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Development in Lithium/Sulfur Secondary Batteries

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Abstract: This paper reviews different modification methods to cathode, anode and electrolyte materials in view of their electrochemical properties for application in lithium/sulfur batteries. In the sulfur electrode, carbonaceous materials, conductive polymer materials, and metal oxide adsorbing materials are employed to enhance conductivity and reduce polysulfide dissolution. The effects of anodes and novel electrolytes, such as gel polymer, solid polymer and solid ceramic electrolytes, are reviewed.

Keywords: Lithium sulfur battery, cathode, modification, polysulfide dissolution.

1. INTRODUCTION

1.1. General Introduction of Lithium Sulfur Batteries

The lithium-ion rechargeable batteries have been widely used in the portable electronic devices such as laptops, cameras and cell phones [1-4]. The rapid growth of electric vehicles has been requiring the development of next generation batteries with high specific capacity and energy density. Lithium/Sulfur (Li/S) cell is one of the most promising candidates for a storage device due to:

(1) Low cost and abundant resources of sulfur;
(2) Non-poisonous and environment friendly;
(3) Wide temperature range of operation;
(4) Intrinsic protection mechanism from over charge, providing safety;
(5) Possibility of long cycling [5].

Furthermore, the Li/S battery yields a high theoretical specific capacity of 1675 $mAh \cdot g^{-1}$ and theoretical specific energy of 2500 Wh/kg (or 2800 Wh/L) on a weight or volume basis respectively [6], based on the Li/S redox couple, $S + 2Li^+ + 2e^- \leftrightarrow Li_2S$ on the assumption of the complete reaction of lithium with sulfur to Li_2S. It differs from conventional lithium batteries For example, the specific capacities of $LiMn_2O_4$, $LiCoO_2$ and $LiNiO_2$ are 126, 149 and 180 $mAh \cdot g^{-1}$, respectively [7], whose values are limited by the extent of lithium intercalation into transition metal oxides [8] - reversible uptake of Li ions and electrons in a solid with minimal change to the structure. Typically, a lithium transition-metal oxide or phosphate is used as a positive electrode that re-intercalates Li^+ at a high potential with respect to the carbon negative electrode [9].

The high capacity and recharge ability of sulfur can be achieved from the electrochemical cleavage and reformation of a sulfur-sulfur bond in cathode [9].

1.2. Problems and Shortcoming about Lithium Sulfur Batteries

The discharge process of the Li/S battery proceeds in two steps [10]: first, the transformation of sulfur to lithium polysulfide (Li_2S_n, $2<n<8$) and followed by the transformation of lithium polysulfide to lithium sulphide (Li_2S) [11-13]. The lithium polysulfide, which is formed during the first discharge step of Li/S battery, is dissolved into the electrolyte, which causes the irreversible loss of the sulfur active material [13-18].

According to Nimon and co-workers [19], when polysulfide was dissolved into an electrolyte, it was also diffused into the lithium anode and reacted with the lithium to reduce the cycling efficiency. Thus, the cyclic behaviour of the Li/S battery becomes very poor mainly due to the polysulfide dissolution into the electrolyte.

In the present paper, we introduce different methods to modify the cathode, electrolyte and anode materials to overcome the problem of polysulfide dissolution into electrolyte.

2. EFFECT OF CATHODE AND MODIFICATION

2.1. New Preparation Methods on Cathode and Modification on Polysulfide Dissolution

The disappointing result from electrochemical reaction caused by the polysulfide could be improved by trapping the polysulfide inside of the cathode with the help of carbonaceous materials, the components in the sulfur cathode.

Carbon particles in the carbon-sulfur composites have a strong adsorption of the polysulfide to additive materials, which have a large surface area and a high porous structure.

In Wang *et al.*'s research [20], the cathode material composites were prepared with a structure of elemental sulfur embedded and trapped in nano-pores and micro-pores of active carbon to overcome the loss of the active mass in the cathode, which showed good cycle ability in rechargeable lithium cell based on gel electrolyte. The

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reversible capacity of the composite was about 440 mAh·g^{-1} and the utilization of sulfur during cycling approached 90%.

