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Galvanostatic investigation of electrochemical processes at the C/RbCu₄Cl₃I₂ interface

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Abstract The kinetics of electrochemical processes at a vitreous carbon electrode in contact with the solid electrolyte RbCu₄Cl₃I₂ has been investigated. In the range of potentials from zero up to the decomposition potential of the electrolyte (0.57 V), the rate of the reversible electrode reaction $\text{Cu}^+ - \text{e}^- \leftrightarrow \text{Cu}^{2+}$ is controlled by slow diffusion of the electronic defects (Cu^{2+} ions or holes) in the electrolyte. The diffusion coefficient of these defects is equal to $1.5 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$. The exchange current density of the electrode reaction is equal to $20 \times 10^{-6} \text{ A cm}^{-2}$.

Keywords Solid electrolyte · Rubidium tetracopper trichloride diiodide · Vitreous carbon electrode · Electrode kinetics · Slow diffusion

Introduction

The electrolyte RbCu₄Cl₃I₂ has the highest conductance (by means of Cu^+ ions) of all studied low-temperature solid electrolytes. Therefore, a powerful device with this electrolyte, which functions at room temperature, can be made.

In copper-conducting solid electrolytes, some electrochemical reactions proceed with the participation of Cu^+ ions, for example:



and these have been investigated explicitly [1, 2, 3]. However, the copper-conducting solid electrolytes always contain Cu^{2+} ion impurities owing to the chemical instability of monovalent copper compounds. Therefore in such electrolytes, including RbCu₄Cl₃I₂, electro-

chemical reaction with Cu^{2+} ion participation may take place [4, 5, 6, 7, 8]:



The investigation of this reaction is of considerable interest, since it is possible to identify Cu^{2+} ions with the hole conductance of copper-conducting solid electrolytes, with some assumptions [7].

The reaction of Eq. 2 is convenient to investigate at the polarization of indifferent (non-copper) electrodes. By potentiostatic investigations of platinum [5] and vitreous carbon [7, 8] electrodes it was found that the equilibrium potential of the reaction rate of Eq. 2 is controlled by slow electronic defect diffusion (Cu^{2+} ions or holes) in the electrolyte.

In the present work a detailed galvanostatic investigation of a vitreous carbon electrode in contact with the solid electrolyte RbCu₄Cl₃I₂ is carried out in the potential interval from zero up to the decomposition potential of the electrolyte, φ_d (for RbCu₄Cl₃I₂: $\varphi_d = 0.57 \text{ V}$ [9]).

Experimental

The solid electrolyte RbCu₄Cl₃I₂ was prepared by the published method [10]. Cells of the type Cu|RbCu₄Cl₃I₂|vitreous carbon were prepared in a dry air (P_2O_5) atmosphere by pressing RbCu₄Cl₃I₂ and copper powders onto a flat vitreous carbon disk (12 mm diameter) under a pressure of $2.2 \times 10^8 \text{ Pa}$. The thickness of the electrolyte layer was equal to ca. 1 mm. A copper wire reference electrode (0.2 mm diameter) was positioned inside the electrolyte. The clamping pressure applied to the cell was ca. $3 \times 10^6 \text{ Pa}$. Before measurements began, the cell was annealed for several hours at 140 °C.

Polarizations of the cells were made with a P-5848 potentiostat (Russia) at room temperature.

Results and discussion

According to the theory of the Hebb-Wagner polarization method [11, 12], the electromotive force of the cell Cu|RbCu₄Cl₃I₂|vitreous carbon should be equal to zero

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under equilibrium conditions. However, the stable pseudo-equilibrium potential of the indifferent electrode vs. copper has a value of about 0.4–0.5 V [5, 6] in reality. This potential is due to the chemical instability of Cu^+ ions in $\text{RbCu}_4\text{Cl}_3\text{I}_2$ and the electrolyte always contains Cu^{2+} ion impurities.

It is necessary to discuss the state of divalent copper in $\text{RbCu}_4\text{Cl}_3\text{I}_2$. In the crystal structure of the electrolyte, this electronic defect can be represented as an electronic hole spreading out over all Cu^+ ions. Some authors [13, 14] discussing hole conduction in $\text{RbCu}_4\text{Cl}_3\text{I}_2$ use this argument. However, if the time of localization of the hole on an individual Cu^+ ion is longer than the time of the hole jump between copper ions, it is possible to consider the electronic defect as the electrochemical active species Cu^{2+} [6]. Other authors [4, 5] use this description of the process.

Since the determination of the state of copper electronic defects does not enter the purpose of this work, we shall further *formally* note these defects as Cu^{2+} ions. Thus it is simpler and habitual to write the equations of electrochemical kinetics.

The vitreous carbon electrode in contact with the investigated $\text{RbCu}_4\text{Cl}_3\text{I}_2$ sample has a pseudo-equilibrium potential φ_0 of about 0.5 V vs. a copper reference electrode.

