Ionic-additive Crosslinked Polymeric Sulfur Composites as Cathode Materials for Lithium-Sulfur Batteries

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ABSTRACT

Lithium-sulfur (Li-S) batteries are one of attractive energy conversion and storage system based on high theoretical specific capacity and energy density with low costs. However, volatile nature of elemental sulfur is one of critical problem for their practical acceptance in industry because it considerably affects electrode uniformity during electrode manufacturing. In this work, polymeric sulfur composite consisting of ionic liquid (IL) are suggested to reduce volatility nature of elemental sulfur, resulting in better processibility of the Li-S cell. According to systematic spectroscopic analysis, it is found that polymeric sulfur is consisting of repeating units combining with elemental sulfur and volatility of them is negligible even at high temperature. In addition, the IL-embedded polymeric sulfur shows moderate cycle performance compared to the cell with elemental sulfur. From these results, it is found that the IL-embedded polymeric sulfur composite is applicable cathode candidate for the Li-S cell based on their excellent non-volatility as well as their superior electrochemical performance.

Keywords : Lithium Sulfur Battery, Polymeric Sulfur, Ionic Additive, Cathode

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1. Introduction

Lithium-sulfur (Li-S) batteries are considered as one of promising energy conversion and storage system because electrochemical reaction of elemental sulfur (S_8) provides high theoretical specific capacity (1672 mA h g^{-1}) with low costs [1-5]. Nevertheless, several critical issues are still remaining for successful utilization of the Li-S cell including low electronic conductivity of elemental sulfur (less utilization of specific capacity and poor rate capability) [6-10], unfavorable polysulfide dissolution and instable anode interface as a result of undesired electrochemical/chemical reaction on lithium metal (which leads to poor cycle performance of the Li-S cell) [11-15]. In addition, volatile nature of elemental sulfur is inadequate for employing in industrial pro-

cess: changes in sulfur loading on electrode (during drying process) significantly affect electrode uniformity, resulting in considerable influence on overall electrochemical performance of the Li-S cell. In this respect, many attempts have been tried to overcome technical problems of the Li-S cell, however, control in volatility of elemental sulfur is still ambiguous even enhancement in volatility of active material is essentially required for their practical adoption.

The elemental sulfur is readily vaporized at ambient temperature with increasing in temperature [16,17]. However, their physicochemical properties are significantly changed at certain temperature: once they expose to extremely high temperature ($> 160^\circ\text{C}$), they readily lose their own volatile nature as a result of formation in long-chain polymeric sulfur [18-20]. It means that polymeric sulfur is one of attractive positive material to replace current used elemental sulfur owing to their non-volatility, resulting in expectation for better processibility [21-23]. With these concepts in mind, modified polymeric sulfur composite combining with ionic liquid (IL) unit is

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designed as an alternative positive material for the Li-S cell. Because the IL is non-volatile and non-flammable [24-27], it is expected that electrode uniformity and safety characteristics of the Li-S cell will be advanced compared to the cell consisting of only elemental sulfur.

2. Experimental

IL-embedded polymeric sulfur is synthesized by slight modification of synthetic method of polymeric sulfur reported in literature [28]. Mixture of 20 g of elemental sulfur (325 mesh, Alfa Aesar) and 2.0 g of 1-ethyl-3-vinylimidazolium bromide (EVIm-Br) was placed in round bottom at room temperature then it was stirred vigorously at 180°C for 2 h. After the reaction completed, they were cooled to room temperature until they are fully solidified. Then, residual EVIm-Br was removed by decantation with acetonitrile (CH₃CN) and further vacuum drying at 100°C for overnight was performed to remove remaining elemental sulfur which is unreacted starting material.

Morphology of IL-embedded polymeric sulfur was characterized by field-emission-scanning electron microscope (FE-SEM, Thermo keytex) and their structural information was analyzed by X-ray diffraction (XRD, Malvern Panalytical, Empyrean). The chemical structure of IL-embedded polymeric sulfur is characterized by Fourier transform infrared spec-

trometer (FT-IR, Bruker, VERTEX70) and Raman spectrometer (Bruker, Senterra, 532 nm), respectively. To evaluate volatility of IL-embedded polymeric sulfur, simple storage test was performed: 10 g of them were placed in round bottom at 150°C oven then weight changes were monitored for seven days.

For electrochemical test, IL-embedded polymeric sulfur was mixed with poly(ethylene oxide) (PEO, MW: 600,000, Aldrich) and conducting agent in MeCN (anhydrous, Aldrich) with a ratio of 50:25:25 (wt.%). Resulting slurry was coated on carbon coated aluminum current collector with a doctor blade then cathode was dried at 60°C for overnight and finally dried for 12 h under vacuum at room temperature. Loading level of cathodes were $3.95 \pm 0.15 \text{ mg cm}^{-2}$. The 2032 coin-type cells were fabricated with a 12-mm-diameter electrode as the cathode, lithium foil as the anode, a poly(ethylene) separator (PE, Asahi), and an electrolyte (TEGDME:DME:DOL=1:1:1 (vol.%) + 1.0 M LiTFSI + 0.3 M LiNO₃, PanaxEtec). Galvanostatic discharging–charging was performed in the potential range of 1.8–2.6 V (vs. Li/Li⁺) at 25°C using a Toscat-3100 battery-testing cyclers.

