ORIGINAL PAPER

**Gennady I. Ostapenko · Antony Cox
Lidiya A. Ostapenko**

Investigation of electrochemical reactions in the solid state cell Cu/RbCu$_4$Cl$_3$I$_2$/C

Abstract Using experimental potential values for a vitreous carbon electrode in contact with the RbCu$_4$Cl$_3$I$_2$ solid electrolyte, the concentration of Cu^{2+} ions in the electrolyte was determined. At 0.5 V, the concentration of Cu^{2+} was 1.25×10^{18} cm^{-3}. The estimated values of the Cu^{2+} ion concentration in RbCu$_4$Cl$_3$I$_2$ (0.8%) and the potential of the vitreous carbon electrode after electrochemical decomposition of RbCu$_4$Cl$_3$I$_2$ (0.606 V) correspond to experimental values of 2% and 0.58 V, respectively. This demonstrates the adequacy of the model describing the electrode potential of Cu^{2+} as a function of the concentration in RbCu$_4$Cl$_3$I$_2$. When the C/RbCu$_4$Cl$_3$I$_2$ interface was polarized, the diffusion coefficient of Cu^{2+} was 1.5×10^{-8} cm^2 s^{-1}. Investigations of the interface between the copper electrode and RbCu$_4$Cl$_3$I$_2$ were carried out by galvanostatic and potentiostatic methods. A 1-μm layer of cuprous oxide, Cu$_2$O, was discovered on the interface of the copper electrode with RbCu$_4$Cl$_3$I$_2$. This layer blocks the course of the electrochemical reaction Cu^0–e$^-$ ⇌ Cu$^+$ with participation of copper metal. The copper electrode behaves as an inert redox electrode at low overvoltages. In this case, at the Cu$_2$O/RbCu$_4$Cl$_3$I$_2$ interface an electrochemical reaction with Cu^{2+} ion participation, Cu$^+$–e$^-$ ⇌ Cu^{2+}, takes place. The results suggest that the reaction rate is limited by slowing the Cu^{2+} diffusion in RbCu$_4$Cl$_3$I$_2$. The initial Cu^{2+} ion concentration in the electrolyte near this interface is about 1.4×10^{17} cm^{-3}. The exchange current density is about $(4 \pm 2) \times 10^{-6}$ A cm^{-2}.

G.I. Ostapenko (✉)
Institute of Radio Engineering & Electronics,
Russian Academy of Sciences,
48 Goncharov Str., Ulyanovsk 432011, Russia
E-mail: ufire@mv.ru

A. Cox
Department of Materials Science and Metallurgy,
University of Cambridge, Cambridge CB3 3QZ, UK

L.A. Ostapenko
Kustanay Agricultural Institute,
28 Abay Str., Kustanay 458015, Kazakhstan

At potentials $\varphi > 8$–10 mV, an electrical breakdown of the Cu$_2$O layer takes place, allowing copper metal to ionize to Cu$^+$. We suggest that at 10 mV $< \varphi <$ 100 mV the rate of this reaction is limited by the formation and growth of copper nuclei and at $\varphi > 120$ mV the reaction rate is limited by charge transfer.

Keywords Solid electrolyte · Rubidium copper chloride iodide · Inert electrode potential · Copper(II) ion concentration · Electrode kinetics

Introduction

Although extensive experimental data about the thermodynamics and kinetics of electrochemical processes in low-temperature Cu$^+$-conducting solid electrolytes is available [1, 2, 3, 4, 5, 6, 7], detailed interpretations of these results are lacking. The following are unresolved phenomena: (1) the nature of the e.m.f. between copper and inert electrodes in electrolytes; (2) the discrepancy by three orders of magnitude between the exchange current density obtained from measurements of the equilibrium potential (2×10^{-6} A cm^{-2} [7]) and those from Tafel plots at overvoltages of > 120 mV (2×10^{-3} A cm^{-2} [6]).

At the same time, it is known that Cu$^+$-conducting solid electrolytes always contain some Cu^{2+} ions [2, 8, 9]. For example, the Cu^{2+} ion content in the RbCu$_4$Cl$_3$I$_2$ solid electrolyte reaches 1–2% of the overall copper [10]. Therefore, in such solid electrolytes, along with the electrode reaction:

$$Cu^0 - e^- \rightleftharpoons Cu^+ \qquad (1)$$

the reaction:

$$Cu^+ - e^- \rightleftharpoons Cu^{2+} \qquad (2)$$

may take place.

The interrelationship of an inert electrode potential with the Cu^{2+} activity in Cu$^+$-conducting electrolytes is here presented. In addition, an investigation of electrochemical reaction kinetics on copper and inert

electrodes in the $RbCu_4Cl_3I_2$ electrolyte is performed and the interpretation of the experimental results is given, taking into account the possibility of reaction 2.

