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Structural and dynamic behavior of lithium iron polysulfide Li_8FeS_5 during charge–discharge cycling

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HIGHLIGHTS

- Structural and dynamic behavior of Li_8FeS_5 during electrochemical cycle is studied.
- Delithiation-induced amorphization results from formation of S-S polysulfide bonds.
- Different processes are suggested for Li extraction and insertion.
- Activation energy for Li ion diffusion in Li_8FeS_5 is estimated to be 0.35 eV.

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ABSTRACT

Lithium sulfide (Li_2S) is one of the promising positive electrode materials for next-generation rechargeable lithium batteries. To improve the electrochemical performance of electronically resistive Li_2S, a Fe-doped Li_2S-based positive electrode material (Li_8FeS_5) has been recently designed and found to exhibit excellent discharge capacity close to 800 mAh g^{-1}. In the present study, we investigate the structural and dynamic behavior of Li_8FeS_5 during charge–discharge cycling. In Li_8FeS_5, Fe ions are incorporated into the Li_2S framework structure. The Li_2S-based structure is found to transform to an amorphous phase during the charge process. The delithiation-induced amorphization is associated with the formation of S-S polysulfide bonds, indicating charge compensation by S ions. The crystalline to non-crystalline structural transformation is reversible, but Li ions are extracted from the material via a two-phase reaction, although they are inserted via a single-phase process. These results indicate that the delithiation/lithiation mechanism is neither a topotactic extraction/insertion nor a conversion-type reaction. Moreover, the activation energies for Li ion diffusion in the pristine, delithiated, and lithiated materials are estimated to be in the 0.30–0.37 eV range, which corresponds to the energy barriers for local hopping of Li ions along the Li sublattice in the Li_2S framework.

1. Introduction

Lithium sulfide (Li_2S) is one of the most promising positive electrode materials for next-generation rechargeable lithium batteries, because of its high theoretical capacity of 1167 mAh g^{-1} (1672 mAh g^{-1} in the conventional S-based notation). Its corresponding electrochemical reaction can be expressed as $Li_2S = S + 2Li^+ + 2e^-$, and involves the S^{2-}/S^0 redox couple at the average potential of 2.15 V vs. Li/Li^+ [1]. However, two well-known problems remain to be solved. The first is that both Li_2S and elemental sulfur S are electronically resistive, which gives rise to relatively poor electrochemical performance in practical applications. The other problem is the dissolution of lithium polysulfide intermediates Li_2S_x ($2 < x < 8$) into a nonaqueous electrolyte solution during the discharge, which causes an internal "shuttle" phenomenon, leading to capacity fading [2,3]. Several attempts to overcome these drawbacks have been reported. Composite electrodes with carbonaceous materials have been designed and developed to enhance the electronic conductivities of Li_2S and S. Nazar's group reported the excellent electrochemical properties of a well-designed sulfur-carbon composite electrode, where sulfur is confined within the pore structure of mesoporous carbon tubes, interconnected by carbon nanofibers to form channels [1]. A Li_2S-C composite electrode prepared

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by spark plasma sintering (SPS) showed excellent initial charge–discharge capacity and cycling stability, along with high coulombic efficiency, in an all-solid-state cell, wherein the use of inorganic solid electrolytes is expected to suppress polysulfide dissolution [4]. A ball-milled Li_2S-Fe composite was first investigated as a positive electrode material by Obrovac and Dahn [5]. Li_2S-Co and Li_2S-Cu composites were also examined [6,7]. Transition-metal (TM) ions such as Fe, Co, and Cu are considered to be effective as conducting agents and/or Li_2S decomposition catalysts. Recently, our group has developed new electrode materials from metal sulfides (TiS_2, FeS_2, and NbS_2), Li_2S and/or S, and demonstrated their good initial charge–discharge capacities and cycle stabilities [8–14]. Sakuda et al. reported the stable initial charge–discharge characteristics of amorphous TiS_4 in a nonaqueous electrolyte solution, which indicated that polysulfide dissolution was suppressed by the formation of metal-sulfur bonds [9]. They further unveiled its unique charge–discharge mechanism, involving structural changes such as the destruction/formation of S-S disulfide bonds and decrease/increase in the coordination number of Ti atoms [14]. Similarly, a Fe-doped Li_2S-based material (Li_8FeS_5) was successfully prepared and exhibited an excellent discharge capacity of ~730 mAh g^{-1} after a stepwise pre-cycling treatment [12]. The structural changes occurring in Li_8FeS_5, which became X-ray amorphous during the charge–discharge cycles, were investigated using X-ray total scattering (XTS) and X-ray absorption spectroscopy (XAS) techniques that provided structural and electronic information about the Fe/S-based framework [12,15]. These studies provided evidence for charge compensation by S ions and formation of strong S-S bonds (as in elemental sulfur) during the lithium deintercalation. However, detailed structural information about the Li environments is still lacking; this information would be important for a full understanding of the delithiation/lithiation mechanism in Li-M-S batteries (where M denotes TM ion). In the present study, we examine the changes in the local structure and dynamics of Li ions in Li_8FeS_5 during the initial charge–discharge cycle using solid-state nuclear magnetic resonance (NMR) spectroscopy as well as ^{57}Fe Mössbauer and X-ray photoelectron spectroscopy (XPS) measurements.

