 4-1. X-ray and Neutron SLDs of studied species. All values are in $10^{-6} \text{ \AA}^{-2}$	36
Table 4-2. Fitting parameters and results of 100 and 50 mg/mL P123 in water. SLD_{set} and volume fraction are fixed. SLD_{set} should be almost identical to SLD_{fit}	42
Table 4-3. Results from core-shell fit to P123 water dispersion SAXS data	44
Table 4-4. Fitting results using spherical core multi-shell fit	50
Table 4-5. Fitting results using the fixed ratio model with mixed IL/PEO core and solvated shell. The samples are sorted with a descending ratio of IL/P123	50
Table 4-6. Fitting results using a summation of a power law and the fixed ratio core multi shell model. The samples are sorted with a descending ratio of IL/P123	52
Table 4-7. Fitting results of SANS data on IL/P123 spherical micelles	57
Table 4-8. GO, P123, and EMImTFSI neutron SLDs and their visibility in the solvents (+: visible, -: invisible).....	59
Table 4-9. Fitting results on compressed composite electrode SANS using a summation of Guinier-Porod model and Gaussian peak or a fractal model. Samples are listed with ascending IL/P123 electrolyte to rGO ratio	63

Chapter 1

Introduction

Energy is vital for today's rapid human development, and non-renewable fossil fuel has always been the predominant source. While the combustion of fossil fuels has greatly boosted the world economy, it has also severely impacted the environment, leading to the development of alternative renewable sources, such as solar and wind energy. However, due to the intermittent nature of these sources, a reliable energy storage system, such as supercapacitors and various types of batteries, is required. Among these, supercapacitors, also known as electrochemical capacitors, have gained significant attention due to their unique characteristics [1]. Supercapacitors exhibit superior cycle life owing to their physical mechanism of energy storage. With higher energy density than traditional capacitors and higher power density than batteries, supercapacitor becomes the perfect option for situations where a burst of energy is frequently needed to be stored or released in a short period of time. For example, in electrical vehicles, they can be utilized for recovering braking power and providing higher power at takeoff at the same time [2]. As shown in Figure 1-1, supercapacitors bridge the gap between capacitors and batteries by offering intermediate power and energy density in between batteries and capacitors.

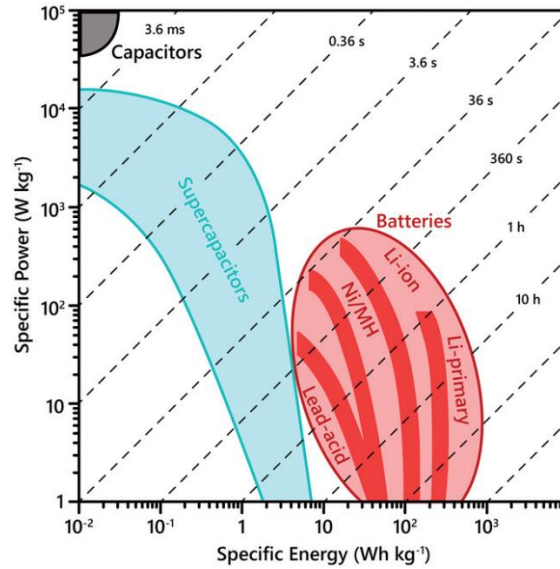


Figure 1-1. Ragone plot showing the power vs. energy density of energy storage devices.
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Supercapacitors are made of two main components, two electrodes and an electrolyte. They can store energy through either electric double-layer charging or electrochemical reactions. The electric double-layer charging originates from the accumulation of charges on the electrodes while a potential is applied across the electric double-layer capacitor (EDLC). On the other hand, the capacitors which store charges through electrochemical reactions are called pseudocapacitors. EDLCs can usually sustain rapid charging/discharging but have relatively lower energy density. While pseudocapacitors could have a higher capacitance, they suffer from shorter cycle life because of the faradaic reactions. In this thesis we will be focusing on EDLCs.

Commercial supercapacitor electrodes are usually made of activated carbon (AC), mainly due to its high specific surface area and good chemical stability. However, despite having a high surface area, its pore size distribution and surface functionality can still limit the

performance of this material. To address these issues, research has been focusing on deriving AC by combining different carbon precursors, activation agents, and processing parameters to find the optimum for a specific system[4]. Another way to address these is to use 2D materials, such as graphene, MXene, etc., with intrinsically high surface area. Graphene, composed of a single layer of carbon atoms arranged in a hexagonal lattice, has attracted great attention from the scientific community ever since its discovery in 2004[5]. Its exceptional electrical conductivity, large specific surface area, and chemical stability make it an ideal material for energy storage applications. However, graphene suffers from restacking, where sheets of graphene are pulled together by strong van der Waals interactions soon after it is produced, causing a dramatic decrease of surface area. Regardless of this issue, graphene still has the potential to significantly improve energy density while maintaining or even enhancing the power density and cyclic stability of the device.

The other key component in a supercapacitor, the electrolyte, can also influence the performance of the supercapacitor. Depending on the electrolyte, the movement of the charged species between the electrolyte and the electrode-electrolyte interaction could be very different. Major types of electrolytes include aqueous, polymeric, etc. Ionic liquid, a liquid salt at room temperature, has the advantage of being non-volatile, and exhibiting a wide electrochemical voltage window and high ionic conductivity over other electrolytes, which makes it a promising candidate for supercapacitor electrolyte.

Our previous work constructed a three-dimensional graphene-ionic liquid structure[6]. The ionic liquid-surfactant electrolyte inserted in between reduced graphene oxide (rGO) sheets as spacers has successfully prevented restacking, thereby maximizing the active material content and improving the capacitive performance of the supercapacitor. However, the high viscosity of the composite electrolyte has a negative impact on the ion movement hence the rate performance of the supercapacitor. Therefore, this thesis aims to investigate the dynamics of

all the species within the composite electrode material. The knowledge gained could be then used to engineer better supercapacitors. In the next chapter, a more detailed background on carbon-based supercapacitor electrodes, ionic liquid electrolyte, characterization techniques, and performance metrics will be given.

Chapter 2

Background

2.1 Supercapacitors

Supercapacitors can be characterized into two types depending on their energy storage mechanism: EDLCs and pseudocapacitors. EDLCs store electric charges in a purely physical way at the double layer formed by electrostatic interaction between the electrode and the charged species in the electrolyte. Pseudocapacitors possess an extra mechanism of charge storage. Through fast and reversible faradaic processes between electroactive groups in the electrolyte and functional groups on the electrode surface, additional charge can be stored compared to EDLCs. However, this could induce instability in the device resulting in shorter cycle life, which could be minimized by careful design of the electrode/electrolyte system.

2.1.1 Electric Double Layer Capacitor

An EDLC is made of two electrodes, one positive and one negative, an electrolyte, and a separator in between, shown in Figure 2-1. The electrolyte should be electrically insulating but ionically conductive, and the separator prevents shorting of the two electrodes while also allowing the ions to move freely across two sides. At stationery, both cations and anions are evenly distributed across the device. When an external potential is applied, electrons move away from the positive electrode and accumulate on the negative electrode. Simultaneously, cations and anions in the electrolyte travel to the negative and positive electrode respectively due to electrostatic interaction.

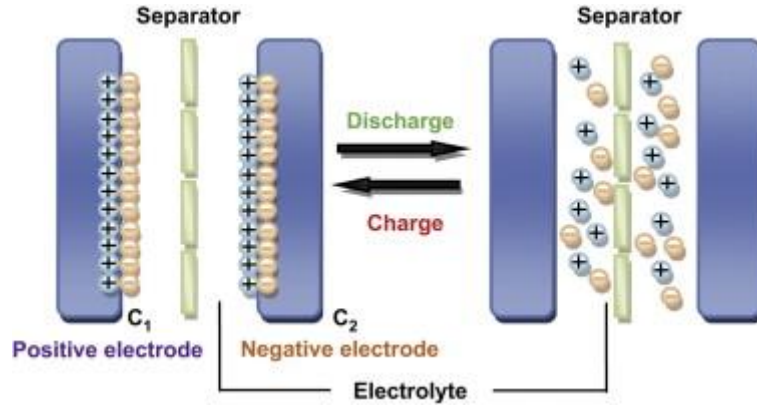


Figure 2-1. Schematic of a supercapacitor. Reproduced with permission from [7]

The “double layer” in EDLC comes from the two sheets of opposite charges at the electrode-electrolyte interface, which were first established by Helmholtz’s theory [8]. This structure is equivalent to a parallel plate capacitor, whose capacitance can be described as the following equation:

$$C_d = \frac{\epsilon \epsilon_0}{d} \quad \text{Equation 2-1}$$

where ϵ is the relative permittivity of the medium, ϵ_0 is the permittivity of free space, and d is the distance between the charged electrodes. In the case of a supercapacitor, this distance is as small as a few electrolyte molecules. The Helmholtz model successfully described the charge separation at the interface with opposite polarity electronic and ionic charges accumulated at each side of the electrode/electrolyte interface. However, it fails to predict the differential capacitance, since factors such as the ion concentration, thermal motion, and applied potential are not considered in the model.

The model was later optimized by Gouy and Chapman by considering the thermal movement of ions[8]. They treated the layer as a diffuse layer. Along with the electrostatic effect, they used a Poisson-Boltzmann equation to describe the concentration and potential profile:

$$\frac{d^2\phi}{dx^2} = -\frac{e}{\epsilon\epsilon_0} \sum_i n_i^0 z_i \exp\left(\frac{-z_i e \phi}{k_B T}\right) \quad \text{Equation 2-2}$$

which then yields:

$$C_d = \left(\frac{2z^2 e^2 \epsilon\epsilon_0 n^0}{k_B T}\right)^{1/2} \cosh\left(\frac{ze\phi_0}{2k_B T}\right) \quad \text{Equation 2-3}$$

where ϕ is the electrostatic potential, z is the charge on each ion, e is the charge on each electron, n_0 is the number concentration of ions in bulk electrolyte, k_B is the Boltzmann constant, and T is the absolute temperature. This model predicts a V-shaped differential capacitance function, with infinite rises of capacitance on extreme potentials. This flaw comes from the initial assumption of point charges, making the ion infinitely close to the electrode surface.

After Gouy and Chapman, Stern perfected the model by combining the Helmholtz layer and the diffusive layer[8]. The Helmholtz layer is a compact layer of ions adsorbed onto the electrode surface, with a minimum separation distance. Further away is the diffuse layer which is similar to that in the Gouy and Chapman model. The capacitance can then be calculated using an equivalent circuit of the Helmholtz capacitor and diffuse layer capacitor in series, which gives:

$$\frac{1}{C_{DL}} = \frac{x_2}{\epsilon\epsilon_0} + \frac{1}{\left(\frac{2\epsilon\epsilon_0 z^2 e^2 n^0}{k_B T}\right)^{1/2} \cosh(ze\phi_2/2k_B T)} \quad \text{Equation 2-4}$$

In which x_2 is the outer Helmholtz plane distance. These double layer models mentioned above are summarized in Figure 2-2 below.

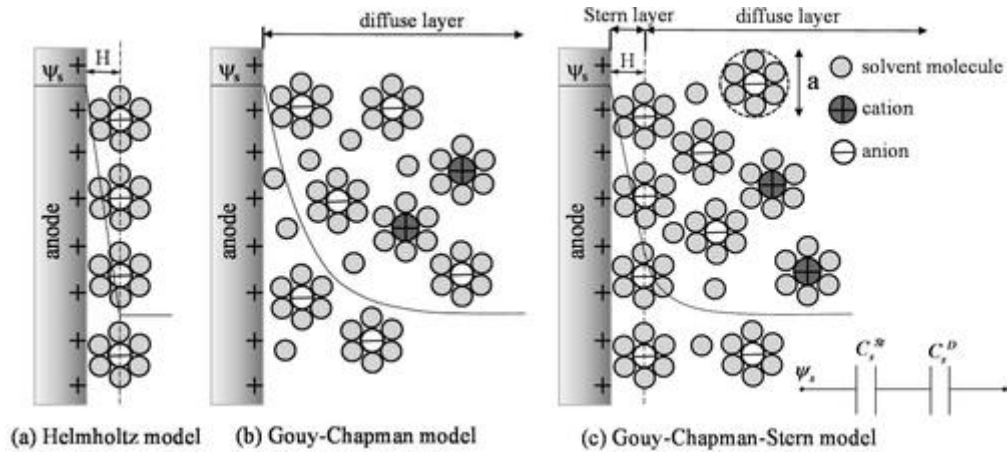


Figure 2-2. Graphical representation of the double layer model by Helmholtz(left), Gouy and Chapman (middle), and Stern (right). Reproduced with permission from [9]

2.1.2 Pseudocapacitor

Pseudocapacitors utilize fast and reversible faradaic mechanisms at or near the electrode surface to store charge. There are three common types: underpotential deposition, redox reaction, and intercalation as in Figure 2-3. Underpotential deposition occurs when the metal ion in the electrolyte adsorbs on to the metal electrode, forming a monolayer. Redox reaction occurs when the electrolyte ions experience the faradaic charge transfer on or near the surface of electrode using the applied potential as the driving force. Intercalation takes place in the bulk of the electrode material in which the ions temporarily reside in tunnels or between layers of the material without breaking its crystallographic structure. The capacitance of pseudocapacitors is usually one or two magnitudes higher than that of the EDLC. However, the power density of pseudocapacitors is much lower because of the faradaic processes. Additionally, the electrochemical reactions could not be perfectly reversible, which causes degradation on the electrolyte and electrodes, hence shorter cycle life.

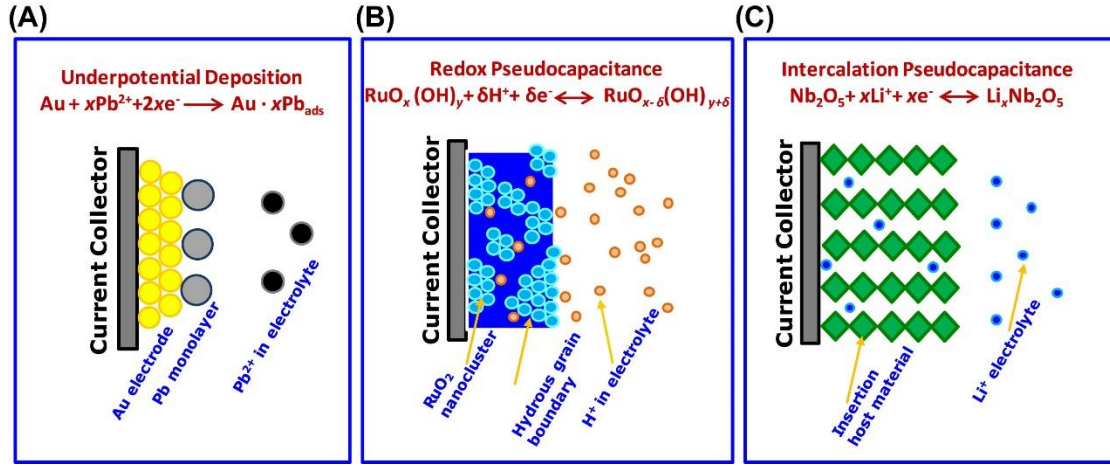


Figure 2-3. Three common types of pseudo-capacitive electrode. Reproduced with permission from [10]

2.2 Performance Evaluation of EDLC

The most important factor of an EDLC is its specific capacitance. The gravimetric capacitance can be estimated from the materials specific surface area (SSA) and the double layer capacitance mentioned previously:

$$C_G = C_{DL} \cdot SSA \quad \text{Equation 2-5}$$

In some cases where the volumetric capacitance might be more important:

$$C_V = C_G / \rho \quad \text{Equation 2-6}$$

In a symmetric supercapacitor, in which the two electrodes are identical, energy density is linearly related to its volumetric capacitance and the square of the operating voltage (U) of the device:

$$E_V = \frac{1}{8} C_V U^2 \quad \text{Equation 2-7}$$

Therefore, to improve the performance of an EDLC, one should maximize the specific surface area, double layer capacitance, material density, and operating voltage window. These

properties are usually linked together and restricted to the material property and processing techniques, so optimizing them for the highest energy density remains challenging. For example, the rate performance, which refers to how well the EDLC charge and discharge at different rates, is determined by the ion mobility in the electrolyte and the electrode pore structure etc. These aspects will be covered in the following sections.

2.3 Electrolyte

Electrolytes play a critical role in the performance and functionality of supercapacitors. Their own property such as the operating voltage window and ionic conductivity have great impact on the key performance metrics of the device, namely energy and power density, cycle life, and efficiency.

There are typically three types of electrolytes based on their physical states: liquid, solid, and quasi-solid. Aqueous electrolytes, a traditional liquid electrolyte, are most used in supercapacitor research due to their lower viscosity and high ionic conductivity. However, the operating voltage of them is mostly restricted by the stability of water hydrolytic stability (1.23 V) with some exception of neutral electrolytes reaching a 2.4 V window[11]. Another liquid electrolyte is organic electrolyte. They have a wider potential window than aqueous-based electrolytes (up to 2.9 V), but they also come with low ionic conductivity, more solvated ions, and low dielectric constant, which requires careful design of the electrode pore sizes[12]. Solid or quasi solid electrolytes, usually polymer-based, are becoming more desirable to resolve the electrolyte leakage issue of liquid electrolytes. Not only do they conduct ions, but they can also serve as the separator. Research on them is still in the early stages. The ion transport mechanism is still under investigation. Up to date, the most frequently reported one, polyvinyl alcohol, is usually combined with one of the other liquid electrolytes to increase its ionic conductivity, so the voltage window will be dependent on the added species.

Ionic liquid has recently been suggested as an alternative electrolyte for energy storage due to their low volatility, high ionic conductivity, and most importantly, wide electrochemical stability window. A more detailed review of ionic liquid as supercapacitor electrolyte will be presented below.

2.3.1 Ionic Liquids

Ionic liquids (ILs) are salts with melting points below 100 °C. An IL consists of an asymmetric organic cation and an inorganic or organic anion. By making different combinations among these ions, it is possible to tune the physical and chemical properties as needed. Common cation and anion options are demonstrated in Figure 2-4 below.

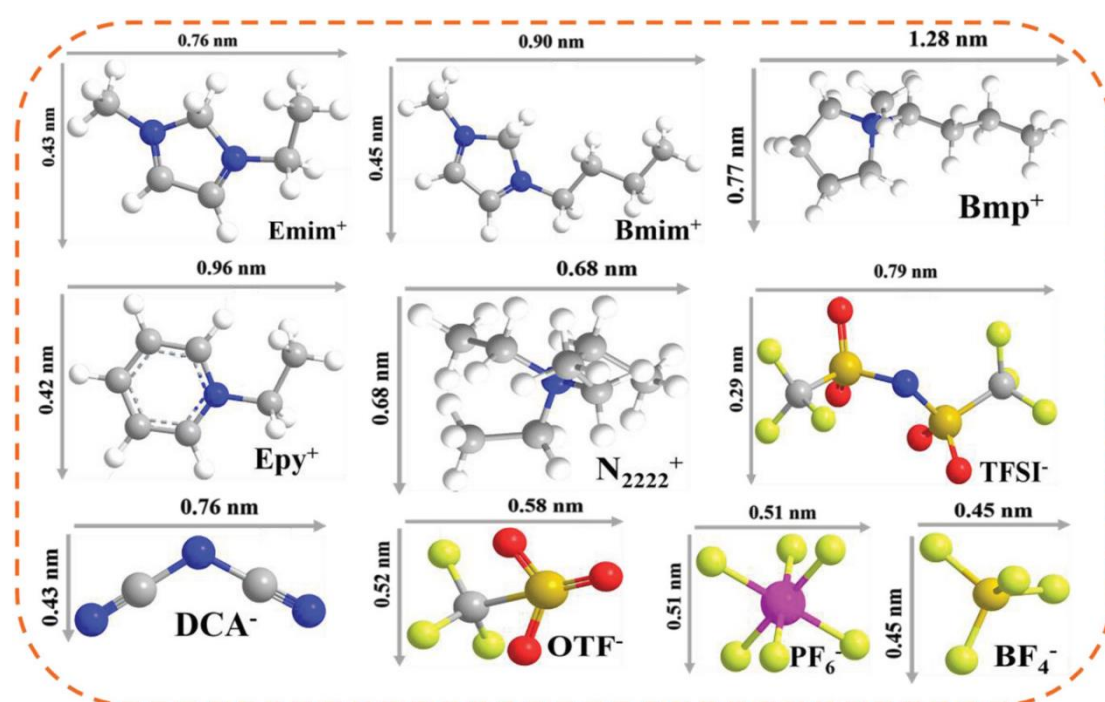


Figure 2-4. Common cations (top) and anions (bottom) in ILs and their ionic sizes. Reproduced with permission from [13]

For supercapacitors, ionic liquid has the highest theoretical operating voltage up to 6 V, which could dramatically boost the energy density of the device[14]. However, their larger ion size and high viscosity result in poorer ionic conductivity than aqueous electrolytes. Therefore,

similar to organic electrolytes, the pore size of the electrode should be optimized for the largest accessible surface area, which will be discussed in the section after.

