Supporting Information

Ionic Conduction and Speciation in $LiPF_6$ and $LiBF_4$ Dimethyl Sulfoxide Electrolytes: Comparison with Propylene Carbonate Electrolytes

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The classical theory of ionic conductivity

In general, the ionic conductivity of dilute electrolytes is described by the Nernst–Einstein (NE, eq. S1) and Stokes–Einstein (SE, eq. S2) relations:

$$\kappa = \sum \frac{z_i^2 F^2}{RT} D_i c_i \qquad (1)$$

$$D_i = \frac{k_B T}{6\pi\eta r_i} \ , \qquad (2)$$

where z_i, D_j, c_i, and r_i are the formal charge, diffusion coefficient, concentration, and radius of ionic species i, η is the solution viscosity, and the other symbols have their conventional meanings. The NE relation states that ionic conductivity is determined by the concentration and diffusivity of charge carriers, while the SE relation describes that diffusivity is governed by the solution viscosity and the size of the mobile species. Therefore, the two classical theories dictate that low viscosity and a high concentration of charge carriers are prerequisites to achieve facile ion conduction. However, the NE relation often fails in concentrated solutions, where conduction behavior is complicated by the presence of various ion pairs and non-vehicular conduction modes (e.g., hopping or the Grotthuss-type mechanism). Indeed, the NE relation underestimated the conductivity of concentrated $LiBF_4$–PC solution in the current work, suggesting the emergence of ion hopping conduction.[1]

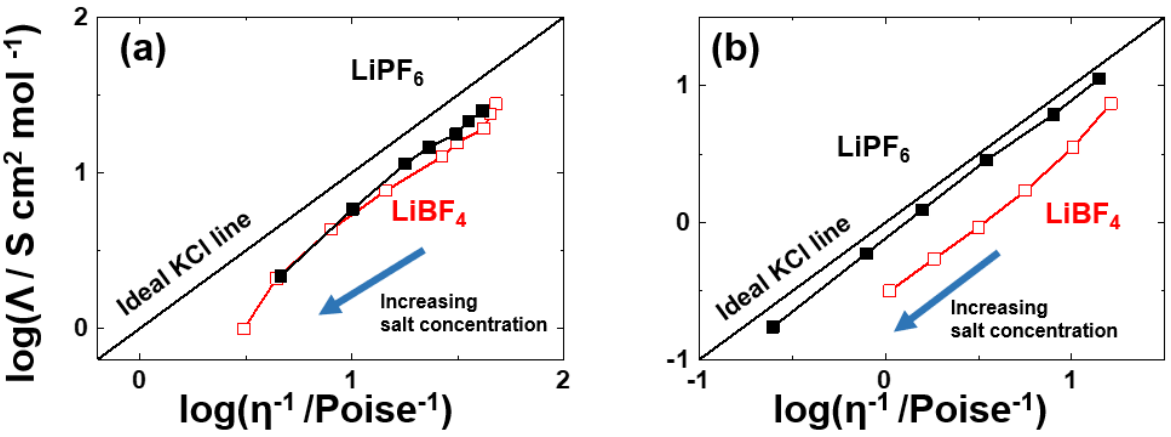

Figure S1. Walden plots of $LiPF_6$– and $LiBF_4$– (a) DMSO and (b) PC solutions at 298 K. (b, Reprinted with permission from Ref. 1, copyright 2018 American Chemical Society)

