Areas of ionic, electronic and mixed conductivity in Nb/Nb$_2$O$_5$/electrolyte system

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The ionic ($J_i$) and electronic ($J_e$) current components of the total current density through the (+)Nb/Nb$_2$O$_5$/electrolyte systems as well as the total current density are calculated using the respective expressions describing the dependence of current on field strength. The areas of electronic, mixed and ionic conductivity during the anodic film growth of (+)Nb/Nb$_2$O$_5$/electrolyte system are determined. The current efficiency during the anodic film growth is calculated and it is presented as a function of the total current density as well. A dependence of the areas of mixed conductivity and of current efficiency on the nature of the electrolyte solution is found out.

**Key words**: anodic Nb$_2$O$_5$ film, electric conductivity, current efficiency.

INTRODUCTION

The current ($J$) that flows in (+)metal/anodic oxide film/electrolyte systems consists of three components: $J = J_i + J_e + J_{dis}$. The ionic current ($J_i$) causes the growth of the anodic film by migration of ions (metal and oxygen containing ones) under the influence of the electric field applied. The electronic current ($J_e$) through the anodic oxide has no effect on the film growth. The dissolution current is negligible ($J_{dis} ≈ 0$) upon anodization in electrolytes not dissolving the film. In all cases, the ionic conductivity is investigated at high current densities (at very high field strengths, respectively). Under these conditions, validation of the so called high field approximation takes place. Moreover, the electronic current density in this case is very low, hence the total current is equal to the ionic one ($J ≈ J_i$).

The dependence of the ionic current on the electric field strength $J_i(E)_{T}$ is described by the Gunter-Schultze-Betz equation [1, 2]:

$$J_i = A_G \exp(B_G E)_T,$$

where $A_G$ and $B_G$ are constants depending on the metal (oxide) nature and on the temperature.

The electronic conductivity is studied usually during anodic polarization of already formed oxide films at potentials lower than the formation voltage, i.e. at comparatively low field strengths. Under such conditions the following empirical equation for the $J_e(E)_{T}$-dependence has been found [3]:

$$J_e = \alpha_e \exp(\beta_e E^{1/2})_T,$$

where $\alpha_e$ and $\beta_e$ are constants depending on the nature of contact electrolyte and on the temperature. Different models [4] have been proposed to explain the mechanisms of the electronic conductivity (Schottky emission, Poole-Frenkel effect, Fowler-Nordheim tunneling). Only the Christov’s model [5] explains a dependence of $J_e$ on the nature and concentration of the contact electrolyte. In this model, the electrolyte was considered as a semiconductor and redox couples in it were assumed to play the role of electron donors.

In this work field strength areas of ionic, electronic and mixed conductivity and current efficiency are determined for the system (+)Nb/Nb$_2$O$_5$/electrolyte.

RESULTS AND DISCUSSION

Numerous data both for the ionic and for electronic conductivity in the (+)Nb/Nb$_2$O$_5$/electrolyte system have been reported in the literature [6–9]. The values of the constants in Eqn. (1) have been determined for ionic current during anodization of niobium [7]. The ionic current does not depend on the electrolyte nature. On the contrary, the electronic current depends on the nature of electrolyte and its concentration [6]. Same dependence has been found recently by Ono et al. [8] for the leakage current, which varies tenfold within pH 1.6–10 range during lower-voltage anodic polarization of anodized Nb in aqueous solutions with different concentration ratios of phosphoric acid and ammonia. The electronic current in the respective system has been measured [6] after anodic film formation using different contact electrolytes. Two contact electrolytes have been implemented, i.e. aqueous borate electrolyte (ABE)

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having pH 6 and non-aqueous ammonium salycilate in dimethylformamide (AS/DMF). Two concentrations of AS/DMF have been used during measurements as well. The values of the constants in Eqns. (1) and (2) determined at 293 K are given in Table 1.

**Table 1. Values of the constants in Eqns. (1) and (2).**

<table>
<thead>
<tr>
<th>System (+)Nb/Nb2O5/electrolyte</th>
<th>Ionic current (Eqn. (1))</th>
<th>Electronic current (Eqn. (2))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$A_i$, A·cm$^{-2}$</td>
<td>$B_i$, cm$^{-1}$</td>
</tr>
<tr>
<td>1.00×10$^{-12}$</td>
<td>3.40×10$^{-6}$</td>
<td>ABE [6]</td>
</tr>
<tr>
<td>0.1 M AS/DMF [6]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.6 M AS/DMF [6]</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The ionic and electronic current densities are calculated using the values of the constants from Table 1 and they are presented in Fig. 1 as a function of field strength.