Background

The preparation of low-temperature Cu^+-conducting solid electrolytes includes melting of an ingredient intermixture at a temperature of approximately 500 °C, pulverizing, pressing and long-life annealing at a temperature of approximately 200 °C [11, 12, 13]. It is known that Cu^+ ions are chemically unstable in such conditions and oxidize to Cu^{2+} ions even in the presence of trace quantities of oxygen. The oxidizing reaction of the $RbCu_4Cl_3I_2$ electrolyte during its preparation is that of CuCl, present in the electrolyte:

$$4CuCl + 0.5O_2 \rightarrow 2CuCl_2 + Cu_2O \tag{3}$$
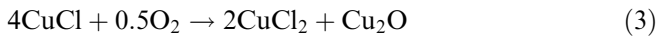
Here, two atoms of copper migrate to the surface of the electrolyte crystal and form cuprous oxide, Cu_2O. In the bulk of the crystal the negatively charged vacancies V'_{Cu} (according to the Kroeger-Vink notation) are formed. $CuCl$ and $CuCl_2$ have practically identical packing of Cl^- ions [14] and form solid solutions [15]. Therefore $CuCl_2$, apparently, does not form an individual lattice. Hence, Cu^{2+} ions ($Cu^{\bullet}_{Cu}$) are formed in the lattice site usually occupied by Cu^+ ions ($Cu^{\times}_{Cu}$). Reaction 2 can now be written as:

$$4Cu^{\times}_{Cu} + 0.5O_2 \rightarrow Cu_2O + 2Cu^{\bullet}_{Cu} + 2V'_{Cu} \tag{4}$$
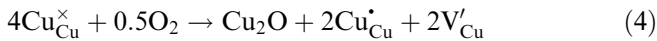
Cu^{2+} dissociation with the formation of an electronic hole ($h^{\bullet}z$) is possible:

$$Cu^{\bullet}_{Cu} \rightleftharpoons Cu^{\times}_{Cu} + h^{\bullet} \tag{5}$$

Hence, the copper electronic defect formed by oxidation of the electrolyte in the crystal structure can be explained as:

1. Electronic holes spread among Cu^+ ions. This is supported by authors [16, 17] considering hole conduction in $RbCu_4Cl_3I_2$.
2. The electrochemically active species Cu^{2+}, if the residence time of the hole for the localized Cu^+ ion state is more than the hopping time of the hole between copper ions [19]. Other authors in the field [2, 18] support this view.

The definition of the state of the copper electronic defects does not enter into the purpose of this work, so the defects will be attributed to Cu^{2+} ions. It is also appropriate to clarify the situation using equations of electrochemical kinetics.

Consideration is now given to the processes that happen at the electrolyte/copper electrode interface. The thermodynamics requires (Hebb-Wagner theory [20]) that the Cu^{2+} activity in the electrolyte should be reduced and correspond to the equilibrium of the reaction:

$$Cu^0 + Cu^{2+} \rightarrow 2Cu^+ \tag{6}$$
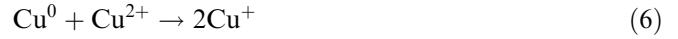
In this case, the e.m.f. between the copper and the inert electrodes will be equal to zero. However, this e.m.f. in realistic cells with low-temperature Cu^+-conducting electrolytes is not always equal to zero. For example, in the interval 400–600 mV the determination of the hole conductivity of electrolytes has been studied [16, 17]. It is clearly stated [19] that the e.m.f. is impossible to remove at annealing temperatures below the melting point of the electrolyte (about 200 °C), even under vacuum. Hence, in these conditions the electrolyte cannot be made to equilibrate with the copper electrode.

The possible reasons for this phenomenon will be addressed. First, the microscopic structure of the $Cu/RbCu_4Cl_3I_2$ interface will be discussed. The presence of a blocking layer on this interface has been underlined [12]. Other authors [4, 5] refer to the presence of an adsorbed oxygen layer. Others again [21] resolutely specify the presence of a copper oxide layer on the copper electrode surface.

Generally, the preparation procedure of the copper electrode does not exclude the presence of copper oxides on its surface. At temperatures less than 500 °C, even under an oxygen pressure about 10^{-3} mmHg, cuprous oxide is formed on copper [22, 23]. During annealing, oxygen chemisorbs on cuprous oxide and there is oxidation of cuprous ions to cupric ions:

$$Cu_2O + 0.5O_2 \rightleftharpoons 2CuO \tag{7}$$

The mechanism of this reaction is similar to the mechanism of reaction 3. Taking into account reaction 5, the following reaction can be noted:

$$2Cu^{\times}_{Cu} + 0.5O_2 \rightleftharpoons Cu_2O + 2V'_{Cu} + 2h^{\bullet} \tag{8}$$
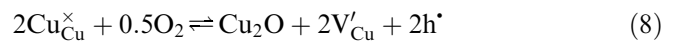
The mobility of the copper vacancies is less than the hole mobility by some orders of magnitude. Therefore cuprous oxide has practically no ionic conductance and is a p-type semiconductor.

The Cu^+ and Cu^{2+} ion concentrations in cuprous oxide on the copper metal surface should correspond to the equilibrium of reaction 6. Therefore, some copper metal atoms transfer from the electrode into cuprous oxide during annealing, with the formation of Cu^+ ions and mobile electrons. These Cu^+ ions occupy the lattice vacancies and the electrons associate with holes. Therefore, in cuprous oxide near the copper electrode, an interface region is formed which is depleted of holes and in some cases even contains mobile electrons [23]. Such a layer depleted of current carriers or even a p-n junction is the barrier layer. This barrier layer has rectifying properties and the structure $Cu/Cu_2O/$ohmic contact is designed for alternating current rectification and is noted as the copper oxide rectifier.

The thermodynamics requires that the cuprous oxide layer in the copper oxide rectifier should be in equilibrium with copper. However, such a rectifier is efficient even at temperatures of 100 °C and more. Hence, the high gradient of the hole (or Cu^{2+} ion) concentration in the cuprous oxide layer is sufficient for a long life. This is explained by the strong stopping of reaction 6 because of the very small value of the copper self-diffusion coefficient in Cu_2O [24] and the Cu^{2+} concentration on the inside of the cuprous oxide layer may be considerable, up to formation of cupric oxide [22, 23].

