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COLLOID CHEMISTRY AND ELECTROCHEMISTRY

Electrodeposition of Rare Earth Metals Y, Gd, Yb in Ionic Liquids

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Abstract—The possibility of yttrium, gadolinium, and ytterbium electrodeposition from solutions of their triflates in different ionic liquids at 100°C was investigated. It was shown that these metals could be deposited on the cathode from electrolytes based on ionic liquids with quaternary ammonium cations, and these metals do not deposit from 1-butyl-2,3-dimethylimidazolium triflate. It was established that, in the case of butyltrimethylamonium triflate usage, metal deposition occurs on a copper electrode, and it does not occur on a platinum electrode, and in 1-butyl-1-methylpirrolidinium triflate, the reduction process is possible on both electrodes. Yb^{3+} reduction occurs step by step via Yb^{2+} formation. It was shown that the limiting stage of the cathode process is adsorption of a metal cation on the electrode.

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Electrochemical reduction of rare-earth metal (REM) cations is a relatively poorly studied problem. Though electrodeposition of REM alloys is a more important task from a practical viewpoint compared to electrodeposition of pure metals, an investigation of the reduction conditions of individual REMs is a necessary condition of a systematic approach to the electrodeposition of their alloys.

In the literature, there is a considerable volume of data on polarography [1] and electrodeposition of REMs from molten salts [2]. Standard potentials M^{3+}/M for all REMs (i.e., Sc, Y, and lanthanides) have rather close values (–2.4...–2.2 V). In spite of this fact, it was reported that there was the possibility of electrodeposition of samarium [3] and europium [4] from electrolytes representing aqueous solutions. Comparatively recently, the possibility of electrodeposition of many of lanthanides both in the pure form and as alloys from nonaqueous solutions (DMF, DMSO) containing their chlorides, nitrates, or tosylates was shown [5, 7, 8].

In [5], the electrodeposition of ytterbium and Yb–Bi alloy from an electrolyte on the basis of DMSO containing 0.1 M $YbCl_3$ was investigated. Ytterbium is deposited from this electrolyte on the copper or platinum cathode as a shiny, well-cohesive precipitate. The cathode process

$$Yb^{3+} + 3e \longrightarrow Yb^0$$

proceeds irreversibly and in one step. Polarographic measurements [6] in $Yb(CF_3SO_3)_3$ solutions in propylene carbonate and acetonitrile show that Yb^{3+} reduction could process also via the formation of Yb^{2+}.

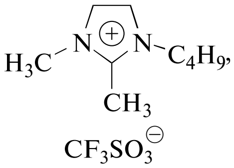
In [7], the electrodeposition of gadolinium and Gd–Co alloy from $Gd(p\text{-}CH_3C_6H_4SO_3)_3$ DMF solution was investigated. According to the authors' data, REM tosylates are easily dehydrated and become nonhygroscopic, which make convenient their usage as a constituent of nonaqueous electrolytes.

Ionic liquids are also an appropriate medium for the electrodeposition of REMs and their alloys. Thus, in [8, 9], the electrodeposition of Al–La alloys from a saturated $LaCl_3$ solution in the ionic liquid (IL) $EMIm^+Al_2Cl_7^-$ was studied. According to the data of [9], the solubility of lanthanum chloride in this IL is 45 mmol/kg. The lanthanum content in the alloys obtained [8] was 0.05–0.5 at %, which is explained both by the low lanthanum concentration in the electrolyte and by the big difference in the deposition potentials of the alloy components. Nevertheless, this amount of lanthanum in the alloy substantially affects the morphology of the cover obtained and results in preferred orientation of crystals.

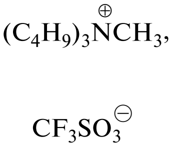
Lanthanum, europium, and samarium electrodeposition from electrolytes on the basis of butyltrimethylammonium triflimide is studied in [10]. Solutions of triflimide trihydrates of the corresponding REMs $M((CF_3SO_2)_2N)_3 \cdot 3H_2O$ with a concentration of 0.04–0.14 M were used as electrolytes. Here, it was reported that the electrolyte contains no more than 0.01% water. It was shown that the reduction of Sm and Eu with a stable intermediate degree of oxidation (+2) occurs in two steps.