3. Results and Discussions

Synthetic scheme for IL-embedded polymeric sulfur is presented in Fig. 1a. Because disconnection of sulfur-sulfur connectivity is always accompanied

Fig. 1. (a) The proposed mechanism of IL-embedded polymeric sulfur. SEM images for surface morphologies of (b) elemental sulfur, and (c) IL-embedded polymeric sulfur.

Fig. 2. (a) XRD patterns, (b) the analysis in FT-IR, and (c) Raman of elemental sulfur (black), and IL-embedded polymeric sulfur (red).

with generation of radical intermediates at elevated temperature prior to formation in long-chain polymeric sulfur [29-32], vinyl-functionalized IL seemed to be appropriate embedding unit to facilitate radical coupling reaction through participation of vinyl group in radical scavenging reaction owing to their favorable reactivity against radical species [33,34]. After synthesis completion, morphology of IL-embedded polymeric sulfur is measured by FE-SEM as shown in Fig. 1b, and 1c. Because elemental sulfur is easily vaporized under vacuum condition, their surface morphology is continuously changed as increasing in exposure time during FE-SEM observation. On the contrary, surface morphology of IL-embedded polymeric sulfur is clearly observed. The XRD patterns of each material clearly indicate their different structural information (Fig. 2a) – γ -phase elemental sulfur seemed to be converted to amorphous phase as a result of formation in new structure. These results indicate that IL-embedded polymeric sulfur has different structure with change in physico-chemical properties compared to its corresponding analogue.

The analysis in FT-IR and Raman spectroscopy also indicate significant clues to confirm a chemical structure of IL-embedded polymeric sulfur (Fig. 2b, and 2c). According to FT-IR analysis, S-S stretching which is electrochemically active sites is clearly seen at 465 cm^{-1} . The S-S stretching is also observed in Raman spectroscopy – Raman signals observed in the IL-embedded polymeric sulfur exactly matched with S-S signals in the elemental sulfur. It means that the IL-embedded polymeric sulfur has S-S connectivity which is significant electrochemically active sites to promote conversion reaction of the Li-S cell. Additional transmittance signals are found at 660 cm^{-1}

Fig. 3. The results of storage test at 150°C : weights loss of sulfur. (black: elemental sulfur, and red: IL-embedded polymeric sulfur)

and 621 cm^{-1} in the IL-embedded polymeric sulfur – this is corresponded to new C-S connectivity arisen from the reaction of elemental sulfur and VEIm-Br [35]. It evidently indicates that elemental sulfur (S-S) is bound to IL units (C-S), resulting in successful synthesis of IL-embedded polymeric sulfur via simple synthesis reaction. The quantitative analysis by elemental analyzer indicates that the sulfur contents in the IL-embedded polymeric sulfur is 92% (not shown in this manuscript). From these results, it can be confirmed that the IL-embedded polymeric sulfur is consisting of 92% of elemental sulfur with combination of 8% of IL.

To evaluate volatility of IL-embedded polymeric sulfur, their storage tests was performed at 150°C (Fig. 3). The elemental sulfur showed decreasing in weight as increasing in storage time because of their high volatility. After seven days, it is observed that

Fig. 4. (a) Potential profiles of the cells at the initial cycle, and (b) cycling behaviors of the cells: elemental sulfur (black), and IL-embedded polymeric sulfur (red).

only 12.4% of elemental sulfur is remaining. On the contrary, none of significant changes in weight are observed in the IL-embedded polymeric sulfur – even after completion of storage tests, 99.9% of the IL-embedded polymeric sulfur existing. It evidently indicates that unfavorable volatile nature of elemental sulfur is completely compensated by changes in chemical structure, leads to modifying physicochemical properties as well as remaining core chemical connectivity of S-S bonding.

The cycle performance of IL-embedded polymeric sulfur is presented in Fig. 4. In a discharge-charge curves, the cell cycled with IL-embedded polymeric sulfur showed identical shape of voltage profile compared to the cell consisting of elemental sulfur. It means that S-S chemical connectivity in the IL-embedded polymeric sulfur is electrochemically available even initial specific capacity of the cell with IL-embedded polymeric sulfur is slightly less than its corresponding analogue. It might be assumed that less specific capacity is coming from different chemical structure of positive electrode material: because at the ends of elemental sulfur is chemically bound to carbon atom in IL units, there are limitation for full utilization of electrochemical conversion of elemental sulfur, resulting in slight decreasing in specific capacity. On the contrary, cycle performance of the cell consisting of IL-embedded polymeric sulfur is slightly better than the cell with only elemental sulfur: 70% of remaining specific capacity (compared to its initial cycle) was observed whereas the cell cycled with elemental sulfur showed 63% of retention at the end of 50th cycles. It means that the IL-embedded ele-

mental sulfur can be used as positive electrode material instead of currently used elemental sulfur for the Li-S cell based on excellent non-volatility and moderate cycle performance.

4. Conclusions

In this work, non-volatile polymeric sulfur composite is investigated as positive electrode material to replace currently used elemental sulfur for the Li-S cell. According to systematic spectroscopic analysis, it is found that polymeric sulfur is consisting of repeating units combining with elemental sulfur and IL through radical coupling reaction. The IL-embedded polymeric sulfur shows negligible volatility at high temperature and their cycle performance is applicable compared to the cell with elemental sulfur. From these results, it is believed that the IL-embedded polymeric sulfur can be used as one of alternative positive electrode based on their excellent non-volatility, resulting in better electrode uniformity for the Li-S cell.

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