

Video Article

Synthesis of Ionic Liquid Based Electrolytes, Assembly of Li-ion Batteries, and Measurements of Performance at High Temperature

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Abstract

The chemical instability of the traditional electrolyte remains a safety issue in widely used energy storage devices such as Li-ion batteries. Li-ion batteries for use in devices operating at elevated temperatures require thermally stable and non-flammable electrolytes. Ionic liquids (ILs), which are non-flammable, non-volatile, thermally stable molten salts, are an ideal replacement for flammable and low boiling point organic solvent electrolytes currently used today. We herein describe the procedures to: 1) synthesize mono- and di-phosphonium ionic liquids paired with chloride or bis(trifluoromethane)sulfonimide (TFSI) anions; 2) measure the thermal properties and stability of these ionic liquids by differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA); 3) measure the electrochemical properties of the ionic liquids by cyclic voltammetry (CV); 4) prepare electrolytes containing lithium bis(trifluoromethane)sulfonamide; 5) measure the conductivity of the electrolytes as a function of temperature; 6) assemble a coin cell battery with two of the electrolytes along with a Li metal anode and LiCoO₂ cathode; and 7) evaluate battery performance at 100 °C. We additionally describe the challenges in execution as well as the insights gained from performing these experiments.

Video Link

The video component of this article can be found at <https://www.jove.com/video/54864/>

Introduction

Li-ion batteries are devices that transform energy between electrical energy and chemical energy and provide a convenient means to store and to deliver energy on demand and on-the-go. Today, Li-ion batteries dominate the portable electronics market because of their high energy density and re-chargeability, and are of interest for large-scale and specialty applications, such as down-hole drilling and automotive.¹⁻⁵ Batteries are composed of four primary components: cathode, anode, separator, and electrolyte. While the chemistry of the two electrodes dictates the theoretical energy density of the battery, the safety and working temperature are mainly limited by the electrolyte material.⁶⁻⁹ Carbonate based organic solvent electrolytes (e.g., dimethyl carbonate (DMC) and ethylene carbonate (EC)) are widely used in Li-ion batteries due to their low viscosity, high conductivity, and high lithium salt solubility. Moreover, certain combinations of the carbonate solvents (DMC/EC) also form a stable solid electrolyte interface (SEI), thereby preventing degradation reactions between the electrolyte and the electrode, and extending battery life. However, carbonate solvents suffer from low boiling points and flash points, limiting the operation temperature of Li-ion batteries to below 55 °C, with potentially severe safety issues when there is a short-circuit.^{10,11}

Ionic liquids are a class of salts that have melting temperatures below 100 °C.¹² In contrast to typical inorganic salts, ionic liquids possess a wide liquid range and can be liquid at room temperature. Ionic liquids are composed of one or multiple organic cationic centers, such as imidazolium, phosphonium, pyridinium, or ammonium and paired with an inorganic or organic anion, such as methansulfonate, hexafluorophosphate, or halide.^{13,14} The wide variety of possible cation and anion combinations allows for a large number of compositions with tunable properties. In addition, the strong ionic interactions within ionic liquids result in negligible vapor pressure, non-flammability, and high thermal and electrochemical stability.^{15,16}

Replacing conventional electrolytes with ionic liquids is one solution that addresses the inherent safety issues in current Li-ion batteries, and could enable high temperature applications.¹⁷⁻²⁷ To illustrate the general synthetic and material processing methods utilized to construct lithium ion batteries containing ionic liquids for high temperature applications, we describe the synthesis, thermal properties, and electrochemical characterization of mono- and di-phosphonium ionic liquids paired with either the chloride (Cl) or bis(trifluoromethane)sulfonimide (TFSI) anion. Different concentrations of lithium bis(trifluoromethane)sulfonimide (LiTFSI) are subsequently added to the phosphonium ionic liquids to give electrolytes. Based on the performance of the phosphonium TFSI electrolytes with added LiTFSI compared to the chloride analogs, a coin cell is constructed with either the mono- or di-phosphonium TFSI electrolytes along with a Li metal anode and LiCoO₂ cathode. Finally, battery

performance is evaluated at 100 °C for the two different coin cell batteries. The detailed procedures, the challenges in execution, and the insights gained from performing these experiments are described below.

Protocol

1. Synthesis of Mono- and Di-phosphonium Ionic Liquids Paired with Chloride (Cl) and Bis(trifluoromethane)sulfonimide (TFSI) Anions

NOTE: The procedure for the mono-phosphonium ionic liquid possessing three hexyl and one decyl alkyl chain surrounding the phosphonium cation is described, and this ionic liquid is abbreviated as mono-HexC10Cl. The same procedure is repeated using 1,10-dichlorodecane to obtain the di-phosphonium ionic liquid in high yield, and this ionic liquid is abbreviated as di-HexC10Cl.