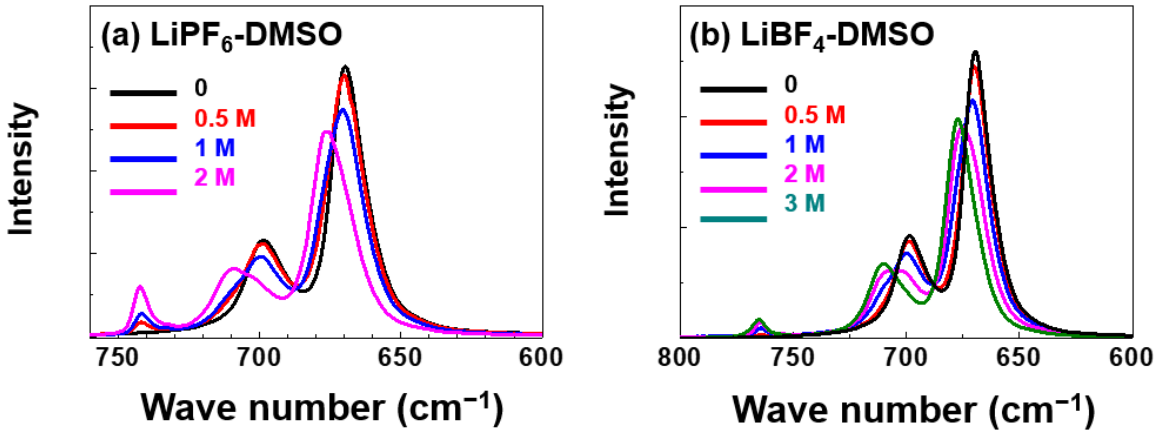

Figure S2. Raman spectra of DMSO solvent and anions in (a) $LiPF_6$–DMSO and (b) $LiBF_4$–DMSO as a function of salt concentration at 298 K.

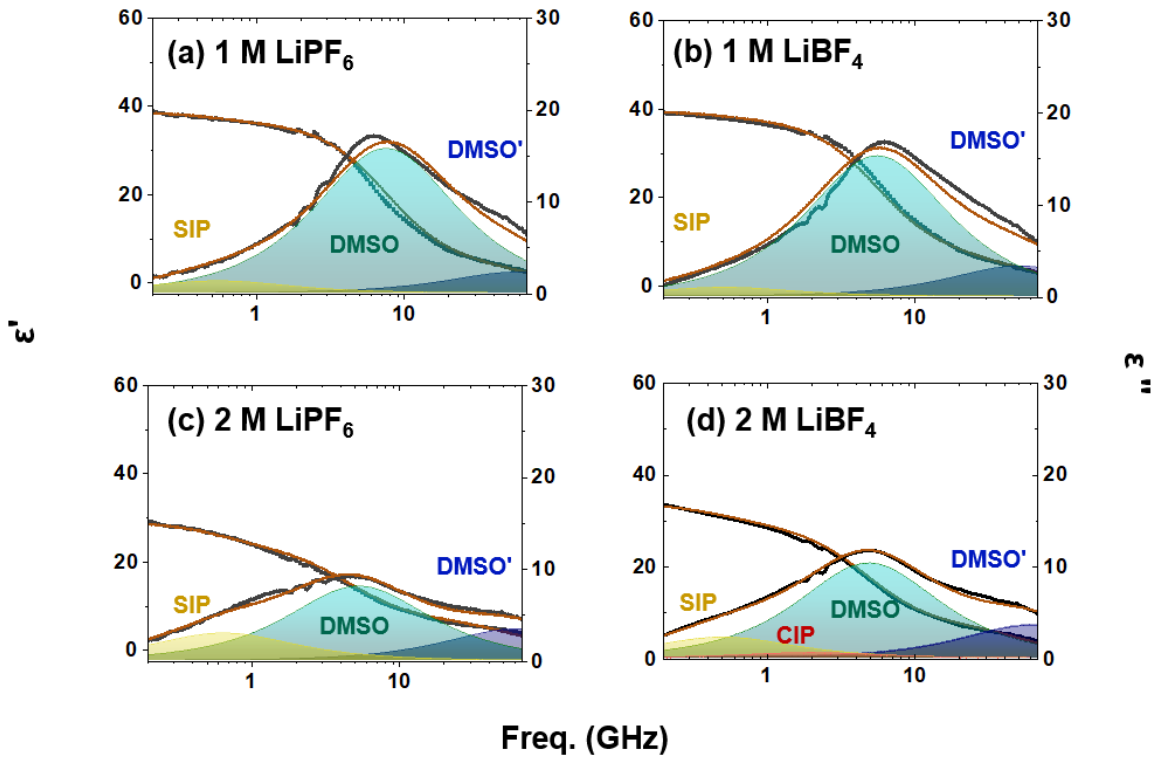

Figure S3. Permittivity ε'(ν) and dielectric loss ε''(ν) of (a) 1 M and (b) 2 M $LiPF_6$–DMSO, and (c) 1 M and (d) 2 M $LiBF_4$–DMSO at 298 K compared with the spectrum calculated with the Debye equation. The highlighted areas show the contributions of the SIP, CIP, and free DMSO solvent (DMSO and DMSO') relaxation process to ε''(ν).