Hence, at the copper electrode/electrolyte interface, the cuprous oxide layer hinders the chemical equilibrium of the electrolyte with copper. Therefore the initial concentration of Cu^{2+} in the electrolyte does not vary and is almost identical in the whole electrolyte sample. It is this concentration that causes a value of the inert electrode potential versus the copper electrode.

The applicability of the equations of classical diffusion kinetics at investigations of cells with low-temperature Cu^+-conducting solid electrolytes is now addressed. The Hebb-Wagner theory hypothesizes the complete equilibrium of the electrolyte with a reversible (here copper) electrode. This requirement should establish the smoothing of the concentration of species (here holes or Cu^{2+} ions) in the whole electrolyte sample. The absence of an initial concentration gradient is one of the main requirements for the application of the equations of classical diffusion kinetics. The chemical equilibrium with a reversible electrode is only a resource for realization of this requirement.

In the investigated cells with low-temperature Cu^+-conducting solid electrolytes there is no chemical equilibrium. However, apparently the initial gradient of the Cu^{2+} concentration in the electrolyte is practically missing because of the blocking of reaction 6 by the cuprous oxide layer. Hence, the application of the equations of diffusion electrochemical kinetics can be justified here.

Experimental

$RbCu_4Cl_3I_2$ was prepared by the method mentioned previously [25]. In this method the mixture RbCl, CuI, $CuCl_2$ and excess copper metal was melted. $CuCl_2$ and copper were allowed to react in the melt and CuCl was formed. The melt was separated from the excess copper using a centrifuge. The granules (at a temperature of 190 °C) were annealed for a few hours.

The surface of a flat copper electrode was hand-ground by corundum powders of various dispersions, polished by diamond paste to an unruffled surface, degreased by ethanol and CaO + MgO aqueous paste and washed with water. The electrodes were annealed at 500 °C under a pressure of 10^{-4} mmHg for 6 h and slowly cooled to room temperature.

Cells of the type $Cu/RbCu_4Cl_3I_2/C$ were prepared in an atmosphere of dry air (utilizing P_2O_5 as dehydrator) by pressing the electrolyte powder under a pressure of 2.2×10^8 Pa. The thickness of the electrolyte layer was about 1 mm. The copper wire reference electrode of 0.2 mm diameter was impressed in the centre of the electrolyte. Copper and vitreous carbon electrodes were positioned onto the electrolyte layer surfaces. The diameter of the cell was 12 mm. The cells were compressed in special equipment under a loading of about 3×10^6 Pa, annealed at 160 °C for 3 h and cooled slowly to room temperature.

All the electrochemical measurements were carried out at 25 °C using a P-5848 potentiostat (Russia) as described elsewhere [26]. The low currents were measured using a sensitive current-voltage follower (TR-1452, Hungary).

Results and discussion

The vitreous carbon electrode

The vitreous carbon electrode in contact with the $RbCu_4Cl_3I_2$ sample produced a stationary potential φ_0 of ~0.50 V versus the copper electrode. Using this value, the quasi-equilibrium concentration of Cu^{2+} ions in $RbCu_4Cl_3I_2$ may be calculated.

The Cu^+ and Cu^{2+} ions are the potential-determining species in $RbCu_4Cl_3I_2$. Consequently, the potential of the copper electrode in $RbCu_4Cl_3I_2$ is:

$$\varphi_{Cu} = \varphi^0_{Cu^{2+}/Cu^+} + \frac{kT}{e}\ln\frac{C_{Cu^{2+},Cu}}{C_{Cu^+,Cu}} \tag{9}$$

where $\varphi^0_{Cu^{2+}/Cu^+}$ is the standard potential of the Cu^{2+}/Cu^+ couple in $RbCu_4Cl_3I_2$, $C_{Cu^{2+},Cu}$ is the Cu^{2+} concentration near the copper electrode, $C_{Cu^+,Cu}$ is the Cu^+ concentration near the copper electrode, k is Boltzmann's constant, T is the temperature and e the elementary charge.

The potential of the vitreous carbon electrode is:

$$\varphi_C = \varphi^0_{Cu^{2+}/Cu^+} + \frac{kT}{e}\ln\frac{C_{Cu^{2+},C}}{C_{Cu^+,C}} \tag{10}$$

where $C_{Cu^{2+},Cu}$ and $C_{Cu^+,Cu}$ are the Cu^{2+} and Cu^+ concentrations near the vitreous carbon electrode. If, for $RbCu_4Cl_3I_2$, $C_{Cu^{2+}} \ll C_{Cu^+}$, then $C_{Cu^+,Cu}\approx C_{Cu^+,C}$, and using Eqs. 9 and 10 the e.m.f. of the $Cu/RbCu_4Cl_3I_2/C$ cell is:

$$\varphi_0 = \varphi_C - \varphi_{Cu} = \frac{kT}{e}\ln\frac{C_{Cu^{2+},C}}{C_{Cu^{2+},Cu}} \tag{11}$$

Using the Cu^+ concentration in the $RbCu_4Cl_3I_2$ lattice ($C_{Cu^+} = 1.585\times10^{22}$ cm^{-3} [11]) and $\varphi^0_{Cu^{2+}/Cu^+} = 0.624$ V (calculated using free energies of relevant reactions [1]), from Eq. 9 at $\varphi_{Cu} = 0$ it is possible to determine $C_{Cu^{2+},Cu} = 4.17\times10^{11}$ cm^{-3}. Substituting this value into Eq. 11, at $\varphi_0 = 0.50$ V, in view of the "lattice saturation" in $RbCu_4Cl_3I_2$, $C_{Cu^{2+}} + C_{Cu^+} = 1.585\times10^{22}$ cm^{-3}, and we obtain:

$$C_{Cu^{2+}}, C = 1.25 \times 10^{18}\, cm^{-3} \tag{12}$$

This Cu^{2+} concentration content in $RbCu_4Cl_3I_2$ is approximately 0.8% relative to the total copper in

$RbCu_4Cl_3I_2$. These data correspond well to the Cu^{2+} content in $RbCu_4Cl_3I_2$, being approximately 2% from measurements of the magnetic susceptibility [10].

