First solvation shell of polymer electrolytes: PEO_4:KSCN

Sittichai Kulawong
Program of Chemistry, Faculty of Science and Technology, Nakhon Ratchasima Rajabhat University,
Nakhon Ratchasima 30000, Thailand
Email: sittichai_kul@hotmail.com

and **Jittima Chaodamrongsakul**
Faculty of Engineering, Vongchavalitkul University, Nakhon Ratchasima 30000, Thailand
Email: jittima_chao@hotmail.com

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ABSTRACT

The local structure of potassium ions were investigated, using experimental measurement of the Extended X-ray Absorption Fine Structure (EXAFS) spectra. This method gives more important information at the atomistic scale including the distance (r) between atom pair around the probed ion and coordination number (N). The coordination number, distances and the Debye-Waller factor (σ^2) of the first shell were focused. EXAFS results revealed that ether oxygen of poly(ethylene oxide); PEO were induced by potassium ion to form an local structure. The first solvation shell in the EXAFS fittings of PEO_4:KSCN consists of five oxygen atoms and two nitrogen atoms.

Keywords: EXAFS, PEO_4:KSCN

1. INTRODUCTION

Solid polymer electrolytes (SPEs) are of great interest in the context of developing a variety of modern electrochemical applications such as high-energy-density batteries, fuel cells and electrochemical devices [1] – [3]. There are several advantages from replacing the aqueous electrolytes of conventional batteries with SPEs. First, polymers have good chemical stability and are generally unreactive with lithium. Second, SPEs can be used as thin layer. Third, their mechanical properties are attractive because SPEs are deformable, flexible, and easily fabricated.

SPEs consist of salts dissolved in solid high molecular weight polymer. Polymer, which can dissolve salt must be comprise of O, N or S atoms because these atoms can interact with cation, and make decompositive salt to have a better ionic conductivity. Poly(ethylene oxide: PEO) is one of the most widely studied host polymer matrix because of its ability to solvate a variety of inorganic salts leading to polymer electrolytes with significant values of ionic conductivity [1] – [12].

Various methods have been employed to find out about the local structure of SPEs. These include thermal methods such as differential scanning calorimetry (DSC), X-ray methods such as X-ray diffraction [13] – [15] and X-ray absorption fine structure (XAFS) [16], [17], solid state NMR methods and vibrational spectroscopic methods such as infrared and Raman [18]. The objective of these various studies is to understand how the structures of the SPEs are implicated to ionic conductivity. Extended X-ray absorption Fine Structure (EXAFS) have been used to investigate the structure of SPEs. The useful information obtains from EXAFS data are the nearest neighbour atoms around the target element and the distances from the target element to these neighbours. Previously, mainly SPEs studied for the heavy metal salts such as PEO:RbI [19, 20], PEO:$NiBr_2$ [21] and PEO:$CuBr_2$ [22]. The distance between metal salts and ether oxygen from PEO (M-O) are nearly invariant at about 2.1 Å. For PEO:$CaBr_2$ system, the M-O distance is slightly larger than heavy metal (2.4 Å) [23]. Another general trend is seen that for high ratios of PEO-metal salt large coordination numbers for the metal ion are seen. Thus Co^{2+} has a coordination number of six (4 oxygens and 2 Br^-) in $PEO_4.CoBr_2$ complex, whereas in the analogous $PEO_{15}.CoBr_2$ the coordination reduces to ~ 3. It can be said that increase in tight coordination by neighbours will lead to low ionic conductivity. Thus EXAFS can provide useful information on the local structure around the metal ion even in the amorphous region.

In this paper, present the local structures around the ionic species of SPEs is characterized using EXAFS which is an averaging technique and gives information such as coordination number and distance of neighbours around an absorbing atom.

2. EXPERIMENTAL SECTION

2.1 Sample preparation

PEO (MW 4 x 10^6 g mol^{-1}, Aldrich) was used as received. The salts, potassium thiocyanate (KSCN, Fluka), were dried in the vacuum oven at ~ 100-120 °C for 48 hours. Stoichiometric amount of PEO and the desired salt were dissolved in methanol and stirred continuously for 24 hours at room temperature. After continuous stirring, the solution was allowed to stand at room temperature for 24 h to facilitate degassing. To obtain thin film of the sample, the gelatinous polymer solution was cast on the glass plate. The films were dried in vacuum oven at 50 °C for 24 hours to remove solvent.