1. While in a glove box under argon, weigh out trihexylphosphine (8.3 g, 29 mmol) using a glass pipet, and dispense into a heavy wall pressure vessel. Next, add 1-chlorodecane (5.22 g, 29.6 mmol) using a glass pipet to the same vessel. Cap the vessel containing the mixture with a PTFE bushing.
2. Heat the resulting mixture under argon to 140 °C for 24 hr while mixing to obtain the mono-HexC10Cl. The mixture will become viscous.
3. Place the mixture under high vacuum at 140 °C while stirring to remove any remaining volatile starting materials to obtain the crude mono-HexC10Cl.
 1. To purify, extract the mono-HexC10Cl from the crude mixture using approximately 10 ml of a 1:1 dichloromethane (DCM) to saturated sodium chloride solution (brine) in a 250 ml separatory funnel. Collect the DCM phase. Repeat the extraction process three times.
 2. Combine the 15 ml of collected DCM solutions containing the product, and evaporate the solvent using a rotary evaporator to obtain the mono-HexC10Cl product.
4. Dissolve the mono-HexC10Cl (7.75 g, 16.74 mmol) in 10 ml of DCM and add LiTFSI (6.25 g, 21.76 mmol), pre-dissolved in 10 ml of deionized water. Cap the resulting mixture and stir it at room temperature for 24 hours.
5. Extract the mono-HexC10TFSI from the mixture using a 250 ml separatory funnel filled with approximately 20 ml of DCM. Repeat the extraction process three times. Combine the DCM solutions.
6. Add 1-2 drops of 1 N AgNO₃ solution to 1 ml of the DCM phase to confirm the complete elimination of chloride anions from the organic phase. A white precipitate will be produced if chloride anions remain in solution. Repeat the extraction step until no white precipitate is produced.
7. Add 1 g of anhydrous MgSO₄ to the DCM solution, stir the mixture, and then decant the dried DCM solution. Next, evaporate the solvent by rotary evaporation. The yield is typically greater than 98%.
8. Repeat the same procedure using 1,10-dichlorodecane to obtain the two di-phosphonium ionic liquids, di-HexC10Cl and di-HexC10TFSI, in high yield.
9. Characterize the ionic liquids using ¹H, ¹³C, and ¹⁹F NMR in deuterated-chloroform (shift 7.24) and submit the samples for elemental analysis and mass spectrometry analysis.

2. Characterization of the Ionic Liquids

1. **Differential scanning calorimetry (DSC)**
 1. Weigh out 5 to 10 mg of the ionic liquid (record the actual mass) and add it to the center of an aluminum sample pan, which is subsequently hermetically sealed. Be sure to complete this step efficiently as the ionic liquids are hygroscopic and the weight will change if left to stand.
 2. Load the sample pan and an unloaded (reference) pan into the differential scanning calorimeter. Be sure to place the sample and reference pan in the appropriate location as determined by the specific DSC used.
 3. Program a temperature ramp and cooling cycle: 1) heat from -70 °C to 200 °C at a heating rate of 10 °C/min, 2) cool to -70 °C at a cooling rate of 5 °C/min, and 3) repeat the heat-cool cycling three times.
 4. By analyzing the thermal trace, determine the melting point (T_m), crystallization (T_c) and glass transition temperatures (T_g) (if applicable).
2. **Thermal gravimetric analysis (TGA)**
 1. Clean and tare the platinum pan on the movable arm of the TGA. Add 5 to 10 mg of the ionic liquid on the pan. Only touch the pan using tweezers.
 2. Heat the sample from 20 to 500 °C at a heating rate of 10 °C/min.
 3. Identify the decomposition temperature where 10% of the original sample weight is lost. For long-term stability studies, heat the sample at a set temperature for a prolonged time and monitor the loss of weight.
3. **Viscosity measurements**
 1. With a glass pipette, place 1 ml of ionic liquid on the Peltier stage of a controlled strain rheometer. Make sure the aluminum plate is fully covered with the ionic liquid.
 2. Use a 20 mm diameter parallel aluminum plate (or cone) and set the gap between the aluminum plate and the top surface of the sample to be 1.0 - 2.0 mm in all of the runs.
 3. To minimize the effect of moisture in the air, perform the measurements in a glove bag filled with nitrogen gas.
 4. Prior to each test, pre-shear the sample at a shear rate of 100 Hz for 10 sec to eliminate any physical memory of the sample, follow with a 15 min equilibrium step in order for the sample to reach a steady state condition.
 5. Determine the linear viscoelastic region (LVR) via an oscillatory strain sweep at a fixed frequency (1 Hz) with a strain amplitude from 0.1 to 10%.
 6. Select a strain that lies in the LVR and perform the oscillatory frequency sweep from 0.1 to 10 Hz. Determine the complex viscosity at a particular frequency and strain.

