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PHYSICOCHEMICAL STUDIES OF SYSTEMS AND PROCESSES

Electrochemical Synthesis of Sodium Hexamethoxyniobate

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Abstract—Anodic dissolution of niobium in anhydrous methanol in the presence of sodium methylate was studied. A method for recovery of niobium methylate from sodium hexamethoxyniobate by the reaction with ammonium chloride was developed.

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The permanent need of the electronic industry in high-purity materials and, in particular, special-purity niobium used in manufacture of niobium slug capacitors enforces a search for new methods for its production and purification. Of particular interest are purification of niobium to remove admixtures of other metals and recovery of pure niobium from the raw metal and alloys. The most promising for this purpose is the electrochemical way to obtain metal alkoxides, followed by their separation. The electrochemical synthesis of niobium alkoxides has been considered previously [1, 2]. A similar method can be used to produce not only simple alkoxides, but also complex compounds, e.g., sodium hexamethoxyniobate $NaNb(OMe)_6$, whose specific properties can serve as a basis for development of a new method for recovery of pure niobium from niobium-containing alloys.

The available published data for this compound are rather scarce. This compound was first obtained by a chemical reaction of sodium and niobium methylates [3]. The principal properties of the substance were described and the electrical properties of its solutions were reported. The existence of $[Nb(OMe)_6]^-$ ions was also demonstrated in [4] by conductometric titration. No evidence about the electrochemical method for synthesis of complexes of this kind could be found in the literature.

In this study, the possibility of obtaining the sodium-niobium methoxy complex by the electrochemical method was considered and its properties and formation mechanism were analyzed.

EXPERIMENTAL

Because, according to [5], the synthesis of alkoxides is sensitive to presence of moisture, methanol of chemically pure grade used in the study was subjected to additional drying by boiling with magnesium shavings [6]. The final content of water was less than 0.01%. LiCl used in the study was also of chemically pure grade. Lithium chloride was dried by calcination at 350°C for 5 h. Sodium methylate was obtained by a direct reaction of metallic sodium (chemically pure) with methanol. The anodes were made of niobium of Nb-1 brand [GOST (State Standard) 16099–80].

Experiments were performed in a diaphragmless electrolyzer having the form of a 90-cm^3 glass cylinder equipped with a thermostating jacket and a cock at the bottom for discharging the electrolyzate. The electrolyzer was hermetically closed with a cover into which a thermometer, gas-discharge pipe with a calcium chloride packing, and current leads to the electrodes were inserted. The niobium anode was mounted below the cathode at a distance of 0.5 cm.

The working area of the anode was 8 cm^2. The cathodes were made of a platinum wire 1 mm in diameter and had a working area of 24 cm^2. Prior to each electrolysis, the electrodes were trimmed and degreased

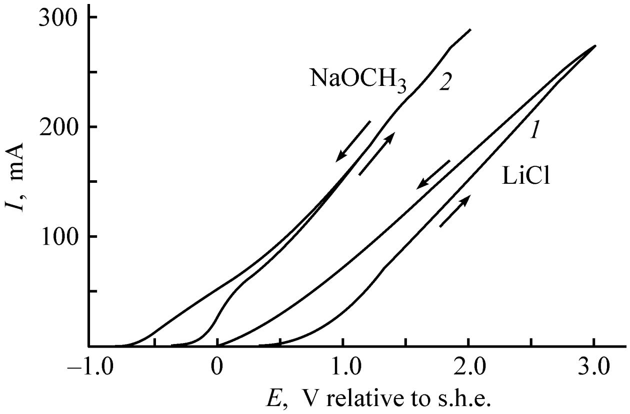

Fig. 1. Voltammetric curves obtained on Nb in 1 M solutions of (*1*) LiCl and (*2*) NaOCH$_3$ in methanol. Temperature 25°C, potential sweep rate 0.2 V s^{-1}; the same for Figs. 2, 3. (*I*) Current and (*E*) potential; the same for Figs. 2, 3.

with Vienna lime, washed with water, and weighed. After an experiment was complete, the electrolyzate was discharged into a leak-proof flask for further processing. The amount of the dissolved metal was found from the loss of mass by the anode.

To isolate niobium pentamethoxide (methylate), the alcohol was evaporated from the electrolyzate and then the product was extracted from the still bottoms with hexane. After the extractive agent was evaporated, a light yellow liquid that crystallized upon cooling remained in the flask. The resulting yellowish crystals had mp 61°C.

Sodium hexamethoxyniobate was isolated by evaporation of the alcohol from the electrolyzate and washing of the remaining white needle-like crystals with hexane.

