APPLIED ELECTROCHEMISTRY AND CORROSION PROTECTION OF METALS

Electrochemical Synthesis of Niobium(V) Ethylate

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Abstract—The effect exerted by the supporting electrolyte and cathode material on the anodic dissolution of niobium in ethanol solutions was studied.

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The goal of this study was to develop an electrochemical method for preparing Nb(V) alkoxide. The latter can serve as the starting material for preparation of ultrapure Nb(V) and Nb(V) oxide, which are widely used in various areas of industry.

The anodic dissolution of a metal in the corresponding alcohol in the presence of a supporting electrolyte is one of promising but insufficiently studied methods of preparing transition metal alkoxides. At the same time, in an extensive monograph [1] reviewing in detail the properties and methods of preparation of all the presently available metal alkoxides, the electrochemical method is given the least attention. Alkoxides prepared by the electrochemical method are listed in a review [2], demonstrating the potential of the method.

As a rule, it is recommended to perform the synthesis in a diaphragmless electrolyzer from electrolytes chosen empirically, with as high electrical conduction as possible. The influence of electrolysis conditions on the yield of alkoxides virtually was not studied. The existing views on the mechanism of the alkoxide formation are controversial. According to Lemkuhl et al. [3], who synthesized iron, cobalt, and nickel alkoxides using alkali metal halides as electrolytes, the initial anodic process is the discharge of halide ions. Then, the atomic halogen reacts with a metal of the anode to form the corresponding halide, which is reduced to the alkoxide on the cathode, i.e., the reaction pattern is as follows:

Anode:

$$\operatorname{Hal}^{-} \rightarrow \operatorname{Hal}^{\bullet} + e, M + 2\operatorname{Hal}^{\bullet} \rightarrow \operatorname{MHal}_{22}$$

Cathode:

$$MHal_{2} \xrightarrow{+e} [MHal_{2}]^{-} \xrightarrow{+e} [MHal_{2}]^{2-} \xrightarrow{+2HOR} H_{2} + 2Hal^{-}$$
$$+ M(OR)_{2}. \tag{1}$$

Based on the general views on the possible mechanism of the formation of transition metal alkoxides by the anodic dissolution in alcohol electrolyte solutions, Shreider et al. [4] suggested the following reactions as the most probable:

Anode:

$$\mathbf{M} - \mathbf{e} \xrightarrow{\operatorname{Hal}^- + \mathbf{OR}^-} \mathbf{M}(\mathbf{OR})_n \operatorname{Hal}_m [+\mathbf{M}(\mathbf{OR})_p \operatorname{Hal}_q \downarrow],$$

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Cathode:

$$M(OR)_{n}Hal_{m} + e \rightarrow M(OR)_{n}Hal_{m}^{-\bullet} \xrightarrow{-Hal} M(OR)_{n}Hal_{m-1}^{\bullet}$$

$$\xrightarrow{+ROH, -1/2H_{2}} M(OR)_{n+1}Hal_{m-1}^{\bullet} \xrightarrow{+e} \dots$$

$$\xrightarrow{+ROH, -1/2H_{2}, -Hal^{-}} M(OR)_{n+m}. \qquad (2)$$

Contrary to Shreider et al. [4], who ruled out the alcohol dissociation with the formation of RO⁻ and a proton with its subsequent reduction on the cathode, Bukhtiarov et al. [5] detected by cyclic voltammetry intense hydrogen evolution during the electrolysis of alcohol solutions in aprotic solvents on the cathode made of transition metals. Based on these observations, Bukhtiarov et al. [5] suggested an alternative mechanism of the alkoxide formation, involving ionization of a metal with the formation of the corresponding cations on the anode and decomposition of an al-

cohol molecule accompanied by evolution of hydrogen and formation of the RO⁻ anion on the cathode. In the bulk of a solution, alkoxide anions react with the metal cations to form alkoxide. The reaction pattern can be presented as follows:

Anode:
$$M^0 \rightarrow M^{2+} + 2e$$
,
Cathode: ROH + e \rightarrow OR⁻ + 1/2H₂,
In solution bulk: $M^{2+} + 2RO \rightarrow M(OR)_2$. (3)

Thus, with rather scarce and controversial data available on the electrochemical formation of transition metal alkoxides, we started a systematic study of this process with niobium ethylate as example. Shreider [4] obtained for the first time niobium ethylate by the electrochemical method involving electrolysis of an ethanol solution of triethylamine hydrobromide with a platinum cathode and a niobium anode. Niobium pentaethoxide was isolated and identified, but the Shreider's experiment is the only example of niobium alkoxide electrosynthesis described in detail in the literature.

This study is the first step of the investigation of the electrochemical synthesis of niobium alkoxide; we examined the anodic dissolution of niobium in an ethanol solution of various electrolytes.

EXPERIMENTAL

According to the published data, alkoxide synthesis is a moisture-sensitive process. Therefore, particular attention was given to the ethanol drying. After performing a number of the experiments, we used in the study the following method.

Water was preliminarily separated from ethanol by distillation of a ternary azeotrope with benzene [6]. Then the solution was treated with sodium metal and diethyl oxalate. After distillation, the ethanol fraction (boiling point point 78.2–78.3°C) contained 0.03–0.05 wt % H₂O. The content of water in the alcohol was determined by Fischer titration.

As supporting electrolytes were used chemically pure grade salts. Tetraethylammonium acetate was prepared by mixing an aqueous solution of tetraethylammonium hydroxide with an excess amount of dilute acetic acid. After that, the solution was evaporated to dryness and the residue was dried at $100-120^{\circ}$ C/5 mm Hg.

The experiments were performed in a diaphragmless electrolyzer in the form of a 90 cm³ glass cylinder equipped with a temperature-control jacket and a magnetic stirrer. The electrolyzer was hermetically closed with a lid, in which a thermometer, an outlet pipe with a calcium chloride tube, and electrode current leads were inserted. A flat niobium anode was arranged between the two cathodes.

The niobium anode (working area 8 cm^2) was made of an Nb-1 niobium sheet [GOST (State Standard) 16099–80], and the cathodes (working area 18 cm^2), of a 1-mm platinum wire. Prior to the electrolysis, the electrodes were weighed after trimming and degreasing with Vienna lime. After the experiment was complete, the solution was removed for further treatment. The weight of the dissolved metal was determined from the weight loss of the anode.

The product was isolated by fractional distillation. First alcohol was distilled off, and then niobium pentaethoxide, a light-yellow liquid, was distilled in a vacuum (boiling point 165°C/1.5 mm Hg).

The current–voltage dependences were measured on an IPC-2000 electronic potentiostat and processed on a computer. For the measurements we used a 45 cm^3 diaphragmless cell equipped with a temperature-control jacket. The electrodes and an outlet rube were inserted into the cell lid. The electrode system consisted of a stationary working electrode made of the corresponding metal (working area 0.5 cm^2), a platinum auxiliary electrode, and a silver chloride reference electrode.

To measure the anodic curve, the cell was charged with an electrolyte solution of the required concentration and was purged with dry argon through the outlet tube for 0.5 h. Then, the trimmed electrode was set into the cell preheated to the required temperature and was polarized by the prescribed program.

To record the cathodic curves in the presence of niobium ethoxide, the electrodes were withdrawn and trimmed prior to each measurement, and niobium ethoxide was added to the electrolyte just before the measurement. The current–voltage curves were processed on a computer.

