Polymer Electrolytes for Rechargeable Lithium/Sulfur Batteries

by

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AUTHOR'S DECLARATION

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

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Abstract

With the rapid development of portable electronics, hybrid-electric and electric cars, there is great interest in utilization of sulfur as cathodes for rechargeable lithium batteries. Lithium/sulfur batteries implement inexpensive, the earth-abundant elements at the cathode while offering up to a five-fold increase in energy density compared with the present Li-ion batteries. However, electrically insulating character of sulfur and solubility of intermediate polysulfides in organic liquid electrolytes, which causes rapid capacity loss upon repeated cycling, restrict the practical application of Li/S batteries.

In this thesis, the gel polymer and solid polymer electrolytes were synthesized and applied in Li/S batteries. A gel polymer electrolyte (GPE) was formed by trapping 1 M lithium bistrifluoromethane-sulfonamide (LiTFSI) in tetraethylene glycol dimethyl ether (TEGDME) electrolyte in a poly(vinylidenefluoride-co-hexafluoropropylene) (PVDF-HFP) /poly(methylmethacrylate) (PMMA) polymer matrix. The electrochemical properties of the resulting GPE were investigated in lithium/sulfur battery. The gel polymer battery exhibited a high specific capacity of 753.8 mAh g^{-1} at the initial cycle, stable reversible cycling and a capacity retention about 80% over 40 cycles along with a high Coulombic efficiency. Comparative studies conducted with the 1 M LiTFSI liquid electrolyte cell demonstrated that a cell with liquid electrolyte has remarkably low capacity retention and Coulombic efficiency compared with the GPE cell. In the further studies, a solid polymer electrolyte (SPE) based on poly- (ethylene-oxide)/nanoclay composite was prepared and used to assemble an all-solid-state lithium/sulfur battery. The ionic conductivity of the optimized electrolyte has achieved about 3.22×10^{-4} S cm^{-1} at 60 ^{o}C. The Li/S cell with this SPE delivered an initial

discharge capacity of 998 mAh g^{-1} when operated at 60 ^{o}C, and retained a reversible capacity of 634 mAh g^{-1} after 100 cycles. These studies has revealed that the electrochemical performance of lithium/sulfur cells, including charge-discharge cyclability and Coulombic efficiency, can be significantly improved by replacing liquid electrolytes with solid polymer and gel polymer electrolytes, which reduce the polysulfide shuttle effect and could protect the lithium anode from the deposition of the electrochemical reaction, leading to higher sulfur utilization in the cell.

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Finally, I would like to express my appreciation for my parents and my parents-in-law. I could not make it without their constant support and love. Most importantly, I want to thank my husband, Yongguang Zhang, for his unconditional love, encouragement and support. He has always been, and continues to be, my biggest stimulation for everything I do.

Dedication

Dedicated to My Parents and husband

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List of Abbreviations

THF: Tetrahydrofuran

KB: Ketjen Black

PVDF-HFP: Poly(vinylidenefluoride-co-hexafluoropropylene)

PMMA: Poly(methylmethacrylate)

LITFSI in TEGDME: Lithium bistrifluoromethanesulfonamide in tetraethylene glycol dimethyl ether

NMP: 1-methyl-2-pyrrolidinone

LiTFSI: Lithium bistrifluoromethanesulfonamide

PAN: Polyacrylonitrile

PVDF: Polyvinylidene fluoride

PEO: Polyethyleneoxide

MMT: Octadecylamine modified montmorillonite nanoclay

XRD: X-ray diffraction

FESEM: Field emission scanning electron microscopy

BET: Brunauer-Emmet-Teller

CV: Cyclic voltammetry

EIS: Electrochemical impedance spectroscopy

Chapter 1

Introduction and Motivation

1.1 Overview and Research Objectives

Rapidly growing consumption of limited fossil fuels and the accompanying global environmental problems demand for the development of alternative ecological and renewable energy sources (RES) and "green" electric transportation. Rechargeable batteries become an important part of the electric grids with such types of energy, allowing mitigating the power and current variation, and diminish the disadvantages of intermittent nature of RES. Secondary Lithium-ion batteries (LIBs) are dominating the market of portable electronics such as cellular phones, notebook computers, camcorders, *etc.* **[1-3]**. To further expand its application for the electric vehicles (EVs) or large energy reserved systems, the development of LIBs with transition metal oxides and phosphates based cathodes, having an inherent theoretical capacity limitation up to 300 mAh g^{-1}, and a maximum practically usable capacity of only 210 mAh g^{-1} has been considered widely **[4-7]**. Along with the mentioned capacity limitations, the transition metals used in these cathodes are expensive, limited in resources and mostly toxic. Compared with them, the elemental sulfur (S) is a more attractive candidate due to its low cost, environmental friendliness, high theoretical capacity of 1672 mAh g^{-1} and theoretical specific energy density of 2600 Wh kg^{-1} **[8]**, making it one of the most promising cathode materials for the next generation of high-energy secondary battery **[9]**.

However, it has been reported that Li/S batteries with organic liquid electrolyte have some problems related to low active material (S) utilization, low efficiency and poor cycle life **[9, 10]**, essentially due to the electronic and ionic insulating nature of S and the solubility of reductive polysulfides in organic electrolyte **[11-14]**. Big effort has been dedicated to improve the sulfur cathodes in the Li/S system; e.g. various types of conductive carbon materials **[12-19]** and conductive polymers **[20-28]** have been used to composite with sulfur as cathodes for Li/S batteries which allowed for partially overcoming the mentioned problems.

It is then surprising that most of the strategies attempted to date to achieve progress with the Li/S battery have been concentrated on the cathode problems, neglecting those associated with the electrolyte.

Therefore, in this thesis, we investigated the electrolyte component of the Li/S cell, and replaced a common liquid organic electrolyte with gel polymer and solid polymer electrolytes. It is considered that a polymer electrolyte may function as separator in a cell, isolating the negative and positive electrodes from each other, reducing the cathode reaction products from diffusing to the anode side [**29**].

In the first part of the thesis, we focus on the preparation and introduction of the gel polymer electrolyte (GPE) into Li/S batteries. GPE is considered as a promising candidate for high energy density electrochemical devices **[30]**, which can successfully separate the electrodes in a battery and minimize the electrolyte leakage problems, while at the same time, it retains the ionic conductive properties of a liquid, such a low internal impedance and high mobility of the charge carrying species **[30]**. In our study, the GPE was formed by trapping 1 mol L^{-1} solution of lithium bistrifluoromethane-sulfonamide (LiTFSI) in tetraethylene glycol dimethyl ether electrolyte in a poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP)/poly(methylmethacrylate) (PMMA) polymer matrix. This PVDF-HFP/PMMA composite membrane was prepared by phase inversion using acetone/water as solvent/non-solvent. The Li│ PVDF-HFP/PMMA GPE│ S/KB composite coin-type battery was assembled and electrochemical performance was explored.

In the second part of thesis, we focus on the preparation and introduction of the solid polymer electrolyte (SPE) into Li/S batteries. Since in the Li/S batteries, sulfur cathode is lithium free, lithium metal is always chosen as an anode. However, there are several problems with lithium metal such as its extremely high reactivity causing flammable instinct characteristic, and dendrites formation on the surface of lithium metal during cycling, resulting in a cell short circuiting, which are very serious safety hazards. Use of a solid state electrolyte that is impermeable for polysulfides can effectively suppress the formation of dendrites. Currently, SPE has drawn wide attention due to its advantages, such as no leakage of electrolyte, high energy density, flexible geometry and safety when used in solid-state rechargeable lithium batteries **[31, 32]**. Herein, we report the preparation of a solid polymer electrolyte based on poly (ethylene-oxide)/nanoclay composite for all solid state lithium/sulfur batteries. The effects of the nanoclay content and the temperature on the conductivity of SPE have been investigated using AC impedance spectroscopy. The electrochemical properties of all solid state Li/S batteries were investigated by cyclic voltammetry (CV) and charge/discharge measurements.

1.2 Outline of the Thesis

This thesis consists of chapters as followings:

Chapter 1 gives an overview of the thesis, including introduction of polymer electrolytes used in Li/S batteries. The main objectives of the research are also listed in this chapter.

Chapter 2 reviews the available literature about principles, the latest developments and new opportunities in polymer Li/S batteries field.

Chapter 3 describes the details the experimental methods and required materials applied in the research.

In Chapter 4, we report on the preparation of novel poly (vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP)/poly(methylmethacrylate) (PMMA) gel polymer electrolyte, and investigation of its physical and electrochemical properties in the structure of Li/S battery.

Chapter 5 presents the solid polymer electrolyte based on poly (ethylene-oxide)/nanoclay composite and the results of its tests in all solid state lithium/sulfur batteries.

Finally, Chapter 6 gives the conclusions of this thesis and present recommendations for the future work.

Chapter 2

Background and Literature

2.1 General Introduction to Polymer Electrolyte for Lithium Sulfur Batteries

With the rapid exhaustion of limited resources such as fossil fuels and their global environmental issues, modern society's sustainability depends on the development of ecological alternative power sources such as solar and wind energy, and low-emission transportation such as hybrid and electric vehicles. High energy-density batteries are an essential part of such systems and there is an insatiable demand for its improvement. Secondary lithium-ion batteries (LIBs) dominate the market for portable electronics (e.g., cellular phones, notebook computers, camcorders) **[1-3]**, but are still not economically attractive for large scale and transportation applications.

Although tremendous progress has been achieved in the field of LIBs, the transition metal oxides and phosphates typically used as cathode materials have maximum theoretical capacity limited to about 200 mAh g^{-1} (of which only 170 mAh g^{-1} can be practically achieved) **[4-7]**. The energy limitations, along with the high cost and ecological concerns of these materials, can restrict their practical application in large scale scenarios.

An alternative technology under intense development is the lithium/sulfur battery (Li/S). Elemental sulfur has higher theoretical capacity (1672 mAh g^{-1}) and specific energy (2600 Wh kg^{-1}) than conventional cathode materials. Sulfur is also a low cost, abundant, and environmentally friendly natural resource **[8]**, making it a very promising cathode material candidate, especially for large scale energy storage applications **[9]**. However, Li/S batteries suffer from inefficient utilization of cathode materials and poor cyclability **[9,10]**, both essentially due to the insulating nature of S and the solubility of polysulfides in liquid organic electrolytes **[11-14]**.

Successful operation of Li/S batteries has been achieved through the development of composites of sulfur with carbonaceous **[5,15-23]** and polymeric **[24-27]** materials. In these composites, the S particles are embedded into the conductive carbon or polymer matrices **[5,21,28]**, which enhance the electronic conductivity of the composite and hinder the dissolution of polysulfides into the electrolyte **[13,14,28-30]**.

Another strategy to improve the capacity and cyclability of Li/S batteries is the electrolyte optimization so as to reduce the loss of sulfur by dissolution in the liquid electrolyte **[14,31-35]**. Among the possible electrolyte modifications, replacement of the common liquid organic electrolytes with polymer electrolytes has proved promising and efficient.

Polymer electrolyte may generally be defined as a membrane that possesses transport properties comparable to that of common liquid ionic solutions **[36]**. Although the study of polymer electrolyte was started in 1973 by Fenton *et al.* **[37]**, its technological importance was appreciated in the early 1980s **[38]**. Since then, a large number of polymer electrolyte systems have been prepared and characterized. It is possible and convenient to group all the polymer systems into two broad categories, *i.e.*, pure solid polymer electrolyte (SPE) and plasticized or gel polymer electrolyte systems (GPE).

The first category, pure solid polymer electrolyte, is composed of lithium salts (e.g., $LiClO_4$, $LiBF_4$, $LiPF_6$, $LiAsF_6$, $LiCF_3SO_3$, $LiN(CF_3SO_2)_2$, $LiC(CF_3SO_2)_3$) dissolved in high molecular weight polyether hosts, (e.g., PEO and PPO) which acts as solid solvents **[39]**. The ionic conduction mechanism of SPE is intimately associated with the segmental motions of the polymer. The second category of polymer electrolyte, gel polymer electrolyte, is characterized by a higher ambient ionic conductivity but poorer mechanical properties when compared with SPE. GPE is usually obtained by incorporating a larger quantity of liquid electrolyte to a polymer matrix that is capable of forming a stable gel polymer host structure.

Polymer electrolytes have several obvious advantages over the liquid electrolytes. Among the advantages of these electrolytes, they include no internal shorting, no leakage of electrolytes and no non-combustible reaction products at the electrode surface existing in the liquid electrolytes **[40-44]**. The pre-requisites for a polymer electrolyte for lithium batteries are: high ionic conductivity at ambient and sub ambient temperatures, good mechanical strength, appreciable transference number, thermal and electrochemical stabilities, and better compatibility with electrodes **[41-43,45]**. In particular, for Li/S battery, it is expected that the polymer membrane can act as a physical barrier, which can help control the dissolution of the sulfide anions from the cathode and also prevent the attack of the same anions at the anode **[46]**.

In this chapter, the preparation and electrochemical properties of polymer electrolytes are studied based on the catalogue of polymer electrolytes. The electrochemical characteristics of the Li/S batteries based on these polymer electrolytes, related to the performance of their cells, are also discussed here.

2.2 Dry Solid Polymer Electrolytes in Li/S Batteries

In dry solid polymer electrolytes, the polymer host itself is used as a solid solvent along with lithium salt and it does not contain any organic liquids. As a polymer host, the high molecular weight poly(ethylene oxide) (PEO)-based solid polymer electrolytes are emerging as the best candidates to be used because of their solvation power, complexation ability and ion transport mechanism directly connected with the alkaline salt (Li^+). However, the ionic conductivity of PEO-lithium salts (LiX) electrolytes at ambient temperature (10^{-7}-10^{-6} S cm^{-1}) is not high enough for most practical applications. In order to overcome this problem, consistent research efforts have been devoted to improve the ionic conductivity of PEO-LiX ($X = ClO_4^-$, $CF_3SO_3^-$, BF_4^-, PF_6^-, *etc.*) solid polymer electrolytes **[42, 47]**.

In Jeon *et al.*'s study **[48]**, $LiClO_4$ was chosen to dissolve in high molecular weight polymer host-PEO which acted as solid solvents. Dry polymer electrolyte made of PEO with tetra(ethylene glycol dimethyl ether) was employed into Li/S cells to study issues such as the fading capacity and low sulfur utilization.

According to the change in morphologies for a composite sulfur cathode, which was obtained by scanning electron microscopy (SEM), a model for the change in morphology of the composite cathode was built as shown in **Figure 2.1**. The authors offered us a mechanism for the capacity fading that was mainly due to the heterogeneity and worsening distribution of sulfur along with cycling.