Mesoporous carbon was reported [21] that it is used in industry as an adsorbing material because of their high surface area. Furthermore, mesoporous carbon has good electrical conductivity.

According to Liang *et al.* [22], a soft-template synthesis method is applied to produce sulfur/caron composite cathode for Li/S rechargeable batteries. This method is first introduced by Liang [23-26] to synthesize mesoporous carbon. After activating mesoporous carbon using potassium hydroxide (KOH), the carbon obtains a hierarchical structure with a bimodal pore size (micropore and mesopore). The bimodal pores play important roles during electrochemical reaction: micropores trap sulfur particles to give high electrical conductivity and to prevent the particles from escaping from cathode; and macropores allow a large number of lithium ions to transport between anode and cathode, which leads to high ionic conductivity. As a result, initial discharge capacity reached 1584 mAh·g^{-1}; this value is greater than the literature value of 1155 mAh·g^{-1}.

Wang *et al.* [27] reported that sulfur-mesoporous carbon composite (S/C) was prepared by heating a mixture of elemental sulfur and synthesized mesoporous carbon. A novel electrolyte was prepared by dissolving lithium bistrifluoromethane-sulfonimidate (LiTFSI) in the synthesized ionic liquid consisting of 1-ethyl-3-methylimidazo-lium bis(trifluoromethylsulfonyl)imide (EMITFSI) at a concentration of 1 mol/L. The S/C composite was tested in both the ionic liquid and the organic solvent electrolytes. And the S/C composites using ionic liquid electrolyte showed better results in the capacity and cyclic stability than that of the conventional organic solvent electrolyte of 1 mol/L LiTFSI-PEGDME.

CMK-3, the most well-known member of the mesoporous carbon family, was studied as CMK-3/sulfur composite in the Li/S battery [9]. It was found that the sulfur was homogeneously distributed in the framework of the mesoporous carbon, which allows ingress of electrolyte within the structure. The empty volume within the pores is also available to accommodate the uptake of Li ions, due to the lower density of Li_2S compared to the sulfur. The insulating sulfur only occupied the empty channels in the mesoporous carbon and does not block the electrical current transporting paths [9].

To reduce the dissolution of the polysulfide into the electrolyte, the polymer, polyethylene glycol (PEG) chains of varying molecular weight, was coated on the external surface of the composite (CMK-3/S), further helped retard diffusion of polysulfide out of the cathode structure. It was found that the cycling stability was improved. The initial discharge capacity was increased to 1320 mAh·g^{-1}, but no fading was observed in the second 10 cycles and the capacity was stabilized at 1100 mAh·g^{-1} on cycling.

Wang *et al.* studied Polyacrylonitrile(PAN) [28] as the reaction precursor with elemental sulfur heating at 280-300°C to obtain a novel conductive sulfur containing material. The composite, with sulfur embedded in this conductive polymer matrix, which was expected to hinder the sulfur and polysulfide from dissolving into the electrolyte, improved the electrochemical kinetics of the sulfur cathode. The lithium battery with PAN/sulfur composites as the cathode active material has high capacity density and good recharge ability. The specific capacity of the composite was up to 850 mAh·g^{-1} at the first cycle. The specific capacity remained above 600 mAh·g^{-1} after 50 cycles, which demonstrated high sulfur utilization and relatively stable cycle behaviour.

PAN, however, shows poor electrical conductivity in the cathode, which limits the high power rate of sulfur composite materials. To solve this problem, further study [29] was done by using the carbon nanotubes (MWCNTs) to set up a highly conductive network in the composite, PAN/sulfur cathode. It was found that MWCNTs not only kept the cathode integrity and accommodated the volume change during charge/discharge processes, but also provided stable channels for electrical and ionic conduction at high power rates. By applying MWCNTs, sulfur utilization and cycling stability of the cathode had been significantly improved. The capacity remained 96.5% of sulfur utilization after 100 cycles. Moreover, the PAN/sulfur composite exhibited excellent high power rate capability up to 7C (386.7 mAh·g^{-1}).

