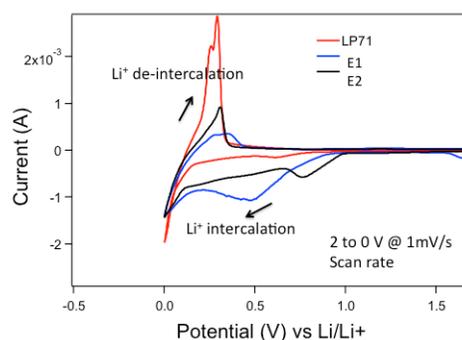


## Project 1: Functional ionic liquid based electrolytes for Li-ion battery applications (2 students)<sup>#</sup> - Lynden Archer

Current state of the art liquid electrolytes in Li-ion batteries for EVs and HEVs are in most cases simple transplants from conventional Li-ion batteries used in portable devices, which were historically optimized for the rate at which they transport ions between 3.3 and 4.2 Volts (typical voltage cutoff for cell phone batteries). These organic carbonates and ethers are used as electrolytes because they have polar groups and possess good affinity for Li-ions, moderate dielectric constants and moderate to low viscosities at room temperature. The choice of electrolyte has a significant effect on the interfacial properties of the electrodes and hence the long term performance and stability of the battery. Graphite the anodic material of choice for Li-ion batteries to pair against current and future cathode materials, accommodates a maximum of one Li ion per six carbon atoms, yielding a theoretical capacity of 372 mAh/g. The intercalation of Li ions into the graphite basal planes occurs around 0.1V vs Li/Li<sup>+</sup>, which is beyond the thermodynamic stability of the organic electrolytes. During this process, the graphite electrode is cathodically polarized to low potential, electrolyte solvent, salt anions and impurities in the electrolyte are reduced to form some insoluble products which deposits on the surface of the anode to form a passivating layer. This process takes place mostly during the first several cycles of a working battery. The thus formed passivating layer termed as a solid electrolyte interface (SEI) layer by Peled [1], is recognized as a crucial factor on the performance of Li-ion batteries.

Recent progress in synthesis, purification, and electrochemical analysis of room temperature ionic liquids (ILs) has established the promise of this unique class of materials as electrolytes for next-generation lithium batteries [2]. ILs are organic salts having melting points below 100°C and generally consist of a bulky cation and an inorganic anion. Because of their unique combination of physicochemical properties, such as negligible vapor pressure, non- or low flammability, good room-temperature ionic conductivity, wide electrochemical stability window, and favorable chemical and thermal stability, ionic liquids possess many synergistic attributes that will ultimately make electrolytes based on ILs materials a viable choice for Li-ion batteries. The vast range of anion and cation chemistries that can be combined to create ILs tailor-made or explicitly designed to complement a specific combination of electrode chemistries, also provides a largely untapped materials library that can address concerns about battery safety. However, ILs have remained unattractive as electrolytes for Li-ion batteries for two reasons: first, the fraction of the ionic conductivity of the electrolyte arising from mobile lithium ions (i.e. the so-called lithium transference numbers) is typically low, making cells using IL electrolytes prone to polarization. Second, most ILs exhibit only moderate total ionic conductivity at and below freezing temperatures, and poor lithium-ion transference due to



**Fig 1.** Cyclic voltamograms of Li-Graphite half cells

the relatively large proportion of mobile cations in the system.

Although ILs are stable at high voltages, their cathodic stability is poor. Thus, one of the challenges is to widen the cathodic stability window of ILs to enable the use of a graphite anode. To understand the electrochemical performance of the IL based electrolytes, we designed different types of electrolyte formulations based on 1-butyl-3-methyl

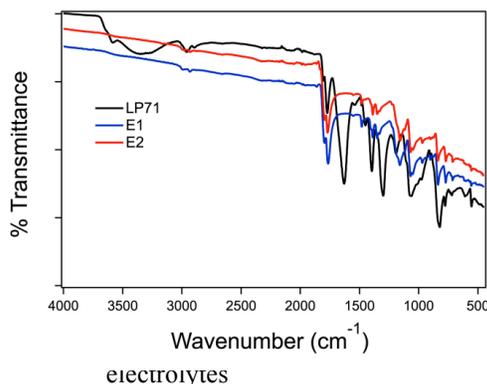
pyrrolidinium bis(trifluoromethylsulfonyl)imide (Pyr<sub>14</sub>TFSI) IL: **E1** (PC:EC: Pyr<sub>14</sub>TFSI 2:2:1 1M LiPF<sub>6</sub> with 2 wt% LiBOB); **E2** (PC:EC: Pyr<sub>14</sub>TFSI 2:2:1 1M LiPF<sub>6</sub> with 10 wt% VC), **E3**: (LP71: Pyr<sub>14</sub>TFSI). These hybrid

