MLF Experimental Report	提出日 Date of Report
課題番号 Project No. 2015A0062 実験課題名 Title of experiment Intermediate-range structure of concentrated lithium electrolyte 実験責任者名 Name of principal investigator Tsuyoshi Yamaguchi 所属 Affiliation Nagoya University	装置責任者 Name of responsible person Toshiya Otomo 装置名 Name of Instrument/（BL No.） NOVA / BL21 実施日 Date of Experiment Nov. 1, 2015 - Nov. 4, 2015

試料、実験方法、利用の結果得られた主なデータ、考察、結論等を、記述して下さい。（適宜、図表添付のこと）
Please report your samples, experimental method and results, discussion and conclusions. Please add figures and tables for better explanation.

1. 試料 Name of sample(s) and chemical formula, or compositions including physical form.

1) Propylene carbonate (PC)-h_6, liquid
2) PC-d_6, liquid
3) PC-m_6 (1:1 mixture of PC-h_6 and PC-d_6), liquid
4) $^{7}LiClO_4$ in PC-d_6 (3 mol/kg), liquid
5) $^{0}LiClO_4$ in PC-d_6 (3 mol/kg, ^{0}Li stands for the mixture of ^{7}Li and ^{6}Li whose scattering length is zero), liquid
6) $^{6}LiClO_4$ in PC-d_6 (3 mol/kg), liquid
7) $^{7}LiClO_4$ in PC-m_6 (3 mol/kg), liquid
8) $^{7}LiClO_4$ in PC-h_6 (3 mol/kg), liquid

2. 実験方法及び結果（実験がうまくいかなかった場合、その理由を記述してください。）
Experimental method and results. If you failed to conduct experiment as planned, please describe reasons.

The neutron diffraction of the above eight samples were measured at NOVA / BL21. All the liquid samples were contained in vanadium cells, which were pressed into planer form whose path length was 2 mm. The energy spectrum of the incident beam was determined from the scattering from a vanadium plate, and the contribution of the scattering from the vanadium cell was subtracted by measuring the scattering from an empty cell. The data accumulation times were varied from 3 to 9 hours, depending on the neutron absorbance of the samples and the condition of the beam source.

Figures 1 and 2 show the variation of the diffraction patterns with changing the isotopes of Li and H, respectively. The diffraction patterns determined from the data at 17° were plotted, and the contribution of the incoherent scattering was not subtracted. The diffraction patterns in the figures were arbitrarily scaled and shifted for visibility. A prepeak was observed at 0.8 $Å^{-1}$ in all the spectra except for that of $^{7}LiClO_4$ / PC-m_6. The strength of the prepeak gradually decreased with increasing the scattering length of lithium from -2.22 fm (^{7}Li) to +2.00 fm (^{6}Li) as is exhibited in Fig. 1. More interesting is the H isotope effects in Fig. 2. Although the prepeak was observed both in PC-d_6 and PC-h_6, the prepeak disappeared in the case of their 1:1 mixture.

2. 実験方法及び結果（つづき） Experimental method and results (continued)

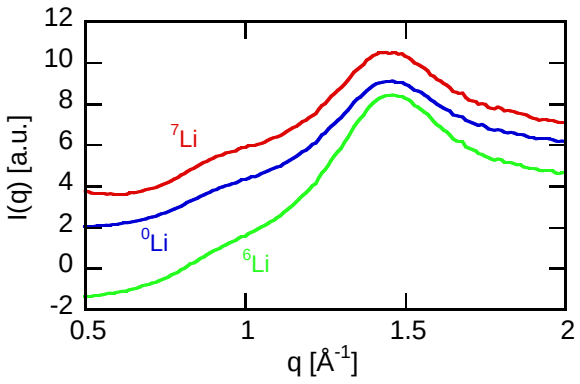

Fig. 1. Li isotope effects on the diffraction patterns of 3 mol/kg $LiClO_4$ / PC-d_6.