In the present work, the electrochemical reduction of yttrium, gadolinium, and ytterbium from their nonaqueous triflate solutions in ionic liquids with the triflate anion ($CF_3SO_3^-$) and cations of different composition further denoted as $BuMe_2ImOTf$ (1),

$Bu_3MeNOTf$ (2), and BMPOTf (3), respectively, is investigated:

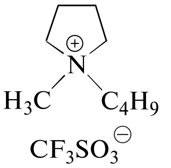


(1)



$(C_4H_9)_3\overset{\oplus}{N}CH_3$, $CF_3SO_3^{\ominus}$

(2)



(3)

EXPERIMENTAL

IL Synthesis

1-Butyl-2,3-dimethylimidazolium chloride. The mixture of 1,2-dimethylimidazolium (19.2 g, 0.2 mol) and *n*-butyl chloride (24 ml, 0.23 mol, 15% excess) was heated in a sealed vial at 110°C for 70 h. The product obtained was dried in vacuum at 130°C and then recrystallized from acetonitrile. Yield—84%.

1-Butyl-1-methylpyrrolidinium chloride. The mixture of 1-methylpyrrolidine (21 ml, 0.2 mol), *n*-butyl chloride (24 ml, 0.23 mol, 15% excess), and acetonitrile (35 ml) was heated in a sealed vial at 100°C for 20 h. The product was crystallized from the solution upon cooling. The mother liquor was treated with activated carbon and partially evaporated to obtain an additional amount of the salt. The salt obtained was dried in vacuum at 100°C until achieving a constant weight. Yield—87%.

Ionic liquids (general procedure). The corresponding chloride (0.1 mol) and potassium triflate CF_3SO_3K (18.8 g, 0.1 mol) were mixed with acetonitrile (200 ml) and refluxed at 80°C for 30 min. The KCl precipitate was filtered, the filtrate was evaporated, and the residue was dried in vacuum under heating. To remove the impurities, the IL was dissolved in 200 ml of CH_2Cl_2, and this solution was extracted with 5 ml of water four to six times (until the absence of Cl^- in the aqueous layer). Then CH_2Cl_2 was distilled and the residue was dried in vacuum (~0.01 mm Hg) at 120°C until the complete cessation of distillation of volatile substances (~20 h).

REM triflates were obtained as described in [6] from trifluoromethanesulfonic acid solution and an excess of the corresponding REM oxide and dehydrated in vacuum (~0.01 mm Hg) at 130°C for about 20 h. The preparation of electrolytes and electrochemical measurements were carried out in an argon atmosphere in a glove box. Electrolytes were 0.1 M solutions of the corresponding REM triflate in the tested ionic liquids (dissolved under heating).

Electrochemical measurements were performed on a setup containing a PI-50-1 potentiostat, PR-8 programmer, and ADC. Platinum foil and copper wire electrodes with an area of ~0.5 cm^2 were used as the working electrodes, and a platinum wire was used as an auxiliary electrode. The electrolyte volume was 3 ml. The reference electrode was a silver wire immersed in the 0.1 M solution of $(C_4H_9)_3(CH_3)N^+Cl^-$ in the ionic liquid used, separated from the main volume of the cell by a membrane representing a porous Al_2O_3 pellet soldered to a glass tube.

RESULTS AND DISCUSSION

The 1,2,3-trialkylimidazolium cation is considered to be electrochemically more stable compared to the 1,3-dialkylimidazolium cation because of the absence of a comparatively labile proton in the 2 position. IL having such type of cation (1,2-dimethyl-3-propylimidazolium triflimide) in particular was suggested as a basis for an electrolyte for lithium accumulators [11]. However, preliminary experiments in $BuMe_2ImOTf$ have shown that REM electrodeposition from REM triflates does not occur in the IL mentioned. Therefore, further measurements were carried out in the IL with aliphatic cations.

