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Room temperature molten fluorometallates: 1-ethyl-3-methylimidazolium hexafluoroniobate(V) and hexafluorotantalate(V)

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Abstract

The first room temperature molten salts containing hexafluorometallate anions of transition metals, 1-ethyl-3-methylimidazolium (EMIm) hexafluoroniobate, EMImNb(V)F_6, and hexafluorotantalate, EMImTa(V)F_6, have been synthesized by the reactions of EMImF·2.3HF with NbF_5 and TaF_5, respectively. They exhibit similar physical properties. Viscosities and conductivities are 49 cP and 8.5 mS cm^{-1} for EMImNbF_6 and 51 cP and 7.1 mS cm^{-1} for EMImTaF_6, respectively at 298 K. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Room temperature molten salt; Ionic liquid; Imidazolium; Hexafluoroniobate; Hexafluorotantalate; Electrochemistry; Organic synthesis

1. Introduction

Since the discovery of an air-stable room temperature molten salt (RTMS, sometimes called ionic liquid), 1-ethyl-3-methylimidazolium tetrafluoroborate (EMImBF_4) [1], a number of RTMS containing fluoroanions have been synthesized ([2–4] and references therein). However, the salts containing fluoroanions of transition metals have not been reported yet. Synthesis of such molten salts is an interesting subject from the viewpoint of electrochemical applications such as electrodeposition and synthetic applications such as catalysis.

The authors have recently reported a series of highly conductive and low viscous RTMS, alkylimidazolium fluorohydrogenates (RR'ImF·2.3HF, RR'Im = alkylimidazoium cations) [5–7]. They are composed of alkylimidazolium cations and $(HF)_nF_{n+1}^-$ anions. EMImF·2.3HF possesses some excellent properties with the highest conductivity of 100 mS cm^{-1} and the lowest viscosity of 4.85 cP at 298 K among the RR'ImF·2.3HF. Studies for practical applications of these salts as electrolytes are now under way. Another possibility is fluorinating agents which simultaneously act as reaction solvents like HF [8]. In addition to these applications, RR'ImF·2.3HF are expected to be good precursors for clean synthesis of other RTMS containing fluoroanions. Alkylimidazolium RTMS are generally prepared by metathesis of starting chlorides or bromides and salts containing fluoroanions. The separation of the dissolved reaction byproduct such as metal chloride and bromide from the main product is sometimes difficult because of the involatile nature of the molten salt. The benefit of the synthesis of RTMS by acid–base reactions of RR'ImF·2.3HF and metal fluorides is the easiness of separation of the reaction byproduct HF from the molten salts which gives high purity of the final products. The reaction of EMImF·2.5HF with BF_3 was reported previously as an alternative way to synthesize EMImBF_4 [9]. It has recently been reported that some solid and liquid EMIm salts containing fluoroanions of main group elements (PF_6^-, SiF_6^{2-}, $Sb_nF_{5n+1}^-$) are obtained with this method [10]. In this paper, we report the syntheses of new RTMS containing group 5 elements, EMImNb(V)F_6 and EMImTa(V)F_6, and some physical and electrochemical properties of them.

2. Results and discussion

During the reaction of EMImF·2.3HF with NbF_5 and TaF_5, the pressure in the reaction vessel increased by the evolution of HF. The exothermic acid–base reactions proceeded vigorously due to strong acidities of the metal pentafluorides. After the reaction ceased, the reactor was heated up to around 340 K to eliminate the hydrogen fluoride completely by evacuation. The reaction of EMImF·2.3HF (5.22 mmol) and NbF_5 (5.27 mmol) gave a pale-yellow liquid (obs. 5.10 mmol, calc. 5.22 mmol). The reaction of EMImF·2.3HF (4.48 mmol) and TaF_5 (4.58 mmol) also gave a

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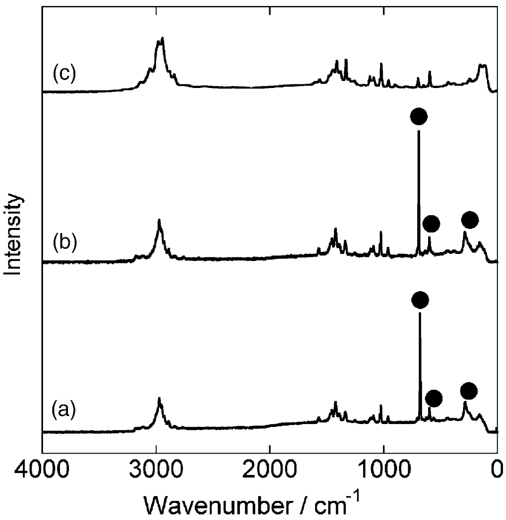


Fig. 1. Raman spectra of $EMImNbF_6$, $EMImTaF_6$ and EMImCl: (a) EMImCl (solid); (b) $EMImNbF_6$; (c) $EMImTaF_6$. The solid circles in the figure indicate peaks ascribed to the fundamental modes of the O_h MF_6 anions.

pale-yellow liquid (obs. 4.38 mmol, calc. 4.48 mmol). The Raman spectra of the liquids in comparison with that of the original EMImCl are shown in Fig. 1. Besides the peaks of $EMIm^+$ cation observed in the EMImCl spectrum (a), sharp peaks ascribed to $\nu_1(A_{1g})$,$\nu_2(E_g)$ and $\nu_5(F_{2g})$ modes [11] of the octahedral $Nb(V)F_6^-$ are observed in the spectrum (b) (680, 598 and 287 cm^{-1}, respectively) and $Ta(V)F_6^-$ in the spectrum (c) (692, 562 and 283 cm^{-1}, respectively). Peaks ascribed to impurities such as binary fluorides or fluoroanions with lower oxidation states are not observed. It is reasonably concluded, the obtained liquids are $EMImNbF_6$ and $EMImTaF_6$ with high purities.

