Supplementary Information (SI)

Solvent effects on Li ion transference number and dynamic ion correlations in glyme- and sulfolane-based molten Li salt solvates

Keisuke Shigenobu [1], Kaoru Dokko [1], Masayoshi Watanabe [2] and Kazuhide Ueno [1,*]

[1]Department of Chemistry and Life Science, Yokohama National University, 79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan

[2] Institute of Advanced Sciences, Yokohama National University, 79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan.

*CORRESPONDING AUTHOR FOOTNOTE: Telephone/Fax: +81-45-339-3951. E-mail: ueno-kazuhide-rc@ynu.ac.jp

Salt diffusion coefficients

The salt diffusion coefficients (D_{salt}) were measured according to past literature.[1] The experiments were performed using the Li symmetric cells prepared in the same way as for the potentiostatic polarisation method, for measuring the Li^+ transference number t_{Li}^{PP}. First, the cell was polarised to 10 mV in potentiostatic mode. After the cell reached the steady state, it was relaxed until the potential returned to its initial value (i.e., the value before polarisation). Here, the potential relaxation plots ($U(t)$) were fitted to Eq. S1 in order to calculate the salt diffusion coefficient within a porous separator (D_S).

$$U(t) = V_0 + ae^{-bt} \quad (Eq. S1)$$

V_0 is the offset potential; a and b are the fitting parameters; and D_S was calculated using the following equation (Eq. S2).

$$D_S = \frac{L^2 b}{\pi^2} \quad (Eq. S2)$$

where L is the thickness of the separator. For the calculation of Onsager coefficients, the salt diffusion coefficients within separator-free electrolytes (D_{salt}) should be used. Here, D_{salt} was obtained by correcting the salt diffusion coefficients within the separator with the tortuosity, τ, of the separator, which is estimated from conductivity data and separator porosity (0,88), as follows:

$$D_{Salt} = \tau D_S \quad (Eq. S3)$$

Calculation of Onsager transport coefficients

Based on the Onsager reciprocal relations, the ionic conductivity σ_{ion} is described as shown below.[2,3]

$$\sigma_{ion} = \sigma_{++} + \sigma_{--} - 2\sigma_{+-} \quad (Eq. S4)$$

Here, three Onsager coefficients (σ_{++}, σ_{--} and σ_{+-}) can be calculated from four parameters (A_1~ A_4) which are defined by the experimentally obtained quantities, σ_{ion}, t^{PP}_{Li}, D_{salt} and $d\Delta\varphi/dln(c)$ [26].

$$A_1 \equiv \sigma_{ion} = \sigma_{++} + \sigma_{--} - 2\sigma_{+-} \#(Eq.S5)$$

$$A_2 \equiv \sigma_{ion} \cdot t^{PP}_{Li} = \sigma_{++} - \frac{(\sigma_{++})^2}{\sigma_{--}} \#(Eq.S6)$$

$$A_3 \equiv \frac{D_{salt} \cdot \sigma_{ion} \cdot c \cdot F^2}{2RT} = \left\{\sigma_{++} \cdot \sigma_{--} - (\sigma_{+-})^2\right\} \cdot \frac{dln(a_{\pm})}{dln(c)} \#(Eq.S7)$$

$$A_4 \equiv \frac{d\Delta\varphi}{dln(c)} \cdot \frac{F^2}{2RT} \cdot \sigma_{ion} = (\sigma_{--} - \sigma_{+-}) \cdot \frac{dln(a_{\pm})}{dln(c)} \#(Eq.S8)$$

Three Onsager coefficients are obtained by solving the above four equations (Eq. S5 ~ Eq. S8).

$$\sigma_{++} = \frac{1}{A_2^2 A_4^2} \cdot \left(A_1 A_2^2 A_4^2 - 2A_1 A_2 A_3 A_4 + A_1 A_3^2 + 2A_2^2 A_3 A_4 - A_2 A_3^2\right) \#(Eq.S9)$$

$$\sigma_{--} = \frac{A_3^2 \cdot (A_1 - A_2)}{A_2^2 A_4^2} \#(Eq.S10)$$

$$\sigma_{+-} = \frac{1}{A_2^2 A_4^2} \cdot \left(-A_1 A_2 A_3 A_4 + A_1 A_3^2 + A_2^2 A_3 A_4 - A_2 A_3^2\right) \#(Eq.S11)$$

The two Onsager coefficients, σ_{++} and σ_{--}, are split into the self-terms and the distinct terms:

$$\sigma_{ion} = \sigma^{self}_{+} + \sigma^{distinct}_{++} + \sigma^{self}_{-} + \sigma^{distinct}_{--} - 2\sigma_{+-} \#(Eq.S12)$$

The self-terms, σ^{self}_{+} and σ^{self}_{-}, are derived from the Nernst–Einstein equation by inserting the experimentally obtained diffusivity data, D_{Li} and D_{anion}.

$$\sigma^{self}_{+} = \frac{cF^2 D_{Li}}{RT}, \ \sigma^{self}_{-} = \frac{cF^2 D_{anion}}{RT} \#(Eq.S13)$$

The distinct terms can be calculated by simply subtracting σ^{self}_{+} (and σ^{self}_{-}) from σ_{++} (and σ_{--}).

