The presence of nano-sized water channel in highly concentrated aqueous electrolyte

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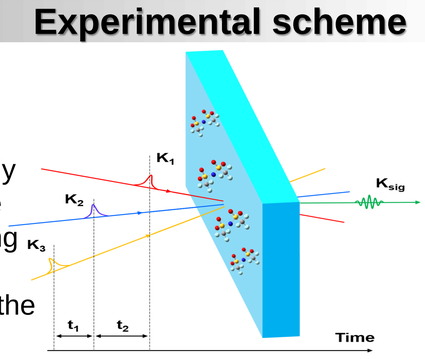
Abstract

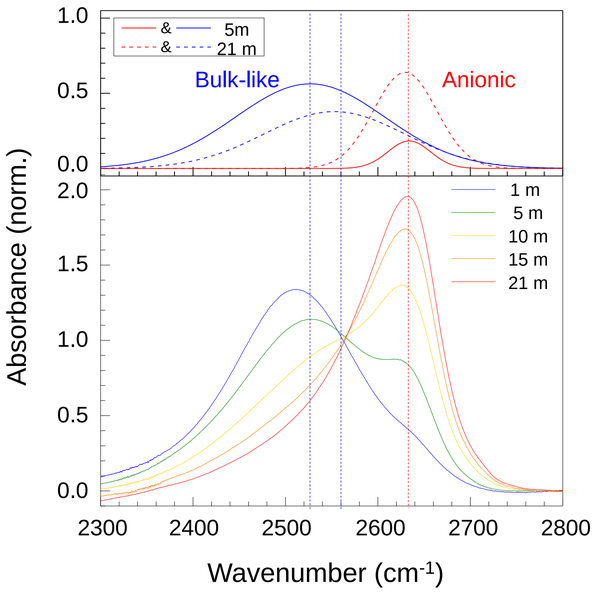
Recent researches on highly concentrated aqueous electrolyte (containing the Bis(trifluoromethane) sulfonimide lithium salt, LiTFSI) suggested that the possibility of application of water-based electrolyte to the lithium-ion battery (LIB). The lithium ion in this water-in-salt lithium-ion battery (LIB) were found to move rapidly even with high viscosity of the superconcentrated electrolyte. It was guessed that water could play a critical role to transport lithium ion in the electrolyte, but it is still ambiguous. It is well known fact that the hydrogen bond is very sensitive to their surrounding and this sensitivity can be helpful to understand the unexpectedly fast flow of lithium cation in highly viscous condition. By carrying out time-resolved IR spectroscopies (femtosecond IR pump-probe and two-dimensional IR spectroscopy), here we show that a considerable amount of water in aqueous electrolyte has bulk-like properties. Complementary MD simulation reveal that this bulk-like water forms the nanometer sized hydrogen-bonding network channels, which are intertwined with ion networks. Furthermore, time-resolved rotational anisotropy, spectral diffusion dynamics, and molecular dynamics simulations of water indicate the presence of interfacial water layer acts as electrical lubricant i.e. reducing electrostatic friction of hydrated lithium ions. We anticipate that the present work provides a guiding principle for developing aqueous electrolytes for LIB.

