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Improvement of electrochemical performance of sulfur-based materials for lithium-sulfur batteries

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Abstract

Lithium ion batteries (LIBs) have been considered as one of the most promising energy storage/conversion devices as desirable power sources for portable electronic devices and transportation such as EV and HEV. However conventional cathode materials (i.e., LiCoO$_2$, LiMnO$_2$, and LiFePO$_4$) have clear limitations for commercialization as above mentioned power sources owing to their limitative theoretical capacity under 300mAhg$^{-1}$. Recently, Sulfur is emerged as an attractive cathode material candidate due to its high capacities of up to 1675mAhg$^{-1}$. In addition, it is abundant and environmentally friendly material which is one of the important factors for next generation batteries. Nevertheless Li-Sulfur batteries have some problems like polysulfide dissolution and involving insoluble polysulfide such as Li$_2$S$_2$, Li$_2$S which are electronically nonconductive. These problems result in capacity fading during charge-discharge process and loss of active material. Therefore many researchers have been dedicated to tackle these problems by developing various methods for sulfur based composite materials (i.e., sulfur-carbon composite, hybrid sulfur composite and sulfur- polymer composite) and additives in electrolyte (i.e., LiNO$_3$, toluene). However, there still remain a number of challenges to avoid polysulfide dissolution and formation of insoluble polysulfide.

In this regard, here we first report the PTCDA organic/Sulfur composite material and demonstrate how we can efficiently reduce polysulfide dissolution and formation of insoluble polysulfide enabling extended cycle life.

In addition, the impacts of the electrolyte additives such as a fluoroethylene carbonate (FEC), LiNO$_3$ and polysulfide to the electrochemical performance and SEI layer of Li-Sulfur batteries were investigated. And also to prevent polysulfide dissolution, SEI layer on cathode was formed by forcing decomposition of electrolyte. To confirm the effects of additive, the surface chemistry with several electrolyte additives were investigated using X-ray photoelectron spectroscopy (XPS). It is found that LiNO$_3$ formed stable protective layer which involved LiN$_3$ species component. This layer prevents polysulfide dissolution and a shuttle effect.
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1. Introduction

As a rapid industrialization progresses, severe pollution problems are emerging. Particularly, the burning of fossil fuels is causing air pollution and bringing a global warming. In the green energy industry, solar heat, wind power and other renewable energies are big issue. Lithium ion batteries (LIBs) have been considered as one of the most promising energy storage/conversion devices for portable electronic devices and transportation such as EV and HEV.¹

Sony Corporation commercialized Lithium ion (Li ion) batteries for the first time in the 1990s. Since then Li ion batteries have been to the fore as power sources for portable electronic devices, (cell phone, laptop and so on) electric vehicles (EVs) and as energy storage systems (ESSs) (Fig 1).

Commercialized Li ion batteries use a transition metal oxide (i.e. LiCoO₂, LiMn₂O₄) or phosphate (LiFePO₄) as a cathode material and graphite as an anode material. During the charging process, Li ions are de-intercalated from the cathode materials and intercalated in the anode materials. This process is reversible during the discharge (Fig. 2). Conventional cathode materials (i.e., LiCoO₂, LiMnO₂, and LiFePO₄) have low theoretical capacity under 300mAhg⁻¹. This acts as a restriction for them to be used for ESS or EV because they require higher energy density and lower cost. So Sulfur is candidate cathode material due to its high capacities of 1675mAhg⁻¹. Moreover, it is abundant in earth and environmentally friendly, which are important factors for next generation batteries.²

Li-Sulfur batteries typically used lithium metal for the anode and sulfur for the cathode. Fig 3 shows schematic illustration for Li-Sulfur batteries. In the negative electrode, the oxidation reaction of lithium metal occurs and the generated lithium ions are transferred to the cathode and react with the sulfur elements during the discharge process.³ Before the discharge process, sulfur exists as S₈ ring. When the sulfur reacts with the lithium ions during discharge, the sulfur – sulfur bonds are cleaved to open the S₈ ring, and changed to polysulfide linear bonding shortening the sulfur chain length. When it is completely reduced, it makes Li₂S as a result.⁴ Figure 4 presents schematic illustration of the overall reaction, given by:

\[
\begin{align*}
S₈ + 2Li⁺ + 2e^- & \rightarrow Li₂S₈  \\
Li₂S₈ + 2Li⁺ + 2e^- & \rightarrow 2Li₂S₄  \\
Li₂S₄ + 2Li⁺ + 2e^- & \rightarrow 2Li₂S₂  \\
Li₂S₂ + 2Li⁺ + 2e^- & \rightarrow 2Li₂S
\end{align*}
\]

High ordered polysulfides such as Li₂Sn (8≤n≤4) correspond to the first plateau (2.15-2.4V) in the voltage profile and they are soluble in the electrolyte. Dissolved polysulfides diffused into Li metal
and can be reduced to Li$_2$S$_2$ and Li$_2$S. Also they can generate shuttle effect and passivation of the Li metal.$^5$

Low ordered polysulfides such as Li$_2$S$_2$ and Li$_2$S correspond to the second plateau (2.1V) in the voltage profile. Li$_2$S$_2$ and Li$_2$S are insoluble in the electrolyte and electronically insulating, so they cover the cathode by acting as a resistance component and make the movement of lithium ions difficult. Generated insoluble polysulfides lead capacity fading during charge-discharge process and loss of active material. $^6$

To overcome these problems, many researchers tried various methods. Browsing the research trends of lithium/sulfur batteries studied recently, studies for producing composite porous carbons, carbon nanotubes, graphene and polymer composites have been researched. These studies improved the efficiency and cycle performance.$^7$
Figure 1. Schematic illustration of the Li-ion battery applications.

