Ionic Conduction Mechanism in High Concentration Lithium Ion Electrolytes

Xiaobing Chen⁺ and Daniel G. Kuroda⁺

⁺ Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803, United States Email: <u>dkuroda@lsu.edu</u>

Contents

MATERIALS AND METHODS	2
Sample Preparation	2
Ionic Conductivity and Viscosity Measurements	2
Fourier Transform Infrared Spectroscopy (FTIR)	2
Two-Dimensional Infrared Spectroscopy (2DIR)	2
Ab-initio Molecular Dynamics Simulations (AIMDS)	2
DFT Calculations	3
Ion Pair Lifetime from AIMD	3
TABLES AND FIGURES	1
Walden product of the samples	4
Potential energy surface for the anion and solvent interacting with the lithium ion	4
Experimental FTIR spectra of the HCEs and their central frequencies	5
ACN Nitrile frequency as function of the anion identity	5
ACN Nitrile frequency as function of the lithium ion speciation	5
Two dimensional IR spectra for the different samples	5
REFERENCES	7

MATERIALS AND METHODS

Sample Preparation

LiFSI (98%, TCI) was used without purification. LiFTFSI (98%, FUJIFILM Wako Pure Chemical), LiTFSI (98%, Alfa Aesar) and LiBETI (98%, TCI) were dried in a vacuum oven under 150 °C for two days. Acetonitrile-D3 (ACN-D3, 99.8% isotope VWR) was dried in molecular sieves overnight before use. The water content in the solvent was tested to be less than 100 ppm of water by Karl Fischer titration.

Solutions of LiFSI, LiFTFSI, LiTFSI or LiBETI in ACN-D3 were prepared at the salt:solvent molar ratio of 1:2. To assist the dissolution of Li salt in ACN-D3, the mixture of salt and solvent was heated at low level on a hot plate until a clear, homogeneous liquid formed. Sample cells for FTIR and 2DIR consisted of the ACN-D3/Li+ solution sandwiched between two CaF₂ windows without spacer. All samples and sample cells were prepared in a N₂-filled glovebox to minimize water contamination from the air.

Ionic Conductivity and Viscosity Measurements

The ionic conductivity of the electrolytes was measured using a YSI 3200 conductivity meter combined with YSI 3250 cell probe. The temperature of the solutions was recorded with the integrated temperature probe of the cell probe. The viscosity of the electrolytes was measured using a Brookfield DV-II+pro viscometer.

Fourier Transform Infrared Spectroscopy (FTIR)

FTIR experiments were performed on a Bruker Tensor 27 equipped with a liquid nitrogen cooled MCT detector and a spectral resolution of 0.5 cm⁻¹. Spectra were averaged over 40 scans.

Two-Dimensional Infrared Spectroscopy (2DIR)

The setup used for 2DIR experiments has been previously detailed in the literature,¹ so only a short description is provided here. The input IR pulses were generated with a Spectra Physics Spitfire Ace Ti:sapphire amplifier at a repetition rate of 5 kHz, in combination with an OPA-800C and difference frequency generation crystal. These input IR pulses were then split into three replicas and later focused on the sample using the well-known boxcars geometry.² The photon echo signal was measured in the $-k_1$ $+ k_2 + k_3$ phase-matching direction. A heterodyned detection was performed using a fourth pulse (local oscillator). The heterodyned signal was measured in a 64-element MCT array detector after dispersing the heterodyned signal in a spectrometer. The photon echo signal was measured as a function of three critical time intervals: the coherence time τ (interval between pulses 1 and 2), the waiting time T_w (interval between pulses 2 and 3), and the coherence time t (interval between pulse 3 and the detected signal). These time intervals were set via computer-controlled translation stages. Here, 2DIR data were collected by scanning τ time from -4 to +4 ps in increments of 5 fs for each waiting time to collect both the rephasing and nonrephasing data by switching the time ordering.² Signals were collected for waiting times from 0 to 5 ps in steps of 0.25 ps. The data collection in waiting time was confined to a maximum of 5 ps due to the presence of heating effects.³⁻⁵ In all of the measurements, the local oscillator always preceded the photon echo signal by ~0.8 ps. The time domain signal, collected as a function of (τ , T_w, λ_t) via a monochromatorarray detection, is transformed into the 2DIR spectra (ω_{τ} , T_w, ω_{t}) by means of Fourier transforms. A detailed explanation of the Fourier analysis has been described elsewhere.⁶