2.3.2 Ionic Liquid Double Layer

Since ILs are liquid made solely of ionic species, their double layer behavior at the polarized surface cannot be described by Stern's model mentioned before. The electrostatic interaction between anion and cation becomes more and more dominant compared to other factors like diffusion driven by concentration gradient. Two specific behaviors have been observed for ionic liquid. At low surface potentials close to the open circuit potential (OCV), the counter ions near the electrode surface have an "overscreening" behavior. The number of counter ions accumulated on the electrode surface is more than the charge needed to neutralize the electrode surface. A second layer of ions which carries the same charge as the electrode then comes on top of the first layer as an effort to maintain local charge neutrality. This alternating sequence repeats, forming an oscillating charge distribution. The second behavior occurs at much higher potential when a single layer of counter ion is not enough to neutralize the surface. Instead, a thicker layer of counter ion accumulates until the electric field decays to the point where it cannot support another layer. This effect is known as crowding or saturation. When this occurs, since the extra layer of ion is further away from the electrified surface, the double layer capacitance becomes lower. Figure 2-5 below demonstrates the molecular arrangement at the electrode surface from overscreening to crowding.

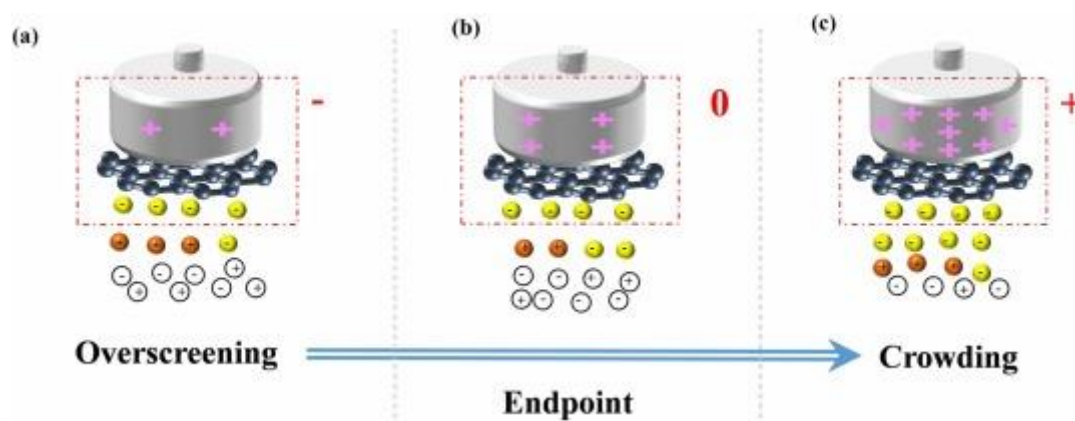


Figure 2-5. Schematic of IL at polarized electrode surface. Reproduced with permission from [15]

These two phenomena have been verified by molecular dynamic studies. Figure 2-6 below shows the result generated by Vatamanu et al. studying alkyimidazolium bis(trifluoromethanesulfonyl)imide on a graphite surface [16]. It is clearly illustrated in the figure that the initial increase in differential capacitance due to overscreening at low bias followed by a sharp drop from crowding as the applied bias increases.

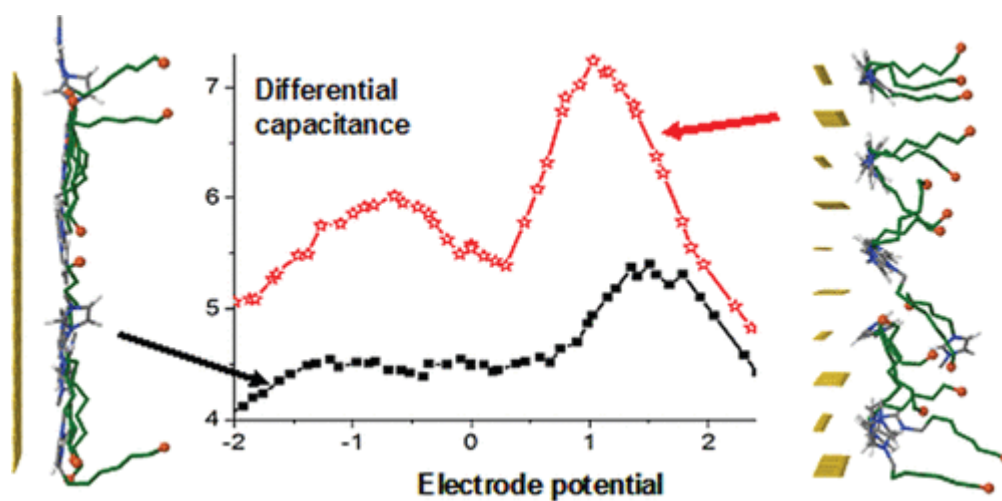


Figure 2-6. Differential capacitance of alkyimidazolium bis(trifluoromethanesulfonyl)imide at graphite surface as a function of electrode potential. Reproduced with permission from [16]

2.4 Electrode Material

The electrodes are the most critical component of a supercapacitor. Their properties determine the type or nature of the supercapacitor and are directly related to the performance of the final device. For EDLCs, carbonaceous materials such as activated carbon, carbon nanotubes, and graphene are commonly used due to their good chemical and thermal stability, high surface area, and high electrical conductivity. On the other hand, pseudocapacitors often utilize the reversible faradaic reaction from conductive polymers or metal oxides. In this thesis, only carbonaceous electrode material for EDLCs will be discussed.

2.4.1 Activated Carbon

Activated carbons are widely used in commercial EDLCs primarily because of their high specific surface area and low cost. They can be derived from a wide range of organic precursors, from agricultural wastes like coconut shell[17], corncob[18] etc. to metal carbides[19]. This is usually done with a two-step thermal process. When heated, the precursor first undergoes pyrolysis (carbonization) which removes most of non-carbon elements. Then with the addition of an activating agent, for example potassium hydroxide or CO₂ gas[20], the converted carbon is slowly etched, forming a hierarchical porous structure. The resulting pores can be categorized based on their sizes. Micropores (< 2 nm) are the smallest and contribute the most to the surface area. Mesopores (2 - 50 nm) and macropores (> 50 nm) are larger pores that provide structural support. Depending on the precursor and processing parameters, the pore size distribution varies. Activated carbon electrodes could achieve specific capacitance ranging from 100 to 300 F/g for aqueous electrolyte and 100 to 150 F/g for organic and ionic liquid electrolytes[21]. This discrepancy mainly comes from the difference in accessible surface area by the charge carriers in the electrolyte. While smaller ions like H⁺ in aqueous electrolytes can adsorb on micropore surfaces, larger ions in organic electrolyte cannot, resulting in lower capacitance and

poor rate performance. Therefore, constructing a well-designed porous structure for the desired purpose is critical to an activated carbon electrode.

2.4.2 Graphene and Graphene-Based Materials

Graphene was first produced and identified in 2004 by Geim et al. by mechanically exfoliating graphite down to one atom thick using scotch tape[5]. This method yielded a single layer of carbon atoms arranged in a 2D honeycomb lattice, namely graphene. Graphene is the building block for all other graphitic materials of dimensionalities from 0D fullerenes to 3D graphite.

Within a graphene lattice, the carbon atoms are tightly bonded to each other with strong covalent bonds under sp^2 hybridization. The fourth valence electron of each carbon atom overlaps with each other forming a delocalized π -electron cloud above and below the graphene sheet. To exfoliate graphite to obtain single layer graphene, one should overcome the weak π - π interaction between two adjacent sheets. Graphene's unique structure gives graphene a lot of extraordinary properties, i.e. good electrical conductivity, high specific surface area, and chemical stability but also put challenges on the synthesis methods. Nevertheless, graphene is still a promising candidate for scalable electrode material.

When made into electrodes and an electrical potential is applied to the graphene sheet, the total double layer capacitance can be divided into two capacitors in series, the quantum capacitance and the geometric capacitance:

$$\frac{1}{C_{DL}} = \frac{1}{C_Q} + \frac{1}{C_G} \quad \text{Equation 2-8}$$

The quantum capacitance (C_Q) is an intrinsic property of the material itself and is positively correlated with the density of states. The geometric capacitance (C_G) is the combined

capacitance of the Helmholtz layer capacitance and diffuse layer capacitance as described in the Stern model of double layer. From the equation, both the quantum capacitance and the geometric capacitance could limit the total capacitance. In the case of pristine graphene, the quantum capacitance is the smaller one, thus the limiting factor[22]. This is because of the low electronic density of state at the Dirac point of pristine graphene which has a positive correlation to the quantum capacitance. Therefore, pristine graphene is not preferred for supercapacitor electrode.

To accommodate this issue, proper modification needs to be applied to the lattice, such as doping and lattice defects[23]. The electronic band structure or the Fermi level of graphene can be shifted, resulting in higher density of state and higher quantum capacitance. One promising approach is to use reduced graphene oxide. Compared to pristine graphene, rGO retains some functional groups and defects after the reduction of graphene oxide (GO) which boosts its quantum capacitance and wettability while it can inherit comparable conductivity to that of pristine graphene, if sufficiently reduced. Therefore, rGO and graphene are often used interchangeably when referred in literature.

rGO can be obtained from the reduction of graphene oxide (GO). The most widely used method to synthesize GO is the Tour's modified Hummer's method in which graphite is chemically oxidized and delaminated [24]. It is rich in oxygen-containing groups, such as ether, carboxyl, and hydroxyl groups. These groups give GO its amphiphilic nature, and keep the sheets separated while dispersed in polar solvents like water and ethanol. Compared to pristine graphene, GO and rGO are much easier to produce on a large scale. However, due to its high density of defects or functional groups, GO must undergo reduction to partially restore the properties of graphene sheets. Common reduction methods include chemical [25], thermal [26], laser [27], plasma [28] etc.

Carbon nanotubes (CNTs) are another close variant to graphene. They are made of rolled up graphene sheets, so they inherit most of graphene's unique properties like electrical and heat conductivity and mechanical strength. There are multiwalled nanotubes, and single walled nanotubes depending on the number of graphene rolls. The hollow interior and inter-tube spaces in the tubular structure of CNTs act as mesopores which are critical to ion transport. However, like graphene, CNTs tend to form bundles due to the van der Waals interaction between tubes.

2.4.3 Review of Graphene Based Electrode

The main challenge to apply rGO in energy storage devices is that when processed into a dense electrode, graphene has the tendency to restack which makes it lose most of the desired properties from graphene, especially the surface area and conductivity. One common approach is to introduce physical spacers between graphene sheets. Examples of these spacers could be metal ions, polymers, carbon nanotubes, and other carbon materials. Table 2-1 below demonstrates a few options along with their performance.

Table 2-1. Examples of physical spacers and their energy storage performance for graphene-based composite supercapacitor electrode

Spacer	Electrolyte	Specific Capacitance	Rate Performance	Reference
Polyaniline	PVA/H ₂ SO ₄	433 F g ⁻¹ at 1.5 A g ⁻¹	91% at 15 A g ⁻¹	[29]
CNT	1 M Na ₂ SO ₄	331 F g ⁻¹ at 0.4 A g ⁻¹	233 F g ⁻¹ at 4 A g ⁻¹	[30]
MnO ₂	1 M Na ₂ SO ₄	310 F g ⁻¹ at 2 mV s ⁻¹	228 F g ⁻¹ at 500 mV s ⁻¹	[31]

Although the introduction of spacers to the system resolves the issue of graphene restacking, it inevitably decreases the proportion of active material and adds complexity to the whole system. The spacer material has an impact on the overall porous structure, the accessible surface area, and the voltage window of the device. Therefore, the choice of spacer is critical and should be carefully evaluated based on specific application.

As discussed previously, ionic liquids have the potential to greatly improve the energy density [29] of supercapacitors due to their high electrochemical voltage window. In 2013, Pope et al. have developed an ionic liquid/graphene composite electrode material [32]. They started with a colloidal mixture of graphene oxide dispersion and a water miscible IL, 1-ethyl-3-methylimidazolium tetrafluoroborate (EMImBF₄). The mixture is then dried off, leaving only ionic liquid and graphene oxide, followed by thermal reduction. Instead of dead weight like some polymeric binders, ionic liquid is employed as the electrolyte and physical spacer simultaneously, yielding a gravimetric capacitance of 140 F/g and a 3 V voltage window. Later, She et al. built upon this method [33]. Using a non-ionic surfactant, they developed an emulsion of hydrophobic 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMImTFSI), in water. Shown in Figure 2-7, the intermolecular interactions between the hydrophobic tails of the surfactant and graphene oxide and between the hydrophilic tails and IL enable the spontaneous assembly of a microemulsion system. After thermal reduction like previous work, the specific capacitance of this composite reaches 302 F/g at 80 wt.% IL composition or 218 F/cm³ at 60 wt.%.

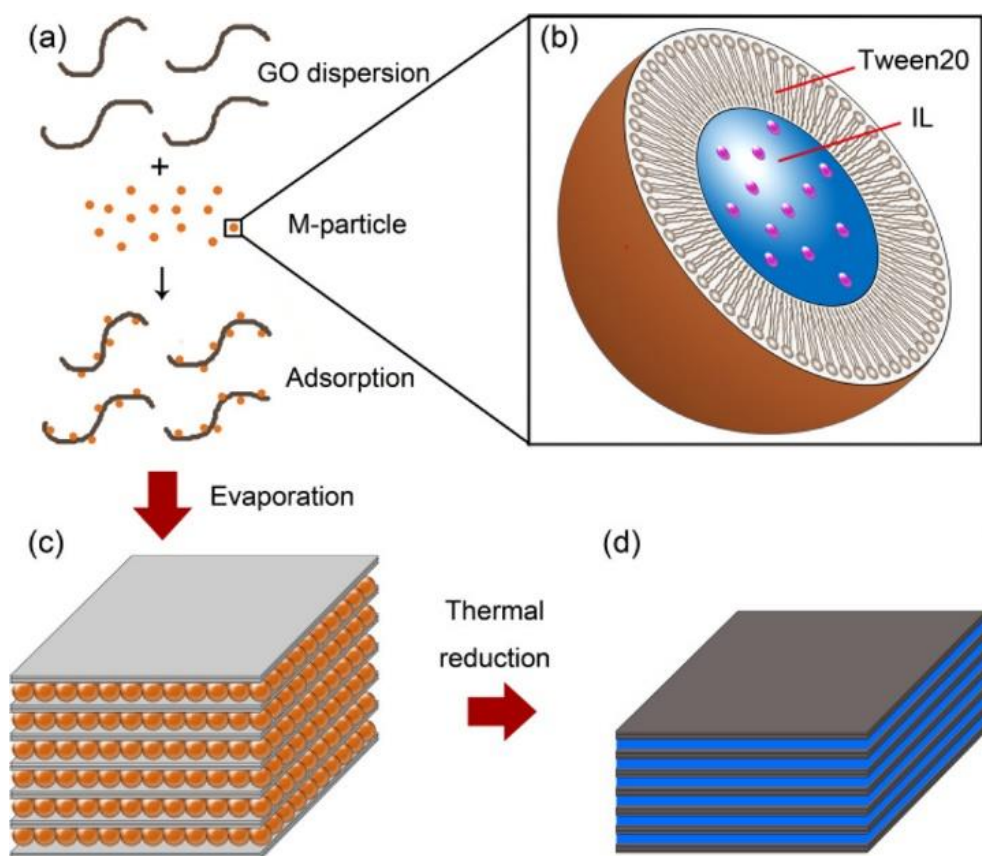


Figure 2-7. Schematic of the fabrication process for IL-mediated rGO electrode used by She et al. Reproduced with permission from [33]

Nevertheless, these two approaches involve heat treatment which inevitably leads to thermal degradation or evaporation of the surfactant and IL. Lashkari adapted to these approaches [6]. They first discovered a dramatic increase of the double layer capacitance between a glassy carbon electrode in IL electrolyte with the addition of non-ionic surfactants [34]. Therefore, instead of dispersing GO in water, they used a Pluronic P123 (poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-poly(ethylene glycol)) solution as the dispersant for rGO. EMImTFSI is then added so that rGO attaches to the hydrophobic chains and EMImTFSI attaches to the hydrophilic chains forming a micelle-like structure as in the previous literature. To anchor this structure and remove the water content, the dispersion is flash-frozen and freeze-dried, yielding a black, fluffy, and powder-like material. This material shows a maximum gravimetric capacitance of 243.8 F/g at 5 mV/s with a voltage window of around 2.5

V in a symmetrical device. However, this material still left offers significant room for improvement, which will be further explored in this thesis.

Another common approach to prevent restacking is to fabricate vertically aligned graphene (VAG) devices. The vertical alignment of graphene sheets not only maintains the separation between layers, but also facilitates efficient ion transport which is important especially when operating in high power devices. Figure 2-8 below shows that this morphology minimizes the ion transport pathway when charged. Ions reside in the channels created by the vertical architecture could access the graphene surface without collapsing or compressing the structure. However, the fabrication of such devices often involves bottom-up techniques like chemical vapor deposition [35], which could be time and energy consuming. An alternative to this morphology is holey graphene. Methods such as chemical etching [36], catalyst oxidation [37], and ion bombardment [38] have been used to perforate graphene sheets, creating nanopores that enable ions to access more surface area through a shorter route to achieve better rate performance.

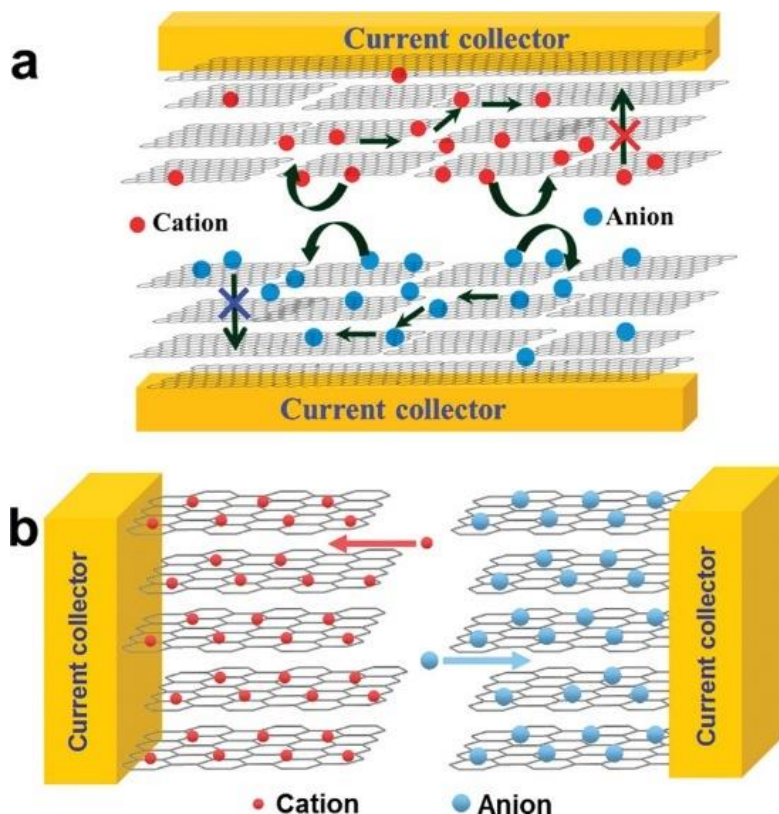


Figure 2-8. Schematic comparison of ion transport between (a) stacked and (b) vertically aligned graphene electrode when charged. Reproduced with permission from [39]

2.4.4 Self-assembly among EMImTFSI/Pluronic P123/Graphene

The composite electrode material reported by Lashkari mentioned above has showed promising results [6]. Now, understanding the interactions among all components become crucial for further tailoring the nanostructures with desired electrode properties. The hydrophobic IL, EMImTFSI, settles in the PEO section of the P123 surfactant possibly through hydrogen bonding as presented in Figure 2-9.

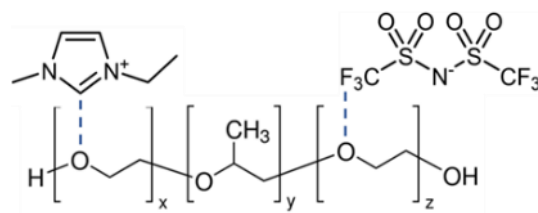


Figure 2-9. Possible interaction between EMImTFSI and Pluronic P123

On the other side, the Pluronic surfactant interacts with graphene or graphene oxide with its PPO section as shown in Figure 2-10 [40], [41].

