Investigation into the role of silica in lithium polysulfide adsorption for lithium sulfur battery

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ABSTRACT

A new type of sulfur electrodes with the ability for polysulfide adsorption was prepared by incorporating silica nanoparticles (SN) or amine functionalized silica nanoparticles (AFSN). AFSN was synthesized by a simple and cost-effective method. The functionalization and surface morphology of silica were confirmed with Fourier transform infrared (FTIR) spectroscopy and scanning electron microscopy (SEM), respectively. Polysulfide adsorption studies were carried out using UV–vis spectrometer, which confirmed the excellent adsorption of polysulfides by AFSN. Interaction of polysulfides with SN or AFSN was studied using FTIR and FT-Raman spectroscopy. The effective polysulfide adsorption by SN and AFSN leads to good and stable cycle performance of lithium sulfur cells. The results show that the incorporation of SN or AFSN with sulfur is a promising method to prepare cathode material for lithium sulfur batteries.

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1. Introduction

The demand for highly efficient energy reservoirs has constantly driven the development of battery systems. As a result, secondary lithium battery systems have been successfully developed with different cathode active materials [1–4]. Battery technology has improved significantly in the last two decades, in terms of size, weight, and flexibility, enabling the revolution of portable electronic devices and providing us with an exceptional quality of life. Nowadays, the non-renewable primary energy source fossil fuel petroleum is experiencing rapid depletion and the unfettered consumption of petroleum releases the greenhouse gas CO_2 when it is burned [5]. Therefore, clean, efficient, and renewable energy for automotive transportation is in high demand. An alternative option for petroleum in vehicles is to use electrical energy generated from renewable sources such as wind or solar. High energy density rechargeable batteries are necessary to store the energy thus produced. However, the cost, weight, size, and safety concerns of lithium ion batteries still hinder the promotion of electric vehicles (EVs). For this reason,

lithium sulfur (Li–S) batteries are regarded as one of the next generation energy storage systems due to high theoretical capacity $(1675 \, \mathrm{mAh \, g^{-1}})$, natural abundance, and the nontoxic nature of sulfur [6]. Despite these advantages, Li–S cells face some challenges. Sulfur cathodes have traditionally suffered from low discharge capacity and low Coulombic efficiency due to some reasons. The electronic conductivity of both sulfur and its final discharge product, lithium sulfide (Li_2S), are low [7]. Also, Li_2S and other discharge products form a layer over the cathode, which reduces the conductivity of cathode and further inhibit the access of lithium ions [8]. The reduction intermediates, lithium polysulfides, that are generated during the discharge process are easily dissolved into organic electrolyte, leading to active material loss [9,10], and because of the concentration gradient between cathode and anode, the polysulfides diffuse through the separator to the anode, where they are reduced to insoluble Li_2S_2 and Li_2S, which passivize lithium anode [11]. In addition, the expansion of cathode during discharge caused by lithium ion intercalation leads to structure collapse [12].

Lots of researches have been carried out to improve the electric conductivity of cathodes and prevent active material loss in order to achieve improved cycle performance of Li–S cells. An efficient way is the use of sulfur–carbon composites in which carbon black [13], microporous carbon [14], mesoporous carbon [15], hierarchical porous carbon [16], graphene [17], hollow carbon spheres [18],

carbon nanotubes [19], or carbon nanofibers [20] act as the host for sulfur accommodation. Other methods such as the use of gel polymer electrolyte [21], sulfur-conducting polymer composites [22], lithium anode protection [23], lithium alloy [24], and high concentration of lithium salt or additives such as $LiNO_3$ in the electrolyte [25] can also improve the performance of Li–S cells. Incorporation of materials which can hold sulfur and polysulfides in the cathode by physical or chemical interaction is another option to overcome the problem of active material loss during the discharge–charge process. Among a large variety of adsorbing materials, silica is of particular interest due to its good stability, high mechanical resistance, and high surface area as an extensively modifiable material. The addition of functional groups on the surface of silica can make it capable of interacting with various organic solvents [26]. For Li–S batteries, silica is a suitable substance that can adsorb polysulfide intermediates within sulfur cathodes by means of weak bonding, and also permit reversible desorption and release of polysulfides [27].

Even though promising methods to prepare efficient cathodes are available for Li–S batteries, research is ongoing to find more commercially viable additives which are cheap and easy to mass produce. In the present work, a novel sulfur cathode with the ability for polysulfide adsorption was prepared by the incorporation of silica nanoparticles (SN) or amine functionalized silica nanoparticles (AFSN).

