Supplementary Information:

Li⁺ Solvation in Glyme-Li Salt Solvate Ionic Liquids

Kazuhide Ueno, a Ryoichi Tatara, a Seiji Tsuzuki, b Sohi Saito, c Hiroyuki Doi, c Kazuki Yoshida, a Toshihiko Mandai, a Masaru Matsugami, d Yasuhiro Umebayashi, c Kaoru Dokko, a Masayoshi Watanabe a

a Department of Chemistry and Biotechnology, Yokohama National University, 79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan

b Research Initiative of Computational Sciences (RICS), Nanosystem Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), 1-1-1 Umezono, Tsukuba, Ibaraki 305-8568, Japan

c Graduate School of Science and Technology, Niigata University, 8050 Ikarashi, 2-no-cho, Nishi-ku, Niigata City, 950-2181, Japan

d Faculty of Liberal Studies, Kumamoto National College of Technology, 2659-2 Suya, Koshi, Kumamoto 861–1102, Japan

AUTHOR EMAIL ADDRESS: mwatanab@ynu.ac.jp
Figure S1. Typical results on the deconvolutions of Raman spectra into four bands at around 810, 835, 850, and 873 cm$^{-1}$, by the Gaussian-Lorentzian function.

Figure S2. Normalized Raman spectra of (a) G3-Li[TFSA] mixtures, (b) G3-Li[OTf] mixtures, (c) G4-Li[BETI] mixtures, (d) G4-Li[TFSA] mixtures, (e) G4-LiClO$_4$ mixtures, and (f) [Li(G4)$_1$]X.
Figure S3. Ionic conductivity plotted against Li salt concentration in the G3-Li[TFSA] and the G3-Li[OTf] mixtures at 30 °C.

Electrode potentials of Li/Li⁺.

The electrode potential $E_2$ was calculated by the following procedure, with $c_f$ values obtained from Raman spectroscopic analysis (Table S1).

Table S1. Estimated value of concentration of free G3 in [Li(G3)n][TFSA] at 30 °C by Raman study.

<table>
<thead>
<tr>
<th></th>
<th>$c_f$ (mol%)</th>
<th>$c_f$ (mol dm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Li(G3)$_3$][TFSA]</td>
<td>2.3</td>
<td>0.071</td>
</tr>
<tr>
<td>[Li(G3)$_{1.2}$][TFSA]</td>
<td>17</td>
<td>0.58</td>
</tr>
<tr>
<td>[Li(G3)$_{1.5}$][TFSA]</td>
<td>22</td>
<td>0.78</td>
</tr>
<tr>
<td>[Li(G3)$_2$][TFSA]</td>
<td>35</td>
<td>1.4</td>
</tr>
<tr>
<td>[Li(G3)$_4$][TFSA]</td>
<td>65</td>
<td>3.0</td>
</tr>
</tbody>
</table>

The potential $E_2^0$ of the reference electrode, Li/Li⁺ in 1 mol dm$^{-3}$ Li[TFSA]/G3 (=Li(G3)$_{4.8}$)[TFSA]) can be written as:

$$E_2^0 = E_2^0 + \frac{2.303RT}{F} \log \frac{1}{3.8} = 0$$

$$\Leftrightarrow E_2^0 = E_2^{0'} + \frac{2.303RT}{F} \log 3.8$$

(Substitution Eq. S1 in Eq. 7, we get:)
where $E_2^{0'}$ is 0, because it represents the reference electrode potential. Thus, we can calculate $E_2$ by substituting $a_{[\text{Li(glyme)}]^+} = c_{\text{Li}}$ and $a_{\text{glyme}} = c_G - c_{\text{Li}}$ in the dilute solutions ($c_{\text{Li}} \leq 1 \text{ mol dm}^{-3}$ for G3-Li[TFSA] mixtures), and $a_{[\text{Li(glyme)}]^+} = c_{\text{Li}}$, $a_{\text{glyme}} = c_f$ in the concentrated regime ($c_{\text{Li}} > 1 \text{ mol dm}^{-3}$) in Figure 9.

Although we assume $a_{\text{Li}^+} (= a_{[\text{Li(glyme)}]^+}) = c_{\text{Li}}$ for the sake of simplicity, the activities can indeed be represented as $a_{\text{Li}^+} (= a_{[\text{Li(glyme)}]^+}) = c_{\text{Li}} \gamma_{\text{Li}}$ with the activity coefficient of Li$^+$ ($\gamma_{\text{Li}}$). If the activity coefficient is taken into consideration, the Nernst equation of the electrode reaction; $\text{Li}^+ + e^- \rightleftharpoons \text{Li}$, can be modified as:

$$E_i = E_i^0 + \frac{2.303RT}{F} \log a_{\text{Li}^+} = E_i^0 + \frac{2.303RT}{F} \log \gamma_{\text{Li}} + \frac{2.303RT}{F} \log c_{\text{Li}}$$

(S3)

The electrode potential ($E_i^{0'}$) in the reference solution of $c_{\text{Li}} = 1 \text{ mol dm}^{-3}$ with the activity coefficient ($\gamma_{\text{Li}, 1\text{M}}$) can be written as:

$$E_i^{0'} = E_i^0 + \frac{2.303RT}{F} \log \gamma_{\text{Li}, 1\text{M}} (= 0)$$

(S4).