Ab-initio Molecular Dynamics Simulations (AIMDS)

The AIMDSs were carried out with the CP2K package (version 3.0).⁷ The electronic structure was calculated via Quickstep module⁷ using the PBE functional with the D2⁸ dispersion scheme and the TZV2P basis set, with Goedecker-Teler-Hutter (GTH) pseudopotentials.⁹⁻¹¹ Periodic boundary conditions were applied to the system, and the Nosé-Hoover thermostat was used to keep the temperature constant at 300 K, with the temperature damping constant of 100 fs. A self-consistent field (SCF) convergence criterion was set to 5.0×10^{-7} hartree. Each system was composed of 10 lithium ions (Li+), 10 anions (FSI⁻, TFSI⁻, or BETI⁻) and 20 acetonitrile-t3 (ACN-T3) in a cubic box with a length of 14.9, 15.9, and 17.8 Å for LiFSI, LiTFSI, and LiBETI systems, respectively. The ACN-T3 (i.e., all hydrogens (H) were replaced by tritium (T)) is required

for 1.0 fs time steps in the AIMDS.^{12, 13} In this paper, the box composition is representative of concentrated lithium electrolyte in acetonitrile with a molar ratio between salt and solvent of 1:2.

The initial lithium solvation shell of LiFSI/TFSI/BETI in ACN-T3, consisting of a Li+ coordinated to 2 acetonitrile molecules and 1 anion in a bidentate configuration (Figure S4), was first optimized to reach the minimum energy by Gaussian 09.¹⁴ The molecular box contains 10 optimized solvation shells randomly placed using Packmol.¹⁵ The box later underwent a minimization run over 5000 cycles, a 2 ns NVT, a 2 ns NPT, and another 2 ns NVT process using AMBER 16 software package¹⁶ and GAFF force field.¹⁷ These preparation steps were required to assure the equilibration of the box. In the AIMDS, each system was equilibrated for ~20 ps, followed by a production run in the NVT ensemble for another ~200 ps.

DFT Calculations

DFT calculations were performed with Gaussian 09 software¹⁴ at the PBE1PBE level of theory using the 6-311++G** basis set.^{12, 13, 18} Structure optimization and frequency calculation were performed in acetonitrile using polarizable continuum model (PCM) to obtain reasonable structures of the contact ion pairs.

Ion Pair Lifetime from AIMD

The ion pair lifetime as determined from the ion pair correlation function ((h(0)h(t))) previously defined for similar systems.^{19, 20}



Figure S1. Walden product as a function of the anion in the lithium salt for samples having a molar ratio of 1:2 lithium ions per solvent molecule. Dashed line is the average of the Walden product among different salts.



Potential energy surface for the anion and solvent interacting with the lithium ion

Figure S2. DFT Frequency of the coordinated CN stretch as a function of the distance between Li+ and N_{anion} (r(Li-N_{anion}), left panel) and between Li+ and N_{ACN} (r(Li-N_{ACN}), right panel) in bidentate solvation shells (see Figure S5). Black, red, and blue symbols represent the results of LiFSI, LiTFSI and LiBETI, respectively. Table S1. Harmonic constant derived from fitting of the potential energy surfaces presented in Figure S2 using a harmonic potential of the form: $V = \frac{1}{2}kdr^2$, with k the harmonic constant.

Anion	Harmonic potential constant (k, in kcal/(mol*Å ²))		
	r(Li-N _{anion})	r(Li-N _{ACN})	
FSI	33	65	
TFSI	39	60	
BETI	37	59	



Experimental FTIR spectra of the HCEs and their central frequencies

Figure S3. Normalized and centered FTIR spectra for LiFSI (black), LiFTFSI (red), LiTFSI (cyan), and LiBETI (green) in ACN. Inset shows the coordinated nitrile stretch band without centering.

*Table S*2. Experimental central frequency of the CN stretch band as function of the anion identity in the lithium salt.

	FSI	FTFSI	TFSI	BETI
ω _{cN} (cm ⁻¹)	2291.5	2289.8	2290.3	2289.5

ACN Nitrile frequency as function of the anion identity



Figure S4. Optimized structure of a contact ion pair with 1 Li+, 1 anion (FSI⁻) and 2 ACN molecules in the bidentate configuration. The pink, red, cyan, yellow, gray, light blue and white colors represent Li, O, N, S, C, F and H, respectively.