Experimental scheme



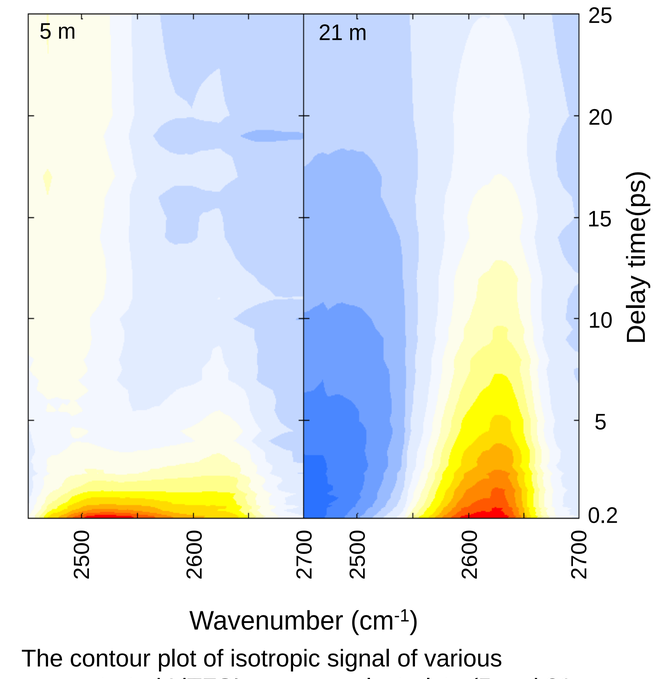
Experimental results

FT-IR spectra

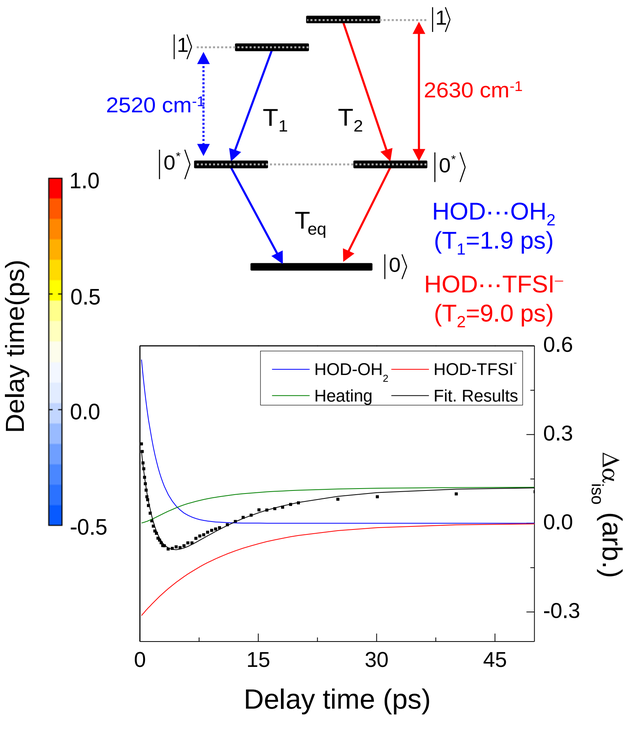


FT-IR spectra of OD stretches in various concentrated LiTFSI aqueous electrolyte (1~21 m, lower pannel) and Gaussian fitting results (5 and 21 m, upper pannel).

IR PP spectra

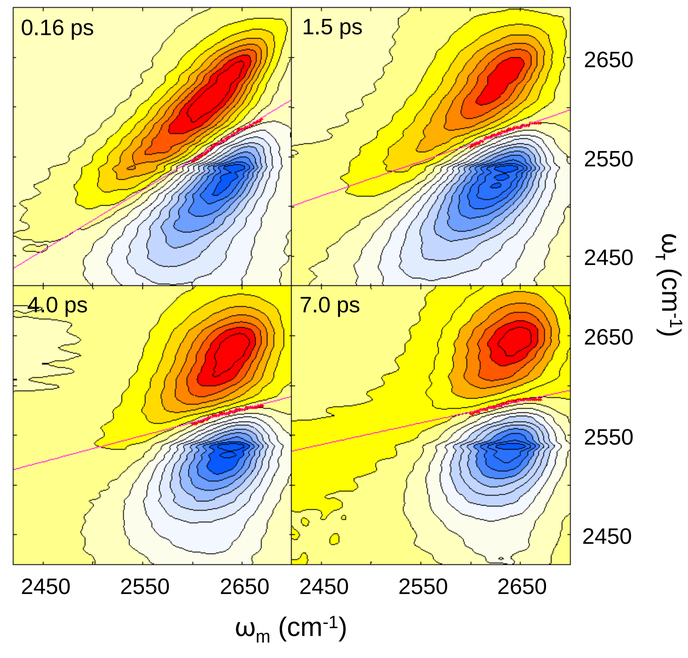


The contour plot of isotropic signal of various concentrated LiTFSI aqueous electrolyte (5 and 21 m) from 0.2ps to 25ps.



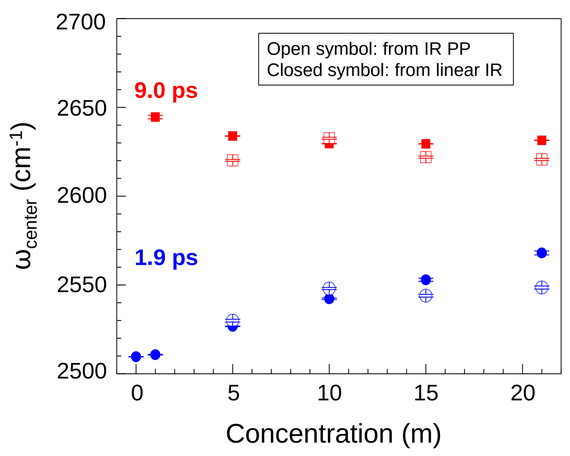
Scheme of global fit to remove the induced heating effect on the isotropic signal and results of fitting w/ Bakker's model (J. Chem. Phys. 125, 144512 (2006))

2D IR spectra



2D IR spectra of 21 m LiTFSI aqueous electrolyte at four representative T_w and corresponding nodal line slope (related with the FFCF)

Analysis



(Left) Center peak frequency and (Right) amplitude fraction of water species
Both information was obtained by Gaussian fit on FT-IR and isotropic signal at several concentration (5~21 m).

