Preparation of Li_2S–$FePS_3$ composite positive electrode materials and their electrochemical properties

Tomonari Takeuchi [a,*], Hiroyuki Kageyama [a], Masahiro Ogawa [b], Kei Mitsuhara [b], Koji Nakanishi [c], Toshiaki Ohta [b], Atsushi Sakuda [a], Hironori Kobayashi [a], Hikari Sakaebe [a], Zempachi Ogumi [c]

[a] National Institute of Advanced Industrial Science and Technology (AIST), Midorigaoka 1-8-31, Ikeda, Osaka 563-8577 Japan
[b] Synchrotron Radiation Center, Ritsumeikan University, 1-1-1 Noji-Higashi, Kusatsu, Shiga 525-8577, Japan
[c] Office of Society-Academia Collaboration for Innovation, Kyoto University, Uji, Kyoto 611-0011, Japan

ARTICLE INFO

ABSTRACT

For an attempt to incorporate phosphorous ions into the Fe-containing Li_2S, we have prepared Li_2S–$FePS_3$ composite positive electrode materials using the combination process of the thermal heating and the mechanical milling. The XRD results showed that the Li_2S–$FePS_3$ composite samples consisted of low-crystalline Li_2S and small amounts of FeP as impurity. The electrochemical tests demonstrated that the Li_2S-rich composite sample cells (Li_2S:$FePS_3$ = 4:1 mol) showed relatively high initial discharge capacity (ca. 780 mAh·g^{-1}) without any pre-cycling treatments. This makes a clear contrast to the Fe-containing Li_2S (Li_2S–FeS_x composite) sample cells, which showed the initial discharge capacity of ca. 330 mAh·g^{-1} and it was enlarged to ca. 730 mAh·g^{-1} after the stepwise pre-cycling treatment. Ex-situ XRD and XAFS measurements showed the reversible changes of the peaks ascribed to Li_2S and the local structures around S atoms during cycling. The incorporation of phosphorous ions into the Fe-containing Li_2S was effective for improving the structural reversibility against Li extraction/insertion reactions, resulting in the improved electrochemical performance of the cells.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Lithium sulfide (Li_2S) is one of the promising cathode active materials for high-energy rechargeable lithium batteries, because it has a high theoretical capacity (ca. 1170 mAh·g^{-1}) and has an advantage that a variety of anode materials without lithium sources (such as graphite, nanostructured silicon) are applicable in the practical battery system [1–13]. However, this material is both electronically and ionically resistive, which gives rise to low active material utilization in the cells. In order to enhance the conductivity of Li_2S cathode, several attempts, such as forming composites with metals (Li_2S–Fe, Li_2S–Cu) [1–3] or carbon (Li_2S–C) [4–9], have been performed. Recently, we have prepared the composites with semiconducting FeS_x ($x = 1$, 2) using the combination process of the thermal heating and the mechanical milling [12]. The obtained Li_2S–FeS_x composite samples consisted of Fe-containing low-crystalline Li_2S, and the Li_2S-rich sample cells (Li_2S:FeS = 4:1 mol) showed the initial discharge capacity of ca. 330 mAh·g^{-1}, which was enlarged to ca. 730 mAh·g^{-1} after the stepwise pre-cycling treatment. Although relatively high discharge capacity was attained, several days were required for the stepwise pre-cycling

treatment. For applying in the practical battery system, it will be advantageous to optimize the composition further so as to obtain the sample showing higher discharge capacity without any pre-cycling treatments.

Recently, incorporation of phosphorus ions into Li_2S was reported to form Li_3PS_4 at the surface of Li_2S particles, which enhanced the ionic conductivity of the active material from ca. 10^{-13} to 10^{-7} S·cm^{-1}, leading to the improved electrochemical performance of the cells [10]. Seamless transport of Li ions and transfer of electrons are basic requirements for electrode materials [14], and the formation of some Li_3PS_4-like components by incorporating phosphorus ions could be effective for improving the cell performance of the Li_2S–FeS_x composites.

In the present work, we have prepared Li_2S–$FePS_3$ composite positive electrode materials for an attempt to incorporate phosphorus ions into the Fe-containing Li_2S. $FePS_3$ was used as a phosphorus source, because this material itself shows relatively high discharge capacity [15–18]. The electrochemical properties and the charge/discharge mechanism of the obtained Li_2S–$FePS_3$ composite samples were examined and compared with those of the previous Li_2S–FeS_x.

