

Direct X-ray Evidence of Electrochemical Induced Intercalation of Substituted Alkylimidazolium and Lithium Cations into Graphite from Ambient-Temperature Ionic Liquids

Paul C. Trulove
Air Force Office of Scientific Research
801 Randolph St. Room 732,
Arlington, VA 22203-1977

Hugh C. De Long
Chemistry Department
US Naval Academy
Annapolis MD 21402

Thomas E. Sutto
NRL, Code 6170, Chemistry Division
Washington D. C., 20603

It has been reported that various 1-ethyl-3-methylimidazolium (EMI^+) and 1,2-dimethyl-3-propylimidazolium (DMPI^+) salts can function not only as electrolytes, but also as the electrochemical intercalates in a simple battery (1,2). Also, it has been reported that these ionic liquids can function as the electrolytes in various types of lithium battery systems, including simple graphite based systems in which Li^+ and the imidazolium cation is reported to intercalate graphite.(3-6) However, no direct X-ray evidence has been reported showing the structure of these intercalates.

In the present study we have attempted to address the lack of direct X-ray evidence of cation intercalation of graphite in ionic liquids. A series of electrochemical charging experiments were conducted on graphitic paper using the ionic liquids EMIBF_4 and DMPIBF_4 , both with and without 0.5 M LiBF_4 present. The ionic liquids, EMIBF_4 and DMPIBF_4 with and without Li^+ were first electrochemically characterized using a three electrode system in which the working electrode was a strip of carefully dried graphitic paper. Cyclic Voltammetry indicated strong intercalative behavior for the substituted imidazolium rings, and poor intercalative behavior for the tetrafluoroborate anion. Studies in which 0.5 M Li^+ was present indicate weak cationic intercalative behavior in EMIBF_4 but much stronger intercalative behavior in DMPIBF_4 . Charge discharge behavior, both with and without Li^+ present were performed in the three electrode system and yielded the following efficiencies: For the EMIBF_4 ionic liquid without Li^+ present, the cationic charge/discharge efficiency was 70%, but dropped down to near 50% with Li^+ present; for the pure DMPIBF_4 without Li^+ present, the cationic charge/discharge efficiency was 75%, but dropped slightly, down to near 70% with Li^+ present.

In order to charge the graphitic paper for the x-ray experiments, a galvanic cell was used, and charged with either the pure, or Li^+ containing ionic liquid. A standard for comparison was similarly prepared using 0.5 M LiBF_4 in propylene carbonate. Pure graphitic paper exhibited a single strong peak near 3.36 \AA , corresponding to the 0 0 2 reflection of 2-H graphite. For the graphite paper charged in propylene carbonate, a first stage intercalate, with diffraction peaks roughly corresponding to that expected for partial forming of a LiC_6 compound were observed.

As can be seen in Figure 1, clear evidence can be seen for the intercalation of the DMPI^+ cation, while only the presence of a weak shoulder could be taken as an indication the EMI^+ intercalated the graphite. Thus, for the paper charged with either EMI^+ or with 0.5 M Li^+ present,

little evidence for intercalation was observed, although the shoulder could be observed on the pure 0 0 2 reflection which correspond to partial intercalation of the graphitic paper. For the DMPI^+ cation, both with and without Li^+ present, strong diffraction peaks were observed corresponding to a 1st stage intercalate for the pure ionic liquid with a c-axis expansion of 7.2 \AA , while with Li^+ present, a multi-staged graphitic intercalate appeared to form.

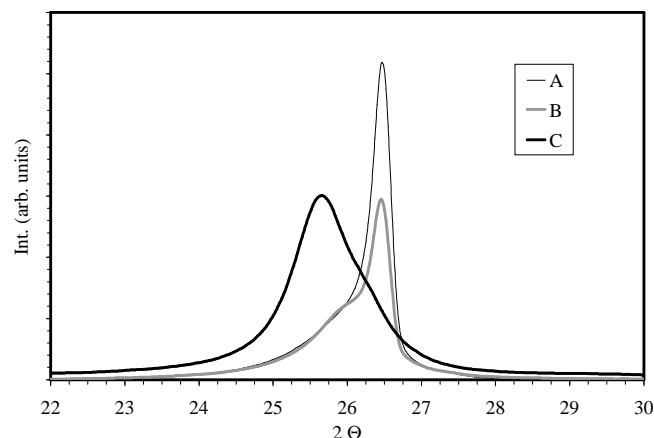


Figure1: X-ray Powder Diffraction Pattern of Graphitic Paper (A.), EMI^+ charged graphitic paper (B.) and DMPI^+ charged graphitic paper (C.). The ionic liquid charging was performed using a galvanic cell containing just the ionic liquid. A scan rate of $0.02^\circ/\text{min}$ was used.

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