MD simulation

MD simulation method

- ✓ Various LiTFSI moleculse(1, 5, 10, 15, 21 m) was dissolved in 1000 H_2O molecules
- ✓ Energy minimization (steepest & conjugate gradient method)
- ✓ NTP equilibration(10 ns)
- ✓ NVT equilibration(200 ns)
- ✓ Production NVT MD (800 ns) cutoff = 10 Å / at T=298 K, P=1atm

QM calculation

- ✓ Atomic charges of the two ions are the restrained electrostatic potential (RESP) charges obtained by carrying out B3LYP/6-311++G(3df,2pd) calculations with Gaussian 09 program.

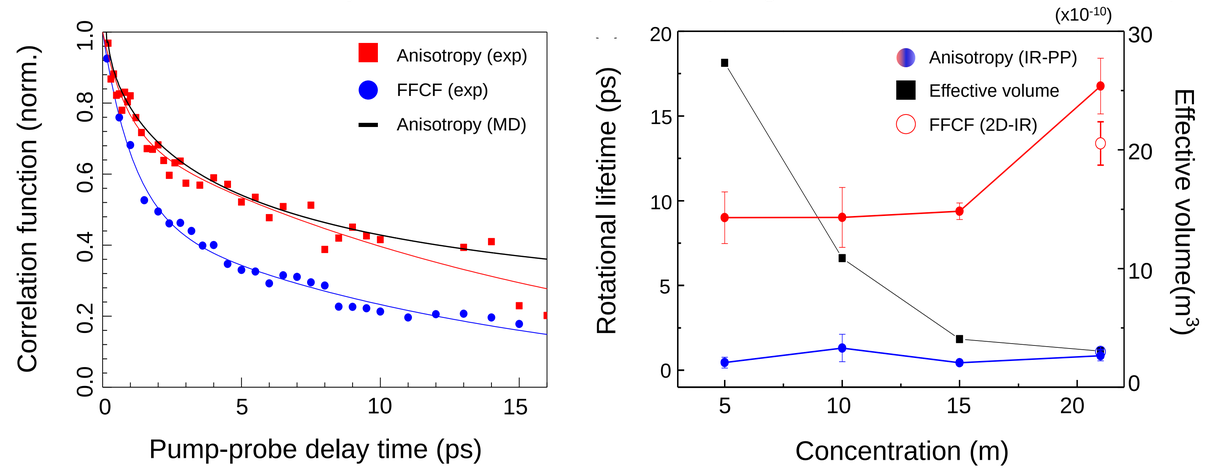
Conc. (m)	D (10^{-10} m^2/s) Simulation	D Experiment		k (mS/cm) Simulation	k Experiment
5	5.04	3.21[a]	4.12[b]	69.00	49.2
10	2.21	1.67[a]	2.27[b]	33.80	32.9
15	0.96	1.08[a]	1.15[b]	-	-
21	0.35	0.394[a]	0.52[b]	6.40	8.2

[a]20°C; [b]30°C

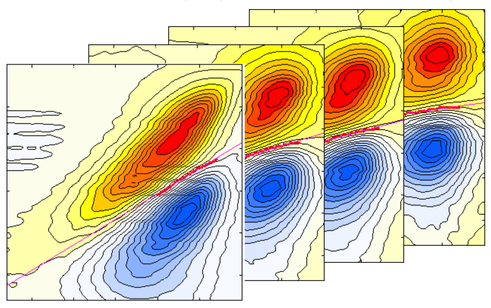
$$D = \lim_{t\to\infty} \frac{1}{6}\sum_{i=1}^{N} \frac{t}{dt} < [R_i(t) - R_i(0)]^2 >$$

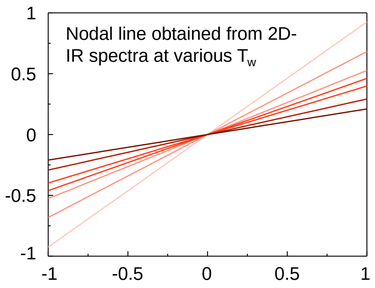
D : Diffusion coefficient
κ : Ion conductivity

$$\kappa = \lim_{t\to\infty} \frac{e^2}{6tkBVT} \sum_{i,j=1}^{N} z_i z_j < [R_i(t) - R_i(0)] >< \left[R_j(t) - R_j(0)\right] >$$