In Fig. 1 the quasi-stationary current-voltage characteristics (CVC) of the vitreous carbon electrode are shown, using the results of potentiostatic measurements. The CVC may be analysed using classical electrochemical diffusion kinetics. At steady-state diffusion, the CVC is described by [27]:

$$\varphi - \varphi_0 = \frac{kT}{e}\ln\left(1 - \frac{i}{i_d}\right) \tag{13}$$

where $(\varphi - \varphi_0)$ is the diffusion overvoltage. This equation was deduced for the case of an excess background electrolyte. Such an electrolyte in this case consists of Cu^+ ions. Here the limiting diffusion current is:

$$i_d = \frac{eD}{L}C_{Cu^{2+},C} \tag{14}$$

where D is the diffusion coefficient of Cu^{2+} and $L = 1$ mm is the thickness of the $RbCu_4Cl_3I_2$ layer in the $Cu/RbCu_4Cl_3I_2/C$ cell.

The current-voltage relation takes the explicit form:

$$i = i_d\left\{1 - \exp\left[\frac{e}{kT}(\varphi - \varphi_0)\right]\right\} \tag{15}$$

In Fig. 1 the experimental CVC is well approximated by Eq. 15 for $i_d = -3\times10^{-8}$ A cm^{-2}. Here the plateau on the CVC characterizes the limiting diffusion current of Cu^{2+} transport to the vitreous carbon electrode. The diffusion coefficient of Cu^{2+} (using Eqs. 12 and 14) is 1.5×10^{-8} cm^2 s^{-1}. In this case, solid state diffusion takes place; therefore, with the use of the Nernst-Einstein relation, Eq. 14 may be rewritten as:

$$i_d = \frac{kT}{e}\frac{\sigma}{L} \tag{16}$$

where σ is the conductivity. From this, the electronic defect conductivity (by means of Cu^{2+} ions or holes) of $RbCu_4Cl_3I_2$ is equal to 1.2×10^{-7} S cm^{-1}.

When current is applied to the vitreous carbon electrode, the electrochemical reaction:

$$Cu^+ - e^- \rightarrow Cu^{2+} \tag{17}$$

takes place, reduction occurring when $\varphi < \varphi_0$ and oxidation when $\varphi > \varphi_0$. In the latter case, $C_{Cu^{2+},C}$ adjacent to the electrode is increased. When $= C_{Cu^{2+},C}$ exceeds the critical Cu^{2+} solubility in $RbCu_4Cl_3I_2$, anodic decomposition of $RbCu_4Cl_3I_2$ on the electrode surface will take place [28]:

$$RbCu_4Cl_3I_2 \rightarrow Cu^+ + RbCuCl_3 + 2CuI \tag{18}$$

Assuming that the reaction products completely cover the electrode surface, one Cu^{2+} from $RbCuCl_3$ will correspond to two Cu^+ from CuI. Hence the ratio $C_{Cu^{2+},C}/C_{Cu^+,C} = 0.5$. At this ratio the calculated potential (Eq. 10) of the vitreous carbon electrode is 0.606 V.

Figure 2 shows the cyclic potentiodynamic curve for $RbCu_4Cl_3I_2$ electrochemical decomposition on a vitreous carbon electrode. In this figure it is observed that the experimental null-current potential ($\varphi_{i=0}$) after decomposition of $RbCu_4Cl_3I_2$ is 0.58 V. The difference between the calculated and experimental potentials (26 mV) is insignificant.

The copper electrode

Considering the copper electrode preparation method in this work, the $Cu/RbCu_4Cl_3I_2/C$ cell may be described by $Cu/Cu_2O/RbCu_4Cl_3I_2/C$. As mentioned above, the Cu_2O layer has practically no ionic conduction. Therefore, during polarization of the copper electrode,
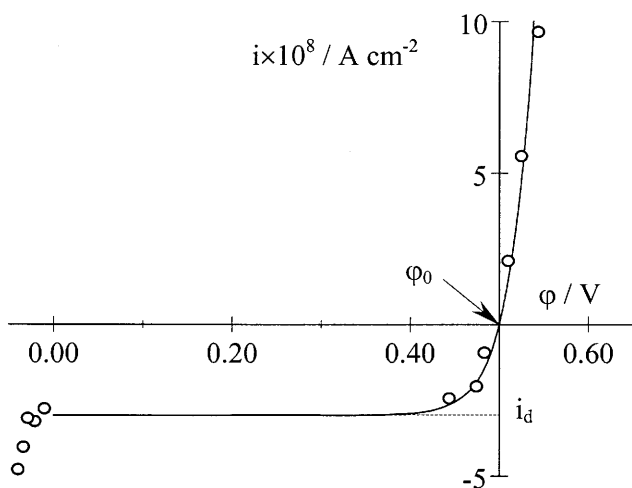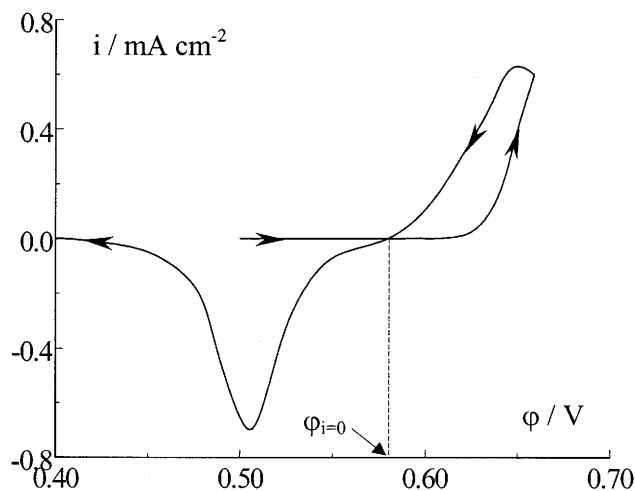

