THE UNIVERSITY OF QUEENSLAND

Master of Engineering Thesis

Gel polymer electrolytes for electrochemical capacitors

Student Name: LIWEI ZHENG

Course Code: ENGG7282

Supervisor: Prof George Zhao

Industry Supervisor: Prof George Zhao

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Abstract

Electrochemical energy storage devices like batteries and electrochemical capacitors (ECs) are critical in our daily life and the development of sustainable energy such as solar and wind. In general, batteries have a high energy density than ECs while the latter has a higher power density than the former. There have been many strategies for enhancing the energy density of ECs. This project aims to study gel polymer electrolytes for improving ECs performance.

This report firstly gives an overview of energy storage devices, followed by summarizing different categories of electrolytes for energy storage applications and several electrochemical measurements were introduced. The PVDF-HFP based gel polymer electrolytes with different ionic liquids and fillers were prepared and their electrochemical performance were measured in a two-electrode system. At last, the perspective of future work is suggested.

The key finds in this thesis project include:

1. PVDF-HFP/ EMIMBF$_4$ + 1 wt% TiO$_2$ gel polymer electrolyte (GPE) achieved the highest ionic conductivity (2.6×10^{-2} S cm^{-1}). The specific capacitance can remain 81% when current density shifting from 0.1 A g^{-1} to 1 A g^{-1}.

2. The addition of filler TiO$_2$ can significantly improve the ionic conductivity of the electrolyte and specific capacitance of the cell while GO as a filler can slightly improve the specific capacitance of the cell.

3. Based on the data, the ionic conductivity of the GPE based on TFSI$^-$ anion is much higher than the GPE based on BF$_4^-$. Moreover, it is revealed that TFSI$^-$ can help improve the rate performance in comparison with BF$_4^-$.

In summary, this work had syntheses different GPEs based on PVDF-HFP, two different ionic liquids and two fillers. Their ionic conductivity and specific capacitance of the cell were compared later. It was found that with the incorporation of fillers, the ionic conductivity and electrochemical performance were proved to improve. Moreover, it is promising for PVDF-HFP/ $EMIMBF_4$ + 1 wt% TiO_2 GPE to meet the commercial demands for ECs.

Acknowledgements

I would like to take this opportunity to thank Prof. George Zhao for his patient teaching and excellent guidance. Under his supervision, I was able to gain the correct information from the literature review and know how to finish a thesis project. As I knew nothing about the electrochemical capacitors and gel polymer electrolytes which are exactly my thesis project focused, he usually sent me some review papers and some basic papers about my project which are really helpful. Besides, Prof. George Zhao gave me a chance to finish a mid-term presentation which was not compulsory for this course. The mid-term presentation helped me summarize the literature review part and get ready for the experimental.

Further thanks must be given to Dr Xiaoming Sun. She was a postdoctoral researcher in UQ. I deeply appreciated her for meeting me every week and dealing with my confused questions. During the one-year thesis project, there were so many times I did not know how to do in the laboratory, Dr Xiaoming Sun always did some important steps at first in case I got hurt.

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Finally, I am very grateful for the support and assistance gave by my parents, friends and family during the process.

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1 Introduction

1.1 Background

The significant consumption of fossil fuels in recent 50 years has resulted in climate change among the whole world. Therefore, it is urgent to develop and use clean energy for sustainable development and the health of our life. Most renewable energy such as wind and solar is intermittent, thus not reliable for use. To solve this problem, energy storage technologies are required to be more effective to store the energy collected and release the energy on demands.

The electrochemical energy storage systems are the most widely used technology. Batteries, fuel cells and ECs are considered as three main kinds of the most crucial electrochemical energy storage devices currently. ECs are the more attractive topic compared with batteries and fuel cells because of its extremely high power density and environmentally safety (Abruña et.al, 2008).

An EC is constituted with three key elements: electrode, electrolytes and separator. The electrolytes play an important role in ECs because electrolytes act as the channels for ions transportation which limit the potential window and power output of an EC. Electrolytes can be divided into liquid electrolytes, solid electrolytes and gel polymer electrolytes. Liquid electrolytes are conventional electrolytes which have been used for the last several decades. However, the safety issue is always the biggest problem of liquid electrolyte. Solid electrolytes are long-time used because of the safety and strong mechanical stability. However, the lower ionic conductivity of solid electrolytes cannot be improved easily. Recently, gel polymer electrolytes have attracted the most attention due to their high ionic conductivity and excellent electrochemical performance.

1.2 Research aims and scope of this project

The specific objectives are to:

- Understand the fundamentals of electrochemical energy storage devices;
- Learn from the literature how to synthesise and characterise gel polymer electrolytes;

- Synthesize gel polymer electrolytes for fabricating energy storage devices;
- Gain experience in conducting a research project;
- Gain experience and skills in writing a scientific report.

In this project, we aim to prepare gel polymer electrolytes based on PVDF-HFP which can be used in ECs. Firstly, different gel polymer electrolytes were synthesised through solution casting method. Secondly, those gel polymer electrolytes were fabricated in a two-electrode electrochemical capacitor to measure their electrochemical performance. The performance of ECs was evaluated in terms of ionic conductivity and specific capacitance.

1.3 Thesis outline

This report contains seven parts as outlined below:

- Chapter 1 Introduction—This Chapter briefly presents an overall introduction including the background and objectives.
- Chapter 2 Literature Review—This Chapter provides a comprehensive review on energy storage devices, electrolytes developments and some experimental methodologies.
- Chapter 3 Research methodology—This Chapter describes the chemicals and several electrochemical measurements used in this project.
- Chapter 4 Experimental — This Chapter demonstrates the experimental details.
- Chapter 5 is Results and Discussions.
- Chapter 6 is Conclusions and recommendations — summarize the highlights of this project and give recommendations for future research.
- Chapter 7 is references.

2 Literature review

2.1 Energy storage devices

Batteries and ECs are commonly used as energy storage devices. They have pros and cons respectively. The choice of the right device always depends on the actual use and practical limitation. The different energy and power outputs, charge and discharge rate are exhibited due to the different energy storing mechanism. Batteries store energy directly by electrochemical reactions while ECs stores energy as the charge on the pair of electrodes. Figure 2.1 shows the different power ratings and energy ratings of different electrochemical storage devices (Fernão Pires et.al, 2014). According to this Figure, ECs have a higher power output and much less discharge time than batteries.

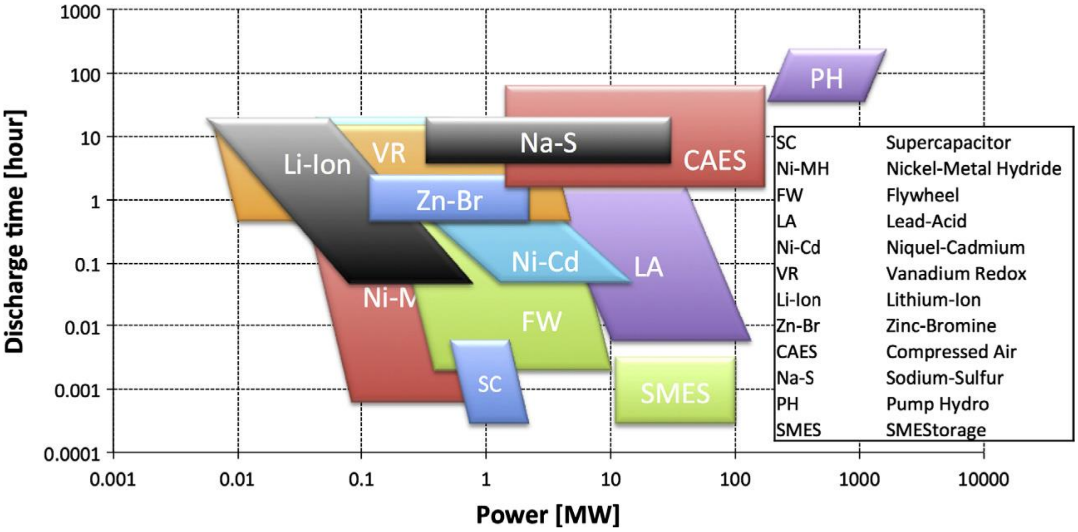

Figure 2.1 Power ratings and discharge times.

2.1.1 Batteries

A battery is composed of an anode (positive electrode), a cathode (negative electrode) and an electrolyte. There are some commercially widely used batteries like lithium-ion, nickel-metal-hydride, and nickel-cadmium batteries. Batteries are able to store much more energy per unit mass than ECs because they store energy by faradic reactions. In these reactions, charge crosses the interface between a battery's electrodes and electrolyte solution which lead to oxidation and reduction. However, batteries cannot be stable and must be replaced after a long-time usage because the redox reaction is supposed to change the structure of the electrode materials.

Lithium-ion batteries (LIBs) are currently used in most applications, such as energy store devices, power tools and medical instruments. LIBs normally use a metal oxide as the cathode while using graphic carbon with a layer structure as the anode. The electrolyte is normally composed of a lithium solution. Figure 2.2 shows the charging and discharging process for a LIB. When the battery is being recharged, the cathode reacts with electrolyte leading to the release of lithium ions into the electrolyte. Meanwhile, the electrons transfer to the cathode. Reverse processes happen when the batteries are discharged.

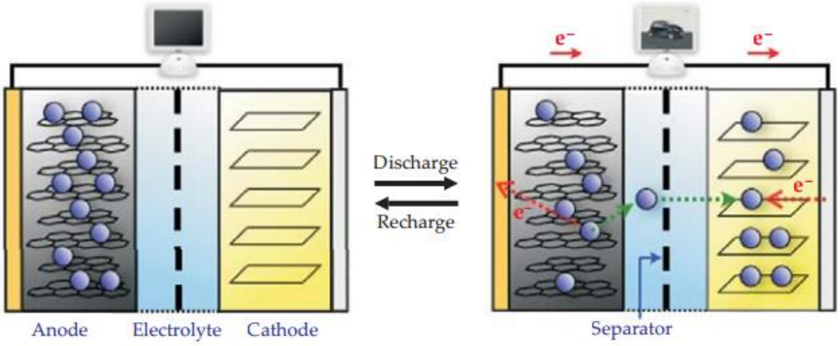

Figure 2.2 Charging and discharging process for a lithium-ion battery (Abruña et.al, 2008)

The energy output of a battery is depended on the operating voltage which is determined by the redox reactions happening on the two electrodes and the charge capacity of electrodes which is determined by different materials. The high energy output of LIB is highly due to the superior electrochemical properties of lithium. On the one hand, as the lightest metal, Li has an excellent charge capacity. On another hand, Li is a strong metal as well. A lithium anode can generate a large operating voltage window between the anode and the cathode.

However, there are some safety issues associated with LIBs. Li metal can form on the anode surface by mistake when the current distribution is not uniform. As a result, short circuits happen. For this reason, different types of batteries are being developed of which some are available commercially while some are still in the experimental stage, such as Lead acid, Sodium Sulphur, Metal-air, Flow batteries (Divya & Qstergaard, 2009)

2.1.2 Electrochemical capacitors (ECs)

ECs have become really different from conventional dielectric capacitors because they have an extremely high power density, long cycle life, and high repaid charging/discharging rate (Yan et.al, 2014). Figure 2.3 the 'Ragone plot' which is the relationship between power density and energy density of different energy devices. ECs have much higher power densities and slightly lower energy density compared with batteries. Besides, ECs are obviously better in another aspect, such as power density, efficiency, charge/ discharge rate and safety (Zhong et.al, 2015).

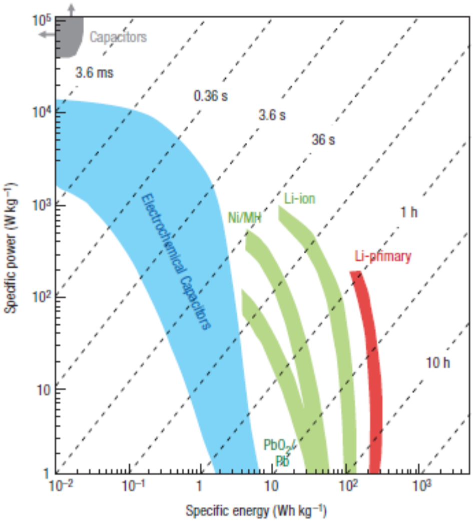

Figure 2.3 Ragone plots for several energy storage devices (dielectric capacitors, batteries and ECs) (Zhong et.al, 2015).

The specific energy (E) and specific power (P) for a single EC can be derived from Eq2.1 and Eq 2.2:

$$E = \frac{1}{2} C_T V^2 \qquad \text{Eq2.1}$$

$$P = \frac{V^2}{4R_S} \qquad \text{Eq2.2}$$

Where V is the cell voltage (in volts), C_T is the total capacitance of the cell (in farads) and R_S is the equivalent series resistance (ESR) (in ohms). The capacitance of the cell is mostly depended by the electrode materials and electrolyte. The cell voltage is associated with electrolyte while the ESR is limited by the different electrodes and electrolytes.

ECs can be further divided into three kinds due to the difference of operation mechanism: electrical double-layer capacitors (EDLCs), pseudocapacitors and hybrid capacitors.