The results of the measurements in $Bu_3MeNOTf$ are shown in Fig. 1. The voltammetric curve in the pure ionic liquid at 100°C has a typical form. The area of electrochemical stability (“electrochemical window”) is situated in the range of potentials of –1.9 to 2.85 V relative to the reference electrode and thus comes to the value of 4.75 V. The peaks at the potentials of 1.2 and 2.2 V apparently correspond to the oxidation of the cathode reaction products since they do not appear if the anode branch of the curve is measured first. A long-term electrolysis of all tested ILs with the copper or platinum cathode at current values of 1–10 mA/cm^2 does not lead to the formation of traces of any precipitate on the electrode.

The polarization curves obtained on Pt at different scanning speeds in the 0.1 M solutions of $Gd(OTf)_3$ or $Y(OTf)_3$ do not reveal any noticeable differences from the background curve. The absence of visible traces of the precipitate on the surface of the electrode under long-term cathode polarization and the coincidence of the branches of the direct and reverse voltammetric curve run apparently indicate the absence of reduction of REM ions to the metal on the platinum electrode. The only cathode process occurring apparently is the reduction of the IL cation.

In the case of the usage of the copper electrode, the situation is different. For Y and Gd, the cathode branch coincides with the background as before, and on the curve for Yb, the broad peak with a maximum value at –0.96 V corresponding to the reaction

$$Yb^{3+} + e \longrightarrow Yb^{2+} \quad (1)$$

is observed. However, after reversing the scanning, a hysteresis (“nucleation loop”) is observed on the curve. The precipitate of a black metal on the surface of the electrode appears. Delineated anode peaks responding to the removal of the metal deposited are absent; this is similar to the data of [10] concerning electrodeposition of lanthanides from IL with triflim-

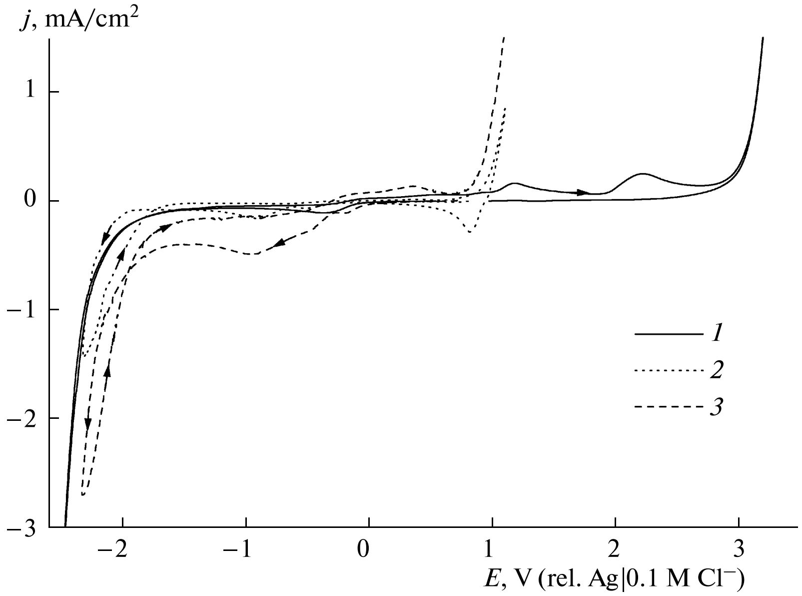


Fig. 1. Voltammetric curves obtained at 100°C and v = 10 mV/s: (*1*) pure IL $Bu_3MeNOTf$, Pt electrode; (*2*) IL + 0.1 M $Gd(OTf)_3$, Cu electrode; and (*3*) IL + 0.1 M $Yb(OTf)_3$, Cu electrode.

