Properties of surface film on lithium anode with LiNO$_3$ as lithium salt in electrolyte solution for lithium–sulfur batteries

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ABSTRACT

The properties and the deposition process of surface film on lithium metal with LiNO$_3$ as lithium salt in electrolyte solution are investigated using X-ray photoelectron spectroscopy (XPS), scanning probe microscopy (SPM), scanning electron microscope (SEM) and electrochemical impedance spectroscopy (EIS). XPS spectra and depth profile of the surface film show that LiNO$_3$ represents a significant role in the formation of the film, which is attributed to the reaction between lithium metal and the electrolyte solution. With the strong oxidation of LiNO$_3$, the surface film consists of both inorganic species such as LiN$_x$O$_y$ and organic species such as ROLi and ROCO$_2$Li. The height and phase images obtained by a SPM system show that the surface film formed with LiNO$_3$ is a homogenous surface film. Combined with EIS spectra and SPM images, the appropriate rate of the reaction between lithium metal and electrolyte solution with LiNO$_3$ is a significant factor to from a homogeneous surface film. The SEM images show that the surface film on lithium metal immersed in electrolyte solution with LiNO$_3$ for several hours becomes smooth and compact. The compact and homogenous surface film formed with LiNO$_3$ brings about the enhanced stability of lithium anode and the improved cycle life of lithium–sulfur batteries.

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1. Introduction

A steady increasing demand for clean and efficient energy storage devices has been present in the past several decades, due to the ever-rising concerns about limited global energy supply and environment and climate changes [1–3]. Due to high volume and gravimetric energy density, lithium batteries are currently developed to power a diverse range of applications, from cars to microchips [1,4]. Furthermore, high energy density is one of the hottest topics of lithium batteries all along. Lithium–sulfur battery is a promising positive battery system due to its high theoretical energy density of about 2600 Wh kg^{-1}, assuming the complete reaction of lithium with sulfur to form Li$_2$S [3,5,6]. In addition, the lithium–sulfur battery has more advantages, such as being non-toxic, low cost and plentiful [7]. Hence, there has been a strong incentive to develop a rechargeable lithium–sulfur battery [3,8,9]. Nevertheless, capacity degradation with increasing cycles has limited its widespread practical realization [3,10], which can be mainly attributed to the high solubility of the polysulfides formed as reaction intermediates in the organic electrolyte solutions during discharge-charge processes [11]. The soluble polysulfides

will migrate through the separator to the lithium anode, with which react quite strongly to form solid precipitates (Li$_2$S$_2$ and/or Li$_2$S). The reaction causes active mass loss and unstable structure of lithium anode [3,12]. Considering of the above challenges, the protection of lithium anode is quite significant to the property improvement of lithium–sulfur battery [12–16].

To add additive in electrolyte solution is a usual and effective method to modify the electrode/electrolyte interfaces in lithium batteries [17]. In lithium–sulfur battery system, lithium nitrate (LiNO$_3$) has been investigated as an effective additive in electrolyte solution to protect lithium anode, because the components of electrolyte solution with LiNO$_3$ react with lithium anode to form protective surface film. The film could prevent the parasitic reaction between lithium anode and polysulfides, which results in active mass loss and the unstable structure of lithium anode [18]. Aurbach has studied component of the film using Fourier transform infrared and X-ray photoelectron spectroscopy [18]. Furthermore, the improved performances of lithium–sulfur battery with LiNO$_3$ have been reported by Wen and co-workers [19]. However, the properties of the film and the preventing mechanism have not been reported in previous publications. In the present work, topography, phase, chemical composition and depth profile of the surface film on lithium anode are studied using X-ray photoelectron spectroscopy (XPS), scanning probe microscopy (SPM), scanning electron microscope (SEM) and electrochemical impedance

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spectroscopy (EIS). On the basis of the data, the effect of $LiNO_3$ on the surface film is discussed in detail. The study in this paper introduces a clear way to employ SEI (Solid Electrolyte Interphase) layer additive in electrolyte solutions for lithium–sulfur battery.

2. Experimental

Lithium metal foil (100 μm, Denway, China) was received and stored in an argon atmosphere glove box. The metal foil was dipped in different electrolyte solutions for 5 h to obtain lithium anodes with different surface film. The treated lithium samples were washed with 1,2-dimethoxyethane (DME, analytically pure, water content $<3.0 \times 10^{-3}$%, Novolyte) and further dried in an argon-filled glove-box for 2 h.

A special transfer system was employed to transfer lithium samples from the glove box to a SEM system (HITACHI S-4800) or a XPS system (K-Alpha 1063, Thermo Fisher Scientific) without exposing them to atmospheric contaminants. The transfer system consists of a special sample tray and a homemade glove box which is connected with the SEM or XPS inlet. The sample tray consists of a sample holder, a rubber sealing gasket and a stainless steel cover. The treated sample was fixed on the holder and sealed in the sample tray in the usual glove box. After that, the sample tray was transferred to the homemade glove box which was filled with argon. The sample holder was sent into the SEM or XPS system after the cover and the gasket were removed. The spectra presented here were obtained by using Al-Kα radiation system, which operated at a power of 72 W (12 kV) with a base pressure of 10^{-9} Torr, and the diameter of the analyzed area on lithium samples was 400 μm. The etching process was performed using an argon ion beam (accelerating voltage 2 keV, ion beam current 6 mA).

Height and phase images of a lithium sample surface were simultaneously obtained in tapping mode by a SPM system (Solver P47-PRO, NT-MDT, Russia) placed in a special homemade glove box full of argon. All SPM images were generated by a pixel dimension of 256×256 and a scan rate of 1 Hz. Furthermore, other scanning parameters were also optimized for obtaining high-quality images.