2.1.2.1 Electrical double-layer capacitors (EDLCs)

EDLCs are electrochemical capacitors which are non-faradaic. They store electrostatic energy by using reversible adsorption between the solution ions and electrodes. EDLCs can generate high static double-layer capacitance and they generally use carbon materials.

Conventional dielectric capacitors cannot store much energy by using reversible adsorption because of the charge storage areas are not large and the distance between the two charged plates is limited. However, ECs can store much more energy based on the electrical double-layer mechanism because of the large interfacial area and long distance. As it shows in Figure 2.4a, the concept of the electrical double layer was firstly modelled by von Helmholtz in the 19th century (Helmholtz, 1853). The model shows that there exist two opposite-charge layers at the interface between electrolyte and electrodes. Figure 2.4b shows that Gouy and Chapman further modified the model by adding other electrolyte ions including cations and anions and the ions layer is called the diffuse layer (Chapman, 1903). After that, Figure 2.4c shows that Stern combined the two models to build a Stern model which shows the compact layer and the diffuse layer (Stern,1924). As a result, the compact layer consists of two kinds of ions: adsorbed ions and adsorbed counterions.

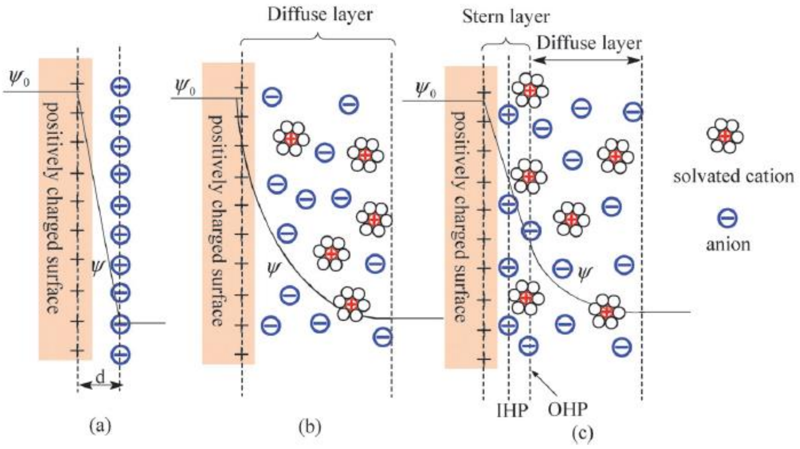

Figure 1.4 Three models about electrical double layers (a) the Helmholtz EDLC model (b) the Gouy–Chapman EDLC model, and (c) the Stern EDLC model (L. L. Zhang & Zhao, 2009).

The capacitance of the Electrical double-layer capacitors (C_{dl}) is a combination of the capacitors from two regions which are the compact layer capacitance (C_H) and the diffusion layer capacitance (C_{diff}). The C_{dl} is:

$$\frac{1}{C_{dl}} = \frac{1}{C_H} + \frac{1}{C_{diff}} \qquad \text{Eq 2.1}$$

The capacitance for an EDLC is can be calculated by Eq 2.2 (Simon & Gogotsi,2010):

$$C = \frac{\varepsilon_r \varepsilon_0 A}{d} \qquad \text{Eq 2.2}$$

Where ε_r is the dielectric constant of the electrolyte, ε_0 is the vacuum dielectric constant, *d* is the thickness of the double layer (the distance between two layers) and *A* is the electrode surface area.

According to this Eq 2.2, there is an effective way to improve specific capacitance by using a porous electrode. A capacitance increase was observed when using porous carbon electrodes and the less pore size electrode uses, the larger specific capacitance was observed. (Simon& Gogotsi, 2010).

2.1.2.2 Pseudocapacitors

The second group of ECs are pseudo-capacitors which store energy by faradaic reactions. In this faradaic system, electrons transfer so fast because ions react instantly in such an atomic structure. Pseudocapacitance is occupied by the transfer of electrons between electrolyte and electrodes. Figure 2.5 shows the mechanism of Pseudocapacitors store energy.

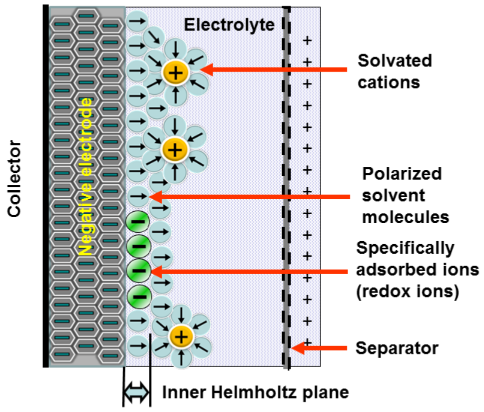

Figure 2.5 Pseudocapacitance with specifically adsorbed ions. Retrieved from https://en.wikipedia.org/wiki/Pseudocapacitance#/media/File:Pseudocapacitance-Priciple.png.

The ruthenium oxide (RuO_2) has attracted many attentions because of it is a typical material producing pseudocapacitance. It has been observed that the specific capacitance of amorphous hydrous ruthenium oxide ($RuO_2 \cdot xH_2O$) (720 Fg^{-1}) is much higher than anhydrous ruthenium oxide (Zheng et.al, 1995). This is because of the redox reactions of ruthenium oxide and ejection on the surface within $RuO_2 \cdot xH_2O$.

$$RuO_x(OH)_y + \delta H^+ + \delta e^- \rightleftharpoons RuO_{x-\delta}(OH)_{y+\delta}$$

where $RuO_{x-\delta}(OH)_{y+\delta}$ and $RuO_x(OH)_y$ are the oxidation product and oxidant.

Compared with EDLC, the biggest change of pseudocapacitance is the faradic system. In this system, electron transfers very fast as the ions instantly interact with the atomic structure of the electrode and make the charging-discharging process much faster than batteries. Because of the redox, pseudocapacitance is observed to be much higher than double-layer capacitance at the same condition.

2.1.2.3 Hybrid ion capacitors

The third type of ECs is hybrid ion capacitors which combine an EC electrode with a battery electrode. It benefits from both capacitors and batteries. More specifically, the hybrid capacitor electrodes usually include a Faradaic electrode and a carbon electrode.

Figure 2.6 shows the cyclic voltammetry (CV) and galvanostatic charge–discharge (GCD) curves of a hybrid capacitor which has both capacitive and battery-type Faradaic electrodes working together. The negative electrode shows both the anodic peak and cathodic peak.

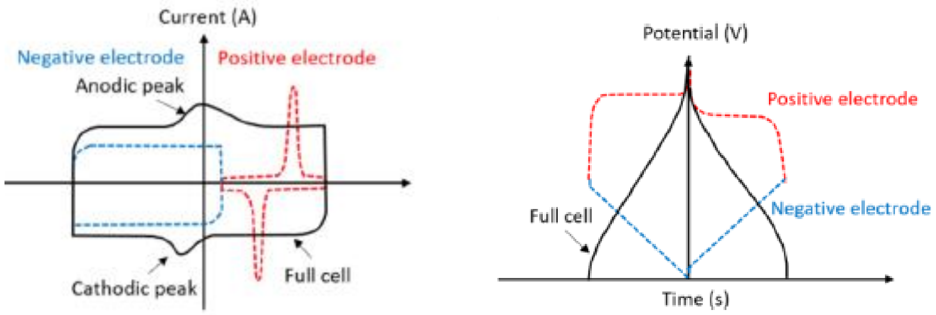

Figure 2.6 CV and GCD curves of a hybrid capacitor (Shao et.al, 2018).

2.2 Electrolytes

An EC is composed of three parts: electrolyte, electrodes and separator (Figure 2.7). As one of the key components, electrolytes provide ionic conductivity and apply transfer channels for ions between two electrodes. The electrolyte within an EC not only can depend on how much the energy and power output, but also play an important role in determining the cycle life, specific capacitance and ionic conductivity as well (Zhong et.al, 2015).

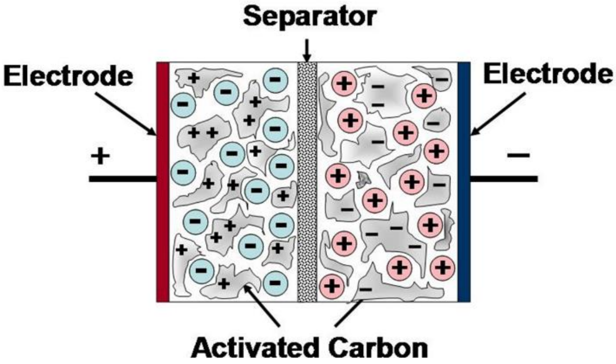

Figure 2.7 Components of an EC.

The nature of electrolytes fundamentally decided by: (1) the ion type and pore size; (2) the ion concentration and solvent type; (3) the interaction between the ions and solvent; (4) the interaction between the electrolyte and electrodes; (5) The electrochemical stable potential window (ESPW). Each of them can affect the performance of the EC. ESPW can directly decide the EC’s operating voltage while ion types and concentration are able to influence the ionic conductivity which is important to the EC’s power density. Furthermore, the better interaction between electrolyte and electrodes can lead to a higher specific capacitance.

For a high-performing EC, we need to improve the relatively low energy density while trying to keep the high power density and a long cycle-life at the same time. Some effective ways can be helpful to achieve the goal: (1) Find an electrolyte with high ionic conductivity and a wide potential window; (2) Develop a premium electrode with high capacitance; (3) Integrate electrolyte with electrodes to optimize the structure.

Generally, electrolytes can be divided into the liquid electrolyte, solid electrolyte and gel polymer electrolyte in the first place due to the different conditions. Figure 2.8 shows the further different kinds of electrolytes used in ECs. In general, liquid electrolytes can be further divided into aqueous electrolytes, organic electrolytes and ionic liquids (ILs) while Solid electrolytes can be grouped into dry solid polymer electrolyte and inorganic electrolyte. Moreover, Gel polymer electrolytes can be distinguished into Hydrogel polymer electrolytes, Organogel electrolytes, Iongel electrolytes and Redox-active gel polymer electrolytes due to different liquid they took to interact with the host polymer.

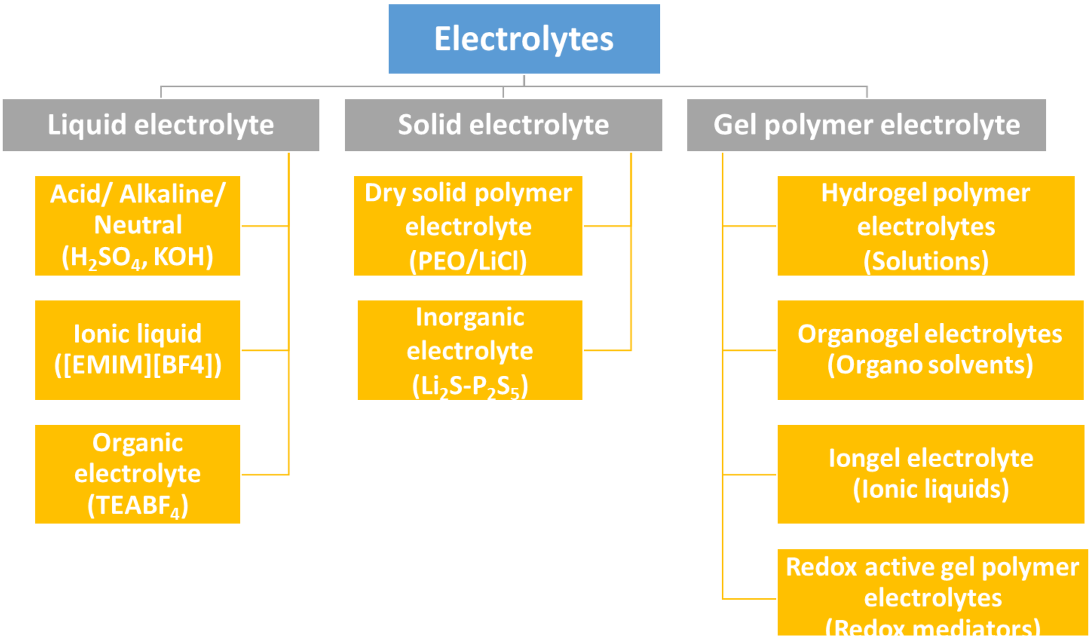

Figure 2.8 Different categories of electrolytes used in ECs.

Liquid and Solid electrolytes are the conventional electrolytes and have been used for the last few decades. However, there is some weakness for them, respectively. Accidents like leakage always happened and caused terrible accidents for the liquid electrolytes-based ECs while the ionic conductivity of the solid electrochemical-based ECs was always so low that cannot be improved. To overcome these problems of the conventional electrolytes, considerable works have been devoted to find and develop new kind of electrolytes to improve the performance of ECs. In this regard, gel polymer electrolytes are gradually becoming a better option for ECs.

2.2.1 Liquid electrolytes

Generally, Liquid electrolyte seems to be an appropriate choice for commercial ECs due to their high ionic conductivity which can lead to a high power density according to Eq 2.2. Compared with Solid electrolytes, Liquid electrolytes seems to be a superior choice for commercial use according to Figure 2.9B. More than 90% of the published literature used Liquid electrolytes as their electrolytes since 2004. The reason might contribute not only the easy synthesis process for ECs based on Liquid electrolyte but the electrochemical performance was able to be excellent (Zhong et.al, 2015). Generally, Liquid electrolytes can be further divided into aqueous electrolytes, organic electrolytes and ionic liquids according to the ion type and solvent type.

