

Supporting Information of "Analysis of Prepeak Structure of Concentrated Organic Lithium Electrolyte by Means of Neutron Diffraction with Isotopic Substitution and Molecular Dynamics Simulation"

Tsuyoshi Yamaguchi,^{a,} Koji Yoshida,^b Toshio Yamaguchi,^b Yasuo Kameda,^c Kazutaka Ikeda,^d and
Toshiya Otomo^d*

^a Department of Molecular Design and Engineering, Graduate School of Engineering, Nagoya
University, Furo-cho, Chikusa, Nagoya, Aichi 464-8603, Japan

^b Department of Chemistry, Faculty of Science, Fukuoka University, Nanakuma, Jonan, Fukuoka 814-
0180, Japan

^c Department of Material and Biological Chemistry, Faculty of Science, Yamagata University, 1-4-12,
Kojirakawa-machi, Yamagata City, Yamagata 990-8560, Japan

^d High Energy Accelerator Research Organization (KEK), Tsukuba, Ibaraki 305-0801, Japan

E-mail: tyama@nuce.nagoya-u.ac.jp (T. Yamaguchi)

CORRESPONDING AUTHOR: E-mail: tyama@nuce.nagoya-u.ac.jp, Tel: +81-52-789-3592, Fax: +81-
52-789-3273.

S1. Calibration of the effects of inelastic scattering

In the present analysis, the inelasticity correction was carried out by employing scattering intensity observed for the null-H₂O (a mixture of H₂O and D₂O with molar ratio of 0.64 and 0.36, the average scattering length of hydrogen atom is 0) sealed in thin walled vanadium cell (2 mm t × 14mm w, wall thickness of 0.1 mm). The scattering intensity from the null-H₂O measured by the NOVA spectrometer was corrected for absorption and multiple scattering and converted to the absolute scale using corrected scattering intensity from a vanadium slab (1.5 mm t). The O-O partial structure factor of liquid water was then subtracted from the corrected scattering intensity from the null-H₂O to obtain the inelasticity correction term for the null-H₂O which is dominated by inelasticity distortion of the scattering intensity from the H atom. The correction term multiplied by the factor α was subtracted from the scattering intensity observed for the LiClO₄ / PC solution to obtain the inelasticity corrected scattering intensity. The factor α was determined so that the corrected scattering intensity data sets for different scattering angles between 13.1 and 27.9° well agree within experimental uncertainties.

S2. Temperature dependence of the structure factor from MD simulation with Model 1

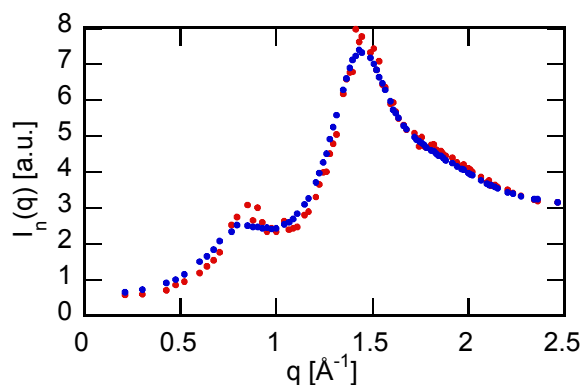


Figure S1. The structure factors, $I_n(q)$, of $^7\text{LiClO}_4$ / PC- d_6 solution at 350 K (red) and 500 K (blue) obtained by MD simulation with Model 1.

Since the temperature of our MD simulation, 500 K, is much higher than that of the experiment, 298 K, one may consider that the structure obtained by the MD simulation does not reflect the structure of the real solution. In order to resolve the question, we performed a simulation run at 350 K using Model 1, and the obtained structure was compared with that at 500 K. The density of the run at two different temperatures were the same, and the lengths of the equilibration and production runs at 350 K were 20 ns and 100 ns, respectively.

The structure factors of $^7\text{LiClO}_4$ / PC- d_6 at two different temperatures were plotted together in Fig. S1 for comparison. The temperature dependence of $I_n(q)$ is small, and we consider that the MD simulation at 500 K captures the essential feature of the liquid structure at 298 K. The scattering of the data is larger at the lower temperature, which is ascribed to the poorer statistics owing to the slower relaxation of the scattering length density mode.

S3. Solvation structure of Li^+ ion in three different models

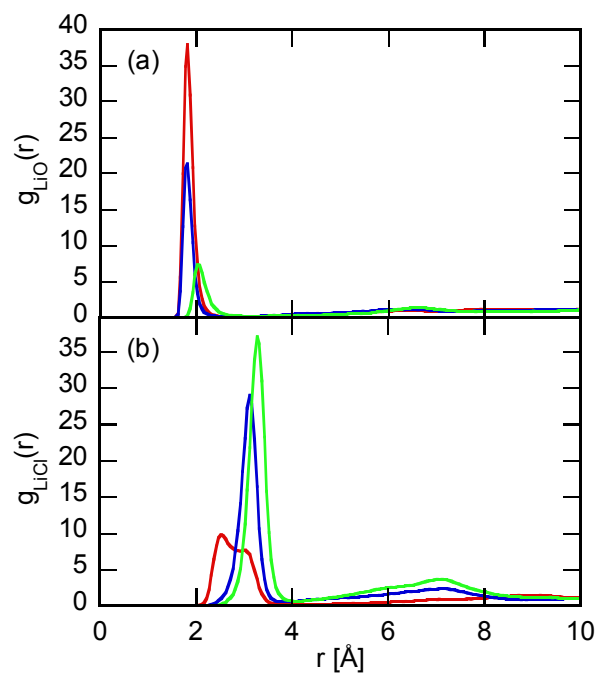


Figure S2. The radial distribution functions between (a) Li-O and (b) Li-Cl atoms calculated by Models 1 (red), 2 (blue) and 3 (green) are plotted, where the O-atom stands for the carbonyl oxygen atom of solvent PC.

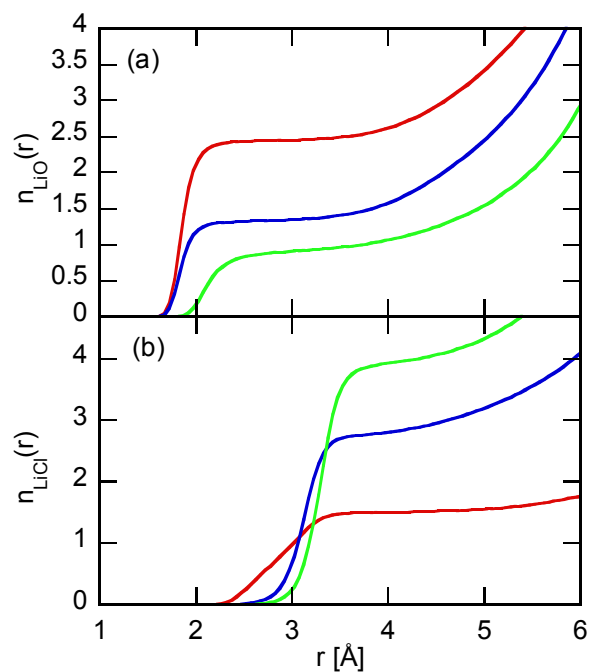


Figure S3. The running coordination numbers between (a) Li-O and (b) Li-Cl atoms calculated by Models 1 (red), 2 (blue) and 3 (green) are plotted, where the O-atom stands for the carbonyl oxygen atom of solvent PC.