AC impedances were measured on a three-electrode cell using an Autolab Electrochemical Workstation (AUT71864) over a frequency range of 10 to 3×10^5 Hz. The perturbation amplitude was 5 mV. The working electrode (2 cm²) was obtained by pressing lithium foil on a nickel substrate. The reference electrode was a lithium chip and the counter electrode (6 cm²) was lithium foil on a nickel meshwork. The distance between the working electrode and the reference electrode was 2 mm. The lithium working electrode surface was polished by anodic stripping (1 mA cm⁻²) for 30 s to form a relatively clean lithium surface before the measurement. The impedance measurement carried out after the lithium sample was immersed in electrolyte solution for different time.

For preparing Li_2S_6 solution, lithium (100 μm, Denway, China) and sulfur (99.98%, Aldrich) in stoichiometric ratio were added into 1,3-dioxolane (DIOX, analytically pure, water content $<3.0 \times 10^{-3}$%, Novolyte) and 1,2-dimethoxyethane (DME, 1:1, v/v) mixed solvents. The mixture was sealed and stirred vigorously for 24 h at 50 °C for the complete reaction of lithium with sulfur. The $LiNO_3$ (99.98%, Alfa) was also added into the mixed solvents and stirred vigorously for 24 h at room temperature to prepare 0.5 M $LiNO_3$/DIOX/DME (1:1, v/v) electrolyte solution.

For preparing sulfur cathode, 60 wt.% of sulfur (99.98%, Aldrich), 25 wt.% of acetylene black (Alfa) and 15 wt% of PVdF (polyvinylidenefluoride) binder were taken in NMP (N-methyl-2-pyrrolidone) solvent and mixed in a spex ball mill at room temperature for 2.5 h at 580 rpm. The slurry was coated on an aluminium current collector, dried for 24 h at room temperature and further at 60 °C under vacuum for 12 h. The sulfur cathode, lithium anode and a
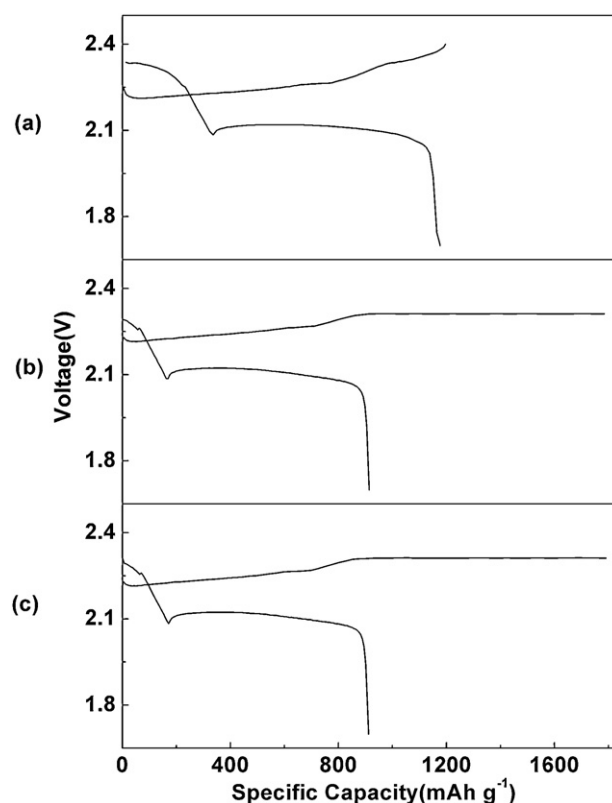

Fig. 1. Charge–discharge curves of lithium–sulfur batteries with lithium anodes immersed in (a) 0.5 M $LiNO_3$/DIOX/DME (1:1, v/v), (b) 1 M $LiN(CF_3SO_2)_2$/DIOX/DME (1:1, v/v), and (c) 0.8 M $LiN(CF_3SO_2)_2$/0.2 M Li_2S_6/DIOX/DME (1:1, v/v).

porous polyolefin separator (Celgard® 2500) were combined into a laminated structure cell and 1 M $LiN(CF_3SO_2)_2$ in 1,3-dioxolane (DIOX) and 1,2-dimethoxyethane (DME, 1:1, v/v) mixed solvents was used as electrolyte solution. The assembled cell was sealed with an appropriate amount of the electrolyte in an aluminum coated plastic pack under vacuum. The galvanostatic charge and discharge tests were performed between 1.7 and 2.5 V at a current density of 0.5 mA cm⁻² using on a multi-channel battery test system (LAND CT2001A).

3. Results and discussion

Fig. 1 shows the charge–discharge curves of lithium–sulfur batteries with lithium anodes immersed in different electrolyte solutions, all lithium anodes used in the experiment were immersed in different electrolyte solution for 5 h before assembled to a cell. The charge–discharge curves represented a typical characterization of lithium–sulfur batteries [20–22]. Two plateaus of discharge process are observed at about 2.4 V and 2.1 V in all batteries. They are corresponding to the reduction of elemental sulfur to form soluble high-order polysulfides and further reduction of the high-order polysulfide to form solid Li_2S solid film respectively [21,23,24]. As shown in Fig. 1a, the high plateau of lithium–sulfur batteries with lithium anode immersed in electrolyte solution containing $LiNO_3$ is obviously longer than that without $LiNO_3$ (Fig. 1b and c). The difference can be attributed to the particular phenomenon in lithium–sulfur batteries. During the first discharge plateau, the higher-order polysulfides diffuse to the lithium anode where they react directly with the lithium in a parasitic reaction to recreate the lower-order polysulfides [25]. The parasitic reaction could lead to the loss of active mass, the loss of