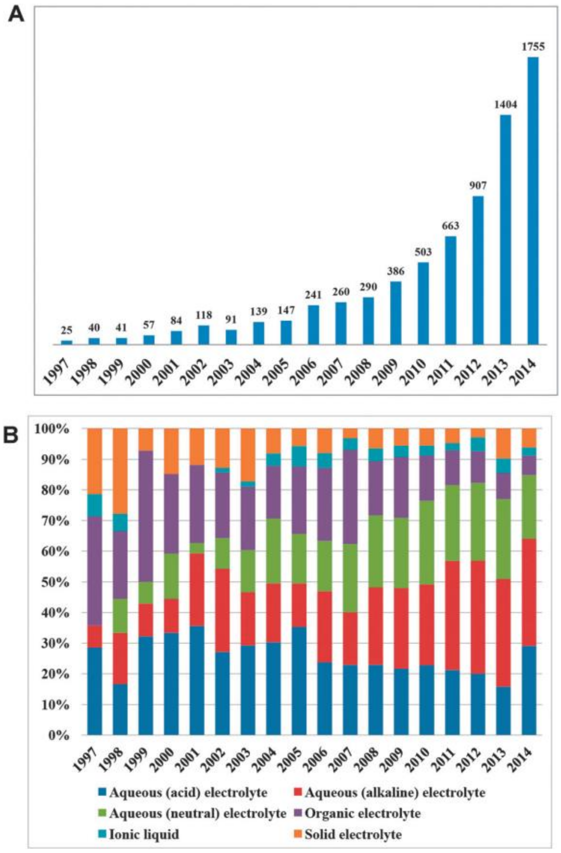

Figure 2.9 (A)Total reported literature related to ECs, (B) different electrolytes usage (Zhong et.al, 2015).

2.2.1.1 Aqueous electrolytes

Aqueous electrolytes are the electrolytes based on water. Compared with an organic solvent and ionic liquids, aqueous electrolytes usually have a high ionic conductivity due to the lower ESR. Typically, the ionic conductivity of aqueous electrolytes can reach 1 S cm^{-1} (Pandolfo & Hollenkamp, 2006).

Aqueous electrolytes normally can be further grouped into acid, alkaline, and neutral solutions (such as KOH, H_2SO_4, Na_2SO_4 and so on). Aqueous electrolytes have a high ionic conductivity due to the mobile ions. Other than that, liquid electrolytes are non-flammable, non-corrosive, safe and convenient to assemble (Zhao & Zheng, 2015). However, the electrochemical stable potential window (ESPW) for aqueous electrolytes are always in a low level which will cause a low energy density.

As listed in Figure 2.9B, acidic electrolytes are the main choice in most ECs studies. H_2SO_4 are the most commonly chose acid electrolyte because of its high ionic conductivity which can reach 0.8 S cm-1 for 1M H_2SO_4 at 25°C (Zhong et.al, 2014). Alkaline electrolytes are another type of the widely used aqueous electrolytes as well. The ionic conductivity of alkaline electrolytes is not low, too. For example, KOH has been investigated most because its ionic conductivity is observed to achieve 0.6 S cm^{-1} (Zhong et.al, 2014). Other than the acidic and alkaline electrolytes, neutral electrolytes are the last kind of aqueous electrolytes. Compared with the other two categories, neutral electrolytes have larger working potential windows and greater safety. Typical, lithium salts, sodium salts and potassium salts are superior choices for neutral electrolytes.

2.2.1.2 Organic electrolytes

Organic electrolytes-based ECs have been focussed in the literature and have been used in the commercial market due to the higher ESPW compared with aqueous electrolytes. The higher potential window can apply a higher both energy density and power density according to Eq 2.1 and 2.2.

Organic electrolytes for ECs usually consist of a conducting salt and an organic solvent. Similarly, the ion size, ion type, solvent type and the interaction between salt and solvent all have an influence on the electrochemical performance of organic electrolyte-based ECs. The different kinds of conducting solvents and organic solvents play a critical role in the overall electrochemical performance.

An idea organic solvent should be able to have a high ESPW and high safety. The most commonly used organic solvents are acetonitrile (ACN) (Figure 2.10) and propylene carbonate (PC) (Figure 2.11) currently. Normally, ACN-based electrolytes have a higher ionic conductivity than the PC-based electrolytes then perform better in specific power output.

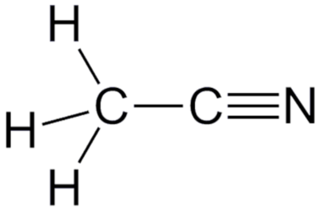

Figure 2.10 Chemical structure of ACN (From Google).

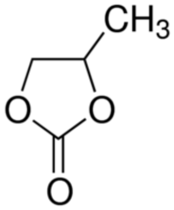

Figure 2.11 Chemical structure of PC (From Google).

A conducting salt can provide different cations and anions for ECs. The different salts have a significant effect on the ionic conductivity, ESPW, the thermal stability of the organic electrolyte. Considered the solubility, conductivity, stability of the conducting salts, $TEABF_4$ (Figure 2.12) has become the top choice.

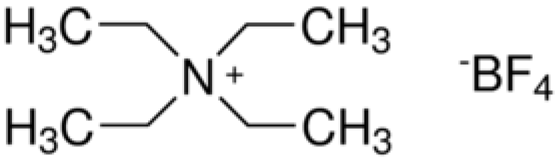

Figure 2.12 Chemical structure of $TEABF_4$ (From Google).

However, there are still some issues when using organic electrolytes for ECs. Compared with ECs using aqueous electrolytes, ECs based on organic electrolytes usually cost more and have a lower specific capacitance, a lower safety as well. Furthermore, an organic electrolyte needs a purification step which aqueous electrolyte don’t need.

2.2.1.3 Ionic liquids

Low-temperature ionic liquids as known as ionic liquids (ILs) are pure organic salts without solvents with melting points below 100 °C. An IL normally consists of an organic cation (such as imidazolium, pyridinium and pyrrolidinium) and an inorganic or an organic anion (such as Cl^-, PF_6^- , BF_4^-) (Figure 2.13). Room temperature ionic liquids (RTILs) which are the ionic liquids whose liquid state can be maintained in room temperature have received significant interests as alternative electrolytes for ECs because they are non-volatile, poorly combustible and heat-resistant which convention electrolytes never have (González et.al, 2016).

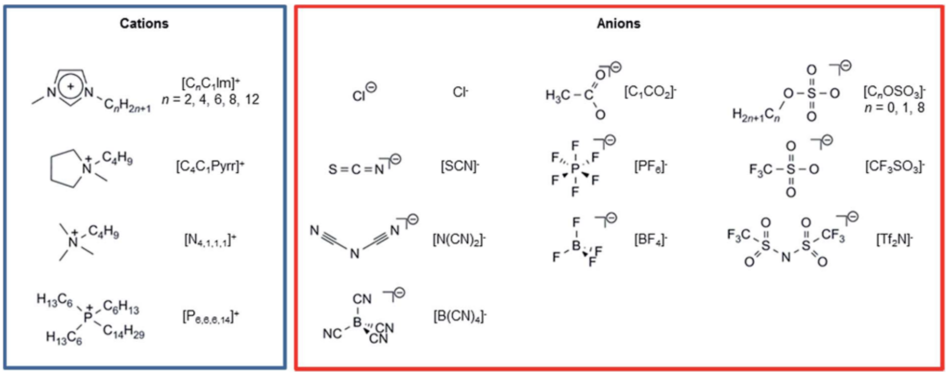

Figure 2.13 Common cations and anions used in the study (Villar-Garcia et.al, 2014)

Compared with aqueous electrolytes and organic electrolytes, ILs are much better at thermal stability, chemical stability, electrochemical stability. Moreover, ILs are safer and flexible due to the huge amounts of cations and anions. The major challenge in developing ILs for ECs is to find and develop ILs with high ionic conductivity and a large ESPW. Sometimes, ionic conductivity is high while the ESPW is narrower. A Large amount of work has been devoted to how to merge these advantages together.

2.2.2 Solid electrolytes

Solid electrolyte-based ECs have attracted more interests recently with the rapidly growing demand of powers for portable electronic and some flexible electronic devices. Compared with liquid electrolytes, the major advantages of solid electrolytes are the simple package and safe due to the leakage-free.

Solid electrolytes can be further divided into dry solid polymer electrolytes (SPE) and inorganic electrolytes. Fig 2.14 shows the component of an SPE. It is composed of a polymer matrix (PEO) and a lithium salt (LiCl) without any solvents. In SPEs, salts ions transport through the polymer while the ions transport in the liquid phase in liquid electrolytes.

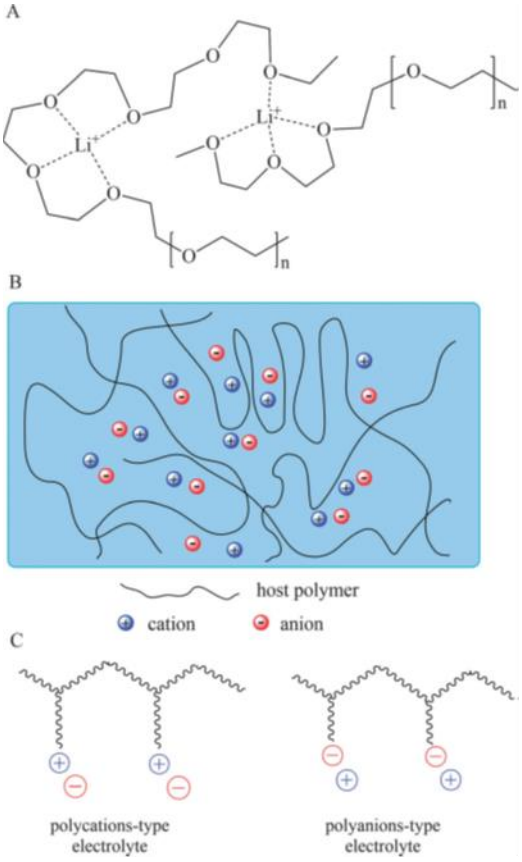

Figure 2.14 Different structure diagrams of (a) a solid polymer electrolyte, (b) a gel polymer electrolyte, and (c) a polyelectrolyte (Zhong et.al, 2014).

When solid electrolytes are used in commercial business, some critical requirements must be followed, such as high ionic conductivity, a high chemical, electrochemical and thermal stability and mechanical strength. However, it is hard to achieve these requirements at the same time. The biggest issue for solid electrolytes is how to merge both the high ionic conductivity and high mechanical strength.

2.2.3 Gel polymer electrolytes

Conventional liquid electrolytes have been the major electrolytes due to their high ionic conductivity for several decades. However, the leakage of electrolytes has led to bad consequences. In this case, solid electrolytes can avoid safety issue but cannot deliver high ionic conductivity. For this reason, combined the advantages of both liquid electrolytes and solid electrolytes, gel polymer electrolytes (GPEs) have been the most studied electrolytes. GPEs can apply energy devices with high flexibility and adjustable shapes.

A GPE is composed of a polymer host matrix and a liquid electrolyte. The polymer host matrix is conductive to apply GPEs with high mechanical functions and high flexibility. Moreover, a good polymer host matrix helps GPEs have a wide electrochemical window. There are so many polymer matrixes has been used, such like poly (ethyl oxide) (PEO), poly (vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) and so many kinds of electrolyte are used as well, such as sulfuric acid (H_2SO_4), tetraethylammonium tetrafluoroborate ($TEABF_4$).

Among the polymer matrixes, the poly (vinylidene fluoride -hexafluoropropylene) (PVDF–HFP) (Figure 2.15)-based GPEs have been focus extensively recently because the PVDF–HFP matrix has a high dielectric constant (ε= 8.4) which is helpful of dissolution of salts and carry more ions.

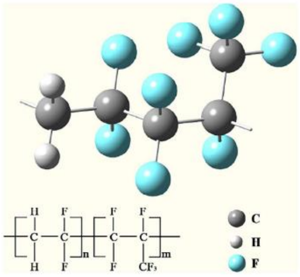

Figure 2.15 Chemical structures of PVDF-HFP (Chen et.al, 2018).

As for the electrolyte, meaning the electrolyte and solvent, providing ionic conducting which can be conducive to the charge on both electrodes. The electrolyte not only helps the electrochemical double-layer and the faradic process but also play an important role in determine ES performance. A good electrolyte can help to improve thermal, chemical and electrochemical stability. Besides, it can provide a high ionic conductivity which can lead to large capacitance eventually. Generally, the electrolyte can be further divided into four categories: aqueous electrolyte, organogel electrolyte, iongel and redox active gel polymer electrolyte. They will be discussed in the following parts.

2.2.3.1 Hydrogel polymer electrolytes

The hydrogel polymer electrolytes are the gel-polymer electrolytes based on water. The Hydrogel can easily trap water in the polymer matrix due to the three-dimensional network.

