Room Temperature Molten Fluorohydrogenates for Electrochemical Systems

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$EMIm(HF)_{2.3}F$, 1-ethyl-3-methylimidazolium fluorohydrogenate, was first reported in 1999[1]. The component ions are shown in Fig. 1 (a, c, d). This salt possesses a high ionic conductivity of 10^2 mS cm^{-1} as well as a wide liquid temperature range below and above room temperature[2]. Since then, we have synthesized a series of room temperature molten fluorohydrogenates and reported their physicochemical properties[3,4]. 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-methylpyrro-lidinium cation as a counter ion (Fig. 1b)[4].

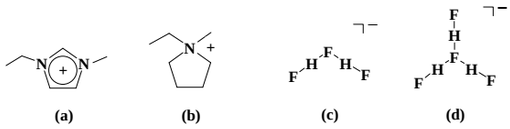
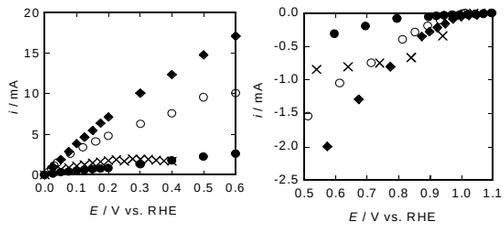


Fig. 1 1-Ethyl-3-methylimidazolium(a), 1-ethyl-3-methylpyrrolidinium cation(b) and fluorohydrogenate anions (c,d).

Studies have been made on their applications as electrolytes of some electrochemical systems such as dye-sensitized solar cells[5], electrical double layer capacitors[6], and most recently, molten salt fuel cells. In the molten salt fuel cell using $EMIm(HF)_{2.3}F$ 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 $EMIm(HF)_{2.3}F$.

Anode: $H_2 + 8(HF)_2F^- \rightarrow 6(HF)_3F^- + 2e^-$
Cathode: $1/2O_2 + 6(HF)_3F^- + 2e^- \rightarrow H_2O + 8(HF)_2F^-$
Total: $H_2 + 1/2O_2 \rightarrow H_2O$

For the cell operation at elevated temperatures, HF-deficient fluorohydrogenates such as $EMIm(HF)_{1.3}F$ is applied. In this case, the combination of fluorohydrogenate anions involved in the cell reaction are altered to HF_2^- and $(HF)_2F^-$. 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 $EMIm(HF)_{2.3}F$ (Anions present are $(HF)_2F^-$ and $(HF)_3F^-$ 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).



(a) (b)

Fig. 2 Polarization curves of (a) H_2 gas and (b) O_2 gas electrodes in $EMIm(HF)_{2.3}F$ at 298 K (♦), in $EMIm(HF)_{1.3}F$ at 373 K (O), in $EMIm(HF)_{1.3}F$ at 298 K (●), in 30 wt% KOH aq. at 298 K (x).

References

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