SHORT COMMUNICATION

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Kinetics of electrochemical reactions on the Ag(Hg)/Ag$_4$RbI$_5$ interface

Abstract The electrochemical behaviour of the Ag(Hg)/Ag$_4$RbI$_5$ interface is investigated by a potentiostatic pulse method. It is found that the rate-determining step of the electrode reaction is electron transfer with an exchange current density of 68 mA cm^{-2} and a transfer coefficient of approximately 0.45. The order of the electrochemical reaction for silver oxidation is estimated from polarization investigations of silver amalgam in various concentrations. From this it is deduced that the mercury is ionized and is implanted in the electrolyte together with silver under anodic polarization: $15Ag + 85Hg - 100e^- \rightarrow 15Ag^+ + 85Hg^+$. From comparison of the electrochemical behaviour of the Ag(Hg)/Ag$_4$RbI$_5$ and Ag/Ag$_4$RbI$_5$ interfaces it is concluded that the rate of anodic silver dissolution on the Ag/Ag$_4$RbI$_5$ interface is limited by crystallization effects.

Keywords Silver amalgam/Ag$_4$RbI$_5$ interface ·
Electrode reaction · Rate-determining step ·
Electrocrystallization · Charge transfer

Introduction

Owing to great interest in low-temperature solid electrolytes during the years 1970–1990, many works were published on the kinetics of a silver electrode in contact with the solid electrolyte Ag$_4$RbI$_5$. These publications can be classified approximately into three groups. In some papers it is stated that the rate-determining step of electrode process is silver electrocrystallization [1, 2]. In others it is asserted that the electrocrystallization is not the rate-determining step [3, 4]. Others state that special theories for solid electrolytes should be developed for the explanation of experimental kinetic laws [5]. At

present, there is no consolidated opinion about the nature of the rate-determining step on the Ag/Ag$_4$RbI$_5$ interface.

At the same time it is known that, on amalgamated electrodes, crystallization effects are eliminated [6]. It has been shown [7, 8] that the rate of an electrochemical reaction will increase considerably on an amalgamated silver electrode in contact with solid electrolytes. It seems that a detailed investigation of the amalgamated silver electrode will allow us to contribute greater clarity concerning the rate-determining step of electrode reactions on the Ag/Ag$_4$RbI$_5$ interface.

In the present work the kinetics of the amalgamated silver and silver amalgam electrodes is investigated by the pulse potentiostatic method.

Experimental

The solid electrolyte Ag$_4$RbI$_5$ was prepared by the known literature method [9]. Cells of the type Ag(Hg)/Ag$_4$RbI$_5$/Ag were prepared in a dry air atmosphere (dehydrator P$_2$O$_5$). At first the Ag$_4$RbI$_5$ pellet was pressed under a pressure of 2.2×10^8 Pa. Then a silver powder was pressed as the counter electrode. The diameter of the cell was equal to 12 mm and the thickness of the electrolyte layer was approximately 1 mm. The silver wire reference electrode of 0.2 mm diameter was pressed inside the electrolyte. The flat amalgamated silver electrode or the silver amalgam was positioned onto the electrolyte as a working electrode.

The concentrated silver amalgam was prepared by long-time contact of silver metal with mercury. Amalgams of others concentrations were prepared by means of dilution of the concentrated amalgam.

Polarization of the cells was carried out 2 h after their assembly by means of a P-5848 potentiostat (Russia) at room temperature. The potentiostatic transients were registered with photorecording by means of an S8-1 oscillograph (Russia).

Results and discussion

Immediately after the cell assembly the working electrode potential was increased slowly to 0.08–0.1 V over 1–2 h, depending on the amalgam concentration. Apparently, mercury reacts chemically with Ag$_4$RbI$_5$ rather

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slowly [8], but it does not interfere with the current crossing the electrode/electrolyte interface.

