S. V. KARPACHEV and S. F. PAL' GUEV

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Abstract

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S. V. KARPACHEV and S. F. PAL' GUEV

ON THE OPERATION OF A GALVANIC CELL WITH A SOLID ELECTROLYTE POSSESSING MIXED CONDUCTIVITY

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It is of interest to consider the influence of electronic conductivity, which exists along with ionic conductivity in the solid electrolyte of a galvanic cell, on the electric power delivered by this cell to an external circuit. Clarification of this question will, it seems to us, broaden the understanding of the role of the electronic conductivity of the electrolyte in the operation of galvanic cells with solid electrolytes.

To simplify the problem posed, we shall solve it for the example of a simple galvanic cell with solid silver bromide as the electrolyte:

$$\mathrm{Ag} \mid \mathrm{AgBr} \mid \mathrm{Br}_2,\ \mathrm{C}. \tag{I}$$

Gaseous bromine, dissolving in solid silver bromide, imparts to the latter electronic conductivity of the p-type (^{1}). In accordance with this, the electromotive force of our cell E will be expressed in the following way (^{2}):

$$E = (1 - \bar{t})E_0. \tag{1}$$

Here E_0 is the thermodynamic value of the electromotive force, i.e., the value it would have in the absence of electronic conductivity in the solid electrolyte; $\bar{t}$ is the mean value of the transport number of electrons or, what is the same thing, of holes in the solid electrolyte.

We shall assume that bromine diffuses from the bromine electrode to the silver electrode through the entire thickness of the electrolyte and that the bromine concentration immediately near the silver electrode is determined by the equilibrium

$$\mathrm{Ag} + \mathrm{Br} \rightleftarrows \mathrm{AgBr}. \tag{2}$$

In this case the quantity $\bar{t}$ may be represented as follows (^{3}):

$$\bar{t} = \frac{\lg \dfrac{\varkappa_0^{(C)} + \varkappa_i}{\varkappa_i}}{\lg \dfrac{C_{\mathrm{Br}}^{(C)}}{C_{\mathrm{Br}}^{(\mathrm{Ag})}}}. \tag{3}$$

In equation (3), $\varkappa_0^{(C)}$ is the electronic conductivity in the electrolyte immediately near the bromine electrode; $\varkappa_i$ is the ionic conductivity, which we shall approximately regard as constant in all cross sections of the electrolyte; $C_{\mathrm{Br}}^{(C)}$ and $C_{\mathrm{Br}}^{(\mathrm{Ag})}$ are the concentrations of bromine dissolved in the electrolyte, respectively near the bromine and silver electrodes, and the concentration $C_{\mathrm{Br}}^{(C)}$ will obviously be in equilibrium with respect to the bromine pressure at the bromine electrode.

Let us calculate the ohmic resistance of the electrolyte, assuming that it is a cylinder of length l with a cross-sectional area of 1 cm^2.

The resistance of a thin electrolyte layer of thickness dx will be $\dfrac{dx}{\varkappa_0 + \varkappa_i}$; the total resistance of the electrolyte R is equal to

$$R = \int_0^l \frac{dx}{\varkappa_0^{(x)} + \varkappa_i}. \tag{4}$$

The quantity $\varkappa_0^{(x)}$ may be written as follows:

$$\varkappa_0^{(x)} = kC_{\mathrm{Br}}^{(x)}, \tag{5}$$

where k is a constant, and $C_{\mathrm{Br}}^{(x)}$ is the concentration of dissolved bromine in the section of the electrolyte located at a distance x from the silver electrode.

We shall assume that the distribution of the bromine concentration along the electrolyte is determined purely by the diffusion process; then the bromine concentration gradient will be constant along the solid electrolyte. Accordingly,

$$\frac{C_{\mathrm{Br}}^{(\mathrm{C})} - C_{\mathrm{Br}}^{(\mathrm{Ag})}}{l} = \frac{C_{\mathrm{Br}}^{(x)} - C_{\mathrm{Br}}^{(\mathrm{Ag})}}{x}, \tag{6}$$

Let us express, with the aid of (6) and (5), the quantity $\varkappa_0^{(x)}$ through x. Substituting the expression obtained into (4) and carrying out the integration, we obtain

$$R = \frac{2.3l}{\varkappa_0^{(\mathrm{C})} + \varkappa_0^{(\mathrm{Ag})}} \lg \frac{\varkappa_0^{(\mathrm{C})} + \varkappa_i}{\varkappa_0^{(\mathrm{Ag})} + \varkappa_i}. \tag{7}$$

If the concentration $C_{\mathrm{Br}}^{(\mathrm{Ag})}$, determined by equilibrium (2), is very small, then in expression (7) the quantity $\varkappa_0^{(\mathrm{Ag})}$ may be neglected, and we shall have

$$R = \frac{2.3l}{\varkappa_0^{(\mathrm{C})}} \lg \frac{\varkappa_0^{(\mathrm{C})} + \varkappa_i}{\varkappa_i}. \tag{8}$$

The resistance of the electrolyte R' in the case where only ionic conductivity $\varkappa_i$ is present in the electrolyte is written as follows:

$$R' = \frac{l}{\varkappa_i}. \tag{9}$$

Let us set the following quantitative ratios, close to reality:

$$\varkappa_0^{(\mathrm{C})} \simeq 10\varkappa_i; \qquad \frac{C_{\mathrm{Br}}^{(\mathrm{C})}}{C_{\mathrm{Br}}^{(\mathrm{Ag})}} \simeq 10^{10}.$$

Under these conditions, approximately,

$$\bar{t} \simeq 0.1, \qquad R \simeq 0.23R'. \tag{10}$$

Let us write expressions for the powers W_0 and W delivered by the galvanic cell to the external circuit, respectively in the absence and in the presence of electronic conductivity in the solid electrolyte; let in both cases the external resistance be R':

$$W_0 = 0.25\frac{E_0^2}{R'}, \qquad W = 0.54\frac{E_0^2}{R'}. \tag{11}$$

It follows from relations (11) that the power delivered by our galvanic cell to the external circuit, in the case where electronic conductivity is present, is, roughly speaking, twice as great as the power delivered to the external—

···external circuit, in the case when electronic conductivity is absent. This circumstance, as is readily seen, is due to the fact that under the condition $C_{\mathrm{Br}}^{(\mathrm{Ag}')} \gg C_{\mathrm{Br}}^{(\mathrm{Ag})}$, owing to the appearance of electronic conductivity, the resistance of the electrolyte decreases substantially more than the electromotive force of the galvanic cell. It should be noted, however, that the distribution of the concentration of bromine dissolved in the electrolyte will, generally speaking, be disturbed under the action of the current flowing through the cell. Therefore the results obtained will be quantitatively valid in the case of comparatively small currents or a high rate of diffusion of bromine in the solid electrolyte.

Thus, under certain conditions, the appearance of electronic conductivity in the solid electrolyte of a galvanic cell may be useful, since it substantially increases the electric power delivered by the cell to the external circuit.

Institute of Electrochemistry, Ural Branch
Academy of Sciences of the USSR

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Note: Figure translations are in progress. See original paper for figures.