Spiro-ammonium Imide Salts as Electrolytes for Lithium Batteries

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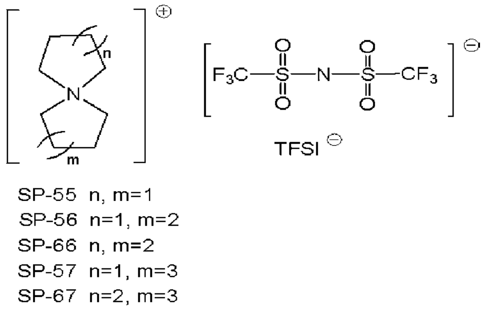
Organic salts based on the bicyclic (spiro) ammonium cation were synthesized with a systematic variation in the size of the rings. The salts show high melting points and plastic crystal phases. The SP-56 salt showed the lowest melting point, highest ionic conductivity, and a reduction potential more positive than that of the Li/Li$^+$ couple; therefore, it was mixed with EC before being employed in a Li/LiFePO$_4$ battery. The battery maintained capacities between 100 and 113 mA h g^{-1} over 100 cycles.

Conventional battery electrolytes incorporate a mixture of linear and cyclic organic carbonate solvents that are volatile and flammable and LiPF$_6$ salt that in the presence of small amounts of water releases HF causing corrosion and undesired chemical reactions, all detrimental to the overall functioning of the battery.[1] Ionic liquids, ILs, are considered as promising alternatives due to their nonvolatility, nonflammability, and also for their chemical, electrochemical, and thermal stabilities.[2] The most studied ILs are those based on heterocyclic or aliphatic (tetraalkyl or dialkyl monocyclic) ammonium cations coupled with negative-charge-delocalizing anions such as BF$_4^-$, PF$_6^-$, or [N(SO$_2$CF$_3$)$_2$]$^-$. When introduced in Li metal or Li ion batteries their electrochemical (cathodic) stability, high viscosity (i.e., low ionic conductivity), and compatibility with the graphite anode turned out to be serious challenges, but molecular engineering of the ammonium cation resulted in ILs with improved cathodic stability and battery cycling performance as in the case of dialkyl-monocyclic ammonium imide salts such as *N*-methyl, *N*-propylpiperdinium imide, PP113.[3,4]

Herein, we extend our study on the effect of the structure of the ammonium cations on the thermal and electrochemical properties and on battery performance of their salts as electrolytes. We report on the salts of an ammonium cation that has two aliphatic rings bonded to the positive-charge-bearing nitrogen atom, known as spiro-ammoniums.

As illustrated in Scheme 1, we synthesized five salts, systematically varying the size of the cation's two rings, by refluxing appropriate amounts of a cyclic amine and a dibromoalkane in a strong basic solution, following the procedure reported in ref 5. ^{1}H and ^{13}C NMR spectra of the synthesized salts showed that three of the five salts (SP-55, SP-56, and SP-66) were obtained in the pure form and in a good yield while those that have the seven-membered ring (SP-57 and SP-67) contained large amounts of the uncyclized compounds. The salts were synthesized with Br$^-$ as an anion which we exchanged for the TFSI$^-$, bis(trifluoromethane sulfonyl) imide, [N(SO$_2$CF$_3$)$_2$]$^-$ anion, due to its renowned negative-charge delocalization and high geometric flexibility that reduces the (lattice energy) melting points of its salts.



Scheme 1. Chemical structure of the five spiro-ammonium imide salts synthesized in this work.

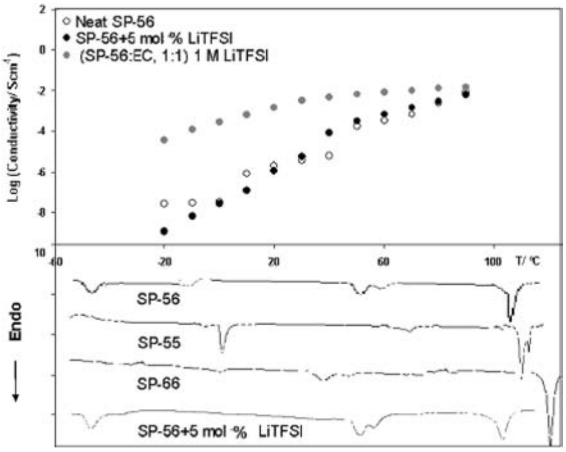


Figure 1. DSC scans of SP-56, SP-55, SP-66, and SP-56 + 5 mol % LiTFSI and ionic conductivity of the neat SP-56 and with additions of LiTFSI alone and with EC.

From Figure 1, showing the DSC scans of the three pure salts (SP-55, SP-56, and SP-66), it can be seen that the salts have melting points above 100 °C and undergo a second-order transition below the melting temperature to plastic crystal phases before the regular crystal phase. The melting points are much lower than those reported for the corresponding salts using Br$^-$ or BF$_4^-$ as an anion.[5,6] For example, the melting points of the SP-55 and SP-66 were lowered from 322 and 248 °C in the case of the bromide down to 113 and 130 °C for the imide salts, respectively. The three salts showed a transition from the regular crystal phase to plastic crystal phases similar to what was reported for other ammonium imide salts with different structures (heterocyclic; aliphatic tetraalkyl, or monocyclic) that originates from the rotation and orientational disorder of the cations (and possibly the anion) while in their lattice sites.[7] This was observed at 8 °C for the SP-55, at 41 °C (very weak) for SP-66, and at −40 °C for the SP-56. The latter showed a second plastic crystal phase starting at 59 °C, which can be attributed to the higher number of possible conformational isomers available to this structure due to the extra methylene groups in one of the