2. Experimental

First, $FePS_3$ was prepared from the sponge-shaped porous iron, and phosphorus and sulfur powders, using the spark-plasma-sintering (SPS) process (SPS-3.20 MK-IV, Fuji Electronic Industrial, Japan), after the method reported previously [11,19]. The $FePS_3$ powder thus

obtained was blended thoroughly with the commercially available Li_2S powder (Mitsuwa Chemicals, Japan) in an 1:4 molar ratio, and the mixture was treated by the SPS process at 600 °C for 3 min under an Ar atmosphere [11,12]. The SPS-treated sample was then blended with acetylene black (AB) powder in a 9:1 weight ratio, followed by mechanically milled for 8 h using a pulverizer [12] (Model No. MC-4A, Ito Seisakusho Ltd., Japan) at a rotation speed of 1000 rpm, to yield the Li_2S–$FePS_3$ composite. Most of the procedures were carried out in an Ar-filled glove box, because Li_2S is very sensitive to atmospheric moisture.

The phase purity of the sample was checked by X-ray diffraction (XRD) measurements (Rotaflex RU-200B/RINT, Rigaku, Japan) using monochromatic Cu Kα radiation within the 2θ range of 10–125°. Before the measurements, each sample was covered with Kapton film in an Ar-filled glove box, and the measurement was carried out within 3 h to suppress the reaction with atmospheric moisture. The RIETAN-2000 program was used for structural refinement with X-ray Rietveld analysis [20]. The elemental composition of the sample was estimated by inductively coupled plasma (ICP) emission spectroscopy (SII Nanotechnology Inc., SPS4000) (for Fe, P, and S) and atomic absorption spectroscopy (Hitachi High-Technologies Co., Z2300) (for Li). The impedance of the Li_2S–$FePS_3$ composite sample was measured using a frequency response analyzer (SI 1260, Solartron Analytical), covering a frequency range from 0.1 Hz to 1 MHz with an applied voltage of 10 mV, after the sample powder was cold-pressed into a pellet with 10 mm diameter and 0.6 mm thickness. The electrical conductivity values, corrected for pellet geometry, were calculated from the intercept of the data points on the real axis of the complex impedance plane plots (Nyquist plots). The valence states and local structures of S and P atoms for the sample electrodes were examined by S and P K-edge X-ray absorption fine structure (XAFS) measurements, which were carried out at the soft X-ray double crystal monochromator beamline, BL-13 of the Synchrotron Radiation Center, Ritsumeikan University [21]. The total electron yield (TEY) method was used and the incident X-ray beam was monochromatized with Si(111) crystal ($2d = 6.270$ Å) pair. The photon energy was calibrated with the strong resonance of K_2SO_4 (S $1s \rightarrow t_2$) appearing at 2481.7 eV [22]. All the samples were sealed in an Ar-filled transfer vessel [21].

The electrochemical lithium extraction/insertion reactions were carried out using lithium coin-type cells. The working electrode consisted of a mixture of an 11.1 mg Li_2S–$FePS_3$ composite (containing 10% (1.1 mg) AB) and a 3.9 mg additional AB powder with a 0.5 mg Teflon powder pressed into a 15 mm diameter tablet under a pressure of 10 MPa. The electrochemical test cell was constructed in a stainless steel coin-type configuration. The negative electrode was a 15 mm diameter and 0.2 mm thick disk of Li foil, and a separator was a microporous polyolefin sheet. The solution of 1 M $LiPF_6$ in a 50:50 mixture of ethylene carbonate (EC) and dimethylcarbonate (DMC) by volume (Tomiyama Pure Chemical Industries Ltd., battery grade) was used as the electrolyte. Each cell was assembled in an Ar-filled glove box, and the electrochemical measurement was carried out at 30 °C initially with charging, after standing overnight on open circuit, using a TOSCAT-3100 (Toyo System) at a current density of 46.7 mA·g^{-1} (0.264 mA·cm^{-2}) (corresponding to 0.04C for $2e^-/Li_2S$) between 3.0 and 1.0 V. Cyclic voltammetry (CV) of the cell was also conducted in a voltage range of 1.0–3.0 V (vs. Li/Li^+) using a potentiostat/galvanostat (Model 1400, Solartron Analytical) at a scan rate of 0.037 mV·s^{-1}.