7. Perform an oscillatory temperature sweep controlled by the instrument software from 10 °C to 95 °C with increments of 5 °C and a 1 min equilibrium at each temperature. Define strain and frequency, for example, to be 1.0% and 1 Hz, respectively. Complex viscosities at different temperatures are read out.
4. **Conductivity measurements**
 1. Dry the ionic liquid at 100 °C under high vacuum for 12 hr to remove trace amounts of moisture before testing.
 2. In a glove box under an argon atmosphere, load approximately 4 ml of the sample in a test tube, be sure to add enough sample to immerse the sensing tape of the conductivity probe completely.
 3. Use a heating block to control the temperature and maintain the stirring during the measurement to maintain homogeneity.
 4. Read the conductivity at each temperature after a 30 min equilibration time.
5. **Cyclic voltammetry (CV)**
 1. Assemble a lithium/lithium/platinum three-electrode system in the glove box under an argon atmosphere.
 2. Charge the vessel with the ionic liquid and make sure all the electrodes are immersed in the ionic liquid. Seal the vessel under argon.
 3. Equilibrate the vessel at the desired temperature for 20 min. Sweep the potential rate at 1 mV/sec between -0.2 V and 6.5 V versus Li⁺/Li.

3. Preparation of the Electrolytes

1. Dry the ionic liquid under high vacuum at 80 °C overnight with rigorous stirring to ensure removal of trace amounts of water.
2. Dry the LiTFSI at 70 °C for three days in a vacuum oven.
3. Transfer the anhydrous ionic liquid and LiTFSI salt to the glove box.
4. Add the ionic liquid (e.g., mono-HexC10TFSI, 4.50 g, 6.4 mmol) and LiTFSI (1.83 g, 6.4 mmol) to an oven-dried flask containing a stir bar. Stir the mixture overnight until it is homogeneous to obtain a concentration of 1.6 M for the electrolyte.

4. Fabrication of the Lithium Ion Coin Cell Battery

1. In the glove box under argon atmosphere, place one spring and one stainless steel disc in the bottom cap of the coin cell. Place a 12.7 mm diameter LiCoO₂ electrode (24 mg) in the stainless steel disc.
2. Soak two pieces of the separators (porous polypropylene membranes) in the above-prepared ionic liquid electrolyte at 60 °C on a hot plate for 15 min.
3. Add the ionic liquid electrolyte to the surface of the LiCoO₂ cathode until the material is fully covered with electrolyte (≈ 0.5 ml).
4. Place the separators soaked in the electrolyte in the center of the coin cell. Then add a few more drops of ionic liquid electrolyte (a few microliters) onto the separators.
5. Cut a piece of lithium metal with a diameter of 12.7 mm in the glove box. Place the lithium metal on top of the separators.
6. Cap the coin cell and seal it with a crimper in the glove box.
7. Transfer the coin cell out of the glove box and rest the cell for 12 hr prior to initiating the battery/electrochemical tests.

5. Performance of the Battery at 100 °C

1. Place the coin cell in an oven operating at 100 °C, which has a small hole in the back wall where the cables from the electrochemical testing station have been threaded. Connect the coin cell to the electrochemical testing station.
2. Leave the cell at 100 °C for 30 min to equilibrate to the temperature.
3. Select galvanostatic charge-discharge cycling on the electrochemical testing station. Set the cycle number to 500.
4. Set the charge current to 500 μA and the voltage upper limit to 4.2 V. Set a rest time of 60 sec at 0 V after each charge.
5. Set the discharge current to 500 μA and the voltage lower limit to 3.0 V. Set a rest time of 60 sec at 0 V after each discharge.
6. Start the charge-discharge cycling at a current of 500 μA between 3.0 V to 4.2 V using the software. Evaluate the charge output against time.

Representative Results

The ionic liquids, mono-HexC10Cl and di-HexC10Cl, were prepared via a nucleophilic reaction, and a subsequent halide exchange reaction gave the mono-HexC10TFSI and di-HexC10TFSI ionic liquids, respectively (**Figure 1A**).¹⁴ All four ionic liquids were colorless and slightly viscous liquids (**Figure 1B**). A representative ¹H NMR of the mono-HexC10TFSI ionic liquid is shown in **Figure 1C**, and along with mass spectrometry and elemental analysis data confirmed the structure.