It has been found that a typical hydrogel polymer electrolyte can be synthesised based on Poly (vinyl alcohol) (PVA) (Figure 2.16) which acts as the polymer matrix. PVA is easy to prepare and can be easily mixed with strong alkaline, strong acid and neutral electrolytes then form hydrogel polymer electrolyte. It was found that the specific capacitance of a hydrogel polymer electrolyte-based EC loss half storage after 40-67 days (Gao &Lian, 2014).

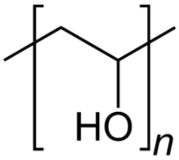

Figure 2.16 Chemical structures of PVA. Rederived from https://en.wikipedia.org/wiki/Polyvinyl_alcohol.

Hydrogels are currently easy to prepare with high hydrophilicity, favourable film forming property and low cost. However, hydrogel polymer electrolyte seems are not stable and a good choice for ECs due to the poor temperature and environmental stability. The electrolytes cannot behave well at high temperatures like 70 °C (Fei et al, 2014) and the performance of an EC based on hydrogel electrolyte would suffer a huge loss after a period (Cheng et al, 2015).

2.2.3.2 Organogel electrolytes

Organogel electrolyte is a high-working voltage electrolyte which is based on organic solvents. Some organic solvents have already been commonly used for a long time, like propylene carbonate (PC), ethylene carbonate (EC) and dimethyl carbonate (DMF). The ratio of polymer and organic solvents usually affect the function of GPEs.

The cell voltages of ESs based organogel electrolyte normally at 2.5–3V which was much higher than those based hydrogel electrolyte ESs (Huang et al, 2007). Compared with hydrogel electrolyte, EC is better based on organogel electrolyte due to the high cell voltages which can result in a high energy density (Ramasamy & Anderson,2014). Compared with hydrogel electrolyte, ECs based organogel electrolyte have a higher cost and lower ionic conductivity (Rodriguez et al, 2013).

Compared with hydrogel electrolyte, the organogel electrolytes performs better in cell voltage and cycling stability which are significant in energy devices. However, the organogel electrolytes are more complex to synthesis and suffer from low ionic conductivity. For these reasons, the organogel electrolytes are widely used in batteries.

2.2.3.3 Redox-active gel polymer electrolytes

Redox-active polymer electrolyte is the third and newest kind of GPE. This electrolyte can help to increase the capacitance of ECs due to more pseudocapacitance. Moreover, the pseudocapacitance not only comes from the electrodes but also from the redox-active electrolyte.

The strategy of detecting redox active electrolyte has been tested in liquid-state, solid-state and gel-state electrolyte based ECs. Furthermore, most studies focus on the redox active GPEs because of they have an obviously higher EC specific capacitance (Fan et al, 2014). Some polymer hosts have been used in the redox active GPEs such like Poly (vinyl alcohol) (PVA) and poly (ethyl oxide) (PEO) while the typical electrolytes which have been found are iodides (e.g., NaI and KI) and organic redox mediators (e.g., hydroquinone and p-benzenediol).

Redox-active GPEs are the special kind of GPEs which contains most redox reactions. Compared with hydrogel electrolyte, except the much higher specific capacitance, they can be produced by an easier procedure under general environment.

2.2.3.4 Ion gels

Ion gels are the last kind of gel polymer electrolyte. Ion gels are relatively new kind of gels compared with hydrogels and organogels. They are normally consisting of a polymer matrix and an ionic liquid. Ion gel is great because of the high ionic conductivity and wide electrochemical stability. Besides that, they also performed well in thermal stability and non-flammability. It is reported that an EC based ion gel can be still stable up to 330–350 °C (Yin et.al, 2015).

Using poly (ionic liquid)s to formulate ion gels has become attractive because the follow advantages: 1) poly (ionic liquid)s have good chemical affinity and miscibility of which can perfectly solidify and girlify organic salts (Winterton, 2005); 2) poly (ionic liquid)s have high ion-ion interactions with the polymer matrix then prevent leakage of the liquid from gel; 3) poly(ionic liquid)s always have a high ionic conductivity which is conducive to practical use (Pont et.al, 2009).

The properties (e.g., conductivity and electrochemical stable potential window (ESPW)) of an ion gel depend on the function of ionic liquid and polymer matrix. Either the IL or the host polymer is crucial for maximizing the performance of an EC based ion gel. Common IL like [EMIM][SCN] and [EMIM][TCB] have already been detected due to their low viscosity (Pandey Hashmi, 2013).

There are three main methods used in synthesizing ion gels: doping of polymers with ILs, in situ polymerization and synthesis of polymeric ionic liquids (PILs) (Ye et.al, 2013).

Figure 2.17 shows the synthesis steps using the doping polymers with ILs method. In the first step, a synthesized polymer was blended with an IL with an appropriate solvent then mix a homogeneous solution. After that, the solution was cast into a predesigned shape and was put into an oven to remove the solvent. This approach applies a convenient way to control the ionic conductivity of the iongel by adjusting the different weight content of the polymer matrix and ionic liquid. For this reason, the content of the ionic liquid is so crucial because it can directly determine the ionic conductivity of the iongel. However, poor mechanical stability and IL leaching will happen if the content of the ionic liquid is overloaded. In conclusion, the key parameter for this method is to adjust the IL/polymeric matrix ration and their compatibility.

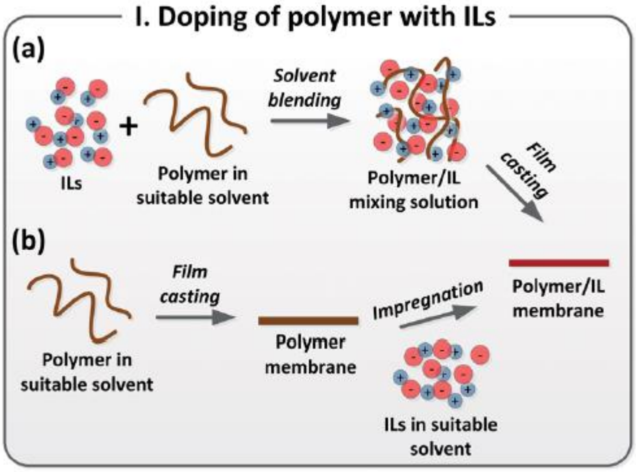

Figure 2.17 Schematic diagram of doping of polymers with ILs (Ye et.al, 2013).

Doing of polymer with ILs method is the most commonly used method for preparing ion gels. This step consists of several steps, firstly dissolve IL and poly ionic liquid into a common solvent, then cast the solution, finally dry it to remove the solvent. This method has a strong advantage that allows electrolyte more versatile and the content of ionic liquid can go up to 60 wt% (Ye et.al, 2013).

Figure 2.18 shows the synthesis steps using the polymerization/crosslinking of monomers in ILs method. In this method, ILs are mixed with the different vinyl monomers and initiators before polymerization. Ion gels can be directly formed due to the high solubility of the vinyl monomers in ILs and the help of the initiators. For this way, the key factor is the compatibility between different polymer matrixes and different ILs.

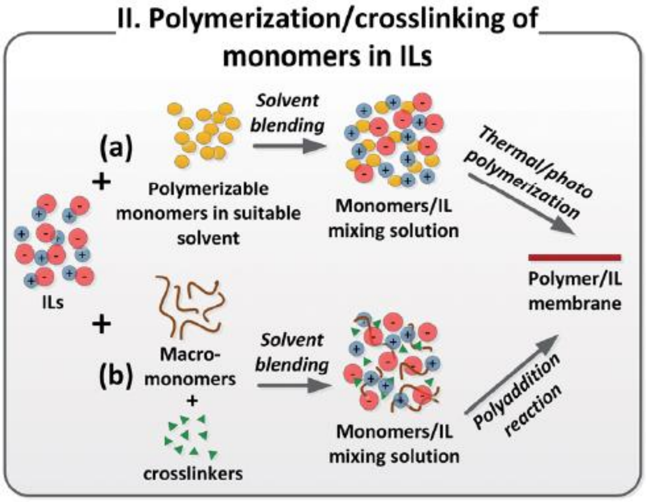

Figure 2.18 Schematic diagram of polymerization/crosslinking of monomers (Ye et.al, 2013).

Ion gels can be synthesised by the polymerization of polymeric IL (PIL) monomers or the modification of currently existing polymers as well (Figure 2.19). When using this method to prepare ion gels, the process is more complicated because this approach involves a number of organic synthesis and purification steps at the monomer level. Meanwhile, the ionic conductivity of the electrolytes synthesised by this method is normally lower compared with another two approaches.

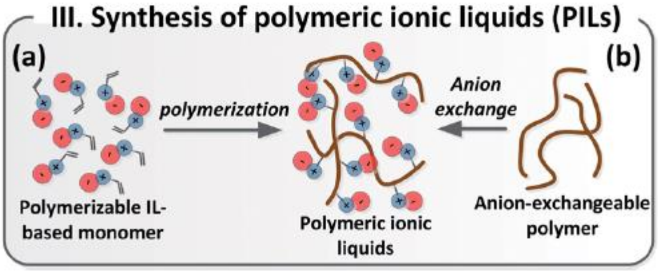

Figure 2.19 Schematic diagram of polymerization of polymeric ionic liquids (Ye et.al, 2013).

Ion gels seem to keep advantages both of hydrogel electrolyte, organogel electrolyte and redox active electrolytes. ECs based ion gels usually exhibited good flexibility, high thermal stability, strong mechanical strength and a great self-recovering ability. However, in some case, EDLCs based ion gels could have a low specific energy density (3.5-4.7 $Whkg^{-1}$) because of the limited cell voltage (Pandey &Hashmi, 2013). For this reason, ion gels might be good choices for ECs.

The biggest problem for ECs is to merge the high ionic conductivity with good mechanical properties. It has been proved that adding some inorganic nanoparticles, such like silica (SiO_2), Graphene oxide (GO) and titania (TiO_2), into the polymer matrix can be conducive to further improve the ionic conductivity and mechanical properties (Croce et.al, 2000) (Figure 2.20). On the one hand, the nanoparticles can act as solid plasticizers to interact with the polymer matrixes to further decrease the crystalline phase and promote the amorphous phase which means more ion-transfer channels were opened (Yue et.al, 2016). On another hand, the nanoparticles can help to improve the ionic liquid uptake (Long et.al, 2016).

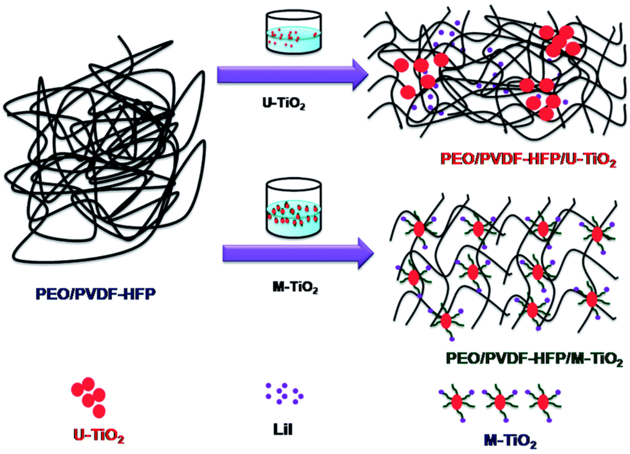

Figure 2.20 Influence of nanoparticles on PVDF-HFP (Prabakaran et.al, 2014).

Graphene oxide (GO) (Figure 2.21) has been remarkable inorganic filler with a large surface area. GO has some excellent properties like thermal stability and mechanical strength. It can help to improve the mechanical strength and chemical stability of the polymer matrix as well. Most importantly, GO has been proven that it can interact well with the polymer matrix and ILs when it was added into polymer/IL solution and especially GO can have a significant positive effect on PVDF-HFP (Zhong et.al, 2015). Recently, more and more experiments about the electrolytes based on PVDF-HFP were finished and new progress is achieved in both ionic conductivity and electrochemical performance.

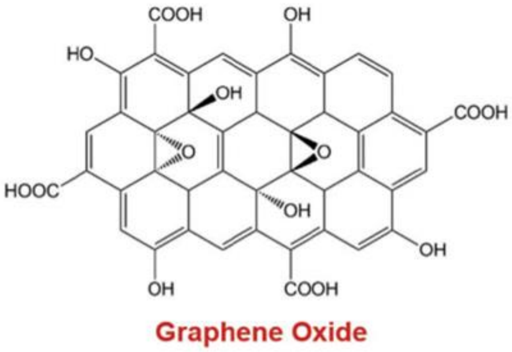

Figure 2.21 Chemical structures of GO (Chen et.al, 2018).

Based on the literature review on the energy storage devices and electrolytes, some conclusions can be drawn as follows:

(1) Batteries and ECs are both commonly used energy storage device. ECs have a much higher power density and lower energy density in comparison with batteries. That drawback, limited energy density can be further improved by optimizing electrodes and electrolytes.

(2) Conventional liquid electrolytes have been the major electrolytes due to their high ionic conductivity for several decades. However, the leakage of electrolytes has led to unsafe consequences. In that case, solid electrolytes can avoid safety issue but cannot deliver high ionic conductivity. With regard to that, combining the advantages of both liquid electrolytes and solid electrolytes, gel polymer electrolytes (GPEs) have been attracting more attention. In addition, the physical properties of GPEs can rend the flexibility and adjustable shapes of the whole device, which may be another merit for its applications.

