Tracking the Transition Behavior and Dynamics of Ionic Transport in Crystalline Ionic Gel Electrolytes**

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Experimental Section

Synthesis of ImiZIL

1-Methylimidazole (99 %) was purchased from Aldrich Co. 1,3-Propane-sultone was a product of TCI Ltd. LiTFSI was supplied by Sigma Aldrich. Acetone (A.C.S. agent) from Junsei Chemical Co. was distilled and stored with fresh 5A° molecular sieves.

ImiZILs were prepared, following below synthetic procedure reported by our previous literature. 1-Methylimidazole (100 mmol, 8.21 g) was mixed and stirred with 1,3-propanesultone (110 mmol, 13.4g) in acetone for 24 hours at room temperature following below scheme. Then the precipitated white solid product was collected by filtration. The product was washed with acetone above three times, then dried under vacuum at room temperature. Yield : 99%.

![Chemical structure](image)

1H-NMR (DMSO-d6, 300 MHz), δ (ppm) = 9.09 (s, 1H, Im), 7.72 (d, 2H, Im), 4.29 (t, 2H, CH2), 3.83 (s, 3H, CH3), 2.39 (t, 2H, CH2), 2.08 (m, 2H, CH2).

Elemental analysis calcld (%) for C7H12N2O3S: C, 41.21; H, 5.93; N, 13.73. Found : C, 41.17; H, 5.89, N, 13.63.

Characterization

The ionic conductivities of ImiZIL–LiTFSI mixtures were measured by the AC impedance spectroscopy over a frequency range of $10^{-1}$ Hz to $10^6$ Hz with 10 mV. A system based on a Solatron 1255 Frequency Response Analyzer was used to measure the ionic conductivity. The conductivity of the sample was obtained from complex impedance analysis. The real and imaginary parts of the complex impedance were plotted and the ionic conductivity was obtained from the bulk resistance found in complex impedance analysis.
From this resistance value in ohms, ionic conductivity is calculated assuming a uniform current distribution in the conductivity cell

\[ \sigma(S/cm) = \frac{L(cm)}{R(\Omega)A(cm^2)} \]  

where \( L \) is the distance between the two measuring electrodes, \( A \) is the cross-sectional area of the sample, and \( R \) is the measured resistance. Ionic conductivities of all samples were measured from 293 K to 363 K. Every result was averaged in the error range of ±4%.

X–ray Diffraction (XRD) data were obtained on a Rigaku D/max III C (3 kW) with a \( \theta/\theta \) goniometer equipped with a CuK\( \alpha \) radiation generator. The diffraction angle of the diffractograms was in the range of \( 2\theta = 10 \text{–} 40^\circ \).

\(^7\)Li and \(^{13}\)C NMR spectra were obtained by using a 400 MHz solid state NMR spectrometer (Bruker, DSX 400) with CP/MAS probe. \( d_6 \)-DMSO was used as solvent.

A spectroscopic instrument was used to analyze reaction as follows. FT-IR spectra were collected on a JASCO FT-IR 4100. The pressure was set as equal for all samples to avoid differences caused by the pressure and penetrating depth. Each spectrum, which was recorded as the average of 13 scans with a resolution of 4 cm\(^{-1}\), was collected from 4000 cm\(^{-1}\) to 650 cm\(^{-1}\). We focused on the spectrum data of 2000 – 650 cm\(^{-1}\) because the bands in this range are strongly related to the imidazolium ring and sulfonate group of ImiZIL and the TFSI anion of LiTFSI.

**PCA**

Principal component analysis (PCA) decomposes the original data matrix into the product of a product of scores and loadings matrices. Score matrix contains information on how samples are related to each other. The loading vectors are usually separated into two categories: significant loadings representing the linear combinations of spectral contributions of actual components and the noise or insignificant vectors. The two matrices are linearly combined with the original data; hence in most discussions of PCA results, the two matrices are explored in parallel.
The fundamental idea of PCA is that the significant part of the data matrix \((A)\) can be expressed as the product of score \((W)\) and loading \((V)\) matrices

\[
A = W V' + E
\]

where \(E\) is the residual matrix often associated with pure noise. Here \(V'\) stands for the transpose of \(V\).