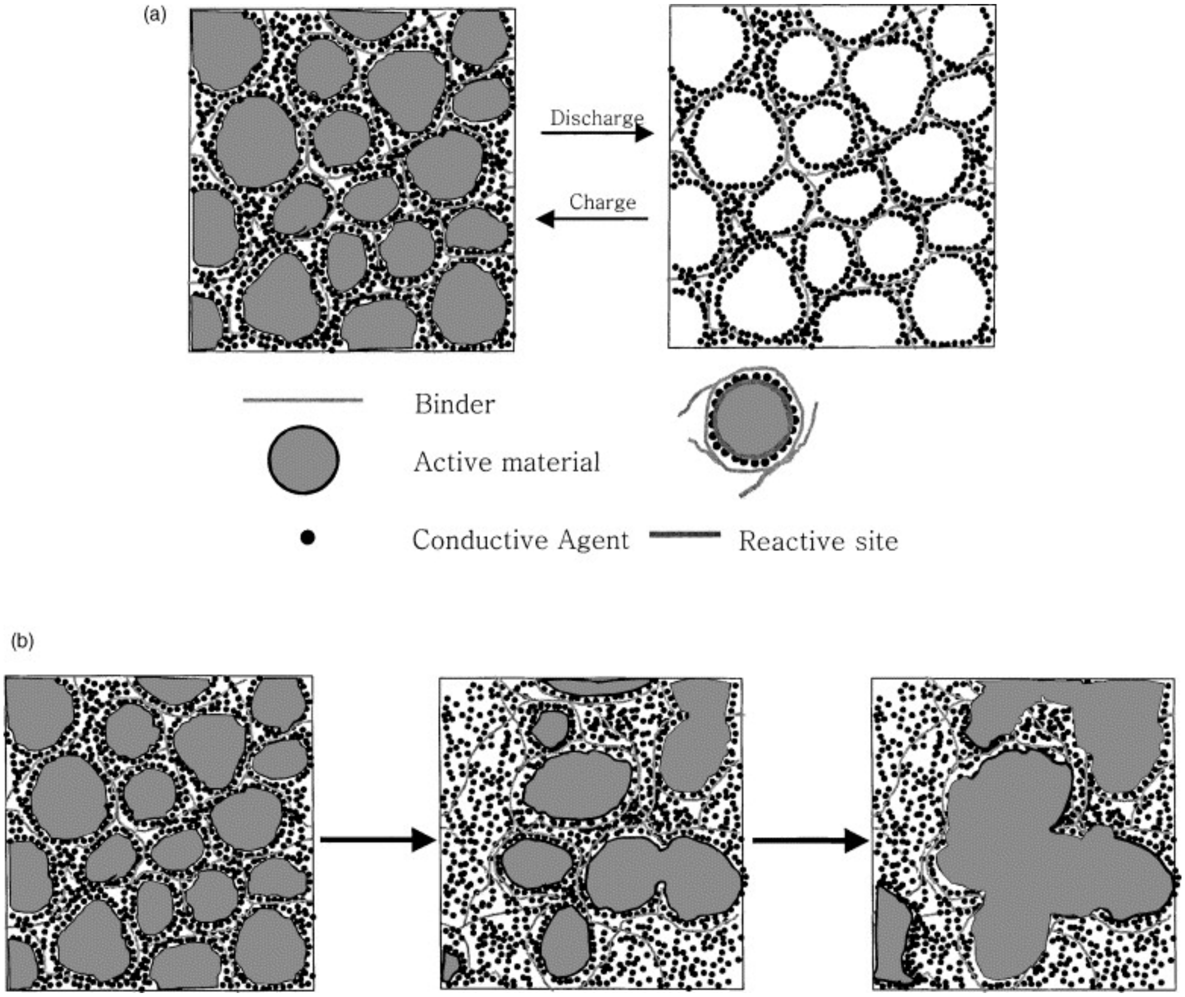

Fig 2.1 Model for morphology change of composite cathode during charge-discharge: (a) ideal case; (b) real case. Reprinted from Ref. 48 with permission from Elsevier.

Some researchers have been trying to further improve the conductivity by the use of inorganic ceramic filler such as Al_2O_3, SiO_2, TiO_2 and ZrO_2 in the host polymer matrix **[49-57]**.

In Shin *et al.*'s study **[58]**, $(PEO)_{10}LiCF_3SO_3$ polymer electrolyte with titanium oxide (Ti_nO_{2n-1}, $n = 1, 2$) was introduced into Li/S system, and they not only investigated the ionic conductivity and interfacial stability of this dry polymer electrolyte but also the discharge characteristics of Li/S cells with $(PEO)_{10}LiCF_3SO_3$ polymer electrolyte. From the results of this study, titanium oxide is a good candidate as ceramic filler in $(PEO)_{10}LiCF_3SO_3$ dry polymer electrolyte. Titanium Oxide filler has a size of sub-micron and several micron consisting of various phases that were prepared by ball milling for 100 h, which were introduced into the $(PEO)_{10}LiCF_3SO_3$ polymer electrolyte. The addition of titanium oxide containing Ti_2O_3, TiO and Ti_2O into the $(PEO)_{10}LiCF_3SO_3$ polymer electrolyte improved the ionic conductivity due to the change of -C-O-C- vibration and ionic structure of polymer electrolyte by the decrease in crystallinity of PEO polymer electrolyte, and the interface resistance between polymer electrolyte and lithium electrode was remarkably decreased by lowering the contact area between lithium and electrolyte.

In Jeong *et al.*'s study **[59]**, $(PEO)_6LiBF_4$ polymer electrolyte was prepared under three different mixing conditions: stirred polymer electrolyte, ball-milled polymer electrolyte and ball-milled polymer electrolyte with 10 wt% Al_2O_3. The Li/S cell containing ball-milled $(PEO)_6LiBF_4$-Al_2O_3 polymer electrolyte delivered a high initial discharge of 1670 mAh g^{-1}, which was better than the cells with stirred $(PEO)_6LiBF_4$ polymer electrolyte or $(PEO)_6LiBF_4$ ball-milled polymer electrolyte. And also the cycle performance of Li/$(PEO)_6LiBF_4$/S cell was also remarkably improved with the addition of Al_2O_3.

$(PEO)_{20}Li(CF_3SO_2)_2N$-$\gamma LiAlO_2$ was prepared and introduced into Li/S battery in Wen *et al.*'s study **[60]**. The all-solid-state Li/S cell with PEO based polymer electrolyte operating at 75 °C exhibited an average capacity of 290 mAh g^{-1} in 50 cycles. The cycle-stability of Li/S polymer battery was improved by amending the method to prepare the sulfur composite cathode by blending sulfur and PEO by thermal melting at 180 °C in a sealed container. The SEM results confirmed the mechanism of capacity fading **[48]**, which suggested that the capacity of Li/S polymer battery was mostly suffered from aggregation of sulfur or lithium sulfide during cycling.

This research group did a further study to combine $(PEO)_{18}Li(CF_3SO_2)_2N\text{-}SiO_2$ polymer electrolyte and sulfur/mesoporous-carbon composite cathode as an all solid state polymer battery **[29]**. The conductivity of the PEO based electrolyte could reach 5×10^{-4} S cm^{-1} at 70 °C. In the sulfur cathode, mesoporous carbon sphere with uniform channels was employed as a conductive agent, and sulfur was penetrated into those channels by a co-heating method. By this, the prepared all solid state polymer battery showed excellent cycling performance with a reversible discharge capacity of about 800 mAh g^{-1} at 70 °C after 25 cycles.

In Hassoun *et al.*'s study **[61]**, the solid electrolyte was prepared by a hot-pressed membrane of poly(ethylene oxide)-lithium triflate $PEO\text{-}LiCF_3SO_3$ composite containing well-dispersed nanosized zirconia, ZrO_2, particles and lithium sulfide, Li_2S. In this composite, the well-dispersed ZrO_2 filler is beneficial to the transport properties of the polymer electrolyte both in terms of enhancement of the ionic conductivity and of lithium transport number, as well as acting as a stabilizer of the lithium metal electrode/electrolyte interface **[62]**. The $PEO\text{-}LiCF_3SO_3$ composite provides the lithium ion transport **[63]** and the addition of Li_2S contributes to enhance conductivity and also prevents sulfide dissolution from the cathode **[64]**. The resulting solid polymer electrolyte was exploited by fabricating a solid-state battery formed with a lithium metal anode and sulfur/carbon cathode. **Figure 2.2** shows that a specific capacity of about 450 mAh g^{-1} (based on the S/C mass) or about 900 mAh g^{-1} (based on the S mass) can be obtained by the Li/SPE/S-C solid state battery.

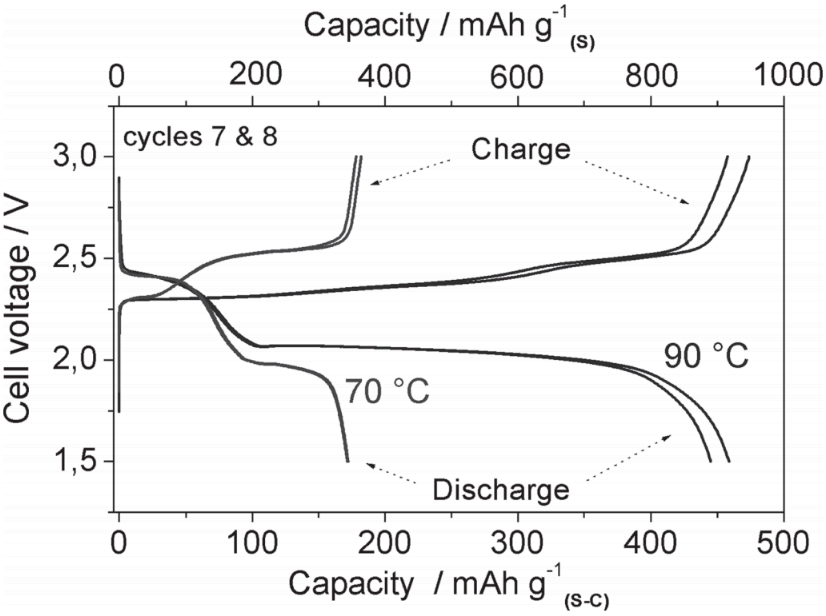

Fig 2.2 Voltage profiles of typical discharge-charge cycles of the Li/SPE/S-C solid-state battery at two temperatures and at a C/20 rate 1.5-3 V voltage range. The specific capacity is reported in terms of total S-C mass and of S mass only. Reprinted by permission from Wiley-VCH Verlag GmbH & Co. KGaA. from Ref. 61.

Recently, Yu *et al.* [**65**] reported the fabrication of all-solid-state Li/S battery containing siloxane cross-linked network solid electrolyte at room temperature. The solid polymer electrolytes (SPEs) were prepared by crosslinking reaction of a homogeneous precursor solution of siloxane cross-linker, tetra (ethylene oxide) dimethyl ether, lithium salt ($LiCF_3SO_3$) and an initiator (benzoyl peroxide, BPO). The resulting solid electrolytes show high ionic conductivity (3.52×10^{-4} S cm^{-1} at room temperature) and good electrochemical stability with lithium (3.85 V vs Li). All-solid-state Li/S battery was prepared by stacking lithium metal anode, solid polymer electrolyte and sulfur cathode in turn as shown in **Fig.2.3**. The battery shows the first discharge capacity of 1044 mAh g^{-1} at room temperature. This first discharge capacity rapidly decreases in 4th cycle and remains at 512 mAh g^{-1} after 10 cycles.

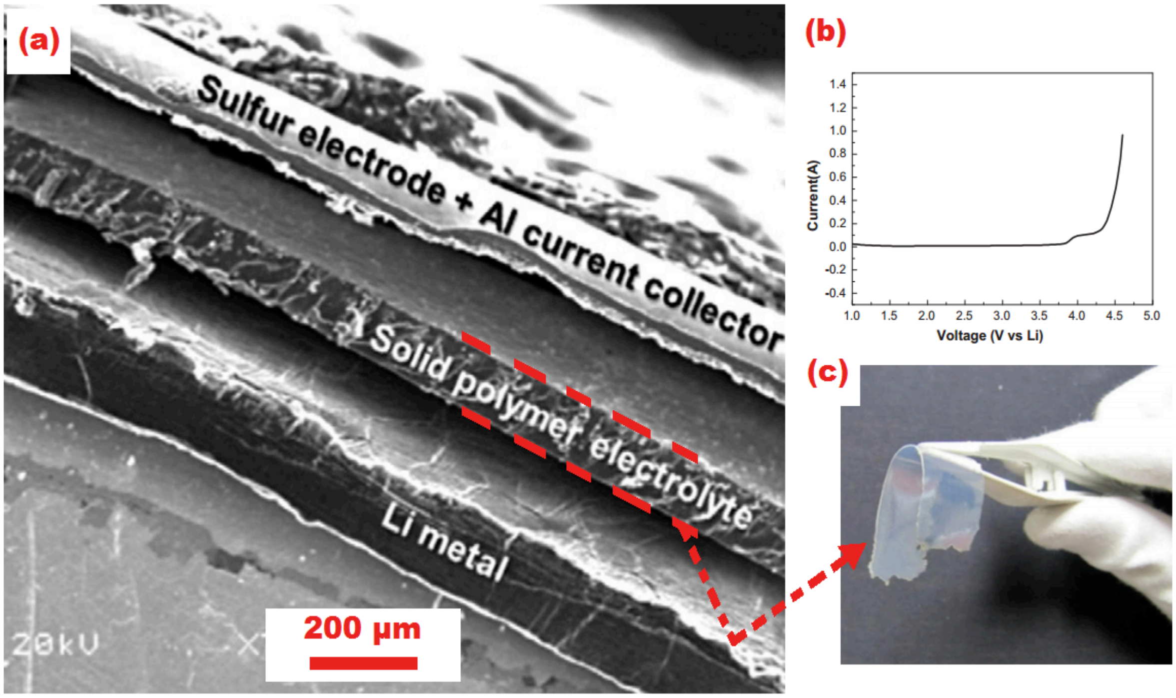

Fig 2.3 (a) Cross-sectional SEM image of all solid state Li/S battery; (b) Linear sweep voltammetry curve of solid polymer electrolyte at room temperature; (c) The photograph of solid polymer electrolyte. Reprinted from Ref. 65 with permission from Elsevier.

In summary, the reason for choosing PEO as the polymer host is mainly due to that PEO usually form stable dry complexes exhibiting a relatively higher ionic conductivity than other solvating polymers **[66]**. The sequential oxyethylene group: -CH_2-CH_2-O-, and the polar groups:-O-, -H-, -C-H-, in the polymer chains can well dissolve the ionic salts **[43,44,63]**. In further studies, new polymer electrolyte structures, based on a modified PEO main polymer chain with grafted polymers, block copolymers, cross-linked polymer networks, which resulted in polymer electrolytes with a lower degree of crystallinity and a low glass transition temperature T_g, can be considered for use into Li/S battery system.

2.3 Gel Polymer Electrolyte in Li/S Batteries

In the point of view of dry solid polymer, the main obstacle is still the ionic conductivity, which is generally below 10^{-3} $S \cdot cm^{-1}$ and not enough for practical application. At room temperature, the all solid state Li/S batteries usually showed poor performance. As a result, gel polymer electrolytes were developed **[67-69]**, which can be regarded as an intermediate state between typical liquid electrolytes and dry solid polymer electrolytes. In gel polymer electrolytes, the liquid component is trapped in the polymer matrix, thereby preventing leakage of liquid electrolyte. Therefore, the pore structure of the polymer membrane is the key component and is especially important for the ionic conductivity. In Li/S battery, to date, several types of polymer membranes have been developed and characterized, such as those based on poly(ethylene oxide) (PEO), poly(vinylidene fluoride) (PVDF) and poly(vinylidene fluoride)-hexafluoropropylene (PVDF-HFP).

2.3.1 PEO-Based Gel Polymer Electrolyte

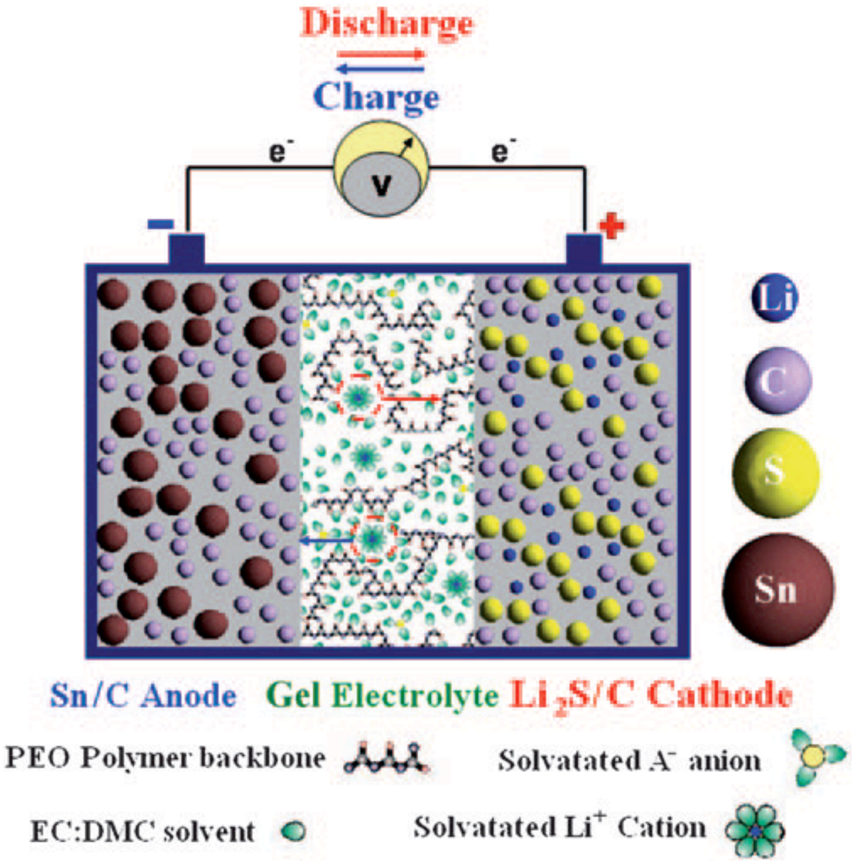

Fig 2.4 Sketch of the Sn/C/CGPE/Li$_2$S/C polymer battery developed herein.

