Piperidinium ionic liquids as electrolyte solvents for sustained high temperature supercapacitor operation

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Piperidinium ionic liquids as electrolyte solvents for sustained high temperature supercapacitor operation

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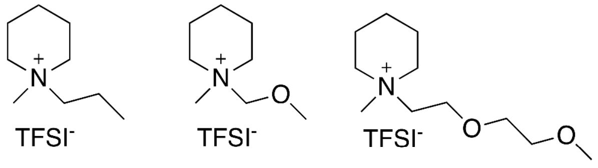
The synthesis and physicochemical properties of a series of non-flammable, thermally stable alkyl ether containing piperidinium ionic liquid electrolytes, containing lithium bis(trifluoromethanesulfonyl) imide, are described along with the superior performance of a lithium ion supercapacitor containing a piperidinium electrolyte compared to a standard carbonate based electrolyte at 100 °C.

Electrical energy storage (EES) device operation at elevated temperatures from 25 to 100 °C is in demand as uses in consumer goods, oil and mining, and automotive expand to meet new market opportunities.[1-7] Currently, the number and variety of such commercially available EES devices are limited. For example, the lithium-thionyl chloride ($LiSOCl_2$) battery is one of the most robust systems available, but $LiSOCl_2$ batteries exhibit high internal resistance and $SOCl_2$ is toxic, corrosive, and hazardous. There have been more successes with supercapacitors (e.g., Evans and FastCap), albeit these devices exhibit reduced cyclability at elevated temperatures.[8, 9] This is a materials-centric and multifaceted problem with significant research efforts directed at synthesizing new electrode, electrolyte, and spacer materials, and evaluating their performance. This challenge is compounded by the desire to have both small portable devices as well as devices that provide high capacity and/or rapid power response. While a number of breakthroughs are reported describing new high energy/power density electrode materials,[3, 5, 10-14] thermally stable separators,[15,16] and electrolytes.[17-20] Electrolytes remain a limiting factor precluding wide-spread practical use in the above-mentioned applications and represent an opportunity for research. Our interest is in thermally stable, non-flammable, non-volatile electrolytes for use in EES devices at elevated operating temperatures. Specifically, we report the: 1) synthesis of a series of non-flammable, thermally stable alkyl ether containing piperidinium ionic liquid electrolytes containing lithium bis(trifluoromethanesulfonyl) imide (LiTFSI); 2) density functional theory calculations of the cation-anion binding energies; 3) temperature and LiTFSI concentration dependence on ion conductivity and viscosity; and, 4) sustained performance of a lithium ion supercapacitor (LIC) at 100 °C.

Our selection of ionic liquids to address this recognized problem in electrolyte deficiencies is supported by a number of reports describing imidazolium and phosphonium based ionic liquids, and their corresponding low vapor pressure and non-flammability.[21,22] Significant research efforts are also underway to identify alternative thermally stable electrolytes such as ionic liquid-carbonate solvent electrolyte mixtures,[23] ethoxy propylene carbonate electrolytes,[24] and solid polymer electrolytes (SPEs),[25] including degradable and environmentally friendly systems.[26] The key attributes responsible for SPE performance are compositions containing a large fraction of oxygen atoms to promote lithium salt dissociation (e.g., poly(ethylene oxide)), possessing low glass transition temperatures to increase segment mobility and ion transport, and exhibiting high thermal decomposition temperatures to ensure non-flammability (≥150 °C).

Piperidinium ionic liquids possess a number of favorable properties including non-flammability, large electrochemical window (-3.8 to 2.5 V vs Pt), and inherent conductivity for use as an electrolyte solvent in electrical energy storage devices.[27, 28] The archetypical piperidinium ionic liquid is N-methyl-N-propyl-piperidinium, **1**, and **1** has been extensively investigated by several laboratories since its first synthesis.[29-31] Inspired by the performance of SPEs, we introduced an alkyl ether chain into the



1 2 3

Figure 1. Chemical structures of the ionic liquids investigated. N-methyl-N-propyl-piperidinium TFSI (**1**), N-methyl-N-methoxymethyl-piperidinium TFSI (**2**), and N-methyl-N-methoxyethoxyethyl-piperidinium

