XAS Study on Lithium-Ion Conducting Li_2O-SeO_2-B_2O_3 Glass Electrolyte

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The need for solid electrolytes suitable for solid state lithium batteries has led investigations into a number of lithium ion conducting glass electrolytes [1]. Many investigations have aimed at the preparation of glass electrolytes with a very high conductivity by using additive doping or mixed former effect.

We previously reported a glass electrolyte Li_2O-SeO_2-B_2O_3 with high lithium-ion conductivity and wide stability window by mixing two network formers [2]. Although investigations were performed on the structure of the electrolyte using FT-IR, it did not provide sufficient understandings on the lithium-ion conduction mechanism because of its structural complexity.

In this study, we performed XAS (X-ray Absorption Spectroscopy) study on the glasses ,$0.5Li_2O$-$0.5(ySeO_2$-$(1-y)B_2O_3)$, to investigate the lithium-ion conduction mechanism. The present work is devoted to identify the local structure modification around selenium atom by Se K-edge EXAFS/XANES spectroscopy, and bonding character changes of oxygen and boron atoms with surroundings by O K-edge, and B K-edge NEXAFS spectroscopy, respectively.

Figure.1 shows the FTs of Se K-edge EXAFS spectra for $0.5Li_2O$-$0.5(ySeO_2$-$(1-y)B_2O_3)$. It shows a typical spectrum for an amorphous compounds with a very short range ordering, the only main peak is related to the first nearest Se-O coordination sphere (~1.6Å). In Figure.1, Se-O main peak intensity decreases with an increase of SeO_2 content, but no peak shift was observed. It is attributed to magnification of network region made of Se-O bonding as SeO_2 content increases, which means the formation and enlargement of Se-O clusters. From the result, it can be concluded that Se-O clusters exist in the mixed anion matrix. And Se-O clusters can provide more conductive environment due to a more polar nature of selenium cation, which in turn lead to an enhancement of Li ion conductivity.

Figure.2 shows the Se K-edge XANES spectra for the glasses. In Figure.2, the edge shifts toward the lower energy as SeO_2 content increases, which means selenium cation becomes more covalent nature. And from the B K-edge NEXAFS spectra, boron edges shift toward the higher energy, which indicates boron cation becomes more ionic nature. Also from the O K-edge NEXAFS spectra, oxygen ion in the network become more negative. From these results, it can be concluded that SeO_2 forms Se-O network and breaks B-O network as the content of SeO_2 increases, which lead to more depolymerized network.

Based on the above observations, the lithium ion conduction mechanism in the system of Li_2O-SeO_2-B_2O_3 glasses will be discussed.

References
[1] M.Ganguli, M.H.Bhat, K.J.Rao, Solid State Ionics 122 (1999) 23.
[2] C.-H.Lee, K.H.Joo, J.H.Kim, S.G.Woo, H.-J.Sohn, T.Kang, Y.Park, J.Y.Oh, Solid State Ionics 149 (2002) 59.

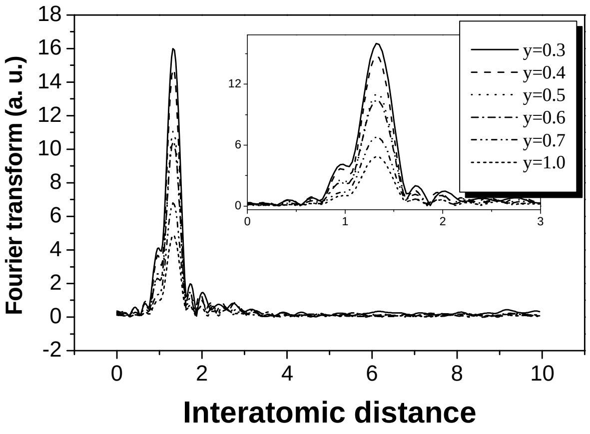

Figure.1 The FTs of Se K-edge EXAFS spectra for $0.5Li_2O$-$0.5(ySeO_2$-$(1-y)B_2O_3)$.

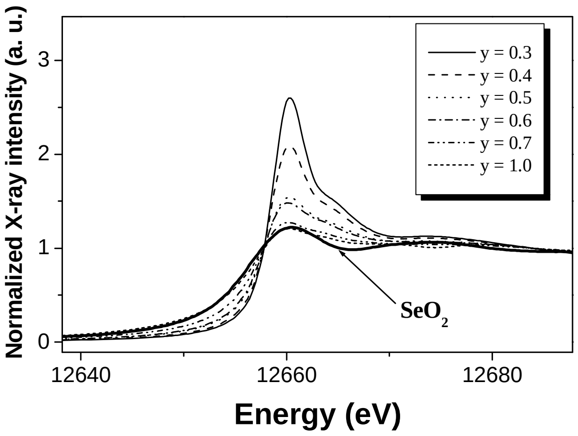

Figure.2 The Se K-edge XANES spectra for $0.5Li_2O$-$0.5(ySeO_2$-$(1-y)B_2O_3)$.