Fig. 1 Current-voltage characteristics of the vitreous carbon electrode in $RbCu_4Cl_3I_2$ versus a copper reference electrode. The *solid line* is the calculated curve according to Eq. 15; the *circles* are the experimental points

Fig. 2 Cyclic voltammogram of $RbCu_4Cl_3I_2$ electrochemical decomposition on the vitreous carbon electrode. Sweep rate 5 mV s^{-1}

reaction 1 cannot take place because of restricted Cu^+ transport to the copper surface. However, the Cu_2O layer has a considerable p-type electronic conduction; therefore an electrochemical reaction may occur at the $Cu_2O/RbCu_4Cl_3I_2$ interface. However, at this interface the copper metal is not present and reaction 1 cannot take place. However, as stated earlier, the solid electrolyte $RbCu_4Cl_3I_2$ always contains some Cu^{2+}. Consequently, only reaction 2 can take place at the $Cu_2O/RbCu_4Cl_3I_2$ interface.

It should be noted that the copper electrode in the $RbCu_4Cl_3I_2$ electrolyte is a semiconductor electrode, since the reaction takes place at the $Cu_2O/RbCu_4Cl_3I_2$ interface, and the copper substrate is an ohmic contact. Such a feature of metal electrodes with oxide layers has been observed previously [29].

The current flow through the $Cu/Cu_2O/RbCu_4Cl_3I_2$ structure depends on the transport of holes in Cu_2O and the transport of copper ions in $RbCu_4Cl_3I_2$. The question of which of these two processes limits the current flow in the $Cu/Cu_2O/RbCu_4Cl_3I_2$ structure should be addressed. As shown above, the copper ion transport in $RbCu_4Cl_3I_2$ is determined by slow Cu^{2+} ion diffusion. The hole transport in Cu_2O is determined by diffusion theory at low voltages [23], and the forward current direction in the copper oxide rectifier at the Cu/Cu_2O interface is designated to be negative. In such a rectifier, at a Cu_2O layer thickness of about 100 μm the limiting current is about 2×10^{-6} A cm^{-2}. During the reverse current the resistance is about 2×10^4 Ω cm^2 at voltages of the order of millivolts [23].

At annealing temperatures lower than 500 °C, the barrier layer thickness is of the order of micrometers [23], which corresponds to the Cu_2O layer thickness used in this work (see below). Therefore it is possible to expect that the limiting current value will increase, and the resistance at low voltages will decrease.

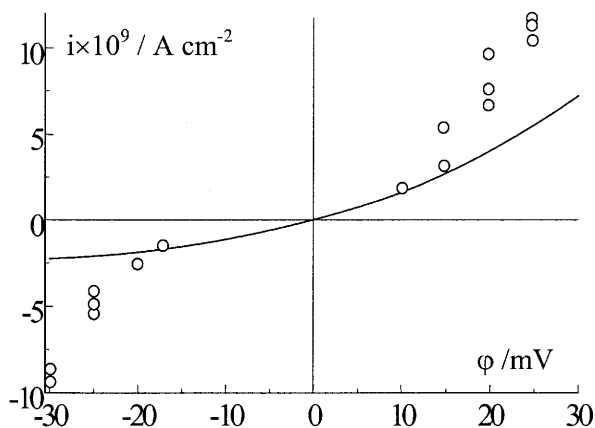In Fig. 3 the CVC for the copper electrode is shown from potentiostatic measurements. Figure 3 shows that the $Cu/Cu_2O/RbCu_4Cl_3I_2$ structure has a non-symmetrical CVC (typical for diffusion processes), i.e. has rectifying properties. However, the limiting current value in the $Cu/Cu_2O/RbCu_4Cl_3I_2$ structure (about 3×10^{-9} A cm^{-2}) is considerably less and the resistance at $\varphi\to0$ (about 10^6 Ω cm^2) is considerably greater than for the Cu/Cu_2O interface (see above). In this structure the forward current is designated as positive across the Cu/Cu_2O interface. It may be inferred that the current flow in the $Cu/Cu_2O/RbCu_4Cl_3I_2$ structure is not limited by the transport in the Cu_2O layer. Hence, this process is limited by slow Cu^{2+} diffusion in $RbCu_4Cl_3I_2$.

In Fig. 4, typical galvanostatic anodic and cathodic "potential φ versus time t" transients are shown for the copper electrode. Before analysis of the experimental galvanostatic transients it should be noted that the double layer charge capacity of the Cu/Cu^+-conducting solid electrolytes interface (4–10 μF cm^{-2} [3, 4]) can be neglected at the polarization times used. The ohmic voltage drop in the electrolyte layer between the working and the reference electrodes may also be neglected.