The anodic current-time (*i-t*) transients for the amalgamated silver electrode after potentiostatic pulses are shown in Fig. 1 (the inclined initial slope is caused by the potentiostat speed). It is seen that the current does not depend on time. Hence, the rate-determining step of the electrode reaction is the charge transfer. The current-voltage characteristics (CVCs) of the amalgamated electrode (Fig. 2, curve 1) conform to the equation for the charge transfer:

$$\ln \frac{i}{1 - \exp{-\frac{zF}{RT}\eta}} = \ln i_0 + \alpha \frac{zF}{RT}\eta \qquad (1)$$

where η is the overvoltage, at the exchange current density $i_0 = 68 \pm 5$ mA cm^{-2} and the transfer coefficient α of approximately 0.45.

The CVCs of the Ag/Ag$_4$RbI$_5$ interface are shown in Fig. 2 (curve 2) for comparison. These CVCs were obtained according to results of similar potentiostatic investigations [2] at transient times of about 0.5–2 ms. At these times the loss of contact on the electrode/electrolyte interface owing to the forming of voids by electrochemical silver dissolution is eliminated. It is seen that under overvoltages of more than 0.1 V these CVCs are described by Eq. 1 for the charge transfer at $i_0 = 20 \pm 2$ mA cm^{-2} and $\alpha \approx 0.45$. However, under overvoltages of less than 0.1 V the CVCs are not described by Eq. 1. Hence, under these overvoltages, crystallization effects probably dominate since at the amalgamated electrode such effects do not exist.

We shall analyse the influence of mercury on the behaviour of the silver electrode. Takahashi and Yamamoto [7] state that mercury reacts with an interstitial silver ion and eliminates the rate-determining step of its interaction with the silver ion vacancy. Raleigh [10] suggests that improvement of the electrode/electrolyte
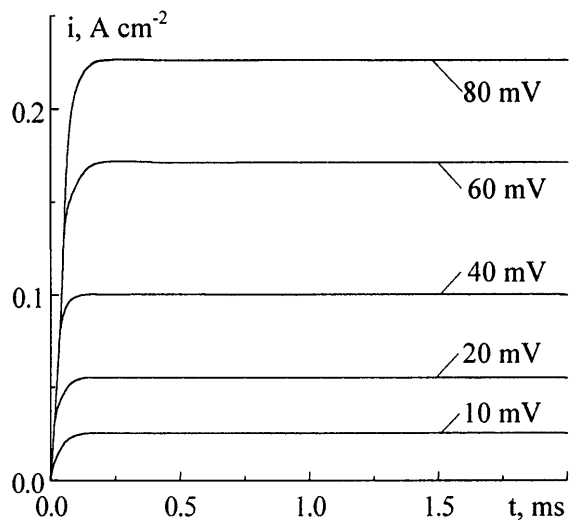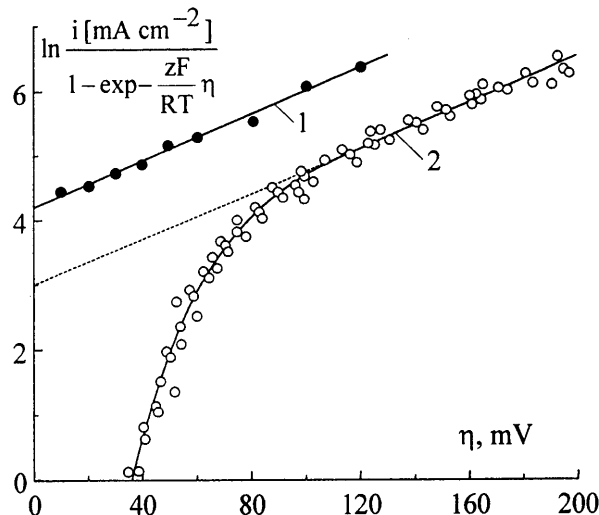
Fig. 2 Current-voltage characteristics on the interfaces: *1* amalgamated silver/Ag$_4$RbI$_5$ and *2* Ag/Ag$_4$RbI$_5$ [2]

microcontact on the fluid interface brings about an increase of the interface effective surface.

To determine the mechanism of any mercury influence we have assumed that mercury can react with Ag$_4$RbI$_5$ not only chemically but also electrochemically. For testing this hypothesis, the anodic behaviour of silver amalgams of various concentrations was also investigated by the potentiostatic method.