Next, the thermal stability of the four ionic liquids were determined (**Table 1**). As a representative ionic liquid, the di-HexC10TFSI will be described in detail. First, DSC was performed to determine if there were any phase transitions between -70 to 150 °C (**Figure 2A**). No glass transition temperature or melting temperature was observed for the di-HexC10TFSI ionic liquid, indicating the wide liquid range and phase stability over this temperature range. In a temperature ramp test using TGA at a heating rate of 10 °C/min, the di-HexC10TFSI ionic liquid did not show a weight loss until 300 °C. The thermal decomposition temperature was determined to be 365 °C (**Figure 2B**).

The electrochemical stability of the mono-HexC10TFSI and di-HexC10TFSI ionic liquids was determined at 100 °C by CV using a three-electrode Li/Li/platinum setup (**Figure 3A**). CV measurements were performed at 100 °C between -0.5 and 6.5 V (versus Li⁺/Li) at a scan rate of 1 mV/sec. The mono-HexC10TFSI and di-HexC10TFSI ionic liquids were stable up to at least 5.0 V versus Li⁺/Li at 100 °C. Above 5.0 V, the decomposition of the TFSI anion occurred.

The viscosities of the ionic liquids at 25 °C were then determined (**Table 1**). Since the viscosities of the mono-HexC10TFSI and di-HexC10TFSI ionic liquids were significantly lower (7 Pa·sec at room temperature) compared to the Cl-based ionic liquids, the remainder of the studies were conducted with these two ionic liquids. LiTFSI was subsequently blended with mono-HexC10TFSI and di-HexC10TFSI, respectively, at a weight percentage of 5% (0.3 M), and the viscosity and conductivity of the electrolytes were measured. At all temperatures between 25 and 100 °C, the di-HexC10TFSI+LiTFSI electrolyte had a higher viscosity than mono-HexC10TFSI+LiTFSI. Increasing the temperature afforded lower viscosities (**Figure 4A**). Similarly, the conductivity values increased at higher temperatures for both electrolytes, with the mono-HexC10TFSI+LiTFSI electrolyte exhibiting greater conductivity values than the di-HexC10TFSI+LiTFSI electrolyte at all temperatures.

Next, the dependence of the viscosity and ionic conductivities on the amount of LiTFSI added (0.3 M and 1.6 M) to the mono-HexC10TFSI+LiTFSI and di-HexC10TFSI+LiTFSI electrolytes was determined as a function of temperature. As shown in **Figure 4B**, the concentration of the LiTFSI salt influenced both the conductivity and viscosity. Higher salt concentrations afforded a more viscous mixture and therefore a less conductive medium. Increasing the temperature significantly decreased the viscosity and, thus, increased the conductivity for all of the compositions. The mono-HexC10TFSI+LiTFSI electrolyte exhibited lower viscosities and higher conductivities than the corresponding di-HexC10TFSI+LiTFSI electrolyte. For example, at room temperature, the mono-HexC10TFSI+LiTFSI electrolyte (0.3 M and 1.6 M) displayed relatively low conductivities (~ 0.01 mS/cm), whereas at 100 °C the conductivities increased by two orders of magnitude and were about 1 mS/cm. Increased amounts of LiTFSI gave lower conductivities and higher viscosities. For example, when the temperature was increased to 100 °C, the conductivity of the 0.3 M mono-HexC10TFSI+LiTFSI (~ 1.7 mS/cm) electrolyte was almost twice the value measured for the 1.6 M composition (~ 1.0 mS/cm).

Prior to the coin cell experiments, CV experiments were performed to determine the electrochemical response of the mono-HexC10TFSI+LiTFSI (0.3 M) and the di-HexC10TFSI+LiTFSI (0.3 M) at 25, 60, and 100 °C in the presence of the Li/LiCoO₂ redox couple, respectively (**Figure 3B**). The voltage was swept from 1.5 to 4.6 V with a current rate of 1 mV/sec. The current increased dramatically from 25 to 100 °C, indicating that as the temperature increased, the viscosity decreased with a resultant lowered internal resistance. The mono-HexC10TFSI+LiTFSI showed a higher current response than the di-HexC10TFSI+LiTFSI at each temperature. The expected LiCoO₂ redox reaction peaks at approximately 3.6 V and 4.1 V were observed. The Li⁺ intercalation and de-intercalation were mostly complete from 2.5 V to 4.6 V, and no obvious material decomposition was observed within this range.