Figure 2. Schematic illustration of the Li-ion battery (Graphite/Li$^+$ electrolyte/LiCoO$_2$).
Figure 3. Schematic illustration for Li-Sulfur batteries.

Figure 4. Schematic illustration of the overall reaction.
CHAPTER II

PTCDA-Sulfur composites.

1. Introduction

Research trend of Li-Sulfur batteries

1.1. Porous carbon-sulfur composites

Nazar et al. synthesized mesoporous carbon-sulfur composites. After mixing sulfur and mesoporous carbons, carbons are filled with sulfur inside the pores. Figure 5 shows schematic illustration for mesoporous carbon-sulfur composites and their cycle performance. This structure improves the electronic conductivity and prevents generation of soluble polysulfides in the electrolyte. Furthermore, nanopores in the structure can accommodate deformation and expansion of structure. The composites showed a high discharge capacity, but still cannot prevent polysulfide dissolution during the cycle. In order to improve this problem, they were coated with a polymer material (PEG), thereby producing Li-Sulfur batteries having a high theoretical discharge capacity.\(^8\)

Ahn et al. reported that sulfur was dissolve into the activated carbon micropores by a solution-based processing. It has an advantage that using an inexpensive activated carbon can reduce the manufacturing cost of the batteries. This composite showed high initial capacity (1364mAh/g at 0.25C) and good cycle performance during 50 cycles. Sulfur was not easily dissolved into the electrolyte because sulfur was well retained in the activated carbon.\(^5\)

Another approach similar to creating a porous hollow spherical carbon composite was prepared by vaporizing sulfur, reported by Archer et al. Figure 6 shows TEM images for mesoporous carbon-sulfur composites and their cycle performance. A porous hollow spherical carbon has a high specific surface area and large internal void spaces. This composite showed high initial capacity (1071mAh/g), capacity retention of 91% during the 100 cycles and shuttle effect was also relaxed. Polysulfide is hardly soluble and exists in small pore sulfur.\(^9\) However, microporous hollow spherical carbon-sulfur composites indicated the different voltage profile between 1.5~2V. It is possible to observe such a phenomenon even in composite form which passed through the heat treatment process of 300 degrees.\(^10\) The reason is that these materials have no longer \(S_8\) structure. Figure 7 TEM represents image for microporous carbons-sulfur composites and their voltage profile.

For the nanoporous carbon-sulfur composite, the following conditions are required in order to improve performance: (1) if pore size is well optimized, it can traps polysulfide and minimize
pulverization. (2) In order to increase the content of sulfur, a large pore volume is required.11

Figure 5. (a) Schematic illustrations for Mesoporous carbons-sulfur composites (b) cycle performance.

Figure 6. (a) TEM images for Mesoporous carbons-sulfur composites and (b) cycle performance.

Figure 7. (a) TEM image for microporous carbons-sulfur composites and (b) voltage profile.
1.2. Graphene-sulfur composites

Graphene has large surface area, chemical stability, and mechanical strength and flexibility, making it a useful growth substrate to anchor active materials for electrochemical energy storage applications.¹²

Zhang et al. synthesized graphene oxide- sulfur (GO-S) nanocomposites. Sulfur was deposited on graphene oxide sheets by chemical reaction. Electrical conductivity improved by combining the functional groups on the graphene oxide and sulfur, and it prohibits polysulfide dissolution in electrolyte. Go network accommodates the volume change of the electrode which occurs in electrochemical reaction of the sulfur and lithium. So the GO-S composites exhibit high initial capacity and excellent capacity retention.¹³

Another approach is combining sulfur and graphene with PEG coating reported by Dai et al. Figure 8 is a diagram of the synthesis step for a graphene-sulfur composite. This composite show good cycling stability and its capacity decreased only by 13% within the 90 cycles. But sulfur with PEG and graphene-sulfur without PEG showed faster capacity decay. The reason is that graphene affects electrical conductivity and traps polysulfide. PEG layer also traps polysulfide and accommodate volume change. So it is important factor for stable cycling performance in this graphene-sulfur composite.¹⁴

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Figure 8. Diagram of the synthesis step for a graphene-sulfur composite.
1.3. Polymer coating

PAN is widely used in the sulfur-containing polymer material. Sulfur-PAN composite is produced via the dehydrogenation process of PAN. Sulfur-PAN composite was prepared from a variety of temperatures at 250–800 °C reported by Wang et al.\(^{15}\) As a result, the composite which was heat-treated at 450 °C showed a capacity retention rate of nearly 90% during 380 cycles. This compound has a structure that sulfur is attached to the PAN chain. As a result, the electrical conductivity is improved, and it exhibits good cycle properties.

