XAFS study for sulfurized alcohol composite positive electrode materials applicable for Li-S batteries

**Hiroyuki Kageyama[1*], Toshikatsu Kojima[1], Tomonari Takeuchi[1],
Kei Mitsuhara[2], Masahiro Ogawa[2], Keisuke Yamanaka[2], Toshiaki Ohta[2],
Ryo Nagai[3], and Akira Ohta[3]**
[1]*National Institute of Advanced Industrial Science and Technology (AIST),*
Midorigaoka 1-8-31, Ikeda, Osaka 563-8577, Japan
[2]*Ritsumeikan University, Noji-Higashi 1-1-1, Kusatsu, Shiga 525-8577, Japan*
[3]*Lithium Ion Battery Technology and Evaluation Center (LIBTEC),*
Midorigaoka 1-8-31, Ikeda, Osaka 563-8577, Japan

1. Introduction

Elemental sulfur is one of the promising cathode active materials for high-energy rechargeable lithium batteries because of its high theoretical capacity (ca. 1670 mAh・g^{-1}) and relatively low cost [1]. However, sulfur cathode has some disadvantages, such as low electrical conductivity and dissolution as polysulfides into electrolyte during electrochemical cycling, resulting in shuttling in Li-S batteries. Several attempts have been performed to solve these problems, and the major improvements have been made by forming composites with carbon matrix, whereby sulfur was physically confined in some fine structures [2]. Despite the improved electrical transfer and the suppressed shuttling of polysulfides, these S-C composites cells still showed gradual capacity degradation. This is originated from the low binding energy between sulfur and carbon matrix [3].

Another type of S-C composites has been developed, based on the concept of embedding sulfur into a conductive polymer matrix, such as sulfurized poly(acrylonitrile) (S-PAN) [4-6]. In these organosulfur materials, sulfur is thought to be incorporated in cavity of molecular scale, which significantly prevents the dissolution as polysulfides, leading to the excellent cycle stability of the cells. Although many kinds of polymer framework have been investigated, there still remain challenges for exploring the organosulfur materials with higher sulfur contents, using inexpensive and non-toxic reagents [3].

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*Present address: Office of Society-Academia Collaboration for Innovation, Kyoto University Uji, Kyoto 611-0011, Japan

In the present work, we have tried to prepare new type of organosulfur cathode materials using primary alcohol. The structure and the electrochemical properties of the obtained sulfurized alcohol composites (SAC) were examined.

2. Experimental

SAC was prepared by refluxing primary alcohol 1-$C_nH_{2n+1}OH$ (n = 3 – 10) (1g) and elemental sulfur (5g) in a glass tube equipped in an electric furnace, which was heated at 400°C. After cooling, the resulting powder was ground and then heated again at 300°C under N_2 flow in order to eliminate residual elemental sulfur to yield the SAC. We also prepared S-PAN after the method reported previously [7]. The obtained SAC was characterized by XRD, TEM observation, elemental analysis, and Raman spectroscopy. Also we made S K-edge XAFS measurements of the SAC together with the reference samples, elemental sulfur, Li_2S and dithiooxamide ($NH_2CSCSNH_2$) (SR Center, Ritsumeikan University) by total electron yield (**TEY**) and partial fluorescence yield (**PFY**) mode, simultaneously. Electrochemical lithium insertion / extraction reactions were carried out at 30°C using lithium coin-type cells with 1M $LiPF_6$ / (EC + DMC) electrolyte at a current density of 30 mA・g^{-1} between 1.0 and 3.0 V initially with discharging.

3. Results and Discussion

The obtained SAC samples were black in color, and the XRD patterns showed no significant peaks, irrespective of the primary alcohol (n-value). High-resolution TEM observations showed no obvious crystalline domains, indicating an amorphous phase. The EDX mapping showed relatively homogeneous distribution of sulfur and carbon in the SAC samples. The elemental analyses indicated that the sulfur content was more than 60 wt%, which was higher than that reported previously for S-PAN (ca. 30 – 53 wt%) [4,5]. The Raman spectra showed some peaks at 480, 1250, 1440cm^{-1}, suggesting the S-S, C-S, and C-C bonds, respectively. Analyses of the D- and G-bands indicated that the C-C bonds mainly consisted of sp^3-type configuration, which makes a clear contrast to the S-PAN where the C-C bonds consisted of mainly sp^2-configuration.

The electrochemical tests for the SAC sample cells showed that the initial discharge capacity was ca. 800 - 1000 mAh・g^{-1}, which was higher than that of S-PAN, due possibly to higher sulfur contents. The charge/discharge mechanism was examined using S K-edge XAFS measurements. Figure 1 and 2 show S K-XANES spectra and radial structure functions around the S atom of the typical SAC sample prepared from l-nonanol and sulfur (**1-nonanol-S**) and those after the early stage discharge-charge cycling together with those of the reference samples, respectively. Three absorption peaks at 2.469 keV, 2.472 KeV, and 2.473 keV in S K-XANES region would be assigned to the transition concerned with S=C< or S_2^{2-}, the internal transition with isolated S or -S-S-S-, and the transition with hybrid orbital of -S-C-H, respectively.