Zhang *et al.* [30] introduced a novel polymer, polyaniline polysulfide (SPAn), which can hold more sulfur in the polymer than the others. The polymer has polyanilline as the backbone chain and 2 four-member rings with S-S bonds as the side chains of aniline. From the structure, it is predicted that the polymer can store high energy when it is used in Li/S battery. The result of Li/S battery with SPAn showed high initial discharge capacity of 980 mAh·g^{-1} and a stable reversible capacity of 403 mAh·g^{-1} after 20 cycles.

In the other research group, Ma *et al.* [31] developed polyaniline/sulfur composite cathode, which was synthesized by situ polymerization. The aniline was polymerized to form a layer of polyaniline on the sulfur surface. The results showed that the composites reached 1134.0 mAh·g^{-1} at the first cycle, which is relatively low compared to the results from the other polymers containing sulfur. The capacity remained 526.9 mAh·g^{-1} after 30 cycles.

In Song *et al.*'s research [10], nano-sized $Mg_{0.6}Ni_{0.4}O$ synthesized by the sol-gel method was used as an additive, which has the polysulfide adsorbing effect. It was explained that the crystal structure of $Mg_{0.6}Ni_{0.4}O$ is the same as MgO, which has the effect of retaining liquid electrolyte in a Li/iron sulphide secondary battery like an electrolyte sponge [32].

Furthermore, $Mg_{0.6}Ni_{0.4}O$ has a catalytic effect of dissociating the chemical bond, which was expected to apply to the Li/S battery considering the dissociation energy of the S-S single bond [32]. As the result, it was found that the capacity and cyclic ability of the Li/S battery at room temperature were improved, when $Mg_{0.6}Ni_{0.4}O$ was used as an additive in sulfur cathode.

Zhang *et al.* [1] reported a novel cathode material created with V_2O_5 and sulfur for Li/S rechargeable batteries to improve electrochemical performance. The cathode material was prepared *via* the sol-gel method. The initial discharge capacity was 473 mAh·g^{-1}. This value is less than that of the sulfur cathode battery, whose initial discharge capacity was

535 mAh·g^{-1}, due to the low specific capacity of V_2O_5. However, the result showed that capacity and the rate capacity were increased and the utilization of active material was improved.

This research group [33] further studied the effect of $Mg_{0.8}Cu_{0.2}O$ addition into the c-V_2O_5/S composite cathode was investigated on the electrochemical performance of Li/S rechargeable batteries. As the result, the cyclic ability and discharge capacity were improved after the addition of $Mg_{0.8}Cu_{0.2}O$. The initial discharge capacities of the cathode with and without additive were 545 and 400 mAh·g^{-1} respectively, which showed that not only did $Mg_{0.8}Cu_{0.2}O$ has the adsorbing effect on polysulfide, but also a catalytic effect on promoting redox reaction of the Li/S batteries.

2.2. Modification on Conductivity of Cathode

To improve the electrochemical results, it is important to retain the polysulfide in the cathode to prevent it from being involved in the redox reaction, which occurs at the surface of the carbon. To do so, the morphology of the carbon matrix must be controlled that it can easily accept the polysulfide, such as uniformity of the carbon matrix and the structural stability [34].

Choi *et al.* [35] presented that carbon nano-fiber (CNF) with an average diameter of 150 nm was added into the cathode to improve cyclic ability. Cathode, with CNF using PEO and PVdF as the binders, showed better cycle property than the one without CNF. As the result, cyclic ability was improved when CNF was added to the cathode because CNF provides a good electrical connection and a structural stability. The cycling life (up to 60th cycle) of SPEAC was more stable than that of CNF because of the suppression of agglomeration of sulfur or lithium sulphide by the addition of CNF.

