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Effectiveness of dioxolane/dimethoxyethane mixed solvent for the fabrication of lithium-sulfur semiflow batteries

Gabriele Tarquini[a], Mariasole Di Carli[b], Livia Della Seta[b], Margherita Moreno[b], Pier Paolo Prosini[b,*]

[a] *Università degli Studi di Roma "La Sapienza", Dipartimento di Scienze di Base e Applicate per l'Ingegneria, via Antonio Scarpa14/16, 00161, Rome, Italy*
[b] *ENEA, Italian National Agency for New Technologies, Energy and Sustainable Economic Development, Casaccia Research Centre, Via Anguillarese 301, 00123 Santa Maria di Galeria, Rome, Italy*

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ABSTRACT

In order to implement a Li/S semiflow battery, a mixture of lithium polysulfide (Li_2S_8) dissolved in dioxolane/dimethoxyethane was studied as a catholyte in Li/carbon battery cells. The Li_2S_8 polysulfide was prepared by stirring Li_2S and elemental sulfur in a 1:1 mixture of dioxolane/dimethoxyethane heated at 80 °C. The mixture of polysulfides was tested in a lithium metal cell. The working electrode was a mixture of Ketjenblack carbon (used as conductive filler) and PTFE. It was found the Li_2S_8 polysulfide immediately converts into Li_2S_4 and sulfur when added to the electrolyte solution. The electrochemical tests showed that the cell retains excellent Coulombic efficiency and good cycling stability. The potential window used during the electrochemical tests plays an important role on the cell performance in terms of stability and capacity. An improvement of more than 500 mAh g^{-1} in the specific capacity retention was observed when the potential window was reduced from 3.0–1.5 V to 2.8–1.7 V. *Post mortem* SEM and EDS analyses confirmed that not only the surface but the whole of the working electrode participates to the electrochemical reaction.

1. Introduction

The lithium-sulfur (Li-S) couple represents one of the most interesting electrochemical storage system due to the high theoretical energy density (2567 Wh kg^{-1}), high theoretical cathode capacity (1675 mAh g^{-1}) and low cost of the sulfur. The reaction between sulfur and lithium, starting with Rauh's 1979 work [1], has been extensively studied in conventional rechargeable batteries [2–8]. Although Li/S batteries have been the subject of numerous improvements, they are still far from reaching the market place due to several drawbacks. Sulfur can take the form of over 30 allotropes. The most common allotrope of sulfur is called octa-sulfur (S_8). During discharge of a Li/S battery the reduction of S_8 proceeds over several soluble polysulfide intermediates (Li_2S_x) before the final precipitation of solid phases, when is reduced in Li_2S and partially in Li_2S_2 [9–10]. Long polysulfide chains can diffuse toward the lithium metal electrode where they are reduced to form shorter polysulfides. Subsequently, these shorter polysulfides can diffuse back to the positive electrode where they are oxidized. As a result, a cyclic process (called "shuttle" mechanism) develops inducing a chemical shortcut of the cell, which causes low Coulombic efficiency and severe capacity fade [11]. Zhang and Read [12] showed that $LiNO_3$, used as a co-salt, is excellent in promoting the formation of a denser and protective passivation film on the Li surface. The film not only increases Li cycling efficiency, but also protects soluble polysulfide anions from chemical and electrochemical reductions on the Li anode. Demir-Cakan et al. [13] in 2013 proposed to use a liquid cathode obtained either by dissolving polysulfides within the electrolyte or by placing sulfur powder in contact with the Li negative electrode. Such a strategy eliminates the detrimental Li_2S formation inside a porous carbon matrix and moreover, leads to the formation of a protective SEI layer at the Li electrode. Nevertheless, both the proposed battery systems suffer from rapid capacity fading. Manthiram et al. [14] proposed for the first time a polysulfide semiflow battery, a configuration with the catholyte circulating at the cathode side like redox flow batteries. The half-flow mode Li/S batteries could be a promising candidate for large-scale storage for renewable energies. Since then, several patents have been proposed for the Li-S pair in flow battery, using both solid sulfur and Li_2S_x polysulfides solution [15–17]. A large amount of polysulfides dissolved in an external tank to the carbon current collector can result in clogging the pores in the carbon electrodes due to the precipitation of high order polysulfides or sulfides upon cycling. This can be overcome by controlling the charge/discharge cut-off potentials to allow only

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* Corresponding author.
E-mail address: pierpaolo.prosini@enea.it (P.P. Prosini).