(3) Among all the categories of GPEs, ion gel seems to be the most promising one due to the high ionic conductivity and wide electrochemical stability. Table 2.1 shows some different Ion gel polymer electrolytes and their electrochemical performance. Doping of polymers with ionic liquids is the most popular method to synthesise an ion gel because it can help ion gel form with a high ionic liquids content which leads to the high ionic conductivity.

Table 2.1 Brief summary of Iongel polymer electrolyte in the literature review.

Method	Polymer	Ionic liquid	Synthesis method	Ionic conductivity/×10^{-3}S cm^{-1}	Specific capacitance	Chemical stable window/V	ref
Doping of polymers with ILs	Poly(diallyldimethylammonium) chloride (PILCl)	LiTFSI	Anion exchange reactions and solution casting	4.2	71.5 F g^{-1} at 0.2 A g^{-1}	3	(Trigueiro et.al, 2014)
	PVDF	EMIMFSI	Solution-casting	2.8	71.7 F g^{-1} at 1.0 A g^{-1}	2.8	(Ortega et.al, 2016)
	PVA	BmImCl	Solution-casting	7.31	28.36 F g^{-1} at 10 mV s^{-1}	4.8	(Liew,2014)
	PVDF-HFP	1-ethyl-3-methylimidazolium tetracyanoborate (EMIMTCB)	Solution-casting	9	34.4 F g^{-1} at 10 MHz	3.8	(Pandey & Hashmi, 2013)
	PVDF-HFP	1-ethyl-3-methyl-imidazolium trifluoromethanesulfonate (EMIMTf)	Solution-casting	6.3	80 F g^{-1} at t 10MHz	1.2	(Pandey, 2010)
	PEGDMA and PEGMA	1-propyl-1-methylpyrrolidinium bis(fluorosulfonyl) imide (P13FSI)	Polymerization of methacrylate and dimethacrylate oligomers solution-casting	1.6	32 F g^{-1} at 2 mV s^{-1}	2.5	(Chaudoy, 2017)
	(PVP/PVDF-HFP)	1-butyl-2,3-dimethylimidazolium tetrafluoroborate ([Bdmim]BF4)	Solution-casting	2.92	133 F g^{-1} at 0.1 Ag^{-1}	2.4	(Syahidah & Majid, 2015)
	PVA	1-butyl-3-methylimidazolium iodide (BmImI)	Solution-casting	9.63	52.8 F g^{-1} at 10 mV s^{-1}	3.8	(Liew et.al, 2016)
	PVDF	1-ethyl-3-methylimidazolium bis(fluorosulfonyl) imide (EMIMFSI)	Solution-casting	2.45	71.7 F g^{-1} at 10 mV s^{-1}	2.8	(Ortega et.al, 2016)
	PEO	1.3-dimethylimidazolium bis (tri-fluoromethyl sulfonyl) imide (DMIMTFSI)	Cross-linking	9.8	79.5 F g^{-1} at 1 A g^{-1}	3.5	(Zhong et.al, 2017)

PEO	1-ethyl-3-methylimidazolium bis (trifluor- omethyl sulfonyl)-imide (EMIMTFSI)	Cross-linking	8.6	84.58 F g^{-1} at 1 A g^{-1}	3.5	(Zhong et.al, 2017)
PEO	1.3-diethylimidazolium bis (trifluoromethyl sulfonyl) imide (DEImTFSI)	Cross-linking	6.7	74.52 F g^{-1} at 1 A g^{-1}	3.5	(Zhong et.al, 2017)
PEO	1-ethyl-3-methylimidazolium tetrafluoroborate (EMIMBF4)	Cross-linking	14	85.69 F g^{-1} at 1 A g^{-1}	3.5	(Zhong et.al, 2017)
PEO	1-propyl-3-methylimidazolium tetra- fluoroborate (PrMImBF4)	Cross-linking	7.3	65.12 F g^{-1} at 1 A g^{-1}	3.5	(Zhong et.al, 2017)
PVA	1-butyl- 3 methylimidazoliumtrifluoromethanesulfonate (BMIMTf)	Solution-casting	2.37	2 F g^{-1} at 10 mV s^{-1}	3.5	(Liew et.al, 2016)
PVDF-HFP	1-butyl3-methylimidazolium tetrafluoroborate (BMIBF4)	Solution-casting		154 F g^{-1} at 1 mA cm^{-2}	2	(Pandey et.al, 2014)
PVDF-HFP	1-ethyl-3-methylimidazolium tetrafluoroborate (EMIMBF4)	Solution-casting	25	190 F g^{-1} at 1 A g^{-1}	3.5	(Yang et.al, 2014)
Poly(diallyldimethylammonium) chloride solution (pDADMAC)	Lithiumbis(trifluoromethanesulfonyl)imide (LiTFSI)	Ion exchange reaction	3	100 F g^{-1} at 1 mA cm^{-2}	3.5	(Tiruye et.al, 2015)
Alginate	1-ethyl-3-methylimidazolium tetrafluoroborate (EMIMBF4)	Solution-casting	20	136 F g^{-1} at 0.2 A g^{-1}	2.5~4	(Soeda et.al, 2015)
PVDF-HFP (Ionic liquid:polymer weight ratio: 5:1)	EMITrif 1-ethyl-3-methylimidazolium (EMI+) and (CF3SO3, Trif)	Doping of polymers with ILs	8	-	0.8	(Fuller et.al, 1997)
PVDF-HFP (Ionic liquid:polymer weight ratio: 10:1)	EMITrif 1-ethyl-3-methylimidazolium (EMI+) and (CF_3SO_3, Trif)	Doping of polymers with ILs	7.3	-	0.8	(Fuller et.al, 1997)
PVDF-HFP (Ionic liquid:polymer weight ratio: 7:1)	EMIMBF4	Doping of polymers with ILs	11	-	-	(Fuller et.al, 1997)
Poly (HEMA)	DVIMbr 1-butyl-3 methylimidazolium hexafluorophosphate (as a solvent)	Thermal polymerization	0.3	125 F g^{-1} at 10 mV s^{-1}	3	(Taghavikish et.al, 2018)

	PVDF-HFP	[HEMIm][BF$_4$]	Solution-casting	0.15	-	-	(Yeon et.al, 2005)
	PVDF-HFP	[HEMIm][PF$_6$]	Solution-casting	0.15	-	-	(Yeon et.al, 2005)
Polymerization of vinyl monomers in ILs	Vinyl monomer	Ionic liquid	Method	Ionic conductivity/×10^{-3}S cm-1	Specific capacitance	Chemical stable window	ref
	2-hydroxyethyl methacrylate (HEMA)	EMIBF$_4$	Thermal polymerization	0.2	-	-	(Noda & Watanabe, 2000)
	2-hydroxyethyl methacrylate (HEMA)	BPBF$_4$	Thermal polymerization	1	-	-	(Noda & Watanabe, 2000)
	methyl methacrylate (MMA)	BMIPF6	Thermal polymerization	0.5	-	-	(Li et.al, 2006)
	methyl methacrylate (MMA)	EMIMTFSI	Thermal polymerization	5	-	-	(Susan et.al, 2004)
Polymerization of polymerizable ILs	Ionic liquid monomer	Additive	Method	Ionic conductivity/×10^{-3}S cm-1	Specific capacitance	Chemical stable window	ref
	1-Methyl-3-{[4-(2-methacryloyloxyethoxy)-1,1-biphenyl-4-oxy] hexyl} imidazolium tetrafluoroborate	A photoinitiator, 2,2-dimethoxy-2-phenylacetophenone, was added	Photopolymerization (light irradiation)		32 F g^{-1}	-	(Hoshino, 2003)
(Meth)acryloyl-based IL monomer	1-bromohexyl-6-acrylate and lithium bis(trifluoromethanesulfonyl)imide	E$_4$A as the crosslinker to improve mechanical strength	Bulk polymerization method		1.4 F g^{-1}	-	(Ogihara, 2006)

N-vinylimidazolium-based IL monomer.	1-Vinyl-3-ethyl-imidazolium bromide	Azobis (2- methylpropionitrile) AIBN as a thermal initiator purification with chloroform	Thermal polymerization		-	-	(Amajjahe et.al, 2003)
	1-Butyl-3-vinylimidazolium bis(trifluoromethylsulfonyl) imide ([bvim][Tf$_2$N])	B-cyclodextrin (B-CD) to achieve high water solubility	Thermal polymerization		-	-	(Amajjahe & Ritter, 2008)
	N-vinylimidazolium tetrafluoroborate (VyImBF$_4$)	AIBN as a thermal initiator	Thermal polymerization	0.016	-	-	(Hirao, 2000)
Styrenic IL monomer.	1-[(4-Ethenylphenyl) methyl]-3-alkylimidazolium Bis(trifluoromethane)sulfonimides	AIBN as a thermal initiator	Thermal polymerization	-	-	-	(Bara et.al, 2007)
	1-[2-(Methacryloyloxy) ethyl]-3-butyl-imidazolium tetrafluoroborate ([MABI][BF$_4$])	AIBN as an initiator. DMF was used as solvent because all poly (ionic liquid) s are soluble in it.	Thermal polymerization	-	-	-	(Tang et.al, 2005)
Crosslinkable	Poly(vinylimidazolium-co-vinylsulfonate)	LiTFSI as a solvent	Neutralization method to prepare the IL monomer	0.00008	-	-	(Yoshizawa et.al, 2002)
	Poly (vinylimidazolium-co-3-sulfopropyl acrylate)	LiTFSI as a solvent	Neutralization method to prepare the IL monomer	0.001	-	-	(Yoshizawa et.al, 2002)
Copolymerization	Poly (HMA-co-MEBIm-BF$_4$)	AIBN, DMF	Thermal polymerization	0.2 at 420 °C	-	-	(Chen et.al, 2009)
	Poly (MEBIm-TFSI-co-MEBIM-BF$_4$)	AIBN, DMF	Thermal polymerization	0.8 at 420 °C	-	-	(Chen et.al, 2009)

3 Research methodology

3.1 Chemical reagents and materials

Poly (vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP, Mw ~ 400,000), ionic liquid 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMIMTFSI, >97.0%), solvent Dimethylformamide (DMF), Poly(tetrafluoroethylene) (PTFE), ionic liquid 1-Ethyl-3-methylimidazolium tetrafluoroborate ($EMIMBF_4$), nanoparticles Titanium oxides (TiO_2) and Graphene oxide (GO). All the materials were used as received.

3.2 Electrochemical performance measurements

3.2.1 Cyclic voltammetry (CV)

Cyclic voltammetry (CV) curve is an effective technique to measure the current and voltage of electrode material. CV curves usually are rectangular for most EDLCs while the curves have peaked for Faradaic redox reaction capacitors.

The specific capacitance C (Fg^{-1}) of the electrodes can be calculated from the Eq 3.1 (Chen et.al, 2002):

$$C = \frac{1}{mv(V_a - V_c)} \int_{V_a}^{V_c} I(V)dV \qquad \text{Eq 3.1}$$

Where *v* represents for potential scan rate, *m* represents for the mass of the electroactive materials in the electrodes, V_a represents for the anodic potential while V_c is the cathodic potential, *I (V)* represents for the response current density and *V* represents for the potential.

3.2.2 Galvanostatic charge–discharge (GCD)

Another common technique using to gain specific capacitance of a capacitor is galvanostatic charge/discharge curves. The curve records different potential and time when applying cyclic current. Besides the current density, the curve is dependent on cycle numbers and the phase structure of electrolyte.

GCD cycling is generally worked using three-electrode systems for capacitors at various current densities. For a GCD capacitor, the specific capacitance (C_{sp}) of the electrodes can be derived using the equation 3.2 (Ng et.al, 2009):

$$C_{sp} = \frac{I}{m(dv/dt)} \qquad \text{Eq 3.2}$$

Where *I* represents for given current density, *dv/dt* is the slope of the discharge curve and *m* is the mass of the electrode.

3.2.3 Electrochemical impedance spectroscopy (EIS)

Electrochemical impedance spectroscopy (EIS) is a technique to calculate the ionic conductivity of a GPE which is significant. Ionic conductivity shows how many ions move inside the GPE. EIS works on an electrochemical working station in a certain frequency range at room temperature. Before the EIS measurement, the GPE membrane needs to be sandwiched between two stainless steel combining a blocking-type cell. The ionic conductivity can be calculated by Eq 3.3 (Taberna et.al, 2003):

$$\sigma = l/(R_b A)(Scm^{-1}) \qquad \text{Eq 3.3}$$

where *A* is the area of the GPE membrane film connected with stainless steel electrode, σ represents for the ionic conductivity, *l* represents for the thickness of the GPE membrane film and R_b is the bulk resistance.

The bulk resistance is the value of the real impedance when means that the imaginary impedance equal zero after you plot the cole-cole plot (the relation between imaginary impedance and real impedance).

4 Experimental

4.1 Preparation of graphene oxide

Graphene oxide (GO) powder was prepared from natural graphite by Modified Hummers' method (Kovtyukhova et.al, 1999). The solid graphene oxide was ready to use. The as-prepared GO is a layered structure with the dimensions of 8 -15 nm and the length of 50 µm.