The basic kinetic parameters of the electrochemical reaction 2 at the $Cu_2O/RbCu_4Cl_3I_2$ interface are now addressed. In the case of diffusion kinetics, the galvanostatic transients are described by the equation [27]:

$$\varphi = \frac{kT}{e}ln\left(1\pm\sqrt{\frac{t}{\tau}}\right) \tag{19}$$
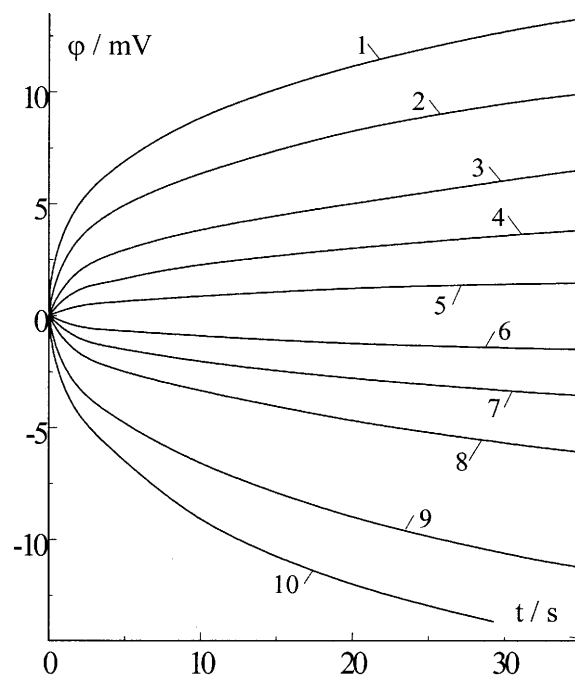
where transition time (in this case) is:

Fig. 3 Current-voltage characteristics of the copper electrode. The *solid line* is the calculated curve according to Eq. 15; the *circles* are the experimental points

Fig. 4 Galvanostatic transients under current densities ($i\times10^9$ A cm^{-2}): *1*, 30; *2*, 20; *3*, 15; *4*, 10; *5*, 5; *6*, –5; *7*, –10; *8*, –15; *9*, –20; *10*, –30
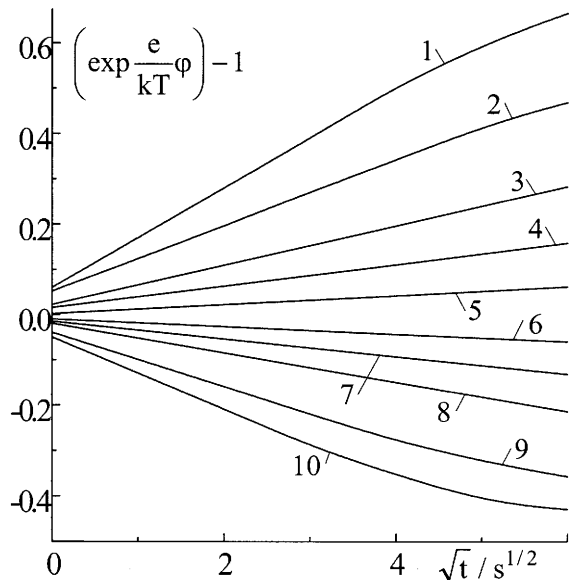
Fig. 5 Galvanostatic transients from Fig. 4 in Eq. 21 coordinates

Fig. 6 Galvanostatic transients from Fig. 5 after deduction of the overvoltage charge transfer η_{ct}

$$\tau = \frac{\pi}{4} D \left(\frac{e}{i_g} C_{0,Cu^{2+}} \right)^2 \tag{20}$$

and where $C_{Cu^{2+}}$ is the initial (before current switching) Cu^{2+} concentration in the electrolyte adjacent to the $Cu_2O/RbCu_4Cl_3I_2$ interface and i_g is the current density. Equation 19 can be rewritten as:

$$\exp \frac{e}{kT} \varphi - 1 = \sqrt{\frac{t}{\tau}} \tag{21}$$

In Fig. 5 the galvanostatic transients from Fig. 4 are shown in Eq. 21 coordinates. Using these coordinates the transients are close to linear at $\varphi < 8$–10 mV. However, the straight lines in Fig. 5 are not extrapolated to zero. Hence, at $t \rightarrow 0$ the overvoltage $\eta \neq 0$. This overvoltage can only be the overvoltage due to charge transfer, η_{ct}. In Fig. 5, η_{ct} does not exceed 2 mV. Therefore, it is possible to estimate the value of the charge transfer resistance ($\theta_{ct} = \eta_{ct}/i_g$) from segments of the ordinates at $t = 0$. Here $\theta_{ct} = (6 \pm 3) \times 10^3 \, \Omega \, cm^2$. Hence, the value of the current exchange density:

$$i_0 = \frac{kT}{e} \frac{1}{\theta_{ct}} \tag{22}$$

is equal to $(4 \pm 2) \times 10^{-6}$ A cm^{-2} at the $Cu_2O/RbCu_4Cl_3I_2$ interface.

The exchange current density of reaction 2 at vitreous carbon in the same sample of $RbCu_4Cl_3I_2$ electrolyte is greater than that at cuprous oxide and is 25×10^{-6} A cm^{-2} [9]. This is due to the fact that the exchange current density on semiconductor electrodes is less than on non-semiconductor electrodes [29].

