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CURRENT GENERATION MECHANISM IN SYSTEMS WITH SOLID POLYMER ELECTROLYTE^{*)}

By

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Abstract

The current generation process in electrolytic cell on interface solid polymer electrolyte-catalyst is described. The potential distribution in the active layer of the porous electrode as a function of the electric conductivity and reduce thickness electrode is investigated. It is shown that a high electrode activity can be achieved by increasing the dispersion of polymer particles in the catalyst-SPE mixture.

In recent years considerable interest has been shown in electrochemical systems with ion-exchange membranes-solid polymer electrolyte (SPE).^{1,2)} In these systems it is very important to elucidate the mechanism of current-generation processes at the catalyst-solid polymer electrolyte interface.

Earlier³⁾ we showed that by using in the active layer of the electrode a mixture of catalyst and dispersed polymer electrolyte particles, it is possible to improve significantly the electrochemical characteristics of the electrodes. In this connection it is of interest to study theoretically the current generation process in such electrodes and to compare the obtained results with experimental data.

A porous electrode with solid polymer electrolyte, which can be used, in particular, in electrolytic cells, is shown schematically on Fig. 1. Let E and E_m be the electrolyte and metal component potentials measured against a reference electrode. Introducing the reduced quantities $\bar{E} = \frac{\alpha FE}{RT}$, $\bar{E}_m = \frac{\alpha FE_m}{RT}$ and $\eta = (\bar{E}_m - \bar{E}) - (\bar{E}_m - \bar{E})_{\text{stat}}$ - the local electrode polarization, it is easy to show that E and E_m satisfy the set of equation

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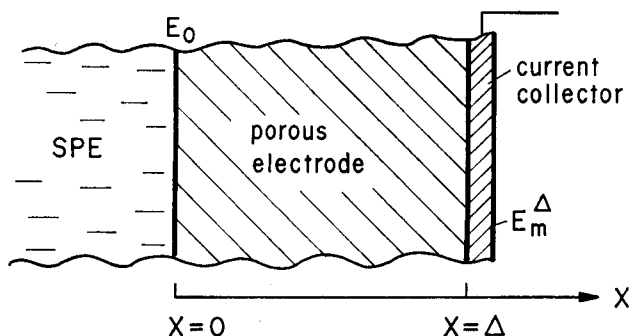


Fig. 1. Schematic diagram of a porous electrode with SPE.

$$-\frac{d^2 E}{dx^2} = \tilde{\rho} i_0 S \operatorname{sh} \eta \quad (1)$$

$$\frac{d^2 E_m}{dx^2} = \tilde{\rho}_m i_0 S \operatorname{sh} \eta \quad (2)$$

where $\tilde{\rho}$ and $\tilde{\rho}_m$ — are the effective resistivities in the electrode of electrolyte and catalyst, i_0 is the exchange current, S is the specific surface of catalyst on which occurs the catalytic process whose current density $j = i_0 S \operatorname{sh} \eta$. The set of equation (1) and (2) is equivalent to the equation

$$\frac{d^2 \eta}{dy^2} = \operatorname{sh} \eta \quad (3)$$

with the boundary conditions :

$$\left. \frac{d\eta}{dy} \right|_{y=0} = -I, \quad \left. \frac{d\eta}{dy} \right|_{y=\Delta/L} = \mathcal{L} L \quad (4)$$

where $y = x/L$, $L = \sqrt{\frac{RT}{\alpha F i_0 S (\tilde{\rho} + \tilde{\rho}_m)}}$ is the characteristic length of the process, $I = y/y_0$ is the reduced current generated in the electrode (total current), $y_0 = \frac{\alpha F \tilde{\rho} L}{RT}$ is the characteristic current, $\mathcal{L} = \frac{\tilde{\rho}_m}{\tilde{\rho}}$.

Usually when integrating equation (3) it is assumed⁴⁾ that instead of (4) the following boundary conditions are used

$$\eta \Big|_{y=0} = \eta_0, \quad \left. \frac{d\eta}{dy} \right|_{y=\Delta/L} = 0 \quad (5)$$

However the specificity of a system with solid polymer electrolyte is that in principle the parameter \mathcal{L} characterizing the electronic resistivity of the metal phase is not necessarily small. According to the literature data^{5,6)}

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the average size of agglomerates of platinum metal blacks used as catalysts in electrodes of electrochemical devices is $0.1 \mu\text{m}$, while the size of the solid polymer electrolyte grains, found by us by means of the sedimentation analysis and electron-microscopic measurements is from ten microns to several hundred. Therefore in the system under consideration the porous layer structure is as shown on Fig. 2. It was found by calculation⁷⁾ that under these conditions $\bar{\rho} = \rho/v$ and $\bar{\rho}_m \approx \beta\rho_m/v$ where parameter $\beta \gg 1$ and increases rapidly with decreasing ratio v_m/v .