Niobium forms penta-, tetra-, and trialkoxy compounds [1], i.e., it may exist in the penta-, tetra-, or trivalent state. With lithium chloride, lithium *p*-toluenesulfonate, triethylamine hydrohalides, or tetraethylammonium quaternary salts in ethanol as electrolytes, the niobium anode dissolves with the formation of a Nb(V) compound. This is confirmed by calculation of the current efficiency and by the lack of solution coloration typical for Nb(III) and Nb(IV) alkoxides [1]. At the same time, it was shown experimentally [1] that, at a cathodic current density from 0.01 to



Fig. 1. Current–voltage curves measured in a 0.5 N solution of LiCl in ethanol (0.027% water) in the presence of Nb(OEt)₅ additions. $T = 25^{\circ}$ C, $V = 0.2 \text{ V s}^{-1}$; the same for Fig. 2. (*I*) Current strength and (*E*) potential (vs. silver chloride electrode); the same for Fig. 2. Cathode: (a) Pt, (b) Ni, and (c) stainless steel. Nb(OEt)₅ concentration (M): (*I*) 0, (*2*) 0.001, (*3*) 0.01, (*4*) 0.02, and (*5*) 0.04.

0.0025 A cm⁻², niobium pentaalkoxide can be reduced to the tetraalkoxide on the cathode, with a colorless solution becoming brown in the course of the electrolysis. After testing a number of cathodic materials (lead, niobium, titanium, stainless steel, molybdenum, nickel, and platinum), we chose metals with the lowest hydrogen overvoltage, platinum and nickel, as the working materials.

The cathodic reduction was also examined voltammetrically. The reduction of niobium pentaethoxide on the cathodes made of different materials was determined by measuring the voltammograms on platinum, nickel, and stainless steel at the cathodic polarization in a 0.5 N solution of lithium chloride supporting electrolyte at different concentrations of niobium pentaethoxide (Figs. 1a–1c). The curves obtained

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| Addi- tion, M | Current, mA | | Current spent for | | | | |
|------------------|-------------|-------|-------------------|--|--|--|--|
| | background | total | reduction, % | | | | |
| Potential –2.0 V | | | | | | | |
| 0.001 | 10 | 10 | 0 | | | | |
| 0.01 | 10 | 12 | 16.7 | | | | |
| 0.02 | 10 | 17 | 41.2 | | | | |
| Potential -2.5 V | | | | | | | |
| 0.001 | 27 | 27 | 0 | | | | |
| 0.01 | 27 | 33 | 15.2 | | | | |
| 0.02 | 27 | 48 | 43.8 | | | | |
| | | | | | | | |

Table 1. Comparison of total currents and currents spent for reduction of niobium pentaethoxide at its different concentrations in solution and at different potentials

Table 2. Effect of the anion on the dissolution of a niobium anode ($S_{\text{work}} = 8 \text{ cm}^2$) at an anodic current density of 0.03 A cm⁻² from a 0.1 M electrolyte with a Pt cathode ($S_{\text{work}} = 18 \text{ cm}^2$) at 35°C

| Electrolyte | Current efficiency by Nb(V), % | Nb(OEt) ₅ yield based on Nb(V) | |
|--|--|--|--|
| $Et_4NClEt_4NAcEt_4NBF_4Et_4NBrLiClLi(CH_3C_6H_4SO_3)$ | 99.16 99.92 97.72 95.79 99.46 95.70 | 42.9 1.71 20.9 0 65.4 23.1 | |

Table 3. Effect of the cation on the current efficiency by Nb(V) in electrolysis with Nb anode ($S_{\text{work}} = 8 \text{ cm}^2$) and Pt cathode ($S_{\text{work}} = 18 \text{ cm}^2$) in a 0.1 M electrolyte at an anodic current density of 0.03 A cm⁻² and 35°C

| Electrolyte | Current efficiency by Nb(V) |
|-------------------------------------|-----------------------------|
| LiCl | 99.46 |
| Et_4NCI $Et_3N \cdot HCI$ | 100.37 |
| Et ₄ NBr | 95.79 |
| Et ₃ N · HBr Bu / NBr | 78.69 |
| Du410DI | 20.02 |

show that niobium pentaethoxide is reduced only on the steel electrode (Fig. 1c). The parameters characterizing this process are listed in Table 1.

