Evaluation of structures of poly(ethylene carbonate) solid polymer electrolytes by small-angle neutron scattering

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Solid polymer electrolytes (SPEs) are expected to be used as next-generation battery materials, but their ionic conductivity has still not reached a practical level. It is important to understand the ion conduction mechanism of SPEs at the molecular level, as well as to improve/modify the polymer species used in SPEs. In many previous studies, poly(ethylene oxide) (PEO) has been widely used as a polymer matrix in SPEs. However, PEO tends to crystallize, and the ionic conductivity of PEO-type SPEs decreases rapidly at around room temperature. To address this issue, we focused on poly(ethylene carbonate) (PEC) as a new polymer species. While PEC has been reported to exhibit excellent ionic conduction/battery properties as SPE [1], its fundamental properties are still not understood well. Based on the above background, the purpose of this study was set to understand the structures of PEC-type SPEs by small-angle neutron scattering (SANS) as part of understanding their fundamental properties.

Poly(ethylene carbonate/ethylene oxide) P(EC/EO) copolymers were synthesized by polymerizing EC monomers [2]. To obtain the contrast in SANS, hydrogenated and deuterated (*h*- and *d*-, respectively) EC monomers were polymerized to prepare *h*- and *d*-P(EC/EO)s, which have the molecular weight of ca. 10 kg/mol and EO/EC monomer unit ratio [EO]/[EC] $\approx$ 2. The *d*- and *h*-P(EC/EO)s were blended at a weight ratio of 90/10 with various weight ratios (w_{Li} = 0~0.67) of lithium salt, lithium bis(trifluoromethanesulfonyl) imide (LiTFSI), for SANS measurements. As for the reference, the corresponding PEO/LiTFSI samples were also prepared. These blended samples were prefilled into an assembled cell by the solvent casting method in our laboratory. SANS measurements were performed at the SANS-U beamline with the sample-to-detector distance at 1 and 8 m, and the wavelength of neutron beam at 7 Å. After a series of measurements at different temperatures (20, 50 and 80 °C) were performed.

Figure 1 shows the SANS profiles of P(EC/EO)/LiTFSI blends at different w_{Li} measured at 20 °C. Figure 1 shows that the SANS data varies with changing w_{Li}. That is, the scattering intensity $I(q)$ in the whole scattering vector q region significantly decreases with increasing w_{Li}. This result itself is reasonable because the concentration of polymers as the scatterer decreases with increasing w_{Li}. We also confirmed that P(EC/EO) chains are basically in amorphous state, which is different from conventional PEO systems. We had previously performed SANS measurements on the same samples at the TAIKAN beamline at J-PARC, and found good agreement between some data measured at SANS-U and TAIKAN. Importantly, the SANS-U data can cover the lower q side than the TAIKAN data, which allows us a more accurate discussion of the P(EC/EO) chain conformations. We are currently analyzing the obtained SANS data, and in the future we will discuss the w_{Li} dependence of the conformations of P(EC/EO) chains in SPEs.

[1] Y. Tominaga, Polymer Journal 2017, 49, 291.
[2] R. F. Storey, D. C. Hoffman, Macromolecules 1992, 25, 5369.

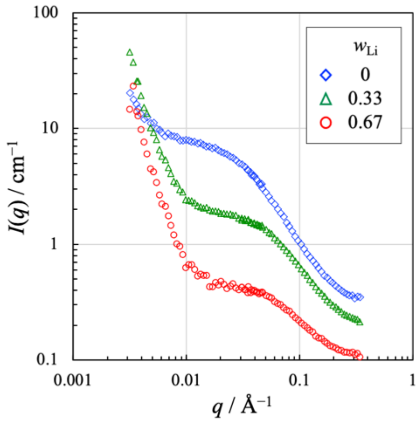

Fig. 1. SANS profiles of P(EC/EO)/LiTFSI with different w_{Li} measured at 20 °C.