It is known that mesoporous carbons trap polysulfide effectively due to their small pore diameter. However, mesoporous carbons have a large surface area for polysulfide dissolution, so capacity decay occurred in mesoporous carbon-sulfur composition. Cui et al. synthesized mesoporous carbon-sulfur composition with PEDOT: PSS coating. Figure 9 shows a diagram of the polymer coating of mesoporous carbon-sulfur composite. It is known that PEDOT: PSS is thermally stable at 85°C for over 1000h with minimal change in electrical conductivity.\(^{16}\) As a result, conductive polymer PEDOT: PSS coating on the surface of mesoporous carbon-sulfur composites was used to minimize the polysulfide dissolution and trap polysulfide effectively. Compared to bare mesoporous carbon-sulfur, PEDOT: PSS coating on the surface of mesoporous carbon-sulfur composites improved cycle performance. It increases initial discharge capacity and improves the capacity retention.

![Figure 9. Scheme of PEDOT: PSS-coated CMK-3/sulfur composite for improving the cathode performance.](image)

Figure 9. Scheme of PEDOT: PSS-coated CMK-3/sulfur composite for improving the cathode performance. (a) In bare CMK-3/S particles (gray: CMK-3, yellow: sulfur), polysulfides (green color) still diffuse out of the carbon matrix during lithiation/delithiation. (b) With conductive polymer coating layer (blue color), polysulfides could be confined within the carbon matrix. Lithium ions and electrons can move through this polymer layer.
2. Experimental

2.1. Preparation of PTCDA/Sulfur composites.
3, 4, 9, 10-perylene-tetracarboxylicacid-dianhydride (>98.0%, TCI) and sulfur (100 mesh, Aldrich) were fully mixed by grinding with a mass ratio of 1:1 in glove box. After that, PTCDA/Sulfur composites were prepared by a ball-mill process. (Steel ball: 20ea, 750rpm, 10h). PTCDA/Sulfur (3:7) composites were synthesized by same process with different ratio.

2.2. Preparation of PTCDA/Sulfur cell.
The PTCDA/Sulfur cathode slurry was prepared by mixing 73% composite material with 18% poly (vinylidene fluoride) (PVDF) (Mw = 534,000, Aldrich) binder in anhydrous N-methyl-2-pyrrolidinone (NMP, Aldrich) and 9% super P (as a carbon additive for conductivity enhancement, Timcal Inc.). The slurry was spread onto aluminum foil (20µm). The coated electrode was dried in convection oven at 80°C for 10h to remove residual organic solvent. The sulfur cathode was not pressed.

2.3. Electrical properties measurements
For electrochemical test of a coin-type half cell, Galvanostatic discharge/charge measurements (WonA Tech WBCS 3000 battery measurement system) were carried out in the potential range between 1.5 and 2.6V versus Li/Li+. 2032 coin-type cells consist of the sulfur cathode as a working electrode and the Li foil as a counter electrode. The Li foil (900µm) anode was prepared in a glove box. The electrolyte used was 1.3M lithium bis(trifluoromethane sulfonyl)imide (LiTFSI) in tetra(ethylene glycol)dimethyl ether (TEGDME) (received from Soulbrain Co. Ltd). The additive used was LiNO₃ (98%, Aldrich).

2.4. Characterization
X-ray diffraction (XRD) data were collected on a Rigaku D/MAX2500V diffractometer using Cu-Kα radiation (λ= 1.5405Å) operated from 2θ = 10~80. TGA curves were recorded on a TA Instrument/ Q500 in a temperature range of 0°C to 1000°C at a heating rate of 10°C/min oxidizing (air) condition. The cross section image of the PTCDA/S particle was examined in Dual-Beam Focused Ion Beam (Quanta 3D FEG) with a Ga LMIS. During the acquirement of FIB images, an EDS was also used to determine in the region under investigation. Attenuated total reflectance-Fourier transform infrared (ATR- FTIR) spectra data were examined in a Varian 670-IR spectrometer with a spectral resolution of 4cm⁻¹ under N₂ atmosphere. The solid-state 12C NMR spectrums were obtained by VNMRS 600/Agilent, USA.
3. Results and Discussion

XRD patterns of the 3, 4, 9, 10-perylene-tetracarboxylicacid-dianhydride (PTCDA), sulfur, PTCDA/S composite are shown in figure 10. It is known that PTCDA has good crystalline properties, and is reported to have different polymorphs. The composite shows the sharp diffraction peaks, while the broad diffraction peaks appear at about 28°. The XRD patterns for the PTCDA/S composite show good accordance with sulfur. It seems that sulfur exists in a crystalline state and the sharp diffraction peaks of PTCDA disappear. So this composite may consist of monolayered PTCDA covering the sulfur.

To understand the inner and outer mixture state of PTCDA/sulfur composites, we examine it via FIB. The morphology cross-section images of PTCDA/S composites are shown in Fig. 11. The sulfur mappings indicate that it exists in the whole area of the composite. So PTCDA is covered on outside surface and dispersed a little inside sulfur. Figure 12 is diagrams of the PTCDA/Sulfur composite.