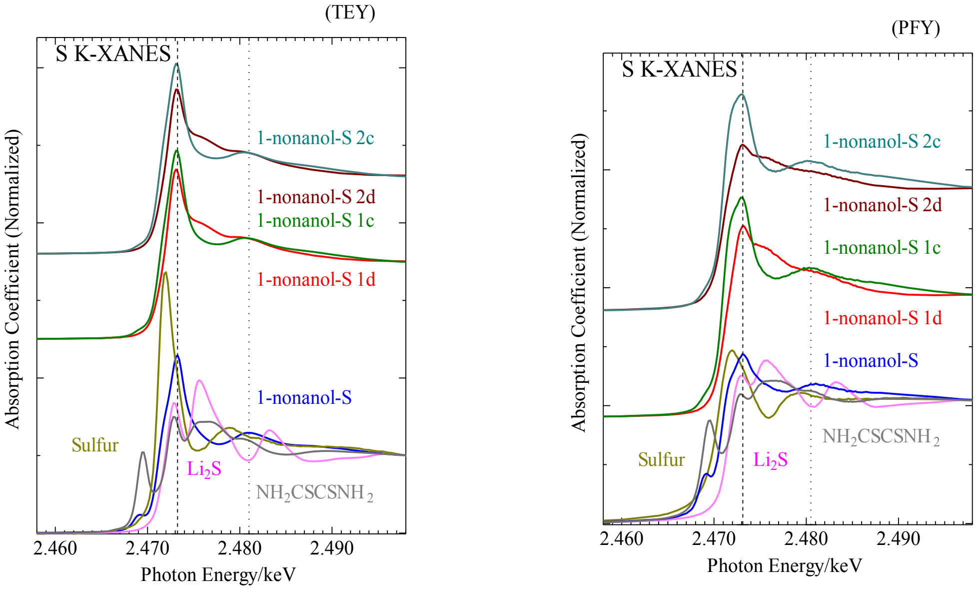

Figure 1. S K-XANES spectra of the typical SAC sample, 1-nonanol-S and those after the early stage discharge-charge cycling; (left) TEY mode, (right) PFY mode.

The peaks at 2.473 keV still remains after the discharge (1d and 2d) while the peak at 2.480

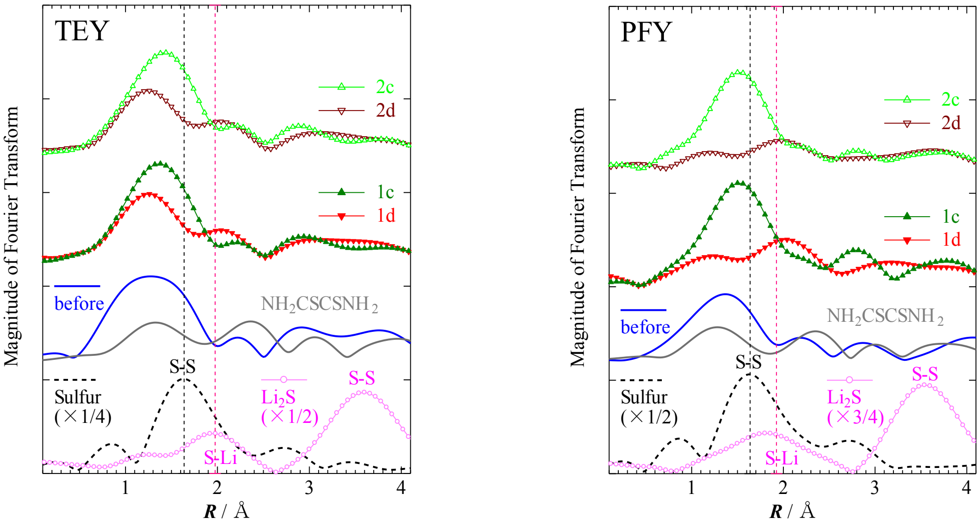

Figure 2. Radial structure functions around the S atoms of the typical SAC sample, 1-nonanol-S and those after the early stage discharge-charge cycling; (left) TEY mode, (right) PFY mode.

keV, which almost disappears after the discharge, reappears after the charge (1c and 2c). Because SAC sample is homogeneous independent of the sample depth from the surface as observed by EDX mapping, the variation of XANES features and patterns of the radial structure functions are virtually similar between surface-sensitive TEY and PFY modes. The radial structure function of as-prepared sample (**before** in Figure 2) has the main peak at similar distance with that of $NH_2CSCSNH_2$, which is fairly shorter than that elemental sulfur while the peak magnitudes are about 1/4 of that of elemental sulfur. This indicates that the main peak would contain contribution from lower Z element than sulfur, for example, carbon. These peak magnitudes decrease after the discharge (1d and 2d) while the distances of the peaks are similar to that of as-prepared sample. Also new peak at distance near to that of S-Li pair of Li_2S appears after the first discharge (1d) and reappears after the second discharge (2d). The main peak magnitudes are recovered after the charge (1c and 2c) and the main peak shifts to longer distance. However, the distance is fairly shorter than that of elemental sulfur. The results of XAFS analysis suggest that the phase with similar local structure around the S atom to that of Li_2S would be formed after the discharge while the bond between the S atom and lower Z element (probably carbon) would not change during the discharge. The C K-edge XAFS analysis of the SAC after discharge/charge, which is in progress, would offer additional information to confirm the discussion above.

In conclusion, new type of organosulfur cathode materials, SAC show different behavior of local structure change during discharge/charge cycling as compared with those of conventional S-C composites and S-PAN. This indicates that the SAC would be potentially promising cathode material as new concept organosulfur substances.

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