The battery is formed by a Sn/C composite anode, a PEO based gel polymer electrolyte, and a Li$_2$S/C cathode. PEO = poly(ethylene oxide). Reprinted by permission from Wiley-VCH Verlag GmbH & Co. KGaA. from **Ref. 64**.

Important progress was recently made by Scrosati and co-workers **[64]**, who built a lithium metal-free new battery version as **Figure 2.4** shows. They also renewed the electrolyte component by replacing the common liquid organic solutions with a gel-type polymer membrane, formed by trapping ethylene carbonate/dimethylcarbonate lithium hexafluorophosphate (EC: DMC/$LiPF_6$) solution saturated with lithium sulfide in a polyethylene oxide/lithium trifluoromethanesulfonate (PEO/$LiCF_3SO_3$) polymer matrix **[70]**.

A dispersed zirconia ceramic filler enhanced the mechanical properties of the gel and improved liquid retention within its bulk **[71]**. Impedance studies **[72]** indicate that the resistance of the as-prepared GPE is low and stable with time with a high conductivity approaching 10^{-2} S·cm^{-1} (**Figure 2.5**). With the assembly of the Sn/C anode, Li_2S/C cathode and PEO based GPE, this polymer battery showed a high initial discharge of about 1200 mAh·g^{-1} at 38 mA·cm^{-2}·g^{-1} (capacity calculated based on Li_2S mass only).

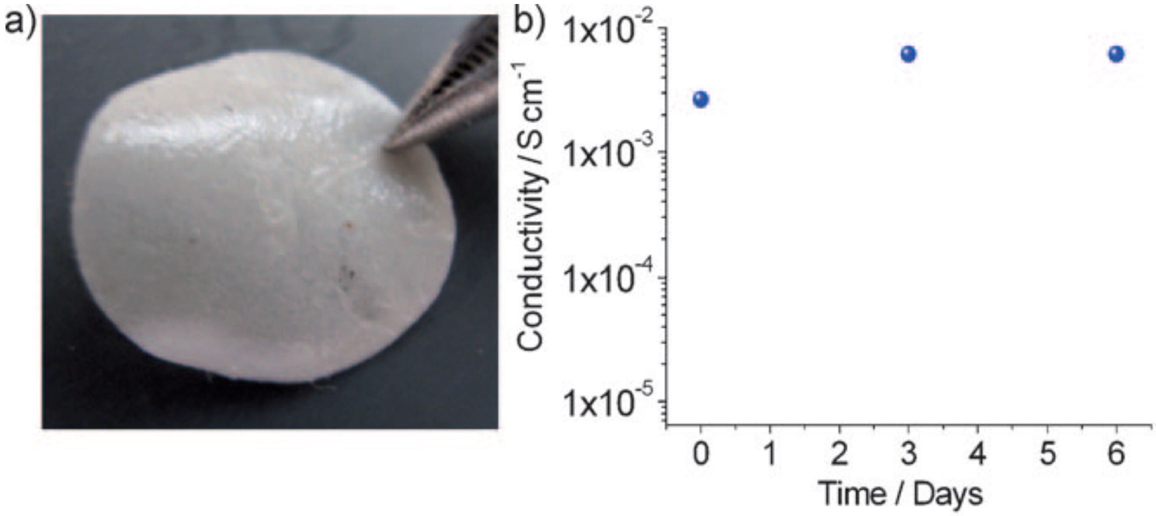

Fig 2.5 Characteristics of the PEO based gel polymer membrane to be used as electrolyte separator in the lithium-sulfur battery: (**a**) Appearance of the membrane; (**b**) Time evolution of the conductivity at room temperature**.** Reprinted by permission from Wiley-VCH Verlag GmbH & Co. KGaA. from **Ref. 64**.

The same research group continued the investigation of this new battery by studying in detail its performance in terms of the basic electrochemistry of the cathode material **[73]**. XRD analysis performed *in situ* in a lithium cell (in **Fig. 2.6**) shows that lithium sulfide can be converted into sulfur during charge and re-converted back into sulfide during the following discharge process. The electrochemical process can be efficiently carried out in polymer electrolyte lithium cells and thus, that the Li_2S-C composite can be successfully used as cathode for the development of novel types of rechargeable lithium-ion sulfur batteries where the reactive and unsafe lithium metal anode is replaced by a reliable, high capacity tin-carbon composite and the unstable organic electrolyte solution is replaced by a composite gel polymer membrane that is safe, highly conductive and able to control dendrite growth across the cell. This new Sn-C/Li_2S polymer battery operates with a capacity of 600 mAh g^{-1} and with an average voltage of 2 V, this leading to a value of energy density amounting to 1200Wh kg^{-1}.

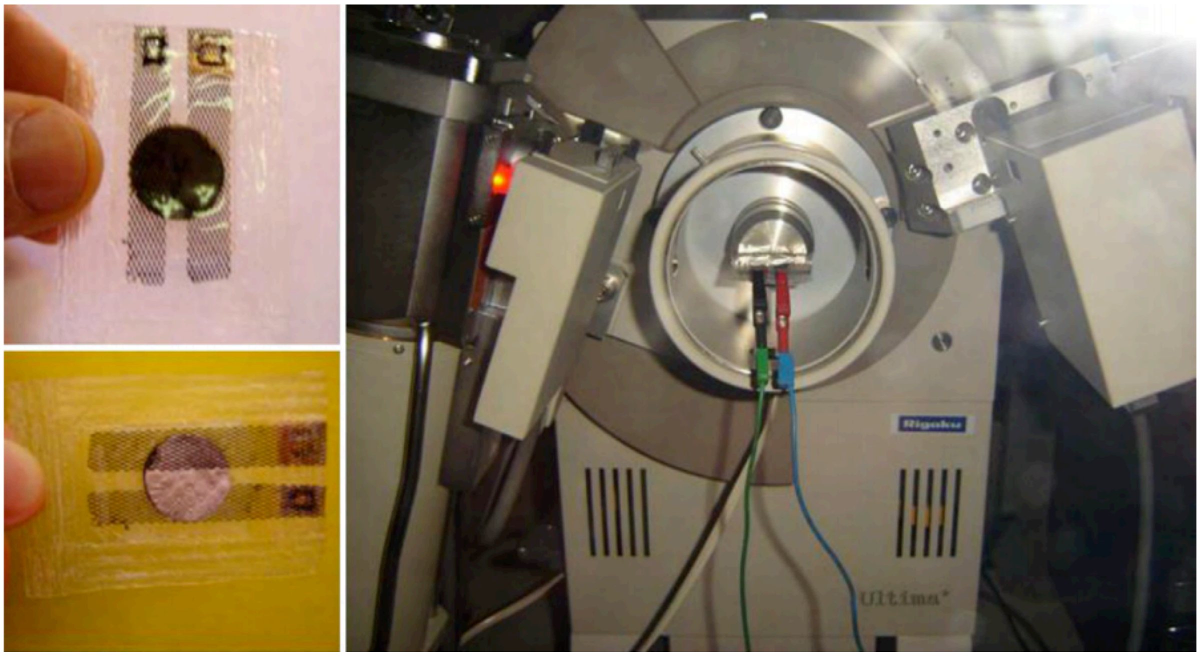

Fig 2.6 Instrumental setup used for the in situ XRD measurements. Reprinted from Ref. 73 with permission from Elsevier.

2.3.2 PVDF-Based Gel Polymer Electrolyte

Poly(vinylidene fluoride) (PVDF) has received great attention as a membrane material with regard to its outstanding properties such as high mechanical strength, thermal stability, chemical resistance, and high hydrophobicity **[74]**. By virtue of its various appealing properties, PVDF has been chosen as a suitable polymer host. PVDF-based polymer electrolytes are expected to be highly anodically stable due to the strongly electron-withdrawing functional group (-C-F). Furthermore, PVDF itself has a high dielectric constant (ε=8.4) for a polymer, which can assist in greater ionization of lithium salts, and thus provide a high concentration of charge carriers **[39,75]**.

A detailed discussion regarding the discharge process of Li/PVDF/S was presented by Ryu *et al.* **[76]**. The PVDF gel polymer electrolyte was prepared by $LiCF_3SO_3$ as lithium-ion resource, tetraglyme as plasticizer, and PVDF as a gelling agent in THF solvent in Ar atmosphere. A freestanding PVDF electrolyte film was obtained after the solvent was evaporated at room temperature. By using PVDF polymer electrolyte, the Li/S cell had two plateaus-like potential regions and a discharge capacity of 1268 mAh g^{-1} at the first discharge. The discharge capacity decreased to 1028 mAh g^{-1} and the upper plateau region disappeared after second discharge. From XRD and DSC results of the sulfur electrode, a model was built as shown in **Figure 2.7** to suggest that elemental sulfur disappeared and changed into Li_2S_n ($n > 4$) at the upper plateau region and Li_2S was formed at the low plateau region.

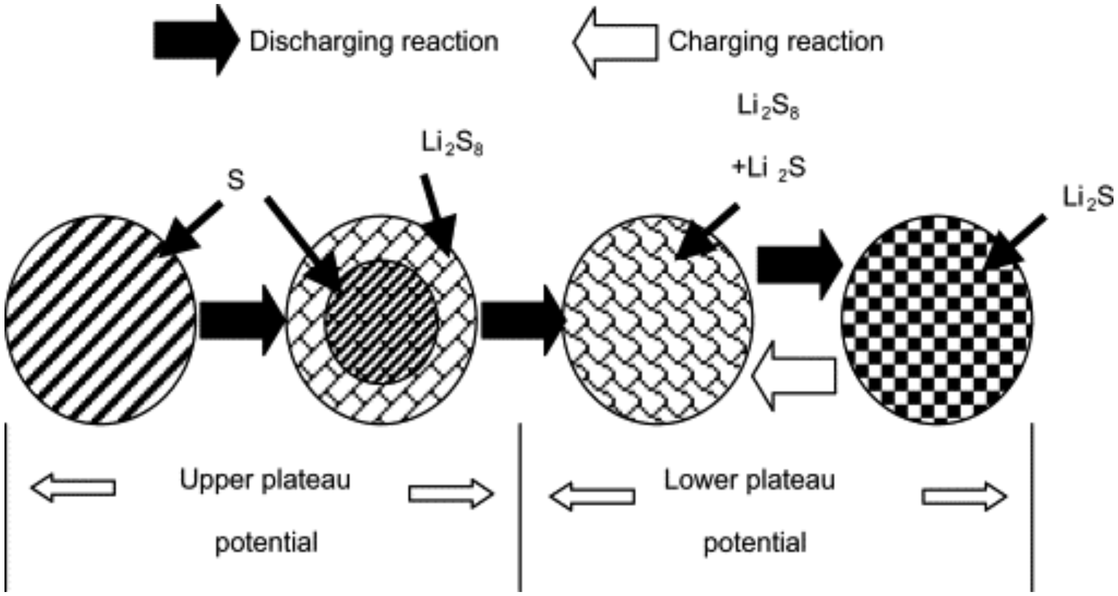

Fig 2.7 The discharge and charge reaction model of lithium/sulfur cell. Reprinted from Ref. 76 with permission from Elsevier.

2.3.3 PVDF-HFP Based Gel Polymer Electrolyte

Poly(vinylidene fluoride)-hexafluoropropylene (PVDF-HFP) has drawn the attention of many researchers due to its appealing properties. The high dielectric constant of $\varepsilon=8.4$ facilitates higher concentrations of charge carriers, and it also comprises of both amorphous and crystalline phases; the amorphous phase of the polymer helps for higher ionic conduction, whereas the crystalline phase acts as a mechanical support for the polymer electrolyte **[77-79]**.

Shin *et al.* **[80]** reported the preparation and performance of PVDF-HFP gel electrolyte in Li/S batteries. The PVDF-HFP gel polymer electrolyte with tetra ethylene glycol dimethylether (TEGDME) as a plasticizer, $LiCF_3SO_3$, $LiBF_4$ and $LiPF_6$ as lithium salt and acetone as solvent was prepared by solvent casting of slurry that mixed PVDF-HFP copolymer with acetone and salt using a ball-milling technique. This polymer electrolyte showed high mechanical property and good ionic conductivity (4.99×10^{-4} S cm^{-1} at room temperature). As ball-milled gel polymer electrolytes were introduced into Li/S cells with sulfur as cathode and lithium as the anode. The first specific discharge capacities with discharge rate of 0.14 mA cm^{-2} at room temperature were about 575 and 765 mAh g^{-1}. The melting temperature of crystalline PVDF-HFP was found to decrease, which may be due to the decrease of crystallinity by scission of the polymer chain during ball milling. Therefore, it was concluded that the ball-milling technique could be a very promising preparative technique for the preparation of slurry for polymer electrolytes.

In Wang *et al*'s study **[15, 24]**, a gel polymer electrolyte was formed by trapping a liquid electrolyte of PC-EC-DEC (1:4:5 v/v) containing 1 M $LiPF_6$ in a dry PVDF-HFP/SiO_2

polymer matrix. And this dry PVDF-HFP/SiO_2 film with abundant pore structure was prepared by phase separation method. The ionic conductivity of resulting gel polymer electrolyte was about 1.2×10^{-3} S cm^{-1} at room temperature. This gel polymer electrolyte was introduced into the cells with sulfur/active carbon composite cathode and sulfur/polyacrylonitrile (S/PAN) composite, respectively. The cell with S/PAN composite cathode exhibited a specific capacity up to 850 mA g^{-1} in the initial and remained above 600 mAh g^{-1} after 50 cycles. With elemental sulfur incorporated in porous carbon, S/C composite exhibited reversible capacity of 440 mAh g^{-1} at current density of 0.3 mA cm^{-2}.

In Jin *et al*'s study **[81]**, P(VDF-HFP) membrane with porous structure was prepared by a simple phase separation process. As shown in **Fig. 2.8**, the white area of the membrane shows homogeneously distributed micropores with a diameter range of 3-5 μm. The micro porous and interconnected skeleton structure provides the membrane the ability to absorb enough electrolytes and functions as a framework to transport Li ions.

The gel polymer electrolyte prepared by combining the porous membrane with N-methyl-N-butylpyrrolidinium bis(trifluoromethanesulfonyl)imide ionic liquid shows good thermal stability, high anodic oxidation potential (>5.0 V vs. Li/Li^+) and good interfacial stability with lithium electrode. The lithium sulfur battery with the GPE delivers an initial discharge capacity 1217.7 mAh g^{-1} and maintains a reversible capacity of 818 mAh g^{-1} after 20 cycles at a current density of 50 mA g^{-1}.

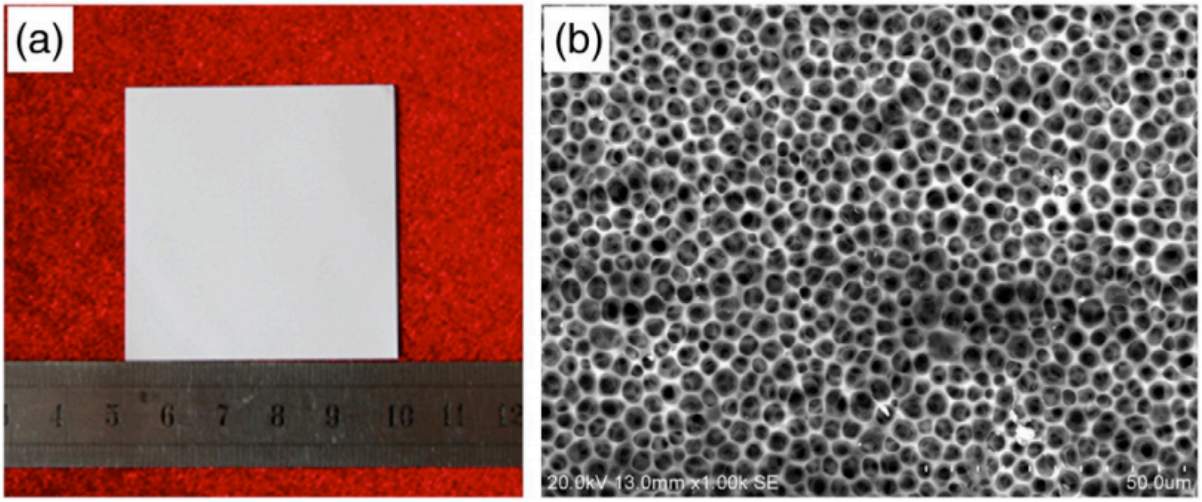

Fig 2.8 Photograph (a) and SEM image (b) of P(VDF-HFP) membrane. Reprinted from Ref. 81 with permission from Elsevier.