To quantify the amount of sulfur in PTCDA/S composite, thermogravimetric analysis (TGA) was used under oxidizing (air) condition. Figure 13 shows the TGA curves of the PTCDA, sulfur and PTCDA/S composite. For the PTCDA/S composites, a multi-step degradation pattern was observed. The first weight loss was the evaporation of sulfur and the second weight loss was the evaporation of PTCDA. Consequently TGA shows the PTCDA/S (1:1) composites range up to 50% sulfur, and shows the PTCDA/S (3:7) composites range up to 70% sulfur.
Figure 10. XRD patterns of the sulfur composites. (a) Sulfur (b) PTCDA (c) PTCDA/S (1:1) composite (d) PTCDA/S (3:7) composite.

Figure 11. (a) SEM image of PTCDA/S composites. (b) EDX elemental mapping images (C, S element) (c) The cross-section image of PTCDA/S. (d) EDX elemental mapping of the cross-section image (C, S element) (c) The cross-section image of PTCDA/S.
Figure 12. Schematic image of the PTCDA/Sulfur composite.

Figure 13. TGA analysis of a sulfur (a), PTCDA/S (3:7) composite (b), PTCDA/S (1:1) composite (c).
NMR is a technique for determining the structure of most organic and some inorganic molecules. Different atoms within a molecule resonate at different frequencies at a given field strength. The observation of the resonance frequencies of a molecule allows us to discover structural information of the molecule. Figure 14 shows solid-state $^{13}$C NMR spectroscopy for PTCDA/S (1:1) and PTCDA. PTCDA has four main bands. The carbon atoms of carbonyl double bonds in anhydride groups are 1. The carbon atoms at the ortho position of carbonyl groups are 2, and the carbon atoms at the meta position of carbonyl groups are 3. The other carbon atoms are 4. Because the carbon and sulfur combination cause carbon-sulfur bonding, it can be confirmed by a new peak formation or existing peak disappearance in NMR spectroscopy. There is no change in peak position, and any new bonding was occurred. This could be checked through FT-IR spectra. Figure 15 show FT-IR spectroscopy for PTCDA (a), PTCDA/S (1:1) (b) and PTCDA/S (3:7) (c). Peak of the PTCDA/S composite is consistent with the PTCDA peak. As a result, new bonds did not occur between PTCDA and sulfur.

Figure 14. Solid-state $^{13}$C NMR spectroscopy for PTCDA/S (1:1) (a) and PTCDA (b).
Figure 15. FT-IR spectroscopy for PTCDA (a), PTCDA/S (1:1) (b) and PTCDA/S (3:7) (c).
Figure 16 shows the galvanostatic cycling at a current density of 167.2 mAg\(^{-1}\) (C/10 rate) in 1.3M LiTFSI dissolved in tetra (ethylene glycol) dimethyl ether (TEGDME) with 1wt% LiNO\(_3\). The initial discharge capacity of PTCDA/S composite with 50wt% sulfur is 745 mAh/g, with 70wt% sulfur is 578 mAh/g and the initial discharge capacity of sulfur is 190 mAh/g.

It is known that sulfur element has very low electronic conductivity due to high electrical resistivity about 2x10\(^{15}\) \(\Omega\cdot\text{m}\). When comparing the sulfur composite, it is possible to verify that it is improved in terms of capacity. It seems that PTCDA of PTCDA/S composite can easily move electrons, so capacity was increased in the case of composite made by mixing sulfur and PTCDA. So the capacity of the 50% sulfur in composite is higher than that of 70% sulfur in composite.

![Figure 16. Electrochemical characterization of PTCDA/S and comparison to reference materials. (a) Voltage profiles of the initial charge/discharge processes for PTCDA/S (1:1), (3:7), between 1.5 and 2.6V vs. Li/Li\(^+\) at 0.1C (b) Voltage profiles of the initial charge/discharge processes for PTCDA (c) Cycleability of PTCDA, sulfur and PTCDA/S composite.](image)
4. Conclusion

In summary, most of the composites for Li-Sulfur batteries are sulfur and carbon species. We create new organic-sulfur composite for Li-Sulfur batteries.

PTCDA/S composite is prepared via simple ball-mill method. Although the capacity is low in comparison with carbon-sulfur composite, this composite shows better cycle performance compared to raw sulfur element. It seems that PTCDA provides electrons for the reaction between sulfur and Li ion, so capacity of PTCDA/S composite was increased. Meanwhile, PTCDA has not been regarded as the roles that retain the structure and prohibit polysulfide dissolution. Further research about composite of sulfur and organic material should be done more.
CHAPTER III

SEI effect on electrochemical performance

1. Introduction

1.1. Electrolytes for Li-Sulfur batteries

Electrolyte of Li-Sulfur batteries has been studied for a variety of electrolyte such as ether, sulfone, carbonates and ionic liquid for better performance. The suitable electrolyte selection is important in the successful utilization of the active material. Because polysulfides easily dissolve in the electrolyte, polysulfides have various chemical reactions in the electrolyte when sulfur and lithium reacts.\(^\text{18}\)