In Fig. 1 the typical anodic and cathodic galvanostatic transients potential φ vs. time t are shown. It is necessary to remark at once that the charging of the double layer capacity of the carbon/solid electrolyte interface ($10\text{--}20\ \mu\text{F cm}^{-2}$ [1]) can be neglected at the investigated times.

In the case of diffusion kinetics the galvanostatic transients are described by the known equation [15]:

$$\varphi - \varphi_0 = \frac{kT}{e} \ln \left(1 \pm \sqrt{\frac{t}{\tau}} \right) \quad (3)$$

where k is Boltzmann's constant, T is the temperature, e is the elementary charge, and τ is the transition time:

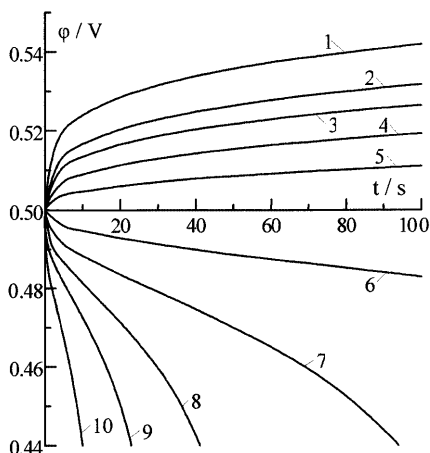


Fig. 1 Galvanostatic transients at current densities ($\mu\text{A cm}^{-2}$) of (1) 6, (2) 4, (3) 3, (4) 2, (5) 1, (6) -1, (7) -2, (8) -3, (9) -4, and (10) -6

$$\tau = \frac{\pi}{4} D \left(\frac{e}{i_g} C_{\text{O,Cu}^{2+}} \right)^2 \quad (4)$$

where $C_{\text{O,Cu}^{2+}}$ is the pseudo-equilibrium concentration of the electronic defects (Cu^{2+} ions or holes) in the electrolyte, D is the diffusion coefficient of these defects, and i_g is the current density. Equation 3 can be rewritten as:

$$\left[\exp \frac{e}{kT} (\varphi - \varphi_0) \right] - 1 = \sqrt{\frac{t}{\tau}} \quad (5)$$

In Fig. 2 the galvanostatic transients from Fig. 1 are shown in Eq. 5 coordinates. In these coordinates the transients are close to linear. Hence in the interval of potentials $0 - \varphi_d$ (at potentials $0 - \varphi_0$, Eq. 1 is blocked, and at $\varphi_0 - \varphi_d$, Eq. 2 is reversible) the rate-determining step of the Eq. 2 electrode reaction is the slow diffusion of electronic defects in the electrolyte.

However, the lines in Fig. 2 are not extrapolated to zero. Hence, at $t \rightarrow 0$ the overvoltage $\eta \neq 0$. This overvoltage can only be the overvoltage of charge transfer, η_{tr} . In Fig. 2, η_{tr} does not exceed 8 mV. Therefore it is possible to estimate the value of the charge transfer resistance, θ ($\theta = \eta_{\text{tr}}/i_g$), from segments of the ordinates at $t = 0$. Here $\theta = (1.3 \pm 0.1) \times 10^3\ \Omega\ \text{cm}^{-2}$. Hence, the value of the current exchange density:

$$i_0 = \frac{kT}{e} \frac{1}{\theta} \quad (6)$$

is equal to $(20 \pm 2) \times 10^{-6}\ \text{A cm}^{-2}$.

In Fig. 3 the galvanostatic transitions from Fig. 2 are shown for "pure" diffusion, i.e. after deduction of the charge transfer overvoltage, η_{tr} . The τ values obtained from the slopes of Fig. 3:

$$\frac{\Delta \left\{ \left[\exp \frac{e}{kT} (\varphi - \eta_{\text{tr}} - \varphi_0) \right] - 1 \right\}}{\Delta \sqrt{t}} = \frac{1}{\sqrt{\tau}} \quad (7)$$

are calculated. In Fig. 4 the transition time vs. the current density is shown in Eq. 4 coordinates. The line slopes:

$$\frac{\Delta \sqrt{\tau}}{\Delta \left(\frac{1}{i_g} \right)} = \frac{\sqrt{\pi D}}{2} e C_{\text{O,Cu}^{2+}} \quad (8a)$$