In summary, gel polymer electrolytes are considered as liquid electrolytes trapped in a polymer membrane. When the bulk of the membrane was composed of connected micropores, the ionic conductivity of the gel polymer electrolyte mainly depended on the property of the liquid electrolyte. Otherwise, if the prepared membrane did not have many connected pores, the transfer of Li^+ mainly happens in the polymer membrane **[82]**. Therefore, in further studies, modifying the pore structure of the membrane and changing the crystallinity of the polymer matrix were developed as the most important strategies to improve Li^+ transport and ion conductivity of GPE in Li/S battery. The former was mainly achieved by optimizing the preparation methods and the latter by modifications of the polymer matrix, such as blending, copolymer and cross-linking, compounding, and adding nanofillers **[82]**.

2.4 Conclusions

Li/S batteries provide much hope, but also many challenges. In general, the main problem in an Li/S battery is its poor cyclic ability, which is mainly caused by polysulfides dissolving into the electrolyte. To solve this problem, the polymer electrolyte is introduced into Li/S battery. As discussed above, with employment of a dry polymer electrolyte and gel polymer electrolyte, the cell showed a better cycle performance. However, problems in Li/S batteries, such as aggregation of sulfur or lithium sulfide during cycling, could not be solved merely by modifying the electrolyte. Together with advances in anodes and cathodes, the development of polymer electrolytes with high conductivity, high compatibility and mechanical strength, can offer a promising future for Li/S batteries.

Chapter 3

Electrochemical Performance of Lithium Gel Polymer Battery with Nanostructured Sulfur/Carbon Composite Cathode

3.1 Introduction

The use of flammable liquid electrolytes in batteries raises safety concerns. Therefore, polymer electrolytes have been studied intensively as an alternative to the liquid systems. Along with safety enhancement, the liquid electrolyte replacement by a polymer membrane provides advantages of much simplified fabrication and modularity in design of batteries **[1]**. Gel polymer electrolytes (GPE) are promising candidates for high energy electrochemical devices **[2,3]**, which can successfully separate the electrodes in a battery and minimize flammable liquid leakage, while maintaining the ionic conduction, i.e., a low internal impedance and high mobility of the charge carrying species **[4]**. In a Li/S battery, it is expected that this gel polymer membrane can act as a physical barrier preventing the direct contact of the electrode components **[5]**. This barrier will also help to control the dissolution of the sulphide anions from the cathode and to prevent the attack of the same anions at the anode **[6]**.

In the present work, we used a mesoporous carbon, ketjen black (KB), with a very high specific area of about 1400 m^2 g^{-1} **[7,8]**, as a conducting additive to prepare a S/C composite cathode. It should be noted that KB is a much cheaper material **[9,10]** compared with the carbon materials used in sulfur composites previously **[11,12]**. GPE was prepared by trapping a solution of lithium bistrifluoromethane-sulfonamide (LiTFSI) in tetraethylene glycol dimethyl ether electrolyte in a poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-

HFP)/poly(methylmethacrylate) (PMMA) polymer matrix prepared by phase inversion using a combination acetone/water as a solvent/non-solvent system. The electrochemical and structural properties of this GPE, its electrochemical performance as an electrolyte for a Li/S cell with a S/KB cathode have been investigated.

3.2 Experimental

3.2.1 Preparation and characterization of S/KB composite cathode

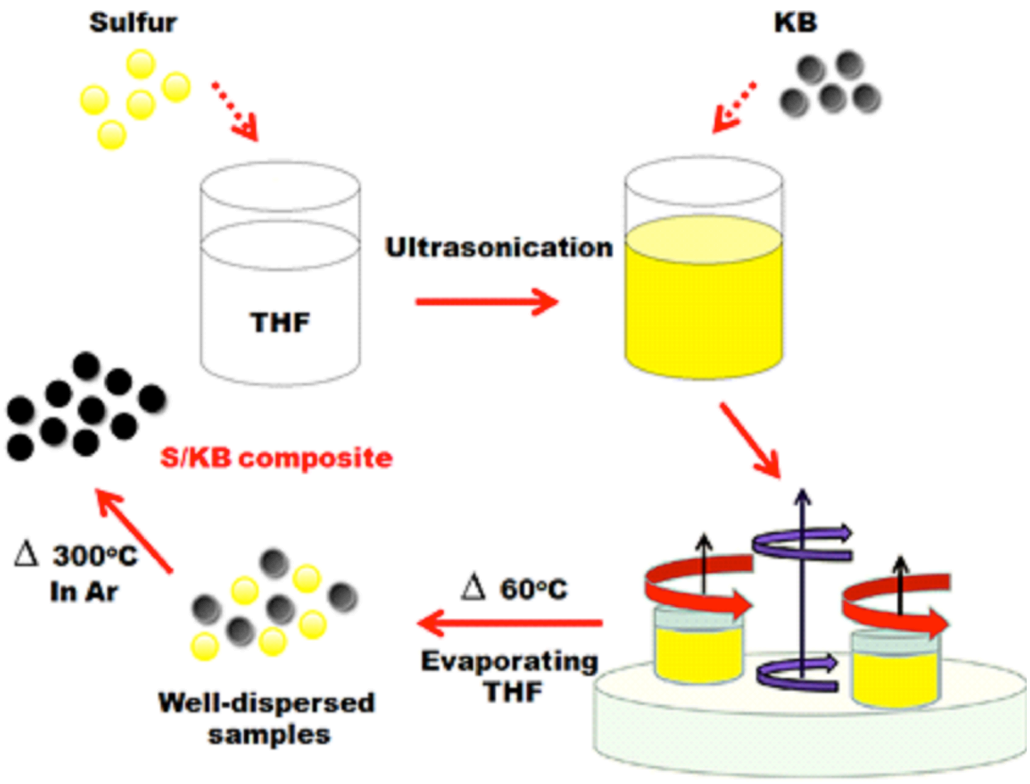

Fig 3.1 Schematics of the preparation of S/KB composite.

The preparation of S/KB composite is schematically represented in **Fig. 3.1**. The S/KB composite was prepared as follows. 0.6 g S was dissolved in 0.05 dm^3 of THF, and the solution was absorbed by gradually added 0.3g KB; the resulting mixture was ball milled at 400 rpm for 2 h. Thereafter, the mixture was dried in a vacuum oven at 60 °C for 6 h to remove the solvent and then heat-treated at 150 °C for 5 h allowing melted S absorption into the pores of KB, and further the temperature was increased to 300 °C and the sample was heated at this temperature for 3 h to evaporate sulfur remained at the KB surface. All the heating processes were performed in a tubular furnace in Ar. The crystalline phases of the samples were determined by X-ray diffraction (XRD, D8 Discover, Bruker) analysis equipped with Cu-Kα radiation. The sample surface morphology was examined by field emission scanning electron microscopy (FE-SEM, Leo-1530, Zeiss). The specific surface area was determined by the Brunauer-Emmet-Teller method (BET, ASAP 2020, Micromeritics). The S content of the samples was analyzed by chemical analysis (Vario Micro Cube, Elementar).

3.2.2 Preparation and characterization of gel polymer electrolytes

The preparation of PVDF-HFP/PMMA polymer matrix is schematically represented in **Fig. 3.2**. In order to prepare GPE, PVDF-HFP and PMMA were dissolved with mass ratio 3:2 in acetone under stirring and ultrasonication. Deionized water was slowly added and the mixture was continuously stirred for 3 h. The resulting slurry was cast on an aluminum plate manually and the solvents were evaporated at ambient temperature overnight, and the resulting membrane was dried under vacuum at 50 °C for 5 h. After this procedure, approximately 80 μm thick, mechanically stable membranes were obtained. The membrane was activated in a glove-box by immersion in a liquid electrolyte, consisting of a 1 mol dm^{-3} solution of LiTFSI in TEGDME. The liquid uptake (%) was determined using the relation $(W_2 - W_1) \times 100 / W_1$, where W_1 and W_2 denote the weights of polymer electrolytes before and after absorbing the electrolyte solution, respectively **[10]**.

The crystalline phases of the prepared films were determined by XRD. Surface morphology of the electrolytes were examined by FE-SEM. Thermal properties of samples were studied by thermogravimetric analysis (TGA, TA instruments, Q-600) by heating with a rate of 10°C min^{-1} from 20 to 510°C under N_2 atmosphere. The ionic conductivity of GPE was determined by EIS over the frequency range from 0.1 Hz to 1 MHz. Polymer membranes were cut into 8 mm diameter disks and sandwiched between two stainless steel blocking electrodes. The electrochemical stability of GPE was investigated by linear sweep voltammetry of the cell with GPE sandwiched between lithium metal and stainless steel electrodes. The voltage is swept from 1 V *vs.* Li^+/Li towards the anodic values with a scan rate of 0.1 mV s^{-1}. Cell assembly and measurement procedures were carried out in a Braun dry box filled with high purity argon.

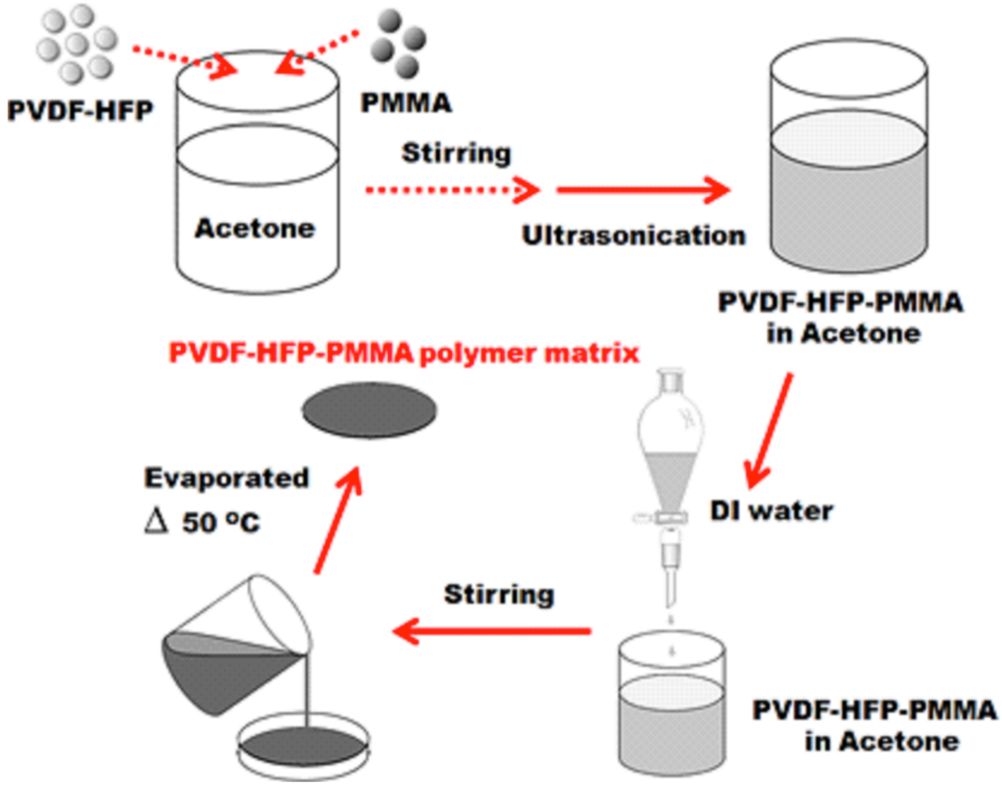

Fig 3.2 Schematics of the preparation of PVDF-HFP/PMMA polymer matrix.

3.2.3 Cell assembling and testing

The electrochemical performance of the S/KB composite cathode was investigated in coin-type cells (CR2032) with PVDF-HFP-PMMA GPE. Each cell was composed of a lithium metal anode and an S/KB composite cathode that were separated by the GPE film. The cathode was prepared by mixing 80 wt% S/KB composite, 10 wt% acetylene black as conductive agent and 10 wt% PVDF as a binder. These materials were dispersed in NMP. The resultant slurry was spread onto a circular nickel foam current collector with 1 cm diameter and then dried in a vacuum oven for 12 h at 60 °C. Finally, the cathode was pressed by a rolling machine in order to achieve good contact between the active material and current collector. The electrodes were prepared to make their weight and thickness approximately the same by precise weighing, pressing and controlling its geometry. The cathode material loading in each electrode was about 5 mg cm^{-2}, and the thickness of the electrode film was about 100 μm. The coin cells were assembled in a dry box filled with argon using the GPE prepared in this work and a microporous polypropylene separator soaked in a liquid electrolyte described above. The cells were tested galvanostatically between 1 and 3 V *vs.* Li^+/Li at a current density of 100 mA g^{-1} (0.06 C). The applied currents and specific capacities were calculated on the basis of the weight of S in the cathode. The EIS measurements were carried out by applying an ac voltage of 10 mV over the frequency range from 0.1 Hz to 1 MHz.

3.3 Results and discussion

3.3.1 Characterization of S/KB composite cathode, polymer matrix and gel polymer electrolyte

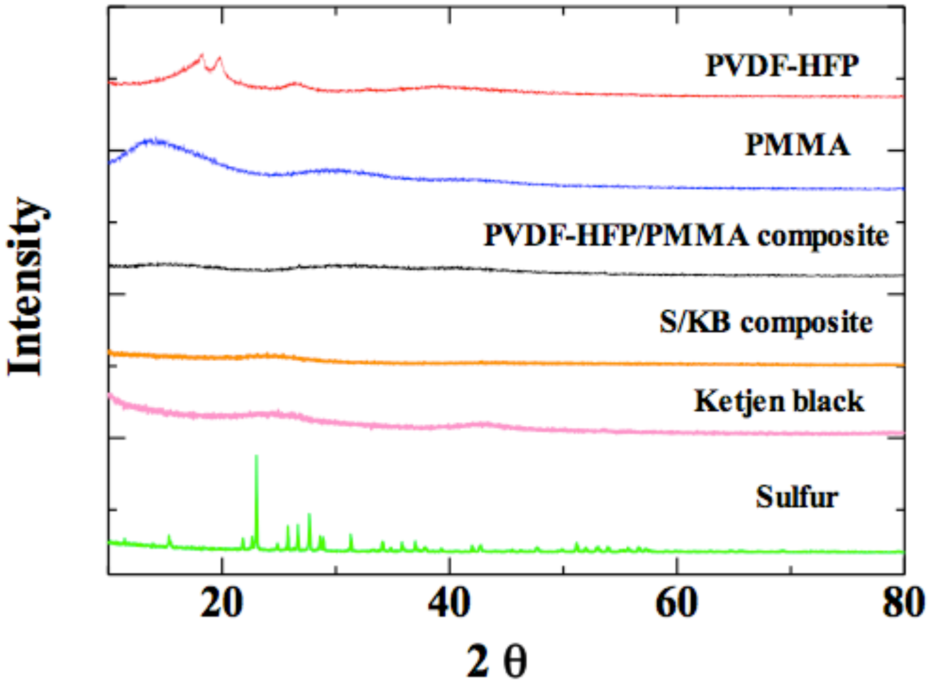

Fig 3.3 XRD patterns of sulfur, KB and S/KB composite.

Figure 3.3 shows the XRD spectra of the starting components used to prepare the composite cathode, S and KB, the S/KB composite, pure PVDF-HFP, PMMA and PVDF-HFP/PMMA composite polymer matrix. It can be seen that the characteristic peaks of S disappear when the carbon composites were prepared via ball-milling and heat treatment. The sublimed sulfur precipitates in a highly crystallized form when cooled to the ambient temperature **[13]**. However, the S/KB composite does not show the peaks of S in XRD spectra. It could be an indication of trapping S into the internal pores of KB. The X-ray diffraction pattern reveals clearly that PVDF-HFP/PMMA composite is less crystalline than pure PVDF-HFP and PMMA. The polymer matrix crystallinity decrease is favorable for the ionic conductivity enhancement of the polymer electrolyte **[6]**.

