ORIGINAL PAPER

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Investigation of the anodic decomposition of the solid electrolyte $RbCu_4Cl_3I_2$

Abstract The process of electrochemical decomposition of the solid electrolyte $RbCu_4Cl_3I_2$ at a vitreous carbon electrode has been investigated. The anodic decomposition of the electrolyte occurs in two steps. At first, the oxidizing electrode reaction of Cu^+ ions to Cu^{2+} ions takes place at potentials higher than 0.57 V and a layer of decomposition products is formed on the electrode surface, including the divalent copper compound $RbCuCl_3$. Then the oxidizing reaction of I^- ions occurs at potentials higher than approximately 0.67 V, with deposition of an iodine layer onto the electrode surface. The deposition rate of the layers of decomposition products is controlled by instantaneous nucleation and two-dimensional growth of the deposit. The total thickness of the passivating layer of decomposition products on the anode is equal to ca. 1 μm.

Keywords Solid electrolyte · Rubidium tetracopper trichloride diiodide · Electrochemical decomposition · Anodic electrocrystallization · Rate-determining step

Introduction

The solid electrolyte $RbCu_4Cl_3I_2$ has high Cu^+ ionic conductivity (0.47 S cm^{-1} [1]) at room temperature. Therefore, batteries with high current density are possible based on this electrolyte, for example the reserve cell collector|$RbCu_4Cl_3I_2$|collector, which is converted before use to the battery collector, Cu|$RbCu_4Cl_3I_2$|I_2,collector by means of electrochemical decomposition of the electrolyte. Hence, investigation of the kinetics of the electrochemical decomposition of $RbCu_4Cl_3I_2$ is of interest.

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On $RbCu_4Cl_3I_2$ decomposition, the deposition of metallic copper occurs on the cathode, which has been investigated explicitly [2, 3]. On the anode, a more complex two-step process takes place [4]. The divalent copper compound $RbCuCl_3$ is first formed and then iodine.

In the present work the kinetics of the anodic electrochemical decomposition of the solid electrolyte $RbCu_4Cl_3I_2$ is investigated.

Experimental

The solid electrolyte $RbCu_4Cl_3I_2$ was prepared by the published method [5]. Cells of the type $^-$C(graphite)|$RbCu_4Cl_3I_2$|C(vitreous carbon)$^+$ were prepared in a dry air (P$_2$O$_5$) atmosphere by pressing $RbCu_4Cl_3I_2$ and graphite powders onto a vitreous flat carbon disk (12 mm diameter) at a pressure of 2.2×10^8 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. 3×10^6 Pa. Before measurements began, the cell was annealed for several hours at 130 °C.

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

Results and discussion

In Fig. 1 it is seen that the cyclic voltammogram of $RbCu_4Cl_3I_2$ anodic decomposition generally has two peaks. At the first decomposition step (peak 1) the oxidizing reaction of monovalent copper occurs:

$$Cu^+ - e^- \rightarrow Cu^{2+} \tag{1}$$

with $RbCuCl_3$ formation, since the equilibrium potential $\varphi_{d,1}$ of this reaction is equal to 0.58 V at the reverse potential after the first peak (Fig. 1, curve 1). In fact, this potential is close to the standard potential $\varphi^\circ_1 = 0.624$ V [6] of Eq. 1. The distinction between $\varphi_{d,1}$ and φ°_1 is possibly explained by the discrepancy between the actual and the standard decomposition conditions.
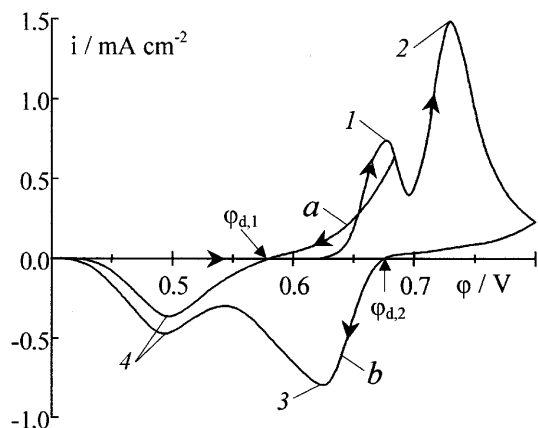
Fig. 1 Cyclic voltammograms of the anodic electrochemical decomposition of the solid electrolyte RbCu$_4$Cl$_3$I$_2$. Potential sweep rate: 5 mV s^{-1}