Substituting Eq. S4 in Eq. S3, we obtain:

$$E_i = E_i^{0'} + \frac{2.303RT}{F} \log \frac{\gamma_{\text{Li}}}{\gamma_{\text{Li}, 1\text{M}}} + \frac{2.303RT}{F} \log c_{\text{Li}}$$

(S5)

In Eq. S5, the first term ($E_i^{0'}$) is 0 because Li/Li$^+$ in 1 mol dm$^{-3}$ Li[TFSA]/G3 is the reference electrode, the second term represents the error caused by the variation of activity coefficient with Li$^+$ concentration, and the third term is a calculable value. Thus, the difference between experimental and calculated values of the electrode potential originated from the second term. Figure S4 indicates that the
activity coefficient ($\gamma_{Li}$) was a little higher than that of the 1 mol dm$^{-3}$ in the lower concentration region (< 1 mol dm$^{-3}$). In the highly concentrated regime, the drastic increase in the electrode potential can also be described by the second term with the activity coefficients in Eq. S5.

In the case of [Li(G3)][TFSA], for example, the experimental data for Li/Li$^+$ electrode potential is 0.230 V, whereas the calculated value is 0.029 V based on Eq. 6, $E = 2.303RT \log \frac{c_{Li}}{F}$ (Figure S4). If the interpretation of the difference between the experimental and calculated values (0.201 V) was imposed to the second term in Eq. S5, $\gamma_{Li}$ must be 2176 times higher than $\gamma_{Li, 1M}$. However, physical meaning of the significantly high $\gamma_{Li}$ is obscure. Instead, we attempted to explain the drastic potential change by considering the activity of the free glymes without imposing the compensation of the activity coefficients.

**Figure S4.** Plots of the experimental and calculated (based on Nernst Equation) value of Li/Li$^+$ electrode potential against common logarithm of the Li salt concentration in [Li(G3)$_n$][TFSA] at 30 °C. Reference electrode was Li/Li$^+$ in 1 mol dm$^{-3}$ Li[TFSA]/G3.

For the modified electrode reaction accompanied by de-solvation process, [Li(glyme)]$^+$ + e$^-$ ⇌ Li + glyme, Nernst equation with the activity coefficients of [Li(glyme)]$^+$ ($\gamma_{[Li(glyme)]^+}$) and glyme ($\gamma_{glyme}$) can be modified as follows:
\[ E_2 = E_2^0 + \frac{2.303RT}{F} \log \frac{a_{[\text{Li(glyme)}^+]} }{a_{\text{glyme}}} = E_2^0 + \frac{2.303RT}{F} \log \frac{\gamma_{[\text{Li(glyme)}^+]}}{\gamma_{\text{glyme}}} + \frac{2.303RT}{F} \log \frac{c_{[\text{Li(glyme)}^+]}}{c_f} \]  
\[ \text{(S6)} \]

The electrode potentials \((E_2')\) in the reference solution with \(c_{[\text{Li(G3)}]^+} = 1 \text{ mol dm}^{-3}\) and \(c_{\text{glyme}} = 3.8 \text{ mol dm}^{-3}\) are;

\[ E_2^{0'} = E_2^0 + \frac{2.303RT}{F} \log \frac{\gamma_{[\text{Li(G3)}]^+,1M}}{\gamma_{G3_{\text{free}},3.8M}} - \frac{2.303RT}{F} \log 3.8 (= 0) \]

\[ \Leftrightarrow E_2^0 = E_2^{0'} - \frac{2.303RT}{F} \log \frac{\gamma_{[\text{Li(G3)}]^+,1M}}{\gamma_{G3_{\text{free}},3.8M}} + \frac{2.303RT}{F} \log 3.8 \]  
\[ \text{(S7)} \]

Substituting Eq. S7 in Eq. S6, we obtain:

\[ E_2 = E_2^{0'} + \frac{2.303RT}{F} \log \frac{\gamma_{[\text{Li(glyme)}^+]}}{\gamma_{[\text{Li(G3)}]^+,1M}} + \frac{2.303RT}{F} \log \frac{\gamma_{G3_{\text{free}},3.8M}}{\gamma_{\text{glyme}}} + \frac{2.303RT}{F} \log 3.8 + \frac{2.303RT}{F} \log \frac{c_{[\text{Li(glyme)}^+]}}{c_f} \]  
\[ \text{(S8)} \]

In Eq. S8, the first term is 0 because Li/Li\(^+\) in 1 mol dm\(^{-3}\) Li[TFSA]/G3 is reference electrode, the second and third terms represent the error caused by the change in the activity coefficients of the complex cation and the free glymes against Li\(^+\) concentration, the fourth term is constant, and the fifth term is a calculable value. The drastic increase in the potential at high concentrations can be explained by the fifth term as \(c_{G3_{\text{free}}}\) in the denominator. However, the difference between experimental and calculated values in Figure 9 could originate from the second and third terms, as well as Eq. S5.