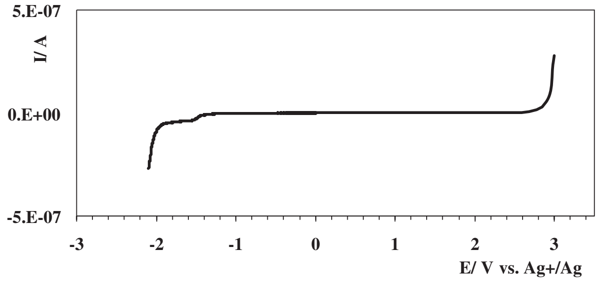


Figure 2. A linear sweep voltammetry scan of neat SP-56 in the molten state (110 °C) using a Pt microelectrode as a working electrode and a silver wire as the counter and the reference electrode at a sweep rate of 50 mV s^{-1}.

rings, which leads to greater disorder and plasticity, similar to what is observed for the pyrazolium imide family.[8] The exact nature of the transitions is currently under investigation by means of powder X-ray diffraction experiments as a function of temperature for the salts in order to elucidate the exact crystal structure and verify the plastic crystal behavior of all the phases. Moreover, it can also be seen in Figure 1 that the addition of 5 mol % of LiTFSI salt to neat SP-56 resulted in a slight decrease in the melting point but showed no effect on the position and magnitude of the regular-to-plastic crystal transition peaks.

The conductivities of the neat salts were measured using an AC impedance spectroscopy technique as a function of temperature. As observed for other organic ionic liquid salts exhibiting plastic crystal behavior,[8] changes in conductivity correlate well with phase transitions observed in the DSC scan. In the case of the SP-56 salt, which showed the highest conductivities throughout the temperature range investigated, a jump in conductivity was observed at 50 °C where it changes from a plastic crystal phase I to another, plastic crystal phase II, giving conductivities reaching 2.0×10^{-6} S cm^{-1} at 20 °C and increasing to 8.1×10^{-3} S cm^{-1} close to melting at 90 °C. The conductivity of the SP-56 salt was measured as a function of added LiTFSI. Upon the addition of 5 mol %, a very slight change in conductivity was observed and it reached 1.2×10^{-6} S cm^{-1} at 20 °C.

A linear sweep voltammetry scan of neat SP-56, conducted using a platinum microelectrode and silver wire as a counter and pseudo-reference electrode, is shown in Figure 2. The voltammetry scan exhibits no electrochemical activity within a window that extends over 5 V. However it also showed that like most ILs that are based on an ammonium cation the salt is reduced at potentials more positive than the Li/Li^+ redox potential.

It is widely accepted that the use of a neat IL alone, without an additive, as an electrolyte in lithium batteries has been proven to be a difficult task. In this case the high melting point and low cathodic stability of the ILs being investigated prevent their usage as electrolytes in the neat form in lithium metal or lithium ion batteries.[9] Consequently, we have chosen ethylene carbonate, EC, for an additive as it is well known for its SEI forming abilities, its high dipole moment and good thermal properties. To a mixture of SP-56 and EC (1:1 by weight) LiTFSI was added (1 M), and the conductivity of the resultant liquid was measured and found to be 1.5×10^{-3} S cm^{-1} at 20 °C that increased to 1.5×10^{-2} S cm^{-1} at 90 °C. This liquid electrolyte was employed in a Li/$LiFePO_4$ battery. The battery showed an initial discharge capacity of 100 mA h g^{-1} that increased to 113 mA h g^{-1} by the 13th cycle and decreased gradually upon further cycling to 105 mA h g^{-1} by the 100th cycle, as shown in Figure 3.

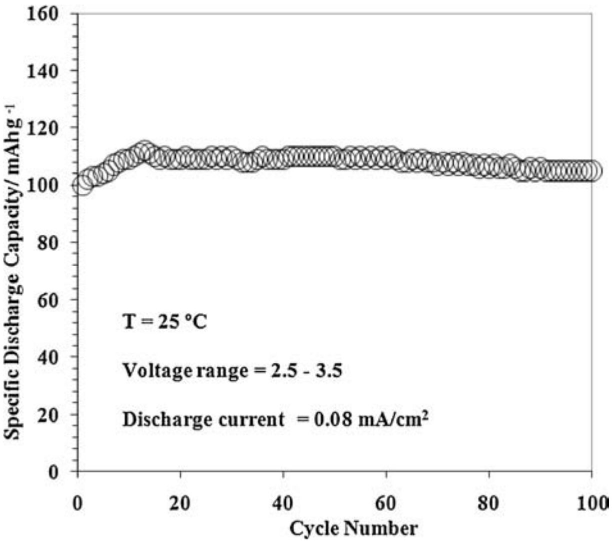


Figure 3. Cycling performance of a Li/$LiFePO_4$ battery using 1 M LiTFSI/SP-56:EC (1:1) as an electrolyte.

In conclusion, we have synthesized new type of organic salts based on a bicyclic (spiro) ammonium cation combined with an imide anion. The salts showed plastic crystal behavior that can support high ionic conductivity below their melting which turned out to be well above ambient temperatures. Lithium batteries using the synthesized salts, which showed low cathodic stability, mixed with conventional solvents delivered promising discharge capacities.

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