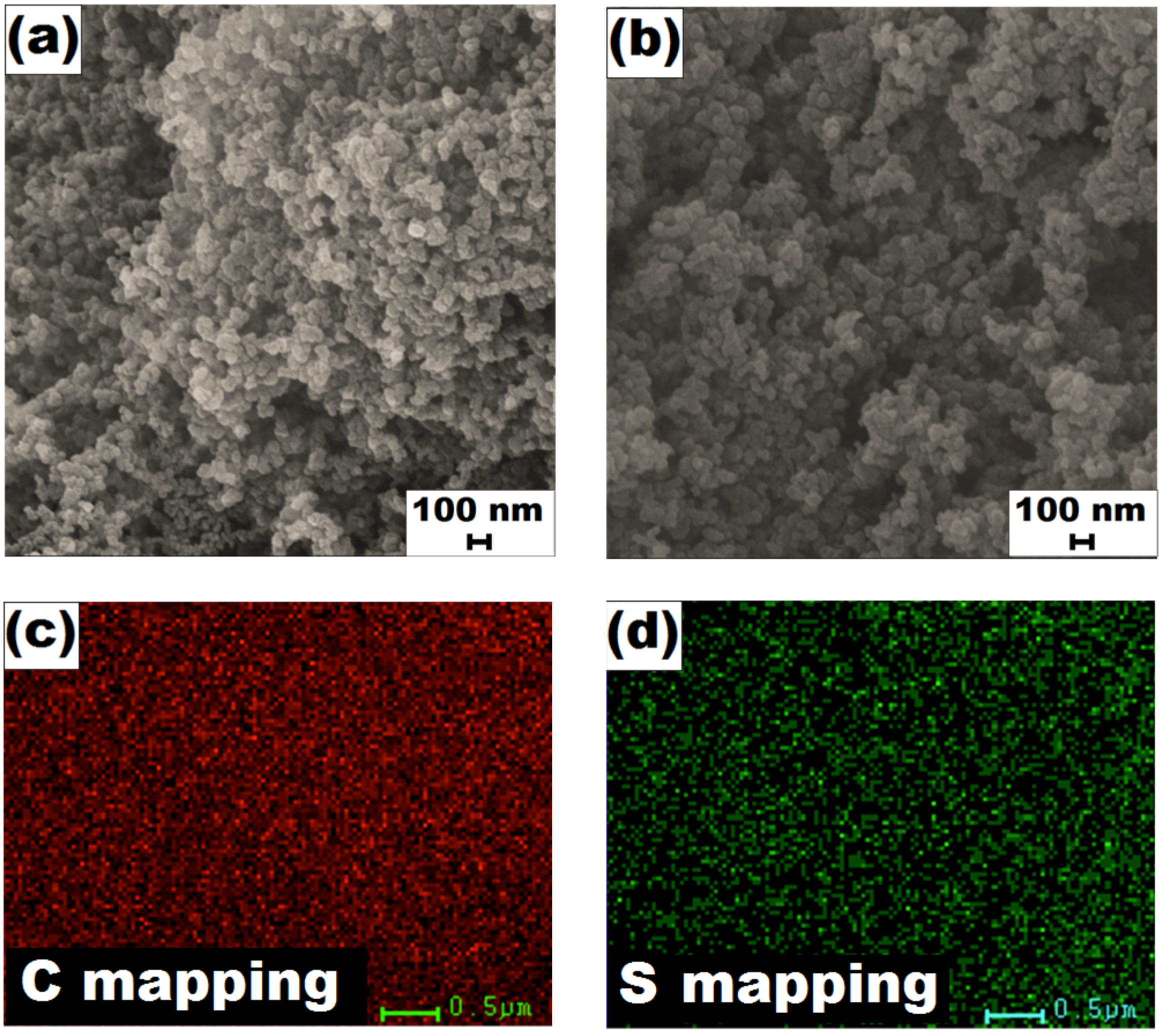

Fig 3.4 SEM images of (a) KB and (b) S/KB composite; EDS mapping showing distribution of (c) C and (d) S elements.

The SEM data in **Fig. 3.4** shows that there is no apparent morphology difference between the KB (**Fig. 3.4a**) and the S/KB composite (**Fig. 3.4b**) containing 43 wt% sulfur (measured by chemical analysis). The KB aggregates have a particle size about 100 nm, and its specific surface area reduces drastically when the S/KB composite is formed, from 1455 to 57 m^2 g^{-1}. These results allow us to suggest that sulfur in the composite remains embedded in the nano- and micro-pores of KB **[8]**. Results of EDS mapping for S and C are also shown in **Fig. 3.4c and 3.4d**, respectively. The bright regions represent these elements distributed in the composite, and indicate that S and C are distributed uniformly within the samples. Chemical analysis has shown that the sulfur content in the S/KB composite was 43 wt%.

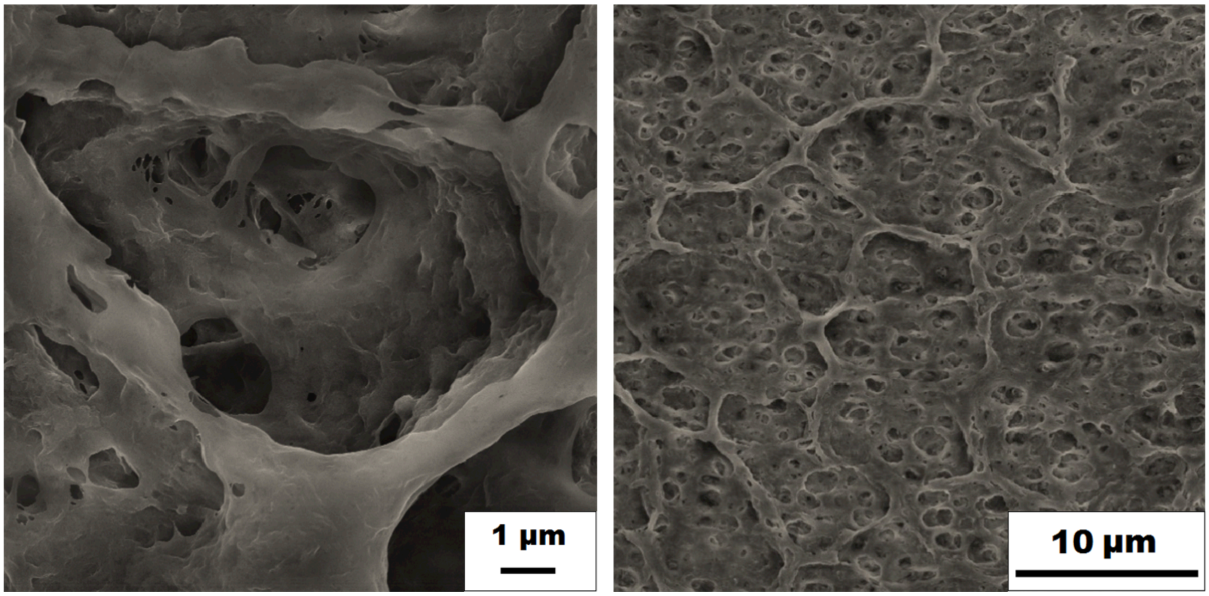

Fig 3.5 SEM images of PVDF-HFP/PMMA composite at different magnifications.

Figure 3.5 presents the SEM photographs of PVDF-HFP/PMMA composite at different magnifications. It can be seen that the polymer matrix has highly porous structure, with the pore diameters from 0.1 to 1 μm. The abundant porous structure increases the surface area of the matrix and could effectively enhance its absorption ability. By the weight increase after dipping in the liquid electrolyte, the liquid content in GPE was determined as 72 wt%. The ionic conductivity of GPE strongly depends on the amount of liquid electrolyte embedded in the pores of polymer membrane **[14]**. The absorbed electrolyte solution acts as medium for the ion conduction through the polymer matrix **[15]**. Therefore, the ability of the polymer matrix prepared in this work to retain a large amount of the liquid electrolyte could be very important to prepare an enhanced polymer electrolyte for the Li/S battery. The GPE prepared in this work was a transparent self-standing film without visible leakage of liquid electrolyte.

The TGA plots of dry PVDF-HFP/PMMA polymer membrane and GPE are shown in **Fig. 3.6**. It can be seen that GPE is thermally stable over 110 °C. Further temperature increase leads to the liquid electrolyte evaporation from the polymer matrix indicated by the weight loss in TGA. The total mass lost during the temperature rise to 250 °C is about 65 wt%, which matches well with the liquid uptake by the polymer matrix calculated above and could be attributed to the evaporation of the solvent. Further mass loss of about 20% has been observed above 300 °C, due to the thermal degradation of PVDF-HFP/PMMA matrix, which also correlates with the TGA plot for a dry PVDF-HFP/PMMA polymer membrane.

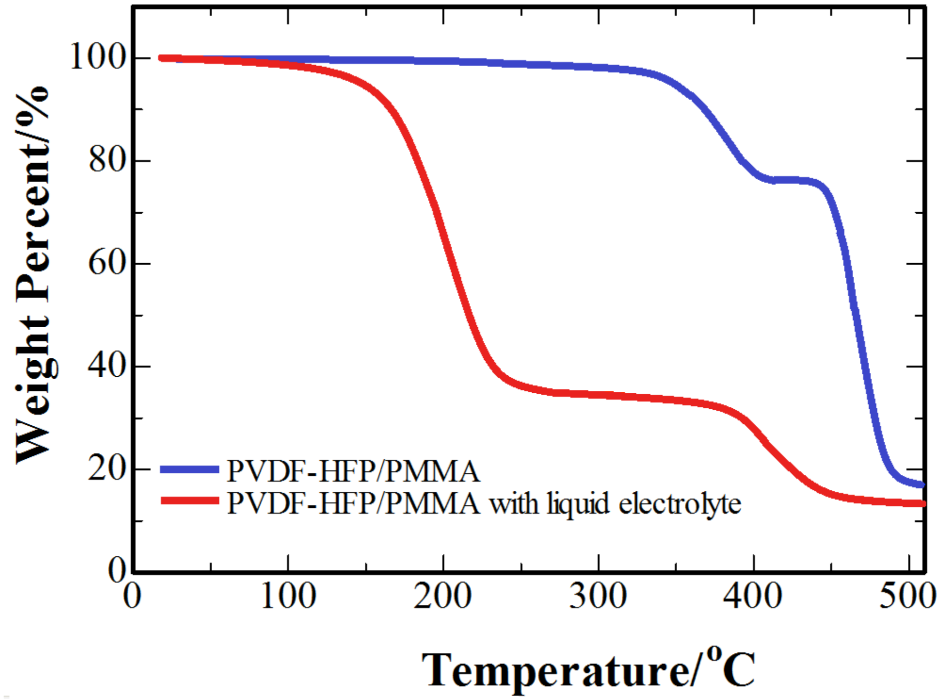

Fig 3.6 TGA plots of PVDF-HFP/PMMA composite and corresponding gel polymer electrolyte.

The ionic conductivity of GPE at a wide range of temperatures was studied by EIS. The typical impedance plot for the PVDF-HFP/PMMA composite is shown in **Fig. 3.7**. One can see that there is no high frequency semicircular portion in the complex impedance plot, which allows us to suggest that the total conductivity is mainly the result of ion conduction **[16]**. The shape of the EIS spectra is convincing evidence of a high integrity of the membrane as well **[17]**. From the complex impedance plot the intercept at the higher frequency side on the *Z'* axis gives the resistance of the bulk electrolyte **[18]**. The ionic conductivity of the gel type electrolyte was calculated from the EIS data by

$$\sigma = \lambda/(R_b \times A)$$

where R_b is the bulk resistance from EIS, λ is the film thickness and A is the surface area of electrode.

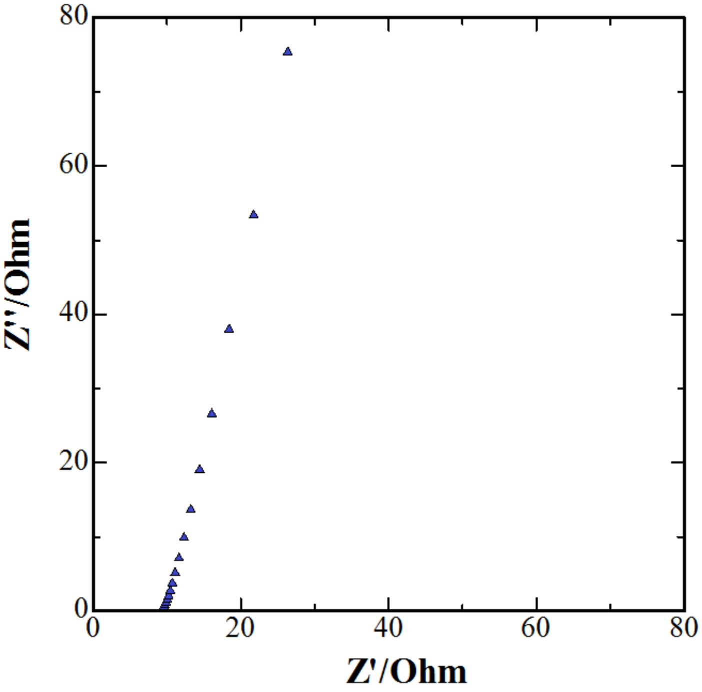

Fig 3.7 Typical ac impedance spectra of as-prepared gel polymer electrolyte.

Figure 3.8 shows the Arrhenius plot of ionic conductivity of the GPE prepared in this work. The electrolyte exhibits high ionic conductivities even at the temperatures below 0 °C, and 3.37 mS cm^{-1} at room temperature. It can be seen that the temperature dependence consists of two linear parts with a transition point about 15 °C, with different activation energies, 9.9 and 4.0 kJ mol^{-1} for the lower temperature and the higher temperature parts, respectively. This could be due to the phase transition phenomena around this temperature, i.e. transition from the amorphous-liquid to the high crystalline-solid state **[6, 17]**.

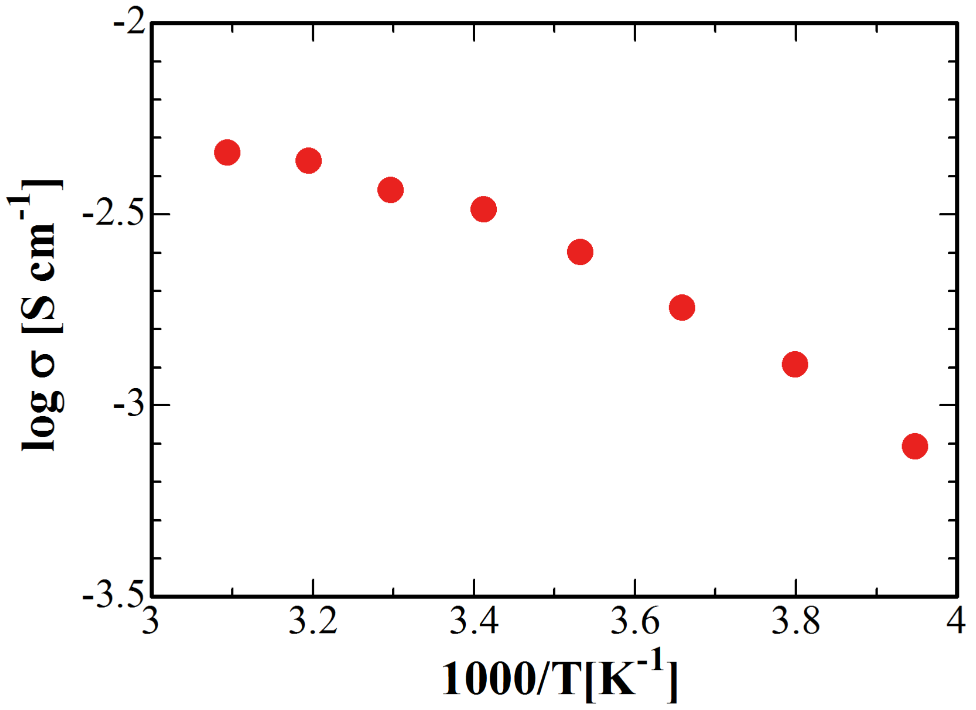

Fig 3.8 Arrhenius plots of ionic conductivity of the GPE prepared in this work.