At the second decomposition step (peak 2), oxidizing reactions of I$^-$ ions take place:

$$I^- - e^- \rightarrow 0.5I_2 \tag{2}$$

since the equilibrium potential $\varphi_{d,2}$ of Eq. 2 is equal to 0.67 ± 0.01 V (Fig. 1, curve 2). This potential is close to the standard potential $\varphi°_2 = 0.72$ V [6] for Eq. 2.

It is apparent that peak 3 in Fig. 1 characterizes the course of Eq. 2 in the reverse direction and peak 4 the course of Eq. 1, also in the reverse direction.

In Fig. 2, typical anodic galvanostatic transients are shown at the electrolyte decomposition. These transients correspond to the mechanism of the decomposition reaction mentioned above. As the current is switched, the electrode potential quickly increases until 0.64–0.66 V and then the first step of the decomposition reaction begins. The difference $(0.64–0.66)–\varphi_d = 0.07–0.09$ V is the overvoltage of the RbCuCl$_3$ phase formation on the vitreous carbon.

The first "saddle" of the transients in Fig. 2 corresponds to the first step of the decomposition reaction. The charge $q_{lay,1}$, which corresponds to this process, is equal to $(7 \pm 0.5) \times 10^{-3}$ C cm^{-2}. The second "saddle" in

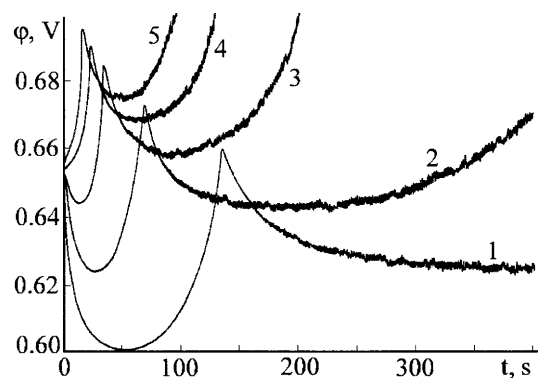Fig. 2 corresponds to the second step of the decomposition reaction. At the site of gaseous iodine formation in the near-electrode space of thickness about 1 μm there arises a pressure of $\sim10^7$ Pa. This pressure exceeds the equilibrium pressure of iodine vapor by five orders of magnitude. Therefore, the iodine should crystallize on the electrode surface. The charge $q_{lay,2}$, which corresponds to this process, is equal to $(32 \pm 2) \times 10^{-3}$ C cm^{-2}. Hence the total thickness of the passivating layer of the decomposition products on the anode is approximately equal to 1 μm.

In Fig. 3 the minimum potentials of the saddles φ_{min} vs. the current density are shown. These dependences are described by the equation:

$$\ln i_g = a + b\varphi_{min} \tag{3}$$

For the first decomposition step, $a_1 = -22.9$, $b_1 = 33$ V^{-1}, and for the second step, $a_2 = -30.6$, $b_2 = 44$ V^{-1}.