4.2 Preparation of gel polymer electrolytes

The gel polymer electrolytes were prepared by a solution casting method. For comparison purpose, two ionic liquids were selected as the plasticizers. The first set looked into the effect of different weight TiO_2 fillers while the second set systematically investigated the influence of the different weight of GO fillers.

For the first set, we aimed to synthesis PVDF-HFP/ A Ionic liquid + TiO_2 GPE. At first, the host polymer PVDF-HFP (0.5g) was dissolved in dimethylformamide (DMF) (8 ml). Then ionic liquid $EMIBF_4$ (0.5g) was mixed in the PVDF-HFP/ DMF solution and again stirred for 2 h at 40°C to form a homogeneous solution. After that, an appropriate amount of TiO_2 (0.5 wt%, 1 wt%, 2 wt%,5 wt% related to the total mass of PVDF) (3.125 mg, 6.25mg, 12.5mg, 25mg respectively) was used for the preparation of GPEs containing TiO_2. The TiO_2 nanoparticles were added to the solution and the mixed solution was sonicated at room temperature until it gets homogeneous. At last, the resultant mixtures were cast onto to predesigned cell and dried in a vacuum oven at 60°C for 12h before characterization. The obtained samples are PVDF-HFP/ $EMIBF_4$ + TiO_2 and PVDF-HFP/ EMITFSI + $TiO_{2.}$

For the second set, similarly, for the synthesis of PVDF-HFP/ A Ionic liquid + GO, the host polymer PVDF-HFP (0.5 g) was dissolved in dimethylformamide (DMF) (8 mL) under stirring at 40°C (use water bath) until a homogeneous solution was obtained. Then ionic liquid $EMIBF_4$ or EMIMTFSI (0.5 g) was mixed in the PVDF-HFP/ DMF solution and again stirred at 40°C until the solution became homogeneous. After that, a certain amount of GO (5 wt% related to the total mass of PVDF) (25 mg) was prepared as a filler for the GPEs. The GO solid was added to the solution and the mixed solution was sonicated at room temperature until it gets homogeneous. At last, the resultant mixtures were cast onto to predesigned cell and dried in a vacuum oven at 60°C for 12h before characterization. For comparison, TiO_2 was replaced by GO, following the same procedures as above mentioned. The obtained samples are PVDF-HFP/ $EMIBF_4$ + GO and PVDF-HFP/ EMITFSI + GO.

4.3 Fabrication of electrochemical capacitor cells

The electrochemical capacitor cells were constructed as a two-electrode cell. As-prepared GPEs films were sandwiched between two working electrodes. The working electrode was prepared by mixing carbon nanotubes (CNT, diameter 8-15 nm, length around 50 μm), carbon black and polytetrafluoroethylene (PTFE, 5 wt%) with a mass ratio 75:15:10. PTFE was used as the solvent to form a slurry with the mixed solids. The slurry was coated onto a stainless mesh (Biyuan co. ltd. China) for the two-electrode measurement and A Whatman filter paper (GF/D) was used as the separator. The area of the electrodes used to fabricate the supercapacitors cells was 1 cm^2 and the mass loading of active materials on each current collector was 2 mg cm^{-2}. The electrodes were dried in a vacuum oven at 110 °C for 10 h before use.

4.4 Electrochemical measurements

The electrochemical performance of the fabricated EDLC cells was measured by CV (cyclic voltammetry), EIS (electrochemical impedance spectroscopy) and GCD (galvanostatic charge-discharge) in the characterization part.

At room temperature, CV, GCD and EIS measurements were tested by using an Autolab PGSTAT 3020 N. CV curves were gained at different scan rates from 5 mV s^{-1} to 200 mV s^{-1}. GCD was running at various current densities in the range of 0.1 A g^{-1} to 4 A g^{-1}. EIS measurements were performed at open circuit potential in the frequency range of 10 MHz to 100 kHz with an amplitude of 5mV.

The mass-based specific capacitance C_s (in F g^{-1}) measured on these two-electrode cells were obtained from the GCD process. The C_s value can be derived by equation 4.1:

$$C_s = 4I\Delta t/2mV \qquad \text{Eq 4.1}$$

Moreover, the areal capacitance C_a (in mF cm^{-2}) can be obtained by equation 4.2:

$$C_a = 4I\Delta t/2SV \qquad \text{Eq 4.2}$$

Where I is the discharge current density, Δt is the discharge time, m is the mass of the active materials on a single electrode, S is the contact area between the active materials and electrode, V is the potential window.

The ionic conductivity of GPEs can be calculated by Eq 3.6.

5 Results and discussions

5.1 Morphology

The as-prepared gel polymer electrolytes membranes after the experimental process which was described in chapter 4, several GPEs were successfully syntheses. Figure 5.1a shows the as prepared PVDF-HFP/ EMIMBF$_4$ + TiO$_2$ polymer membrane while Figure 5.2a is the as prepared PVDF-HFP/ EMIMBF$_4$ + GO polymer membrane. The two membranes were at gel condition and flexible. The TiO$_2$ polymer membrane was almost transparent and GO polymer membrane was black because of the colour of solid GO filler.

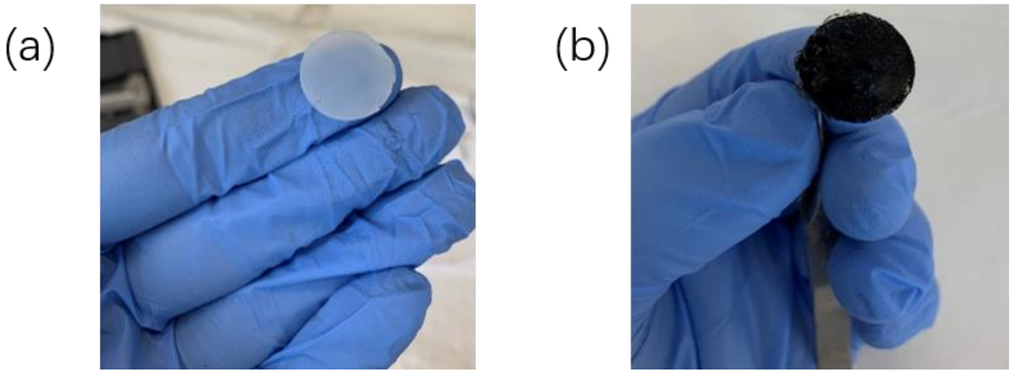

Figure 5.1 (a) As-prepared gel polymer electrolyte membrane consisted of PVDF-HFP/ EMIMBF$_4$ + TiO$_2$

(b) As-prepared gel polymer electrolyte membrane consisted of PVDF-HFP/ EMIMBF$_4$ + GO

In total, we had syntheses PVDF-HFP based gel polymer electrolytes as shown in Table 5.1. There were two ionic liquids used: EMIMBF$_4$ and EMIMTFSI. Different kinds and weight rate fillers were compared. At first, the effect of different content of TiO$_2$ (0.5 wt%, 1 wt%, 2 wt%, 5 wt%) to PVDF-HFP and EMIMBF$_4$ was systematically discussed. For comparison purpose, EMIMBF$_4$ was replaced by EMIMTFSI to investigate the effect of the different ionic liquids. In addition, another filler solid GO was introduced to GPE to further study the difference between TiO$_2$ and GO.

Table 5.1 Eight different groups of GPE

Group number	Polymer matrix	Ionic liquid	Fillers
1	PVDF-HFP	EMIMBF$_4$	-
2	PVDF-HFP	EMIMBF$_4$	5 wt% GO

3	PVDF-HFP	$EMIMBF_4$	0.5 wt% TiO_2
4	PVDF-HFP	$EMIMBF_4$	1 wt% TiO_2
5	PVDF-HFP	$EMIMBF_4$	2 wt% TiO_2
6	PVDF-HFP	$EMIMBF_4$	5 wt% TiO_2
7	PVDF-HFP	EMIMTFSI	-
8	PVDF-HFP	EMIMTFSI	5 wt% GO

5.2 Electrochemical performance of PVDF-HFP/ $EMIMBF_4$ GPE in symmetric cells

It is reported that a PEO/$EMIMBF_4$ gel polymer electrolyte membrane has been synthesized and the ionic conductivity can reach 14 mS cm^{-1} (Kim et.al, 2017). In this project, at first, a PVDF-HFP/ $EMIMBF_4$ group was set and tested. Figure 5.2a shows different CV curves in the 0 to 1.8 V potential range at various scan rates from 5 to 200 mV s^{-1} at room temperature. From Figure 5.2a, we can see that all CV curves show an almost rectangular shape which indicated the EDL mechanism. Figure 5.2b shows different GCD curves at different current densities in the range of 0.1 to 4 A g^{-1}. The EC cell was charged limited up to 1.8V. All the figures seem to be triangles and discharge characteristics of the cell was found to be linear. According to the GCD curves, specific capacitance values at different current densities were calculated. The specific capacitance is 9.5 F g^{-1} at a current density of 0.1 A g^{-1} and 3 F g^{-1} at a current density of 1 A g^{-1}, respectively. Figure 5.2c shows the rate capability. Fig 5.2d shows the Nyquist plot of the cell. It consists of an almost vertical line in the low-frequency region and a half-circle in the high-frequency region. The vertical line indicates the capacitive behaviour of the EC cell. The half-circle in the high-frequency region showed the details about the bulk and interfacial properties of the EC cell. The low equivalent series resistance R_s obtained from this Nyquist plot can further help to gain ionic conductivity.

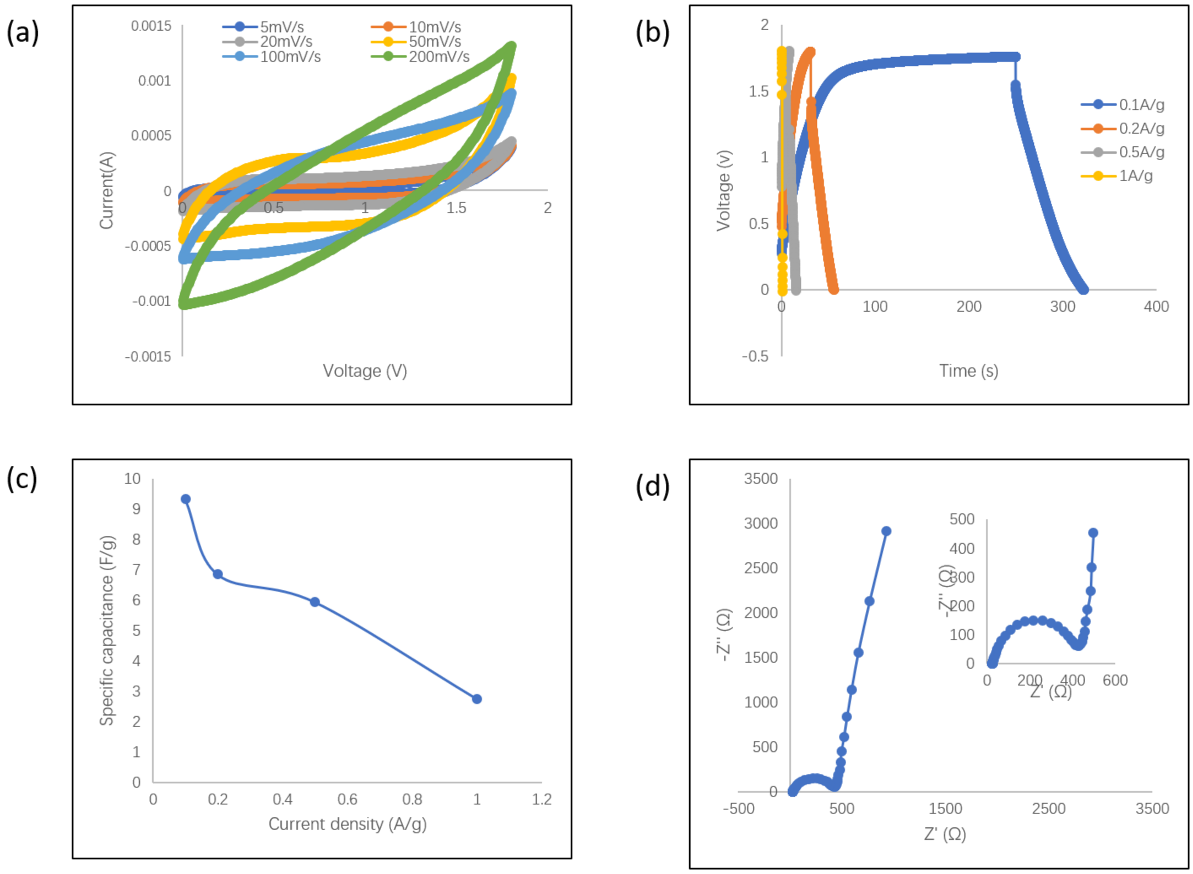

Figure 5.2 More electrochemical performance figures of the PVDF-HFP/ EMIMBF$_4$ GPE based-cell: (a) CV curves at scan rates from 5 mV s^{-1} to 200 mV s^{-1}, (b) GCD curves at current densities from 0.1 A g^{-1} to 1 A g^{-1}, (c) Rate capability, (d) EIS graph (Nyquist plot inset, at high-frequency region).