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Electronic Supplementary Information (ESI) available: Details of synthesis, flammability test, coin cell fabrications and DFT calculations. See DOI: 10.1039/x0xx00000x structure of **1** and synthesized similar analogues containing one, **2**, or two ether atoms, **3**. With this structural change, we hypothesize that the benefits associated with SPEs will also be seen in these ionic liquids, with a concurrent reduction in viscosity and increase in conductivity compared to **1**.[32, 33]

Ionic liquid **1** was purchased from Iolitec Inc. and used without further purification, while **2** and **3** were synthesized following modifications of previously published works.[34, 35] Ionic liquid **2** was synthesized by addition of bromomethyl methyl ether (20 mmol) to a 1.0 M solution of N-methylpiperidine (20 mmol) in ethyl acetate, while under argon and protected from light. The solution was heated to 50 ^{o}C for 12 hours. The corresponding bromide product was recrystallized using minimal dichloromethane (DCM)/ethyl acetate.[34] Lastly, the bromide anion was exchanged for the TFSI anion by dissolving equimolar amount of the product with LiTFSI in 70 mL of DCM/H_2O (1:1). The mixture was stirred overnight at room temperature, and the water phase was washed three times with DCM. The organic phase was subsequently dried over $MgSO_4$. Product **2** was isolated in 27% yield. Ionic liquid **3** was synthesized in a similar manner, except N-methylpiperidine (9.0 mmol) was cooled to 0 ^{o}C in a dark vessel under argon, and 1-bromo-methoxyethoxy ethane was added over 30 minutes (9.00 mmol). The mixture was stirred for 12 hours at room temperature and unreacted material was removed *in vacuo* to obtain the corresponding bromide product.[35] The TFSI analog was obtained following the description above. The product was subsequently passed through an activated charcoal column and isolated in 70 % yield. The composition and structure of each ionic liquid were confirmed by NMR and mass spectrometry (see ESI). Piperidinium ionic liquids **2** and **3** are non-flammable, as they do not ignite when exposed to an open flame (see ESI).

Prior to performing the supercapacitor experiments, the thermal stability, viscosity, and conductivity of **1**, **2**, and **3** were measured. Before each test, the samples were dried at 80 ^{o}C while under vacuum for at least 6 hours. Thermal Gravimetric Analysis (TGA) on samples heated from 20 to 500 ^{o}C at a rate of 10 ^{o}C min^{-1} revealed decomposition temperatures of 386, 288, and 356 ^{o}C for **1**, **2**, and **3**, respectively. The substitution of an oxygen atom for a methylene in the composition reduces the decomposition temperature, and compounds **2** and **3** are less stable than **1**, with **2** being the least stable. Though all are stable at 100 ^{o}C. DSC analysis shows no T_m or T_c for **2** or **3**, indicating the compositions are a liquid over a wide temperature range, unlike **1** which has a T_m and T_c at 19 and -23 ^{o}C, respectively.

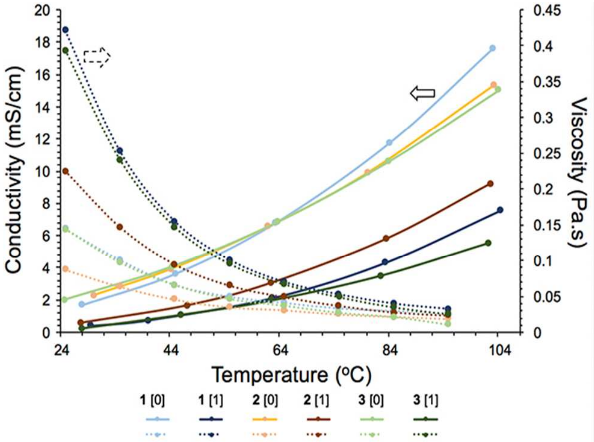

Figure 2. Conductivity and viscosity data for **1**, **2**, and **3** with 0.0 M and 1.0 M LiTFSI salt concentration as a function of temperature. The conductivity and viscosity data are represented by solid and dotted lines, respectively, with the color of the line corresponding to the ionic liquid and the darker shades reflecting increased LiTFSI salt concentration (N>3). Individual graphs for the conductivity and viscosity as well as for the 0.5M LiTFSI compositions are found in the ESI.

