Surface Modification of Sulfur Cathodes with PEDOT:PSS Conducting Polymer in Lithium-Sulfur Batteries

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Sulfur powder was coated with poly(3,4-ethylenedioxythiophene)–poly(styrenesulfonic acid) (PEDOT:PSS) using a wet mixing process in water. The modified sulfur material was investigated for use as a cathode in lithium-sulfur (Li-S) batteries. The surface modification with the conducting polymer was identified with Fourier transform infrared (FTIR) spectra, scanning electron microscopy (SEM), and high-resolution transmission electron microscopy (HR-TEM) analyses. Electrochemical evaluation revealed that surface modification with PEDOT:PSS leads to increases in initial capacity and improvements in the rate capability and cyclability of sulfur electrodes. Electrochemical impedance spectroscopy (EIS) measurements certified a decreased resistance of the PEDOT:PSS-coated sulfur electrode compared to a pure sulfur electrode, indicating that surface modification with a conducting polymer effectively enhanced the electrochemical performance of sulfur electrodes in Li-S batteries.

Our society is increasingly in need of high-energy-density batteries for next-generation electric vehicles and portable electronic devices. At present, cathode materials such as LiCoO₂, LiFePO₄, and LiMn₂O₄ in lithium-ion batteries (LIBs) barely meet the requirements of electric vehicles, hybrid electric vehicles, and energy storage systems, owing to their limited specific capacity (< 170 mAh g⁻¹). These lithium transition metal oxide cathodes are further limited by their heavy weight and less than single-electron reactions per mole. Therefore, new lighter-weight materials with multi-electron reactions must be explored in order to meet the high energy density and low costs needed for modern technology.

Among various candidates, sulfur seems promising as a cathode material, as it is lightweight, abundant throughout the world, and in possession of a higher theoretical capacity (1675 mAh g⁻¹) and energy density (2600 Wh kg⁻¹) than commercial LIB systems, due to its two-electron reaction through the formation of Li₂S₅. However, lithium-sulfur (Li-S) batteries have some disadvantages, including the dissolution of lithium polysulfides from sulfur-based cathodes, the shuttle mechanism at slow charge/discharge rates, and the insulating nature of sulfur (S × 10⁻³⁰ cm⁻¹ at 25°C). Among these drawbacks, the shuttle mechanism is known as one of the most major problems in Li-S cells. The formation of high-solubility lithium polysulfides, such as Li₂S₈, Li₂S₆, Li₂S₄, and Li₂S₂, occurs during the discharge process. These highly soluble polysulfides easily diffuse into the anode side of the cell due to the concentration gradient; in the anode side, the compounds reduce to form Li₂S and Li₂S₂. Subsequently, these insoluble compounds, deposited on the anode, react with polysulfides carried in the cell’s electrolyte, resulting in the formation of soluble medium-chain ions. These ions diffuse back to the sulfur cathode, and the process (known as the shuttle mechanism) repeats. Additionally, these precipitates (Li₂S₂, Li₂S) formed in the redox reaction tend to aggregate gradually on both the anode and cathode surfaces, reducing the amount of active material and consequently leading to a poor cycle life over repeated cycling.

In order to solve these problems, the Nazar group reported the use of a mesoporous carbon (CMK-3) as a reservoir for the sulfur cathode. A variety of studies have been performed with porous carbon, carbon nanotubes/nanowires, hollow carbon spheres, and graphene in order to prevent the dissolution of lithium polysulfides and enhance the electrical conductivity of the Li-S system. Other approaches employ conducting polymers such as polyacrylonitrile (PAN), polypyrrole (PPy), or poly(3,4-ethylenedioxythiophene) (PEDOT). Yi Cui et al. and Wang et al. studied the effect of a coating of conducting polymer on a sulfur/carbon and sulfur/graphene composites, respectively, using an additional heat-treatment process to obtain carbon/sulfur materials before coating with poly(3,4-ethylenedioxythiophene)–poly(styrenesulfonic acid) (PEDOT:PSS). Although the previous reports mentioned above addressed the improved electrochemical performances of sulfur electrodes, the incorporation of carbon or graphene materials lead to the decrease in volumetric energy density of sulfur electrodes. The PEDOT:PSS, however, is promising for its environmental friendliness and stability, as well as its good thermal stability and electrical conductivity. The compound retained its electrical conductivity during testing at 80°C for 1000 h. Also, PSS in PEDOT:PSS is generally known to enhance the solubility in aqueous media and form a homogeneous film or layer as compared to the PEDOT:PSS itself, suggesting the improved characteristics in surface-modification.