3. Results and discussion

The $FePS_3$ powder, prepared from the sponge-shaped porous Fe, and P and S powders, was dark gray in appearance, and its lattice parameters ($a = 5.9445(18)$ Å, $b = 10.293(3)$ Å, $c = 6.7172(9)$ Å, $\beta = 107.122(17)°$), estimated from the XRD peak positions, were consistent with those reported previously for stoichiometric $FePS_3$

($a = 5.947(1)$ Å, $b = 10.300(1)$ Å, $c = 6.7222(8)$ Å, $\beta = 107.16(1)°$ [23]). By the SPS treatment at 600 °C with Li_2S, it changed to a grayish black powder, followed by changed to a black powder (Li_2S–$FePS_3$ composite) after milling with AB. Fig. 1 shows the XRD patterns for the SPS-treated Li_2S + $FePS_3$ and the Li_2S–$FePS_3$ composite sample. Some intermediate phases, such as Li_2FeS_2, $Li_7Fe_2S_6$, and Li_7PS_6, were formed after the SPS treatment, and they disappeared after the milling process, resulting in the formation of mainly low-crystalline Li_2S and small amounts of FeP. Probably, the initial $FePS_3$ reacted with Li_2S to form the intermediate phases (Li_2FeS_2, $Li_7Fe_2S_6$, and Li_7PS_6), which might decompose and/or become some amorphous phase with much reduced crystallite-size by the following milling process, and finally resulting in the formation of partly Fe- and P-containing low-crystalline Li_2S and partly FeP (or some amorphous Li–Fe–P–S phase). The lattice parameter of low-crystalline Li_2S, $a = 5.7016(6)$ Å, was consistent with that reported previously for stoichiometric Li_2S ($a = 5.7158(1)$ Å [24]). The FeP content, estimated by the X-ray Rietveld analysis, was ca. 8 mol%. The atomic ratio of the Li_2S–$FePS_3$ composite sample, estimated by ICP and atomic absorption spectroscopy, was Li:Fe:P:S = 8.0(1): 1.1(1):1.0(1):6.3(1), which was similar to the starting composition with a slight loss (ca. 10%) of S atoms (initially Li:Fe:P:S = 8:1:1:7 for Li_2S:$FePS_3$ = 4:1). These results indicate that the Fe and P ions might be substituted for Li ions in the low-crystalline Li_2S (or might be present at interstitial sites in Li_2S), because the FeP content estimated by the X-ray Rietveld analysis (ca. 8 mol%) was much lower than that estimated from the measured atomic ratio (ca. 20 mol%). The crystallite size, estimated from the peak width at half maximum of the 111 peak (2θ ~ 27°), was ca. 42 nm. Such low crystallinity was due to the high mechanical stress applied by the pulverizer [12]. The electrical conductivity of the Li_2S–$FePS_3$ composite, estimated from the complex impedance plane plots, was ca. 1.5×10^{-3} S·cm^{-1} at room temperature, which was comparable to those of the Li_2S–FeS_x composite samples (10^{-2}–10^{-3} S·cm^{-1} [12]).

The basic electrochemical behavior of the Li_2S–$FePS_3$ composite sample was characterized by cyclic voltammetry. As shown in Fig. 2(a), the oxidation/reduction pair at 2.6/2.4 V was observed, and it was attributable to the redox reaction of sulfur (S^{2-}/S^0 or S^{2-}/S_2^{2-}) [8,9,12]. Some small reduction peaks observable at 1.8 and 1.3 V were not assignable evidently in the present stage. The charge and discharge curves for the Li_2S–$FePS_3$ composite sample cells are shown in Fig. 2(b). The charge curve showed a plateau at ca. 2.5 V, which is similar to that of the previously reported Li_2S–FeS cells, possibly corresponding to the oxidation of sulfur (S^{2-}/S^0 or S^{2-}/S_2^{2-}) [8,9,12]. And the charge capacity was ca. 520 mAh·g^{-1}, which corresponds to ca. 89% of the calculated value (ca. 580 mAh·g^{-1}) for the Li_8FeP_7 (Li_2S:$FePS_3$ = 4:1), assuming that all the Li ions contained are delithiated and contribute to the electrochemical reaction. The subsequent discharge curve showed a rather
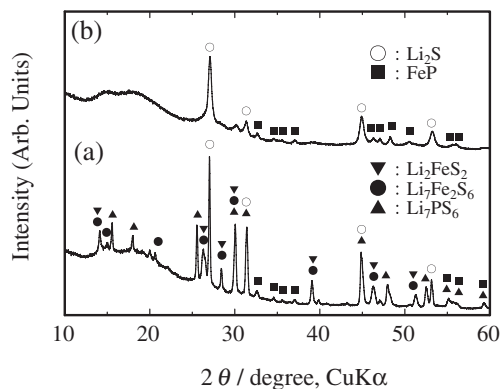

Fig. 1. XRD patterns (Cu Kα radiation) for (a) SPS-treated Li_2S + $FePS_3$ and (b) Li_2S–$FePS_3$ composite sample (Li_2S:$FePS_3$ = 4:1).