Given the lower viscosity and higher conductivity as well as the electrochemical stability between 2.5 and 4.6 V, both the mono-HexC10TFSI+LiTFSI and di-HexC10TFSI+LiTFSI electrolytes were used as the electrolytes for evaluation in coin cell batteries. The battery design, components, and assembled structure are shown in **Figure 5A** with the two stainless steel current collectors located at the ends to create the sandwich-like battery. Li metal serves as the anode sitting on the bottom current collector, which is separated from the LiCoO₂ cathode by two porous polypropylene membrane separators. The separators were soaked in the ionic liquid electrolyte prior to construction of the battery. The gasket and spacers, or springs, were then used to create an airtight seal of the battery and to hold and align the battery components together. All the battery components as well as the LiCoO₂ were dried in a vacuum oven at 70 °C overnight to remove moisture. The electrolyte to be tested was dried at 100 °C under high-vacuum overnight before use. All of the assembling steps were performed in the glove box under an argon atmosphere. Once assembled, the coin cell was sealed and the battery removed from the glove box.

We next performed charge-discharge cycling (CD) to evaluate the specific capacity and cycle life of the battery. The performance of the mono-HexC10TFSI+LiTFSI and the di-HexC10TFSI+LiTFSI electrolytes with 0.3 M of LiTFSI in Li/LiCoO₂ cells at 100 °C was first determined as both electrolytes gave the highest conductivities at this LiTFSI concentration. As shown in **Figure 5B**, the batteries failed within 10 cycles. The coin cell containing the mono-HexC10TFSI+LiTFSI electrolyte showed a higher initial capacity of approximately 140 mAh/g and then decreased by about 20% with each additional cycle. The cycling of the coin cell with the di-HexC10TFSI+LiTFSI electrolyte started at a lower capacity, due to the higher viscosity of the electrolyte, but then decreased, although not as sharply as for the coin cell containing the mono-HexC10TFSI+LiTFSI electrolyte. The battery suddenly failed after cycle seven. The mono-HexC10TFSI+LiTFSI electrolyte showed higher specific capacity and more stable cycling than the cell with the di-HexC10TFSI+LiTFSI electrolyte. The poor performance for both ionic liquids was attributed to the low concentration of LiTFSI. Thus, the concentration of the LiTFSI for the mono-HexC10TFSI+LiTFSI electrolyte was increased to 1.0 M and 1.6 M, and the experiment was repeated. Significantly improved battery performance was obtained (**Figure 5C**). Specifically, the use of both the 1.0 M and 1.6 M mono-HexC10TFSI+LiTFSI electrolytes demonstrated dramatically reduced capacity decay at 100 °C in the coin cell. About 90% of the capacity remained after 20 cycles for the coin cell containing the mono-HexC10TFSI+LiTFSI (1.6 M) electrolyte. The results from the coin cell with the 1.0 M electrolyte formulation were similar: stable cycling occurred during the first 15 cycles and then a sudden decrease to 100 mA/g occurred at cycle 20. A higher concentration of LiTFSI was necessary to maintain capacity at the high temperature.

To further investigate the cycle life of the batteries, an extended galvanostatic charge-discharge cycling experiment was conducted with the coin cell containing the mono-HexC10TFSI+LiTFSI (1.6 M) electrolyte with a current rate of C/7, corresponding to a full charge/discharge of the cathode capacity in 7 hours. The battery operated for a month at 100 °C and cycled 70 times (**Figure 5D**). The initial high capacity of ~ 135 mAh/g decreased to 70 mAh/g after 70 cycles.

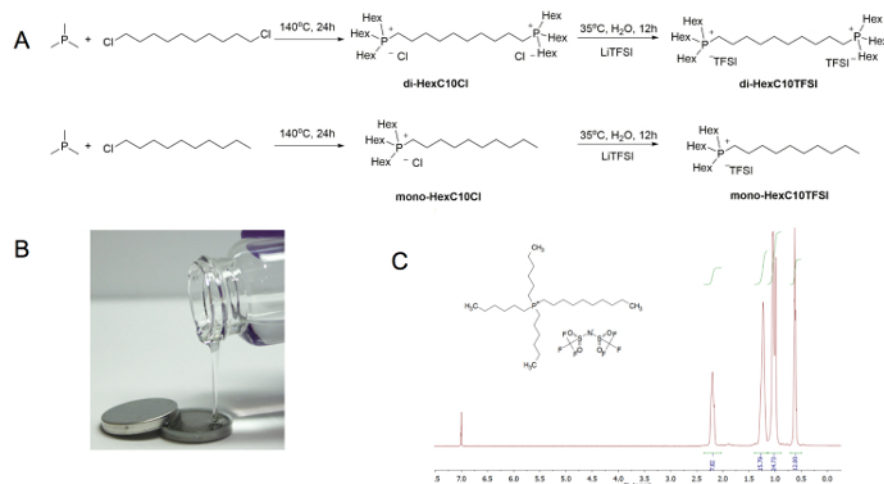


Figure 1. Synthesis and structural characterization of a phosphonium ionic liquid. (A) Synthetic route to the monoHexC10TFSI ionic liquid; (B) Photograph of a purified mono-HexC10TFSI ionic liquid; and (C) ¹H NMR spectrum for mono-HexC10TFSI. [Please click here to view a larger version of this figure.](#)