The content of sodium methylate in the still bottoms was found by their dissolution in water and titration of the resulting solution with an alkali. The content of niobium in the still bottoms was found by their dissolution in water, addition of an acid, and gravimetric determination of the precipitated niobium pentaoxide.

Voltammetric measurements were made with an IPC computer-controlled electronic potentiostat in a 45-cm^3 cylindrical diaphragmless glass cell equipped with a thermostating jacket. Electrodes and a gas-discharge pipe were inserted into the cell cover. The electrode system comprised a niobium stationary working electrode with an area of 0.5 cm^2, platinum auxiliary electrode, and silver chloride reference electrode.

For measuring the anodic polarization curve, an electrolyte solution of a required concentration was poured into the cell and bubbled with dried argon via the gas-discharge pipe for 0.5 h. Then the required temperature was set and a trimmed electrode was placed in the cell and polarized in accordance with the preset program.

NaNb(OMe)$_6$ was synthesized as follows. Prior to electrolysis, the niobium anode was thoroughly degreased and weighed. The electrolyzer was charged with an electrolyte solution [1.1 g of NaOCH$_3$ in 90 ml of methanol (0.54 M solution)]. The content of moisture in the solution was less than 0.05 wt %. The electrolysis was performed at a constant current strength of 1 A and temperature of 18–20°C. In the course of electrolysis, the solution remained transparent, with the electrolyzer voltage equal to 10 V at the beginning of a run and increasing to 11 V by its end. In 7 h 16 min, the current was switched off and the niobium anode was weighed. The loss of mass by the anode was 4.14 g, which corresponds to a 89% current efficiency by pentavalent niobium. Methanol was evaporated from the electrolyzate under a reduced pressure (15 mm Hg). A white crystalline substance identified as NaNb(OMe)$_6$ remained in the still bottoms.

A known method for obtaining alkoxides of the aliphatic series consists in anodic dissolution of a metal in an appropriate alcohol containing a supporting electrolyte that makes the system electrically conducting [1]. Previously, a method for synthesizing niobium pentamethoxide by dissolution of a niobium anode in methanol in the presence of lithium chloride has been developed. With certain conditions satisfied, niobium pentamethoxide can be obtained with a current efficiency exceeding 95% [2].

A study of the influence exerted by the nature of a supporting electrolyte on the niobium dissolution potential in methanol solutions by cyclic voltammetry (CVA) revealed an anomalously high dissolution rate of niobium in the presence of sodium methylate. Figure 1 shows CVA curves for niobium dissolution in the presence of lithium chloride and sodium methylate. It can be seen from the CVA curve that, in the presence of NaOCH$_3$, the onset of niobium dissolution is shifted to the region of negative potentials by approximately 750 mV. Because of this circumstance, the current of anodic dissolution of niobium at a potential of 1 V in the presence of NaOCH$_3$ exceeds that in the presence of LiCl by more than a factor of 2. The so pronounced shift of the niobium dissolution potential may indicate that niobium ions formed at the anode are bound into a stable complex.

Results of a preparative synthesis of sodium hexamethoxyniobate ($NaOCH_3$ concentration 0.5 M, voltage 6–11 V, current density 0.125 A cm^{-2}, temperature 25–30°C)

Run no.	Na : Nb molar ratio	Current efficiency by Nb(V)	Yield of $NaNb(OMe)_6$	Fraction of niobium bound into sodium hexamethoxyniobate	Yield* of $Nb(OMe)_5$
		%			
1	1 : 1	99.9	99	99	0
2	1 : 2.5	98.8	97	41.6	55.3
3	1 : 5	97.2	98	18.9	79.09

* Isolated by extraction with hexane after the evaporation of methanol.

The occurrence of two anodic processes is the most clearly reflected by the voltammetric curve obtained in the presence of lithium chloride with a minor addition of lithium methylate (Fig. 2). It can be seen that, in this case, the dissolution of niobium begins at a more negative potential, a region of limiting currents appears, and the onset of the second reaction is observed when the niobium dissolution potential in the presence of lithium chloride is reached. It follows from the voltammetric curve obtained in the presence of the methoxy complex (Fig. 3) that the niobium dissolution potential lies in the intermediate region between the dissolution potentials in the presence of $NaOCH_3$ and LiCl. However, the process rate is lower.

The data obtained suggest that, in anodic polarization of the niobium electrode, the dissolution of the metal is substantially facilitated in complexation with methylate ions, whereas the reaction with chloride ions is more hindered, which leads to an increase in the potential. In the absence of ions reacting with niobium, the dissolution rate is lower.