Various types of electrolytes have been evaluated for their appropriateness in Li-Sulfur batteries.\(^\text{19}\) Carbonate-based electrolyte doesn’t operate in lithium sulfur batteries, because the nucleophilic attack of the carbonyl group by the polysulfide anion. On the other hand, ether solvents (i.e. 1, 3-dioxolane (DOL), 1, 2-dimethoxyethane (DME), tetra (ethylene glycol) dimethyl ether (TEGDME)) which have a high solubility of polysulfide, show good ionic conductivity and low viscosity suitable for Li-Sulfur battery. Sulfone based electrolytes (i.e. EMS) are considered to be highly stable with regard to oxidation at the cathode, but research about its effects for sulfur electrode was still lacking.

Shin and Cairns have researched ionic liquid based electrolytes. Ionic liquid is normally mixed with ether solvent (i.e. PEGDME) so that it reduces viscosity and improves the ionic conductivity.
1.2 electrolyte additive for Li-Sulfur batteries

The application of Li–sulfur batteries is difficult due to its low cycling efficiency and deposited dendrite on Li metal. The reaction of freshly deposited Li with the electrolyte components and polysulfide makes these problems. Electrolyte additives have been studied to improve charge-discharge performance of Li-Sulfur by forming a stable SEI layer on the electrode.\textsuperscript{20}

Lithium nitrate (LiNO\textsubscript{3}) is one of the most important electrolyte additives in lithium sulfur batteries. Specific chemical reaction of LiNO\textsubscript{3} has not been fully elucidated yet. It has been suggested that a stable passivation layer (Li\textsubscript{x}NO\textsubscript{y} and Li\textsubscript{x}SO\textsubscript{y}) is formed with the oxidizing additives on the lithium metal surface.\textsuperscript{21} Figure 10 shows schematic of decomposition mechanism of LiNO\textsubscript{3} on the Li anode.

This passivation layer can effectively improve coulombic efficiency close to 98–99\% and delay the reduction of polysulfide species. Thus the shuttle effect no longer takes place when LiNO\textsubscript{3} is present in the electrolyte.\textsuperscript{22}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure17.png}
\caption{Diagram of decomposition mechanism of LiNO\textsubscript{3} on the Li anode.}
\end{figure}
2. Experimental

2.1. Preparation of ECG/Sulfur composites.

Edge-carboxylated graphene nanosheets were prepared via ball milling [18]. The ECG/S composite was prepared following a melt-diffusion strategy. ECG (1.0g) and sulfur (1.0g) were ground together. After then, the mixture was heated to 155℃. The weight ratio of sulfur /carbon was adjusted to be equal.

2.2. Preparation of ECG/Sulfur cell

The ECG/Sulfur cathode slurry was prepared by mixing 73% composite material, with 18% poly (vinylidene fluoride) (PVDF) (Mw = 534,000, Aldrich) binder in anhydrous N-methyl-2-pyrrolidinone (NMP, Aldrich) and 9% super P (as a carbon additive for conductivity enhancement, Timcal Inc.). The slurry was spread onto aluminum foil (20µm). The coated electrode was dried in convection oven at 80°C for 10h to remove residual organic solvent. The sulfur cathode was not pressed.

2.3. Electrical properties measurements

For electrochemical test of a coin-type half cell Galvanostatic discharge/charge measurements (WonAtech WBCS 3000 battery measurement system) were carried out in the potential range between 1.5 and 2.6V versus Li/Li⁺. 2032 coin-type cells consist of the sulfur cathode as the working electrode and the Li foil as the counter electrode. The Li foil (900µm) anode was prepared in a glove box. The electrolyte used was 1.3M lithium bis(trifluoromethane sulfonyl)imide (LiTFSI) in tetra(ethylene glycol)dimethyl ether (TEGDME) (received from Soulbrain Co. Ltd). The additive used was FEC (fluoroethylene carbonate) (received from Soulbrain Co. Ltd), LiNO₃ (98%, Aldrich), Polysulfide.
2.4. Characterization

X-ray diffraction (XRD) data were collected on a Rigaku D/MAX2500V diffractometer using Cu-K\textalpha radiation (\(\lambda=1.5405\text{Å}\)) operated from \(2\theta = 10\text{°} - 80\text{°}.\) Scanning electron microscope (SEM) data were examined in a Cold field-emission SEM (Cold FE-SEM) instrument.

The cross section image of the ECG/S particle was examined in Dual-Beam Focused Ion Beam (Quanta 3D FEG) with a Ga LMIS. During the acquisition of FIB images, an EDS was also used to determine in the region under investigation.

The cell was tested by cyclic voltammetry (SP-150, NeoScience) in the range of 1.5-4V vs. Li/Li\textsuperscript{+} using a scan rate of 0.5mV/s.