It is pertinent that the electrolyte has a wide electrochemical stability window, which determines the voltage range of its applicability. Linear sweep voltammetry experiments **[19]** showed that the GPE prepared in this work is electrochemically stable up to 4.5 V (**Fig. 3.9).** As the potential is swept towards the anodic values, an abrupt current rise was observed at about 4.5V, which could be attributed the electrolyte decomposition at the inert electrode interface. This value of the stability window of the GPE appears to be high enough to use PVDF-HFP/PMMA GPE films in Li/S batteries, where the working voltage upper cutoff is limited within 3 V *vs.* Li$^+$/Li.

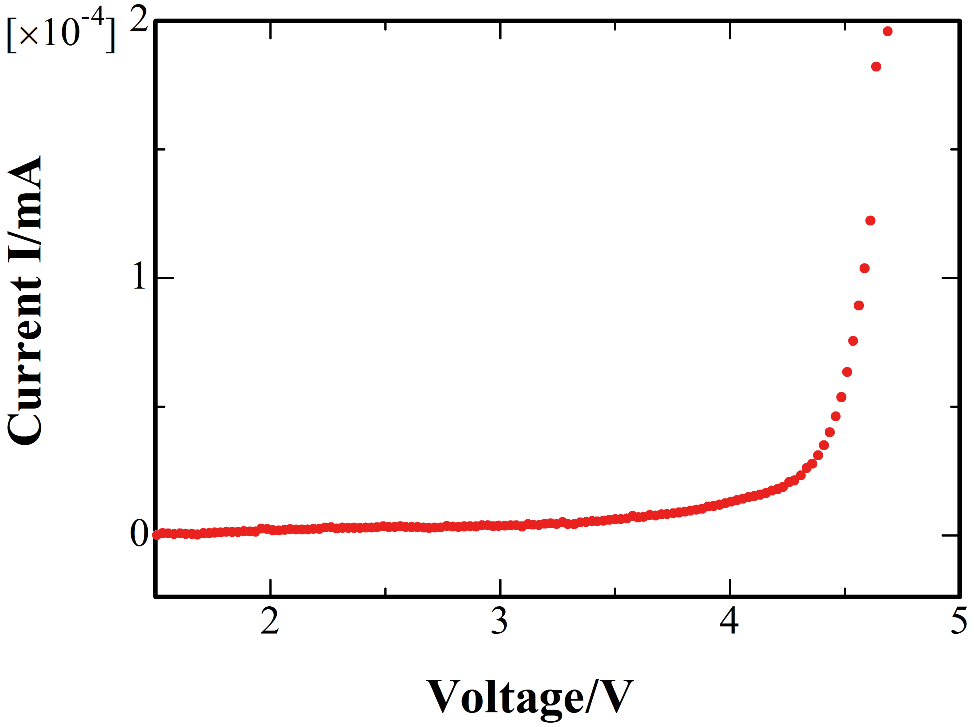

Fig 3.9 Linear sweep voltammetry of Li/GPE/SS cell (scan rate 0.1 mV s^{-1}).

3.3.2 Electrochemical properties of Li\PVDF-HFP-PMMA GPE\S/KB composite cells

Figures 3.10a and 3.10b present the charge-discharge curves of the Li/S batteries with gel polymer electrolyte and liquid electrolyte at 1st, 10th and 20th cycles, respectively. It can be seen that both systems exhibit characteristic potential profiles of charge-discharge of sulfur cathode in lithium battery **[20]** with two potential plateaus of the electrochemical activity, which could be attributed to the multiple electrochemical reactions in the Li/S battery **[21-23]**. The first electrochemical reaction is presented at about 2.5 V and related to the formation of higher-order lithium polysulfides (Li_2S_n, $n \geq 4$), which are soluble in the liquid electrolyte **[21-23]**. The following electrochemical transition of these polysulfides to lithium sulfide Li_2S is reflected as a prolonged plateau around 2 V in the potential profiles, and this reaction kinetics is slower than that of the polysulfide formation **[21-24]** which is reflected by the length of the plateaus.

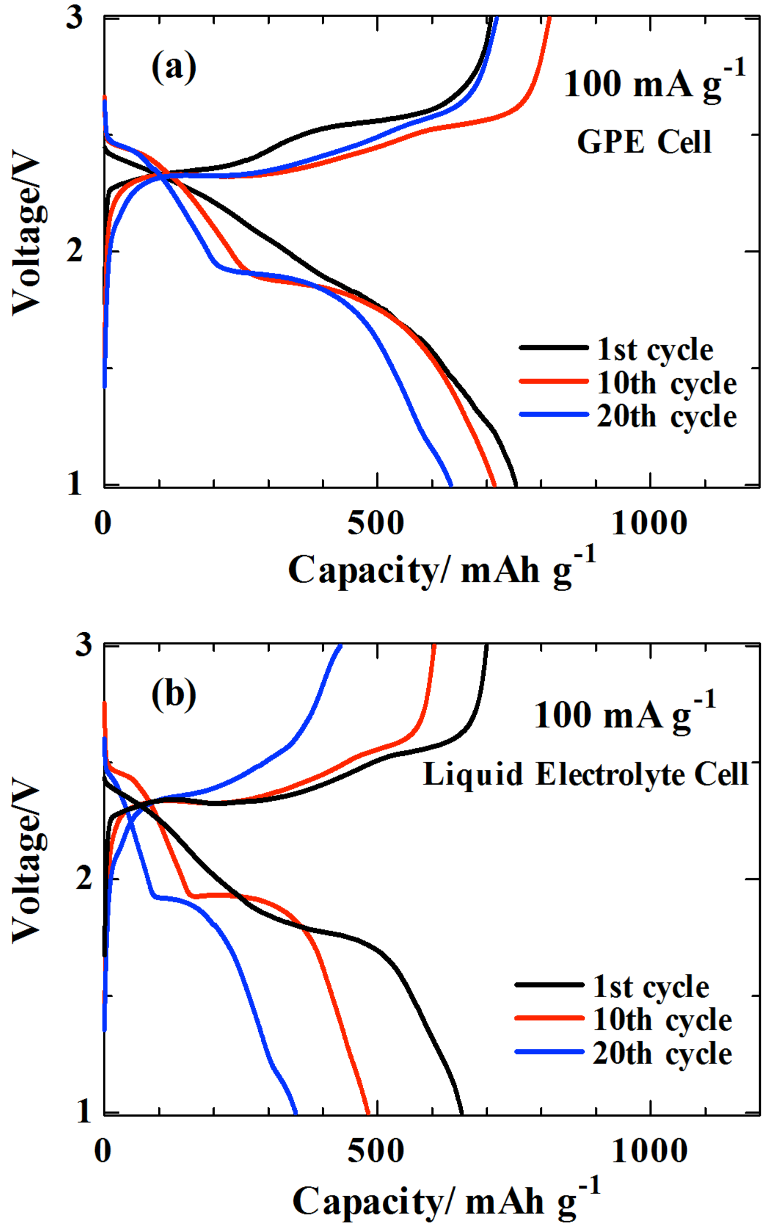

Fig 3.10 Charge-discharge profiles of (a) GPE and (b) liquid electrolyte cells at galvanostatic charge-discharge at a current density of 100 mA g^{-1} (0.06 C).

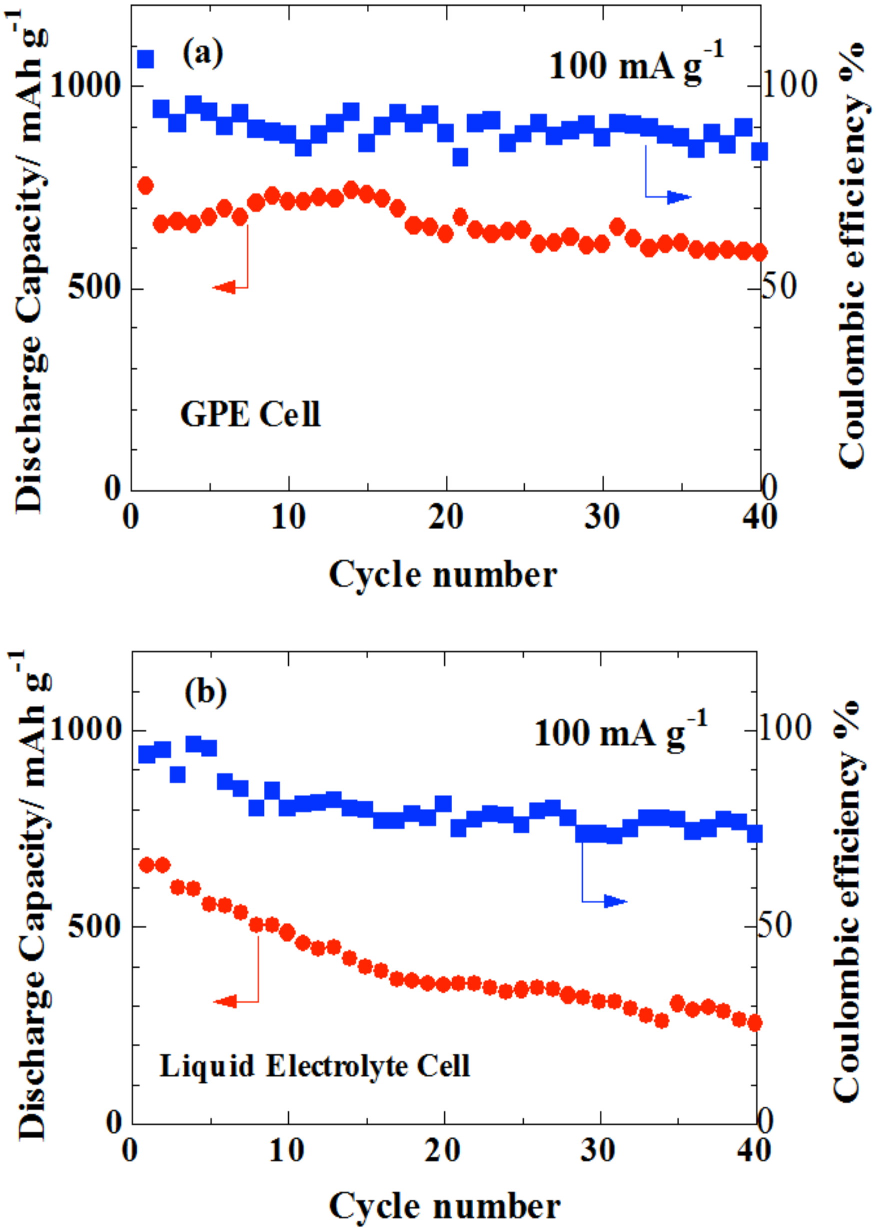

Fig 3.11 Cyclability of (a) GPE and (b) liquid electrolyte cells at galvanostatic charge-discharge at a current density of 100 mA g^{-1} (0.06 C).

One can see from **Fig. 3.11a** and **3.11b**, that the cyclability of the GPE cell is remarkably enhanced compared with the liquid electrolyte counterpart, and the GPE cell retains about 80% of its initial capacity over 40 cycles, while the discharge capacity of the liquid electrolyte battery drastically fades upon cycling. The performance improvement of the cell with the GPE could be attributed to the suppression of the shuttle effect by a GPE film acting as a physical barrier between cathode and anode in the cell preventing the soluble polysulfide migration. Consequently it enhances the net cathode reaction reversibility positively affecting its Coulombic efficiency.

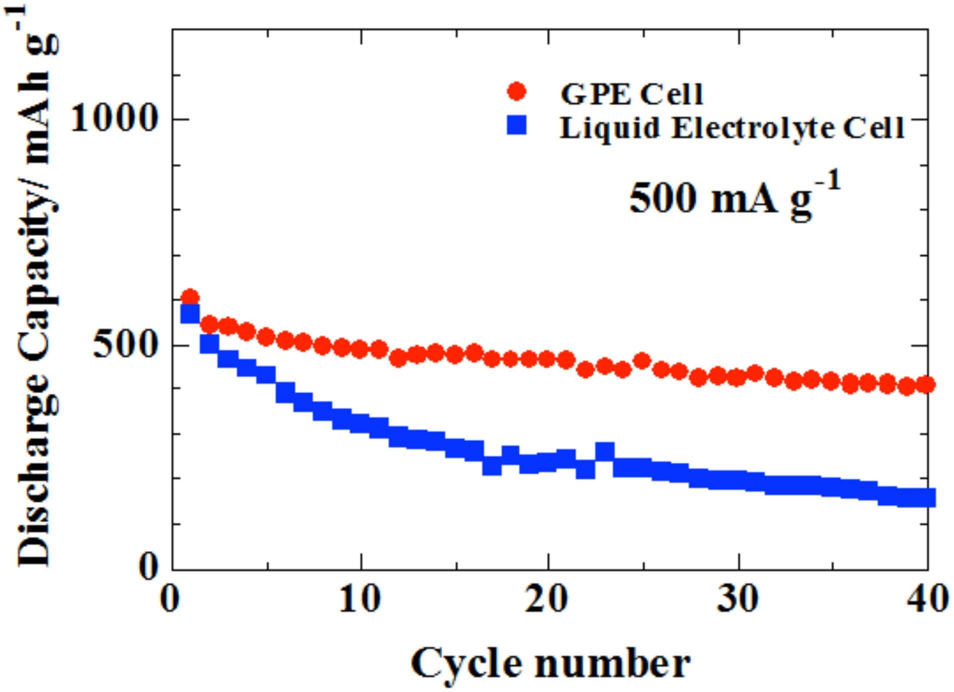

Fig 3.12 Comparative data on cyclability of GPE and liquid electrolyte cells at galvanostatic charge-discharge at a current density of 500 mA g^{-1} (0.3 C).

The effect of use of the GPE in a cell with S/KB composite cathode on its kinetic behavior was further evaluated. The cycle performance of the GPE cell and the liquid electrolyte cell were examined at 500 mA g^{-1} (0.3 C). As expected, the discharge capacity of both types of cells has been decreased by the C-rate increase, and this performance reduction for both types of electrolytes has very similar level. Therefore, the capacity reduction upon C-rate increase is attributed to the kinetic limitations of sulfur cathode **[25]**. Although both type of the cells exhibit similar initial capacities, it can be seen from **Fig. 3.12** that the GPE cell shows a remarkably enhanced cycle performance at the higher current density cycling compared with the liquid electrolyte cell. The further increase in C-rate lead to a more rapid capacity reduction of both GPE and liquid electrolyte cells, that we also relate to the conductivity limitations of sulfur cathode.

The ac impedance measurements performed for both types of the cells are shown in the inset of **Fig. 3.13** The GPE cell exhibits higher total impedance compared with the liquid electrolyte cell. Although the GPE lithium ion transport capabilities at high rates are limited and result in a lower achievable cell capacity **[26]**, we found that the GPE developed in this work had comparable trend in capacity decrease with the C-rate, and delivers the same level initial discharge capacity as its liquid electrolyte counterpart. This phenomenon could be expected in a Li/S battery, because the kinetic limitations of low conductive sulfur cathode could prevail over the diffusional limitations caused by the use of a GPE membrane instead of liquid electrolyte.

The results of this work allow us to suggest that the electrochemical performance enhancement of the Li/S battery by the use of GPE could be attributed to the suppression of polysulfide dissolution by a GPE film acting as a physical barrier between cathode and anode, and limitation of the shuttle effect.

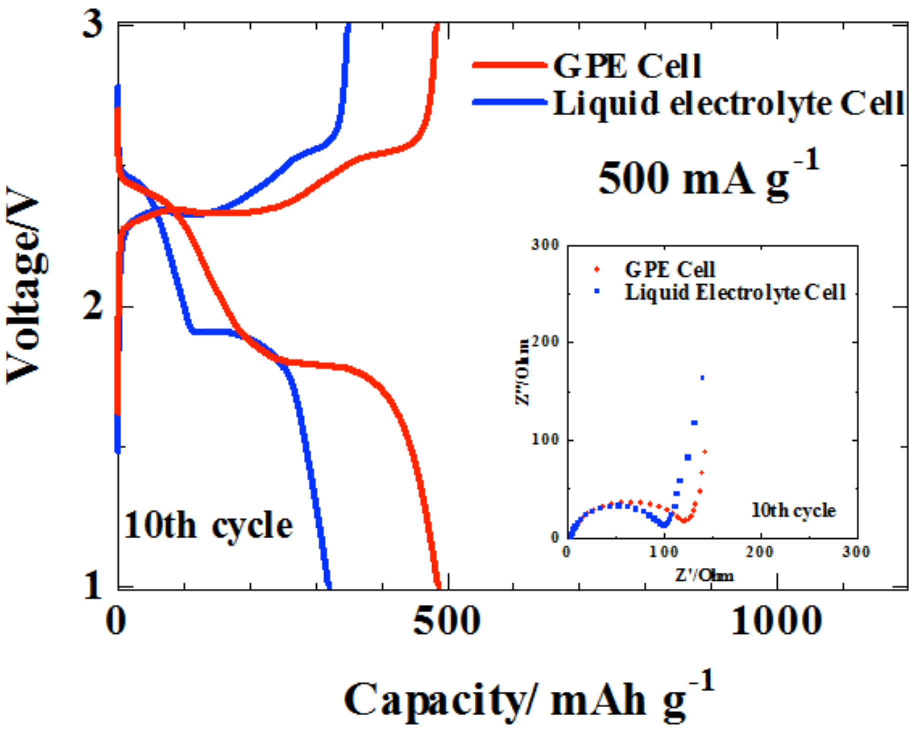

Fig 3.13 Charge-discharge profiles of GPE and liquid electrolyte cells at galvanostatic charge-discharge at a current density of 500 mA g^{-1} (0.3 C). Inset in: EIS data for GPE and liquid electrolyte cells.