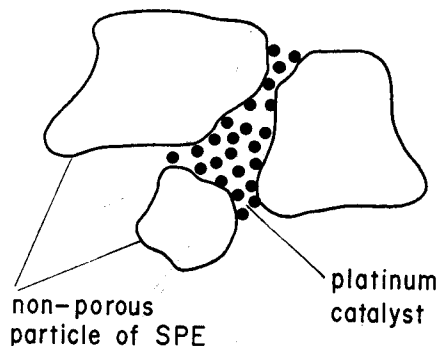


Fig. 2. Electrode structure (active layer) model.

We demonstrated that the theoretical conclusions given above agree well with the results of experimental measurements of electronic resistances in catalyst mixture with SPE. Figs. 3 a and 3 b show the dependences for the ionic and electronic resistances of the electrode active layer consisting of a mixture of ion-exchange membrane powder and platinum-palladium black. Depending on the preparation method, the ionic resistance of the mixture can be within $50 \sim 250 \text{ ohm}\cdot\text{cm}$ and is practically independent of the catalyst content in the mixture (Fig. 3 a) since in the range of the

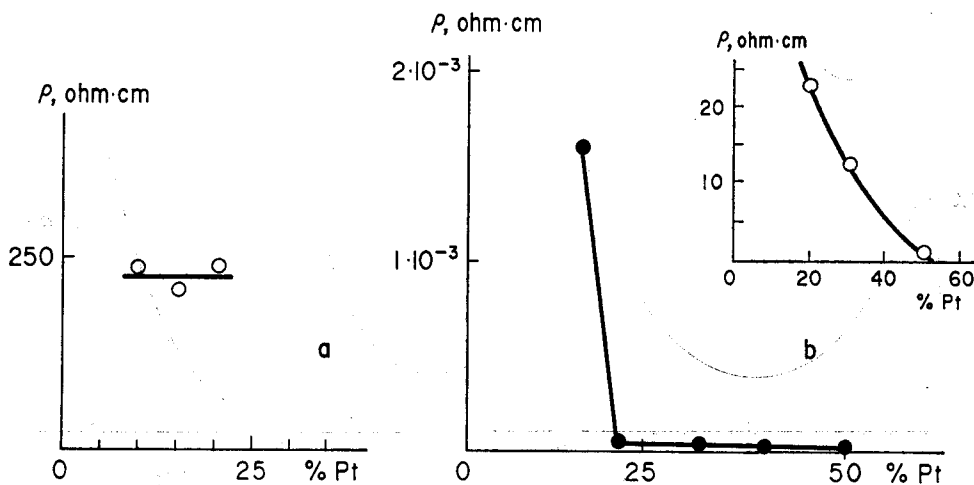


Fig. 3. Dependence of the ionic (a) and electronic (b) resistances of the composition from SPE and catalyst (platinum-palladium) on the weight content of metal in the mixture.