X-ray photoelectron spectroscopy (XPS) used Thermo Fisher on the elementary chemical state and depth profile of the ECG/S. Before the XPS examined, the cathode surface was cleaned by dimethyl carbonate (DMC) (Soulbrain) to remove the electrolyte salt.
3. Results and Discussion

To emphasize the role of electrolyte on cycle performance of Li-sulfur batteries, the Edge-carboxylated graphene nanosheets (ECG) and sulfur composites are used for the evaluation of electrochemical performance. XRD patterns of ECG, sulfur, ECG/S composites are presented in figure 18 (a). Figure 18 (b), (c) present SEM images. ECG is expanded and consists of several layers of graphene sheet so it has an amorphous structure. After sulfur impregnation into ECG layer, the composite peaks seem to little be broad.

Figure 19 is a diagram of the ECG/S structure. To understand the inner and outer mixture state of ECG/sulfur composites, we examine it via FIB. The morphology cross-section images of ECG/S composites are shown in Fig. 20b. The sulfur mappings indicate that it exists through the whole area of the layered ECG. So sulfur is covered on outside surface and also it exists in interlayer of ECG.

![Figure 18. (a) X-ray diffraction patterns of ECG/S composite compared to the pristine ECG (b)SEM micrographs of ECG, (c) SEM micrographs of ECG/S.](image-url)
Figure 19. Diagrams of the ECG/S structure.

Figure 20. (a) SEM image of ECG/S composites. (b) The cross-section image of ECG/S (c) EDX elemental mapping images of C element) (d) EDX elemental mapping images of S element).
To confirm the redox reaction of the additives in electrolyte, we performed CV test. Figure 21 compares the cyclic voltamograms (CV) of the TEGDME electrolyte with different additives. Increasing voltage process caused the oxidation process. In the case of TEGDME electrolyte, decomposition occurs around 3.7V. While in the case of TEGDME electrolyte with FEC and LiNO₃ additive, oxidation peak is moved to lower potential. The additive is decomposed before the electrolyte is decomposed, so it is found that the SEI layer is formed stable on the cathode. However, in the case of polysulfide, reaction process to increase the voltage is reduced to sulfur, so stable SEI layer is not formed on cathode.

Figure 21. Cyclic voltamograms of different electrolyte (a) 1.3M LiTFSI in TEGDME (black), 1.3M LiTFSI in TEGDME with 5wt% FEC additive (blue), and 1.3M LiTFSI in TEGDME with 1wt% LiNO₃ additive (bluish-green) (b) 1.3M LiTFSI in TEGDME with 5wt% PS additive (red), and 1.3M LiTFSI in TEGDME with 1wt% LiNO₃, and 5wt% PS (dark red).
Figure 22 shows the galvanostatic cycling at a current density of 167.2 mAg\(^{-1}\) (C/10 rate) in 1.3 M LiTFSI dissolved in tetra (ethylene glycol) dimethyl ether (TEGDME). In the case of TEGDME electrolyte, due to the effect of polysulfide that is dissolved more and more, cycle is hard to proceed (Fig 22 a, b). In case of figure 22 c and d, it underwent electrolyte decomposition first, but polysulfide dissolution into electrolyte is not prevented. It seems that state of the electrolyte is so unstable due to salt dissolution, it is hard to proceed cycle.

Figure 22. Electrochemical performances of ECG/S cell with a 1.3 M LiTFSI in TEGDME electrolyte. (a) Voltage profiles. (b) Electrochemical cycle life time including the coulombic efficiency and the specific discharge capacity. (c) Voltage profile of electrolyte decomposition first. (d) Electrochemical cycle life time including the coulombic efficiency and the specific discharge capacity.
The FEC is typically known as an anode material additive. FEC formed a stable SEI layer on anode, so it improved capacity retention and coulombic efficiency. We expected that, in li-Sulfur batteries, SEI layer to be formed on the Li metal, thereby suppressing the reaction between polysulfide and Li metal. However the cycle of cell with 1.3M LiTFSI dissolved in TEGDME with 5wt% FEC additive is also hard to process and shuttle effect occurred (Fig 23 a, b). Figure 24 shows the XPS spectra for the SEI layer formed on the cathode and Li metal (anode). It is known that Fig. 24 d, g show that after 1500s etching, the peak centered at 55.5eV is assigned to LiF. FEC is decomposed, and SEI layer is formed on the Li metal. But this SEI layer can’t suppress the reaction between polysulfide and Li metal (anode). In the cathode side, it seems that the various by-products form a layer. Figure 24 (a) is schematic illustration for the formation of SEI layer on the cathode.