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soluble lithium polysulfides to be present in the catholyte, which would reduce the energy density of the overall systems but could prolong the cycle life. A different approach was followed by Yang et al. [18] that developed a lithium/polysulfide semi-liquid battery with lithium polysulfide (Li_2S_8) using an ether solvent as catholyte and metallic lithium as anode. The catholyte was designed to cycle only in the potential range between sulfur and Li_2S_4. This novel strategy resulted in excellent cycle life and compatibility with flow battery design. They also used $LiNO_3$ additive to passivate the lithium surface and eliminate internal shuttle effect. In such a way they were able to achieve over 2000 cycles with a constant capacity of 200 mAh g^{-1}. Chen et al. [19] reported a flow cathode that exploits highly concentrated sulfur-impregnated carbon composite, to achieve a catholyte volumetric capacity five times higher than the all-vanadium flow batteries and 3–6 times higher than the demonstrated lithium-polysulfide approaches. The battery was able to discharge a specific capacity as high as 800 mAh g^{-1} when cycled at 2.5 mAh cm^{-2}. Short-chain polysulfides, *e.g.*, Li_2S_2, are generally insoluble in aprotic solvents and their precipitation of insoluble onto the carbon current collector may shorten the cell lifespan by blocking the flow channels. Starting from this consideration Pan et al. [20] tried to increase Li_2S_2/Li_2S solubility in a DMSO based electrolyte. They reported that DMSO based electrolyte enables both high solubility of lithium polysulfide species, especially for the short-chain species, and good cycling performance for the battery. A stable capacity as high as 1200 mAh g^{-1} was obtained for over 60 cycles. In this paper we demonstrate that the cell loaded with the dioxolane/dimethoxyethane (DOL-DME) based electrolyte containing the polysulfides cycled for more than 50 cycles with high initial specific capacity (1551 mAh g^{-1}), high Coulombic efficiency (higher than 99%) and low capacity fading (0.3% per cycle).

2. Experimental section

2.1. Preparation of the working electrode

An electrode tape was prepared by mixing 90 wt% ketjen black (KJB) carbon powder and 10 wt% poly tetra fluoro ethylene (PTFE, Teflon®). In order to obtain a plastic material, the carbon and the PTFE were mixed in an agate mortar for 20 min. The resulting mixture was calendered to form a tape with a thickness ranging between 40 and 80 µm. Circular electrodes with a diameter of 10 mm were punched from the tape and used for the electrochemical characterization.

2.2. Synthesis of Li_2S_8

Lithium sulfide (Li_2S, 99.9%, Acros Organics) and elemental sulfur (Furuuchi Chem.; 99.9%) were weighted in a 1:7 mole ratio and suspended in a 1:1 mixture of 1,3-dioxolane (DOL, 99.5%, Sigma Aldrich) and 1,2-dimethoxy ethane (DME, 99%, Sigma Aldrich). The DOL/DME mixture was heated at 80 °C under magnetic stirring for 48 h to obtain a homogeneous dark red solution. The concentration of Li_2S_8 was 0.5 M.

A 1.0 M solution of lithium bistrifluoromethanesulfonylimide (LiTFSI) and 0.1 M of lithium nitrate ($LiNO_3$) in a 1:1 mixture of DOL/DME was used as electrolyte. The catholyte solution was prepared by adding 10 ml of the Li_2S_8 solution to 40 ml of electrolyte: the final concentration of Li_2S_8 in the catholyte solution was 0.1 M.