5.3 Electrochemical performance of PVDF-HFP/ EMIMBF$_4$ + 5 wt% GO GPE in symmetric cells

Given that the ionic conductivity and specific capacitance can be further improved by the addition of nanoparticles GO (Ahmad et.al, 2018). The second group was set with 5 wt% GO. Figure 5.3a shows different CV curves in the 0 to 1.8 V potential range at various scan rates from 5 to 200 mV s^{-1} at room temperature. From Figure 5.3a, we can see that all CV curves show an almost rectangular shape which indicated the EDL mechanism. Figure 5.3b shows different GCD curves at different current densities in the range of 0.1 to 4 A g^{-1} at room temperature. The EC cell was charged limited up to 1.8V. All the figures seem to be triangles and discharge characteristics of the cell was found to be linear. According to the GCD curves, specific capacitance values at different current densities were gained. According to the GCD curves, specific capacitance values at different current densities were gained. The specific capacitance values decreased from 19 F g^{-1} at a current density of 0.2 A g^{-1} to 5 F g^{-1} at a current density of 1 A g^{-1}. Figure 5.3c shows the rate capability. Fig 5.3d shows the Nyquist plot of the cell. It consists of an almost vertical line in the low-frequency region and a half-circle in the high-frequency region. The vertical line indicates the capacitive behaviour of the EC cell. The half-circle in the high-frequency region showed the details about the bulk and interfacial properties of the EC cell. The low equivalent series resistance R_s can be obtained from this figure which can further help to gain ionic conductivity.

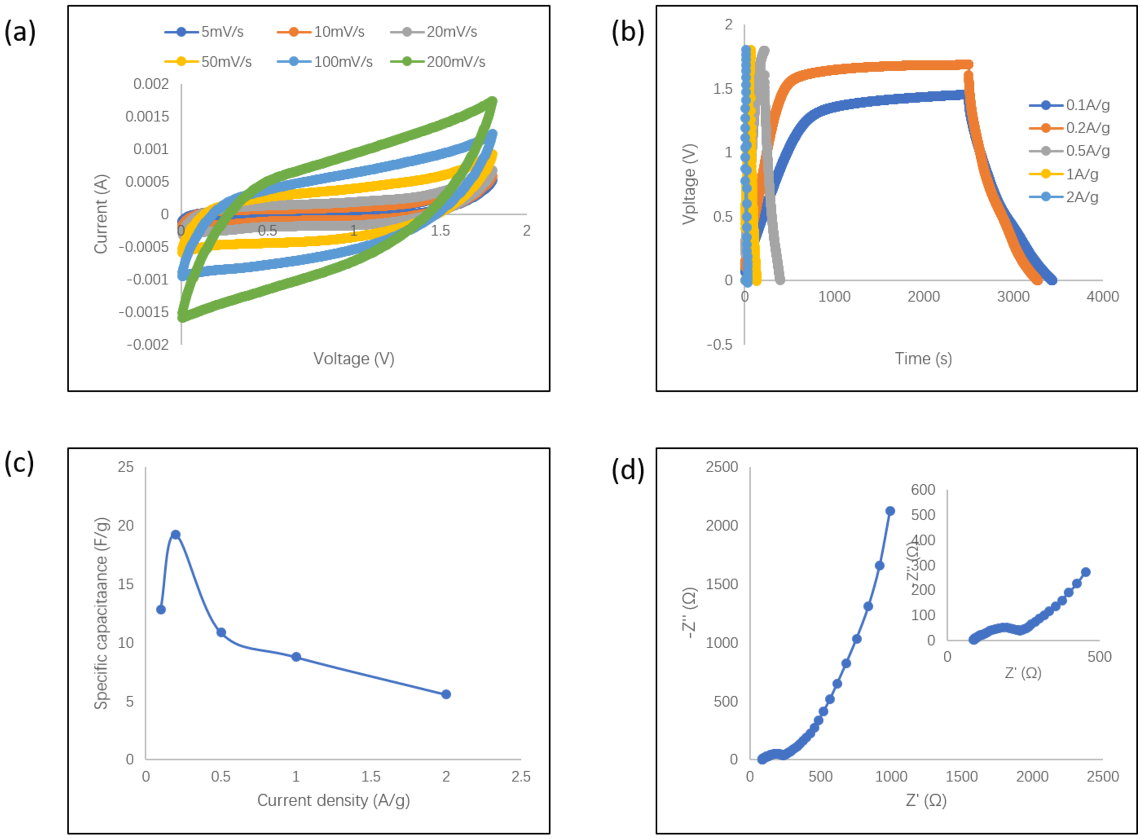

Figure 5.3 More electrochemical performance figures of the PVDF-HFP/ $EMIMBF_4$ + 5 wt% GO GPE based-cell: (a) CV curves at scan rates from 5 mV s^{-1} to 200 mV s^{-1}, (b) GCD curves at current densities from 0.1 A g^{-1} to 1 A g^{-1}, (c) Rate capability, (d) EIS graph (Nyquist plot inset, at high-frequency region).

5.4 Electrochemical performance of PVDF-HFP/ EMIMBF4 + 0.5/1/2/5 wt%TiO_2 GPE in symmetric cells

In the comparison of GO, nanoparticles TiO_2 was considered as a better choice than GO to improve ionic conductivity and specific capacitance (Song et.al, 2015). Figure 5.4a shows different CV curves in the 0 to 1.8 V potential range at various scan rates from 5 to 200 mV s^-

^{1} at room temperature. From Figure 5.4a, we can see that all CV curves show an almost rectangular shape which indicated the EDL mechanism. Figure 5.4b shows different GCD curves at different current densities in the range of 0.1 to 4 A g^{-1} at room temperature. The EC cell was charged limited up to 1.8V. All the figures seem to be triangles and discharge characteristics of the cell was found to be linear. According to the GCD curves, specific capacitance values at different current densities were gained. It can be clearly found that the highest specific capacitance was obtained from the PVDF-HFP/ EMIMBF4 + 1 wt% TiO_2 group and the specific capacitance values decreased from 12.2 F g^{-1} at a current density of 0.1 A g^{-1} to 11.2 F g^{-1} at a current density of 1 A g^{-1}. Figure 5.4c shows the comparison of rate capability. The PVDF-HFP/ EMIMBF4 + 1 wt% TiO_2 group showed a much better rate capability than the other three gel polymer electrolytes. Fig 5.4d consists of an almost vertical line in the low-frequency region and a half-circle in the high-frequency region. The vertical line indicates the capacitive behaviour of the EC cell. The half-circle in the high-frequency region showed the details about the bulk and interfacial properties of the EC cell. The low equivalent series resistance R_s can be obtained from this figure which can further help to gain ionic conductivity.

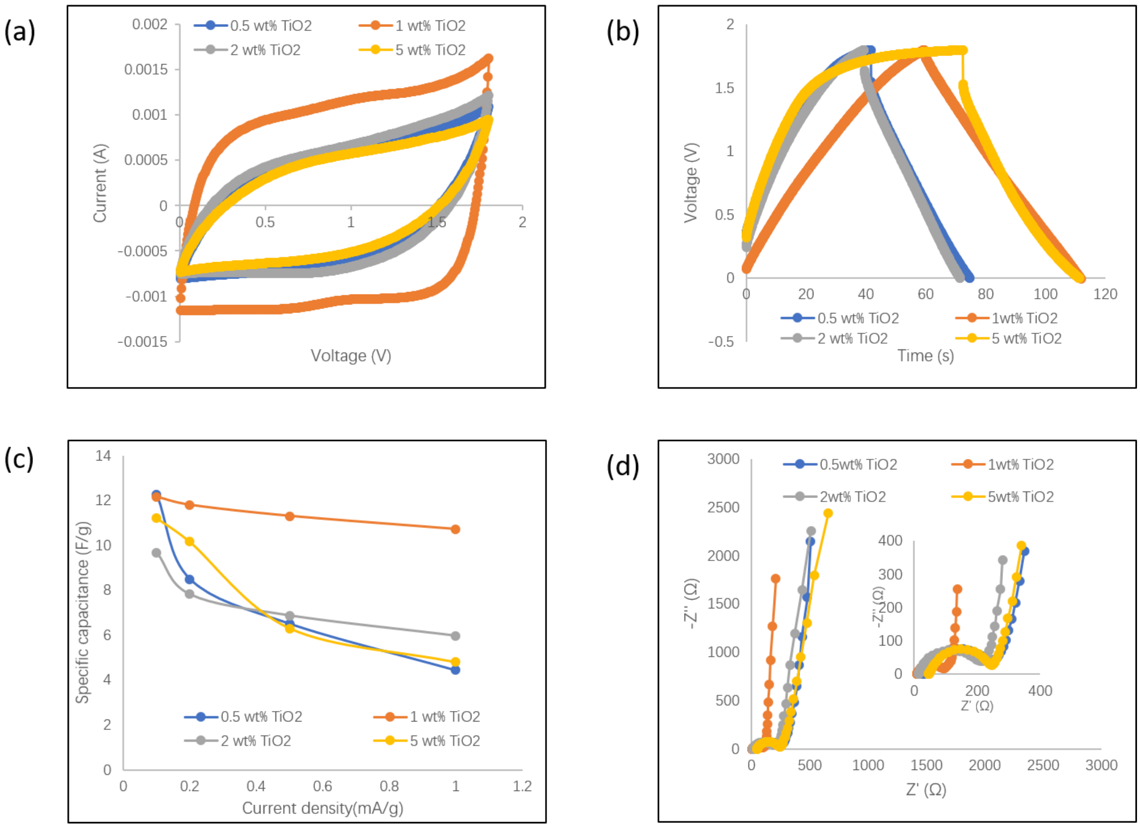

Figure 5.4 More electrochemical performance figures of the PVDF-HFP/ EMIMBF4 + 0.5/1/2/5 wt%TiO_2 GPE based-cells: (a) CV curves at scan rates of 10 mV s^{-1} for four groups, (b) GCD curves at current densities at 0.5 A g^{-1} for four groups, (c) Rate capability for four groups, (d) Nyquist plot for four groups.

The specific information of specific capacitance, ionic conductivity and rate capability of different TiO_2 content groups is given in Table 5.2. All four groups show a higher specific capacitance compared with the one without fillers. The ionic conductivity went to the peak between 1 wt% and 2 wt% TiO_2 group and even reach $2.6{\times}10^{-2}$ S cm^{-1}. In terms of the rate capability, the 1 wt% TiO_2 group can remain 81% of the capacitance from 12.5 A g^{-1} to 10 A g^{-1}.

Table 5.2 Electrochemical performance results for TiO_2 groups

TiO_2 content / wt%	Specific capacitance / F g^{-1} at 0.2 A g^{-1}	Ionic conductivity / S cm^{-1}	Rate capability (% remaining from 0.1 A g^{-1} to 1 A g^{-1})
0.5	12.25	$9{\times}10^{-3}$	36
1	12.00	$2.6{\times}10^{-2}$	81
2	9.50	$1.8{\times}10^{-2}$	62

5	11.25	6×10^{-3}	56

5.5 Electrochemical performance of PVDF-HFP/ EMIMTFSI GPE in symmetric cells

It is revealed that the ionic conductivity of ion gel can be easily improved with the change of anions. It is considered that anion $TFSI^-$ is a better choice than anion $BF4^-$ to further improve the ionic conductivity (Shaplov et.al, 2015). For Group 7, the gel polymer electrolytes with different IL anions were compared in this project. EMIMTFSI instead of $EMIMBF_4$ was added to the polymer matrix. Figure 5.5a shows different CV curves in the 0 to 1.8 V potential range at various scan rates from 5 to 200 mV s^{-1} at room temperature. From Figure 5.5a, we can see that all CV curves show an almost rectangular shape which indicated the EDL mechanism. Figure 5.5b shows different GCD measurement graphs at different current densities in the range of 0.1 to 4 A g^{-1} at room temperature. The EC cell was charged limited up to 1.8V. All the figures seem to be triangles and discharge characteristics of the cell was found to be linear. According to the GCD curves, specific capacitance values at different current densities were gained. The specific capacitance values decreased from 11.5 F g^{-1} at a current density of 0.1 A g^{-1} to 2 F g^{-1} at a current density of 1 A g^{-1}. Figure 5.5c shows the rate capability. Fig 5.5d shows the Nyquist plot of the cell. It consists of an almost vertical line in the low-frequency region and a half-circle in the high-frequency region. The vertical line indicates the capacitive behaviour of the EC cell. The half-circle in the high-frequency region showed the details about the bulk and interfacial properties of the EC cell.