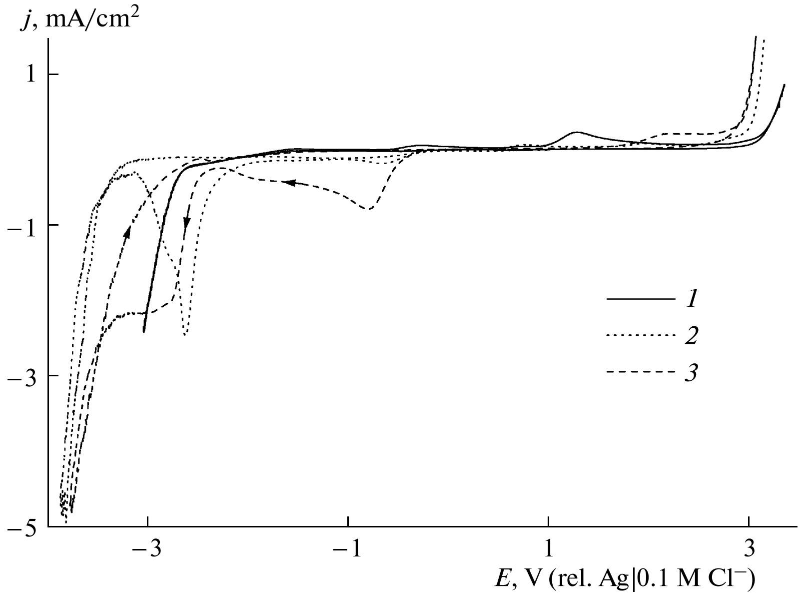


Fig. 2. Voltammetric curves obtained on Pt at 100°C and v = 10 mV/s: (*1*) IL BMPTOf, (*2*) IL + 0.1 M $Gd(OTf)_3$, and (*3*) IL + 0.1 M $Yb(OTf)_3$.

ide anion. At potentials higher than 0.9 V, the anodic dissolution of copper is obviously observed.

The solutions of REM triflates in the BMPOTf IL were also studied. The polarization curve on Pt in the pure IL is shown in Fig. 2. The electrochemical window is situated in the region of potentials of −2.6 to 3.0 V; i.e., their extension is different from that for the previous IL by 0.85 V, which indicates the greater stability of the cyclic structure cation compared to the linear cation. In the temperature range of 20–120°C, the width of the window remains almost constant.

On the voltammetric curves for Pt electrodes in the Y and Gd salt solutions in this IL, the pronounced cathode peak with a maximum value of −2.6 V apparently corresponding to the reaction

$$M^{3+} + 3e \longrightarrow M^0.$$

is observed. It is typical that the voltammetric curve branch corresponding to the cathode reaction of the