2.2 EXAFS measurement and data analysis

The experimental potassium *K*-edge XAS spectra used in this work for PEO_4:KSCN film was measured at beamline BL-8 of the Synchrotron Light Research Institute (Public Organization) in Nakhon Ratchasima, Thailand. The ring current was 100 mA, and the ring energy 1.2 GeV. The data was collected in transmission mode using a Si(111) double crystal monochromator. Two ionization chambers, one of 10 cm length and the other 40 cm length, filled with 250 mbar N_2 were used to monitor the incoming and outgoing intensities of X-rays respectively. For this sample, 2 eV steps was used in the pre-edge region and EXAFS region, while 0.2 eV steps was employed from 60 eV below the edge to 60 eV above the edge. Energy calibration was performed with the standard anhydrous KI compound. A total of 3 scans (each scan lasted approximately 30 minutes) were collected and the scans were averaged after after E_0 determination before further data analysis to improve the signal to noise ratio. The EXAFS data processing was carried out with ATHENA software [24]. Phase shift and backscattering amplitudes of K-O and K-N interactions were calculated by FEFF7.0 software [25]. The EXAFS data fitting done by FEFFIT software were accomplished with single and multiple scattering paths calculated by FEFF7.0, and the EXAFS parameters were extracted from the raw data with the FEFFIT software. The fittings were done both in *r* space (*r* is interatomic distance from the absorber atom) and *k* space (*k* is the wave vector).

3. RESULTS AND DISCUSSIONS

The background subtracted and normalized EXAFS spectra for PEO_4:KSCN system is plotted as $k^2\chi(k)$ vs. *k* in Figure 1 (solid curve). Plots of the radial structure function (RSF) for PEO_4:KSCN system is shown in Figure 2 (solid curve). A prominent first coordination shell at about 2 Å was observed. The sample has a broad and skewed peak after 3 Å. To model the first solvation shell of PEO_4:KSCN, crystal structure of PEO_4:KSCN was used as a reference material. FEFF simulations and best fits of the first solvation shell using PEO_4:KSCN crystal were shown in Figure 1 and 2 (dash curve). In curve-fitting procedures, the first-shell Debye-Waller factors, the amplitude reduction and the edge energy were adjustable. Therefore, three adjustable parameters (Debye-Waller factor, the amplitude reduction and the edge energy) were floated in the fits of experimental EXAFS data to theory. In the FEFFIT documentation, it is strongly suggested that E_0 should be allowed to float to correct for problems such as incomplete core-hole shielding, angular variations in valence charge distribution, and charge transfer effects. The best-fit results for the experimental EXAFS data are shown in Table 1. Fits were obtained in *k* and *r* space with an R-factor of less than 0.02, which indicates excellent agreement between theory and experiment [4]. The EXAFS data were fit using both K-O and K-N coordination shells. Oxygen and nitrogen atoms achieve the best fit of the first solvation shell in PEO_4:KSCN system, the coordination number were estimated to 5 and 2, respectively. Accordingly, the distance of K^+-O and K^+-N were 2.53-3.11 and 2.68-2.88 Å, respectively. Fig. 3 show the possible structure of the local environment around potassium in PEO_4:KSCN system.

The coordination number and average distance of oxygen and nitrogen atoms obtained from the fits agree very well with the results mentioned in crystal structure of PEO_4:KSCN [15]. Crystal structure of PEO_4:KSCN shows the PEO chain adopts a helical arrangement which encloses the potassium ion. The oxygen atoms are located in the inner surface of the tunnel cavity so as to provide appropriate coordination environment for the potassium conformation. The coordination around the potassium is seven. Seven-coordinate environment around the potassium is completed by five ether oxygens from PEO (K^+-O = 2.63-3.09 Å) and two nitrogens from the SCN^- ions (K^+-N = 2.74-3.05 Å) [15].