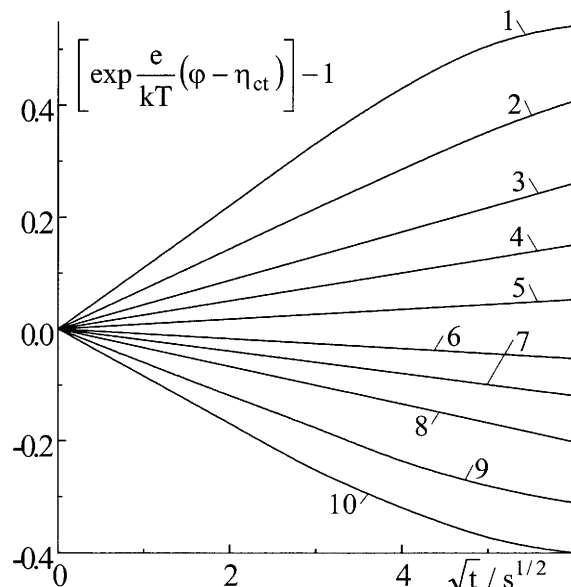In Fig. 6 the galvanostatic transients from Fig. 5 are shown for "pure" diffusion, i.e. minus the charge transfer overvoltage η_{ct}. Values of τ from the straight lines slopes:

$$\frac{\Delta\{[\exp \frac{e}{kT} (\varphi - \eta_{ct})] - 1\}}{\Delta \sqrt{t}} = \frac{1}{\sqrt{\tau}} \tag{23}$$

in Fig. 6 are calculated. In Fig. 7 the transition times versus current density are shown in Eq. 20 coordinates. The slope:

$$\frac{\Delta \sqrt{\tau}}{\Delta(\frac{1}{i_g})} = \frac{\sqrt{\pi D}}{2} C_{0,Cu^{2+}} \tag{24}$$

in this figure depends on the diffusion coefficient and the initial Cu^{2+} concentration in the electrolyte adjacent to the $Cu_2O/RbCu_4Cl_3I_2$ interface. If we assume that the diffusion coefficient ($D = 1.5 \times 10^{-8}$ cm^2 s^{-1}) is constant in the range 0.1–1% Cu^{2+}, the initial Cu^{2+} concentration
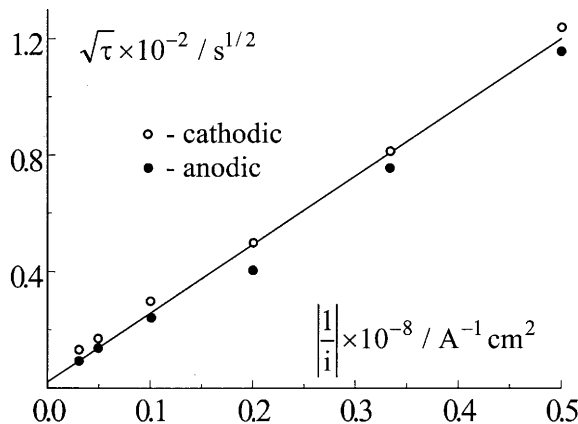

Fig. 7 Transition times versus current densities

in the electrolyte near the $Cu_2O/RbCu_4Cl_3I_2$ interface using Eq. 24 from the slope in Fig. 6 is $C_{Cu^{2+}} = 1.4 \times 10^{17}$ cm^{-3}. Using this value, in Fig. 3 the calculated CVC is shown by a solid line according to Eq. 15 at $\varphi_0 = 0$ for slow diffusion of Cu^{2+} in the electrolyte.

It is observed in Figs. 5 and 6 that the experimental galvanostatic transients do not correspond to Eq. 19 at $\varphi > 8$–10 mV. At potentials in the cathodic region of Fig. 3 there are currents which are higher than the limiting current of the Cu^{2+} ion diffusion. Evidently, in these conditions an electrical breakdown of Cu_2O occurs with destruction of this layer. Thus, the immediate contact of copper metal with the electrolyte occurs and the $Cu/Cu_2O/RbCu_4Cl_3I_2/C$ cell is converted into the $Cu/RbCu_4Cl_3I_2/C$ cell, allowing reaction 1 to proceed.

The breakdown voltage U in the copper oxide rectifier is approximately 4 V [23] at a thickness d of the Cu_2O layer of ca. 100 μm. Consequently, the electric intensity, at which the breakdown happens, $E = U/d$, is 4×10^2 V cm^{-1}. From here it is possible to estimate a value for d in the $Cu/Cu_2O/RbCu_4Cl_3I_2/C$ cell. At $U = 10$ mV and at the estimated E, the thickness of the Cu_2O layer in this cell is about 0.25 μm. It is a reasonable value, taking into account the rather low oxygen pressure and the temperature during the copper electrode annealing.

In Fig. 8 the typical potentiostatic cathodic transients are shown for the copper electrode. The estimated breakdown of the Cu_2O layer by reaction 1 is confirmed by these types of transients at $\varphi > 10$ mV. Such transients are characteristic of a new phase formation on the electrode surface [30]. Hence, the deposition-dissolution of metal copper takes place at these potentials.

On the potentiostatic transients in Fig. 8, the current i_{in} at $t \to 0$ is proportional to the growth rate of the copper deposit layer thickness, and the current i_{end} at $t \to \infty$ is proportional to growth rate of dendrites on the electrode surface [30]. The current i_{in} is insignificant at voltages exceeding the breakdown voltage (Fig. 8a), i.e. in this case the copper dendrites grow only in points on the passive electrode surface where the breakdown has

occurred. In Fig. 8b, the current i_{in} is comparable with i_{end}. Hence, the passivating layer is destroyed on the entire electrode surface at cathodic overvoltages of 30 mV and above, and the thickness of the copper deposit layer increases together with dendrite growth. Evidently, as shown elsewhere [6], in this situation the reaction 1 rate is limited by the rate of nuclei and deposit growth.