Table 1 shows that the current spent for the reduction of niobium pentaethoxide depends on the concentration of the substance in a solution and does not



Fig. 2. Current–voltage curve obtained on Nb in a 0.5 N solution of Et_4NCl in ethanol (0.027% water).

noticeably depend on the cathodic current density in the examined range. Thus, the current–voltage curves obtained are in agreement with the results of the preparative electrolyses.

The effect of the electrolyte on the efficiency of the anodic dissolution of Nb was studied in two series of experiments. The fact that the solution remains colorless indicates that the dissolution occurs to Nb(V). In the first series of the experiments (Table 2) we studied the effect of the anion, with tetraethylammonium as cation. As seen from Table 2, niobium dissolves at a current efficiency exceeding 95% [as calculated for Nb(V)]. Hence, the anion only slightly affects the anodic dissolution of niobium. The effect of the cation is also weak, at least in the case when niobium is dissolved in chloride solutions (Table 3). The further study showed that, whereas the supporting electrolyte affects the dissolution of a niobium anode only slightly, its influence on the formation of niobium alkoxide is decisive. Table 2 shows that niobium ethylate is best formed in chloride solutions, whereas in bromide solutions it is not formed at all. Although with tetraborate and acetate anions the alkoxide is formed, its yield (based on Nb) is considerably lower than in chloride solutions. We do not have sufficient data yet to account for this trend, and the study in this area is being continued.

To study the anodic process in more detail, we measured the current–voltage curves. One of typical cyclic voltammograms obtained at anodic polarization of a niobium electrode in an ethanol solution of tetra-ethylammonium is shown in Fig. 2. The voltammogram has a clear hysteresis. At forward potential scanning, the dissolution is not observed up to 1.2 V, whereas at the reverse scanning the electrode dissolution continues down to 0.25 V. Presumably, the anodic polarization breaks the passivation film on the elec-

Table 4. Potentials of the niobium transition from the active to the passive state in solutions of various compositions.* Solvent: ethanol containing 0.027% water

| Flactrolyta | E _a | Ep | ΔE | | |
|--|----------------------|----------------------|----------------------|--|--|
| Electrolyte | V | | | | |
| LiCl Et ₄ NCl Et ₄ NOOCCH ₃ | 0.65 1.20 1.60 | 0.30 0.25 0.40 | 0.35 0.95 1.20 | | |

*
$$\Delta E = E_a - E_p$$

trode surface, making the electrode active. The potential of the onset of the niobium dissolution at forward scanning can be designated as the potential of transition to the active state, and the potential of the passivation at reverse scanning, as the passivation potential E_p . The similar effect was also observed for solutions of lithium chloride and tetraethylammonium acetate (Table 4). As can be seen, the supporting electrolyte significantly affects the potential of transition to the active state, but does not noticeably affect the passivation potential. From the viewpoint of easiness of niobium anode activation, it is preferable to use lithium chloride as electrolyte.

The experiments performed showed that the current efficiency in dissolution of a niobium anode depends only slightly on the supporting electrolyte and is close to 100% [as calculated for Nb(V)] in all the media studied. This result and the closeness of the passivation potentials for different electrolytes show that, contrary to Lemkuhl's suggestion, niobium ionization rather than oxidation of the anion takes place in the course of the anodic process. Another important observation consists in that the yield of niobium ethylate based on Nb significantly depends on the supporting

electrolyte anion. Probably, the anion is involved in the synthesis reaction. Presumably, the intermediate formation of alkoxy halides, suggested in [4], plays a certain role in the alkoxide synthesis.

CONCLUSIONS

(1) The anodic dissolution of niobium is accompanied by transition of niobium into the pentavalent state. The supporting electrolyte affects only slightly the current efficiency of the metal dissolution.

(2) The supporting electrolyte strongly affects the yield of niobium alkoxide. The highest yield is observed in chloride electrolytes.

(3) To avoid the reduction of Nb(V) to Nb(IV), it is advisable to use cathode materials with the lowest hydrogen overvoltage.

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