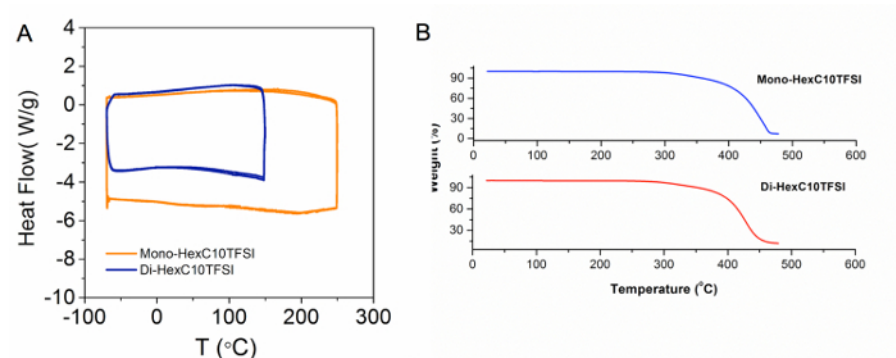


Figure 2. Thermal stability characterization data for the mono-HexC10TFSI and di-HexC10TFSI ionic liquids. (A) Heat flow as a function of temperature from -70 to 150 °C, as measured by DSC; and (B) Weight loss as a function of temperature, as measured by TGA. [Please click here to view a larger version of this figure.](#)

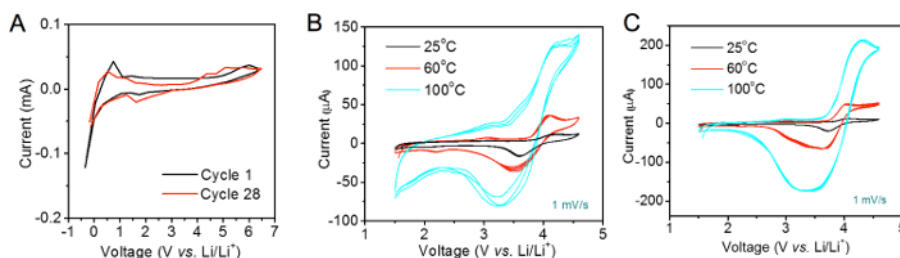


Figure 3. Cyclic voltammetry experiments. (A) Cyclic voltammetry of monoHexC10TFSI at 100 against Pt; (B) Cyclic voltammetry of di-HexC10TFSI at various temperatures in LiCoO₂/Li redox couple; and (C) Cyclic voltammetry of mono-HexC10TFSI+LiTFSI at various temperatures in LiCoO₂/Li redox couple. Reprinted with permission from Chemical Sciences²⁷. [Please click here to view a larger version of this figure.](#)

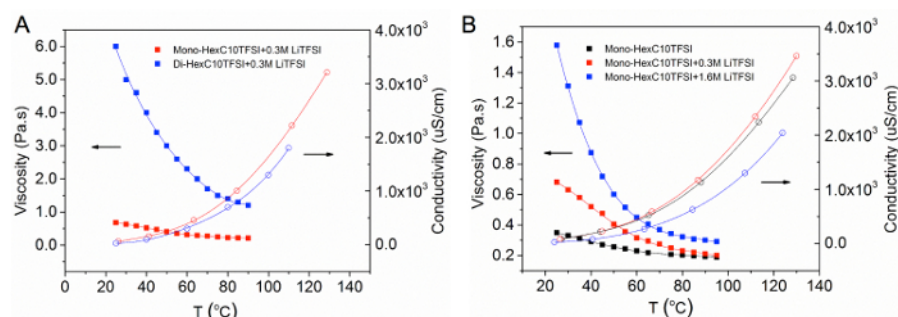


Figure 4. Conductivity and viscosity measurements. (A) di-HexC10TFSI+LiTFSI (0.3 M) and mono-HexC10TFSI+LiTFSI (0.3 M) as a function of temperature, (B) mono-HexC10TFSI+LiTFSI loaded with different concentrations of LiTFSI as a function of temperature. Reprinted with permission from Chemical Sciences²⁷. [Please click here to view a larger version of this figure.](#)