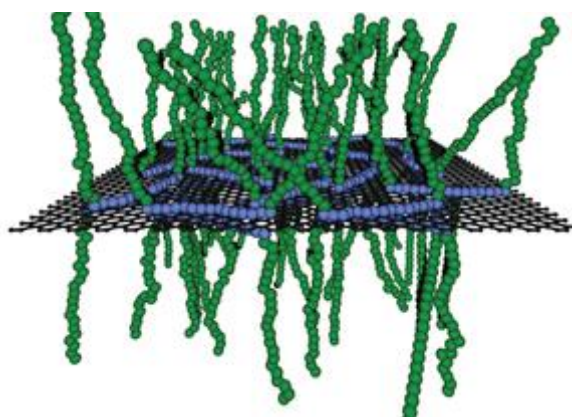


Figure 2-10. Pluronic surfactant attached to graphene surface. Reproduced with permission from [40]

When water becomes absent from the system, the Pluronic surfactant settles on GO surfaces. Lashkari et al. has reported an increase in thickness and reduction in surface roughness as more surfactant attaches to GO surface. While with the presence of IL, high concentration of surfactant and IL could result in large aggregates tens of nanometers in height [42].

2.5 Motivation and Thesis Objectives

Supercapacitors are energy storage devices that offer great power density but relatively low energy density. Therefore, the objective in supercapacitor research should be built around improving its energy density while maintaining the power density. This thesis aims to

investigate the nanostructure characteristics of the composite electrode material developed by Lashkari mentioned above [6].

The rGO/EMImTFSI/P123 composite electrode material has shown superb energy density from the wide voltage window of ionic liquid and tunable specific capacitances. Yet there are still a few aspects that have not been fully understood shown in Figure 2-11. First, the structure yielded from the processing steps has not been characterized in detail. When compressed, a significant volume of air is trapped in the bulk of the electrode. Second, a delayed peak performance is observed from the cycle stability test on the material. As shown below, the performance of the material reaches its maximum after 1700 cycles (work-in cycles) which is probably due to the high viscosity of the electrolyte which hinders mass transport within the electrode.

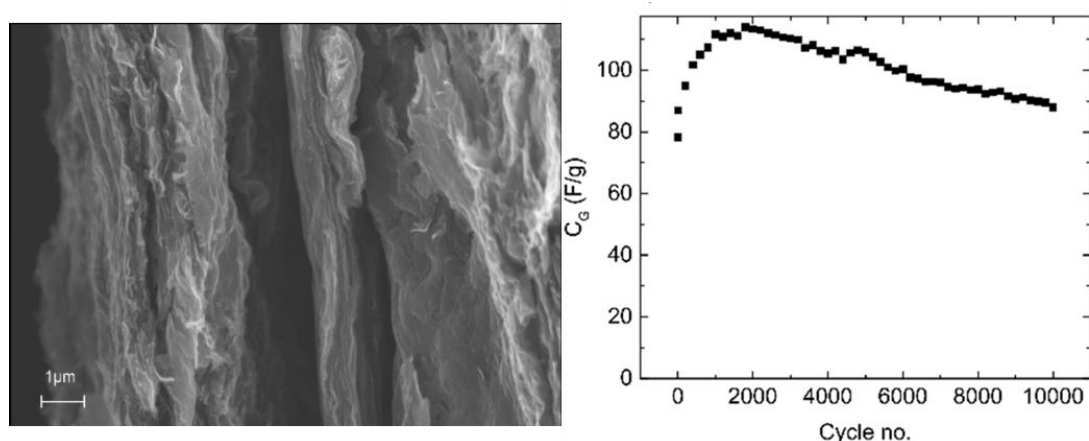


Figure 2-11. Cross-sectional SEM (left) and cycle stability test (right) of the composite electrode fabricated by Lashkari et al. Reproduced with permission from [6]

In the following chapters, this electrode material is reproduced and evaluated. The processing procedure will be broken down into stages and studied using small angle scattering techniques in the next chapter to better understand the self-assembly of this material in water. Later, the effect of long-term cycling, i.e. the degradation of the electrolyte, is studied by the measurement of its differential capacitance over its stability window by EIS. Lastly, heavy ion

bombardment is employed on prepared electrodes to perforate holes on graphene sheets aiming to enhance interplanar ion transportation. This may enable the external IL to be driven in to the bulk of the electrode by the applied potential more rapidly, thereby eliminating the delayed peak performance discussed earlier.

2.6 Thesis Layout

In Chapter 3, the material reported in [6] is reproduced. The procedure is explained in detail, discussing potential structural changes occurring between steps. The performance metrics of it are analyzed in more detail, raising possibilities for improvement and further justifying the objective of this thesis.

In Chapter 4, we analyzed the impact of rGO, EMImTFSI, and P123 concentrations on the self-assembling process in an aqueous media using small angle X-ray and neutron scattering methods. Scattering intensity spectra were acquired on aqueous dispersions of the three species and their mixtures. The spectra were first evaluated by their shape and then fitted using given knowledge on the structure. The micelle dimensions of IL/surfactant emulsions at different concentrations and ratios were measured and compared. The crumpling of GO in water is reflected by its spectra and the effect of the addition of P123 is studied. Dynamic light scattering (DLS) measurements were used to verify the results. Finally, the full mixture of the three species was measured at various background levels, and its structure was determined according to the spectra and compared to previous proposed models.

In Chapter 5, the cycling degradation behavior of the IL/surfactant electrolyte is studied using electrochemical impedance spectroscopy. The voltage window of the electrolyte is determined on a glassy carbon electrode. Then it is cycled slightly beyond the window while the double layer capacitance and ionic conductivity are measured. This chapter also explores the potential of using heavy ion bombardment on a pressed electrode to perforate holes on

graphene sheets as an attempt to boost the rate performance and reduce the number of work-in cycles of the material. The impedance spectra were also recorded and compared to the results in Chapter 3.

Chapter 3

Evaluating Graphene-Based Supercapacitor Composite Electrode Fabrication Using Ionic liquid/Non-ionic Surfactant Electrolyte as Spacer Material

3.1 Introduction

Introducing physical spacers in between graphene sheets has proven to be an efficient method to improve the SSA of rGO composite electrode material. Preliminary studies by Lashkari et al. demonstrated that through the self-assembly of the surfactant with non-surface-active IL to rGO surface under water medium, a maximum C_G of 247.3 F/g and an ESW window of up to 3.5 V can be achieved with optimized mass balancing [6]. The addition of the surfactant to the system not only grants surface activity to non-surface-active IL but has a beneficial effect on the double layer capacitance as well [34]. Although the composition that yields to the best performance has been determined in their study, more work needs to be done to fully understand the composite at each processing step and its life cycle, allowing potential improvements.

In this chapter, the electrode material synthesized by Lashkari et. al [6] is reproduced step by step to provide a solid background on subsequent analyses in the following chapters. Its performance is evaluated in a symmetric supercapacitor cell. The preparation of materials and the results presented were carried out by me.

3.2 Materials and Method

Materials

Graphene oxide was synthesized from graphite flakes (Alfa Aesar, 99.9% purity, -10 mesh) using Tour's modified Hummers' method. A commercial rGO is purchased from Angstrom Materials Inc. The surfactant, Pluronic P123, was purchased from Sigma-Aldrich, and the IL,

1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMImTFSI), was purchased from Io-Li-Tec (99.5% purity). Both of which were used as received.

Preparation of rGO/P123/IL composite electrode

The graphene oxide was chemically reduced using hydrazine reduction method as detailed by Stankovich et al. 50 ml of 2 mg/ml GO dispersion in water was heated in a round bottom flask and 200 μ l hydrazine hydrate (35 wt. %) was added to the dispersion when the temperature reached 70 °C. The dispersion was left overnight at 98 °C. The resulting rGO was then filtered and washed with DI water. The filter cake was collected. It was found that the procedure above yields 50 mg rGO each batch which is then divided into two equal portions for two batches of composite material.

The general preparation procedure for the composite material is summarized in the schematic Figure 3-1. To prepare the beginning dispersion, all components are combined in the following manner. First, 5% of the commercially available rGO is added as a conductive additive to the lab prepared rGO dispersion. The rGO mixture is added to an aqueous dispersion of P123 to a total volume of approximately 100 mL. The dispersion was ultrasonicated for 30 min at 60% amplitude using Sonics Vibra-cell. Then, EMImTFSI was added to the dispersion and ultrasonicated for another 30 min. The final dispersion was sprayed into liquid nitrogen using an atomizer to flash freeze the assembled composite structure. The resulting frozen slurry is then collected and freeze dried, which yields a fluffy black powder. The main procedure of interest, highlighted, is the preparation of the dispersion, namely the structure of the complex formed among rGO, P123, and IL, as the remainder of the process occurs in the solid phase, where molecular movement is minimal.

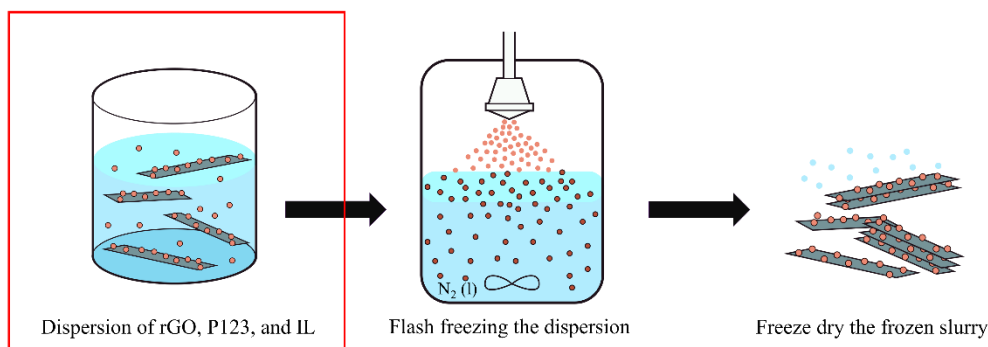


Figure 3-1. Schematic diagram of the preparation of rGO/P123/EMImTFSI electrode material

Electrochemical Characterization

To assemble a supercapacitor, the composite powder was pressed onto a carbon coated aluminum current collector (single carbon layer, Landt instruments) using a 1/2-inch pellet pressing die (MTI corp.) and force of 5 tons (metric) at approximately 1 mg rGO/cm² loading. Inside an argon-filled glovebox, the electrodes pellets are sandwiched in a stainless steel two-electrode split test cell (TMAX Battery Equipments) with a glass fiber separator wetted by 100 μ L of EMImTFSI in between.

The cell is then characterized by CV and EIS on a Biologic SP-300 potentiostat. The gravimetric capacitance is calculated using the following equation:

$$C_G = \frac{2 \int I dV}{m \cdot \Delta V \cdot v} \quad \text{Equation 3-1}$$

where I and V are the current and potential respectively, m is the mass of active material on one electrode, ΔV is the voltage window, and v is the scan rate set for the CV test.

Other characterization

X-ray diffraction was performed on a Rigaku MiniFlex benchtop X-ray diffractometer (Cu $K\alpha$).

3.3 Results and Discussion

Figure 3-2 shows the XRD profiles for as prepared rGO and the composite material. Both samples show a broad reflection at around 24° which corresponds to the (002) plane of graphite ($d = 0.358, 0.372$ nm). A tiny shift to the left of 1.0° is observed on the composite spectrum. Compared to graphite ($d = 0.34$ nm), this shift could be due to a different degree of reduction or weakened restacking of the rGO sheets by the surfactant. The ionic liquid would not affect the XRD spectra due to their amorphous nature.

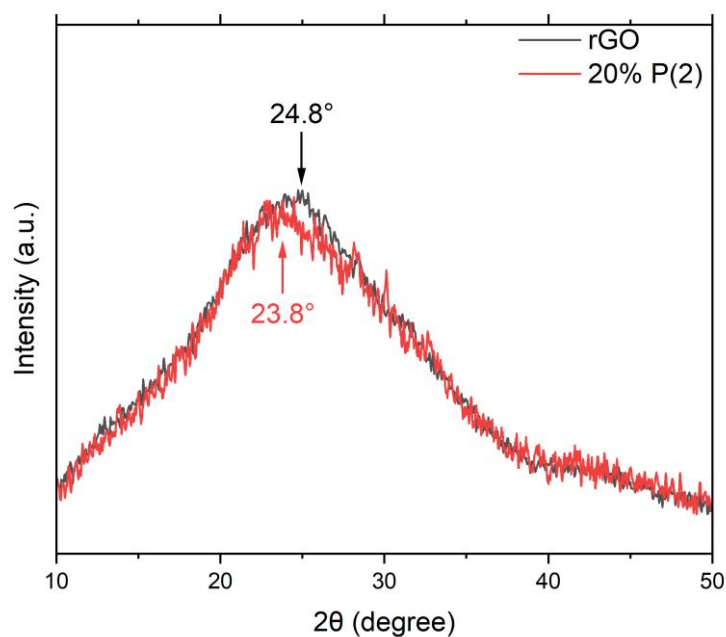


Figure 3-2. XRD spectra of rGO and 20% P(2) composite (containing 20 wt% P123 relative to rGO, with IL at twice the weight of P123). The peaks correspond to the (002) plane of graphite

The measured CV profile of the composite electrode material with the highest volumetric capacitance determined in [6] is shown in Figure 3-3. The composite is made with rGO:P123:IL at a weight ratio of 4:1:2, denoted as 20% P (2) in the literature. This abbreviation is used to

record two key parameters during processing: the amount of P123 absorbed on rGO and the overall electrolyte composition. The CVs maintain their rectangular shape up to 100 mV s^{-1} scan rate while holding 65% of its gravimetric capacitance at 5 mV s^{-1} shown in the figures below. The gravimetric capacitances measured on the 10th cycles are significantly lower than the values reported in [6], indicating that it was still in its work-in process.

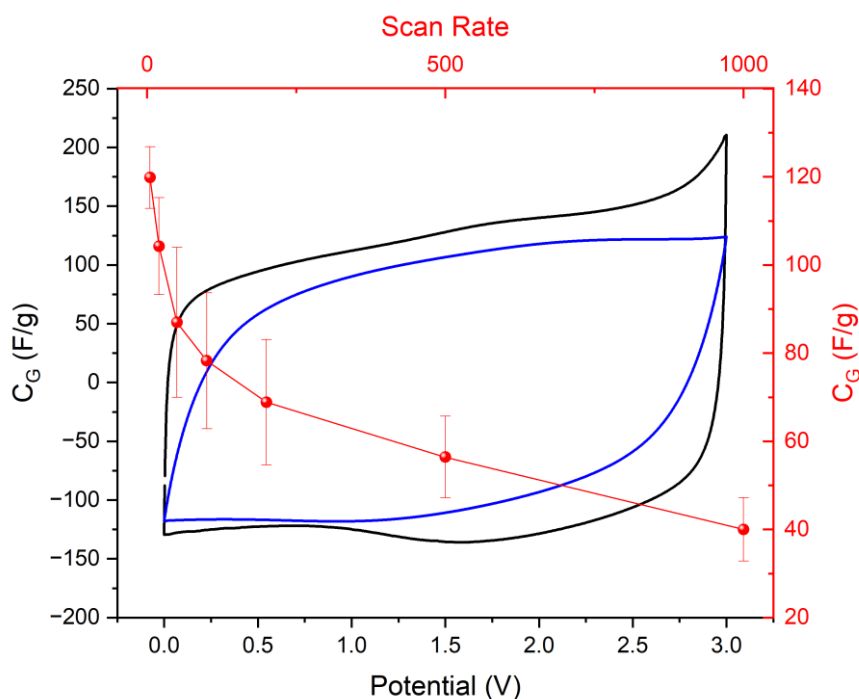


Figure 3-3. Rate performance of 20 % P(2) composite electrode evaluated by CV. CVs measured at 5 mV s^{-1} and 100 mV s^{-1} and rate performance summary up to 1000 mV s^{-1}

Comparing the cycling stability using the CV plot and EIS spectra in Figure 3-4, a gradual expansion of the area enclosed by the CV curves can be seen. The EIS spectra before and after cycling shows significant differences. The as-prepared electrode shows the characteristic 45° Warburg-like impedance which suggests a diffusion-controlled process, while in the cycled electrode, it performs more towards an ideal capacitor with an almost vertical tail. This matches with the claim in the original work in which the absence of such behavior is found in samples with higher IL to P123 ratio.

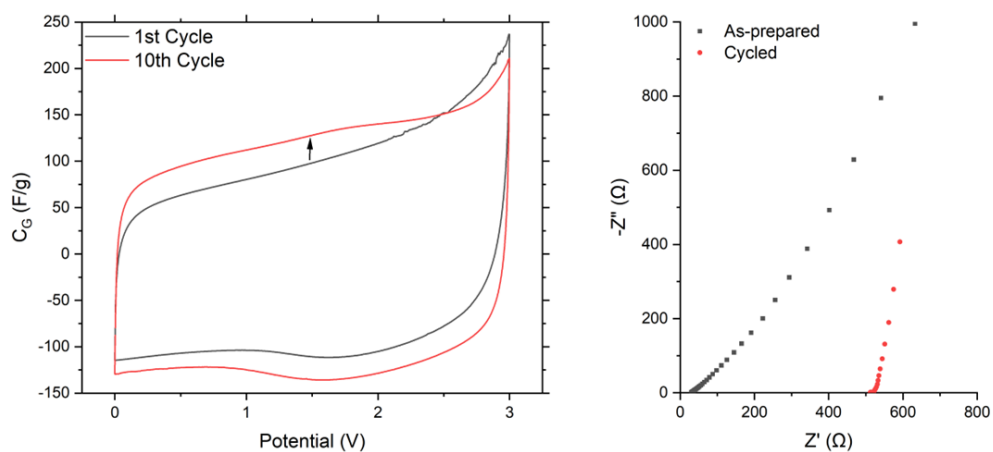


Figure 3-4. Impact of work-in cycles on the electrode electrochemical performance. CV expansion from 1st cycle to 10th cycle (left) and EIS comparison before and after rate testing with an offset of 500 Ω on the x-axis (right)

Chapter 4

Small Angle X-ray and Neutron Scattering Study in Aqueous Assemblies of Graphene Oxide with Pluronic Surfactant and Hydrophobic Ionic Liquid

4.1 Introduction

The previous chapter has elaborated on the processing procedure and electrochemical performance of the composite material. There is significant room for improvement in processing procedure and device performance as we still lack an understanding of how the three species orient themselves in each stage of assembly. This motivates us to use small angle scattering (SAS) to characterize the structure during the assembly at the nano scale, namely small angle X-ray scattering (SAXS) and small angle neutron scattering (SANS).

When penetrating the samples, X-rays scatter from electrons and neutrons scatter from nuclei. SAS measures the angular distribution of the radiation scattered through the sample. The key parameter affecting the intensity of scattering is the scattering length density (SLD, ρ) which is a volumetric average of the scattering length (b_i) of all the atoms in space:

$$\rho = \frac{\sum b_i}{V} \quad \text{Equation 4-1}$$

The intensity profile comes from the difference in SLD of the scattered particles to the surrounding medium:

$$I \propto (\Delta\rho)^2 \quad \text{Equation 4-2}$$

Therefore, by using a solvent with a strong contrast to the particle, SAS can determine the spatial orientation of the atoms in it, for example, the separation of hydrophilic and hydrophobic regions in an aqueous micelle. This contrast variation is used extensively in SANS by adjusting

the SLD of the solvent with its deuterated counterpart. As demonstrated in Figure 4-1, by selectively adjusting the SLD of the background or solvent, the core and shell can be characterized separately by the neutron beam. While there have been plenty of studies by SAS on block copolymers [43], [44], [45] and/or GO/rGO dispersions [46], [47], [48], little is known about the mixture containing these materials with ILs. The presence of ILs could possibly influence the self-assembly behavior of surfactant micelles as well as the flattening of GO/rGO sheets due to the surfactant. Understanding these mixtures is crucial to improve the processing parameters for better electrode material.