3.4 Conclusions

The PVDF-HFP/PMMA polymer membranes prepared by phase separation exhibited abundant pore structure and high ability to absorb liquid electrolyte exceeding 72 wt%. The ionic conductivity of the resulting gel electrolyte was about 3.37 mS cm^{-1} at room temperature. The S/KB composite cathode was prepared via a combination of ballmilling and mild temperature heat treatment. The final composite cathode contained about 43 wt% sulfur with the major part of sulfur incorporated into the internal pores of mesoporous KB. The composite cathode was used to assemble lithium cells with liquid and PVDF-HFP/PMMA GPE electrolytes. The GPE exhibited remarkably enhanced performance compared with the cell with liquid electrolyte. The GPE cell delivered a specific capacity of 753.8 mAh g^{-1} at the initial cycle and retained about 80% of this capacity over 40 cycles. The GPE cell exhibited enhanced Coulombic efficiency compared with the liquid electrolyte cell. The electrochemical performance enhancement was attributed to the effect of GPE membrane reducing the sulfur dissolution and shuttle effect. The GPE had higher impedance than liquid electrolyte; however, the C-rate tests have shown the capacity reduction in both GPE and liquid electrolyte cells in the same level. Therefore, the capacity decrease with C-rate was attributed to the kinetic limitation due to low conductivity of sulfur cathode.

Chapter 4

Synthesis of Poly(ethylene-oxide)/Nanoclay Solid Polymer Electrolyte for all Solid State Lithium/Sulfur Battery

4.1 Introduction

Currently, solid polymer electrolyte (SPE) has drawn wide attention in solid-state rechargeable lithium batteries, due to its advantages, such as no leakage of electrolyte, high energy density, flexible geometry and safety **[1,2]**. Till now, a number of related investigations have reported the use of polymer/nanoclay composite in SPE **[3,4]**. As layered host, nanoclay can provide a huge interfacial contact area, which not only sustain the mechanical properties of SPE, but also increase the solubility of lithium salts, due to higher dielectric property **[3,4]**.

In this chapter, we reported a novel all solid state lithium/sulfur battery system, a sulfur composite cathode combined with PEO/MMT solid polymer electrolyte. The electrochemical properties of all solid state Li/S batteries were investigated by Cyclic voltammetry and charge/discharge measurements.

4.2 Experimental

4.2.1 Preparation and characterization of solid polymer electrolytes

The PEO/MMT polymer electrolyte preparation is schematically presented in **Fig. 4.1**. LiTFSI was first dissolved in acetonitrile at room temperature. PEO was dissolved in acetonitrile (EO/Li molar ratio = 20:1) at 60 ˚C for 12 h, followed by addition of MMT particles at the ratio of 5 wt% of the total $PEO_{20}LiTFSI$. After ultrasonication and stirring, the homogeneous solution was cast on a Teflon™ dish and dried in a vacuum oven at 60˚C until all solvent had evaporated. The thin PEO/MMT film was vacuum dried at 120˚C for 2 h to ensure total removal of moisture.

The ionic conductivity of SPE was determined by EIS over the frequency range from 0.1 Hz to 1 MHz. SPE were sandwiched between two stainless steel blocking electrodes.

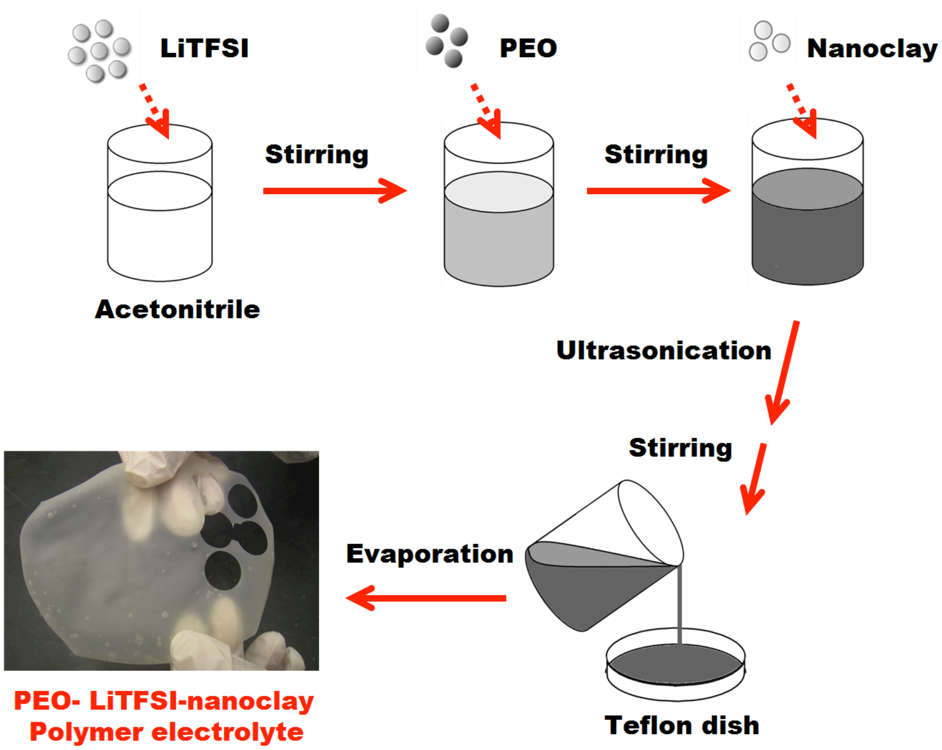

Fig 4.1 Schematic of preparation of the PEO/MMT polymer electrolyte.

4.2.2 Preparation and characterization of S/PAN/$Mg_{0.6}Ni_{0.4}O$ composite cathode

The active material was synthesized by heating a mixture of PAN, sulfur and $Mg_{0.6}Ni_{0.4}O$ as described previously **[5]**. The composite cathode comprised of active material S/PAN/$Mg_{0.6}Ni_{0.4}O$, acetylene black conductive agent, PEO binder, and LiTFSI at a mass ratio of 55:25:15:5, dispersed in NMP. The resultant slurry was spread onto a circular piece of nickel foam with 1 cm in diameter. After drying in a vacuum oven for 12 h at 60 ^{o}C, the cathode was pressed at 8 MPa in order to achieve good contact between the active material and nickel foam.

4.2.3 Cell assembling and testing

The electrochemical performance of Li/S batteries was investigated using coin-type cells (CR2032) composed of lithium metal anode and sulfur composite cathode separated by prepared PEO/MMT composite polymer electrolyte. The coin cells were assembled in a MBraun glove box filled with argon. The cells were tested galvanostatically between 1 and 3 V *vs*. Li^+/Li at certain current density, on a multichannel battery tester. Applied currents and specific capacities were calculated on the basis of the weight of S in the cathode.

4.3 Results and discussion

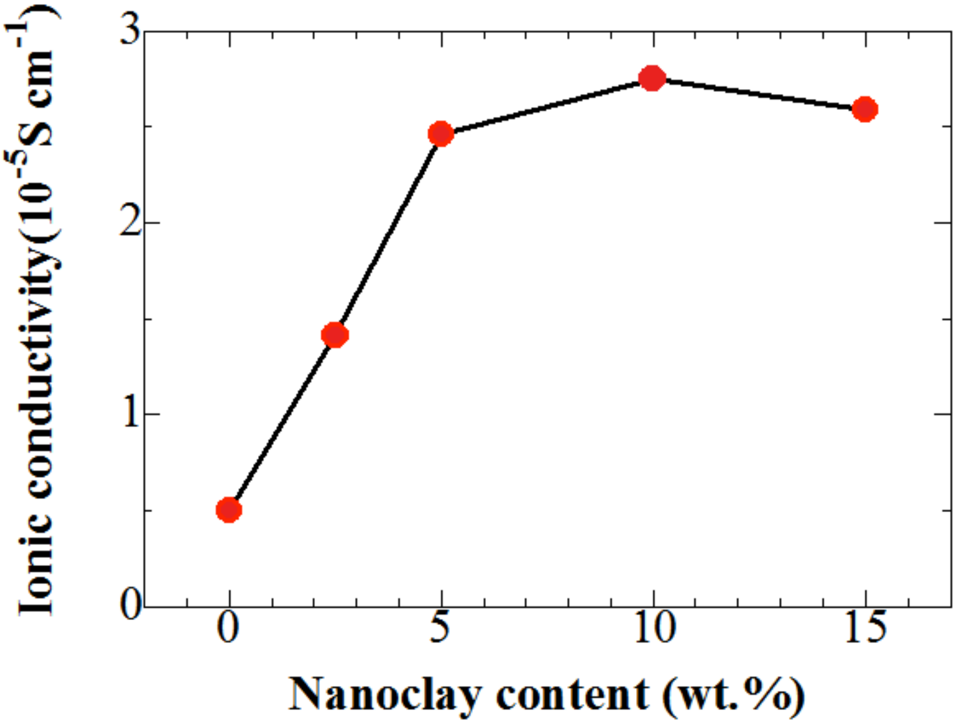

Fig 4.2 The influence of the amount of nanoclay on ionic conductivity.

The dependence of the PEO/MMT solid electrolyte ionic conductivity on the content of nanoclay is depicted in **Fig. 4.2**. The ionic conductivity was mostly enhanced at low amounts of MMT, reaching the maximum value of 2.75×10^{-5} S cm^{-1} at 25 ^{o}C for the composite containing 10 wt% MMT. A slight decrease in conductivity was observed when the amount of MMT was increased to 15 wt%, consistent with the behavior previously reported for the PEO/$LiClO_4$/MMT system **[6]**. It has been reported that the incorporation of nanoclays into polymeric materials increases the amorphous content of the polymer in the composite facilitating the movement of Li^+ ion due to enhanced chain segmental motion **[6]**. Additionally, in the cationic charges on the surface of clay platelets act as Lewis acid centers and compete with Li^+ cations to form complexes with the polymer. This causes a structural modification of PEO/MMT nanocomposite, creating Li^+ conducting pathways at the surface of the clay and lowering of ionic coupling, which in turn promotes the lithium salt dissociation. However, beyond 10 wt.% the insulating nature of MMT overcomes the favorable effects it imparts on the Li^+ ion motion and reduces the overall ionic conductivity of the composite.

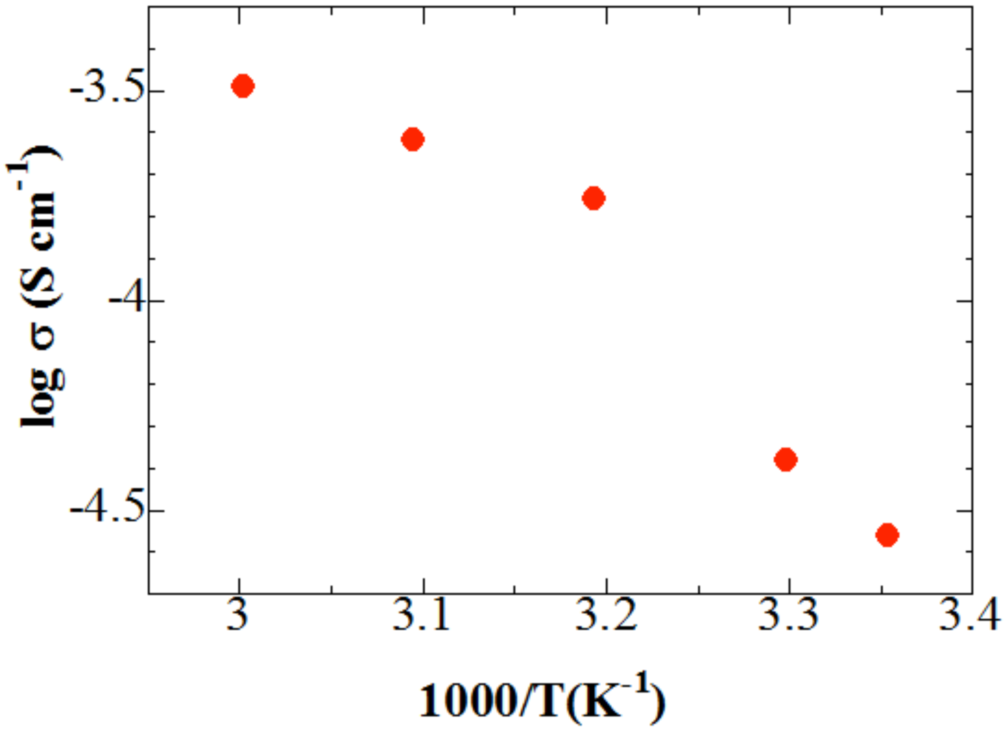

Fig 4.3 The influence of temperature on ionic conductivity.

Figure 4.3 shows the logarithmic temperature dependence of the ionic conductivity for the PEO/MMT system. The linear behavior of the curves suggests that the conductivity obeys the Arrhenius equation $\sigma = \sigma_0 \exp(-E_a/RT)$, where R is the gas constant, σ is the conductivity of polymer electrolyte, σ_0 is the pre-exponential factor, and T is the testing temperature in absolute scale **[7]**. The temperature dependence displays two linear regions with different activation energies, 42 kJ mol^{-1} and 12 kJ mol^{-1} for the lower and the higher temperature regions, respectively. The higher activation energy at lower temperatures is related to the sluggish kinetics of charge transfer and slow Li$^+$ diffusion. Nevertheless, the conductivity of

PEO/MMT polymer electrolyte reaches 3.22×10^{-4} S cm^{-1} at 60 °C, a value that meets the operation requirements of an all solid state sulfur cell [**8-10**].

Figure 4.4 shows a typical cyclic voltammograms (CV) of an all solid state Li/S cell at 60 °C. No electrochemical processes were observed in addition to those related to the Li-S reactions, implying that the PEO/MMT solid polymer electrolyte is electrochemically inactive within the studied potential region. This confirms the electrochemical stability of as prepared solid polymer electrolyte in the voltage range of its applicability. Furthermore, a pronounced reduction process is observed in the first cycle, possibly due to side reactions of formation of the solid electrolyte interface (SEI). These processes are seemingly inherent only to the first reduction because they are not present in the following cycles. After initial activation, the cell exhibits two major stages of the redox processes which agrees with the literature data **[11, 12]** and can be attributed to the transition of S to polysulfides (Li_2S_8, Li_2S_6, Li_2S_4, Li_2S_2), and their further transformation into lithium sulfide (Li_2S), respectively. Additionally, after the initial cycle, the heights of the main peaks remain at a similar level, indicating good reversibility of the system.