Table S1. Parameters used for deriving the concentrations of ion pairs using the Cavell equation.

Ions/Solvent			Reference
radius (r)	Li^+	0.69	[2]
[Å]	PF_6^-	2.45	[2]
	BF_4^-	2.30	[2]
	PC	2.76	[3]
	DMSO	2.73	[4]
polarizability (α)	Li^+	0.032	[2]
[$Å^3$]	PF_6^-	2.77*	—
	BF_4^-	2.77	[2]
	PC	8.55	[5]
	DMSO	8.28	[4]

* Note that the polarizability of PF_6^- is not available in the literature and is thus assumed to be the same as that of BF_4^-.

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Deriving the concentration of ion pairs (C_{SIP} and C_{CIP}) from dielectric strength (S_{SIP} and S_{CIP})

The following equations are quoted from J. Barthel and R. Buchner's work.[2]

The concentration of ion pairs (C_{IP}) can be derived from their dielectric strength (S_{IP}) as below:

$$C_{IP} = \frac{2\varepsilon_s + 1}{\varepsilon_s} \frac{k_B T \varepsilon_0}{N_A} \frac{(1 - \alpha_{IP} f_{IP})}{\mu_{IP}} S_{IP} \tag{3}$$

where μ_{IP} is the dipole moment, f_{IP} is the reaction-field factor, and α_{IP} is the polarizability of the ion pair.

Here, f_{IP} is given by the following expression:

$$f_{IP} = \frac{3}{4\pi\varepsilon_0 ab^2} \frac{A(1-A)(\varepsilon_s - 1)}{\varepsilon_s + (1-\varepsilon_s)A} \tag{4}$$

where A is

$$A = -\frac{1}{p^2 - 1} + \frac{p}{(p^2-1)^{1.5}} \ln(p + \sqrt{p^2 - 1}) \tag{5}$$

and p (= a/b) is the ratio of major half-axis a = (r_{cation} + r_{anion}+ h)/2 to minor half-axis b = c = max[r_{cation}, r_{anion}] of an ellipsoid, which is an appropriate structural assumption.[2] The r_{cation} and r_{anion} terms are the radius of cation and anion, respectively, and h is the distance between the ion centers (= r_{cation} +r_{anion}+2nr_s), where r_s is the radius of a solvent molecule and n is the number of solvent molecules between the cation and anion (n = 0 for CIP and 1 for SIP).[2]

The polarizability of ion pairs, α_{IP}, is estimated to be $\alpha_{IP} = \alpha_{cation} + \alpha_{anion} + n\alpha_s$, where α_{cation}, α_{anion}, and α_s are the polarizability of the cation, anion, and solvent, respectively. The radius and polarizabilities of the ions and solvent are taken from the literature.[3–6]

The dipole moment of ion pairs, μ_{IP}, is given as below:

$$\mu_{IP} = \mu_0 - \mu_{ind} - n\mu_s \tag{6}$$

where μ_0 is the uncorrected dipole moment simply given by μ_0 = z·e_0·h for symmetric electrolytes, where z_{cation} = |z_{anion}|= z and e_0 is the elementary charge.

The induced dipole moment, μ_{int}, is given by the following equation.

$$\mu_{ind} = \frac{(4\pi\varepsilon_0)h^4 e_0(|z_{anion}|\alpha_{cation} + z_{cation}\alpha_{anion}) + 2h\alpha_{cation}\alpha_{anion}e_0(|z_{anion}| + z_{cation})}{(4\pi\varepsilon_0)h^6 - 4\alpha_{cation}\alpha_{anion}} \quad (7)$$