In Han's research [34], multi-walled carbon nano-tubes (MWCNT), prepared by thermal chemical vapour deposition, were used as an inactive additive material for elemental sulfur cathodes for Li/S rechargeable batteries. MWCNT, as a conductive agent in the cathode, was used to increase the retention of soluble polysulfide on cathode and to increase the stability of the carbon matrix, which could provide the increase of both sulfur utilization and cyclic ability of the sulfur batteries. It was explained that the assembly of the relatively long and thin carbon nano-tubes can generate three dimensional network structures with regular pores, which helped retention of the polysulfide in the cathodes. The sulfur/MWCNTs electrode retained high specific capacity at high discharge rate due to an electronically conducting network developed from the MWNTs which are more effective than that of acetylene black.

For the past decades, researchers have been developing novel conductive polymer-sulfur cathode materials has a potential to be one of the active components for the Li/S rechargeable batteries. The addition of the polymer to the sulfur cathode increases the conductivity and stability; therefore, good cyclic ability was obtained.

Conductive polypyrrole (PPy) coating on the surface of the sulfur powder improved the conductivity of S-PPy electrode. Furthermore, PPy could also act as a binder, increasing the contact between particles.

Sulfur-polypyrrole(S-PPy) was synthesized *via* chemical polymerization using sodium ptoluenesulphonate as the dopant, 4-styrenesulphonic sodium salt as the surfactant, and $FeCl_3$ (0.1 M) as the oxidant [36]. PPy nanoparticles coated on the surface of sulfur powder may have trapped the highly polar polysulfide species. As a result, the composite showed good electrochemical properties, improvement of cyclic ability of the cell and increment of the initial discharge capacity from 1100 to 1280 mAh·g^{-1} after coating with the polypyrrole.

Wire-, ribbon-, and sphere-like nanostructures of polypyrrole have been synthesized by solution chemistry methods in the presence of various surfactants (anionic, cationic, or nonionic surfactant) with various oxidizing agents [ammonium persulfate (APS) or ferric chloride ($FeCl_3$), respectively [37].

By using cationic surfactants as soft templates, a novel nanowire of sulfur-polypyrrole positive electrode is prepared *via* simple heating method [38]. The result of the electrochemical performance of Li/S battery showed the initial discharge capacity of 1222 mAh·g^{-1} for the sulfur electrode with PPy as matrix and the remaining capacity of 570 mAh·g^{-1} after 20th cycles. With these results, it was concluded that good electrochemical properties were found when PPy nano-wire was used in rechargeable lithium batteries.

A tubular polypyrrole (T-PPy) fibre as another type of conductive matrixes was introduced by Liang *et al.* [39]. During the co-heating process, which was applied in this paper, the capillary force allowed the sulfur to penetrate into the T-PPy fibre matrix. They have found that the electrochemical behaviour of the composite mostly depended on the location and the content of sulfur. The result showed that the reversible capacity of 650 mAh·g^{-1} was maintained for over 80 cycles for the S/T-PPy composite with 30 wt% sulfur and initial discharge capacity was 1151.7 mAh·g^{-1}. Therefore, the enhanced conductivity, the favourable distribution of the nano-sized sulfur in the T-PPy and the stable retention of polysulphides lead to the improvement of the cycling stability of the sulfur based electrode.

2.3. Effect of Binder

The uniform combination of active sulfur and conductive carbon is very important for a high performance sulfur cathode. Among the components in the sulfur cathode, the binder plays an important role in improving cell performance, especially in regards to the cycle life. A high performance binder should have high adhesion ability for the electrode materials to the current collector, as well as the ability to form a good electric network between the active material and conductive carbon, to facilitate the electron transport as well as the diffusion of the lithium ion [40].