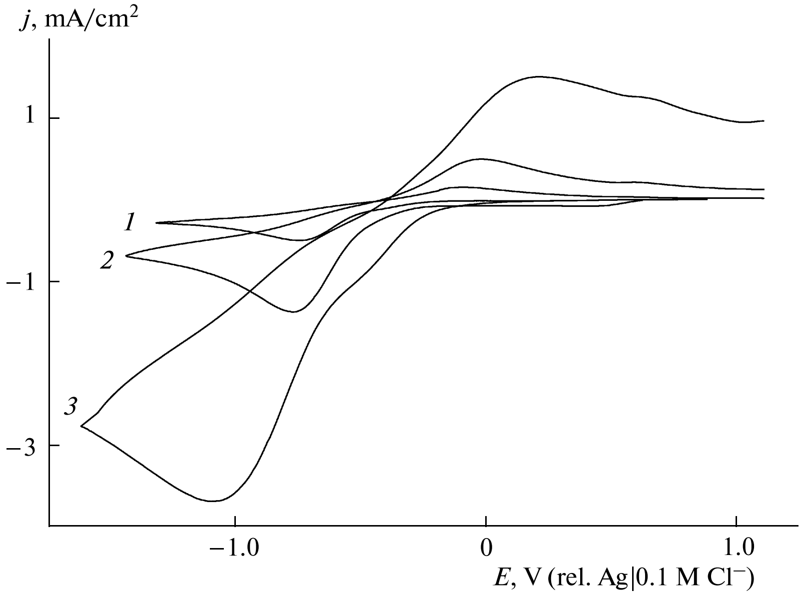


Fig. 3. Voltammetric curves obtained for 0.1 M $Yb(OTf)_3$ solution in IL BMPOTf on Pt at 100°C at different scanning speed: (*1*) 5, (*2*) 20, and (*3*) 50 mV/s.

IL itself shifts to the region of more negative potentials. This can be explained also by partial passivation of the deposited metal surface with water or oxygen impurities. As the scanning speed is increased, the peak is broadened, and its maximum shifts to the region of more negative potentials, and at a value of $v > 50–80$ mV/s, it merges with the region of the curve corresponding to the cathode reaction of IL itself. In the electrolyte containing Yb^{3+}, a peak with a maximum value of –0.8 V corresponding to the formation of Yb^{2+} is also observed. On the reverse run of the voltammetric curve, pronounced anodic peaks are not observed. However, in the case of reversal of scanning at a lower potential (Fig. 3), it is possible to observe Yb^{2+} oxidation, and the absence of the corresponding anode peak on the curve in Fig. 2 obviously indicates that all initially formed Yb^{2+} is subjected to further reduction. The curves obtained on the copper electrode hardly differ in the region of copper electrode stability ($E < 0.9$ V) from that obtained on the platinum electrode.

The dependences of the cathode peak values on the potential scanning speed are shown in Fig. 4. For ytterbium, the dependence shown relates to the peak corresponding to reaction (1). The linear character of these dependences indicates that the limiting stage of the cathode reaction is adsorption of the metal cation [12].

The investigation of formation of thicker metal layers on the copper electrode was performed both in potentiostatic and in galvanostatic conditions. It was found that the deposited metal forms a tenuous black precipitate.

Thus, the results show that the ionic liquids with the triflate anion can be used for the electrodeposition of REMs and, apparently, their alloys. The best results were obtained in the IL 1-butyl-1-methylpyrrolidinium triflate, having the widest electrochemical window compared to the other two ILs tested. It was shown that Yb^{3+} reduction occurs step by step via the formation of Yb^{2+}. Linear dependences of the cathode peak amplitude on the potential scanning speed indicate that the limiting stage of the cathode process in all

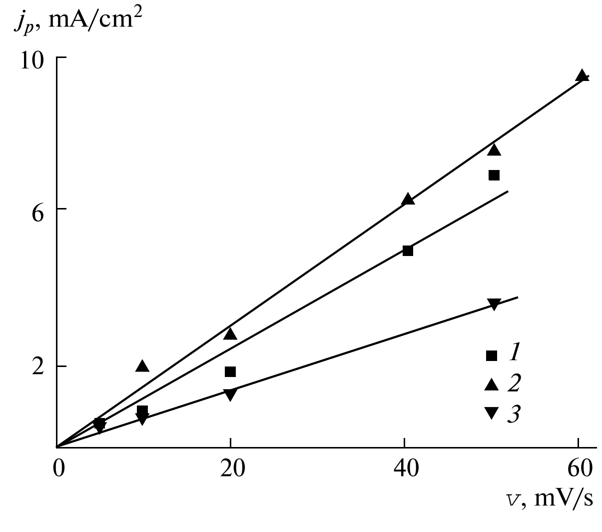


Fig. 4. Dependences of the cathode peak value on the potential scanning speed (100°C, Pt electrode) for the following reactions: (*1*) $Y^{3+} + 3e \longrightarrow Y^0$, (*2*) $Gd^{3+} + 3e \longrightarrow Gd^0$, and (*3*) $Yb^{3+} + e \longrightarrow Yb^{2+}$.

cases is adsorption of the metal cation on the electrode.

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