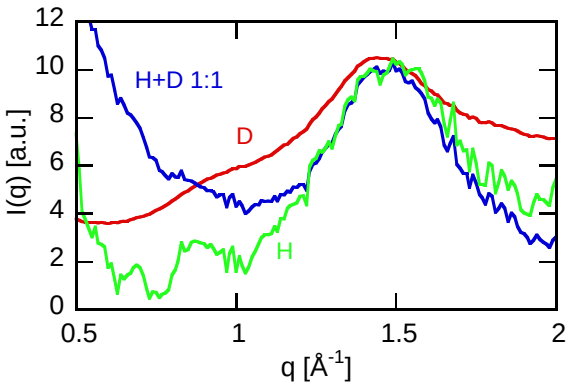

Fig. 2. H isotope effects on the diffraction patterns of 3 mol/kg $^{7}LiClO_4$ / PC.

The prepeak was not observed in neat solvent irrespective of the isotopes of the H-atom, indicating that the intermediate-range structure corresponding to the prepeak was formed by the dissolution of the lithium salt.

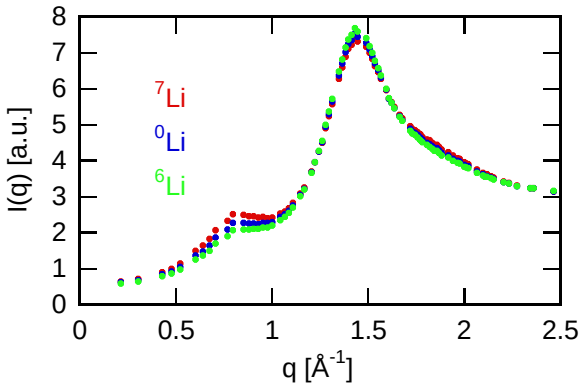

Fig. 3. Li isotope effects on the diffraction patterns of 3 mol/kg $LiClO_4$ / PC obtained by MD simulation.

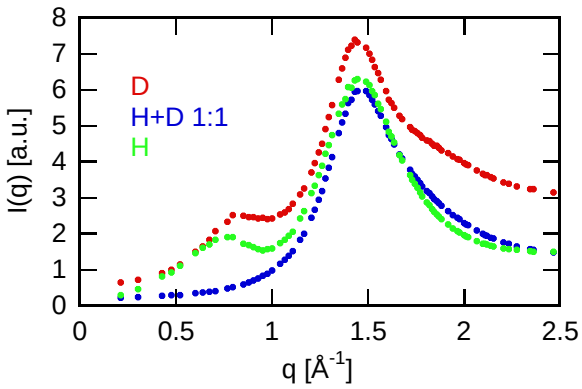

Fig. 4. H isotope effects on the diffraction patterns of 3 mol/kg $LiClO_4$ / PC obtained by MD simulation.

MD simulation study on $LiClO_4$ / PC solution was also performed for the comparison with the diffraction experiment. Several potential models of $LiClO_4$ were tested to reproduce the prepeak structure, and the temperature of the simulation system was elevated up to 500 K to enhance the sampling efficiency. The results of the MD simulation were shown in Figs. 3 and 4. The trends of the experimental isotope effects were reproduced by the MD simulation fairly well. In particular, the disappearance of the prepeak in $LiClO_4$ / PC-m_6 was reproduced as is demonstrated in Fig. 4. A detailed analysis showed that the prepeak originates in the contrast between the ionic and nonpolar domains. Since the scattering length density of the nonpolar domain is larger than that of the ionic domain, the increase in the scattering length of Li decreases the contrast, which leads to the decrease in the prepeak. The partial substitution of D in $LiClO_4$ / PC-m_6 diminishes the contrast, and the contrast was inverted by the further substition in $LiClO_4$ / PC-h_6, resulting in the reappearance of the prepeak.

Further analyses of the experimental data are now in progress to extract the coherent diffraction pattern by subtracting the contribution of the incoherent scattering.