electrolytes are compared with state-of-the-art electrolyte **LP71** (EC:DEC:DMC: 1M LiPF<sub>6</sub>). Figure 1 shows the slow scan cyclic voltammograms for graphite electrode (graphite electrodes were received from Argonne National Lab and used as received) in a CR2032 coin cell. In case of IL electrolytes, considerable cathodic current is observed, which may be related to IL reduction or formation of a thicker SEI layer. To understand this further, FTIR spectra was collected on the electrochemically cycled graphite anodes (see Figure 2). A qualitative FTIR peak analysis indicates that the graphite surface contains organic and inorganic products. Signature peaks at ~1773 cm<sup>-1</sup> can be related to C=O stretching vibrations from [RCO<sub>2</sub>Li]. Similarly, peaks at 1630 and 1300 cm<sup>-1</sup> corresponds to C-O-C stretching vibrations and peaks at 1050 cm<sup>-1</sup> due to C-O stretching vibrations. These peaks indicate the presence of alkyl carbonates. Peaks at 820 cm<sup>-1</sup> can be related to Li-O stretching vibrations, which may be related to presence of LiCO<sub>3</sub>. These results are in agreement with literature reports [3]. As reported by others, the success of ILs as electrolyte solvents against graphite anode, depends strongly on the protective SEI formation. Both the additives (LiBOB and VC) used are effective in creating the necessary SEI to stop the intercalation of PC and IL molecules into the basal planes of graphitic carbon [4].

The focus of this project is to identify the SEI enabling functional ionic liquids and extending the temperature range of the ionic conductivity of the electrolyte solutions by tuning the melting/crystallization points of the solvent via IL-functionalized additives.

The objective of this research project is to develop functional ionic liquid based electrolyte combinations that exhibit high ionic conductivity, excellent cathodic stability and high thermal stability for applications in Li-ion batteries. We propose to achieve these objectives by optimizing non-flammable electrolyte formulations based on ionic liquids, organic co-solvents and nano-particle additives that overcome simultaneously, effective SEI layer formation issues and cation co-intercalation problems associated with ILs on the graphite anodes. The final goal of this research is to demonstrate the feasibility of these ionic liquid electrolyte systems in Li-ion full cells.

To achieve these goals, we will pursue the following technical objectives during the proposed Masters of Engineering Project research:



**Fig 2.** FTIR spectrum of graphite anodes after electrochemically cycled with different electrolytes

1. Thermal characterization of different mono and di-functional ionic liquids: piperdinium and pyrrolidinium, as the cations and FSI, TFSI as anions and characterizations of functionalized IL additives and their effect in tuning the thermal properties (melting and crystallization temp) of the electrolyte solutions to extend the temperature liquid range.
2. Investigation of physical and electrochemical properties of non-flammable electrolytes based on functional ionic liquids.
3. Understand the solid electrode interface (SEI) layer formation on graphite anode with several electrolyte combinations using spectroscopic and electrochemical methods. Determine how specific functional groups (e.g. vinyl, silane and nitrile) present on the ILs, influence cathodic stability during the cycling of graphite-lithium half-cells.
4. Investigation of electrochemical performance of hybrid ionic liquid electrolytes in full cells

Electrolytes will be prepared by mixing the functional ionic liquids with aprotic solvents (PC, EC, DEC) and appropriate amount of Li salt in the glove box. All constituents will be dried in the vacuum oven prior to the electrolyte preparation.

Physical and electrochemical properties of the electrolyte (viscosity, conductivity, flammability, thermal stability, wettability and process ability etc.) may be tuned by using various ratios of the ionic liquids. From these studies, optimized sets of ionic liquid blend electrolytes will be studied in Li-graphite half cells/graphite-LiCoO<sub>2</sub> full cells to enhance the thermal stability, cycle life and columbic efficiencies.

We will subject the electrolyte formulations to a suite of tests to evaluate how variables within our control affect performance and to develop design rules for optimizing their properties. Specifically, we will characterize wettability using a *Wilhelmy plate contact-angle device* that allows us to monitor the time-dependent mass change of separators immersed in a reservoir of hybrid IL electrolytes. These measurements will also allow us to determine the interfacial tension of the electrolyte/separator film interface.

A *dielectric spectrometer* will be used to characterize the dc ionic conductivity over a comparable temperature range. The dc measurements will be complemented with frequency-dependent dielectric loss and storage measurements that allow the loss tangent to be determined, and from the loss maximum and measured dc conductivity, the concentration of mobile ions. Viscosity and flammability of the electrolytes will also be measured as a function of IL type and concentration.

Apart from the above described characterization methods, we will investigate the thermal properties (thermal degradation, melting, crystallization and glass transition temperatures) using *Thermo gravimetric analysis* (TGA) and Differential scanning calorimetry (DSC). *X-ray diffraction and Raman spectroscopic* studies will be applied to reveal the interactions between the electrolyte solvents with the functional ILs and these results will be used to optimize their structure.