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 MLF Experimental Report	提出日 Date of Report July 31, 2017
課題番号 Project No. BL21 2016B0014 実験課題名 Title of experiment Li⁺ solvation structure in glyme-Li salt molten complexes 実験責任者名 Name of principal investigator Kazuhide Ueno 所属 Affiliation Yokohama National University	装置責任者 Name of responsible person Toshiya Otomo 装置名 Name of Instrument/(BL No.) BL 21 NOVA 実施日 Date of Experiment February 18-21, 2017

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. [Li(G3)][OTf]; G3: triglyme, OTf: triflate, 2 different isotopes (⁶ Li/ ^{nat} Li). LiClO ₄ /3SL concentrated electrolytes; ClO ₄ : perchlorate, SL: sulfolane, 2 different isotopes (⁶ Li/ ^{nat} Li) 1.0 M LiTfSA in DMF-d ₇ solution, TfSA: bis(trifluoromethylsulfonyl)amide, 2 different isotopes (⁶ Li/ ^{nat} Li) 3.2 M LiTfSA in DMF-d ₇ solution, 2 different isotopes (⁶ Li/ ^{nat} Li) LiTfSA/2SL concentrated electrolytes; 2 different isotopes (⁶ Li/ ^{nat} Li) LiTfSA/4DMSO-d ₆ concentrated electrolytes, 2 different isotopes (⁶ Li/ ^{nat} Li)

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. Experimental Method: Cylindrical Vanadium cells with 6mm in inner diameter was used for ¹ H-enriched samples while the cylindrical cells with 10 mm in inner diameter was used for deuterated samples. Neutron scattering measurements were performed at room temperature using the NOVA spectrometer installed at BL21 of the MLF. The exposure time was set to 4-8 h for ⁶ Li-enriched samples whereas it was allowed to be 2-4 h for ⁷ Li-enriched samples at the condition of accelerator beam power of 150 kW. Data were analyzed in a similar way as reported in our previous works. Despite large absorption cross section, absorption correction for ⁶ Li-enriched sample has already been confirmed to work satisfactorily with our data analysis program. Inelasticity contributions involved in scattering data for solvents could be cancelled out by taking difference between observed scattering cross sections for ⁶ Li- and ⁷ Li-enriched samples. The first-order difference function, ΔLi(Q), was derived from the difference between ⁶ Li- and ⁷ Li-enriched samples. The environmental distribution function around Li ⁺ (i.e., radial distribution function of Li ⁺) was obtained from Fourier transform of the observed ΔLi(Q).
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2. 実験方法及び結果(つづき) Experimental method and results (continued)

Results:

[Li(G3)][OTf] has melting point above room temperature, but is prone to forming a supercooled liquid (i.e., it remain as liquid at room temperature for long time). However, [Li(G3)][OTf] was partially crystallized in the Vanadium cell during measurements for the long exposure time, and the strong diffraction peak emerged in the obtained data unfortunately. Despite small signal-to-noise ratio, we could analyzed the $\Delta\text{Li}(Q)$ data for [Li(G3)][OTf] with ^{67}Li isotopic substitution, its Fourier transform gave a strong peak at $r = 2.11 \text{ \AA}$ in the distribution function of lithium ions, $G_{\text{Li}}(r)$.

The much clearer results with high signal-to-noise ratio were obtained for the samples with deuterated solvents, such as 1.0 M LiTFSA in DMF-d7 solution, 3.2 M LiTFSA in DMF-d7 solution, LiTFSA/4DMSO-d6 concentrated electrolyte. Li-O distance was reflected as a nearest neighbor peak at 1.96 \AA for LiTFSA/4DMSO-d6 concentrated electrolyte. A strong peak was observed at $r = 1.93 \text{ \AA}$ corresponding to Li-O distance for both 1.0 M and 3.2 M LiTFSA in DMF-d7 solutions, independent of the salt concentration. Probably, Li-Li correlations corresponds to 3.00 and 2.92 \AA for 1.0 M and 3.2 M LiTFSA in DMF-d7, respectively.

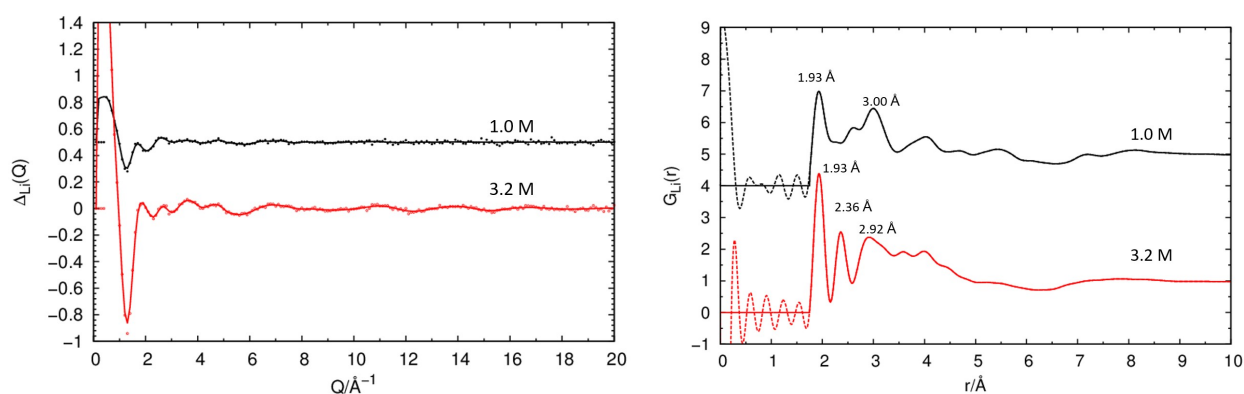


Fig. $\Delta\text{Li}(Q)$ (left) and $G_{\text{Li}}(r)$ (right) of lithium ions for 1.0 M LiTFSA in DMF-d7 and 3.2 M LiTFSA in DMF-d7 solutions.

We successfully obtained reasonable data for the other samples with protonated solvents, such as $\text{LiClO}_4/3\text{SL}$ concentrated electrolytes, LiTFSA/2SL concentrated electrolytes. Fourier transform of the $\Delta\text{Li}(Q)$ data showed a peak at 1.91 and 1.86 \AA for $\text{LiClO}_4/3\text{SL}$ concentrated electrolytes and LiTFSA/2SL concentrated electrolytes, respectively, although these analysis needs to be optimized in more detail.

Further analysis of liquid structure of these concentrated electrolytes will be performed on molecular dynamic simulation on the basis of the obtained distribution function of lithium ions here. This will lead to understanding the poor solubility of lithium polysulfides species in these concentrated electrolytes, and the feedback allows us to newly design the more appropriate liquid electrolytes for high-energy density and long-lived lithium sulfur battery.