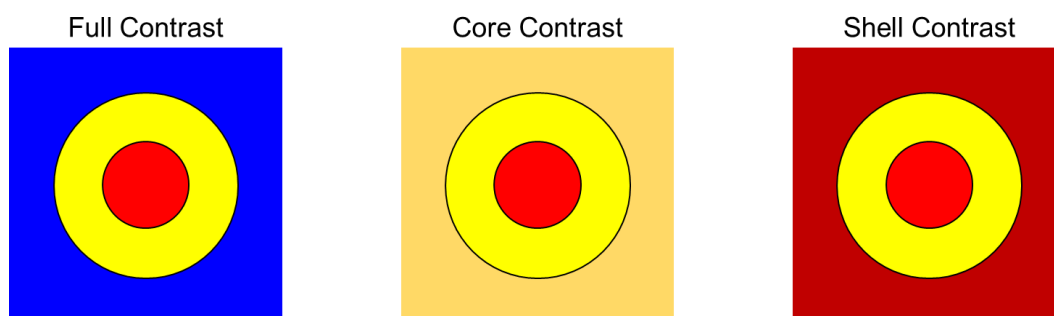


Figure 4-1. Schematic of contrast variation in SANS

4.2 Materials and Method

Materials

Graphene oxide was synthesized from graphite flakes (Alfa Aesar, 99.9% purity, -10 mesh) using Tour's modified Hummers' method. The surfactant, Pluronic P123, was purchased from Sigma-Aldrich, and the IL, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMImTFSI), was purchased from Io-Li-Tec (99.5% purity). Both of which were used as received. Solid composite electrodes were prepared as described in Chapter 3 and compressed into thin films ($\sim 20 \mu\text{m}$) with a roller press.

Characterization

SAXS and SANS data were obtained on pure surfactant, graphene oxide, surfactant/IL, and GO/surfactant/IL solution. Water is used as the primary solvent for SAXS, and for SANS a mixture of H₂O and D₂O is used to achieve different SLDs of 0.3×10^{-6} , 1.6×10^{-6} , and $5.0 \times 10^{-6} \text{ \AA}^{-2}$ for better contrast to different species. SAXS was performed on I22 SAXS Pilatus detector, Diamond Light Source, in Oxfordshire, United Kingdom, at 12.5 keV with a sample-to-detector distance of 2.87 m, giving a q range from $0.0025 \text{ \AA}^{-1}$ to $3 \text{ \AA}^{-1}$. SANS was conducted in monochromatic mode on the Bilby instrument with a q range of 0.0015 to $0.7 \text{ \AA}^{-1}$ at the Australian Centre for Neutron Scattering (ACNS), Australia's Nuclear Science and Technology Organisation (ANSTO) in Sydney, Australia[49]. Measurements were performed at 25 °C unless otherwise stated.

Supplementary dynamic light scattering (DLS) measurements were performed on a VASCO particle size analyzer (Cordouan Technologies).

Data Analysis

The data collected from small angle scattering instruments is a 2D map of scattered intensity. Figure 4-2 shows how a sample pattern of fully orientated cylinders is translated to the 1D profile on the axis of interest from the 2D scattering pattern. All data presented in this chapter are isotropic, meaning that the intensity profiles are indifferent regardless of the angle.

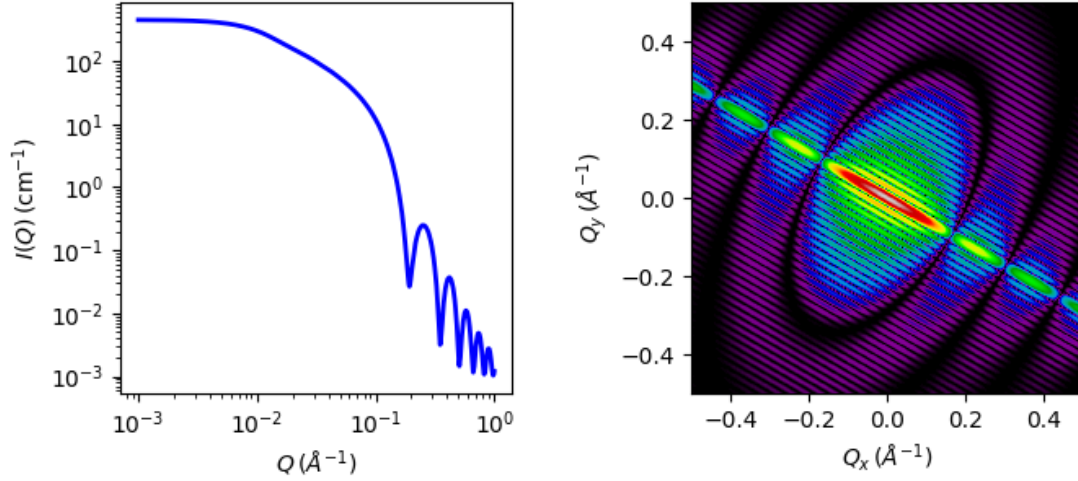


Figure 4-2. Sample 1D (left) and 2D (right) scattering intensity plot of a sample fully orientated dispersion of cylinders [50]

In the 1D spectrum, the scattered intensity of the beam is plotted as a function of the scattering vector, q :

$$q = \frac{2\pi}{\lambda} \sin \frac{\theta}{2} \quad \text{Equation 4-3}$$

where λ is the wavelength of the incident X-ray or neutron beam and θ is the scattering angle.

The scattered intensity (I) can generally be expressed as:

$$I(q) = \text{scale} \times P(q)S(q) + \text{background} \quad \text{Equation 4-4}$$

where $P(q)$ is the form factor, and $S(q)$ is the structure factor. The scale is dependent on the concentration of all the species in the solution and the SLD contrast. The form factor function is determined by the atomic distribution in one nanoparticle (shape), and the structure factor is related to the correlation of these particles within the system. In systems like ideal liquid or dilute dispersions, particles do not interact with each other except through collisions, so the structure factor can be neglected ($S(q) = 1$) and the scattering profile is purely governed by the form factor. On the other hand, in colloidal dispersions for example, the structure factor

would play a crucial role in capturing the interaction between particles (such as electrostatic and Van der Waals forces), which depends on factors like particle charge, effective radius and volume fraction. The dependency of the scattering intensity to the SLD contrast enables the possibility of contrast variation study in which one component can be contrast-matched (invisible) while others remain visible. In this study, water/D₂O have been mixed at selected ratios to simplify the visible structure. The SLDs of all components studied are summarized in Table 4-1 below.

Table 4-1. X-ray and Neutron SLDs of studied species. All values are in $10^{-6} \text{ \AA}^{-2}$

	X-ray	Neutron
Polypropylene oxide (PPO)	9.48	0.35
Polyethylene oxide (PEO)	10.49	0.64
EMImTFSI	13.16	2.41
GO	17.20	5.25
H ₂ O/D ₂ O	9.44/9.43	-0.56/6.38

Raw data obtained has been reduced and radially averaged to 1D on an absolute scale using standard instrument procedures using the Mantid software. Modelling of the scattering data was performed using the software ‘SasView’ (<https://www.sasview.org/>), and all form factors were used without further modification.

4.3 Results and Discussion

In this section, the spectra from small angle scattering measurements are initially evaluated based on their shape to identify a suitable model. Subsequently, dimensional information is

extracted through fitting. A general starting model for a polymer dispersion is the Guinier-Porod model [51], which could account for unimers, spheres, rods, pellets, or any intermediate shapes in between. It consists of a Guinier regime (low q) which provides information on the particle dimensionality and shape, and a Porod regime (high q) which points to the surface roughness. Figure 4-3 demonstrates the SANS data collected on a 0.5% Pluronic P85 block copolymer dispersion in D₂O [51]. The solubility of the copolymer was tuned by adjusting the temperature of the dispersion. As the temperature increased, the solubility went down. Looking at the slope in the Guinier region, the conformation of the polymer was unimers at 283 K with no characteristic slope, spherical micelles at 323 K with a slope of 0, cylindrical micelles at 343 K with a slope of -1 and lamellar micelles at 363 K with a slope of -2. The only limitation to this model is that it cannot handle the oscillations characteristics in compact monodisperse scattering objects precisely, for example micelles, in which case a model developed specifically for that structure should be used.

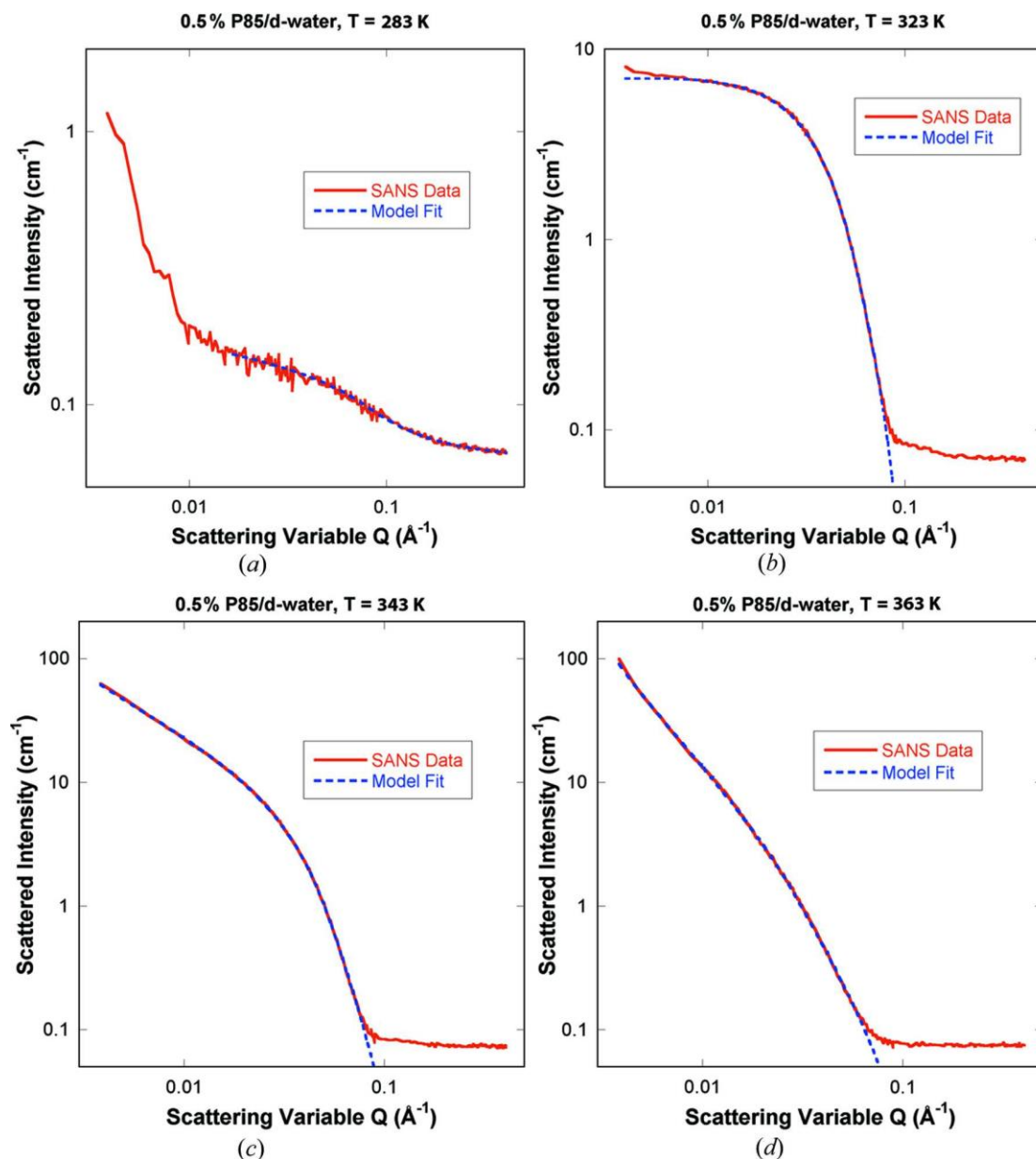


Figure 4-3. Sample Guinier-Porod model fits to the SANS data from 0.5% P85/D2O at various temperatures: (a) unimers (b) sphere (c) cylinder (d) lamellar. Reproduced with permission from [51]

Pluronic P123

Pluronic P123 is a non-ionic surfactant with two hydrophilic PEO blocks on two ends and a hydrophobic PPO block in the middle. Within a specific temperature and concentration range, P123 forms micelles in water. To study the P123 micelles, solutions were prepared at 5, 20, 50, and 100 mg/mL, which translates to 0.862, 3.45, 8.62, and 17.2 mM, for SAXS, and 2.4 mg/mL

for SANS. These concentrations are chosen as they are within the same range used during electrode processing. At room temperature (293 K), these concentrations are above the critical micelle concentration (CMC) of P123 [45]. While water ($9.43 \times 10^{-6} \text{ \AA}^{-2}$) is the solvent, polyethylene oxide (PEO) region ($10.49 \times 10^{-6} \text{ \AA}^{-2}$) is more visible than polypropylene oxide (PPO) region ($9.48 \times 10^{-6} \text{ \AA}^{-2}$).

The scattering spectra of the four concentrations are demonstrated in Figure 4-4. All the samples show the characteristic oscillation at intermediate q value ($\sim 0.04 - 0.05 \text{ \AA}^{-1}$). At high q values, the instrument detection limit is reached, resulting in a noisy background region. At low q values, the intensity drop is likely due to the solvent background subtraction applied as the signal in water is very similar to that of P123. The two lower concentration samples showed an almost linear region with a slope of -2.37 at intermediate q region which could suggest a fractal object, or incomplete micelles. The plateau at low q is still observed as the other samples indicating a spherical structure.

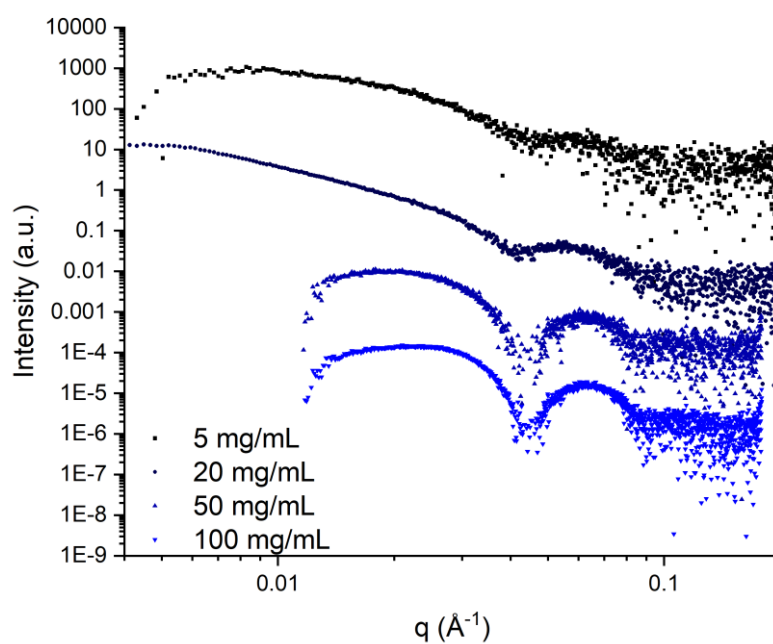


Figure 4-4. SAXS data of P123 at 5, 20, 50, and 100 mg/mL in water

Starting with a simple sphere model for the 100 mg/mL sample, the fit is illustrated in Figure 4-5. The oscillation strength in the high q region is stronger than predicted. This suggests that the distribution of PEO and PPO in the particles is arranged to enhance oscillation. Therefore, a spherical core shell structure is considered.

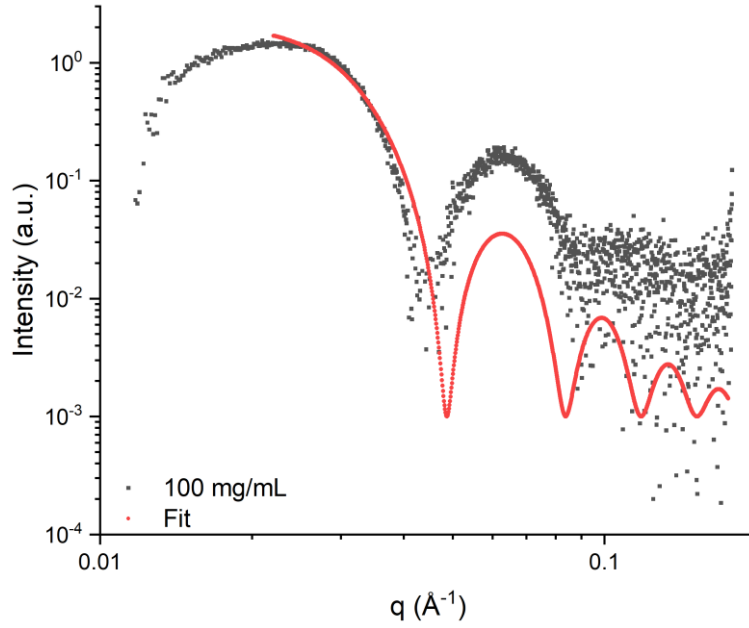


Figure 4-5. Spherical fit to 100 mg/mL P123 in water

As PEO is hydrophilic, it is expected to interact with water and form the outer shell of the micelle. Its volume expansion by water needs to be calculated to precisely determine its effective interaction radius in the solvent, since the water molecules get incorporated into the PEO shell also count towards the volume fraction of the micelle. To achieve this, a constraint is applied between the volume fraction of the micelle and the shell SLD. Assuming the PPO does not interact with water at all, the following relation stands given the dry mass density and SLD of all species:

$$SLD_{shell} = 9.43 + \frac{0.265c}{\phi - 0.6972c} \quad \text{Equation 4-5}$$

where c is the concentration of P123 in g/mL and ϕ is the volume fraction of all the micelles. Using this relation, the radius of PPO core and thickness of PEO shell is fitted, and a theoretical SLD is calculated. The fitting results from the 100 mg/mL sample are displayed in the Table 4-2. Comparing the set SLD and fit SLD, it can be concluded that the real SLD is approximately

$9.60 \times 10^{-6} \text{ \AA}^{-2}$, so this number will be carried on for all later fittings. This calculated value is expected to be slightly smaller than the actual value, because the assumption of water-free PPO core will cause an underestimation of PEO content in the shell, thus lower calculated SLD. From this, a water volume fraction of 84% can be estimated which is within reasonable range from a literature value of 77% [43]. The dimensions of the micelles at the two concentrations are almost identical. The fitted profile is shown in Figure 4-6.

Table 4-2. Fitting parameters and results of 100 and 50 mg/mL P123 in water. SLD_{set} and volume fraction are fixed. SLD_{set} should be almost identical to SLD_{fit}

$SLD_{set} (10^{-6} \text{ \AA}^{-2})$	Volume Fraction ϕ	Radius $r (\text{\AA})$	Thickness $t (\text{\AA})$	$SLD_{fit} (10^{-6} \text{ \AA}^{-2})$
100 mg/mL				
10.00	0.116212	55.5	27.7	9.59
9.70	0.167869	57.7	28.9	9.59
9.60	0.225603	58.4	33.0	9.56
9.58	0.246388	55.1	39.7	9.52
9.55	0.290554	54.5	44.6	9.51
50 mg/mL				
9.70	0.083934	58.3	29.8	9.59
9.60	0.112801	59.8	31.2	9.58
9.58	0.123193	60.0	43.0	9.58
9.57	0.129503	60.1	32.6	9.57

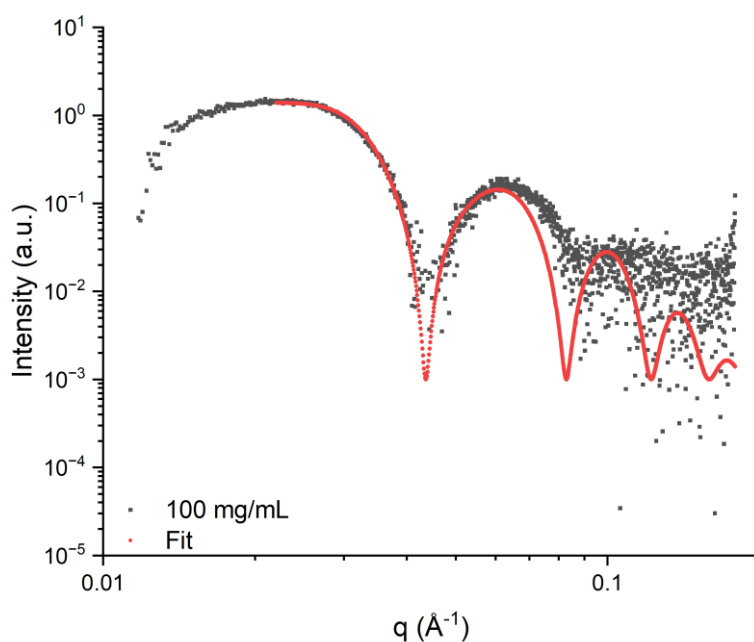


Figure 4-6. Core-shell model fitting for 100 mg/mL P123 in water

To investigate the nature of the linearity at low q , the same micelle structure as the higher concentrations is used to account for the spherical plateau i.e. 59.3 Å in radius, 32.8 Å in thickness. The Guinier-Porod model is then added to describe the behavior of the free-floating surfactant (unimers) in the solvent. Using this summation of the two form factors, the fitted curves are shown below. Fitting from the Guinier-Porod model gives structural information on the free-floating chains as shown in Table 4-3, and the fitted profiles are demonstrated in Figure 4-7. The radii of gyration of P123 at 20 and 5 mg/mL are found to be 17.9 nm and 6.9 nm, respectively. This discrepancy arises from the concentration difference as Guinier-Porod model is most suited for dilute solutions in which particles do not interact with each other. Nevertheless, this increase in R_g suggests the formation of larger tangled polymer chains or incomplete micelles which coexist with complete micelles in the solution. When the concentration further increases, micelles become the more stable structure. Fitting on SANS

data collected on a dispersion of 2.4 mg/mL P123, which eliminates the structure factor effect, suggested an R_g of 6.4 nm. This agrees with the SAXS results.