In contrast to the process of electrosynthesis of niobium pentamethoxide in the presence of lithium chloride, in which both anodic and cathodic reaction products are involved and niobium methylate is formed in the solution bulk upon their mixing [2], the hexamethoxy complex is probably formed directly at the anode in the course of the anodic reaction

$$Nb + 6OMe^- \xrightarrow[-5e]{} [Nb(OMe)_6]^-.$$

The preparative electrolyses performed in the study with 0.1 M NaOMe as a supporting electrolyte demonstrated that niobium is converted to the pentavalent state in a nearly quantitative yield, but no free niobium pentamethoxide is formed until the concentration of Nb(V) in solution reaches a value of 0.1 M. Niobium pentamethoxide starts to appear only after the Nb : Na molar ratio in solution exceeds 1 : 1 (see table).

Sodium hexamethoxyniobate is stable in a methanol solution; however, a similar compound with the ammonium cation does not exist. On the basis of this property, the compound obtained in this study was used to isolate niobium methoxide by the exchange reaction

$$NaNb(OCH_3)_6 + NH_4Cl \rightarrow Nb(OCH_3)_5 + NaCl\downarrow + CH_3OH + NH_3\uparrow.$$

The reaction was performed in a methanol solution of the complex to give niobium pentamethoxide in 87% yield.

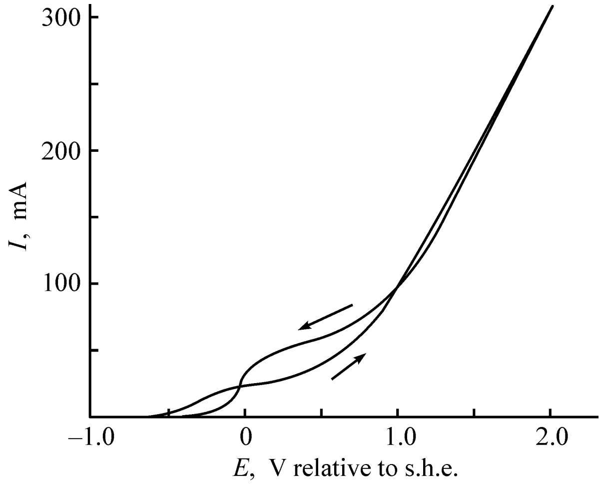

Fig. 2. Voltammetric curve obtained on Nb in a 1 M solution of LiCl in methanol containing 0.1 M $LiOCH_3$.

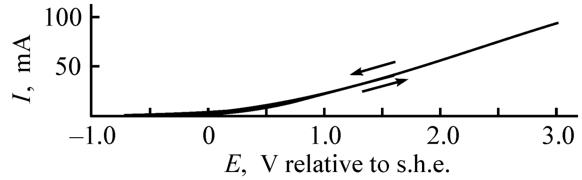

Fig. 3. Voltammetric curve obtained on Nb in a 1 M solution of $NaNb(OCH_3)_6$ in methanol.

Sodium hexamethoxyniobate is formed as white thin needle-like crystals. The substance is well soluble in methanol and insoluble in benzene and hexane. The methanol solution is electrically conducting, which indicates that this compound dissociates by the equation

$$NaNb(OMe)_6 \rightarrow Na^+ + [Nb(OMe)_6]^-.$$

An elemental analysis and calculation gave the following:

Found, %: Na 7.4, Nb 30.6.
$NaNb(OMe)_6$.
Calculated, %: Na 7.6, Nb 30.79.

Crystalline sodium hexamethoxyniobate is comparatively well soluble in water to give a weakly opalescent solution that is stable at room temperature. Evaporation of water yields coarse cubic crystals containing no carbon. Presumably, such a behavior is accounted for by instantaneous hydrolysis to give a hydroxo complex $NaNb(OH)_6$, which is well soluble in water and insoluble in a water–methanol solution.

The possibility of obtaining a compound stable in aqueous solution may be of interest for separation of niobium from admixtures of other metals.

CONCLUSIONS

(1) Sodium hexamethoxyniobate $NaNb(OMe)_6$ was electrochemically synthesized for the first time.

(2) It was demonstrated that the anodic dissolution of niobium is substantially facilitated in the presence of sodium methylate as a supporting electrolyte, compared with solutions containing lithium chloride, because of the formation of complexes with methylate ions directly in the anodic process.

(3) It was shown that pure niobium methoxide $Nb(OMe)_5$ can be obtained in the reaction of the $NaNb(OMe)_6$ formed with ammonium chloride.

(4) It was demonstrated that a water-soluble hydroxo complex $NaNb(OH)_6$ is formed in hydrolysis of $NaNb(OMe)_6$.

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