**2D IR COS**

Generated by a cross-correlation analysis of dynamic fluctuations of IR signals induced by an external perturbation such as temperature, time, stress, concentration, etc., 2D IR COS is defined by two independent wavenumbers.\(^{12}\) 2D IR COS is a well-established analytical technique that provides considerable utility and benefit for elucidating physical interactions such as intra- and intermolecular interactions and various spectroscopic studies of complex systems such as the formation mechanism of nanoparticles, biomineralization, self/supramolecular assembly, and nanoconfinement.\(^{13}\) Some of the notable features of generalized 2D correlation spectra are: simplification of complex spectra consisting of many overlapped peaks; enhancement of spectral resolution by spreading peaks along the second dimension; establishment of unambiguous assignments through the correlation of peaks of selectively coupled by various interaction mechanisms; and determination of the sequence of the spectral peak emergence. The intensity of a 2D correlation spectrum \(X(v_1, v_2)\) is expressed by the dynamic spectrum of a system \(\tilde{y}(v, t)\), following equations (3) and (4).

\[
X(v_1, v_2) = \langle \tilde{y}(v_1, t)\tilde{y}(v_2, t') \rangle \tag{3}
\]

\[
\tilde{y}(v, t) = y(v, t) - \bar{y}(v) \tag{4}
\]

Where \(y(v, t)\) is the perturbation-induced variation of a spectral intensity measured at a spectral variable along the external perturbation \(t\), and \(\bar{y}(v)\) is the reference spectrum chosen as the averaged spectrum. In order to simplify the mathematical manipulation, \(X(v_1, v_2)\) is treated as a complex
number function consisting of two synchronous \( \Phi(\nu_1, \nu_2) \) and asynchronous 2D correlation \\
\( \Psi(\nu_1, \nu_2) \) intensities, respectively as follows.

\[
X(\nu_1, \nu_2) = \Phi(\nu_1, \nu_2) + i\Psi(\nu_1, \nu_2)
\]

\[
= \frac{1}{\pi(T_{\text{max}} - T_{\text{min}})} \int_{0}^{\infty} \tilde{Y}(\nu_1, w) \cdot \tilde{Y}^*(\nu_2, w) dw
\]

(5)

Where \( \tilde{Y} \) and \( \tilde{Y}^* \) are the Fourier transform and the conjugate of the Fourier transform of \( \tilde{y}(\nu, t) \), respectively.

In a synchronous 2D spectrum, the intensity of the auto peaks located at the diagonal positions represent the overall susceptibility of the corresponding spectral region to change in spectral intensity as an external perturbation is applied to the system, while the intensity of the cross-peaks located at the off-diagonal positions of a synchronous 2D spectrum reveal simultaneous or coincidental changes of spectral intensities observed at two different spectral variables (\( \nu_1 \) and \( \nu_2 \)). In contrast, an asynchronous 2D spectrum consisting of only cross peaks provides useful information in order to interpret the mechanisms and kinetics of chemical/physical interactions: the relative temporal relationship or order of the actual sequence of reorientation processes. The intensity of an asynchronous 2D correlation spectrum represents sequential, or successive, changes of spectral intensities measured at \( \nu_1 \) and \( \nu_2 \). An asynchronous cross peak develops only if the intensities of two spectral features change out of phase (i.e., delayed or accelerated) with each other. If the signs of synchronous and asynchronous cross peaks are the same, the intensity change at \( \nu_1 \) occurs before \( \nu_2 \). If the signs of synchronous and asynchronous cross peaks are different, the intensity change at \( \nu_1 \) occurs after \( \nu_2 \). In this work, kinetically conformational changes and their interrelations in the process of proton transport could be obtained from 2D IR COS.
Fig. S1. Photo image of pristine ImiZIL and LiTFSI, and binary ImiZIL–LiTFSI gel electrolyte

A homogeneous, transparent gel film prepared at the equivalent molar ratio of ImiZIL–LiTFSI indicates the mixing of ImiZIL–LiTFSI at a molecular level. In order to evaluate intrinsic properties of binary gel electrolyte, most of impurities such as water were removed by vacuum evaporation.
Fig. S2. XRD of ImiZIL-LiTFSI mixtures with respect to mole fraction of ImiZIL.
Fig. S3. (a) $^7$Li NMR of ImiZIL-LiTFSI mixtures and (b) $^7$Li line width with respect to mole fraction of ImiZIL.
**Fig. S4.** $^{13}$C NMR spectra of ImiZIL–LiTFSI mixtures with respect to mole fraction of ImiZIL.
**Fig. S5.** FT-IR spectra of ImiZIL-LiTFSI mixtures as a function of chemical compositions. Inset is the enlarged FT-IR spectra of ImiZIL-LiTFSI mixtures in the range of 1800 – 900 cm\(^{-1}\). 0 means a molar ratio of ImiZIL-LiTFSI of 4 to 1, 1 of 3 to 1, 2 of 2 to 1, 3 of 1 to 1, 4 of 1 to 2, 5 of 1 to 3, and 6 of 1 to 4.

**Ref.**