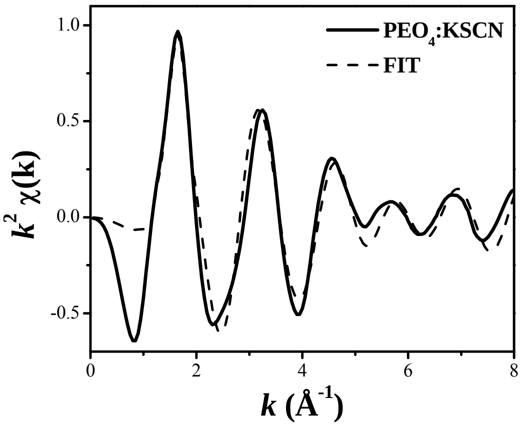

Fig. 1 *Plot of* $k^2\chi(k)$ *vs. k for* PEO_4*:KSCN. The observed spectra (solid curve) were fit by using the parameters from crystal structure* PEO_4*:KSCN (dash curve).*

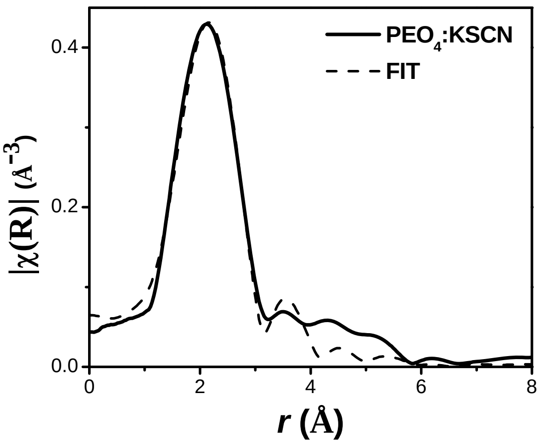

Fig. 2 *Radial structure function for* PEO_4*:KSCN. The observed spectra (solid curve) were fit by using the parameters from crystal structure* PEO_4*:KSCN (dash curve).*

Table 1 *EXAFS parameters of* PEO_4*:KSCN system.*

Sample	Atom	Distance	N	σ^2(Å^2)	E^0Shift(eV)
PEO_4:KSCN	oxygen	2.53 ± 0.10	0.98	0.002	+ 1.60
	nitrogen	2.68 ± 0.06	0.93	0.015	+ 2.23
	oxygen	2.86 ± 0.07	1.03	0.004	+12.33
	oxygen	2.89 ± 0.06	1.11	0.005	+10.73
	oxygen	2.89 ± 0.05	1.01	0.004	+ 6.75
	nitrogen	2.88 ± 0.10	0.97	0.018	- 19.38
	oxygen	3.11 ± 0.01	1.00	0.012	- 10.54

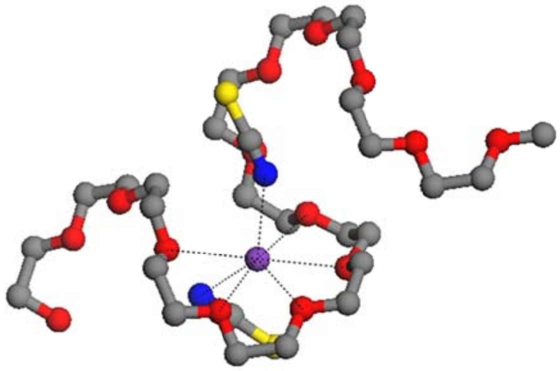

Fig 3. *View of the structure of the PEO$_4$:KSCN complex. Violet sphere, potassium; dark blue, nitrogen; yellow, sulfur; gray, carbon; red, oxygen.*

4. CONCLUSIONS

PEO$_4$:KSCN was examined by EXAFS to determine the local coordination structure around the potassium ion. The best-fit structure for the first solvation shell in the PEO$_4$:KSCN was found to consist of five oxygen atoms and two nitrogen atoms.

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Sittichai Kulawong got a B. Sc. (Chemistry) in 2004 from Ubon Ratchathani University, Thailand, M. S. (Chemistry) in 2008 from Suranaree University of Technology, Thailand, and Ph. D. (Chemistry) in 2013 from Suranaree University of Technology, Thailand. Currently he is a lecturer in the Science and Technology, Nakhon Ratchasima Rajabhat University.

Jittima Chaodamrongsakul got a B. Sc. (Chemistry) in 2000 from Burapha University, Thailand, M. S. (Chemistry) in 2004 from Suranaree University of Technology, Thailand, and Ph. D. (Chemistry) in 2012 from Suranaree University of Technology, Thailand. Currently she is a lecturer in Department of Engineer, Vongchavalitkul University.