Based all the studies of lithium-sulfur battery system, PEO and PVDF are the most commonly used binder, but both of them still have revealed some problems [40]. The PEO-based sulfur cathode usually presents poor adhesion properties [41, 42] and low ionic conductivity at low temperature [43]. The PVDF binder is readily dissolved in the organic electrolytes, especially at elevated temperatures, resulting in an increase in the interfacial resistance [44]. Besides that, the PVDF binder must be dispersed in some high boiling solvent such as N-methyl-2-pyrrolidone (NMP), which tends to be difficult to vaporize, so the drying process of the cathode might lead to the loss of active sulfur at temperatures higher than 80 °C under vacuum [40].

Sun *et al.* developed a water-soluble gelatin macromolecule was adopted as the binder in the fabrication of the sulfur cathode in lithium-sulfur batteries [40]. This gelatin was formed by the covalent linkage of several amino acids into a stable peptide, where the sequence of the peptide chain was determined by the protocol used in its production. The structure and electrochemical performance of the two types of sulfur cathodes, with gelatin and poly (ethylene oxide) (PEO) as binders, respectively, were compared in 1M $LiClO_4$ DME/DOL (V/V=1/1) electrolyte. The results showed that the gelatin binder had multifunctional effects on the sulfur cathode: it not only functioned as a highly adhesive agent and an effective dispersion agent for the cathode materials, but also an electrochemically stable binder. The gelatin binder-sulfur cathode achieved a high initial capacity of 1132 $mAh{\cdot}g^{-1}$, and remained at a reversible capacity of 408 $mAh{\cdot}g^{-1}$ after 50 cycles, all of which were better than with the PEO binder-sulfur cathode under the same conditions.

Wu *et al.* studied Ball milling in combination with heat treatment was used to prepare sulfur-based composite cathode materials incorporating multi-walled carbon nanotubes (MCNTs). The effect of MCNT content and binder type on the capacity, cyclability and self-discharge behavior of a sulfur-based cathode were systematically investigated [45]. Results showed that the appropriate amount of MCNTs was 5%-8% (w, mass fraction) and the use of β-cyclodextrin as a water-soluble binder resulted in the best electrochemical performance. When the Li-S battery was half charged at room temperature, there was almost no self-discharge during storage for 30 days. The charging capacity was 687.7 $mAh{\cdot}g^{-1}$ during the 1st cycle and 623.8 $mAh{\cdot}g^{-1}$ during the 100th cycle for the cathode at a current rate of 0.1C. Therefore, 90.7% of the capacity was retained.

3. EFFECT OF ANODE AND MODIFICATION

The use of elemental lithium as the anode in lithium-sulfur batteries remains a major problem due to safety concerns arising from the formation of lithium dendrites during cycling, which can penetrate the separator and lead to thermal runaway [46]. One way to avoid this safety issue in the lithium/sulfur system is to use a high-capacity anode material other than elemental lithium while replacing sulfur in the cathode with its lithiated counterpart, lithium sulfide (Li_2S) [46].

The electrochemical behavior of Li_2S-C cathode in combination with a tin-carbon composite and a gel-type polymer electrolyte was investigated [47]. This new Sn-C/Li_2S polymer battery operates with a capacity of 600 $mAh{\cdot}g^{-1}$ and the energy density of 1200 $Whkg^{-1}$. XRD analysis performed in situ in a lithium cell shows that lithium sulphide can be converted into sulfur during charge and re-converted back into sulfide during the following discharge process. Li_2S-C composite can be 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 [47].

A novel nanostructured rechargeable battery consisting of a Li_2S/CMK-3 mesoporous carbon cathode and a silicon nanowire anode was prepared to replace sulfur in the cathode [46]. An initial discharge specific energy of 630 $Whkg^{-1}$ based on the mass of the active electrode materials was realized Silicon nanowire anodes are demonstrated to be ideal for this battery system due to their high capacity, low reaction potential, and moderate cycle life. This new battery system avoids the intrinsic safety issues associated with the use of lithium metal in previous lithium/sulfur batteries [46].