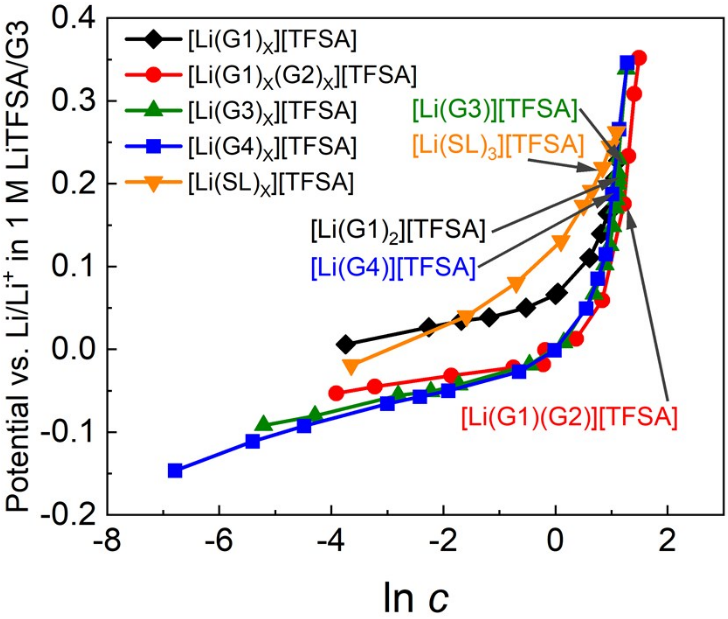

Figure S1. Plots of the Li/Li$^+$ electrode potential against natural logarithm of the Li salt concentration in mixture of LiTFSA in the solvents at 30 °C. The reference electrode was Li/Li$^+$ in 1 mol dm^{-3} Li[TFSA]/G3.

Numerical data

Table S1. Six experimentally obtained parameters for the calculation of Onsager transport coefficients. σ_{ion}, D_{Li}, and D_{TFSA}, of [Li(G3)][TFSA], [Li(G1)$_2$][TFSA] and [Li(G4)][TFSA] are obtained from ref. 16. σ_{ion}, D_{Li}, and D_{TFSA}, of [Li(SL)$_2$][TFSA] and [Li(SL)$_3$][TFSA] are obtained from ref. 18.

Sample	σ_{ion} [mS cm^{-1}]	t_{Li}^{PP}	D_{Li} [10^{-7} cm^2 s^{-1}]	D_{TFSA} [10^{-7} cm^2 s^{-1}]	D_{salt} [10^{-7} cm^2 s^{-1}]	$\frac{d\Delta\varphi}{dln(c)}$
[Li(G3)][TFSA]	1.1	0.028	0.77	0.54	0.53	0.78
[Li(G4)][TFSA]	1.6	0.028	1.26	1.22	0.69	0.65
[Li(G1)$_2$][TFSA]	3.7	0.35	3.25	2.81	5.83	0.35
[Li(G1)(G2)][TFSA]	3.4	0.31	2.78	2.91	6.36	0.74
[Li(SL)$_2$][TFSA]	0.4	0.68	0.35	0.22	0.93	0.17
[Li(SL)$_3$][TFSA]	1.0	0.69	0.98	0.74	2.88	0.19

Table S2. Normalised five transport coefficients of all the electrolytes at 30 °C.

Sample	$\sigma_{+}^{self}/\sigma_{ion}$	$\sigma_{-}^{self}/\sigma_{ion}$	$\sigma_{++}^{distinct}/\sigma_{ion}$	$\sigma_{--}^{distinct}/\sigma_{ion}$	σ_{+-}/σ_{ion}
[Li(G3)][TFSA]	0.79	0.56	−0.65	−0.45	−0.21
[Li(G4)][TFSA]	0.80	0.77	−0.64	−0.39	−0.23
[Li(G1)$_2$][TFSA]	0.94	0.81	−0.32	−0.73	−0.15
[Li(G1)(G2)][TFSA]	1.02	1.07	−0.34	−1.02	−0.13
[Li(SL)$_2$][TFSA]	0.91	0.57	−0.16	−0.48	−0.08
[Li(SL)$_3$][TFSA]	0.81	0.61	−0.03	−0.54	−0.08

List of Symbols

Symbol

A_i Onsager coefficient derivatives

$a_{\pm}$ mean ion activity

c salt concentration (mol dm^{-3})

D_{anion} self diffusion coefficient of anion derived from PFG-NMR (cm^2 s^{-1})

D_{Li} self diffusion coefficient of Li^+ derived from PFG-NMR (cm^2 s^{-1})

F Faraday constant (96485 C mol^{-1})

N_A Avogadro constant (6.022×10^{23} mol^{-1})

R universal gas constant (8.314 J mol^{-1} K^{-1})

T temperature (K)

Greek

σ_{ion} total ionic conductivity measured by ac impedance spectroscopy (mS cm^{-1})

σ_{ij} Onsager coefficients derived from species i and j (mS cm^{-1})

σ^{self} Onsager coefficients derived from Nernst–Einstein equation, self-term (mS cm^{-1})

$\sigma^{distinct}$ Onsager coefficients of distinct term (mS cm^{-1})

References

1. Villaluenga, D. M. Pesko, K. Timachova, Z. Feng, J. Newman, V. Srinivasan and N. P. Balsara, *Journal of The Electrochemical Society*, 2018, **165**, A2766-A2773.
2. F. Wohde, M. Balabajew and B. Roling, *Journal of The Electrochemical Society*, 2016, **163**, A714-A721.
3. D. Dong, F. Sälzer, B. Roling and D. Bedrov, *Physical Chemistry Chemical Physics*, 2018, **20**, 29174-29183.