Next, the viscosity and conductivity of the neat ionic liquids, **1**, **2**, and **3** as well as electrolyte compositions of **1**, **2**, and **3** with 0.5 and 1.0 M LiTFSI were measured as a function of temperature from ≈ 25 to 100 ^{o}C. The conductivity is directly correlated to the temperature, but inversely correlated to the added LiTFSI concentration; the opposite trend is observed for viscosity (Figures 2, S4-S8, S10-S14). As the temperature is increased, the viscosity values for **1**, **2**, and **3**, and the electrolyte mixtures decrease. The mixtures exhibit Newtonian behaviour (See ESI). The ionic liquids containing ether groups within the alkyl chain display a greater decrease in viscosity compared to **1**. For instance, at 25 ^{o}C **1**, **2**, and **3** with 1.0 M LiTFSI salt possess viscosities of 0.42, 0.22, and 0.39 Pa.s, respectively. At lower temperatures, ionic liquid electrolyte **2** exhibits the lowest viscosity value. At higher temperatures, the difference between the three ionic liquid electrolytes diminishes and all three ionic liquid electrolytes display nearly the same viscosity of approximately 0.03 Pa.s. The conductivity of ionic liquids **1**, **2**, and **3** increase with increasing temperature, and it is clear that the incorporation of the ether group increases the conductivity of the ionic liquid as both **2** and **3** possess conductivities slightly higher than **1**. At 25 ^{o}C, ionic liquids **1**, **2**, and **3** possess conductivities of 1.40, 2.29, and 1.99 mS/cm, respectively. Upon addition of LiTFSI to the ionic liquids, the conductivity values of all three electrolytes decrease. Ionic liquid **2** with 1.0 M LiTFSI possesses a conductivity value of 0.56 mS/cm at 25 ^{o}C, while **1** and **3** with 1.0 M LiTFSI salt both have a value of ≈ 0.25 mS/cm. At 105 ^{o}C, the conductivity difference between electrolytes **2** and **1** is more pronounced with the values being 9.2 and 7.5 mS/cm, respectively. The conductivity value for electrolyte **3** with 1.0 M LiTFSI is 6.2 mS/cm at 105 ^{o}C and lower than **1**. For comparison, the conductivity and viscosity values of propylene carbonate (PC) with 1.0 M LiTFSI , a conventional electrolyte, at 25 and 80 ^{o}C are 4.8 mS/cm, 0.006 Pa.s, and 10.8 mS/cm, and 0.003 Pa.s, respectively (See Figures S9 and S15).[36] The conductivity values measured at room temperature for these electrolytes are similar to literature values (see Tables S4, S5, and S6).[23, 31, 37, 38]

Calculations using density functional theory (DFT; Gaussian 16; B3LYP-D3BJ/6-311G(d,p) using B3LYP-D3BJ/6-31G(d) optimized geometries) were next performed to gain further insight into observed viscosity and conductivity trends with the piperidinium ionic liquids.[39] The inclusion of empirical dispersion and basis set superposition error corrections are important for calculations relevant to ionic liquids.[40, 41] The cation-anion binding energies for **1**, **2**, and **3** are similar in magnitude and approximately 3X lower than that calculated for LiF (Table 1). The weak electrostatic interaction energies are consistent with **1**, **2**, and **3** being liquids at 25 ^{o}C and the reduction in viscosity with increasing temperature, as sufficient energy is added to the system to overcome the interaction energies. Similarly, the conductivities of **1**, **2**, and **3**

Table 1. Calculated binding energies for the ion pairs.