Table 4-3. Results from core-shell fit to P123 water dispersion SAXS data

Concentration (mg/mL)	Form Factor(s)	r_{PPO} (Å)	t_{PEO} (Å)	R_g (Å)
100	Spherical Core-Shell	60.1	32.6	-
50	Spherical Core-Shell	58.4	33.0	-
20	Spherical Core-Shell Guinier-Porod	59.3*	32.8*	169
5	Spherical Core-Shell Guinier-Porod	59.3*	32.8*	69

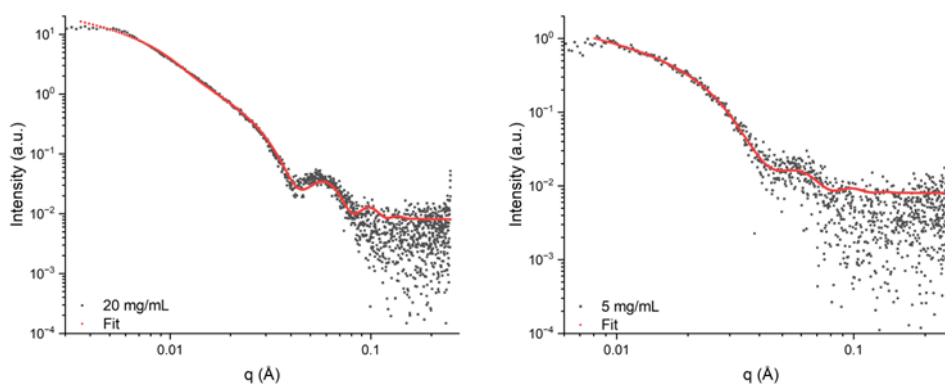


Figure 4-7. Core-shell plus Guinier-Porod fits for 20 mg/mL and 5 mg/mL P123 in H_2O

Graphene Oxide

SAS techniques are highly effective for studying the morphology of graphene oxide (GO) in aqueous environments as it provides information on the spatial distribution of atoms in the particle. When GO sheets are dispersed in water, they exhibit complex conformations, including folding, bending, and crumpling, due to interactions with the solvent and inter-sheet forces. SAS can capture these morphological changes by analyzing the scattering intensity profile,

which reflects the overall shape and surface characteristics of the GO sheets. More specifically, the distinct slopes in the scattering curve provide clues about its structural conformation. Thus, fitting SAS data to appropriate models is critical to understanding GO and the dynamics of its composites in water.

Here, to tune the solvent SLD in our measurement for better contrast between intact graphene and functional groups, we collected SANS data on a GO water dispersion at 2.4 mg/mL with three different solvent SLDs: 0.3×10^{-6} , 1.6×10^{-6} , and $5.0 \times 10^{-6} \text{ \AA}^{-2}$, achieved by mixing different ratios of H₂O and D₂O, shown in Figure 4-8. As the solvent SLD increases, the slope of the scattering pattern gets steeper. This change is due to the different contrast of atoms in GO to the solvent. Carbon and oxygen atoms have similar neutron scattering length densities of 6.65×10^{-6} and $5.80 \times 10^{-6} \text{ \AA}^{-2}$, respectively, while the hydrogen atom has a neutron SLD of $-3.74 \times 10^{-6} \text{ \AA}^{-2}$. Therefore, when the solvent SLD is $5.0 \times 10^{-6} \text{ \AA}^{-2}$, the scattering intensity from a hydrogen atom ($-3.74 \times 10^{-6} \text{ \AA}^{-2}$) is approximately 75 times that of the carbon and oxygen atoms ($\sim 6 \times 10^{-6} \text{ \AA}^{-2}$) as the square of the scattering length density difference, so the GO particles can be treated as ‘clouds’ of hydrogen atoms floating around in the solvent. This inhomogeneous distribution of scattering objects can be modelled effectively using a mass fractal model. The mass fractal dimension (D_f) of the GO particles using the mass fractal model is found to be 2.79 which matches literature value [48]. Looking at the other two solvent SLDs data, the slope in the low q region approaches -2 which is consistent with the plate-like orientation of carbon atoms. The slight deviation from -2 slope suggests minor structural features, such as sheet aggregation, folding, or wrinkling of GO.

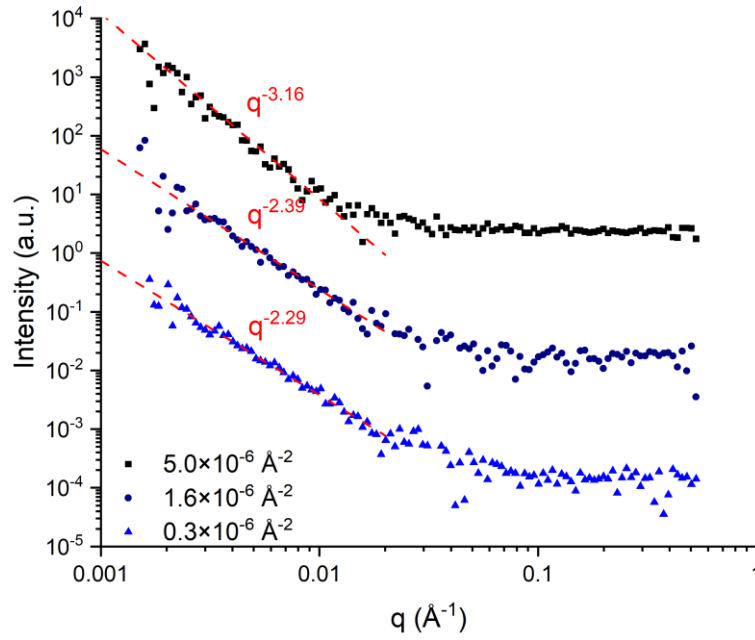


Figure 4-8. SANS data of GO in H_2O/D_2O mixture with $SLD = 0.3 \times 10^{-6}$, 1.6×10^{-6} , $5.0 \times 10^{-6} \text{ \AA}^{-2}$ with linear fit in the low q region

For a more precise model, a thin cylindrical (disk) core shell structure is used as in Figure 4-9. Since most of the oxygen containing groups (hydroxyl and epoxy) in the bulk of the graphene sheet extends out of plane, it is modeled as the ‘face’ as shown in the schematic. The edge is decorated with carboxyl and hydroxyl groups which are represented by the ‘rim’. To fit the model, the thickness (length) of the graphene basal plane is fixed at $3.35 \text{ \AA}$ which is the thickness of graphene monolayer, along with a neutron SLD of $7.557 \times 10^{-6} \text{ \AA}^{-2}$. The fitting results are demonstrated in Figure 4-10. The higher SLD in the rim (GO edges) suggests a higher H/O density on the face layer. This is in agreement with the GO structural model proposed by Dimiev, Alemany, and Tour in which the carboxyl group ($-\text{COOH}$) dominates the edges while dangling H at defect sites and hydroxyl groups ($-\text{OH}$) that extend out of the basal plane contribute to the faces [52]. This also explains why the measurements deviated from the disk model in the spectra obtained at 1.6×10^{-6} and $5.0 \times 10^{-6} \text{ \AA}^{-2}$. The scattering intensity from

the randomly distributed H atoms are less dominant at $0.3 \times 10^{-6} \text{ \AA}^{-2}$, making the whole structure appear more like a flat disk.

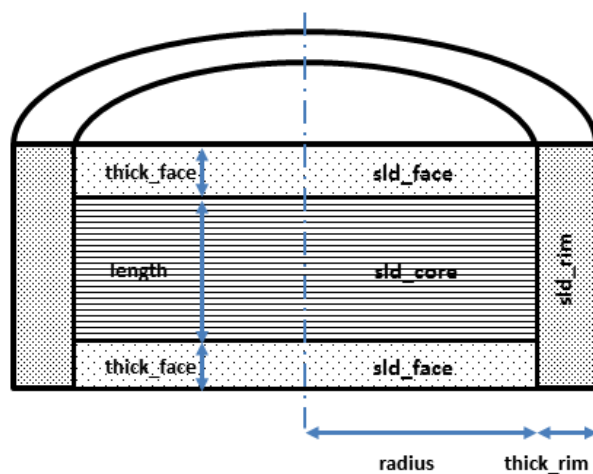


Figure 4-9. Schematic of the cylindrical (disk) core shell model used to model GO [50]

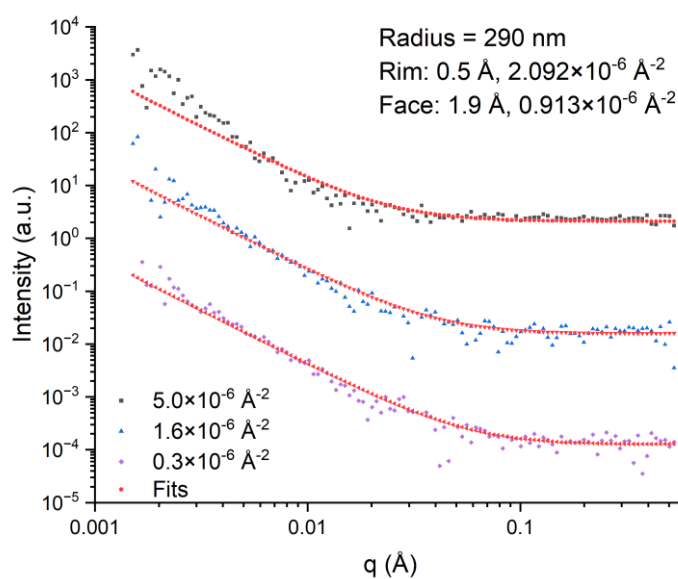


Figure 4-10. Cylindrical core shell fits on 2.4 mg/mL GO in water/D₂O dispersion. Inset text is the fitting result that best fits all three measurements

P123/EMImTFSI Micelle

EMImTFSI is a water immiscible IL, but with the presence of P123, it could be emulsified into nanosized droplets inside the P123 micelle and dispersed in water. Using SAS techniques could give us more insight into how the concentration of the two species affects the overall dimension of the micelles as well as the distribution of the ions within the micelles. Both SAXS and SANS measurements were made on this IL/P123 dispersion with weight ratios ranging from 1:1 to 3:1. This information could clarify the structure of the surfactant in bulk IL electrolyte.

The SAXS profiles of these samples have two distinct shapes which are shown in Figure 4-11. On the left-hand side, where the samples have relatively low P123 and IL concentrations, the curves have an oscillatory behavior in the high q region near the instrument limit and a plateau in the low q region. While on the right, instead of a plateau, the high concentration profiles showed a tilted linear trend in the low q region.

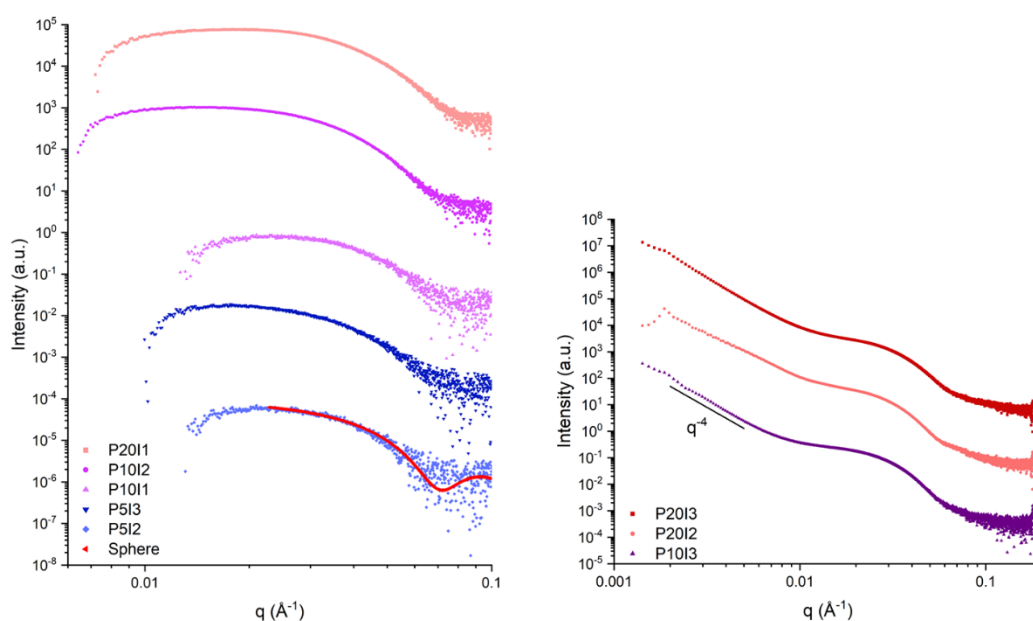


Figure 4-11. SAXS data of P123 and EMImTFSI in water. Left and right figures show two distinct scattering patterns. The red line in the left figure is a sample fit of a sphere. The numbers after P and I in the sample abbreviations denote for the concentration of P123 in mg/mL and EMImTFSI to P123 ratio respectively

Disregarding the drop at extremely low q values from data processing and the noisy background region at high q values in the lower concentration samples, the patterns indicate a spherical structure. Considering that the IL ions interaction with the PEO region of P123 is favored due to the shielding effect of the extra methyl group in PPO [53], the IL droplet is interacting with one layer of PEO, followed by PPO and another PEO layer. Because the surfactant concentration is relatively low so that cylindrical or lamellar micelles are not favored as reported in [51], which is also reflected from the plateau in the low q region, the spherical micelle structure in Figure 4-12 is considered.

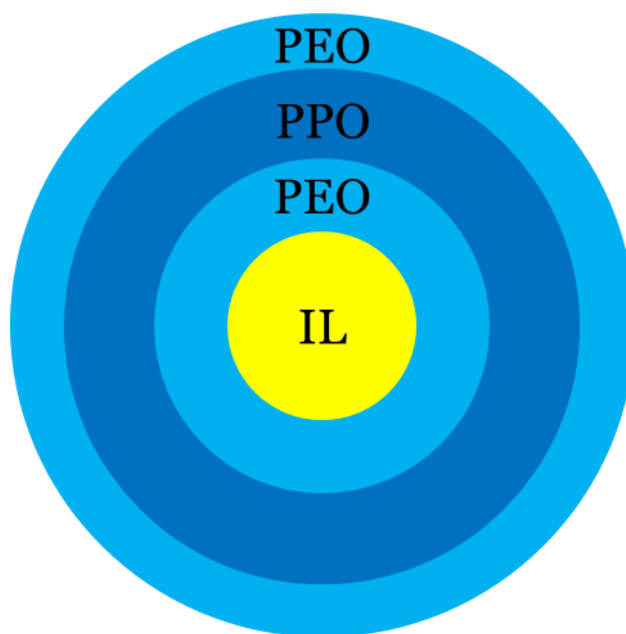


Figure 4-12. Schematic of EMImTFSI/P123 micelle in water

To model this structure in SasView, a spherical core multi shell model is employed. For the lower concentration samples shown in the top figure, the fitting assumes a homogenous micelle dispersion, and water only interacts with the outer PEO layer. Also to reduce the total number of fitting parameters and avoid overfitting, the IL droplet and the inner layer of PEO are treated as the core, and the shell does not include water as well. Given these assumptions, the fitting results are recorded in Table 4-4. This is obviously not a realistic fit, especially to the

P5I2, P5I3, and P10I1 samples, as the PPO volume becomes negligible. However, the general trend is that the increasing amount of IL results in an increase in micelle radius.

Table 4-4. Fitting results using spherical core multi-shell fit

Sample	Core Radius (Å)	PPO Thickness (Å)	PEO Thickness (Å)	Total (Å)
P5I2	52.15	0.00	23.75	75.90
P5I3	44.93	0.00	34.48	79.41
P10I1	50.95	0.00	17.56	68.51
P10I2	52.34	21.21	9.28	82.83
P20I1	45.92	22.41	5.40	73.73

To extract more information from the data, more details from previous fits are implemented (16% solid content in outermost shell), and the volumetric ratio of each layer is fixed by applying a fixed ratio between the thicknesses. In this case, the PEO layers are set to distribute equally inside the core and outside the PPO layer. The fitting results are summarized in Table 4-5 below. The total micelle size is found to be smaller with an increasing IL/P123 ratio, which is in contradiction with the trend previously found. This may come from the assumption of the solvated PEO shell. When IL/P123 ratio increases, the swelling of the PEO shell is less significant, resulting in a smaller micelle size. This fitting method has yielded more significant results compared to the one above. Though some excess features in the fitted profile were absent in the actual measurement, this core-shell model is still found to produce a better fit than a simple sphere model shown in Figure 4-13, as the spherical fit extends outside of the error bar. Therefore, this core-shell (micelle) model will be carried out in later analysis.

Table 4-5. Fitting results using the fixed ratio model with mixed IL/PEO core and solvated shell. The samples are sorted with a descending ratio of IL/P123

Sample	Core Radius (Å)	PPO Thickness (Å)	PEO Thickness (Å)	Total (Å)
P5I3	58.2	5.8	5.5	69.5

P5I2	63.5	8.9	7.9	80.3
P10I2	61.3	8.6	7.6	77.5
P10I1	56.9	13.5	10.7	81.1
P20I1	54.5	12.9	10.2	77.6

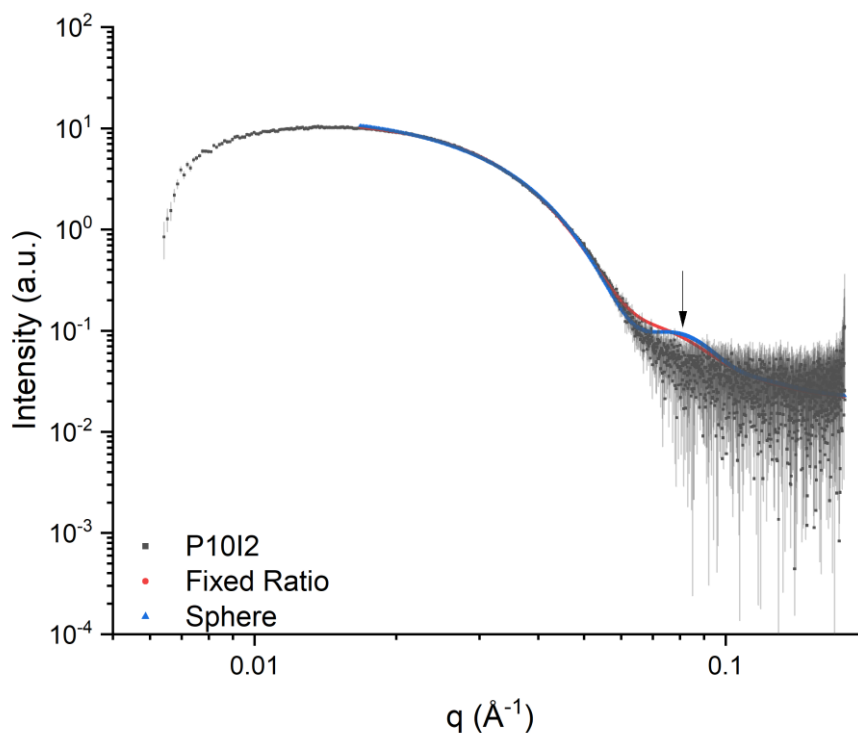


Figure 4-13. The fixed ratio fit compared to spherical fit on P10I2. Arrow denotes where the fit deviates outside the error bar

As demonstrated in Figure 4-11, the three other scattering patterns obtained from P123/IL with relatively higher concentrations all demonstrate a linear behavior in the low q region, in addition to the singular peak in the other samples. The slope of these linear regimes approaches -4. Note that this is not the same slope as mentioned before in the P123 fitting, as the Porod model only applies to the high q region. A slope of -4 in the low q region typically corresponds to large (high correlation length) and dense (high SLD) aggregates beyond the detection limit of the instrument. This suggests that at high IL content, there is not enough P123 to encapsulate IL in the form of spherical micelles, thus forming larger aggregates. To fit these data, a

summation of a power law with -4 slope and the fixed ratio core multi shell model used previously is used, and the results are displayed in Figure 4-14 and Table 4-6 below.