Some physical properties are summarized in Table 1. Their molar volumes are nearly the same. This means that the molecular volumes of these anions are almost identical since the cations are the same in these salts. The similarity of the other physical properties shown in Table 1 should be caused by the coincidence of the volume and molecular geometry of NbF_6^- and TaF_6^- which would give similar electrostatic interactions between the cations and anions in the liquid salt. The conductivities and viscosities of the salts are comparable to those of $EMImN(CF_3SO_2)_2$ [12]. A larger density of fluorotantalate than that of fluoroniobate is obviously due to the difference of the atomic weights of the central atoms. A difference was found in their thermal behavior. $EMImNbF_6$ exhibits a grass transition at 181 K whereas $EMImTaF_6$ does not, although their melting temperatures are close to each other.

Table 1
Some physical properties of $EMINbF_6$ and $EMITaF_6$

	$EMINbF_6$	$EMITaF_6$
Melting point (K)	272	275
Glass transition temperature (K)	181	–
Density at 298 K (g cm^{-3})	1.67	2.17
Molar volume at 298 K (cm^3 mol^{-1})	190	187
Conductivity at 298 K (mS cm^{-1})	8.5	7.1
Viscosity at 298 K (cP)	49	51

A typical cyclic voltammogram of Pt electrode immersed in $EMImTaF_6$ is shown in Fig. 2. The electrochemical window of $EMImTaF_6$ is about 4.5 V. A redox couple observed at around -1.8 V versus Ag/Ag^+ reference electrode is probably ascribed to the redox of Ta(IV)/Ta(V). Further electrochemical analyses are now under way. Although direct electrochemical reduction of Ta(V) to metallic Ta is not possible in the neat salt, a large electrochemical window is advantageous for applications of electrochemical systems such as batteries and capacitors. The synthetic procedure used in the present study can be widely applied to prepare RTMS containing fluoroanions with high purity.

3. Experimental

A T-shaped reactor made of fluoroethylelne-propylene copolymer (FEP) tubes, a perfluoroalkylvinylether copolymer (PFA) connector and valves was used as a reaction vessel. Hygroscopic materials were treated in a glove box of argon atmosphere. NbF_5 (Ozark–Mahoning, purity 99%) and TaF_5 (Ozark–Mahoning, purity 99.5%) were used as supplied. $EMImF{\cdot}2.3HF$ was synthesized as previously

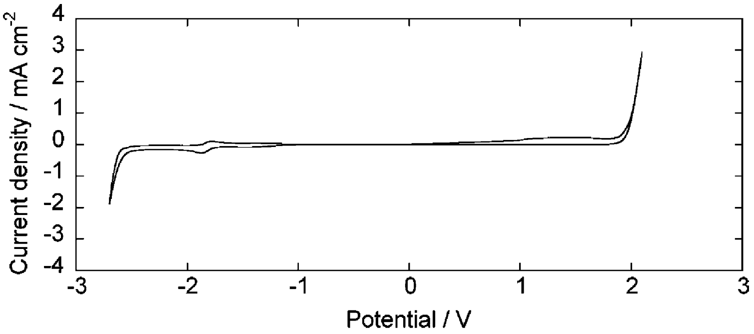
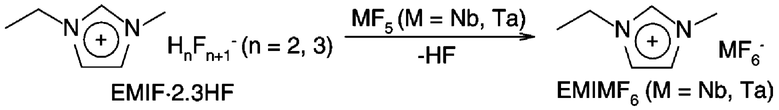


Fig. 2. Cyclic voltammogram of Pt electrode immersed in $EMImTaF_6$. Working electrode: Pt plate, counter electrode: glassy carbon rod, reference electrode: Ag wire immersed in $AgTaF_6$-saturated $EMImTaF_6$.



Scheme 1.

reported [5,6]. Equimolar EMImF·2.3HF and NbF_5 or TaF_5 were reacted at ambient temperatures (Scheme 1). Both the reactions were highly exothermic and careful control was necessary. A small portion of the solid fluoride in one of the tubes of the reactor was transferred into the molten salt in the other. Occasionally the tube was cooled by ice water to control the reaction rate.

Raman spectra of the samples were obtained by a BIO-RAD FTS-175C spectrometer using Nd:YAG laser. Electrochemical measurements were performed using a Pt working electrode and a glassy carbon counter electrode with the aid of Hokuto Denko, HZ-3000 electrochemical measurement system. A reference electrode was made of silver wire immersed in $AgTaF_6$-saturated $EMImTaF_6$. $AgTaF_6$ was prepared as reported previously [13]. Conductivity was measured by impedance technique using a calibrated cell with platinum disk electrodes. Viscosity measurement was performed using an Ostwald viscometer made of FEP. DSC analysis was conducted by Shimadzu DCS-60 differential scanning calorimeter.

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