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X-ray-absorption studies of organodisulfide redox polymeric electrodes

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We have measured the near-edge x-ray-absorption fine-structure (NEXAFS) spectra of the K edge of sulfur in organodisulfide redox polymeric electrodes in both charged and discharged states. The formation and scission of S—S bonding during the charge-discharge cycle were observed through NEXAFS spectroscopy.

INTRODUCTION

A series of disulfide polymers, as a new class of solid-state cathode materials, has been studied recently[1-3] showing high energy densities and long cycle life in solid-state lithium batteries. For most of the cathode materials used in solid-state lithium batteries, the charge-discharge process is based on intercalation chemistry. The energy storage in organodisulfides, on the other hand, is believed to take place by the scission and formation of S—S bonds coupled with the movement of Li^+ ions into and out of the polymer matrix. Up to now, no direct spectroscopic evidence has been provided for this process. We are developing *in situ* techniques to study the relationship between the electrochemical properties and the structural changes during the charge-discharge cycle of disulfide polymers. Compared with other spectroscopic methods, such as ir and Raman, near-edge x-ray-absorption fine-structure (NEXAFS) spectroscopy has the advantages in providing information about the interatomic bonding and coordination geometry with high element selectivity. The penetrating nature of the x-ray probe makes it suitable for *in situ* studies. We report here our preliminary results of NEXAFS studies of disulfide polymers above the sulfur K edge in both charged and discharged states. Using corresponding lithium and potassium organodisulfide salts as a reference system, the formation and scission of S—S bonding during charge-discharge cycles were studied.

EXPERIMENT

Two systems of organodisulfide polymers have been studies: (1) trithiocyanuric acid monomer, lithium and potassium trithiocyanurate salt, and poly(trithiocyanuric acid); and (2) 2,5-dimercapto-1,3,4-thiadiazole, its lithium and potassium salts, and polymer. The chemical structures of the polymers for these two systems are shown schematically in Fig. 1(a). The 2,5-dimercapto-1,3,4-thiadiazole and trithiocyanuric acid were purchased from Aldrich Chemical Co. and were recrystallized from a mixed solvent of THF and hexane. The corresponding disulfide polymer was prepared in an ethanol solution of lithium hydroxide with an equivalent amount of iodine. The lithium and potassium thiolate was prepared by addition of equivalent hydroxide to the mercapto compound.

The composite cathodes were made by mixing the disulfide polymers with $LiBF_4$ salt, ethylene oxide-grafted polysiloxane, and ultrafine carbon black. The cathodes were assembled in cells with $LiBF_4$-acetonitrile as electrolyte, and lithium foil as anodes. The NEXAFS spectra for unreacted polymer cathodes were taken before the composite cathodes were assembled into electrochemical cells. The assembled cells had an open circuit voltages of about 3 V. The cells were discharged for two hours with 0.3 mA/cm^2 current to a voltage of 0.25 V. The recharged state was obtained by reversing the current through the cell until 3 V was reached. NEXAFS measurements were made in both discharged and recharged states for poly(trithiocyanuric acid) and in a discharged state for poly(2,5-dimercapto-1,3,4-thiadiazole). Before the NEXAFS measurements, the cathodes were removed from the cells, and then rinsed and dried.

The NEXAFS measurements were made at beam line X19A at the National Synchrotron Light Source. The data were collected as fluorescence excitation spectra using a large solid angle ionization chamber as the fluorescence detector. As the incident x-ray energy is scanned through the sulfur K edge, the ejected photoelectrons sequentially probe the empty electronic levels of the sample being studied, resulting in fine structure in the near-edge absorption spectrum. The relaxations of these excited states take place by the emission of Auger electrons or fluorescence photons. The spectrum depends on bonding, valence, and coordination geometry of the sulfur atom in the compound. However, unlike the NEXAFS spectra for low-Z atoms such as carbon and oxygen, where the individual spectral features can be assigned to particular transitions,[4] the interpretation of NEXAFS spectra for sulfur is more complicated. Reference systems are, therefore, required for spectral interpretation. In order to relate the spectral change to the microscopic structural change of the disulfide polymers during the electrochemical oxida-