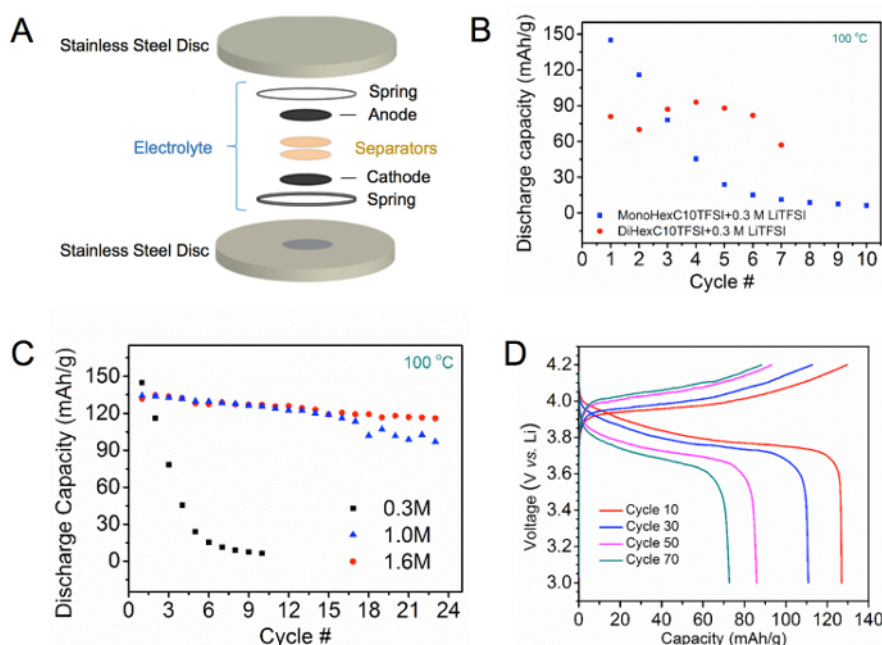


Figure 5. Coin cell battery experiments. (A) Schematic of the coin cell battery; (B) Discharge capacity as a function of cycle number for a battery containing the mono-HexC10TFSI+LiTFSI (0.3 M) and di-HexC10TFSI+LiTFSI (0.3 M) at 100 °C; (C) Discharge capacity as a function of cycle number for a battery containing the mono-HexC10TFSI doped with different concentrations of LiTFSI at 100 °C; (D) Galvanostatic charge-discharge cycling for a battery with the mono-HexC10TFSI+ LiTFSI (1.6 M) composition at 100 °C, current rate at C/7. Reprinted with permission from Chemical Sciences²⁷. [Please click here to view a larger version of this figure.](#)

IL	T_g^a	T_m^a	T_d^b	Viscosity (Pa·sec) at 25 °C, 1 Hz
	(°C)	(°C)	(°C)	
mono-HexC10Cl	-	-	340	9.0×10^2
mono-HexC10TFSI	-	-	355	3.0×10^{-1}
di-HexC10Cl	-30	60	385	2.6×10^5
di-HexC10TFSI	-	-	375	5.2×10^0

Table 1. Properties of Ionic Liquids under Investigation.

^a Determined from -70 to 150 °C; it indicates that a T_g or T_m was not observed in the temperature range tested.

^b The temperature at 10% weight loss. Samples are protected by nitrogen during test.

Discussion

Our approach to develop non-flammable and high temperature functional Li-ion batteries involves the synthesis of new ionic liquid electrolytes and their subsequent evaluation in prototypical coin cells. Specifically, mono-HexC10TFSI and di-HexC10TFSI based electrolytes were tested in a coin cell possessing a Li metal anode and LiCoO₂ cathode. The critical steps within this approach are to: 1) identify the lead electrolyte

according to a set of design specifications; 2) maintain dryness and ensure water does not enter the cell; and 3) develop a cell assembling procedure that affords a working battery.