For the figure 25 c and d, electrolyte decomposition occurred first and SEI layer was formed on the cathode. It seems that this layer is too thick. The layers act as a resistive component and this cell has a low capacity. Figure 25 shows the XPS spectra for the SEI layer formed on the cathode and Li metal (anode). Figure 25 (d), (g) show that LiF peak disappeared due to decomposition of FEC. But this SEI layer can’t suppress the reaction between polysulfide and Li metal (anode). The SEI layer on the cathode, it seems that inner SEI layer is mainly composed of LiF species due to decomposition of FEC and outer SEI layer is mainly composed of Li$_2$CO$_3$ species. Figure 25 (a) is schematic illustration for the formation of SEI layer on the cathode.
Figure 23. Electrochemical performances of ECG/S cell with a 1.3M LiTFSI in TEGDME with 5wt% FEC additive electrolyte. (a) Voltage profiles. (b) Electrochemical cycle life time including the coulombic efficiency and the specific discharge capacity. (c) Voltage profile of electrolyte decomposition first. (d) Electrochemical cycle life time including the coulombic efficiency and the specific discharge capacity.
Figure 24. (a) Schematic illustration for the formation of SEI layer on the cathode. XPS spectra of the cathode surface after 10 cycles in (b) C1s, (c) F1s, (e) C1s, etching 1500s, (f) F1s, etching 1500s, XPS spectra of the Li metal (anode) surface after 10 cycles in (d) Li1s 0s, (g) Li1s 1500s.
Figure 25. (a) Schematic illustration for the formation of SEI layer on the cathode. XPS spectra of the cathode surface after 10 cycles in (b) C1s, (c) F1s, (e) C1s, etching 1500s, (f) F1s, etching 1500s, XPS spectra of the Li metal (anode) surface after 10 cycles in (d) Li1s 0s, (g) Li1s 1500s.
The LiNO₃ has already been identified as a good additive for Li-Sulfur batteries. LiNO₃ make passivation film on lithium metal and suppress the redox shuttle of polysulfide, resulting in improved capacity retention and coulombic efficiency. The cycle of cell with 1.3M LiTFSI dissolved in TEGDME with 1wt% LiNO₃ additive gives significantly better capacity retention and cycleability than FEC additive (Fig 26 a, b). Figure 27, 28 shows the XPS spectra for the SEI layer formed on the cathode and Li metal (anode).

Figure 27 shows the XPS spectra for the SEI layer formed on the cathode. In the case of the SEI layer on the cathode, it seems that SEI layer is mainly composed LiN₃ species and various components. Figure 27 (a) is schematic illustration for the formation of SEI layer on the cathode.

Figure 28 shows the XPS spectra for the SEI layer formed on the cathode. For the SEI layer on the cathode, it seems that inner SEI layer is mainly composed of LiN₃ species due to decomposition of LiNO₃ and outer SEI layer is composed of ROCO₂Li species. Unlike FEC additive, when the SEI layer decomposition of LiNO₃ additive produced in the cathode, to prevent the shuttle phenomenon and good cycle performance. But, the Li metal side, it can be confirmed that coulombic efficiency increases unlike don’t decomposition electrolyte. It may be because perfect SEI layer wasn’t formed and it seems that some of LiNO₃ was decomposed on cathode side. Figure 28 (a) is schematic illustration for the formation of SEI layer on the cathode.
Figure 26. Electrochemical performances of ECG/S cell with a 1.3M LiTFSI in TEGDME with 1wt% LiNO₃ additive electrolyte. (a) Voltage profiles. (b) Electrochemical cycle life time including the coulombic efficiency and the specific discharge capacity. (c) Voltage profile of electrolyte decomposition first. (d) Electrochemical cycle life time including the coulombic efficiency and the specific discharge capacity.
Figure 27. (a) Schematic illustration for the formation of SEI layer on the cathode. XPS spectra of the cathode surface after 10 cycles in (b) C1s, (c) Li1s, (d) C1s, etching 1500s, (e) Li1s, and etching 1500s.
Figure 28. (a) Schematic illustration for the formation of SEI layer on the cathode. XPS spectra of the cathode surface after 10 cycles in (b) C1s, (c) Li1s, (d) C1s, etching 1500s, (e) Li1s, and etching 1500s.
The polysulfide has already been identified as an additive for Li-Sulfur batteries. The cycle of cell with 1.3M LiTFSI dissolved in TEGDME with 5wt% polysulfide additive shows significantly unfavorable capacity retention and cycleability (Fig 29 a, b). When polysulfide plays a role as active materials, this cell increases initial capacity. But polysulfide dissolution occurs during the cycle, so many polysulfides are dissolved in electrolyte.

For other additives, increasing the voltage, salt is decomposed and contributes to the formation of the SEI layer. However, in the case of the polysulfide, when it comes to increasing the voltage, it will go through a process of polysulfide reduction to sulfur. Therefore, increasing the voltage, stable SEI layer isn’t formed on the cathode and it cannot result in better cycle performance (Fig. 29 c, d)

If a small amount of polysulfide is added, the capacity is predicted to increase because polysulfide plays a role as active materials.

Figure 29. Electrochemical performances of ECG/S cell with a 1.3M LiTFSI in TEGDME with 5wt% PS additive electrolyte. (a) Voltage profiles. (b) Electrochemical cycle life time including the coulombic efficiency and the specific discharge capacity. (c) Voltage profile of electrolyte decomposition first. (d) Electrochemical cycle life time including the coulombic efficiency and the specific discharge capacity.
The experiments were carried out to put together additives both for expression of the additional capacity of polysulfide and the effect of stable SEI layer formation of LiNO\textsubscript{3} additive. The cycle of cell with 1.3M LiTFSI dissolved in TEGDME with 1wt% LiNO\textsubscript{3} additive and 1wt% polysulfide shows significantly better capacity retention and cycleability than LiNO\textsubscript{3} additive (Fig 30 a, b).