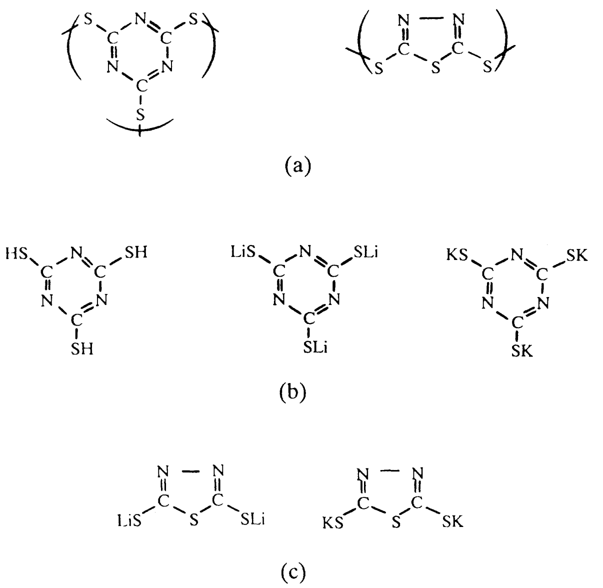

FIG. 1. (a) Chemical structures of poly(trithiocyanuric acid) (left), and poly(2,5-dimercapto-1,3,4-thiadiazole) (right). (b) Chemical structures of trithiocyanuric acid (left), lithium trithiocyanurate (middle), and potassium trithiocyanurate (right). (c) Chemical structures of lithium salt of 2,5-dimercapto-1,3,4-thiadiazole (left) and potassium salt of 2,5-dimercapto-1,3,4-thiadiazole (right).

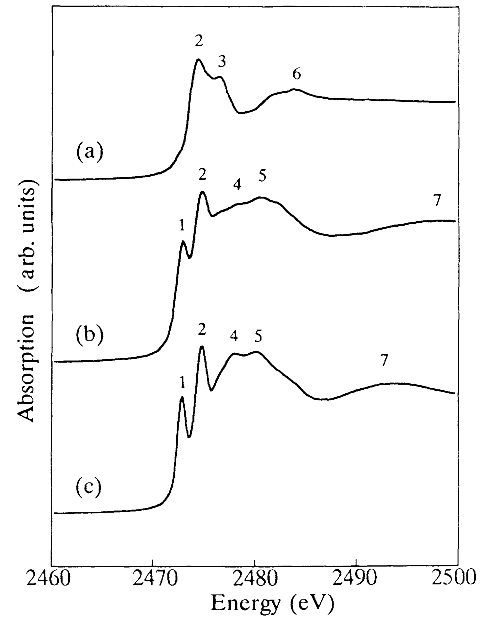

FIG. 2. NEXAFS spectra near the sulfur K edge of (a) trithiocyanuric acid, (b) lithium trithiocynaurate, and (c) potassium trithiocyanurate.

tion and reduction, we have studied the spectra of several selected reference systems. For each of the disulfide polymers, the NEXAFS spectra of corresponding monomeric lithium and potassium salts were taken as references for $S-Li^+$ and $S-K^+$ bonding. The chemical structures of the studied compounds are given in Figs. 1(b) and 1(c).

RESULTS AND DISCUSSION

The NEXAFS spectra of trithiocyanuric acid, and lithium and potassium salts are plotted in Fig. 2 as a reference system. The spectrum of trithiocyanuric acid, lithium trithiocyanurate, and potassium trithiocyanurate are marked as curves (a), (b), and (c), respectively. The spectra of alkali-metal salts in curves (b) and (c) are quite different from the spectrum of trithiocyanuric acid in curve (a) First, the most obvious differences are the new features labeled 1, 4, 5, and 7 for the alkali-metal salts. Second, the intensity of features 3 and 6 is substantially reduced in curves (b) and (c) when compared to curve (a). All of the new features are stronger in curve (c) than in curve (b) where lithium was replaced by potassium in the salts. This strongly indicates that these features are characteristic peaks of sulfur-alkali-metal bonding. The preedge feature 1 at 2471.5 eV could be assigned to a π^* transition related to S=C double bond. This feature was not observed in curve (a) which is consistent with an absence of S=C double bond for the trithiocyanuric acid form.

When the protons are replaced by the alkali-metal ions, such as Li^+ or K^+ in the trithiocyanurate salts, the redistribution of charge induces a resonance structure. The lithium or potassium might be bonded to the nitrogen atoms instead of the sulfur atoms, causing a double bond flip from C=N to C=S. This double bond resonance results in a π^* transition in spectra (b) and (c), labeled 1 in Fig. 2.