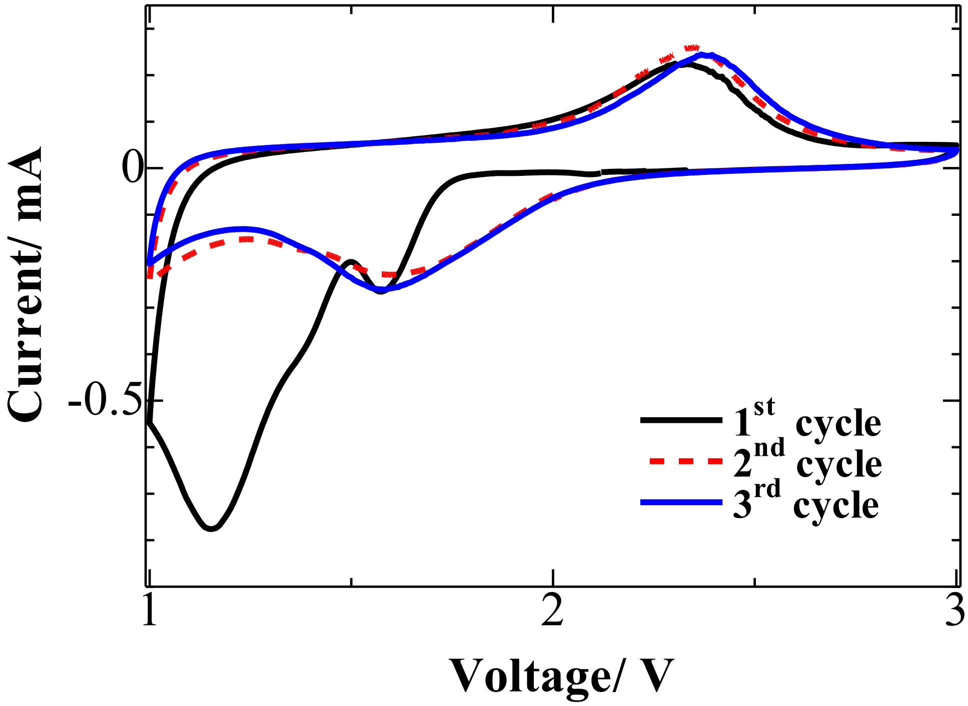

Fig 4.4 Initial CV profiles of all solid state Li/S cell at 60 ^{o}C. The measurement is conducted at a scan rate of 0.1 mV s^{-1} in the voltage range of 1.0 to 3.0 V vs. Li^{+}/Li.

In order to investigate the electrochemical performance of the all solid state Li/S cells, galvanostatic charge/discharge cycling tests were carried out at 60 ^{o}C and the representative results are shown in **Fig. 4.5**. The system delivered a specific capacity of 998 mAh g^{-1} in the first discharge at 0.1C, and a reversible capacity of 591 mAh g^{-1} was obtained in the second cycle (**Figure 4.5a**). The voltage profiles for the 2nd and 3rd cycles show similar behavior, namely, the discharge curves do not present the typical two plateaus related to the step-wise reactions between lithium and polysulfides. This is consistent with the CV results discussed above. The cycling performance of the cells with PEO/MMT solid polymer electrolyte was also carried out at 60 °C as shown in **Fig. 4.5b**. An initial increase of capacity is observed for the first 20 cycles at 0.1 C, suggesting a gradual activation of the solid polymer electrolyte electrochemical properties during the charge/discharge processes. We speculate that this is due to the slow penetration and transport of the lithium ion through the cathode and solid polymer electrolyte interface. After 100 cycles, the system still maintains a reversible specific discharge capacity of 634 mAh g^{-1}, equivalent to a 63.5 % capacity retention from the initial discharge capacity.

4.4 Conclusions

A poly(ethylene-oxide)/montmorilonite composite was prepared and evaluated as solid electrolyte for lithium/sulfur batteries. A five-fold increase in ionic conductivity was observed by addition of 10 wt.%. All solid state Li/S batteries containing PEO/MMT solid polymer electrolyte displayed good cycling performance, retaining a reversible specific discharge capacity of 634 mAh g^{-1} after 100 cycles at 0.1 C rate.

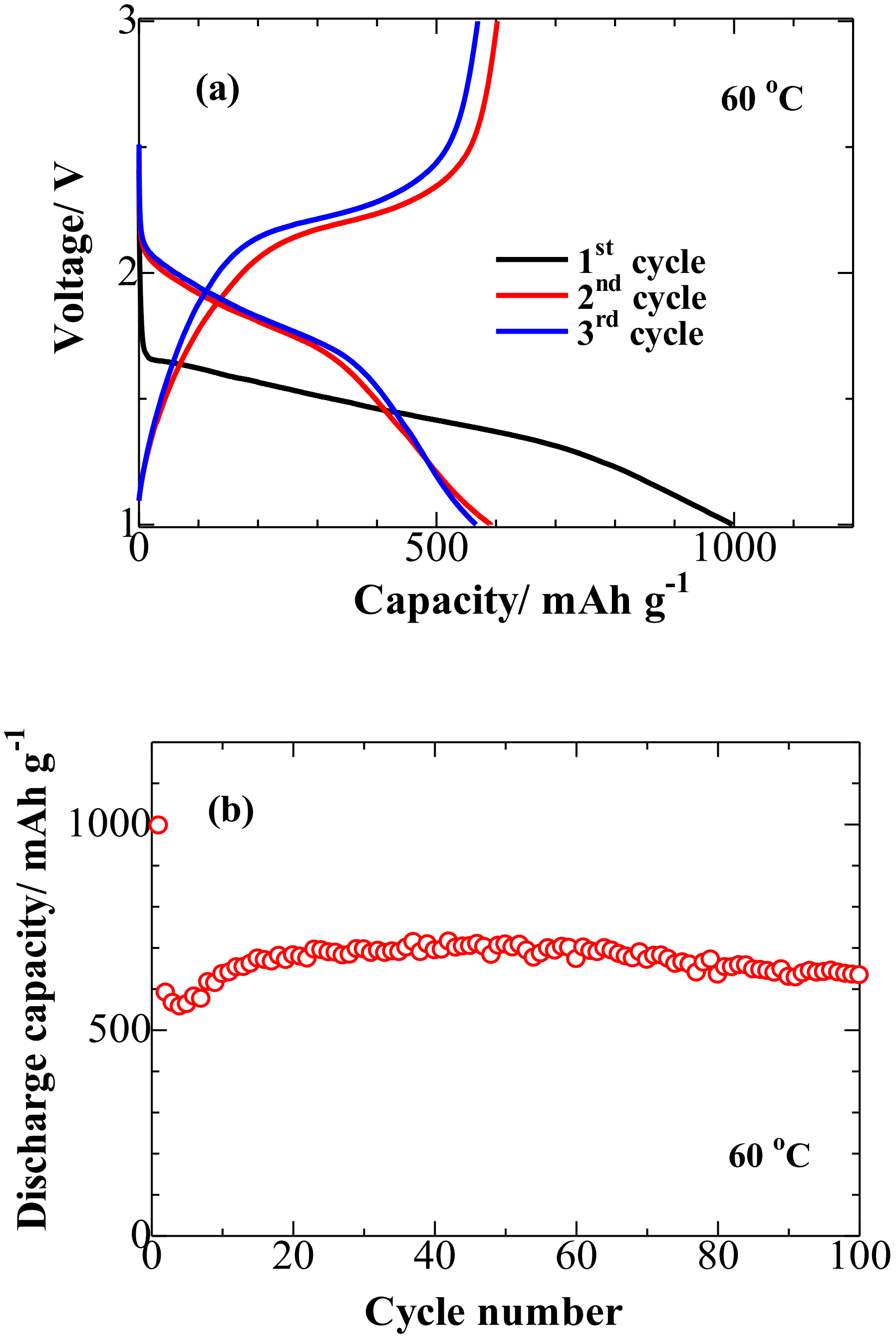

Fig 4.5 (a) Charge/discharge profiles (at 0.1 C) of all solid state Li/S cell at 60 °C; (b) Cycle performance (at 0.1 C) of all solid state Li/S cell at 60 °C

Chapter 5

Final Conclusions and Future Directions

With the development of portable electronic devices and electric vehicles, and demands of storage of renewable energy sources, low cost, safe, abundant in resources, and high energy-density lithium/sulfur batteries have attracted tremendous attention of the researchers and battery companies worldwide. In contrast to the most of other works published on Li/S batteries and focused on the optimization of sulfur cathode, in the present thesis, we worked on the development of the novel polymer electrolyte for Li/S batteries.

The replacement of conventional liquid electrolytes with a polymer membrane along with the improvement of the cell operation, contributes to the battery safety through absence of the electrolyte leakage. Furthermore, the use of polymer electrolytes provides the battery with the advantages of typical plastic batteries, such as ease of fabrication, modularity in design, and free dimensional orientation (no danger of the electrolyte leakage). Therefore, the following polymer electrolytes have been studied.

The PVDF-HFP/PMMA films prepared in this work by phase separation had abundant pore structure and high absorption ability towards liquid electrolytes. The polymer matrix with absorbed liquid electrolyte presented a self-standing film with good mechanical properties. The ionic conductivity of this resulting GPE was about 3.37 mS cm^{-1} at room temperature.

The S/KB composites were used as active cathode materials and were prepared via mechanical milling and thermal treatment. The composite with 43 wt% of sulfur possessed the structure with the most of sulfur incorporated in the micro-pores of KB. This composite cathode showed a good cyclability in rechargeable lithium cell with the GPE prepared in this work. A specific capacity up to 870 mAh g^{-1} in the initial cycle and a reversible capacity of about 510 mAh g^{-1} could be delivered by this cell.

In further studies, a solid polymer electrolyte based on poly (ethylene-oxide)/nanoclay composite was prepared for all solid state lithium/sulfur battery application. Effects of the nanoclay content and the test temperature on the ionic conductivity of the PEO/nanoclay solid polymer were investigated. The ionic conductivity of the resulting solid polymer electrolyte was about 3.22×10^{-4} S cm^{-1} at 60 °C temperature, which could be considered as satisfying the operation requirement for all solid state lithium/sulfur cells. The all solid state Li/S batteries with the PEO/MMT solid polymer electrolyte, prepared in this work, exhibited good cycling, with a reversible capacity of 634 mAh g^{-1} over 100 cycles at 0.1 C rate.

The results obtained in this study on the gel polymer Li/S and the solid polymer Li/S batteries represent a new paradigm of integrating a polymer electrolyte into Li/S batteries, which could be extended to the use of other types of solid electrolytes, and opens the opportunities in generating liquid electrolyte-free Li/S batteries. These developments represent promising steps towards the engineering of viable Li/S batteries. However, the author suggests that other promising opportunities remain to further develop this research, and some of them are briefly described as follows:

Despite being largely studied, the gel polymer electrolytes still need further improvement. Gel polymer electrolytes generally consist of a polymer matrix and a liquid electrolyte. However, the use of organic molecular solvent as liquid electrolyte in the polymer matrix has potential risks of flammability. Due to the substantial improvement of the conductivity of ionic liquids and thermal and electrochemical properties of polymers, the incorporation of ionic liquids into gel polymer electrolytes could be considered as a promising way to prepare high performance Li/S batteries.

Gel polymer electrolytes are prepared by activating the porous polymeric film with liquid electrolyte. The absorbed liquid electrolyte fills the pores of the membrane and facilitates pathways for the ionic conductivity. The solid polymer matrix offers mechanical integrity even with the microporous structure up to some extent. Both high porosity and the liquid electrolyte content significantly contribute towards a higher ionic conductivity. The ionic conductivity of GPE increases with increase in the absorbed liquid electrolyte amount, i.e. the ratio of gel phase; the later greatly depends on the porosity and pore structure of a polymer membrane and its increase reduces the polymer matrix mechanical strength. Thus, the ionic conductivity and mechanical stability of GPEs are mutually exclusive. The conductivity of GPE increases at the expense of its mechanical strength. Addition of ceramic fillers such as SiO_2, Al_2O_3, $BaTiO_3$, and ZrO_2 was found to enhance the mechanical strength, thermal stability and conductivity of GPEs when used as an inorganic additive. This approach could be considered as one of the next work in the development of high performance Li/S battery.

At present, the main restriction of use of solid polymer electrolytes are their low ionic conductivity at ambient temperatures and a low Li^+ transference number under the equilibrium conditions, which is due to the low segmental mobility of the polymer chains complexed with a lithium salt. Typically, the conductivity of bulk polymeric systems used nowadays, independently of the chemical nature of the polymer matrix, remains in the range of 10^{-7}-10^{-5} S cm^{-1} at ambient temperature, whereas the conductivity of the order of 10^{-3} S cm^{-1} or higher is considered as the target for a commercial applicability: appreciable conductivities could be achieved only at temperatures above 70 ^{o}C. Therefore, the study of novel efficient solid polymer electrolytes is important.

Ceramic-type solid electrolytes are characterized as non-flammable, forming a favorable SEI film, and could be prepared in a wide range of compositions. Nevertheless, the major advantage of these materials is their ionic conductivity that is generally higher than that of the corresponding polymer systems. Considering the electrochemical performance in lithium ion batteries, we believe that the solid-state lithium sulfur cell with the ceramic solid electrolyte could be very perspective and promising as high-energy density battery for safe, low-cost energy storage applications.

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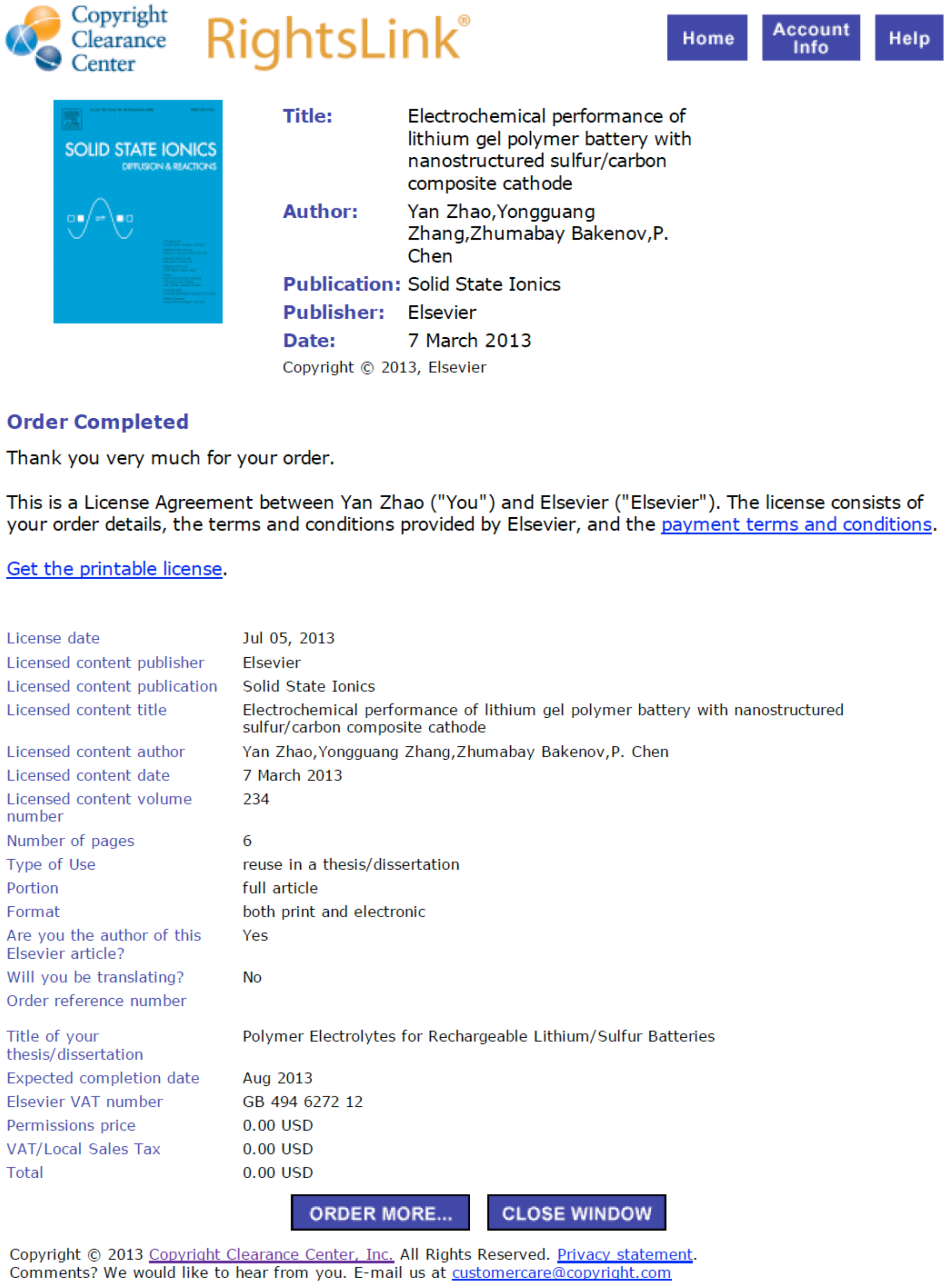

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