Due to the large number of ionic liquids available and given the different combinations of cations and anions, a reiterative process is undertaken which involves selection of an ionic liquid, evaluation of performance, and then optimization or alteration of the ionic liquid composition. An ideal electrolyte material should possess the following characteristics: 1) wide electrochemical window, within which the electrolyte is stable; 2) high ionic conductivity and low electronic conductivity to facilitate ion transport between the electrodes and inhibit self-discharge; 3) chemical and thermal stability so that the electrolyte is compatible with other cell components such as separators, electrodes and their substrates, *etc.*, and to increase the cell safety; 4) non-flammability and low vapor pressure to avoid cell pressure build-up and fire during cell failure; and 5) low toxicity and low cost. High thermal stability of the electrolyte is critical for safe operation and a high cycle number for batteries operating at temperatures greater than 25 °C. Traditional electrolyte materials are carbonate based solvents which are flammable and volatile, and, thus, cannot be used in high temperature batteries.²⁸ Polymer electrolytes are also being investigated as they possess the merits of non-volatility and non-flammability. However, polymer electrolytes are usually solid structures and have lower conductivities ($< 10^{-4}$ S/cm) compared to ionic liquids and carbonate based solvents.^{29,30}

According to the requirements for the ideal electrolyte material described above, the selection of the electrolyte can be challenging. Often these requirements contradict each other and trade-offs must be taken to maximize the battery performance. A representative challenge that we encountered involved the selection of the lithium salt concentration. We initially chose 0.3 M as the concentration to be used in the battery as it yielded the highest conductivity. Any increase in the salt concentration beyond 0.3 M increased the viscosity and lowered the conductivity due to an increase in mass. However, we observed that this low salt concentration limited charge-discharge cycling, whereas the use of higher concentrations, such as 1.0 M and 1.6 M (which possessed lower conductivity values), gave longer stable cycling in the coin cell. Attempts to increase the Li salt concentration beyond 1.6 M were unsuccessful, as we were at the solubility limit. Additionally, using this procedure, the cathode, anode, and separator, along with the electrolyte, can be exchanged and varied to evaluate other battery configurations.

Moisture is known to deteriorate battery performance and shorten the cycle life as well as influence the physical properties of the material (*e.g.*, viscosity). Thus, all the materials comprising the battery should be prepared and characterized under anhydrous conditions and under the protection of argon gas. For example, a rigorous drying procedure is used to remove trace amounts of moisture from the ionic liquids and the Li salts. For these reasons, the ionic liquids are always dried at 100 °C for 24 hours with rigorous stirring under high-vacuum overnight before use. The rheological studies are performed in a sealed glove bag filled with nitrogen to ensure that the ionic liquids are not exposed to air, as the ionic liquids are hygroscopic and easily absorb water. Hence, all the materials involved should be handled or prepared in the glove box or protected by inert gas (argon) under anhydrous conditions. Special cautions should also be taken when handling the glass containers and transferring the ionic liquid in and out of the glove box. Finally, all of the hardware battery components are dried in a vacuum oven at 70 °C overnight to remove moisture before assembly in the glove box.

Several technical difficulties were encountered when assembling the ionic liquid based batteries as a result of the viscous nature of the ionic liquids compared with the readily flowing carbonate solvents. When soaking the separators in the ionic liquid prior to cell assembly, it is difficult to wet all the separator pores. Thus, we heated the separators in the ionic liquid to 60 °C for 15 minutes while stirring to ensure complete wetting of the separator. Likewise, the crevices/pores in the electrodes must also be filled with sufficient ionic liquid electrolyte to ensure good contact with other components of the battery. In order to obtain consistent results, several drops of ionic liquid are dispensed to fully cover the surface and the electrode is heated to 60 °C for 15 minutes before integrating the LiCoO₂ electrode into the battery. These steps are critical as insufficient amounts of electrolyte will afford a short circuit during coin cell operation. Before testing, it is important to have the assembled battery rest at room temperature for 12 hours to ensure that the electrolyte is dispersed throughout the battery.

With proper handling of all materials to ensure dryness, thoroughly covering all components of the coin cell battery (*e.g.*, electrode and separators) with the electrolyte, and allowing the coin cell battery to equilibrate, a coin cell battery can be fabricated that is suitable for testing ionic liquid electrolytes at high temperatures. If failure occurs or unusual results are obtained, review the above steps and suggestions, and repeat the experiments. Limitations can also arise due to the inherent properties of the materials used to construct the coin cell battery. For example, if tests are performed above 100 °C, the separators and electrodes need to be changed.

In conclusion, protocols are described to prepare phosphonium-based ionic liquid and lithium bis(trifluoromethane)sulfonimide salt electrolytes, and to assemble a non-flammable and high temperature functioning lithium-ion coin cell battery. The viscosity, thermal stability, conductivity, and electrochemical stability of mono-phosphonium and di-phosphonium ionic liquids are measured. Preparation of a coin cell battery containing either the mono-phosphonium+LiTFSI or the di-phosphonium+LiTFSI electrolytes, and subsequent battery testing at 100 °C revealed the influence of the lithium salt concentration on successful cycling. These validated experimental procedures will facilitate the study of high temperature batteries, especially those that employ viscous and anhydrous electrolytes.

Disclosures

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