Although the origin of the transitions corresponding to features 4 and 5 are unclear, these transitions are clearly related to the alkali metals since they appeared in all spectra where S-alkali metal bonding is expected. The narrowing of feature 2, and the disappearance of feature 3 in curves (b) and (c) is caused by the breaking of symmetry of the electric field surrounding the sulfur atom when the C—S—H bond was replaced by $C-S-Li^+$. This breaking of symmetry would prevent certain transitions such as that corresponding to feature 3, create new transitions such as that corresponding to features 4 and 5, and remove the degeneracy of the final $3p$ states of sulfur atoms. This, in turn, will narrow the white line, labeled feature 2. Feature 7 is attributed to multiple-scattering effects due to the changing of first shell scatterers from sulfur atoms to alkali-metal atoms. It is, therefore, sensitive to the nature of scatterers. The intensity increases and the center of the peak moves to lower energy when Li ions are replaced by K ions.

The reference NEXAFS spectra of 2,5-dimercapto-1,2,4-thiadiazole, its lithium and potassium salts are plotted in Fig. 3 as curves (a), (b), and (c), respectively. Curve (a) in Fig. 3 is similar to curve (a) in Fig. 2 except that feature 3 is stronger and unresolved from feature 2. As one can see from Fig. 1(a), all three sulfur atoms in trithiocyanuric acid are equivalent. However, in 2,5-dimercapto-1,3,4-thiadiazole, the sulfur atom in the ring

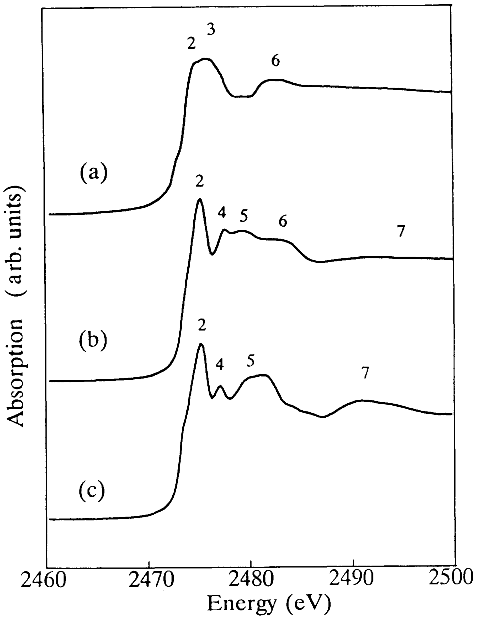

FIG. 3. NEXAFS spectra near the sulfur K edge of (a) 2,5-dimercapto-1,3,4-thiadiazole, (b) lithium salt of 2,5-dimercapto-1,3,4-thiadiazole, and (c) potassium salt of 2,5-dimercapto-1,3,4-thiadiazole.

has different bonding and environment from the other two on both sides. Therefore, the detailed features in curve (a) of Fig. 3 are smeared out. The spectra for lithium and potassium salts in curves (b) and (c) are also similar to those in Fig. 2 for trithiocyanurate salts, except that no preedge feature 1 was observed. This implies an absence of S=C double bonds from resonance conjugation in 2,5-dimercapto-1,3,4-thiadiazole salts. As discussed above, features 4 and 5 appeared as signatures of S-alkali metals bonding in both curves (b) and (c).

The NEXAFS spectra of unreacted, discharged, and recharged composite cathodes using poly(trithiocyanuric acid) are plotted in Fig. 4 as curves (a), (b), and (c), respectively. The spectrum for the unreacted polymer cathode is essentially the same as for the monomer in curve (a) in Fig. 2. Although the spectrum of the discharged cathode in curve (b) does not fully resemble the spectrum of lithium trithiocyanurate in curve (b) in Fig. 2, most of the important spectroscopic characteristics related to S—Li$^+$ bonding are observed, including the sharp preedge feature 1 at 2471.5 eV, a strong feature 4 centered at 2480 eV, a broad feature 7 around 2495 eV, as well as the disappearance of feature 3. This is strong evidence for the electrochemical reduction taking place through the depolymerization in which the S—S bonds are broken and replaced by S—Li$^+$ bonds. The electrochemical reversibility of this reaction can be seen in curve (c), which was measured after recharging the battery electrochemically. In curve (c), all the features related to S—Li$^+$ bonding are weakened while feature 2, related to S—S bonding, grows stronger and broader compared with curve (b). This is a clear indication of the formation of S—S bonding through electrochemical polymerization during recharging. Curve (c) can be represented as a mixture of curves (a) and (b). This indicates that the electrochemical reaction is not completely reversible. We are planning to improve our sampling technique in order to further study the reversibility of the reaction with more cycles.