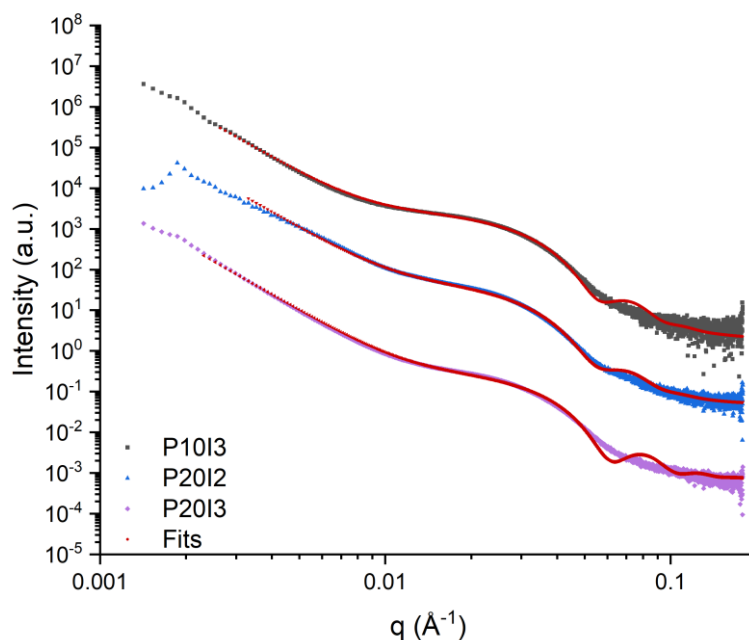


Figure 4-14. Fits from more concentrated samples with summation of power law and core multi shell model

Table 4-6. Fitting results using a summation of a power law and the fixed ratio core multi shell model. The samples are sorted with a descending ratio of IL/P123

Sample	Core Radius (Å)	PPO Thickness (Å)	PEO Thickness (Å)	Total (Å)
P10I3	76.0	7.6	7.2	90.8
P20I3	71.1	7.1	6.7	84.9
P20I2	60.1	8.5	7.5	76.1

Combining the results from both fits, the IL/PEO core size is summarized in the bar chart in Figure 4-15. The core size is plotted instead of the total micelle size since IL has a much stronger contrast than the other species in the system, giving more precise insight into the

micelle dimensions. It is found that higher IL and P123 concentrations produce larger droplets within the concentration range we studied. More IL would increase the core size, and more P123 reduces the core size, except for the 5 mg/mL P123 samples.

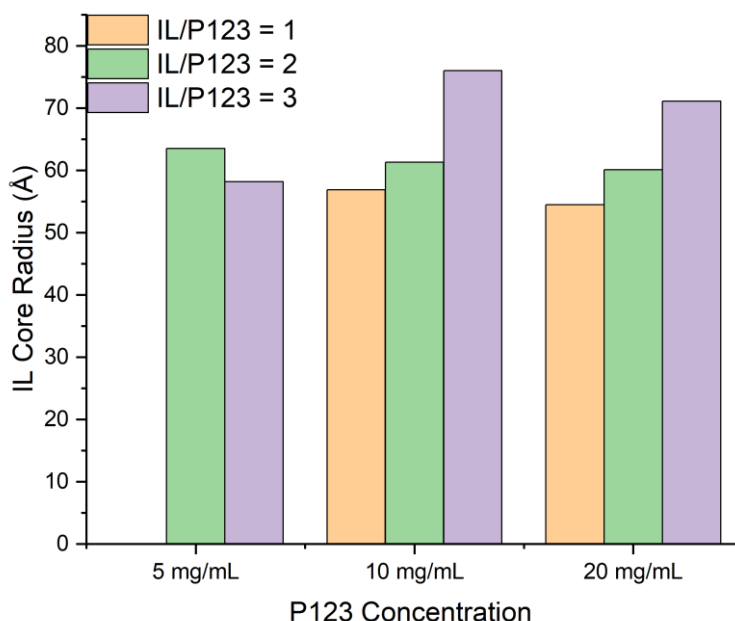


Figure 4-15. Impact of IL and P123 concentrations on IL droplet sizes

Comparing the SANS fitting results in the figure above to DLS measurements on the 20 mg/mL P123 sample series shown in Figure 4-16, the DLS measured the micelle sizes (18.6 nm, 18.6 nm, 26.9 nm respectively) to be slightly larger than that of the SAXS. This is because DLS measures the hydrodynamic size of the particle which represents the entire spatial range the molecule occupies as it diffuses through the solvent. While in SAS techniques, the radius of gyration is the primary size parameter which is a mass-weighted range of distribution, with the diffuse layer being partially disregarded. Even so, the same trend is observed. A bimodal size distribution is found in P20I1, which arises from micelles with and without an IL core. The micelle sizes of P20I1 and P20I2 with the IL core are identical, and from P20I2 to P20I3, an increase in micelle size is observed. Note that signals are caught above 100 nm only in P20I2

and P20I3 which could explain the -4 slope in their low q region. These aggregates could potentially adsorb on graphene surfaces as observed in [42]. However, they could result in inhomogeneity in the final composite, damaging the performance.

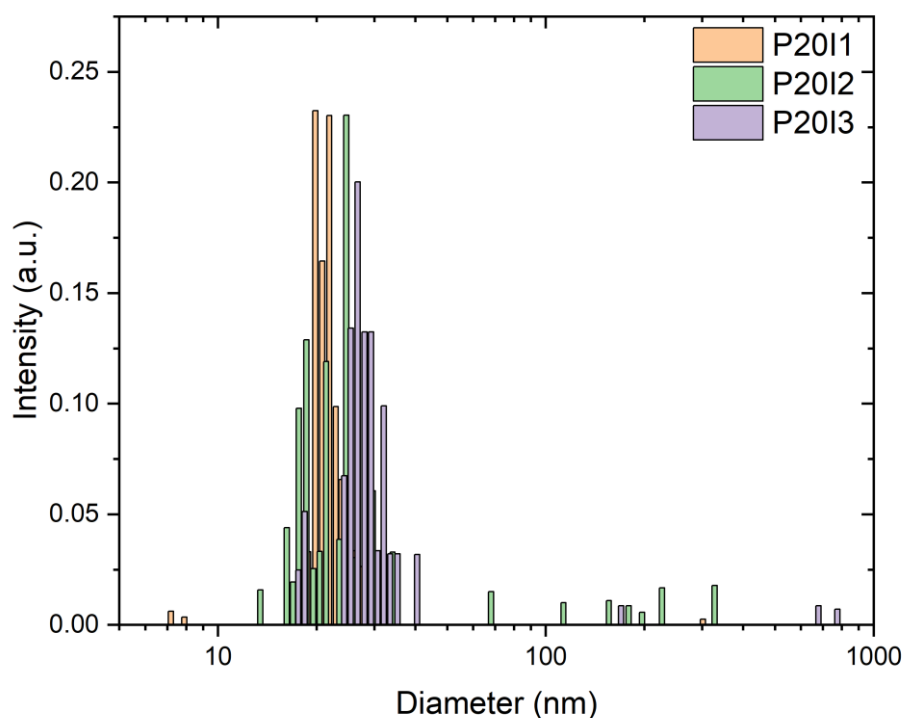


Figure 4-16. DLS measurements on P20I1, P20I2, and P20I3 micelle sizes

In addition to SAXS analysis, SANS data collected on mixtures with the same ratio but below CMC is investigated to eliminate the effect of the structure factor. Using the same core multi-shell model as established in this section previously, the fitting is demonstrated in Figure 4-17, and the fitting parameters are presented in Table 4-7. Note that all the measurements were done at solvent $SLD = 5.0 \times 10^{-6} \text{ \AA}^{-2}$, as this is the only solvent SLD that produces reasonable signal. With increasing IL/P123 ratio, the micelle becomes smaller. Note that in the 3:1 sample, the IL droplet becomes significantly smaller, because the concentration of the surfactant (0.6 mg/mL) is too low to adsorb IL molecules and form micelles. When the concentration is

doubled, a decrease in micelle size is seen. These trends are in contradiction to previous observation in SAXS. This could be a result of favored compact structure forming as the concentration nears the CMC. Nevertheless, a spherical micelle conformation is favored in the interaction between IL and P123 in water, even at concentrations below the CMC.

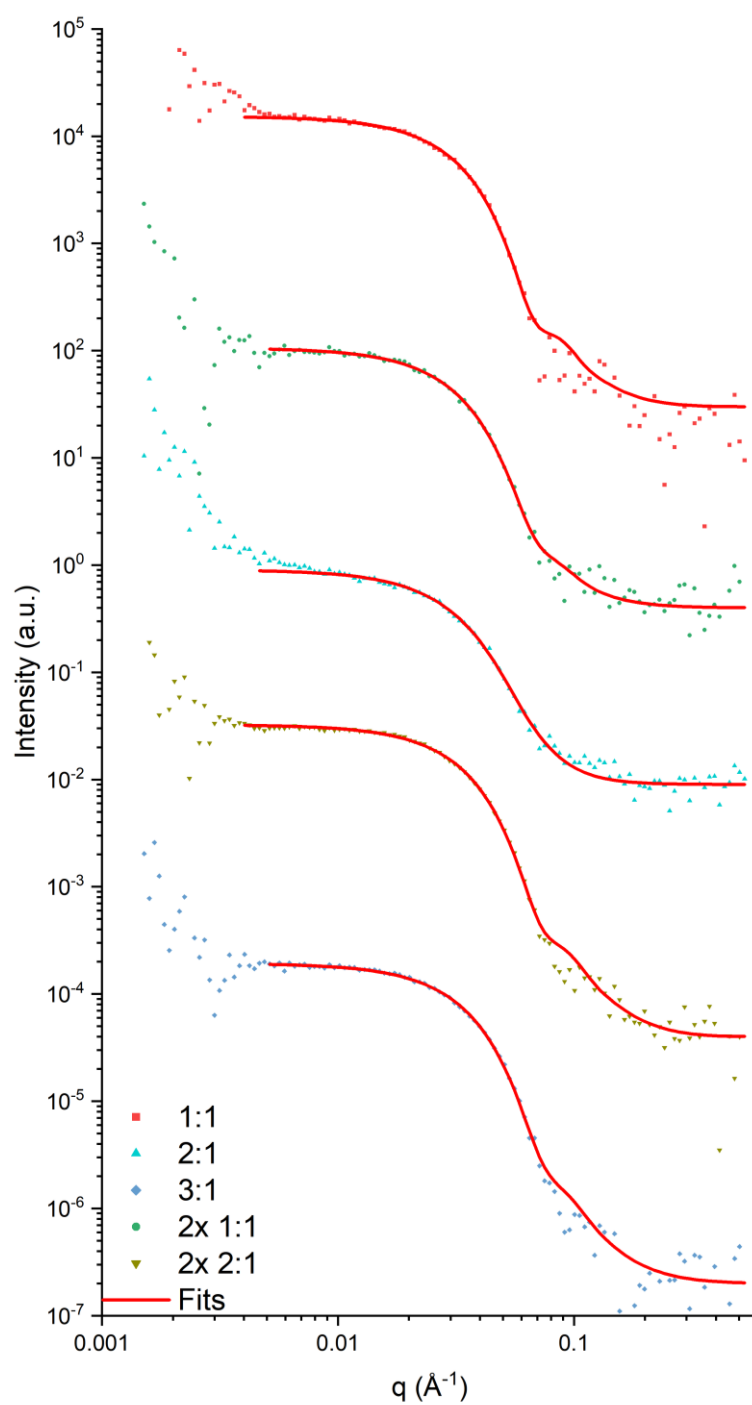


Figure 4-17. The fixed ratio fits to SANS data at solvent $SLD = 5.0 \times 10^{-6} \text{ \AA}^{-2}$ from dilute IL/P123 samples. The ratios in legend correspond to IL/P123 ratio. The total concentration is 2.4 mg/mL, or 4.8 mg/mL if labeled 2x

Table 4-7. Fitting results of SANS data on IL/P123 spherical micelles

Sample	Core Radius (Å)	PPO Thickness (Å)	PEO Thickness (Å)	Total (Å)
1:1	43.2	10.2	8.1	61.5
2:1	43.5	6.1	5.4	55.0
3:1	22.8	2.3	2.1	27.2
2x 1:1	39.2	9.3	7.4	55.9
2x 2:1	40.8	5.7	5.1	51.6

GO/P123/EMImTFSI Dispersion

In this section, the interaction of graphene oxide with the P123/IL mixture studied above is studied with SANS. Previous studies on polymeric surfactant and graphene oxide have shown that the surfactant effectively flattens the GO sheet in dispersion, and it could also be concluded from Figure 4-18 below by the -2 slope in the low q region [48]. In this case the solvent SLD at $5.0 \times 10^{-6} \text{ Å}^{-2}$ made the GO sheet invisible. Instead of forming spherical micelles, P123 adsorbed onto GO and formed a flat layer. It has also been reported that the hydrophobic interaction between GO and PPO is favored [54], so it is expected that GO and IL occupies the hydrophobic and hydrophilic section of the surfactant respectively. In this study, the SANS profiles were acquired on dispersion of GO/IL/P123 at fixed compositions to get a better understanding of how they assemble into the electrode material of our interest.

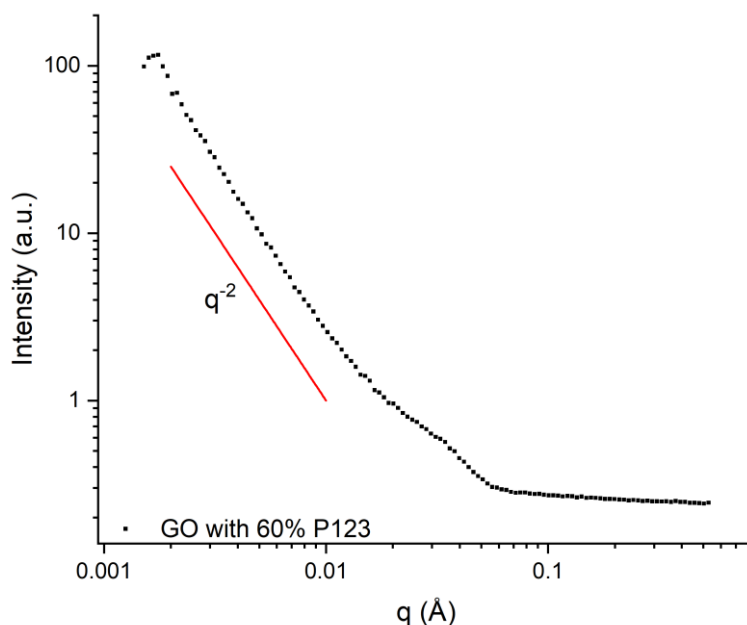


Figure 4-18. SANS data collected at $5.0 \times 10^{-6} \text{ \AA}^{-2}$ of GO/P123 particles.

Figure 4-19 demonstrates the scattering profile of a composite with GO:P123:IL ratio of 2:3:3. As summarized in Table 4-8, the measurements taken at 0.3×10^{-6} , 1.6×10^{-6} , $5.0 \times 10^{-6} \text{ \AA}^{-2}$ are ignoring P123, P123/IL (partially), and GO respectively, as certain species becomes invisible to neutron when its SLD is close to that of the solvent. The slope of the top two patterns demonstrates a slope of -2 which in the low q region suggests a flat and planar structure, GO in this case. In the measurement at $5.0 \times 10^{-6} \text{ \AA}^{-2}$, in which the planar structure of GO is invisible, a spherical/micellar plus planar structure was observed. Subsequent fitting yields a radius of 62 $\text{\AA}$ and a sheet thickness of 4.1 $\text{\AA}$. The radius obtained is likely the radius of the IL/PEO droplet according to previous results on micelle sizes, and the sheet thickness corresponds to the layer adsorbed onto GO. Given this knowledge, the overall structure of this composite in dispersion can be constructed as shown in Figure 4-20. P123 attached to GO surface and flattened it, while large spherical IL/P123 micelles were embedded on the PEO layer. This model also suggests a planar arrangement of the small IL droplets, as in the $0.3 \times 10^{-6} \text{ \AA}^{-2}$ measurement, minimal

spherical signals were caught. This model could also explain the work-in cycles phenomenon observed in the previous chapter. Since the GO surface cannot be fully occupied by spherical IL, an external IL source is needed to fully construct the double layer. Compared to the observation of a ‘spherical cap’ of adsorbed IL/P123 complex through AFM in [42], The difference between these two arises from the high surface tension of water on the IL/P123 interface, causing the spherical morphology observed by SAS.

Table 4-8. GO, P123, and EMImTFSI neutron SLDs and their visibility in the solvents (+: visible, -: invisible)

Neutron SLD ($10^{-6} \text{ \AA}^{-2}$)		D ₂ O/H ₂ O		
		0.3	1.6	5.0
GO	5.2	+	+	-
P123	0.4	-	-	+
EMImTFSI	2.4	+	-	+

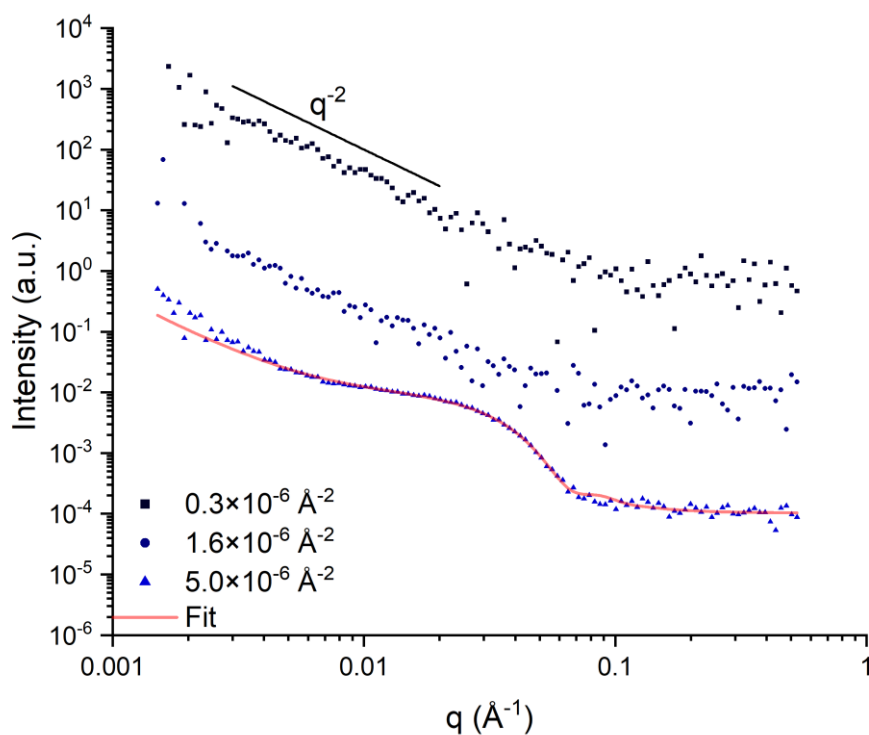


Figure 4-19. SANS data GO/P123/IL composite dispersed in H_2O/D_2O mixture with solvent SLD = 0.3×10^{-6} , 1.6×10^{-6} , $5.0 \times 10^{-6} \text{ \AA}^{-2}$

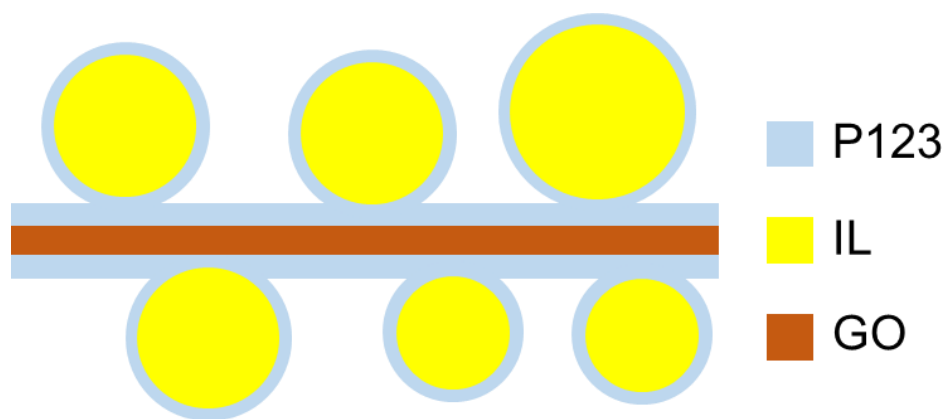


Figure 4-20. Proposed structure of GO/P123/EMImTFSI composite particle dispersion in water.