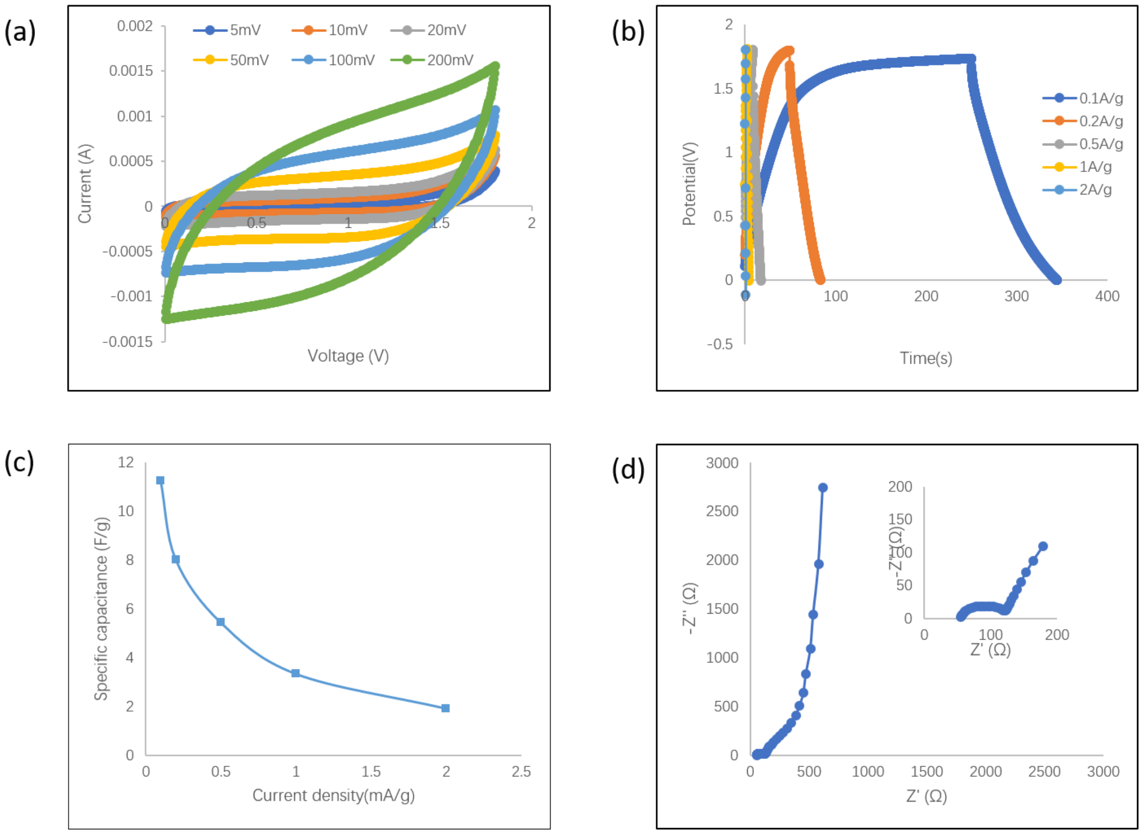

Figure 5.5 More electrochemical performance figures of the PVDF-HFP/ EMIMTFSI GPE based-cell: (a) CV curves at scan rates from 5 mV s^{-1} to 200 mV s^{-1}, (b) GCD curves at current densities from 0.1 A g^{-1} to 1 A g^{-1}, (c) Rate capability, (d) EIS graph (Nyquist plot inset, at high-frequency region).

5.6 Electrochemical performance of PVDF-HFP/ EMIMTFSI+ 5 wt% GO GPE in symmetric cells

Similarly, the addition of nanoparticles GO was considered for EMIMTFSI groups as well. 5 wt% GO was added into PVDF-HFP/EMIMTFSI in Group 8. Figure 5.6a shows different CV curves in the 0 to 1.8 V potential range at various scan rates from 5 to 200 mV s^{-1} at room temperature. From Figure 5.6a, we can see that all CV curves show an almost rectangular shape which indicated the EDL mechanism. Figure 5.6b shows different GCD curves at different current densities in the range of 0.1 to 4 A g^{-1} at room temperature. The EC cell was charged limited up to 1.8V. All the figures seem to be triangles and discharge characteristics of the cell was found to be linear. According to the GCD curves, specific capacitance values at different current densities were gained. The specific capacitance values decreased from 6.5 F g^{-1} at a current density of 0.1 A g^{-1} to 1.5 F g^{-1} at a current density of 0.5 A g^{-1}. Figure 5.6c shows the rate capability. Fig 5.6d shows the Nyquist plot of the cell. It consists of an almost vertical line in the low-frequency region and a half-circle in the high-frequency region. The vertical line indicates the capacitive behaviour of the EC cell. The half-circle in the high-frequency region showed the details about the bulk and interfacial properties of the EC cell.

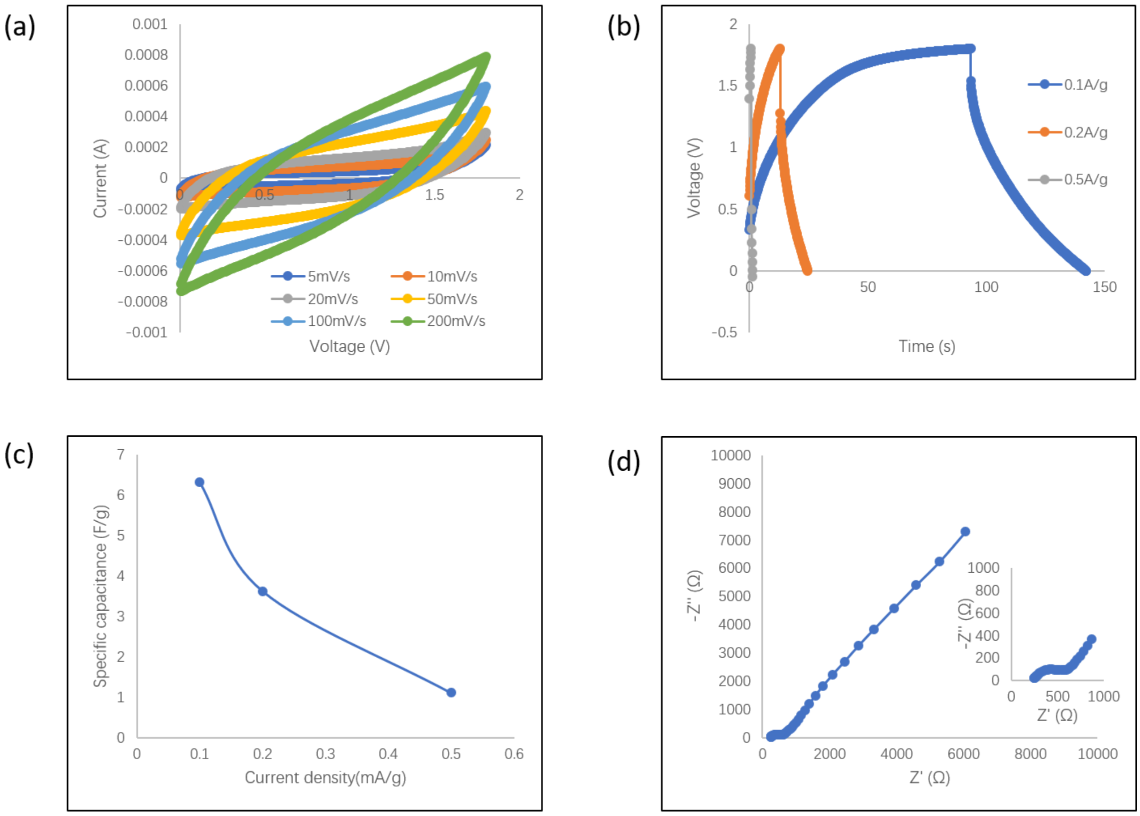

Figure 5.6 More electrochemical performance graphs of the PVDF-HFP/ EMIMTFSI+ 5 wt% GO GPE based-cell: (a) CV curves at scan rates from 5 mV s^{-1} to 200 mV s^{-1}, (b) GCD curves at current densities from 0.1 A g^{-1} to 1 A g^{-1}, (c) Rate capability, (d) EIS graph (Nyquist plot inset, at high-frequency region).

6 Conclusions and recommendations

In summary, we prepared PVDF-HFP based gel polymer electrolytes using solution casting method. The as-prepared GPEs with different ionic liquids and fillers were compared as the electrolytes for electrochemical capacitors. CV, GCD and EIS techniques were employed to evaluate the electrochemical performance. PVDF-HFP was used as the polymer matrix and $EMIMBF_4$/ EMIMTFSI acted as the plasticizers. Furthermore, two kinds of fillers (GO and TiO_2) were selected to improve the ionic conductivity. In particular, various contents of TiO_2 (0.5 wt%, 1 wt%, 2 wt%, 5 wt%) were investigated.

The electrochemical performance (specific capacitance, ionic conductivity and rate capability) of as-prepared GPEs were summarized in Table 6.1.

Table 6.1 Electrochemical performance test results for eight groups

Group number	Polymer matrix	Ionic liquid	Fillers	Specific capacitance / F g^{-1} at 0.2 A g^{-1}	Ionic conductivity / S cm^{-1}	Rate capability
1	PVDF-HFP	$EMIMBF_4$	-	9.5	9×10^{-3}	0.7
2	PVDF-HFP		5 wt% GO	13	2.5×10^{-3}	0.43
3	PVDF-HFP		0.5 wt% TiO_2	12.25	9×10^{-3}	0.36
4	PVDF-HFP		1 wt% TiO_2	12	2.6×10^{-2}	0.81
5	PVDF-HFP		2 wt% TiO_2	9.5	1.8×10^{-2}	0.62
6	PVDF-HFP		5 wt% TiO_2	11.25	6×10^{-3}	0.56
7	PVDF-HFP	EMIMTFSI	-	11.25	6×10^{-3}	0.4
8	PVDF-HFP		5 wt% GO	6.25	1×10^{-3}	0.2

Based on these results, here are some conclusions we can draw:

(1) Among all as prepared GPEs, PVDF-HFP/ $EMIMBF_4$ + 1 wt% TiO_2 GPE achieved the highest ionic conductivity (2.6×10^{-2} S cm^{-1}). The specific capacitance can remain 81% when current density shifting from 0.1 to 1 A g^{-1}. That is possible because of the excellent interaction between PVDF-HFP, $EMIMBF_4$ and 1 wt% TiO_2. The highest specific capacitance (13 F g^{-1}) among all the cells is found from the PVDF-HFP/ $EMIMBF_4$ +5% GO GPE. That might due to the porous structure of GO which can adsorb more ions resulting in a higher capacitance.

(2) Based on the data, the ionic conductivity of the GPE based on $TFSI^-$ anion is much higher than the GPE based on BF_4^- since $TFSI^-$ significantly lowered the glass transition temperature of the polymer. Moreover, it is indicated that $TFSI^-$ can help improve the rate performance in comparison with BF_4^-.

(3) The addition of filler TiO_2 can significantly improve the ionic conductivity of the gel polymer electrolyte and specific capacitance of the cell while GO as a filler can slightly improve the specific capacitance of the cell only but without enhancement of ionic conductivity. The reason can be attributed that TiO_2 can effectively reduce the crystallinity of PVDF-HFP copolymer and facilitate more liquid electrolyte uptake then enhance electrolyte uptake. In this project, TiO_2 seems to be a better filler than GO given the specific capacitance, ionic conductivity and rate capability.

In this project, PVDF-HFP/$EMIMBF_4$ comprising various contents (0.5 wt%, 1 wt%, 2 wt%, 5 wt%) of filler TiO_2, PVDF-HFP/$EMIMBF_4$ with filler GO and PVDF-HFP/EMIMTFSI with GO based-gel polymer electrolytes were synthesized by solution casting method. The effect of fillers (GO and TiO_2) and filler contents on the ionic conductivity and electrochemical performance were systematically investigated. With the incorporation of fillers, the ionic conductivity and electrochemical performance was improved. Particularly, PVDF-HFP/ $EMIMBF_4$ + 1 wt% TiO_2 GPE achieved the highest ionic conductivity at room temperature (2.6×10^{-2} S cm^{-1}) and the specific capacitance can remain 81% when current density shifting from 0.1 to 1 A g^{-1}. The specific capacity of assembled EC using PVDF-HFP/ $EMIMBF_4$ + 1 wt% TiO_2 GPE is 12 F g-1 at 0.2 A g^{-1}. PVDF-HFP/ $EMIMBF_4$ + 1 wt% TiO_2 GPE is promising as electrolytes for ECs.

Further study in depth is deserved to prepare advance gel polymer electrolytes. Even though we demonstrated gel polymer electrolyte with a high ionic conductivity, there are still some problems can be further studied:

(1) PVDF-HFP is a good polymer matrix for gel polymer electrolytes due to its high dielectric constant. However, there is still a long way for PVDF-HFP based GPE acting for commercial use. The high ionic conductivity of PVDF-HFP based GPE is in some degree at the cost of mechanical strength. It is deserved to consider how to balance the mechanical strength and ionic conductivity in practice.

(2) In comparison with solid polymer electrolyte, gel polymer electrolytes have high chemical and thermal stability, non-flammability and flexibility. Moreover, the ionic conductivity can be even 100 times higher than SPEs. However, the low mechanical strength of GPEs are still a critical problem and that is the main reason that GPEs cannot be used in commercial ECs at this stage. Adding inorganic fillers to GPEs is considered an effective way to improve mechanical stability as well as the ionic conductivity. Inorganic fillers play the roles of crosslinking centres. However, the content of the filler should be carefully adjusted appropriately since few fillers cannot work effectively and too many fillers will affect the ionic conductivity. Furthermore, the physical and chemical properties of the filler (pore size, morphologies) should be taken into consideration as well.

(3) In this thesis project, only CNTs were employed as electrode materials. The electrode materials are a significant part for determining the electrochemical performance especially the capacitance of an EC. The matching relationship between electrodes and electrolytes should be considered as well in order to maximize the electrochemical performance of ECs.

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