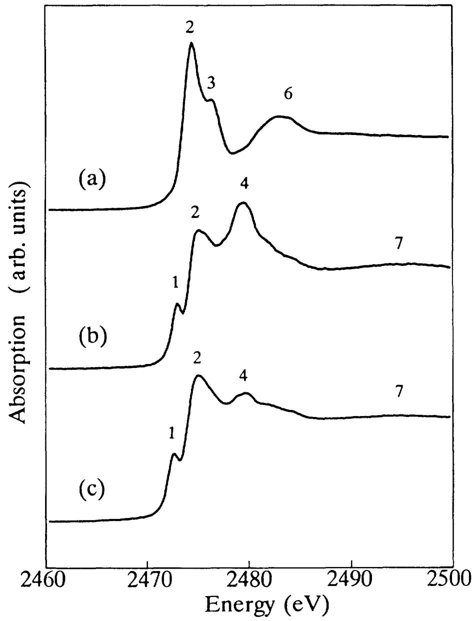

FIG. 4 NEXAFS spectra near the sulfur K edge of poly(trithiocyanuric acid) electrode in (a) an unreacted state, (b) a discharged state, and (c) a recharged state.

Figure 5 shows the spectra of poly(2,5-dimercapto-1,3,4-thiadiazole) in (a) an unreacted state and (b) a discharged state. Curve (a) in Fig. 5 for the unreacted

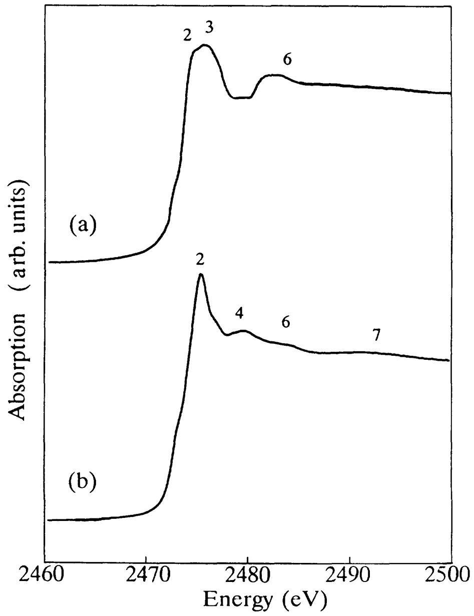

FIG. 5 NEXAFS spectra near the sulfur K edge of poly(2,5-dimercapto-1,3,4-thiadiazole) in (a) an unreacted state and (b) a discharged state.

polymer cathode is basically the same as curve (a) in Fig. 3 for the monomer. After discharge, represented by curve (b), the intensity of features 3 and 6, which are related to S—S bonding, are substantially reduced. At the same time, the intensity of features 4 and 7, which are related to S—Li$^+$ bonding are increased. The results clearly show scission of S—S bonding and the formation of S—Li$^+$ bonding during the discharge. Since no NEXAFS spectra were taken for the recharged state of poly(2,5-dimercapto-1,3,4-thiadiazole), we cannot comment on the reversibility of the discharge-charge cycle of this compound. The *in situ* NEXAFS studies of the redox processes of these disulfide polymers are planned.

CONCLUSION

NEXAFS studies of organodisulfide polymers above the sulfur *K* edge provides detailed spectroscopic information about the S—S and S—Li$^+$ bonding change during the charge-discharge cycle, which is important for understanding the operation of lithium-disulfide polymer batteries. The results of this study clearly show that the discharge-charge process in the organodisulfide polymer cathodes takes place by electrochemical polymerization and depolymerization through the formation and scission of S—S bonding. This study also demonstrates the power of NEXAFS spectroscopy in investigating and monitoring the electrochemical reactions.

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