INVESTIGATION OF THE STABILITY OF LOW-TEMPERATURE IONIC LIQUIDS WITH HIGH-ACTIVITY ANODES

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High-activity anodes such as lithium alloys [Li(Al), Li(Si)] are used in high-temperature (thermal) batteries that operate in the temperature range of 400^o to 550^{o}C. This technology has potential applicability for use in powering instruments while drilling in geothermal and oil/gas boreholes. Temperatures can range from 240^o – 400^{o}C in the former case and ambient to 250^{o}C in the latter case. The wide temperature range for the oil/gas boreholes makes the use of room-temperature molten salts attractive as electrolytes. However, before these ionic liquids can be used in such an environment, the compatibility of these ionic liquids with high-activity anodes must be determined.

Low-temperature ionic liquids appear to be good candidates as electrolytes for lithium and lithium-ion rechargeable cells. These electrolytes exhibit wide liquidus range, good conductivity, good thermal stability (to >300^{o}C in some cases), and good electrochemical stability (wide electrochemical window). In addition, they are nonflammable and do not present a safety hazard. This paper presents preliminary compatibility studies of imidazolium-based and pyrazolium-based tetrafluoroborate ionic liquids with alkaline-earth metal anodes and Li-alloy anodes (44 %Li/56% Si and 20% Li/80% Al). The results of preliminary cycling tests of carbon/$LiMn_2O_4$ cells based on the 1-ethyl-3-methylimidazolium tetrafluoroborate ($EMIBF_4$) electrolyte are reported for several temperatures, along with comparative data for a standard electrolyte used for Li-ion cells (1M $LiPF_6$ electrolyte in ethylene carbonate/dimethyl carbonate).

The compatibility experiments were carried out in evacuated Pyrex® tubes sealed under vacuum. The tubes containing ionic liquid and the anode material were heated and changes in the melt were followed visually as a function of time. Melting points of the melts were measured to determine the effect of anode materials on the melt. For some melts, NMR spectra were also obtained. The results obtained showed that $EMIBF_4$ is stable in contact with lithium alloys for long times at room temperature, with only a small change in melting point after several weeks. At temperatures of 150^{o}C and 200^{o}C, however, the melt reacted very rapidly with the alloys and turned brown/red and could not be crystallized when cooled below room temperature. It was also shown that the reaction is much faster with the Li(Al) compared to the Li(Si) alloy. However, it was observed that 1,3 dimethyl-2-propylimidazolium tetrafluoroborate was more stable towards lithium alloys than the $EMIBF_4$ melt under identical conditions.

With pyrazolium-based ionic liquid (1,2-dimethylpyrazolium tetrafluoroborate – $DMPBF_4$), it was observed that the reaction with Li(Si) at 200^{o}C was slow. The melt showed only a slight coloration and a small decrease in melting point after 8 hours contact. However, at temperature of 225^{o}C and 250^{o}C, the reaction was much faster. NMR spectra of the melt obtained after contact with the Li(Si) and Li(Al) alloys at 225^{o}C indicated decomposition of the melt. However, it was demonstrated that $DMPBF_4$ is more stable with calcium and magnesium metals than with the lithium alloys. These preliminary results show that although all the ionic liquids studied are thermally stable to >300^{o}C, their stability in contact with the high-activity anode materials depends on the electrode material and temperature.

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