Room Temperature Molten Fluorohydrogenates for Electrochemical Systems

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EMIm(HF)$_3$F, 1-ethyl-3-methylimidazolium fluorohydrogenate, was first reported in 1999. The component ions are shown in Fig. 1 (a, c, d). This salt possesses a high ionic conductivity of $10^3$ mS cm$^{-1}$ as well as a wide liquid temperature range below and above room temperature. Since then, we have synthesized a series of room temperature molten fluorohydrogenates and reported their physicochemical properties. We have recently succeeded in extending the electrochemical window of the salt to $-5$ V without significantly decreasing the conductivity of the salt by employing nonaromatic cyclic 1-ethyl-3-methylpyrroloidinium cation as a counter ion (Fig. 1b) $^5$.

![Fig. 1 1-Ethyl-3-methylimidazolium(a), 1-ethyl-3-methylpyrroloidinium cation(b) and fluorohydrogenate anions (c,d).](image)

Studies have been made on their applications as electrolytes of some electrochemical systems such as dye-sensitized solar cells, electrical double layer capacitors, and most recently, molten salt fuel cells. In the molten salt fuel cell using EMIm(HF)$_3$F electrolyte, proton transfer does not occur but hydrogen transfer occurs via fluorohydrogenate anions shown in Fig. 1. Electrode reactions proposed are given below in the case of EMIm(HF)$_3$F.

Anode: $\text{H}_2 + 8(\text{HF})_3\text{F} \rightarrow 6(\text{HF})_3\text{F} + 2e^-$

Cathode: $1/2\text{O}_2 + 6(\text{HF})_3\text{F} + 2e^- \rightarrow \text{H}_2\text{O} + 8(\text{HF})_3\text{F}$

Total: $\text{H}_2 + 1/2\text{O}_2 \rightarrow \text{H}_2\text{O}$

For the cell operation at elevated temperatures, HF-deficient fluorohydrogenates such as EMIm(HF)$_3$F is applied. In this case, the combination of fluorohydrogenate anions involved in the cell reaction are altered to HF$_2$and (HF)$_3$F. Due to the stronger H-F bonds in average in the HF-deficient system, the electrode reactions involving the recombination of H-F bonds in the fluorohydrogenate anions are kinetically unfavorable compared to EMIm(HF)$_3$F (Anions present are (HF)$_2$F and (HF)$_3$F) at ambient condition. However, stabilization of the anions in the HF-deficient system increases the thermal stability at elevated temperatures, which compensates the kinetic dis-advantage of the system (Fig. 2).

References