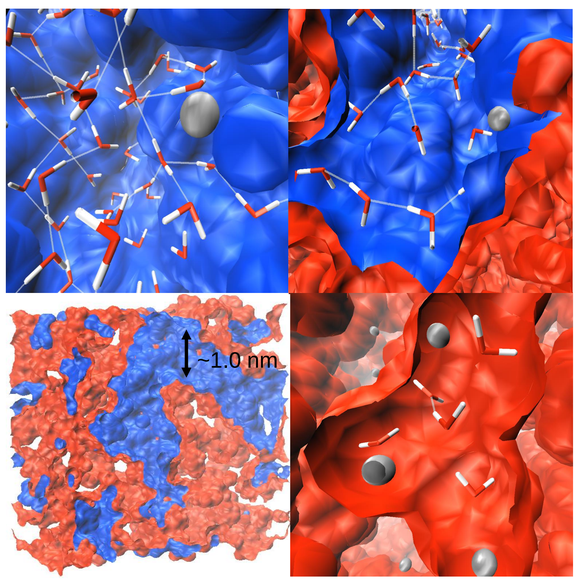
(Left) Rotational (anisotropy, PSPP) and spectral diffusion (FFCF, 2D-IR) correlation function and (Right) rotational decaying constant and corresponding effective volume of water in ionic system.





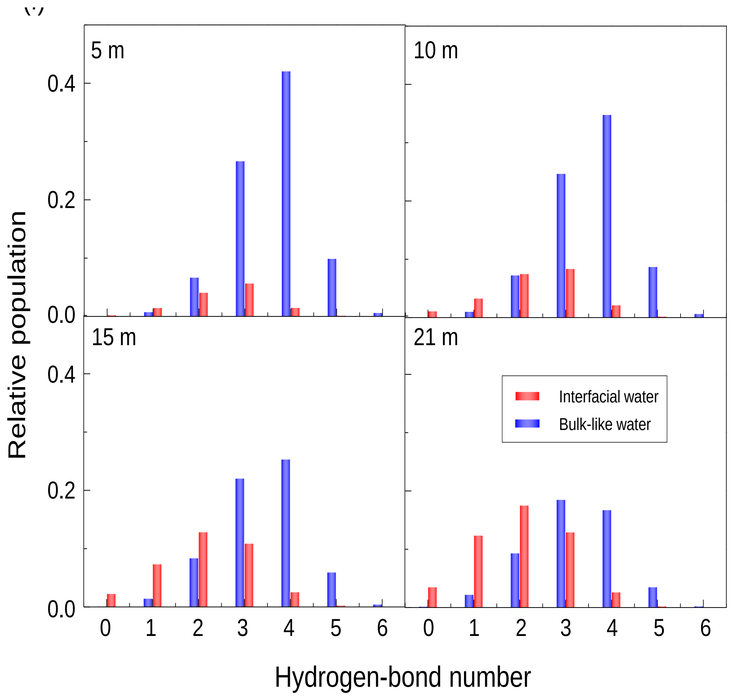
$$\tau_D = \left[\frac{k_B T}{V_{eff}\eta}\right]$$

$$R(t) = 0.4C_2(t) = \left[\frac{\Delta\alpha_{\parallel} - \Delta\alpha_{\perp}}{3P(t)}\right]$$



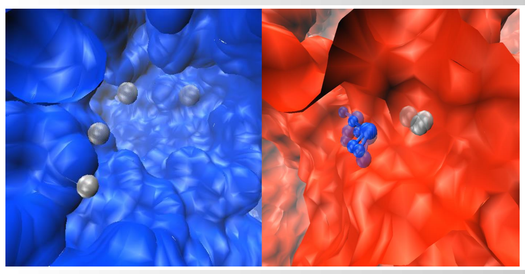
Blue surface& Licorice : water molecule
Red surface : TFSI anion Silver CPK : Li ion

MD snapshot of 21 m LiTFSi aqueous solution.
(Li+: grey, TFSI-: red and water: blue)
(In clockwise) water channel, interface, anionic domain and whole shot.



Histogram of H-bond number per water molecule and relative population of bulk-like water and interfacial water molecules

Discussion & Conclusion



- ✓ With the local sensitivity of OD stretch, it was revealed that the substantial amount of water still remained as 'bulk-like' water even at 21m concentrated LiTFSI aqueous electrolyte.
- ✓ The anisotropy(rotational dynamics) and 2D-IR spectra figured out there are two rotational relaxation pathway; one is wobbling-in-a cone (the rotation of OD is restricted in cone) and the jump rotation of OD to another S=O functional group.
- ✓ With MD simulation, the bulk-like water is expected to plays important role to transport the Li^+ ion and anionic water will be the lubricant for transporting the Li cation by preventing the direct coulombic interaction between Li cation and TFSI anion.

This work was supported by the Institute for Basic Science (IBS) R023-D1

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