Figure 31 shows the XPS spectra for the SEI layer formed on Li metal (anode). Figure 31 (a) is schematic illustration for the formation of SEI layer on the cathode. It is known that the peak centered at 54.9eV is assigned to LiN\textsubscript{3}, the peak centered at 55.5eV is assigned to LiF, and the peak centered at 689.5eV is assigned to Li\textsubscript{x}PF\textsubscript{y}. In case of the SEI layer on Li metal, it seems that inner SEI layer is mainly composed of LiF species and LiN\textsubscript{3} species outer SEI layer is mainly composed of Li\textsubscript{x}PF\textsubscript{y} species.

Figure 32 shows the XPS spectra for the SEI layer formed on Li metal (anode). Figure 32 (a) is schematic illustration for the formation of SEI layer on the anode. The SEI layer on Li metal, it seems that inner SEI layer is mainly composed of LiF species and LiN\textsubscript{3} species outer SEI layer is mainly composed of Li\textsubscript{x}PF\textsubscript{y} species. The SEI components of the Li metal are the same to compare the cell was allowed forced to be formed SEI on cathode or not. But it can be confirmed that the content of LiN\textsubscript{3} is reduced compared to prior (Fig. 32 b,c,d,e). Because almost the whole LiNO\textsubscript{3} was used decomposition to form the SEI layer on the cathode. So it seems that inner SEI layer is mainly composed LiN\textsubscript{3} species outer SEI layer is composed Li\textsubscript{2}CO\textsubscript{3} species(Fig 33 b,c,d,e) Figure 33 (a) is schematic illustration for the formation of SEI layer on the cathode.
Figure 30. Electrochemical performances of ECG/S cell with a 1.3M LiTFSI in TEGDME with 1wt% LiNO$_3$ and 5wt% PS additive electrolyte. (a) Voltage profiles. (b) Electrochemical cycle life time including the coulombic efficiency and the specific discharge capacity. (c) Voltage profile of electrolyte decomposition first. (d) Electrochemical cycle life time including the coulombic efficiency and the specific discharge capacity.
Figure 31. (a) Schematic illustration for the formation of SEI layer on Li metal.
XPS spectra of the cathode surface after 10 cycles in (b) F1s, (c) Li1s, (d) F1s, etching 1500s, (e) Li1s, etching 1500s.
Figure 32. (a) Schematic illustration for the formation of SEI layer on Li metal. XPS spectra of the cathode surface after 10 cycles in (b) F1s, (c) Li1s, (d) F1s, etching 1500s, (e) Li1s, etching 1500s.
Figure 33. (a) Schematic illustration for the formation of SEI layer on the cathode.
XPS spectra of the cathode surface after 10 cycles in (b) C1s, (c) Li1s, (d) C1s, etching 1500s, (e) Li1s, etching 1500s.
4. Conclusion

In summary, the effects of the several electrolytes for Li-Sulfur batteries were described. XPS spectra data confirmed that the SEI layer is formed on the cathode and Li metal. It is found that the SEI layer with FEC additive electrolyte mostly consists of LiF species. SEI layer by FEC isn’t formed stably so it can’t suppress polysulfide dissolution and the reaction between polysulfide and Li metal.

It is found that the SEI layer with LiNO₃ additive electrolyte mostly consists of LiN₃ species. Furthermore various components such as alkyl carbonate (ROCO₂Li), Li₂CO₃, Li₂O, Li₂O₂ and LiₓPFₙ make up the SEI layer. LiNO₃ additive formed stable SEI layer, so it can prevent the continuous transport of electrons from Li metal to soluble polysulfide (Li₂Sn, 8≤n≤4).

In case of polysulfide, small amount of polysulfide act a role of the active materials. As a result, it increases the capacity. But large amounts of polysulfide cause shuttle effect. Consequently, the electrolyte with LiNO₃ and polysulfide additive showed best cycle performance among them. Because LiNO₃ additive formed stable SEI layer so polysulfide can play a role of additional capacity.
References


12. Meng-Qiang Zhao, X.-F. L., †,‡ Qiang Zhang,* † Gui-Li Tian, † Jia-Qi Huang, † Wancheng Zhu, † and; FeiWei, Graphene/Single-Walled Carbon Nanotube Hybrids: One-Step Catalytic Growth and Applications for High-Rate Li-S Batteries. ACS NANO 2012, 6 (12), 10759-10769.


16. Yuan Yang, § Guihua Yu, ‡ Judy J. Cha, † Hui Wu, † Michael V. Gorbachev, ‡ Yan Yao, † Zhenan Bao, ‡,* and; Cui, Y., Improving the Performance of Lithium Sulfur Batteries by Conductive Polymer Coating. ACS NANO 2011, 5 (11), 9187-9193.

17. Han, X.; Chang, C.; Yuan, L.; Sun, T.; Sun, J., Aromatic Carbonyl Derivative Polymers as High-Performance Li-Ion Storage Materials. Advanced Materials 2007, 19 (12), 1616-1621.


