

ON HOLE CONDUCTIVITY ESTIMATION IN Cu⁺-CONDUCTING SOLID ELECTROLYTES

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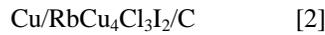
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Cu⁺-conducting solid electrolytes always contain the Cu²⁺ ion impurity owing to chemical instability of monovalent copper. It is possible to present the Cu²⁺ ion in the crystal structure as the Cu⁺ ion with a hole, localized on it.

Usually hole conductivity σ_h is determined by the Hebb - Wagner method (1). The theory of this method guesses an establishment of the thermodynamic equilibrium with a reversible electrode. In particular, the concentration of holes or Cu²⁺ ions in the electrolyte should correspond to equilibrium of reaction:



and to be identical in all sites of the electrolyte sample. In this case the uncurrent potential ϕ_0 of the carbon electrode in the cell:



should be equal to zero vs copper.

However, ϕ_0 is not equal to zero and makes 0.4...0.5 V in realistic cells [2] even at long-lived annealing. Therefore, potential range 0.4...0.6 V was used for the estimation of RbCu₄Cl₃I₂ hole conductivity (2-4). The obtained values of conductivity are incorrect, since some electrochemical RbCu₄Cl₃I₂ decomposition is possible at these potentials (5).

In this work it is offered to improve the estimation procedure of hole conductivity using lower potentials.

If $\phi_0 \neq 0$, a gradient of Cu²⁺ concentration takes place in the electrolyte, i.e. the Cu²⁺ concentration near carbon is much greater than the one near copper. Let us consider the reasons of absence of the thermodynamic equilibrium of electrolyte with copper. The oxide Cu₂O layer substantially always takes place onto surface of the copper electrode. Then the cell [2] can be renamed as:



The Cu²⁺ concentration in Cu₂O on the Cu/Cu₂O interface ($C_{\text{Cu}^{2+}}^{\text{Cu/Cu}_2\text{O}}$) corresponds to the thermodynamic equilibrium [1]. However, self-diffusion copper coefficient in Cu₂O very low. Therefore, Cu²⁺ concentration in Cu₂O on the Cu₂O/RbCu₄Cl₃I₂ interface ($C_{\text{Cu}^{2+}}^{\text{Cu}_2\text{O/RbCu}_4\text{Cl}_3\text{I}_2}$) can be much higher (The

Cu/Cu₂O/Ohmic contact copper-oxide rectifier is efficient at high temperatures for a long time). Using an electrochemical measurements it is shown, that in a cell [3] $C_{\text{Cu}^{2+}}^{\text{Cu/Cu}_2\text{O}} = 4.2 \times 10^{11} \text{ cm}^{-3}$, $C_{\text{Cu}^{2+}}^{\text{Cu}_2\text{O/RbCu}_4\text{Cl}_3\text{I}_2} =$

$1.4 \times 10^{17} \text{ cm}^{-3}$ and $C_{\text{Cu}^{2+}}^{\text{RbCu}_4\text{Cl}_3\text{I}_2/\text{C}} = 1.3 \times 10^{18} \text{ cm}^{-3}$. Hence,

the Cu²⁺ concentration gradient practically is completely focused in the Cu₂O layer and this gradient is negligible in the electrolyte.

The absence of the initial concentration gradient of active particles is the basic requirement at the

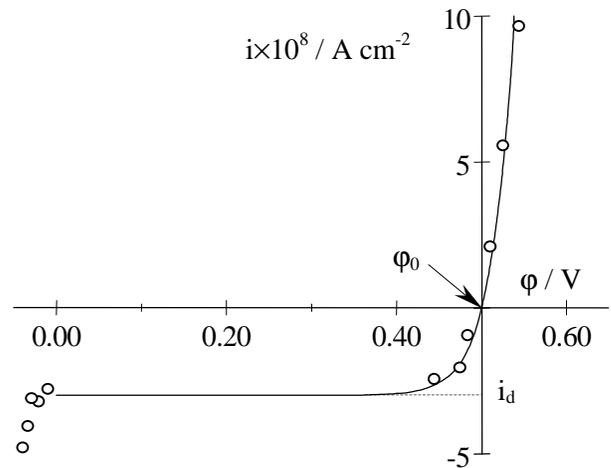
derivation of equations of diffusion kinetics. Therefore here it is possible to use the equation of a current-voltage characteristics (CVC) of the carbon electrode for the slow diffusion case:

$$i = i_d \left\{ 1 - \exp \left[\frac{e}{kT} (\phi - \phi_0) \right] \right\}, \quad [4]$$

where the cathodic limiting current:

$$i_d = \frac{eD_{\text{Cu}^{2+}}}{L} C_{\text{Cu}^{2+}}, \quad [5]$$

where $D_{\text{Cu}^{2+}}$ is the Cu²⁺ diffusion coefficient in the electrolyte. In figure it is visible, that the experimental CVC is well approximated by Eq. [4] at $\phi_0 = 0.5 \text{ V}$ and $i_d = -3 \times 10^{-8} \text{ A cm}^{-2}$.



The value of the RbCu₄Cl₃I₂ hole conductivity it is usually calculated using an anodic uprising branch of the CVC. However this branch is not in the recommended potential range, in which the electrolyte electrochemical decomposition is possible. Therefore, hole conductivity can be more correctly estimated using value of the limiting current i_d , since at cathodic currents the decomposition is impossible. Using the Nernst-Einstein relation, Eq. [5] may be rewritten:

$$i_d = \frac{kT}{e} \frac{\sigma_h}{L}$$

where L is the thickness of the RbCu₄Cl₃I₂ layer in the cell [2]. From here, using i_d value, we gain:

$$\sigma_h = 1.2 \times 10^{-7} \text{ S cm}^{-1}.$$

Thus, the use of the limiting current value allows to exclude the influence of electrochemical decomposition on estimated σ_h value. Besides the i_d value is easy for determining by means of single measuring of a flash current in the cell [2].

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