Ionic Liquids	Binding Energy (kcal mol^{-1})[1]
N-methyl-N-propyl-piperidinium TFSI, **1**	-11.44
N-methyl-N-methoxymethyl-piperidinium TFSI, **2**	-11.50
N-methyl-N-methoxyethoxyethyl-piperidinium TFSI, **3**	-9.87
LiTFSI	-10.22, -11.02, -14.11
LiF	-2.34

[1] Energy calculations were performed in Gaussian 16 with a polarizable continuum model (PCM) with a dielectric constant ε = 15.2. Three configurations were found for LiTFSI and the resulting range of binding energies is reported. The binding energy for LiTFSI in a PCM with a dielectric constant ε = 78.4, more similar to PC, was calculated to be -6.73, -6.02, -7.14.

increase at elevated temperatures as the ions move more freely. However a direct correlation between the small differences in binding energy values of **1**, **2**, and **3** and viscosity/conductivity data is not observed. This observation may be the result of the piperidinium ionic liquid molecular weight or size being a greater contributor to the outcome (e.g., **3** has a larger mass and viscosity compared to **2**) or a limitation of the DFT method.[42] Addition of LiTFSI to **1**, **2**, and **3** increases the viscosity values as there is more material per volume. The conductivity values also decrease with added LiTFSI in a concentration dependent manner. This result is consistent with the increased viscosity with added LiTFSI. Additionally, given that the binding energy of LiTFSI is on par with **1**, **2**, or **3**, a portion of LiTFSI and the electrolyte move as neutral pairs in the electrolyte. For comparison, the calculated binding energies are lower in a higher dielectric constant medium (e.g., PC), suggesting the ions are separated. These neutral pairs reduce the rate of ions flowing through the electrolyte affording a decrease in conductivity as the concentration of LiTFSI is increased. Again raising the temperature provides energy to overcome these electrostatic interactions, and the conductivity increases as more ions move as single species and not pairs. This explanation does not completely describe the conductivity-temperature dependence relationship, as the conductivity values for **1**, **2**, or **3** do not converge at a single high temperature value. Additional calculations are ongoing to understand the finer details of cation-anion pairing.

Given the thermal stability, lack of thermal transitions, lower viscosity, and higher conductivity of ionic liquid electrolyte **2** with 1.0 M TFSI compared to **1** and **3**, we selected electrolyte **2** and evaluated its performance in a supercapacitor at 25 °C and 100 °C compared to PC with 1.0 M LiTFSI. The supercapacitors were fabricated using a method previously described.[24] The Celgard separators were soaked in 100 uL of the ionic liquid electrolyte at 60 °C for 15 minutes to ensure that the viscous electrolyte fully penetrated the separators. The cells were assembled and the capacitance values measured using a multichannel Princeton Applied Research VersaStat MC Battery tester. The cells were equilibrated at room temperature or 100 °C for 30 minutes, and tested within an electrochemical window of 0 to 2.5 V at current densities equal to 1, 2, 5 and 10 A/g. Charge-discharge cycling was performed to calculate the energy and power densities, and discharge capacitance to analyse the cycle life.

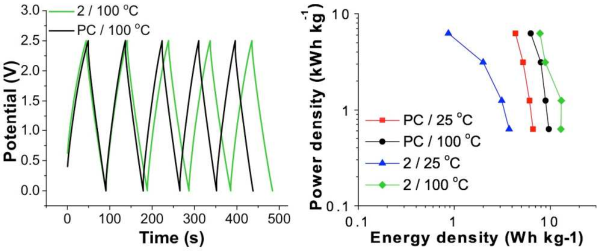

Figure 3. (left) First five charge and discharge cycles of a supercapacitor with electrolyte **2** with 1.0 M LiTFSI at 100 °C. (right) Ragone plot for supercapacitors containing electrolyte **2** or PC (1, 2, 5 and 10 A/g) at 25 and 100 °C.

The first five charge-discharge cycles of the supercapacitor with electrolyte **2** and PC at 100 °C show a similar dynamic range (Figure 3 – left; see Figure S16 for data at 25 °C). The Ragone plot for the PC and electrolyte **2** at 25 °C and 100 °C (Figure 3-right) reveals that the supercapacitor containing electrolyte **2** exhibits a lower energy density (at 1 A/g) of 3.73 Wh/kg compared to 6.61 Wh/kg for PC at 25 C. At 100 °C, the energy density for the supercapacitor containing electrolyte **2** increases to 12.91 Wh/kg and is greater than 9.65 Wh/kg for the supercapacitor containing PC. Increasing the temperature offers a 3.5X improvement in energy density at a current density of 1 A/g. At 100 °C, the supercapacitor containing electrolyte **2** also performs well at higher current densities (10 A/g) affording an energy density of 7.81 Wh/kg.