Ikonopisov and Machkova [10] have proposed that the relation of the ionic to the electronic current can be used for determining the areas of ionic, electronic and mixed conductivity. According to their conclusions, when a certain current component (ionic or electronic) is fifty times greater than the other, it could be assumed as a predominant one. In the range between $J_e = 50J_i$ and $J_i = 50J_e$ an area of mixed conductivity is observed. Since the electronic current depends on the nature and concentration of the electrolyte solution, the change of electrolyte is expected to influence the ranges of conductivity areas.

The areas of electronic, mixed and ionic conductivity are outlined for three different contact electrolytes. An example for ABE is presented in Fig. 2.

The values of electric field strength limiting the mixed conductivity area are presented in Table 2. The table data reveal that the area of mixed conductivity for the system under consideration has the same value for the three electrolyte solutions. The electrolyte nature only affects the area’s boundaries shift.

**Table 2. Electric field boundaries of the conductivity areas in the system (+)Nb/Nb2O5/electrolyte.**

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Field strength $E$×10$^{-6}$, V·cm$^{-1}$</th>
<th>Electronic conductivity ($J_i = 50J_e$)</th>
<th>Mixed conductivity ($J_i = 50J_e$)</th>
<th>Ionic conductivity ($J_i = 50J_e$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABE</td>
<td>$E &lt; 2.63$</td>
<td>2.63–5.71</td>
<td>$E &gt; 5.71$</td>
<td></td>
</tr>
<tr>
<td>0.1 M AS/DMF</td>
<td>$E &lt; 2.33$</td>
<td>2.33–5.35</td>
<td>$E &gt; 5.35$</td>
<td></td>
</tr>
<tr>
<td>0.6 M AS/DMF</td>
<td>$E &lt; 2.01$</td>
<td>2.01–5.08</td>
<td>$E &gt; 5.08$</td>
<td></td>
</tr>
</tbody>
</table>

The determination of the current efficiency ($\lambda$) for three electrolytes can be performed by the following expression:

$$\lambda = \frac{J_i}{J_i + J_e}.$$  

The dependence of current efficiency ($\lambda$) on the total current density ($J$) for the three contact electrolytes is shown in Fig. 3. The results show that the current efficiency depends on the nature and concentration of the contact electrolyte as it is expected in advance. The results presented allow outlining the values where the total current ($J$) is mainly ionic ($\lambda > 98\%$) and the growth of anodic Nb$_2$O$_5$ is efficient. Moreover, when $\lambda < 2\%$ $J$ is predominantly electronic then negligible changes in the oxide thickness should be expected. The lowest values of the efficiency are those obtained during anodic polarization
of Nb/Nb$_2$O$_5$ in ABE.

systems makes possible to define the current ranges where the anodic film formation is carried out at high efficiency. Moreover, the ranges of the electric field (working voltage, respectively), wherein the electrolyte capacitors are expected to be reliable, can also be estimated by the method employed.

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REFERENCES


ZONI NA ЙОННА, ЕЛЕКТРОННА И СМЕСЕНА ПРОВОДИМОСТ В СИСТЕМАТА Nb/Nb$_2$O$_5$/ЕЛЕКТРОЛИТ

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(Резюме)

Йонната ($J_i$) и електронна ($J_e$) компонента на тока, както и тоталната плътност на тока ($J$), протичащ в системата (+)Nb/Nb$_2$O$_5$/електролит, са пресметнати чрез уравненията, описващи тяхната зависимост от силата на електричното поле. Определени са зоните на електронна, смесена и йонна проводимост по време на формирането на анодни оксидни филм в системата (+)Nb/Nb$_2$O$_5$/електролит. Пресметнатата ефективност на тока по време на нарастването на анодните филми е представена като функция от тоталната плътност на тока. Намерено е, че зоната на смесена проводимост както и ефективността на тока зависят от природата и концентрацията на контактния електролит.