

Ionic Conduction at Interfaces of Solid Electrolytes and Electrodes

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Abstract

Ionic conduction of nano composites of solid electrolytes and electrochemically active materials was studied. The conductivity of nano Li_2SiO_3 was enhanced by heterogeneous doping of nano TiO_2 while nano Li_xTiO_2 reduced the conductivity. Addition of FePO_4 decreased the activation energy of the conduction, which is accompanied by lattice expansion of Li_2SiO_3 in the composite. The results may be accounted for by ionic transfer through the interface given rise to by difference of chemical potential of lithium ions between the solid electrolytes and the active materials.

Introduction

To improve performance of all-solid-state lithium secondary batteries, it is important to understand phenomena at interfaces between electrode and electrolyte materials and fabricate ideal interfaces. At the solid-solid interfaces, formation of electrical double layer by difference of chemical potential and the change of ionic conduction behavior by disorder of crystal structure are expected. In the present study we prepared nano-composites of active materials and a solid electrolyte that have large interface area, and report the local structure and ionic conduction at nano heterogeneous interface.

Experimental

Li_2SiO_3 was employed as a Li^+ conductor, whose nano particle (ave. 54 nm in diameter) was obtained by ball-milling of commercial powder (particle size: 1~10 μm). Electrochemically active TiO_2 , Li_xTiO_2 or FePO_4 nano particles was mixed with the Li_2SiO_3 nano particles using a ball-mill. As TiO_2 nano particle, anatase TiO_2 (JRC-TIO-1, Ishihara Sangyo) with an average particle size of 11 nm was used. Li_xTiO_2 ($x \sim 0.01$) nano particle was obtained by chemical lithiation to the TiO_2 nano particle using $n\text{-BuLi}$. FePO_4 nano particle was prepared by delithiation of LiFePO_4 (average particle size 800 nm) using NO_2BF_4 . Each nano particle was annealed at 500°C under

an Ar flow before mixing in order to remove adsorbates and defects formed by ball-milling. Average particle sizes of the nano particles were estimated by SEM and BET surface area. Crystal structure of the nano particles and the composites was characterized by XRD, and ionic conductivity was measured by two-terminal AC method. The samples were handled under an Ar atmosphere.

Results and Discussions

SEM-EDX analyses confirmed that $\text{Li}_2\text{SiO}_3\text{-TiO}_2$ composite was uniformly mixed. XRD indicated that crystal structures of both Li_2SiO_3 and TiO_2 were not changed by the mixing process. As shown in Fig. 1, ionic conductivity was enhanced by mixing TiO_2 and reached maximum when 40% of TiO_2 was mixed. Activation energies of all samples were same (~ 1.2 eV), meaning that ionic conduction mechanism was same, i.e., vacancy migration. The results suggest the ionic conductivity in the $\text{Li}_2\text{SiO}_3\text{-TiO}_2$ system is enhanced by the space charge layer effect, which is supposed to be given rise to by difference of chemical potential of lithium ions between the active materials and the solid electrolytes. To investigate this model, Li_xTiO_2 that exhibits higher chemical potential of lithium, $\mu(\text{Li}^+)$, than TiO_2 , and FePO_4 with lower $\mu(\text{Li}^+)$ were used as the active materials. As shown in Fig. 2, ionic conductivity decreased by Li_xTiO_2 mixing. This is because vacancies didn't increase at the interface and insulating Li_xTiO_2 decreased total ionic conductivity of the composite. This model was also supported by the fact that the crystal structure and the activation energy of the conductivity didn't change. On the other hand, FePO_4 increased the ionic conductivity and decreased the activation energy. XRD patterns showed expansion of the unit cell volume of Li_2SiO_3 by 1.3%. This suggests that FePO_4 trapped many lithium ions strongly, and thus generated many negative vacancies expanded the lattice by the electrostatic repulsion, which decreased the migration enthalpy of the vacancies.

Conclusion

It was found that difference of $\mu(\text{Li}^+)$ between active materials and electrolytes caused change in the vacancy concentration and ionic conductivity.

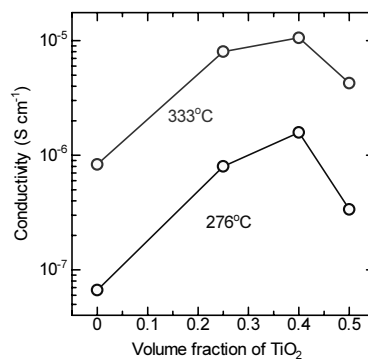


Fig. 1 Composition dependence of conductivity of $\text{Li}_2\text{SiO}_3\text{-TiO}_2$ nano-composites.

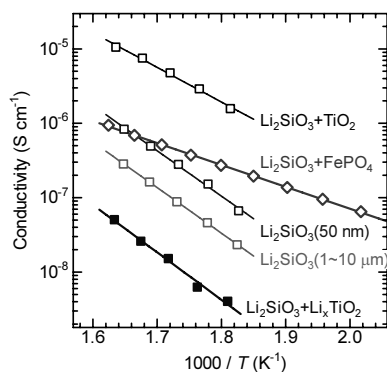


Fig. 2 Temperature dependence of the conductivity of each composite.