Solid Composites

To correlate the structure of the pressed solid composite electrodes used in supercapacitors, the electrode powders were roller-pressed to thin films ($\sim 20 \text{ \mu m}$) and characterized by SANS

to identify characteristic structures within. Figure 4-21(left) demonstrates the collected data on all composites along with rGO and IL-free composite as the control. The number on the left below each curve is the slope on the left most end. The SANS profiles showed a shift in concavity in the low-to-intermediate q region except for 20% P(12), 40% P(2), and 60% P(2), indicating the onset of a new feature. This is more pronounced in the Kratky plot in Figure 4-21(right). The shift for rGO occurs at a correlation length of roughly 100 Å. As more surfactant/IL is introduced, the transition point shifts towards lower q /higher correlation length. This likely corresponds to the size of the small aggregates formed after freeze drying the dispersion. A small number of rGO sheets are held together by the P123/IL electrolyte, and when compressed, voids may form between these aggregates. The slopes in the high q region remain negative instead of a plateau in the dispersion samples. This suggests structures at a much smaller scale as the background intensity should remain constant in the high q region.

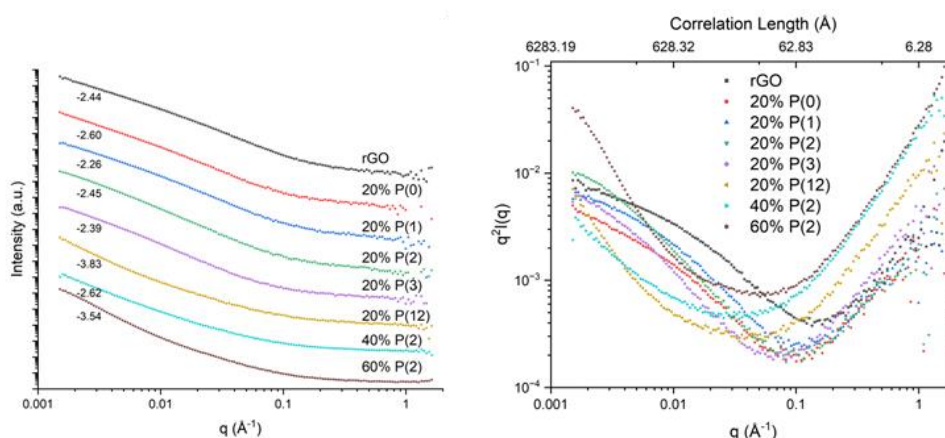


Figure 4-21. SANS profiles of solid composite electrodes (left) and corresponding Kratky (q vs. $q^2 I(q)$) plots (right)

To account for these features across all ranges, a Gaussian peak is applied in addition to the Guinier-Porod model. The Gaussian peak can capture local ordered structures/crystallinity, for example restacked rGO sheets. It is also found that the features identified previously in the high q region can be captured by a broad peak as the size of local ordered structure may span multiple orders of magnitude. This model applies to the samples with lower IL/P123 content,

and the fitting results are summarized in the table below. The correlation length of rGO is within the magnification of restacked rGO. With the addition of the surfactant, the correlation length increases dramatically since without water the surfactant promotes sheet aggregation. When IL is then introduced but limited, it acts like a spacer as expected. However, when all the small aggregates are pressed to each other, IL cannot access all inter-aggregate space. With increased IL content, the excess IL fills up the space and holds everything together causing the extremely large correlation length as in 20%P(3). This matches with the observation in previous electrochemical measurements in which work-in cycles are needed to reach peak performance when insufficient IL is used. In the Guinier-Porod fit, R_g only increases with the addition of IL instead of P123, which also suggests that the interlayer and inter-aggregate spaces are filled and expanded with IL droplets. The Porod exponent above 3 suggests a surface fractal behavior by IL/P123, which also support the above argument.

In the case of excess IL or P123 (20% P(12), 40% P(2), and 60% P(2)), such model does not produce a reasonable fit. Excess electrolyte completely occupies rGO surfaces and inter-aggregate spacing. The composite transforms to a dispersion of rGO in IL/P123 electrolyte from IL/P123 electrolyte in rGO matrix. The fitting parameters are presented in Table 4-9 with sample fits in Figure 4-22. The fractal dimension below 3 suggests a mass fractal. With increasing amount of IL/P123 the fractal dimension approaches 3 which means denser structure, as the excess electrolyte fills up the void spaces. Combined with the increase in volume fraction, this fractal contrast likely originates from IL/P123 that is not packed by rGO sheets. As shown in Figure 4-23, during compression, the excess IL/P123 comes out from inter-layer space and fills up the inter-aggregate space. This is desirable for the electrode material as it fully utilizes the rGO surface.

Table 4-9. Fitting results on compressed composite electrode SANS using a summation of Guinier-Porod model and Gaussian peak or a fractal model. Samples are listed with ascending IL/P123 electrolyte to rGO ratio

Sample	Correlation Length (Å)	R_g (Å)	Guinier Dimensionality ($3 - s$)	Porod Exponent (d)
rGO	36.7	23.2	0.60	2.98
20% P(0)	1112.3	23.2	0.45	3.08
20% P(1)	321.2	30.9	0.51	3.09
20% P(2)	516.6	34.9	0.28	3.19
20% P(3)	7793.7	36.6	0.32	3.19
	Correlation Length (Å)	Radius (Å)	Fractal Dimension (D_f)	Volume Fraction
40% P(2)	3152	17.0	2.56	0.0643
20% P(12)	5742	14.8	2.87	0.206
60% P(2)	2778	8.5	2.95	0.629

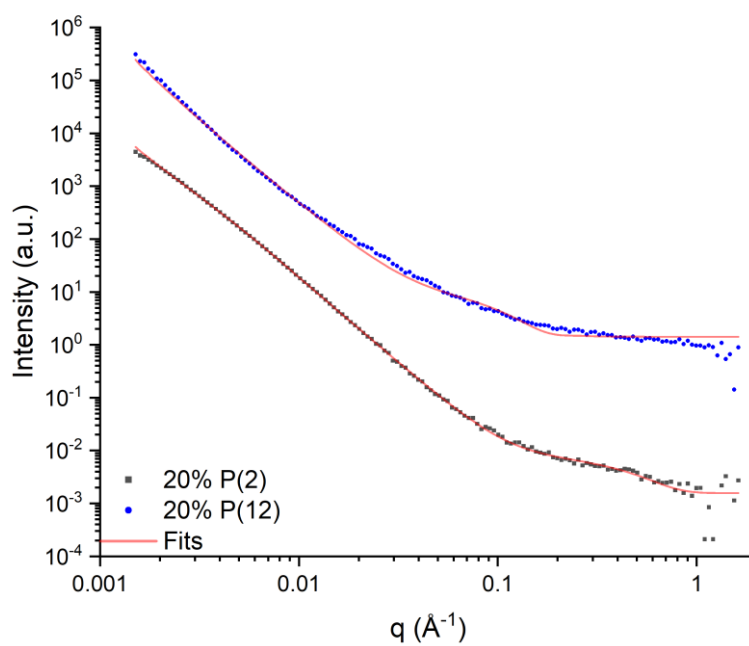


Figure 4-22. Guinier-Porod plus Gaussian fit to 20% P(2) and fractal fit to 20% P(12) solid composite SANS profiles



Figure 4-23. Effect of electrode preparation (compression) on composite structure

4.4 Conclusion

The complex dispersion system of P123, EMImTFSI, and GO was studied under small-angle X-ray and neutron scattering. The self-assembly of the block co-polymer P123 micelle in water is studied at varying concentration along with the addition of ionic liquid EMImTFSI. An intermediate state of P123 micelle formation is observed up to 20 mg/mL, while at higher concentrations the dimension of the micelle is relatively constant. The addition of the ionic liquid did not have an impact on the shape of the micelle based on their low q plateau, so they were modelled with a layered core-shell structure given that IL interacts with PEO. The ratio of IL to P123 was the determining factor for the micelle radius. At a fixed concentration of P123 above the CMC, the higher the ratio, the larger the micelle. While at concentrations below the CMC, the opposite is seen. GO has been successfully modeled with a cylinder core shell model based on previously developed theories with minor deviation due to folding and wrinkling which could be flattened by the addition of P123. Finally, a complete sandwich model was proposed by evaluating the shape of the SAS given the knowledge on the interaction between all components. In addition, the solid composite is evaluated with SANS. Higher IL composition is favored as a surface-fractal-like distribution of electrolyte in the IL/P123 content sample. At higher IL/P123 contents, the scattering becomes a mass fractal becoming almost fully dense in 60% P(2).

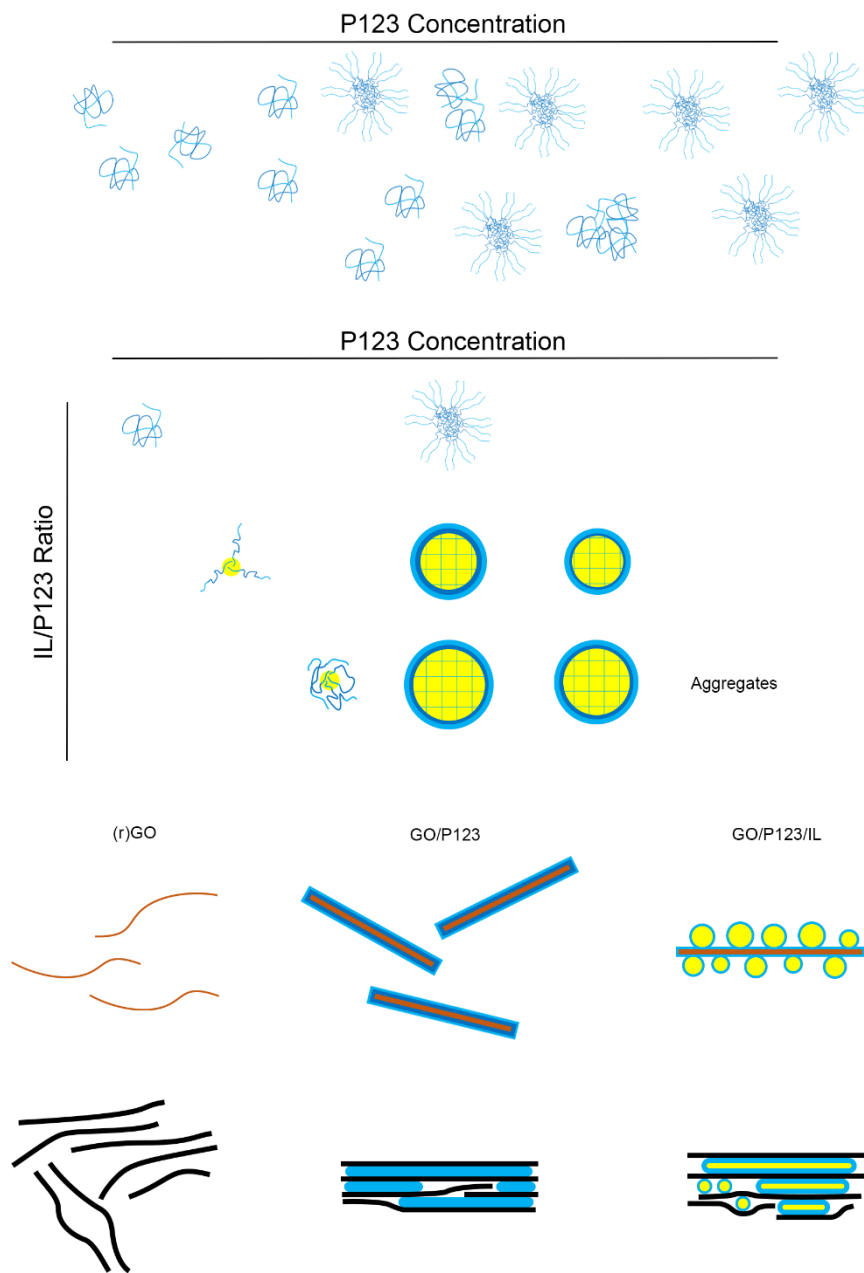


Figure 4-24. Summary of the self-assembly process among (r)GO/P123/IL and their solid composite structures

Chapter 5

Long Term Electrochemical Performance of Ionic Liquid/Non-Ionic Surfactant Electrolyte and Ion Bombarded Graphene-Based Electrode

5.1 Introduction

Room temperature ILs, characterized by their negligible vapor pressure, wide electrochemical stability window, and excellent thermal stability, offer a versatile platform for designing high-performance electrolytes. When combined with non-ionic surfactant, it shows increased double layer capacitance due to the weakened ionic correlation. The surfactant also imparts surface activity to non-surface-active IL, enabling its effective application on materials like graphene. Though this also comes with reduced stability window and increased viscosity, the overall impact on electrochemical performance can still be positive in energy storage devices.

Though this electrolyte has shown promising results in previous studies [6], the impact of electrochemical degradation on its properties has yet to be fully explored. Electrochemical degradation is a critical factor in determining the long-term performance of electrolytes where repeated charge-discharge cycles can lead to gradual deterioration. Degradation mechanisms can involve chemical breakdown, ion migration, structural changes, or the formation of unwanted by-products, all of which can significantly affect the ionic conductivity, stability, and overall efficiency of the electrolyte. This becomes especially important when the interaction between the ionic liquid and the non-ionic surfactant in the electrolyte introduces additional complexities. The surfactant molecules may undergo degradation, altering the IL wetting behavior on graphene, potentially compromising the electrolyte's integrity. Some of these factors could even lead to accelerated degradation and alter the electrolyte's effectiveness over time.

This chapter aims to investigate the electrochemical performance of the IL/non-ionic surfactant electrolyte during electrochemical degradation. By understanding how these properties evolve, the structural change at the double layer could potentially be identified. In addition, heavy ion bombardment was performed on the composite electrodes as an approach to overcome the deteriorated ionic conductivity and delayed peak performance from the high viscosity brought by the surfactant and improve the ionic conductivity.

5.2 Materials and Methods

Materials

Pluronic P123 and N-Methyl-2-pyrrolidone (NMP, 99.0%) were purchased from Sigma-Aldrich, and the IL, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMImTFSI), was purchased from Io-Li-Tec (99.5%). Dichloromethane (DCM, 99.9%) is purchased from Honeywell. All of which were used as received.

Methodologies

Electrolyte samples were made by mixing the required amount of surfactant and IL with DCM (DCM/IL: 1/1 weight ratio) in a glass vial, then stirring them using a Teflon stir bar for 1 hour, followed by drying under flowing dry nitrogen overnight. This mixing procedure was adopted since it was proven to yield the most uniform and thermodynamically stable mixture. The final mixture was then dried under vacuum at 110° C for 7 hours to remove any excess water and solvent impurities.

Three electrode measurements were carried out on the electrolytes in a clean, glass electrochemical cell (BASi Research Products, VC-2) which was covered with a Teflon cap and sealed using a silicon O-ring. A 3 mm diameter glassy carbon (GC) electrode was used as the working electrode, a Pt mesh as counter electrode and a silver wire (BASi Research Products)

was used as a pseudoreference electrode. The GC was polished before use on three different micro-cloth pads using a 1, 0.3 and 0.05 MicroPolish powder and sonicated in ultrapure water for 10 min. The Pt mesh counter electrode was cleaned by performing cyclic voltammetry in 0.5 M sulfuric acid and then sonicating in acetone and ultrapure water for 10 min. The silver wire was placed in an enclosed glass capillary with CoralPor porous glass tip and rinsed with fresh EMImTFSI after each use.

Ion bombardment samples were prepared as described in [6], also in Chapter 3. The composite powder of rGO/P123/EMImTFSI containing approximately 1 mg of rGO was pressed onto each 1/2-inch carbon coated aluminum current collector by 50 kN force. The ion beam irradiation was done at the Grand Accelérateur National d'Ions Lourds (GANIL) in Caen, France. The electrodes are loaded into the samples holder as shown in Figure 5-1. The ion beam perforated the pressed electrode perpendicularly through the holes exposed. The samples were irradiated homogeneously with Xe ions across the surface until the target flux is reached.

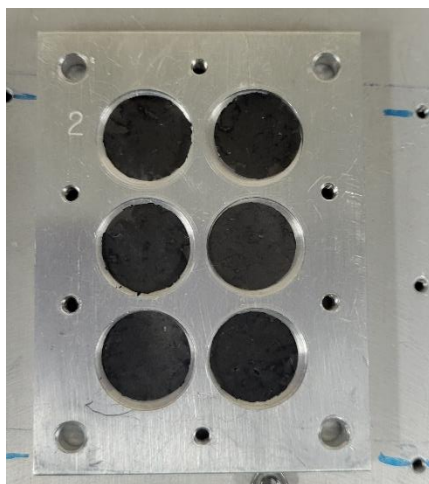


Figure 5-1. Sample holder for ion bombardment chamber.

Electrochemical testing, CV and EIS, was performed using a Biologic SP-300 potentiostat. Transmission electron microscopy (TEM) images were captured on the bombarded samples after the electrochemical testing. The composite electrode material was washed off the current

collector using DCM and centrifuged so that the electrolyte could be removed in the supernatant. 10 mL NMP is added to the dispersion, replacing DCM, to better disperse rGO. The DCM is then removed by heating at 60 °C. The final dispersion is drop casted onto copper TEM grids for characterization.

5.3 Results and Discussion

The electrochemical windows of EMImTFSI and P123/IL composite electrolytes were tested with cyclic voltammetry. Figure 5-2 demonstrates the shrinkage of the electrochemical stability window by the introduction of P123 into EMImTFSI. Note that to speed up the electrochemical degradation of the electrolyte, a cut-off current density of approximately 2 mA/cm² is used instead of the recommended 1 mA/cm² for ionic liquids [55] or even lower [34]. Few minor peaks are observed on both the pure EMImTFSI and composite electrolyte: a pair of weak redox peaks at -0.7 V vs. reference and a broad oxidative peak around 1.2 V. The redox couple is observed since the 0th cycles and its peak current remains the same before and after cycling, so they are likely caused by sample impurities which are also electrochemically active. On the other hand, as cycling progresses, the oxidative peaks gradually became more and more prominent, especially in the pure EMImTFSI. This trend is observed for both of the composite electrolyte, which is believed to come from the decomposition product generated beyond the stability window [34].

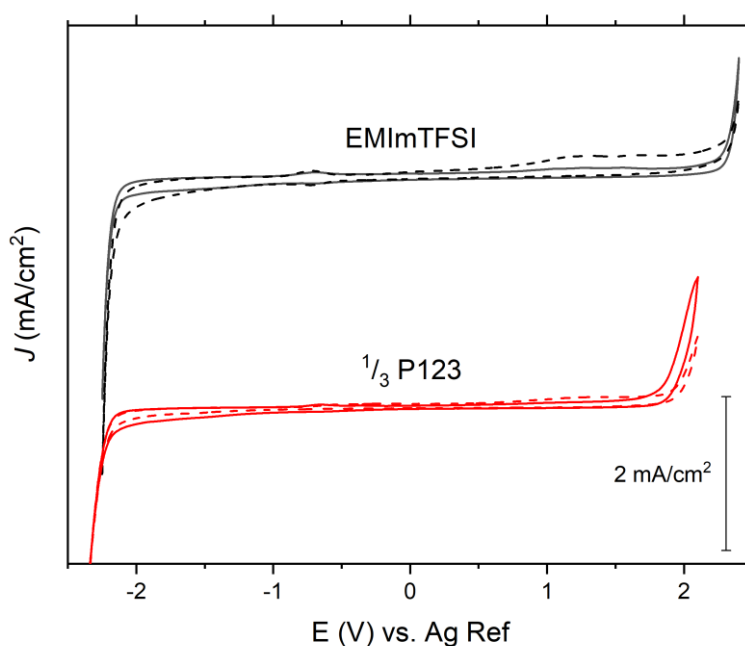


Figure 5-2. Comparison of CVs for pure EMImTFSI (black) and EMImTFSI/P123 composite (red) electrolyte within their electrochemical voltage window. Solid and dashed lines represent the 0th and 1000th cycle respectively.

To study the effect of electrochemical degradation on electrolyte performances, EIS data were collected before and after 1000 cycles on these electrolytes using a perturbation of 10 mV at frequencies ranging from 7 MHz to 0.1 Hz. Figure 5-3 (left) shows the Nyquist impedance plot along with its admittance plot collected on the composite electrolyte at OCV while the fitting of the experimental data is also presented by the dashed line. The plot displays a tilted straight line which becomes curved at low frequencies, while in the high frequency domain, the plot also shows some unexpected behavior which is clearly indicated by the Nyquist admittance plot at the bottom. Both of these frequency ranges should be dropped in future analysis. The red dots in the impedance plot are the fitting of the experimental data to a resistor-constant phase element (R-CPE) equivalent circuit at selected frequency range. This is able to determine the differential capacitance of the electrolyte at the electrode surface which has been demonstrated in previous literatures [34], [56].