In this study, we performed direct surface modification of commercial sulfur powders with a PEDOT:PSS conducting polymer by a simple wet mixing method to investigate the effect of conducting polymer without carbon support on sulfur electrodes. The PEDOT:PSS-coated sulfur cathodes were evaluated on the basis of various electrochemical properties, such as rate capability, cyclability, and impedance, to confirm the modified material’s efficacy in Li-S battery applications.

Experimental

Commercial yellow sulfur powder was purchased from Sigma-Aldrich, and PEDOT:PSS (2 wt% solution in water) was prepared. PEDOT:PSS-coated sulfur was prepared by the wet mixing of sulfur and the required amount of PEDOT:PSS in a water-based solvent to obtain 1 wt% PEDOT:PSS-coated sulfur powders. After wet mixing for 30 min, ethanol was added; further mixing for 1 h removed water and ethanol. The resulting powder was dried overnight at 60°C. The X-ray diffraction (XRD, Rigaku Ultima IV) data were recorded using monochromatic Cu–Kα radiation at 40 kV and 100 mA, to study the structural phases in each sample. The diffraction patterns were recorded at a scan rate of 2°/min between 10° and 90°. The morphology of the surface of the pristine sulfur and of the PEDOT:PSS coating on the modified powder was characterized by scanning electron microscopy (SEM). Transmission electron microscopy (TEM, FEI Company-Tecnai G2) observations were performed to confirm the existence of PEDOT:PSS on the surface of the modified sulfur powder. To further analyze the sulfur content
of the compounds, Fourier transform infrared spectroscopy (FTIR, IS 10, Thermo) was performed.

The electrochemical performance was investigated using CR2032 coin-type cells assembled in a room held at constant temperature and humidity. The modified sulfur cathode materials were mixed from 60 wt% cathode powder (as prepared above), 20 wt% acetylene black, and 20 wt% polyvinylidene fluoride (PVDF) binder in an N-methyl-2-pyrrolidone solvent. After the viscous slurry was seamlessly cast on Al foil, the electrode was dried in a vacuum oven at 120 ◦C and pressed under a constant load. The coin cells were then assembled with the lithium-metal foil as the counter electrode. The electrolyte was 1.0 M bis(trifluoromethane)sulfonimide lithium salt (LiTFSI) and 0.3 M 1,3-dioxolane (DOL) and dimethoxymethane (DME).

To measure the electrochemical performance of the cells, including properties such as rate capability and cyclability, galvanostatic charge-discharge and AC impedance analysis of the cells was estimated and the outcome data was fitted using Z-View software. AC impedance analysis was performed, as shown in Fig.3c and 3d to certify the presence of the PEDOT:PSS coating layer on the modified sulfur powder. The inset in Fig. 3c exhibits the smooth and homogeneous surface of unmodified sulfur, whereas the inset in Fig. 3d indicates that a heterogeneous material is formed on the surface of the modified sulfur powder particles. Fig. 3e and 3f indicate EDS spectrum of the pristine and PEDOT:PSS coated sulfur at the selected spot shown in Fig. 3c and 3d. The small peaks assigned to Cu atom are observed due to the copper grid for supporting the sulfur powders. The EDS spectrum reveals that the coating materials on the surface of the sulfur powder particles are PEDOT:PSS, as indicated by the peaks at 1161 cm⁻¹, 1120 cm⁻¹, and 1057 cm⁻¹, which are attributed to the C–O–C bond stretching in the ethylenedioxy group in the PEDOT monomer, and the weak vibration at 1038 cm⁻¹ is assigned to C–O bond stretching. Fig. 2 reveals that surface-coating was successfully achieved without any degradation of the parent sulfur and PEDOT:PSS materials.

In order to confirm the morphology and physicochemical features of the surface-coated sulfur materials, SEM and HR-TEM were carried out for the pristine and 1 wt% PEDOT:PSS-coated sulfur powders. Fig. 3a and 3b demonstrate typical SEM images of the pristine and PEDOT:PSS-coated sulfur, respectively. PEDOT:PSS-coated sulfur powders exhibit a homogeneously rough and bumpy surface without severe agglomeration, whereas the pristine sulfur materials possess a relatively clear and smooth surface morphology. Careful observation of TEM images and energy dispersive spectroscopy (EDS) analyses were performed, as shown in Fig. 3c and 3d to certify the presence of the PEDOT:PSS coating layer on the modified sulfur powder. The inset in Fig. 3c exhibits the smooth and homogeneous surface of unmodified sulfur, whereas the inset in Fig. 3d indicates that a heterogeneous material is formed on the surface of the modified sulfur powder particles. Fig. 3e and 3f indicate EDS spectrum of the pristine and PEDOT:PSS coated sulfur at the selected spot shown in Fig. 3c and 3d. The small peaks assigned to Cu atom are observed due to the copper grid for supporting the sulfur powders. The EDS spectrum in Fig. 3e and 3f for the designated spots marked in Fig. 3c and 3d reveals that the coating materials on the surface of the sulfur powder include carbon contents, certifying that successful coating of sulfur powder with PEDOT:PSS was achieved.