The number of nuclei per unit of electrode surface increases with increasing overvoltage [30]. At $\varphi > 100$ mV, virtually each copper atom on the electrode surface becomes a nucleus. Evidently, in these conditions, the reaction 1 rate is limited by charge transfer with the exchange current density of the order of milliamps per square centimeter [6]. It is three orders of magnitude greater than the value of the exchange current density for reaction 2.

Conclusions

A layer of cuprous oxide occurs on the interface between the copper electrode and the $RbCu_4Cl_3I_2$ solid electrolyte. This layer hinders establishment of a chemical equilibrium of the electrolyte with copper. Therefore the Cu^{2+} concentration in the electrolyte does not significantly vary, even at long annealing times. The Cu^{2+} concentration in the $RbCu_4Cl_3I_2$ sample is about 1.25×10^{18} cm^{-3} adjacent to the vitreous carbon electrode and 1.4×10^{17} cm^{-3} adjacent to the copper electrode.

The galvanostatic transients and CVC of the electrodes are satisfactorily described by the equations of classical diffusion kinetics. Hence the concentration gradient of Cu^{2+} is directed through the Cu_2O layer. The small initial gradient of the Cu^{2+} concentration in the electrolyte is not important according to the equations for electrochemical cells with low-temperature Cu^+-conducting solid electrolytes.

Experimental Cu^{2+} concentrations in $RbCu_4Cl_3I_2$ (from measurements of the magnetic susceptibility of $RbCu_4Cl_3I_2$), the e.m.f. of the cells and the electrochemical decomposition potential of $RbCu_4Cl_3I_2$ correspond well to the values calculated in this work. This lends support to the model describing the dependence of inert electrode potentials with Cu^{2+} concentration in $RbCu_4Cl_3I_2$.

Fig. 8 Potentiostatic transients under various cathodic potentials (mV): **a** 13; **b** 70
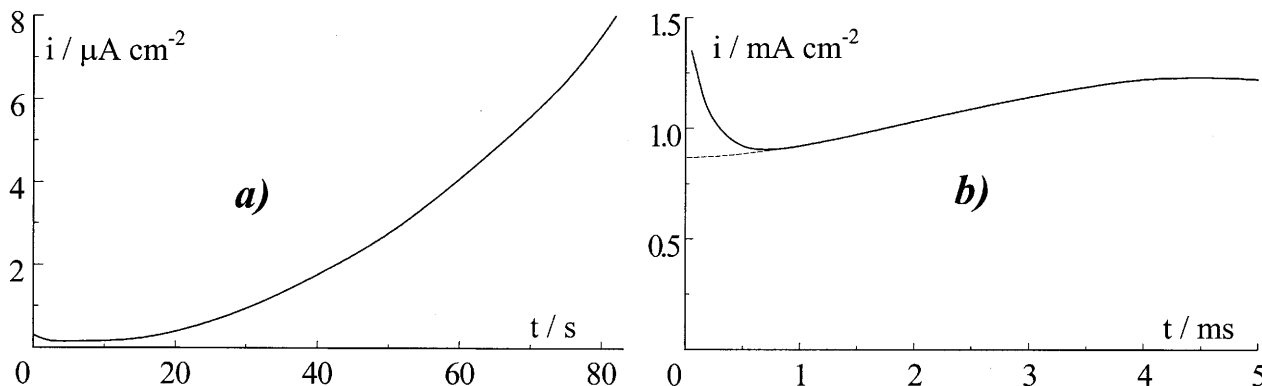
We suggest that, at potentials below the decomposition potential of the $RbCu_4Cl_3I_2$ electrolyte, the process on the $C/RbCu_4Cl_3I_2$ interface is controlled by slow diffusion of the copper electronic defects in the electrolyte. The diffusion coefficient of these defects is equal to 1.5×10^{-8} cm^2 s^{-1}. The electronic defect conductivity (by means of Cu^{2+} ions or holes) of $RbCu_4Cl_3I_2$ is equal to 1.2×10^{-7} S cm^{-1}.

The Cu_2O layer blocks the course of the electrochemical reaction $Cu^0 - e^- \rightarrow Cu^+$ with participation of metal copper. Therefore, at low overvoltages, the copper electrode behaves as an inert redox electrode.

On the $Cu_2O/RbCu_4Cl_3I_2$ interface the electrochemical reaction $Cu^+ - e^- \rightarrow Cu^{2+}$ takes place at low overvoltages. Experimental results suggest that the rate of this reaction is limited by slow Cu^{2+} diffusion in $RbCu_4Cl_3I_2$. The exchange current density of the reaction is about 4×10^{-6} A cm^{-2}.

The electrical breakdown of the Cu_2O layer on the copper electrode takes place at potentials $\varphi > 8$–10 mV and the reaction with participation of copper metal is deblocked. We suggest that the rate of this reaction is limited by the formation and growth of the copper nuclei at 10 mV $< \varphi < 100$ mV. The reaction rate is limited by charge transfer at $\varphi > 120$ mV.

The exchange current densities on the copper electrode from measurements at high and low overvoltages are considerably different, since they characterize different electrochemical reactions.

The information obtained may be useful for investigation and development of electrochemical cells with other solid electrolytes having two-step oxidation mechanisms of an electroactive species.

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