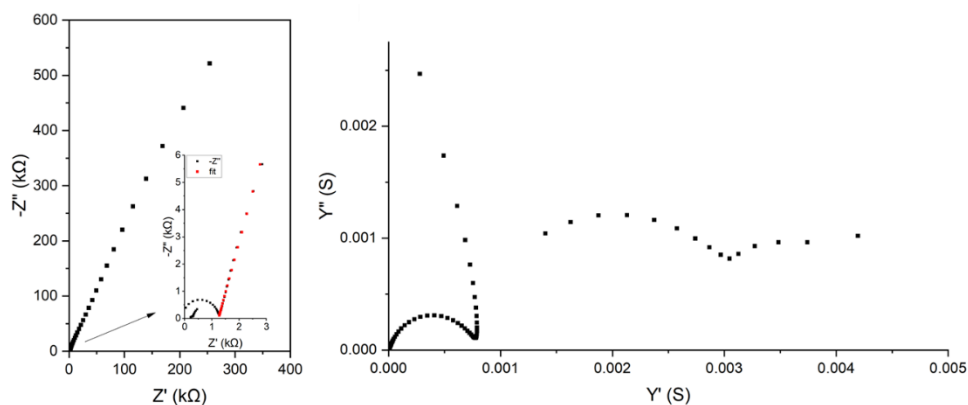


Figure 5-3. Nyquist impedance (left) and admittance (right) plot of P123/EMImTFSI electrolyte

Figure 5-4 shows the Nyquist plots obtained from fresh and cycled electrolyte at various potentials. In the fresh electrolyte, the impedance spectra follow general CPE behavior with a tilted tail. Interestingly the spectrum at -0.6 V vs. reference deviates the most at low frequencies which could correspond to the minor redox couple observed in the CV plot. On the other hand, in the cycled electrolyte the spectra became more and more tilted as the potential moves further away from OCV until a secondary semicircle could be extrapolated, indicating the onset of the decomposition of the IL. Comparing the two plots, the cycled electrolyte has shown reduced capacitive behavior suggested by the reduced slope across the potential range measured.

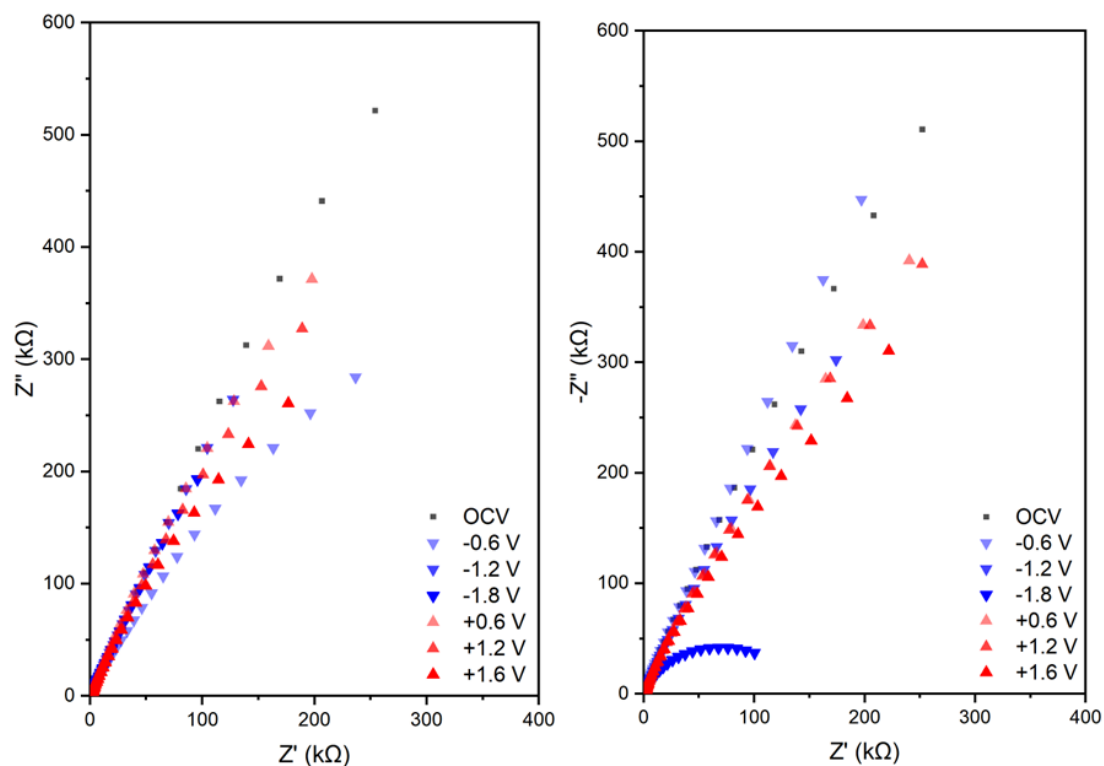


Figure 5-4. Comparison of EIS spectra at selected potential before (left) and after (right) cycling

As shown in Figure 5-5, after 1000 cycles, EMImTFSI turned from colorless to a faint yellow color, whereas in the composite electrolyte, a yellow liquid byproduct settles at the bottom of the vial which could be homogenized with gentle mixing. This liquid is then characterized by ^1H nuclear magnetic resonance (NMR) spectroscopy and Raman spectroscopy. The NMR spectrum of the EMImTFSI after cycling remained identical. This suggests that the EMIm $^+$ cation remains intact while the TFSI $^-$ anion is degraded. In the composite electrolyte, however, a mild upfield shift to the right is observed with no new peaks forming. This is the result of chain scission of the P123 chain. With shorter chains, the shielding effect becomes weaker, allowing oxygen to withdraw more electrons around the proton and causing the upfield shift.

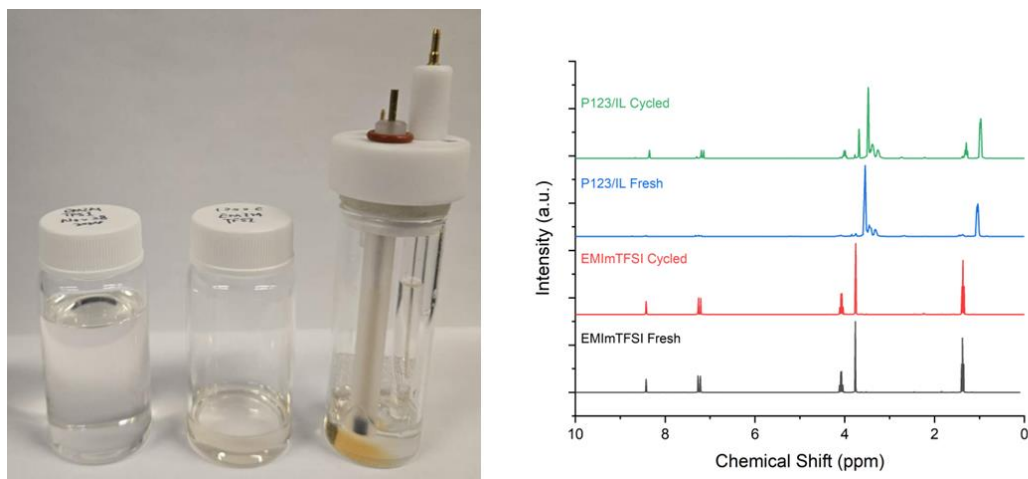


Figure 5-5. Effect of cycling on the physical appearance (left) and NMR spectra of P123/EMImTFSI electrolytes

As it is found that cycling only negatively impacts the capacitive behavior of the composite electrolyte, which eliminates the electrolyte effect on the performance of the device, the ionic transport becomes the most probable cause of the delayed peak performance. As an attempt to resolve this issue, ion bombardment has been performed on the pressed electrode. The CVs at 5 mV/s of the bombarded electrodes are shown in Figure 5-6. The flux 10^{11} ions cm^{-2} has produced the most capacitive electrode. However, this is only half the capacitance of the material before bombardment which will be investigated later in this chapter.

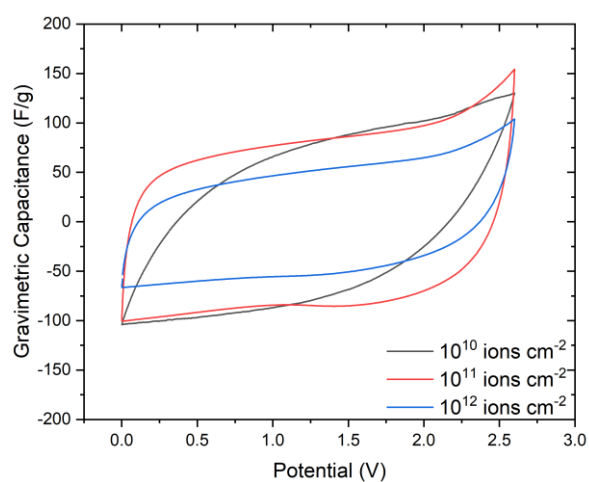


Figure 5-6. CVs of bombarded samples measured at 5 mV/s

Despite the poor capacitance from the bombardment, their charge transfer resistances (R_{ct}), obtained from the semicircle size in EIS high frequency region, were tracked for 1000 cycles in Figure 5-7. Compared to the original material which only has single-digit R_{ct} , these bombarded samples are extremely resistive, matching their CV shapes which deviate from a rectangle.

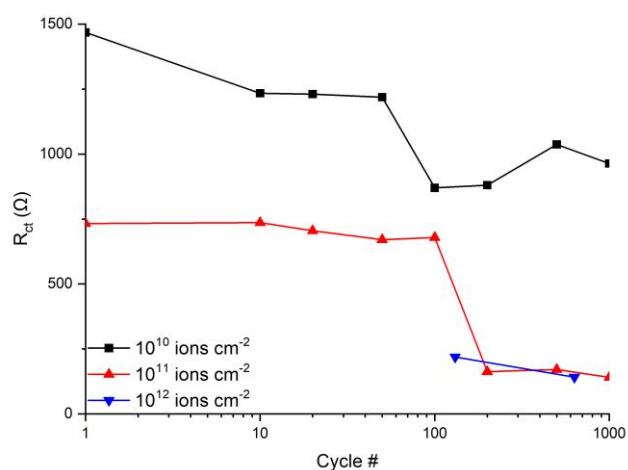


Figure 5-7. Approximated R_{ct} of samples at different fluxes from EIS spectra at OCV

Looking at the TEM images captured on the 10^{11} ions cm^{-2} sample in Figure 5-8, no clear holes can be observed. The Raman spectra also showed no increase on the I_D/I_G ratio before and after bombardment. The reason for this might be the result of the incident beam which in this case is 0° . At this incident angle, the ion beam may penetrate the graphene sheet without leaving any damage. Foller has demonstrated ion induced defects on drop casted GO using a minimum angle of incidence at 1° [57]. Without any effect on the graphene, the high energy heavy ion potentially shatters the ionic liquid molecules [58] or P123 [59], causing the high R_{ct} and reduced voltage window measured above. The sudden decrease of R_{ct} at around 100 cycles is a result of the fresh IL electrolyte replenished during cell assembly gradually replacing the damaged electrolyte as the cycling progresses.

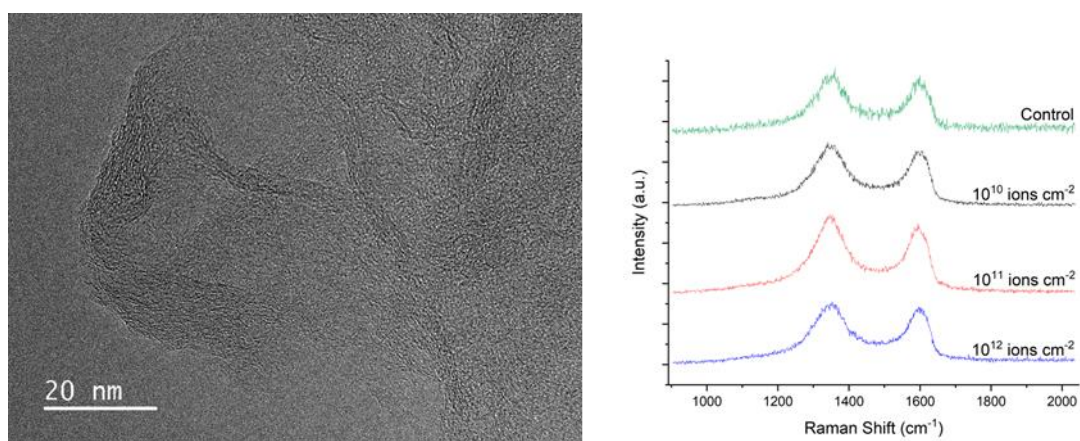


Figure 5-8. TEM image of bombarded sample (10^{11} ions cm^{-2}) (left) and Raman spectra of all bombarded samples compared to as prepared sample (right)

5.4 Conclusion and Future Work

In this chapter, the degradation effect of the electrolyte is briefly evaluated by EIS spectroscopy. It was found that cycling beyond the electrochemical stability window deteriorates the capacitive behavior of the electrolyte. Chemical analysis through NMR confirmed that the cation structure remained intact.

The attempt to improve the rate performance of the composite electrode material by ion bombardment was unsuccessful due to the incident angle of the ion beam. Additionally, the ion beam caused damage to the P123 and EMImTFSI molecules, leading to increased resistive behavior observed in CV. However, continuous cycling demonstrated an improvement as fresh ionic liquid (IL) was electrostatically driven into the electrode.

Chapter 6

Conclusions and Future Works

This thesis explored the preparation and performance of graphene-based composite electrode materials utilizing a P123/EMImTFSI electrolyte, with a focus on understanding the material's structural dynamics and electrochemical performance.

The self-assembly of the complex dispersion system comprising P123, EMImTFSI, and graphene oxide (GO) was thoroughly studied using small-angle X-ray and neutron scattering. Detailed models were proposed to describe the conformation of all particles formed in a water media. P123 unimer-micelle intermediate structures were captured, which stabilize at higher concentrations. The ionic liquid was shown to integrate with the hydrophilic regions of the micelles, forming spherical bilayer structures whose size is determined by the IL-to-P123 ratio. Furthermore, GO was successfully modeled using a cylinder core-shell model with deviations due to folding and wrinkling. The surfactant P123 was found to be able to flatten (r)GO sheets. These findings provide a deeper understanding of the assembly process and the resulting material architecture. Previously studied solid composite compositions are found not able to reach the full potential of rGO electrode as the surfaces were not fully covered by IL/P123 electrolyte.

Electrochemical measurements revealed the impact of long-term cycling and electrolyte degradation on performance. Cycling beyond the electrochemical stability window was found to degrade the capacitive behavior of the electrolyte, although NMR analysis confirmed the cation structure remained intact. Continuous cycling, however, improved performance by electrostatically driving fresh ionic liquid into the electrode, partially mitigating degradation effects.

Efforts to enhance the rate performance of the material through ion bombardment yielded mixed results. While the approach aimed to create perforations in graphene sheets to facilitate interplanar ion transport, the ion beam's incident angle caused damage to P123 and EMImTFSI molecules, leading to increased resistive behavior. Despite this, the findings highlight the potential of this strategy to improve ion accessibility and address delayed peak performance in such systems.

Future works

Although this study provides a detailed exploration of the self-assembling process, the actual structure formed within a compact electrode remains unexamined. Future investigations could address this gap using quasi-elastic neutron scattering (QENS) to analyze the molecular dynamics of electrolytes at graphene surfaces when fully packed to a dense electrode. This approach would enable a deeper understanding of the adsorption of the electrolyte in a real electrode and eventually how capacitance depends on the self-assembly of mixed electrolytes at the interface. In addition, despite failed as demonstrated in Chapter 5, it is still worth trying to synthesize the same material with holey graphene to evaluate the effect of improved ion transport on the device performance.

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Author: Jenei Váttamás, Oleg Borodin, Dmitry Bedrov, et al

Publication: The Journal of Physical Chemistry C

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Decorating Graphene Oxide with Ionic Liquid Nanodroplets: An Approach Leading to Energy-Dense, High-Voltage Supercapacitors

Author: Zimin She, Debasis Ghosh, Michael A. Pope

Publication: ACS Nano

Publisher: American Chemical Society

Date: Oct 1, 2017

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Ultrathin Planar Graphene Supercapacitors

Author: Jung Joon Yoo, Kaushik Balakrishnan, Jingsong Huang, et al

Publication: Nano Letters

Publisher: American Chemical Society

Date: Apr 1, 2011

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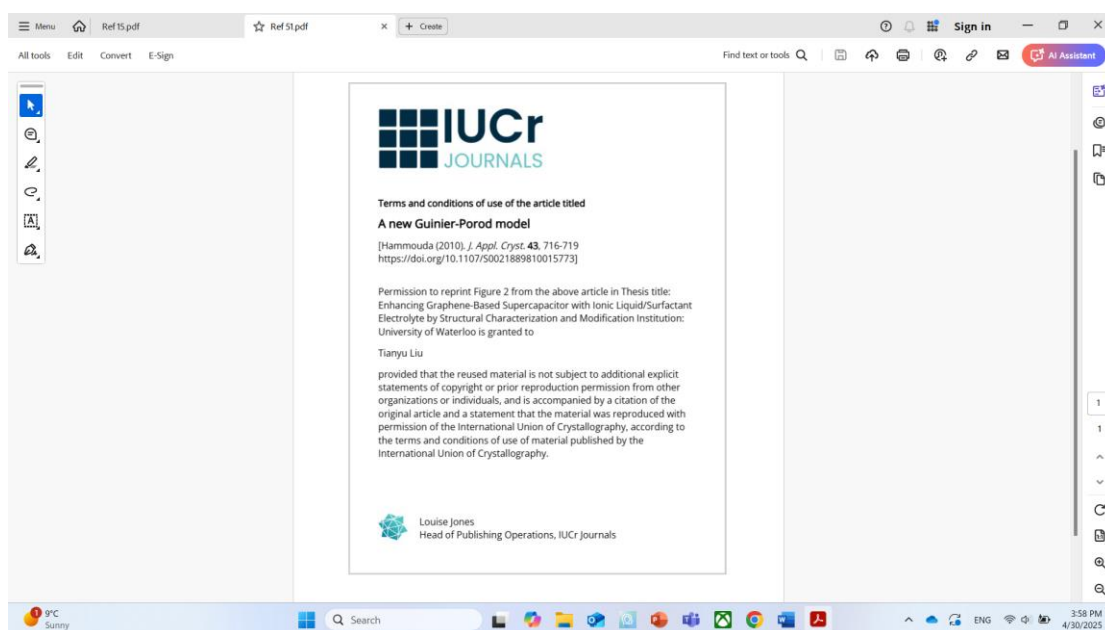
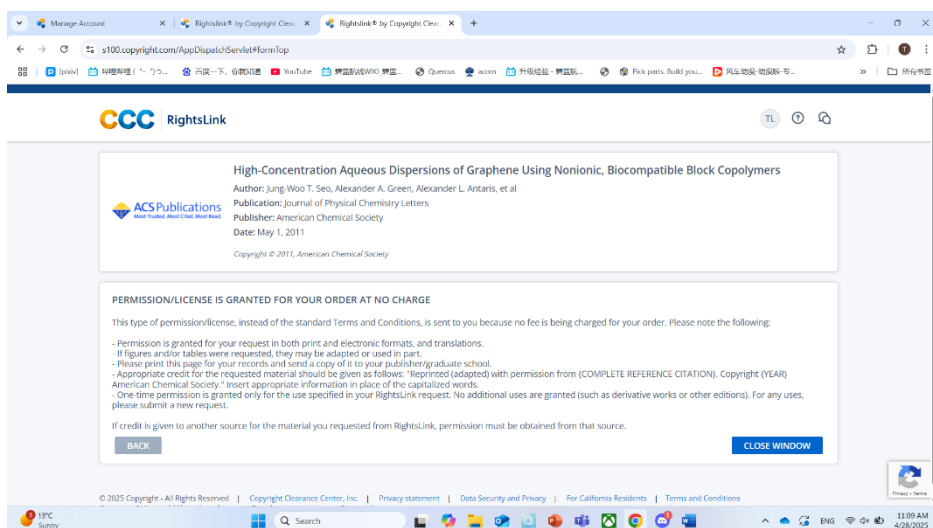
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