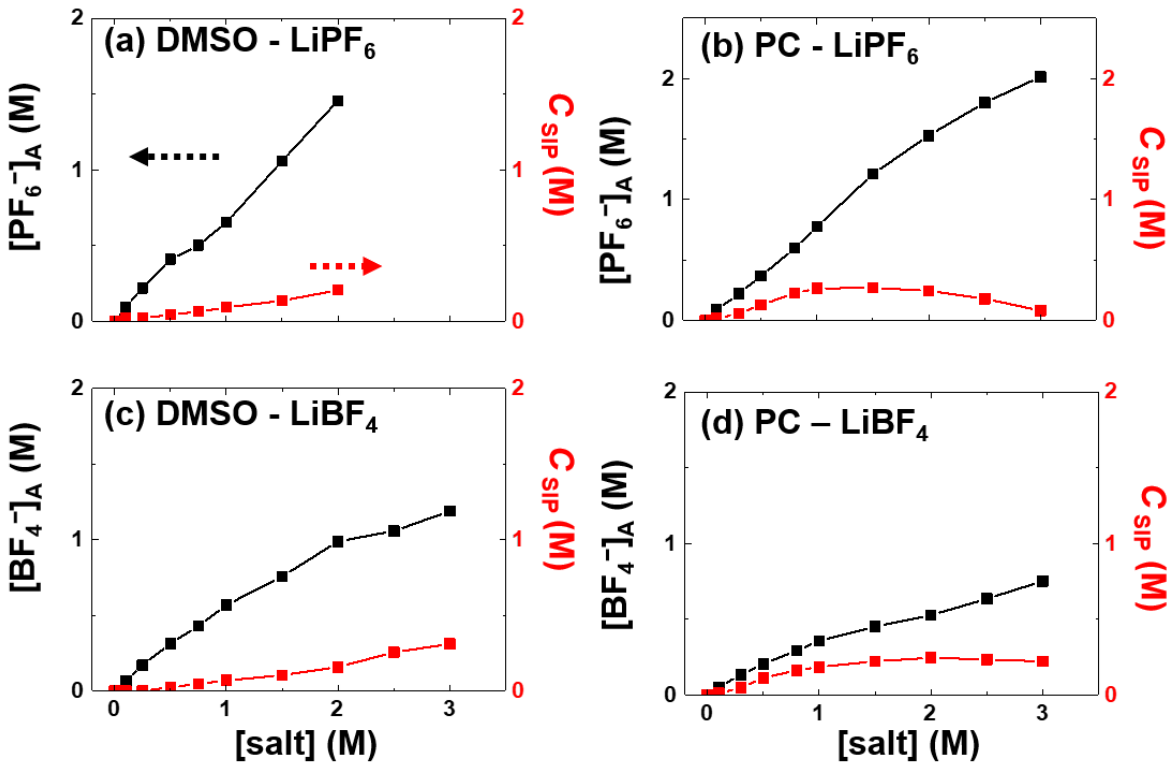

Figure S4. Comparison of the anion concentration obtained from Raman measurements and SIP concentration derived from the dielectric strength of DRS measurements: $[PF_6^-]_A$ vs. C_{SIP} in (a) $LiPF_6$–DMSO and (b) $LiPF_6$–PC. $[BF_4^-]_A$ vs. C_{SIP} in (c) $LiBF_4$–DMSO and (d) $LiBF_4$–PC. (b and d, Reprinted with permission from Ref. 1, copyright 2018 American Chemical Society)