At 25 °C, the initial capacitance values after five cycles for the supercapacitors with the PC and **2** electrolytes are 36.7 and 16.1 F/g, respectively (Figure 4-left). After 2000 cycles at 25 °C, the capacitance values for both the capacitors remain constant with minimal loss over time, with the PC based supercapacitor providing greater capacitance. Raising the temperature significantly changes the capacitance of the supercapacitors. At 100 °C, these values correspondingly decrease to 36.1, and increase to 36.5 F/g for PC and **2**, respectively (Figure 4-right). Increasing the temperature affords a 2.2X enhancement in performance for **2** attributed to the decrease in electrolyte viscosity and increase in electrolyte conductivity, while a slight performance decrease occurs with the PC based supercapacitor. In contrast to the data collected at 25 °C, at 100 °C the capacitance values for the PC based supercapacitor decrease by 28% from 36.1 to 26.0 F/g after 2000 cycles with subsequent device failure at approximately 3200 cycles. This result is consistent with previous reports on PC based electrolytes operating at 60 °C or 70 °C where capacitor degradation occurs at higher temperatures.[43, 44] The supercapacitor with electrolyte **2** cycles for more than 10000 cycles at 100 °C with a 30% decrease in capacitance.

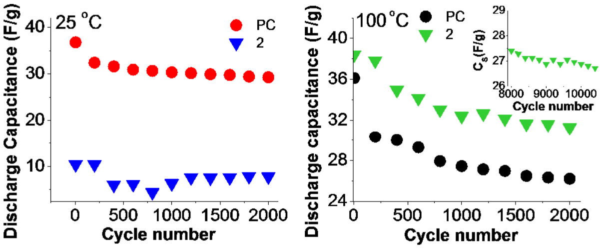

Figure 4. (left) Capacitance values as a function of cycle number for supercapacitors with electrolytes **PC** and **2** with 1.0 M LiTFSI at 25 °C. (right) Capacitance values as a function of cycle number for supercapacitors with electrolytes **PC** and **2** with 1.0 M LiTFSI at 100 °C from 0 to 2000 cycles and continued operation (insert) to 10000+ cycles.

In summary, we describe the physicochemical characteristics of piperidinium ionic liquids possessing an alkyl ether chain as electrolytes, when combined with LiTFSI, for lithium ion supercapacitors. Replacing the alkyl chain with an alkyl ether within the piperidinium ionic liquid composition lowers the decomposition temperature, although all of the compounds are stable to >250 °C, and eliminates phase transitions (T_m or T_c) affording a material which is a liquid over a wide temperature range. The conductivity of the piperidinium ionic liquids are inversely correlated to added LiTFSI concentration but directly correlated to temperature; viscosity displays the opposite relationship. The differences in electrolyte viscosity is most pronounced at lower temperatures, while at high temperatures all the electrolytes possess low values similar to each other. The conductivity of the electrolytes increases with increasing temperatures, and electrolyte **2** exhibits the largest value of 9.2 mS/cm. DFT calculations reveal weak cation-anion binding energies between the piperidinium ionic liquid and TFSI, relative to LiF. A carbon electrode base lithium ion supercapacitor containing electrolyte **2** operates for 10000+ charge-discharge cycles and provides 28 F/g of capacitance at 100 °C, while an analogous device with a PC electrolyte fails after 3200 cycles. These findings support the continued development and performance evaluation of ionic liquid electrolytes for electrical energy storage devices operating at elevated temperatures.

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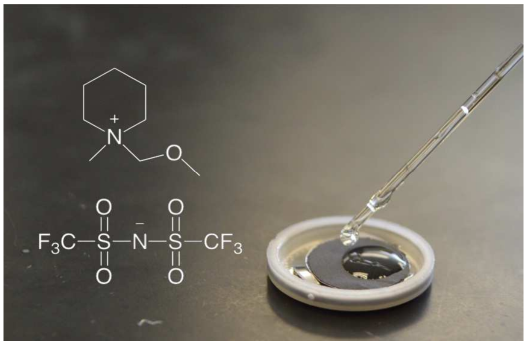

A supercapacitor with a piperidinium ionic liquid and LiTFSI electrolyte operates for 10000+ cycles at 100 °C

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