2.3. Electrochemical measurements

Electrochemical characterizations were performed with LIR2016 type coin cell, using lithium foil as a counter-reference electrode and the KJB carbon tape as the working electrode. A Whatman glass microfiber filter (Grade GF/A) was used as separator. The separator was soaked by 30 µl of catholyte solution. The sulfur content in the catholyte was about 1.20 mg cm^{-2}. Cycling tests were automatically carried out with a battery cycler (Maccor 4000). Cyclic voltammetry (CV) test was performed with a scan rate of 0.25 mV s^{-1}, in the potential range of 2.8 to 1.7 V using an electrochemical workstation (Solartron Analytical 1287 Electrochemical interface). All materials and cells were handled and assembled in a controlled atmosphere at 20 °C in a dry room (R.H. < 0.1% at 20 °C).

2.4. Chemical–physical characterization

The morphology of the working electrode was studied by scanning electron microscopy (SEM). High-magnification microphotographs were taken using an AURIGA, CrossBeam Workstation dual-column focused ion beam–SEM and a JEOL JSM-5510LV. The specimens were directly mounted onto a conductive double face carbon tape, which was previously mounted on a slab. The surface chemistry was mapped with an X-ray energy-dispersive spectroscopy (EDS) system (IXRF EDS-2000).

UV–visible absorption spectroscopic data were collected on a Beckman DU 530 UV–vis spectrophotometer with wavelength range from 900 to 300 nm. Before the UV–vis experiments the polysulfide catholyte samples were diluted to 1.0 mM.

3. Results and discussion

3.1. UV–vis spectroscopy

Lithium polysulfide solutions are complex systems with multiple equilibria characterized by continuous redox reaction, disproportion, and dissociation reactions [21]. The organic solvent used to dissolve the polysulfides plays an important role in determining the nature of the polysulfides present in solution since it is capable of selectively stabilizing a particular type of polysulfide with respect to another. The UV–vis analysis is a suitable method for detecting and identifying polysulfides in organic solvents [22] and it can provide information on the average concentration of polysulfide solutions. The UV–vis analysis carried out over different periods of time can also permit to evaluate the stability of the polysulfides. Fig. 1 reports the evolution of UV–vis absorbance spectra of the catholyte solution recorded during the period of five hours in order to evaluate its stability. The main absorption bands, located at 331 and 419 nm, are associated with the presence of Li_2S_4 while those at 351 and 479 nm, related to the presence of Li_2S_6 [23] are not visible. The intensity of the peak at 331 nm remains stable during the whole experimental time, while the intensity of the peak at 419 nm rapidly decreases after the first hour remaining almost constant in the further measurements. The elevated initial absorbance value recorded

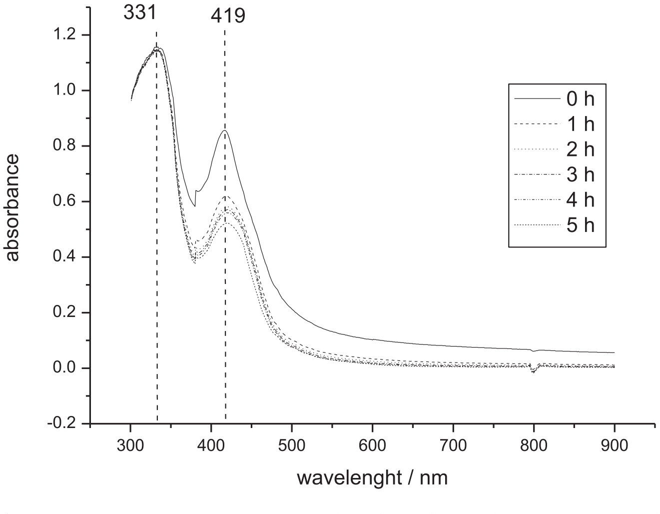

Fig. 1. UV/Vis spectra of 0.1 mM Li_2S_8 in electrolyte solution of DOL-DME from fresh solution to 5 h.