The anodic CVCs of silver amalgams are shown in Fig. 3. It is seen that the position of the polarization curves depends on the amalgam concentration c_{Ag}. It enables us to estimate the order of the silver electrochemical oxidizing reaction [6]:

$$Z_{Ag} = \frac{\partial \ln i}{\partial \ln c_{Ag}} \quad \text{under} \quad \eta \gg \frac{RT}{zF} \qquad (2)$$

The dependence $\ln i$ vs. $\ln c_{Ag}$ under a potential $\varphi = 200$ mV is shown in Fig. 4. The slope of this straight line, i.e. Z_{Ag}, is equal approximately to 0.15. For a fluid metal electrode at unit valence for an electron transfer
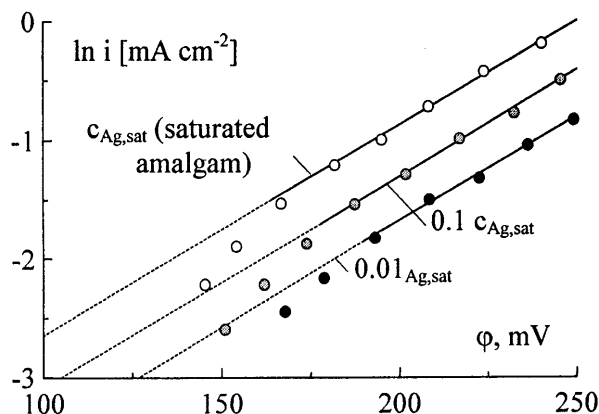
Fig. 1 Potentiostatic current-time transients on the amalgamated silver/Ag$_4$RbI$_5$ interface under various overvoltages η

Fig. 3 Current-voltage characteristics on the silver amalgam/Ag$_4$RbI$_5$ interface at various amalgam concentrations
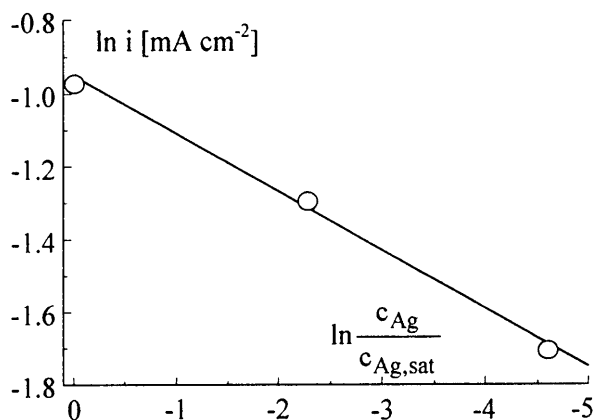
Fig. 4 Currents under $\varphi = 200$ mV vs. amalgam concentration (from Fig. 3)

reaction, the order of the electrochemical reaction is equal to the stoichiometric number of the oxidized silver. Hence, 0.15 silver atoms are required for one electron transfer. It is necessary to assume that the deficiency of charge is delivered by mercury atoms according to the empirical equation:

$$15Ag + 85Hg - 100e^- \rightarrow 15Ag^+ + 85Hg^+ \qquad (3)$$
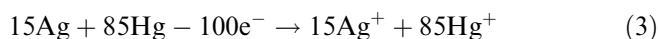
Hence, mercury is ionized and is implanted into the electrolyte together with silver under anodic polarization of the $Ag(Hg)/Ag_4RbI_5$ interface.

Conclusions

The rate-determining step on the $Ag(Hg)/Ag_4RbI_5$ interface is the electron transfer. Mercury together with silver is ionized and is implanted into Ag_4RbI_5 under anodic polarization.

The rate-determining step of silver anodic dissolution is limited by crystallization effects on the Ag/Ag_4RbI_5 interface under overvoltages of less than 0.1 V.

These laws of the investigated electrochemical reactions are well described by the classical equations of electrochemical kinetics and the development of special equations is not required for description of the electron transfer reaction for solid electrolytes.

These results could be useful in investigations of other solid state electrode reactions with the participation of metal electrodes.

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