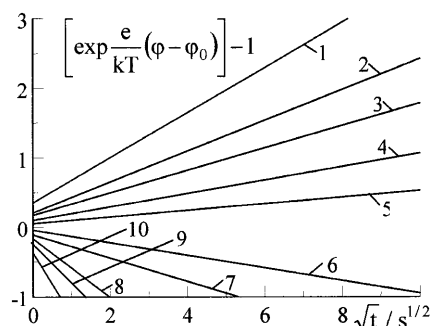


Fig. 2 Galvanostatic transients from Fig. 1 in Eq. 5 coordinates

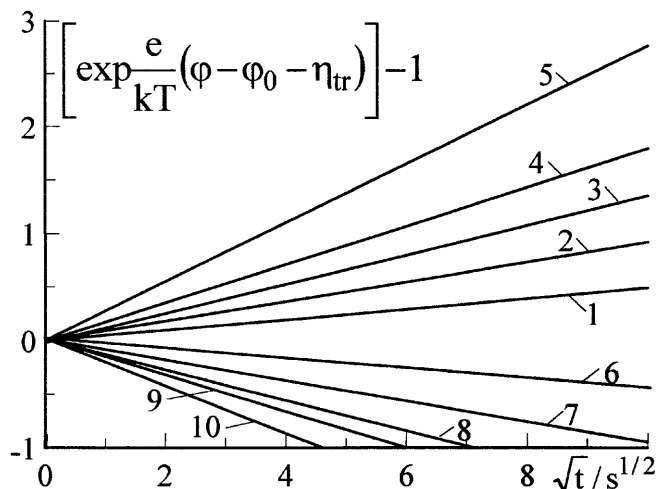


Fig. 3 Galvanostatic transients from Fig. 2 after deduction of the charge transfer overvoltage, η_{tr}

in this figure depend on the diffusion coefficient and the equilibrium concentration of the electronic defects (Cu^{2+} ions or holes).

The value of the equilibrium concentration of the electronic defects (Cu^{2+} ions or holes) is interdependent on the pseudo-equilibrium potential of the vitreous carbon electrode:

$$\varphi_0 = \varphi_{\text{Cu}^{2+}/\text{Cu}^+}^0 + \frac{kT}{e} \ln \frac{C_{\text{O,Cu}^{2+}}}{C_{\text{O,Cu}^+}} \quad (8b)$$

where $\varphi_{\text{Cu}^{2+}/\text{Cu}^+}^0$ is the standard potential of the $\text{Cu}^{2+}/\text{Cu}^+$ couple and $C_{\text{O,Cu}^+}$ is the equilibrium concentration of Cu^+ ions in the electrolyte. At $\varphi_0 = 0.5$ V, $\varphi_{\text{Cu}^{2+}/\text{Cu}^+}^0 = 0.624$ V [16] from thermodynamic data and $C_{\text{O,Cu}^+} = 1.59 \times 10^{22} \text{ cm}^{-3}$ [17] from this equation:

$$C_{\text{O,Cu}^{2+}} = 1.25 \times 10^{18} \text{ cm}^{-3} \quad (9)$$

Substitution of this value into Eq. 8a yields $D = (1.5 \pm 0.5) \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$. Here it is necessary to note that Eq. 3 is deduced for the case of background electrolyte surplus. The Cu^+ ions are such “an electrolyte” in our case. These ions eliminate the electrical field gradient in the $\text{RbCu}_4\text{Cl}_3\text{I}_2$ bulk and so we investigate only the electronic defect diffusion.

Conclusions

The rate-determining step for the electrochemical process at the vitreous carbon/ $\text{RbCu}_4\text{Cl}_3\text{I}_2$ interface in the interval of the potential from zero up to the electrolyte decomposition potential is the diffusion of the electronic defects (Cu^{2+} ions or holes) in the electrolyte. The results of galvanostatic experiments presented in this work correspond well to results for potentiostatic investiga-

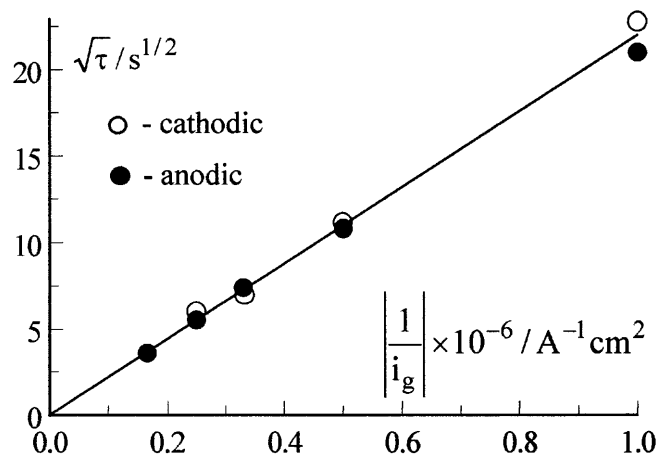


Fig. 4 Transition time vs. current density

tions [8]. The solid electrolytes are the best materials for the study of diffusion processes, since there is no convection in them. Therefore the galvanostatic transients correspond well to the classical equations of diffusion kinetics even at relatively long times.

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