Fig. 4 presents the typical charge/discharge curves of the pristine and PEDOT:PSS coated sulfur for the first and second cycles evaluated at 0.1 C. For the first cycle, the initial discharge and charge
The capacities of the pristine sulfur are 919 mAh g\(^{-1}\) and 881 mAh g\(^{-1}\), respectively. The discharge and charge capacities of the PEDOT:PSS-coated sulfur were found to be 1100 mAh g\(^{-1}\) and 1075 mAh g\(^{-1}\), respectively. Both the unmodified and modified electrodes show two characteristic plateaus during the discharge process in the first cycle, consisting of a short plateau at 2.2 V and a longer plateau at 2.0 V. Typically, the short plateau corresponds to the formation of soluble lithium polysulfides, and the long plateau is related to the shuttle mechanism that creates lithium polysulfides and precipitates (Li\(_2\)S\(_4\), Li\(_2\)S\(_6\), Li\(_2\)S\(_8\), Li\(_2\)S\(_2\), and Li\(_2\)S) from S\(_8\) throughout the redox reaction within the Li-S cell.\(^{15}\) Interestingly, the short plateau at 2.2 V in the charge/discharge cycle of pristine sulfur shows an unstable fluctuation in profile, whereas that of PEDOT:PSS-coated sulfur exhibits a flat profile, possibly due to the suppressed elution of polysulfides, as well as the stabilization of the sulfur by the PEDOT:PSS coating.\(^{32}\) For the long plateaus below 2.1 V, the pristine sulfur electrode experienced a gradual voltage drop, although the PEDOT:PSS-coated sulfur electrode maintained a relatively flat voltage during the discharge process of the first cycle. During the charge process, solid Li\(_2\)S and Li\(_2\)S\(_2\) oxidize via delithiation and then form subsequent soluble liquid materials such as Li\(_2\)S\(_3\), Li\(_2\)S\(_4\), Li\(_2\)S\(_6\), Li\(_2\)S\(_8\), and Li\(_2\)S\(_{10}\).\(^{6}\) Owing to the polarization of the phase transition from insoluble Li\(_2\)S\(_2\) and Li\(_2\)S to soluble lithium polysulfides, the plateau during the delithiation process is located at a higher potential compared to the plateau during the lithiation process. During the second charge/discharge cycle, both samples exhibit higher coulombic efficiency compared to the first cycle, due to the lack of elution of lithium polysulfides (which mostly occurs in the first cycle). The pristine sulfur electrode exhibits discharge and charge capacities of 785 and 778 mAh g\(^{-1}\), respectively, while capacities of 954 and 945 mAh g\(^{-1}\) were obtained for the PEDOT:PSS-coated sulfur electrode during the second cycle, implying that coating with a conducting polymer provides more utilization of the sulfur cathode as well as increased capacity. Although the PEDOT:PSS-coated sulfur electrode without any additional carbon or graphene support exhibit the less improvement in performances, as compared to the previous reports,\(^{32,33}\) which employs the additional carbon supports as well as the conducting polymer, the prominent improvement in electrochemical performances is still confirmed via surface-modification of sulfur electrodes with PEDOT:PSS conducting polymer.

The electrochemical performance of the pristine sulfur and PEDOT:PSS-coated sulfur was analyzed at a variety of charge rates from 0.1 to 2 C as shown in Fig. 5. After 2 C-rate test, the electrochemical performance at 0.1 C-rate is followed. Although both...
Fig. 6. The cycling performance of S and S/PEDOT:PSS composite electrodes at 0.2 C.

Electrodes experience a prominent drop in capacity at the second cycle and gradual capacity decrease during the first five cycles, stable electrochemical performance was obtained at given rates from 0.2 to 2 C. After 2 C-rate test, the electrochemical evaluation at 0.1 C-rate indicates the capacity decrease, as compared to the capacity values at 0.1 C-rate of initial cycles. The PEDOT:PSS-coated sulfur cathode shows a slight decrease in capacity, whereas the pristine sulfur electrode exhibits a significant decrease in capacity with respect to increases in charge rate. At the high current density of 2 C, the pristine and PEDOT:PSS-coated sulfur exhibit capacities of 94.5 and 564.3 mAh g\(^{-1}\), respectively, which corresponds to 10% and 50% retention as compared to the initial capacities evaluated at 0.1 C. These results suggest that the PEDOT:PSS coating considerably improves electron transport in the cell, possibly due to the combined network as well as the enhanced stability between the conducting agent and the sulfur.