2. Experimental

SN (Aldrich) was vacuum dried at 60 °C for 12 h before use. For the preparation of AFSN, 0.1 mol of (3-aminopropyl) trimethoxysilane (Aldrich) and 0.4 mol of tetraethyl orthosilicate (Aldrich) were reacted in the presence of 2-propanol and nonionic surfactant for 4 h at 25 °C [28]. The precipitate was filtered, washed with distilled water, and then dried at 60 °C for 24 h. 1 mM Li_2S_8 solution was prepared by mixing stoichiometric amount of Li_2S, and sulfur in 1,2-dimethoxyethane (DME, Soulbrain Co., Ltd.): 1,3-dioxalane (DIOX, Soulbrain Co., Ltd.) (1:1 volume ratio) in argon atmosphere for 24 h. In order to verify the adsorption ability of SN and AFSN, 0.1 g of SN or

AFSN was added during the preparation of 4 ml of 1 mM Li_2S_8 solution. Then the mixture was filtered and washed with DME/DIOX until the filtrate became colorless. The solid thus obtained was vacuum dried at 50 °C for 5 h.

The surface morphologies and elemental distribution of the samples were recorded with scanning electron microscopy (SEM) coupled with energy dispersive spectroscopy (EDS) (SEM, Hitachi S-4800). Brunauer–Emmett–Teller analysis (BET, ASAP 2010) was used to measure the specific surface area of the silica samples. The interaction of lithium polysulfides with SN and AFSN was studied using Fourier Transform infrared (FTIR, VERTEX 80v, Bruker Optics) and Fourier transform Raman (FT-Raman, LabRam HR800 UV) spectroscopies. The adsorption properties of SN and AFSN were measured using UV–vis spectroscopy (UV–vis Optizen 3220UV).

Sulfur cathodes were prepared by mixing sulfur, SN or AFSN, Ketjen black (KB) conductive carbon, and polyvinylenedifluoride (PVdF, Aldrich) binder (60:10:20:10) in N-methyl-2-pyrrolidone (NMP, Samchun) for 45 min in a ball milling machine, cast on aluminum foil, and dried at 50 °C for 12 h. Bare sulfur cathode was also prepared for comparison using the above method with sulfur/KB/PVdF in 60:30:10 weight ratio. Electrochemical impedance spectra (EIS) of the cells were measured using Zahner IM6 frequency analyzer at room temperature over the frequency range of 10 m Hz–2 MHz at an amplitude of 20 mV. Swagelok cells were constructed with lithium metal as anode (300 μm thick, Cyprus Foote Mineral Co.) and sulfur composite cathode separated by Celgard® membrane with 1.0 M lithium bis(trifluoromethane-sulfonyl) imide (LiTFSI, Aldrich) in DME/DIOX (1:1, v/v) electrolyte. The cells were cycled between 1.5 and 2.8 V using an automatic galvanostatic charge–discharge unit, WBCS3000 battery cycler (WonA Tech. Co.) at room temperature at a current density of 0.1 C. The cell assemblies were carried out in an argon-filled glove box with a moisture level <10 ppm.

3. Results and discussion

Preparation and functionalization of SN with amine group were confirmed with FTIR spectroscopy and a comparison of SN and
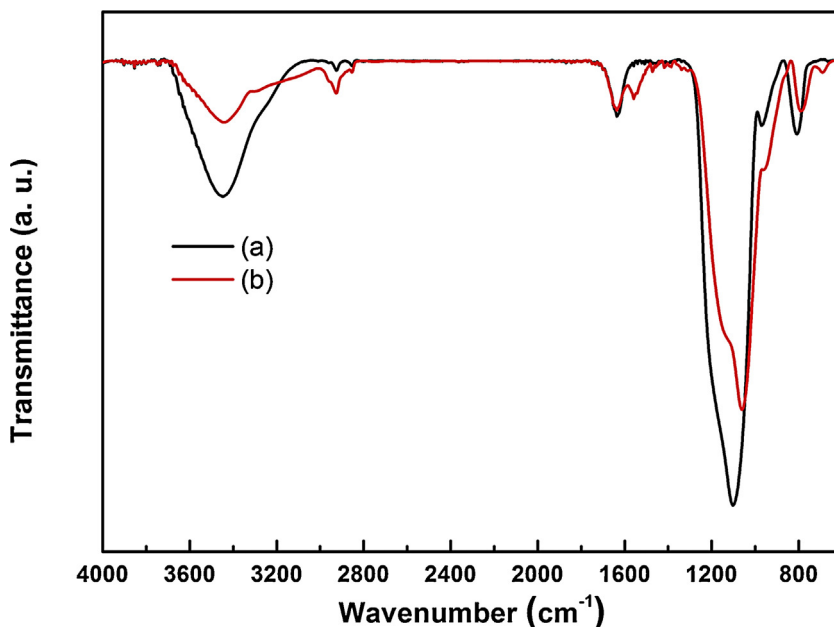

Fig. 1. FTIR spectra of (a) SN and (b) AFSN.