When identifying the law of formation and growth of new phases on the electrode surface, it is necessary to take into account that these phases are dielectrics. This should yield a gradual decrease of the working electrode surface in time, and its passivation. In this case the anodic electrocrystallization of layers of the non-conducting compound can occur in two ways: progressive nucleation and two-dimensional growth of the deposited layers on the electrode surface, or instantaneous nucleation and two-dimensional growth. Under galvanostatic conditions we find [7] for the first case:

$$\varphi = \frac{-a + \ln i_g + 2/3[\ln(2/3) - 1]}{b}$$
$$- \frac{\ln\left\{(1-\theta)[-\ln(1-\theta)]^{2/3}\right\}}{b} \tag{4}$$

and for the second case:

$$\varphi = \frac{-a + \ln i_g + 1/2[\ln(1/2) - 1]}{b}$$
$$- \frac{\ln\left\{(1-\theta)[-\ln(1-\theta)]^{1/2}\right\}}{b} \tag{5}$$

Fig. 2 Galvanostatic transients of the anodic electrochemical decomposition of the solid electrolyte RbCu$_4$Cl$_3$I$_2$ at the current densities (mA cm^{-2}): (1) 0.05, (2) 0.1, (3) 0.2, (4) 0.3, (5) 0.4
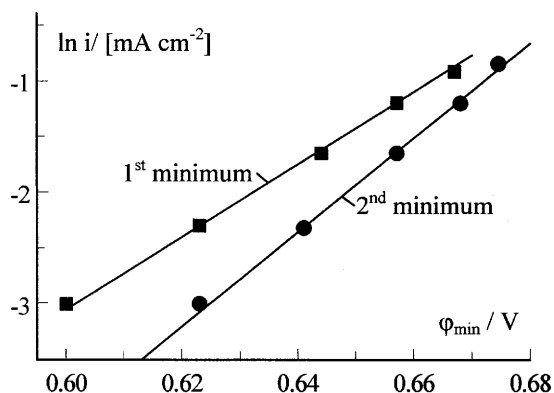

Fig. 3 Minimum potentials of the galvanostatic transients from Fig. 2 vs. the current density
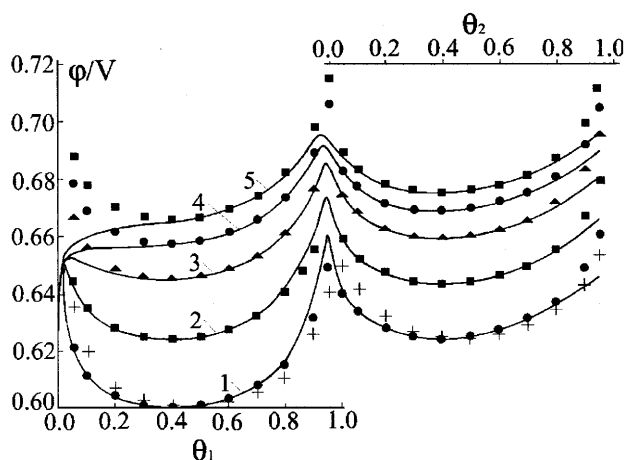
Fig. 4 Electrode potential vs. relative coverage of the electrode surface by the deposited layers, from Fig. 2. For explanation, see the text

where the relative coverage of the electrode surface by the deposited layer is:

$$\theta = \frac{i_g t}{q_{\text{lay}}} \tag{6}$$

In Fig. 4 the galvanostatic transients from Fig. 2 are shown, where the relative coverage θ_1 is for the first decomposition step and θ_2 is for the second step. The theoretical transients in Eq. 5 coordinates is shown by the solid line. The experimental transient according to Eq. 4 for transient 1 is designated by crosses and the one according to Eq. 5 is designated by circles. It is apparent that the experimental transient 1 is approximated better by Eq. 5. Other signs designate the experimental transients for other current densities. It is also seen that all the experimental transients are approximated satisfactory by Eq. 5.

Hence, both steps for the anodic decomposition of $RbCu_4Cl_3I_2$ are controlled by instantaneous nucleation and the two-dimensional growth of layers of the decomposition products.

Conclusions

The anodic decomposition of the electrolyte occurs in two steps. The rate-determining stage of both steps is instantaneous nucleation and two-dimensional growth of product layers of $RbCu_4Cl_3I_2$ decomposition products. The total thickness of the passivating layer of the decomposition products on the anode is equal to ca. 1 μm. The kinetics of the decomposition is determined only by crystallizing effects and does not depend on ion transport in the solid electrolyte.

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