

Structures and Properties of 1-ethyl-3-Methylimidazolium Salts of Fluorocomplex Anions

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Room temperature molten salts (often called room temperature ionic liquids) have received an attention for their interesting characteristics such as nonvolatility, nonflammability and wide liquid-state temperature range.

Room temperature molten fluorohydrogenate using 1-alkyl-3-methylimidazolium, *N*-alkyl-*N*-methyl pyrrolidinium and *N*-alkyl-*N*-methylpiperidinium cations have been reported [1-3]. They exhibit the same vacuum stable composition, (cation)⁺(HF)_{2,3}F⁻, at room temperature.

We have synthesized some room temperature molten salts by the fluoroacid-base reactions of EMIm(HF)_{2,3}F (EMIm: 1-ethyl-3-methylimidazolium) and binary fluorides [4,5]. EMIm(HF)_{2,3}F itself is a room temperature molten salt composed of EMIm cation and (HF)₂F⁻ and (HF)₃F⁻ anions which act as fluorobases against Lewis acid fluorides to form the salts containing fluorocomplex anions. EMIm salts of BF₄⁻ (m.p.: 288 K), PF₆⁻ (m.p.: 333 K), AsF₆⁻ (m.p.: 326 K), NbF₆⁻ (m.p.: 272 K), TaF₆⁻ (m.p.: 275 K), and WF₇⁻ (m.p.: 258 K) have been synthesized with this method. The reaction of the obtained EMImWF₇ and large excess of H₂O gives EMImWOF₅. EMImWOF₅ is also formed by the reaction of EMIm(HF)_{2,3}F and WOF₄. EMImSbF₆ (m.p.: 283 K) is synthesized by the reaction of EMImCl and KSbF₆.

Crystal structures of EMImAsF₆, EMImSbF₆, EMImNbF₆ and EMImTaF₆ were determined by single-crystal X-ray diffraction. EMImAsF₆ and EMImSbF₆ are isostructural with EMImPF₆ [6]. EMImNbF₆ and EMImTaF₆ are isostructural with each other but their structures are different from EMImPF₆-structure. ORTEP diagram of the structure of EMImTaF₆ is shown in Fig. 1. The melting point of the salt decreases almost linearly with increase in size of the hexafluoroanion. EMImWF₇ also obeys this tendency, although EMImBF₄ does not. The tetrahedral BF₄⁻ is considered to have a different interaction with the cation from those of hexa- or heptafluoroanions.

Electrochemical stability of the obtained salt depends on the stability of the anion against reduction. Figure 2 shows cyclic voltammograms of Pt of glassy carbon electrode in the EMIm salts of fluorocomplex anions. In the cases of EMImWOF₅, EMImWF₇, EMImNbF₆ and EMImSbF₆, the anions are more easily reduced than EMIm cation, whereas BF₄⁻ and TaF₆⁻ anions are more stable than EMIm cation, giving wide electrochemical windows of 4.5 V.

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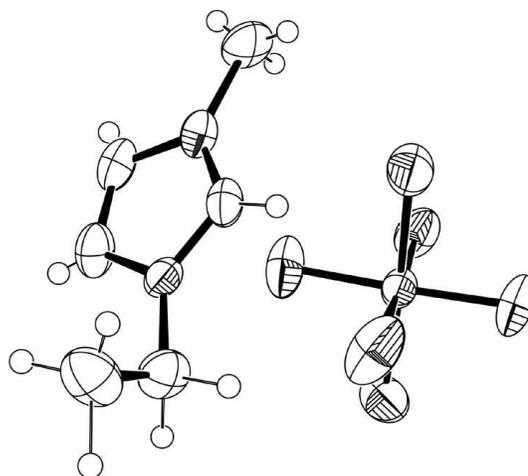


Fig. 1 ORTEP diagram of the structure of EMImTaF₆.

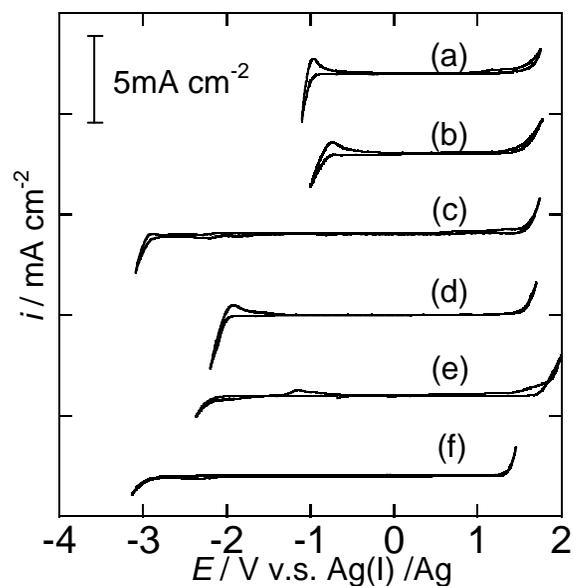


Fig. 2 Cyclic voltammograms of glassy carbon electrodes in (a) EMImWOF₅ and (b) EMImWF₇ and Pt electrodes in (c) EMImTaF₆, (d) EMImNbF₆, (e) EMImSbF₆ and (f) EMImBF₄.