2. Experimental

The Fe-doped Li_2S-based material, Li_8FeS_5, was prepared as follows [12,15]: first, iron sulfide (FeS) was prepared from sponge-shaped porous Fe and S powders by the SPS method [16]. The obtained FeS powder was blended thoroughly with Li_2S powder in a molar ratio of 1:4, and the mixture was sintered by the SPS process at 600 °C for 3 min under Ar atmosphere. Finally, the sintered sample was mechanically milled for 8 h at 1000 rpm with acetylene black (AB) in a weight ratio of 9:1, to yield the Li_8FeS_5-carbon composite active material. The working electrode consisted of a mixture of the composite active material (including AB), additional AB powder, and styrene-butadiene rubber (SBR)-based binder in 71.6:25.2:0.03 wt ratio; the mixture was spread onto an Al foil with heptane and then dried under vacuum overnight. The electrode sheet was pressed into a typical thickness of ~45 μm at 10 MPa. A foil of metallic lithium (0.2 mm in thickness, > 99.9%, Honjo Metal) was used as the negative electrode, and a microporous polyolefin sheet was chosen as the separator. A solution of 1 M $LiPF_6$ dissolved in a 1:1 vol ratio mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) was used as the electrolyte solution (Tomiyama Pure Chemical Industries Ltd., battery grade). Coin-type or laminate-type cells were assembled in an Ar-filled glove box. The electrochemical measurements were performed at 30 °C. The cells were galvanostatically cycled between 2.6 and 1.0 V vs. Li/Li^+ at a current density of 46.7 mA g^{-1}. Then, they were carefully disassembled at selected charge/discharge states in a glove box and rinsed with DMC to remove the residual electrolyte solution.

X-ray diffraction (XRD) measurements were carried out by the Debye-Scherrer method using a SmartLab X-ray diffractometer (Rigaku) equipped with a multilayer mirror optics for the Mo K_α source and a D/tex Ultra one-dimensional silicon strip detector. The samples were scratched off the electrode sheets and sealed in 0.5 mmϕ borosilicate glass capillaries in a glove box.

NMR spectra were acquired on a DD2 600 spectrometer (Agilent Technologies) at a magnetic field of 14.1 T. *Operando* ^{7}Li NMR measurements were performed with a homemade wide-bore static probe, where a flat laminate-type cell was placed horizontally in the center of a 10 mm-diameter solenoid coil. A Hahn echo pulse sequence was used, with a first pulse width of 4.0 μs and an echo decay of 8 μs. Each spectrum was averaged over 30 min. ^{7}Li magic-angle spinning (MAS) NMR spectra were acquired with a wide-bore T3 MAS probe (Agilent Technologies). The powder samples were packed into 1.2 mmϕ MAS ZrO_2 rotors with airtight caps in a glove box, and spun at a spinning rate of 60 kHz during the measurements. A rotor-synchronized Hahn echo pulse sequence (π/2-τ-π-τ-acq.) was used, with a π/2 pulse width of 1.0 μs and relaxation delay of 50 s. Spin-lattice relaxation times (T_1) were acquired with the saturation-recovery technique in the temperature range from −40 to 80 °C. All spectra were referenced to a 1 M LiCl solution at 0.0 ppm.

^{57}Fe Mössbauer spectra were acquired at room temperature in constant acceleration mode with a ^{57}Co (Rh) source and a proportional counter mounted on a WissEl MB-500 Mössbauer bench. α-Fe was used for velocity calibration. The powder samples were pressed and sealed under Ar atmosphere. The spectra were deconvoluted assuming doublet components with two equivalent Lorentzian-shaped lines, from which the Mössbauer hyperfine parameters (isomer shift, IS and quadrupole splitting, QS) were extracted.

XPS measurements were performed on a PHI5000 VersaProbe II (ULVAC-PHI) photoelectron spectrometer with monochromated Al K_α radiation (1486.6 eV). The electrode sheet samples were transferred to an ultra-high vacuum sample chamber ($< 4 \times 10^{-7}$ Pa) without exposing them to air. The pass energy was set to 23.5 eV. Dual-beam charge neutralization (simultaneous irradiation with low-energy electron and Ar^+ ion beams) was applied to avoid sample charging. The spectra were acquired before and after Ar^+ ion sputtering (4 kV for 5 min). The binding energies were calibrated with respect to the C 1s signal from acetylene black at 284.6 eV. The S 2p photoelectron spectra were analyzed after Shirley-type background subtraction.

3. Results and discussion

3.1. Sample characterization and charge–discharge profile

Fig. 1 shows the scanning electron microscope (SEM) image of the Li_8FeS_5 electrode, along with energy-dispersive X-ray spectrometry (EDS) images at S and Fe K-edges. The EDS images indicate that S and Fe atoms are uniformly dispersed in the active material. The chemical composition of the sample was determined to be $Li_{7.8}Fe_{1.0}S_{4.8}$ by inductively coupled plasma-atomic emission spectrometry (ICP-AES) analysis [12]. The electrical conductivity of Li_8FeS_5 was in the range 10^{-2} to 10^{-3} S cm^{-1}, which was much higher than that of Li_2S ($< 10^{-10}$ S cm^{-1}) [12]. Therefore, the Fe doping in Li_2S increased the electrical conductivity, as expected.

Fig. 2 shows the charge–discharge profile of the $Li//Li_8FeS_5$ cell for the initial cycle. Different sampling points are plotted in the figure. The charge capacity at 2.6 V was approx. 600 mAh g^{-1}, which is smaller than the theoretical capacity of 789 mAh g^{-1}, revealing the $Li_{\sim 2}FeS_5$ composition of the material. Two voltage plateau (or sloping) regions were observed during the discharge process. The discharge capacity delivered during the upper voltage plateau reached 600 mAh g^{-1}, corresponding to the full reinsertion of Li ions in the material at 1.6 V. Additional capacity was delivered at the second voltage plateau of ~1.4 V, and the capacity reached approx. 780 mAh g^{-1} at 1.0 V. The material composition was close to $Li_{\sim 10}FeS_5$.