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

Chr. A. Girginov[1], A. S. Zahariev[2], A. A. Girginov[1]*

[1] *Department of Physical Chemistry, University of Chemical Technology and Metallurgy,
8 Kliment Ohridski Blv., 1756 Sofia, Bulgaria*
[2] *Department of Chemistry, Technical University of Sofia, 8 Kliment Ohridski Blv., 1000 Sofia, Bulgaria*

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 ($J_{dis} \approx 0$) 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 ($J \approx J_i$).

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]:

$$J_i = A_G . \exp(B_G E)_T , \qquad (1)$$

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]:

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

where α_e and β_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 DISSCUSION

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)

* To whom all correspondence should be sent:
E-mail: assen@uctm.edu

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).

System (+)Nb/Nb₂O₅/electrolyte				
Ionic current (Eqn. (1))		Electronic current (Eqn. (2))		
A_G, A·cm^{-2}	B_G, cm·V^{-1}	Electrolyte	α_e, A·cm^{-2}	β_e, cm$^{1/2}$·V$^{-1/2}$
1.00×10^{-12} [7]	3.40×10^{-6} [7]	ABE [6]	3.10×10^{-9}	3.07×10^{-3}
		0.1 M AS/DMF [6]	1.10×10^{-9}	2.74×10^{-3}
		0.6 M AS/DMF [6]	1.90×10^{-9}	2.83×10^{-3}

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.
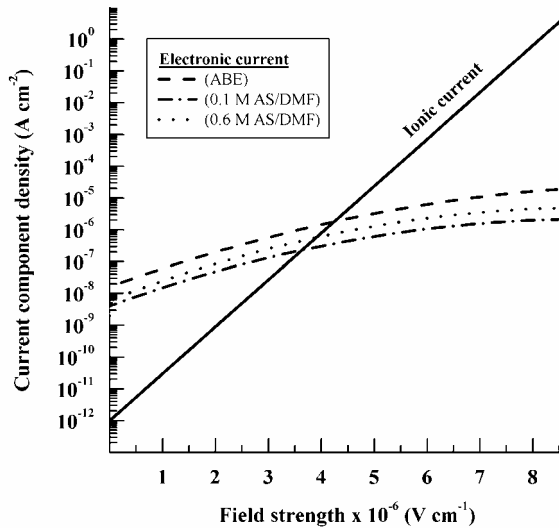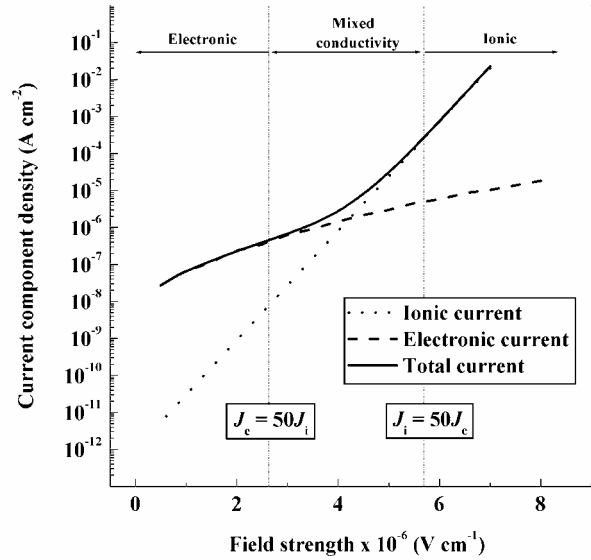

Fig. 1. Ionic and electronic current densities *vs.* field strength for the system (+)Nb/Nb₂O₅/electrolyte.

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.

Fig. 2. Ionic, electronic and total current densities *vs.* field strength for the system (+)Nb/Nb₂O₅/ABE.

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

Electrolyte	Field strength $E \times 10^{-6}$, V·cm^{-1}		
	Electronic conductivity ($J_e = 50J_i$)	Mixed conductivity	Ionic conductivity ($J_i = 50J_e$)
ABE	$E < 2.63$	2.63–5.71	$E > 5.71$
0.1 M AS/DMF	$E < 2.33$	2.33–5.35	$E > 5.35$
0.6 M AS/DMF	$E < 2.01$	2.01–5.08	$E > 5.08$

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

$$\lambda = \frac{J_i}{J_i + J_e} . \qquad (3)$$

The dependence of current efficiency (λ) 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 Nb₂O₅ 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.

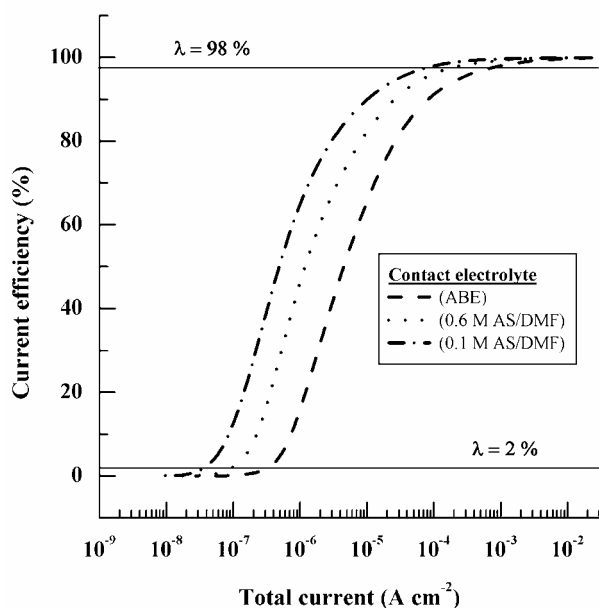

Fig. 3. Current efficiency as a function of total current density for three contact electrolytes.

CONCLUSION

The determination of ranges of ionic and electronic conductivity for the (+)Nb/Nb$_2$O$_5$/electrolyte 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.

REFERENCES

1. A. Güntherschulze, H. Betz, *Z. Phys.,* **91,** 70 (1934).
2. A. Güntherschulze, H. Betz, *Z. Phys.,* **92,** 367 (1934).
3. S. Ikonopisov, *Electrochim. Acta,* **14,** 761 (1969).
4. V. Trifonova, A. Girginov, *J. Electroanal. Chem.* **107,** 105 (1980).
5. S. Christov, *J. Electroanal. Chem.* **105,** 275 (1979).
6. S. Ikonopisov, N. Elenkov, *J. Electroanal. Chem.,* **86,** 417 (1978).
7. M. Lohrengel, *Mater. Sci. Eng.*, **R11**, 243 (1993).
8. S. Ono, K. Kuramochi, H. Asoh, *Corros. Sci.*, **51**, 1513 (2009)
9. K. Nagahara, M. Sakairi, H. Takahashi, K. Matsumoto, K. Takayama, Y.Oda, *Electrochim. Acta,* **52,** 2134 (2007).
10. S. Ikonopisov, M. Machkova, *Compt. Rend. Acad. Bulg. Sci.*, **37,** 1661 (1984).

ЗОНИ НА ЙОННА, ЕЛЕКТРОННА И СМЕСЕНА ПРОВОДИМОСТ В СИСТЕМАТА Nb/Nb₂O₅/ЕЛЕКТРОЛИТ

Кр. А. Гиргинов[1], А. С. Захариев[2], А. А. Гиргинов[1]*

[1] Катедра „Физикохимия", Химикотехнологичен и металургичен университет, бул. „Климент Охридски" № 8, 1756 София
[2] Катедра „Химия", Технически университет - София, бул. „Климент Охридски" № 8, 1756 София

(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.