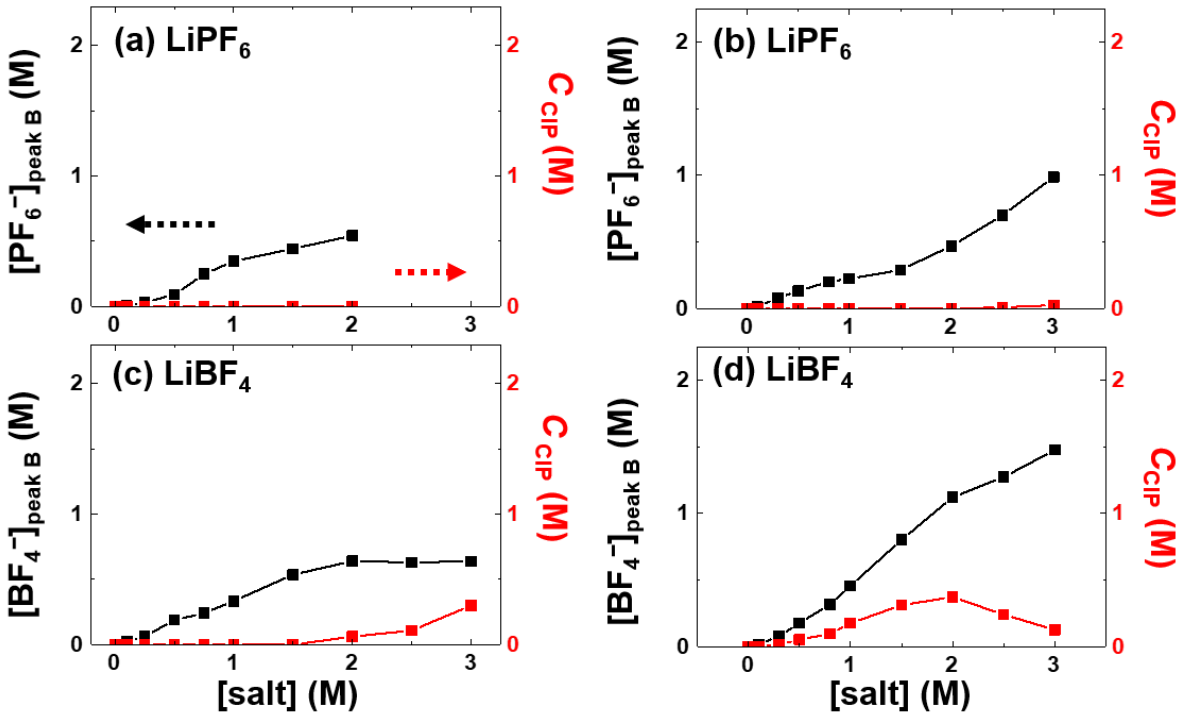

Figure S5. Comparison of the anion concentration obtained from Raman measurements and CIP concentration derived from the dielectric strength of DRS measurements: $[PF_6^-]_B$ vs. C_{CIP} in (a) $LiPF_6$–DMSO and (b) $LiPF_6$–PC. $[BF_4^-]_B$ vs. C_{CIP} in (c) $LiBF_4$–DMSO and (d) $LiBF_4$–PC. (b and d, Reprinted with permission from Ref. 1, copyright 2018 American Chemical Society)

Table S2. Experimental values of the PFG-NMR self-diffusion coefficients (10^{-10} m^2 s^{-1}) for ^{1}H (DMSO), ^{7}Li (lithium ion), and ^{19}F (anion) with various salt concentrations at 298 K.

	$LiPF_6$–DMSO			$LiBF_4$–DMSO		
[salt] (M)	^{1}H	^{7}Li	^{19}F	^{1}H	^{7}Li	^{19}F
0	7.218	—	—	7.516	—	—
0.1	6.961	3.170	6.216	7.309	3.238	6.869
0.25	5.938	3.121	5.653	6.627	3.213	6.497
0.5	4.952	2.702	4.671	6.096	2.771	5.291
0.75	4.219	2.333	4.081	5.326	2.436	4.755
1.0	3.516	1.947	3.402	4.951	2.059	3.706
1.5	1.693	1.021	1.570	3.008	1.397	2.314
2.0	0.660	0.414	0.567	1.424	0.837	1.364
2.5	—	—	—	0.661	0.444	0.644
3.0	—	—	—	0.320	0.232	0.304

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(1) Hwang, S.; Kim, D.-H.; Shin, J. H.; Jang, J. E.; Ahn, K. H.; Lee, C.; Lee, H., Ionic Conduction and Solution Structure in $LiPF_6$ and $LiBF_4$ Propylene Carbonate Electrolytes. *J. Phys. Chem. C* **2018**, *122*, 19438-19446.
(2) Barthel, J.; Hetzenauer, H.; Buchner, R., Dielectric Relaxation of Aqueous Electrolyte Solutions. I. Solvent Relaxation of 1: 2, 2: 1, and 2: 2 Electrolyte Solutions. *Ber. Bunsenges. Phys. Chem.* **1992**, *96*, 988-997.
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