Fig. 6 demonstrates the cycling performances of the pristine and PEDOT:PSS-coated sulfur electrodes, evaluated at the same charge and discharge rate of 0.2 C. Both electrodes show a large decay in capacity, especially during the second cycle because of the dissolution of lithium polysulfide compounds during the initial cycles (as addressed in Fig. 4), but the conducting polymer-coated electrode suppressed the capacity drop in the second cycle. The PEDOT:PSS-coated electrode displayed a capacity retention of 87.8%, whereas the pristine electrode retained 81.7% of its original capacity during the second cycle. After 50 cycles, the PEDOT:PSS-coated sulfur electrode displayed the capacity of 565.7 mAh g\(^{-1}\), although the pure sulfur electrode exhibited an inferior capacity around 292.1 mAh g\(^{-1}\), which corresponds to capacity retentions of 60.9% and 41.1%, respectively, as compared to the capacity in the first charge-discharge cycle.

Fig. 7 shows Nyquist plots of a Lithium-sulfur pouch cell in electrochemical impedance spectroscopy (EIS) measurements for the pristine and PEDOT:PSS-coated sulfur before and after one cycle. The solid symbols indicate the measured data, while the lines represent the plot obtained from fitting with software in EIS evaluation. The data was fitted with an equivalent circuit, as shown in the inset of Fig 7. The impedance spectra in Fig. 7a is composed of the one depressed semicircle in the medium-frequency region which corresponds to the charge transfer resistance of the interface between the sulfur electrode and electrolyte, and the inclined line (Warburg impedance) in the low frequency region corresponds to semi-infinite diffusion. The impedance spectra in Fig. 7b has the two depressed semicircle and inclined line (Warburg impedance). The depressed semicircle in the higher frequency is associated with the interfacial charge-transfer resistance, and the depressed semicircle in the lower frequency indicates the formation of lithium-poly-sulfide (Li\(_2\)S and Li\(_2\)S\(_2\)).39,40 All elements shown in a specific equivalent circuits in Fig. 7 represent that \(R_c\) is the resistance of the electrolyte, \(R_w\) is the charge transfer resistance, \(R_1\) is the deposit diffusion resistance of Li\(_2\)S (or Li\(_2\)S\(_2\)), CPE1 and CPE2 are constant phase elements, and \(Z_w\) is the Warburg diffusion impedance of the polysulfides within the cathode. The semicircle from the high- to medium-frequency region corresponds to the charge transfer resistance and formation of Li\(_2\)S\(_2\) and Li\(_2\)S, while the straight inclined line at low frequency relates to the diffusion process of lithium ions within the cathode materials.37–39 Before the cycle, it is apparent that the PEDOT:PSS-coated sulfur electrode exhibits a lower charge transfer resistance than the pristine sulfur cathode, possibly owing to the conducting polymer. Both electrodes exhibit the highly decreased impedance values after 1 cycle, as compared to those before cycle, because the sufficient penetration of the electrolyte into the electrodes is achieved by the active process during electrochemical reaction. After 1 cycle, both electrodes provide considerably reduced charge transfer resistance values, but the PEDOT:PSS-coated electrode still exhibits a lower resistance value compared to the pristine one. This result indicates that the PEDOT:PSS coating improves the conductivity of sulfur powder, and this effect, in turn, provides an enhancement in electrochemical performance with better reversible capacity in Li-S cells.

Conclusions

Sulfur cathodes were surface-modified with PEDOT:PSS by a simple wet coating technique to suppress the formation of lithium polysulfides and improve the electrochemical performance of lithium-sulfur batteries. The physical and chemical features of the surface-modified sulfur materials were confirmed by FTIR spectra, SEM, and HR-TEM images. PEDOT:PSS-coated sulfur electrodes exhibited an increase in initial capacity and an improvement in rate characteristics. After 50 cycles, a PEDOT:PSS-coated sulfur electrode maintained a capacity of 566 mAh g\(^{-1}\), while the pure sulfur electrode delivered a capacity of 292 mAh g\(^{-1}\). The EIS measurement revealed that the surface modification with the conducting polymer provided a lower resistance and better electrical conductivity to the sulfur electrode, which resulted in better electrochemical behaviors in Li-S battery applications.

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