4. EFFECT OF ELECTROLYTE

4.1. New Electrolyte

The sulfur, which has a crown-like ring structure, forms various lithium polysulfides as a result of the reduction, which are generally soluble in the electrolyte phase [48-50]. For the successful operation of a lithium-sulfur battery, the electrolyte should satisfy many requirements, i.e. high ionic conductivity, good polysulfide solubility, low viscosity, electrochemical stability, chemical stability toward lithium, and safety [48]. Different types of new electrolytes such as polymer electrolyte and ceramic electrolyte have been evaluated for their suitability in Li/S cells.

Polymer electrolytes can be introduced to restrain the dissolution of polysulfides into the electrolyte. Polymer electrolytes explored for this purpose are commonly complexes of a lithium salt (LiX) with a high-molecular-weight polymer such as polyethylene oxide (PEO). But PEO tends to crystallize below 60°C, whereas fast ion transport is a characteristic of the amorphous phase. So the conductivity of PEO-LiX electrolytes reaches practically useful values (of about 10^{-4} S cm^{-1}) only at temperatures of 60-80°C [51]. Some researchers have been tried to solve the problems with the use of nano-scale ceramic filler such as Al_2O_3, SiO_2, and TiO_2 in PEO based polymer electrolyte [51-53]. The additive improved the conductivity of PEO base electrolytes as well as their interfacial resistance between the electrolyte and the lithium electrode.

Croce *et al.* [51] prepared the conductivities of around 10^{-4} S cm^{-1} at 50°C and 10^{-5} S cm^{-1} at 30°C in a PEO-$LiClO_4$ mixture containing powders of TiO_2 and Al_2O_3 with particle sizes of 5.8-13 nm. Another approach is to decrease the crystallinity of the polymer in order to improve the polymer chain mobility [54].

Smith *et al.* have reported that high energy mechanical milling conducted at ambient and cryogenic temperature can decrease the molecular weight and glass transition temperature in poly(methylmethacrylate) (PMMA) or poly (ethylene propylene) (PEP) [55].

Jeong *et al.* [56] found that ball milled PEO-base polymer electrolytes with ceramic filler displayed higher ionic conductivity and interfacial stability than that without ceramic fillers. PEO-$LiBF_4$ polymer electrolyte with nano-

Al_2O_3 prepared by ball milling for was further investigated in the discharge process of lithium/sulfur battery. The cycle performance and initial discharge capacity of Li/ $(PEO)_6 LiBF_4$ /S cell was remarkably improved by the addition of Al_2O_3 [54]. The initial discharge capacity of lithium sulfur cell using BCPE was 1670 mAh·g^{-1}, which was approximately equal to the theoretical capacity. These improvements of cell performance were attributed to the stability of 2.1V plateau, thus Al_2O_3 filler stabilized formation of Li_2S and improved utilization of sulfur.

Wang *et al.* [57] prepared PVDF-HFP gel electrolyte used in rechargeable lithium battery based on the sulfur/active carbon cathode, which showed good cyclability. And elemental sulfur was embedded and trapped in nano-and micro-pores of active carbon. The reversible capacity of the composite was about 440 mAh·g^{-1} and the utilization of sulfur during cycling approaches 90%.

PVDF-TG-LiX polymer electrolytes comprised of polyvinylidene fluoride-hexafluoropropylene (PVDF-HFP) copolymer, tetra (ethylene glycol) dimethyl ether as 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 [58]. The PVDF-TG-$LiPF_6$ polymer electrolytes prepared by ball-milling, for, 12h, in particular, resulted in a maximum value in the ionic conductivity, which was 4.99×10^{-4} S cm^{-1} at room temperature. The melting temperature of crystalline PVDF decreased due to the decrease of crystallinity by scission of the polymer chain during ball milling. This gel polymer electrolyte was employed into Li/S battery based on the S cathode and Li anode. The initial discharge capacity can reach to 765 mAh·g^{-1} at the rate of 0.14 mA cm^{-2}.