Table S3. DFT frequencies and intensities for uncoordinated and coordinated CN stretch in the bidentate solvation shell (Figure S4) formed with different sulfonylimide anions.

Species	ω _{CN} (cm ⁻¹)	I (km/mol)
	2403.66	73.19
LI(ACIN) ₂ (FSI)	2404.05	214.89
Li(ACN)₂(TFSI)	2403.83	210.98
	2404.01	69.01
Li(ACN)2(BETI)	2403.03	172.43
	2403.44	95.90
ACN	2378.15	62.15

ACN Nitrile frequency as function of the lithium ion speciation



Figure S5. Ion pairs. From left to right: mixed, double monodentate, and bidentate configurations. Pink, red, cyan, yellow, gray, light blue and white colors represent Li, O, N, S, C, F and H atoms, respectively. *Table S4*. Frequency of the CN stretch of ACN in three configurations shown in Figure S5.

Configurations	ω _{CN} (cm ⁻¹)	l (km/mol)
mixed	2404.20	136.17
double monodontate	2403.26	148.95
double monodentate	2403.60	112.85
hidantata	2403.83	210.98
biuentate	2404.01	69.01

Two dimensional IR spectra for the different samples



Figure S6. Expanded 2DIR spectra. From top to bottom panels, there show the spectra of LiFSI, LiFTFSI, LiTFSI and LiBETI. The waiting times shown from left to right are 0, 2 and 5 ps. The x-axis is probe frequency $(\omega_t \text{ cm}^{-1})$ while the y-axis is pump frequency $(\omega_\tau \text{ cm}^{-1})$.

REFERENCES

- 1. Y. Cui, K. D. Fulfer, J. Ma, T. K. Weldeghiorghis and D. G. Kuroda, *Phys. Chem. Chem. Phys.*, 2016, **18**, 31471-31479.
- 2. P. Hamm and M. Zanni, *Concepts and Methods of 2D Infrared Spectroscopy*, Cambridge University Press, Cambridge, 2011.
- 3. J. C. Rushing, F. M. Leonik and D. G. Kuroda, J. Phys. Chem. C, 2019, 123, 25102-25112.
- 4. S. Park, M. B. Ji and K. J. Gaffney, J. Phys. Chem. B, 2010, 114, 6693-6702.
- 5. K. P. Sokolowsky and M. D. Payer, J. Phys. Chem. B, 2013, 117, 15060-15071.
- 6. Y. S. Kim, J. P. Wang and R. M. Hochstrasser, J. Phys. Chem. B, 2005, 109, 7511-7521.
- 7. J. VandeVondele, M. Krack, F. Mohamed, M. Parrinello, T. Chassaing and J. Hutter, *Comput. Phys. Commun.*, 2005, **167**, 103-128.
- 8. S. Grimme, J. Comput. Chem., 2006, 27, 1787-1799.
- 9. S. Goedecker, M. Teter and J. Hutter, *Physical Review B*, 1996, 54, 1703-1710.
- 10. G. Lippert, J. Hutter, P. Ballone and M. Parrinello, J. Phys. Chem., 1996, 100, 6231-6235.
- 11. J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, 77, 3865-3868.
- 12. K. Leung and J. L. Budzien, Phys. Chem. Chem. Phys., 2010, 12, 6583-6586.
- 13. T. P. Pollard and T. L. Beck, J. Chem. Phys., 2017, 147.
- 14. M. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci and G. Petersson, *Journal*, 2009.
- 15. L. Martinez, R. Andrade, E. G. Birgin and J. M. Martinez, J. Comput. Chem., 2009, 30, 2157-2164.
- 16. D. Case, R. Betz, D. Cerutti, T. Cheatham, T. Darden, R. Duke, T. Giese, H. Gohlke, A. Goetz and N. Homeyer, *Journal*, 2016.
- 17. J. M. Wang, R. M. Wolf, J. W. Caldwell, P. A. Kollman and D. A. Case, *J. Comput. Chem.*, 2004, **25**, 1157-1174.
- 18. N. Chapman, O. Borodin, T. Yoon, C. C. Nguyen and B. L. Lucht, J. Phys. Chem. C, 2017, 121, 2135-2148.
- 19. M. Kohagen, M. Brehm, J. Thar, W. Zhao, F. Muller-Plathe and B. Kirchner, J. Phys. Chem. B, 2011, **115**, 693-702.
- 20. Y. Zhang and E. J. Maginn, J. Phys. Chem. Lett., 2015, 6, 700-705.