All solid-state batteries using sulfide solid electrolyte (SE) are of great advantage than the batteries of liquid electrolytes, because solid-solid contact causes no dissolution problem and the same constituent components make the SE/electrode interface easier [59]. Thio-LISICON ($Li_{3.25}Ge_{0.25}P_{0.75}S_4$) synthesized by solid-state reaction was used as a solid electrolyte [60]. Electrode framework was investigated using various type of carbons; meso-porous carbons with two and three-dimensional structures, CMK-3, and carbon replica [61]. The all solid-state lithium battery with the composite electrode of sulfur and CMK-3 showed a reversible capacity of 1000 mAh·g^{-1} with significant degradation of charge-discharge capacities after several cycles. The degradation of the charge-discharge characteristics was due the sulfur existed outside of the meso-pore of the carbon framework structure [59].

4.2. Additive on Electrolyte

For the liquid electrolyte, most often, a single organic solvent does not meet all the requirements of an electrolyte in a Li/S cell and optimization based on a mixture of solvents.

The effect of incorporating varying amounts of toluene additive in 1M $LiCF_3SO_3$ in tetra (ethylene glycol) dimethyl ether (TEGDME) liquid electrolyte on the electrochemical performance of Li/S cell at room temperature was studied [62]. It was found that the addition of toluene in low amounts was an effective means to enhance the electrochemical performance of 1M $LiCF_3SO_3$ in TEGDME electrolyte in Li/S cells at room temperature. Electrolytes with toluene have higher redox currents resulting from increased ion mobility and ionic conductivity. Toluene addition enhanced initial discharge capacity; a maximum of 750 mAh·g^{-1} (45% of the theoretical specific capacity of sulfur) was obtained with 5% of toluene, which was 1.8 times that of the cell without toluene. The electrolyte with 5% toluene exhibited a stable cycle performance with the highest discharge capacity and charge-discharge efficiency. AC impedance analyses of Li/S cells with the electrolytes showed that toluene addition resulted in a lower initial interfacial resistance and a fast stabilization of electrode/electrolyte interfaces in the cell [62].

Tetra ethylene glycol dimethylether (TEGDME) electrolyte was used to improve the performance of Li/S batteries [63]. A Li-S cell with stainless-steel current-collectors exhibited severe self-discharge behaviour. After 30 days of storage, the open-circuit voltage (OCV) dropped from 2.5 to 2.2V and the discharge capacity decreased to 72% of the original capacity. With the analysis of the self-discharged sulfur electrodes by SEM, XRD, and DSC, it was concluded that polysulfides are formed from the lithium and sulfur ions, and are which are linked to the corrosion of the stainless-steel current-collector. Stainless steel is not an appropriate material for use as the current-collector for the sulfur electrode in the Li-S cell. The self-discharge rate of the Li-S cell can be decreased by using a gold-coated current-collector, which can provide corrosion resistance.

These studies from Aurbach *et al.* showed the impact of the presence of $LiNO_3$ in solution on the surface chemistry of Li electrodes: Its direct reduction to form surface Li_xNO_y species and the oxidation of sulfur species to form various Li_xSO_y surface moieties [64]. This impact explains the positive effect of $LiNO_3$ in preventing the shuttle mechanism that avoids full charging of sulfur electrodes in Li-S cells: The enhancement of Li passivation, which diminishes the possible reduction in polysulfide species in solutions by the reactive lithium electrodes.

CONCLUSION

Li/S battery provides us much hope, but also many challenges. In general, the main problem in Li/S battery is having poor cyclic ability, which is mainly caused by polysulfides dissolving into the electrolyte. To solve this problem, together with advances of the anode and the electrolyte, the materials, such as active carbon, can be chosen with sulfur as a composite cathode in the Li/S battery to contain the most polysulfides. Besides that, certain materials with high conductivity that cover the surface of the sulfur particles encourage a long cycle life. Promisng results have been achieved by modifying the cathode in the Li/S battery. Evenly distributing sulfur in the composite cathode, enhancing the conductivity of the composite cathode, and stabilizing the retention of polysulfides, along with the use of a non-metal lithium metal will lead to the employment of sulfur based cathode batteries in the commercial world

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