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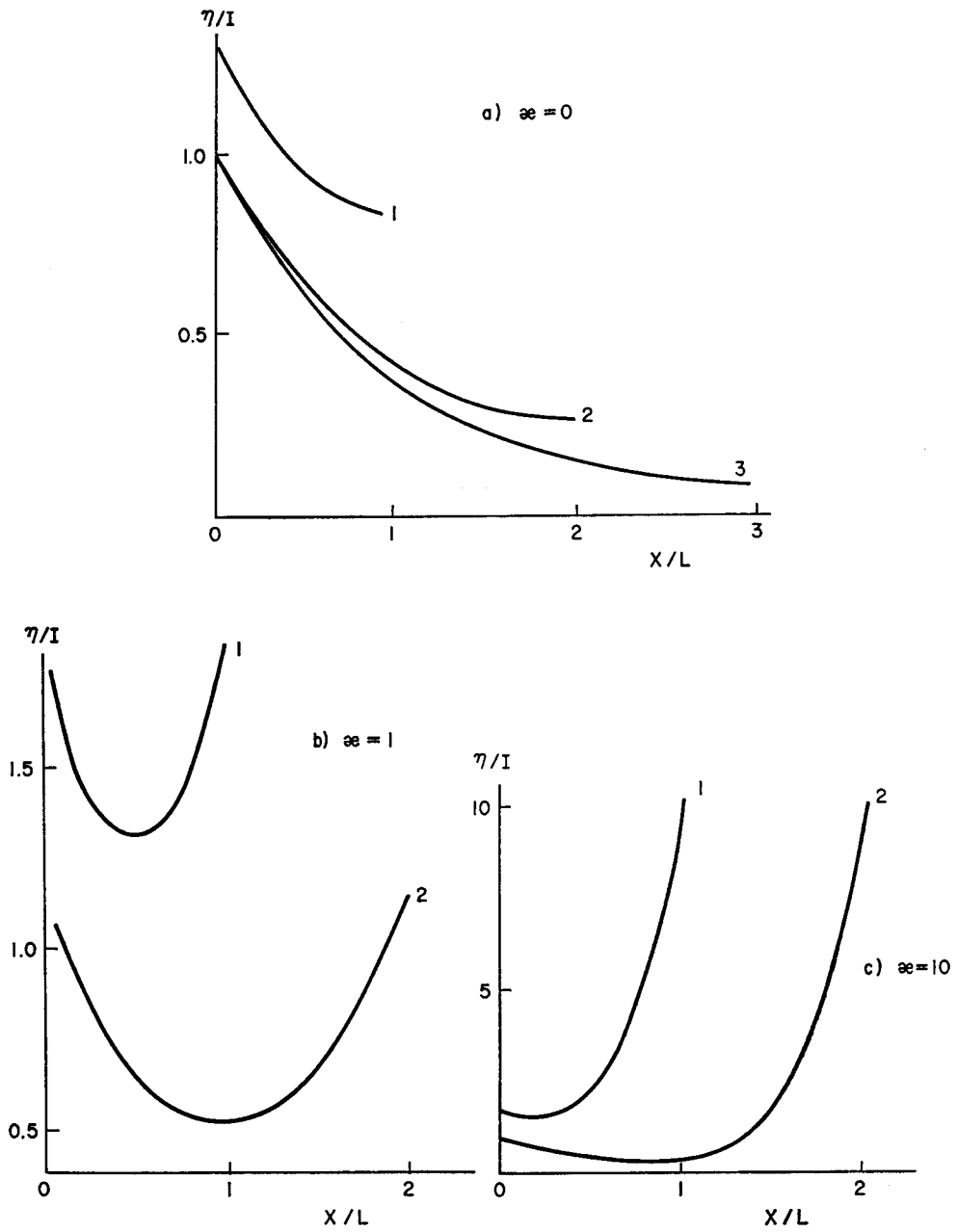


Fig. 4. Potential (current) distribution along the active layer coordinate as a function of the effective electric conductivity (α) and reduced electrode thickness (d/L) at $\alpha = 0$ (a), $\alpha = 1$ (b) and $\alpha = 10$ (c).

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ratios examined the volume fraction of SPE varies but insignificantly. At first, with decreasing catalyst amount, the electronic resistance of the mixture changes slightly, but when metal content is less than 20% it rises sharply (Fig. 3 b). Thus in the range of the catalyst content in the mixture 10~50% the parameter \mathcal{X} varies from 440 to 4×10^{-3} (at $\rho=250$ ohm.cm), so that for analysis of the equation (1~3) the boundary conditions (4) should be chosen.

Confining ourselves to the low polarization region, we obtain (instead of equation (3) :

$$\frac{d^2\eta}{dy^2} = \eta \quad (6)$$

whose solution gives :

$$\eta = I \frac{\text{ch}(\Delta+x) + \mathcal{X} \text{sh } x}{\text{sh } \Delta} \quad (7)$$

Fig. 4 shows the electrode polarization distribution from its thickness at different \mathcal{X} (from 0 to 10). These data indicate that with increasing \mathcal{X} the current generation zone recede from the front to the rear side. At $\mathcal{X}=1$ both front and rear electrode sides contribute to current generation, in the middle part however current generation is not large.

Formula (7) alone is insufficient for making numerical estimates of the electrochemical activity of a porous electrode with SPE. It should be noted that in the system under consideration it is possible to measure experimentally not the quantity η_0 but the potential difference $E_0 - E_m$ (Fig. 1). Let us show that the current can be related to this quantity. Integrating twice (2) in the low polarization region and taking into account expression (7), we obtain

$$E_m^0 - E_m^A = \frac{\mathcal{X}}{1-\mathcal{X}} I \left[\Delta - (1-\mathcal{X}) \frac{\text{ch } \Delta - 1}{\text{sh } \Delta} \right] \quad (8)$$

and the electrode polarization (see expression (7)) is given by

$$\eta_0 = E_0 - E_m^0 = I \frac{\text{ch } \Delta + \mathcal{X}}{\text{sh } \Delta} \quad (9)$$

Therefore, excluding from (8) and (9) the quantity E_m^0 we find the difference needful

$$E_0 - E_m^A = I \left[\left(1 - \mathcal{X} \frac{1-\mathcal{X}}{1+\mathcal{X}} \right) \text{cth } \Delta + \frac{\mathcal{X}}{1+\mathcal{X}} \left(\Delta + \frac{2}{\text{sh } \Delta} \right) \right] \quad (10)$$

Fig. 5 shows the dependence of the electrochemical activity of the electrode on its thickness for a number of parameter \mathcal{X} values. The curve

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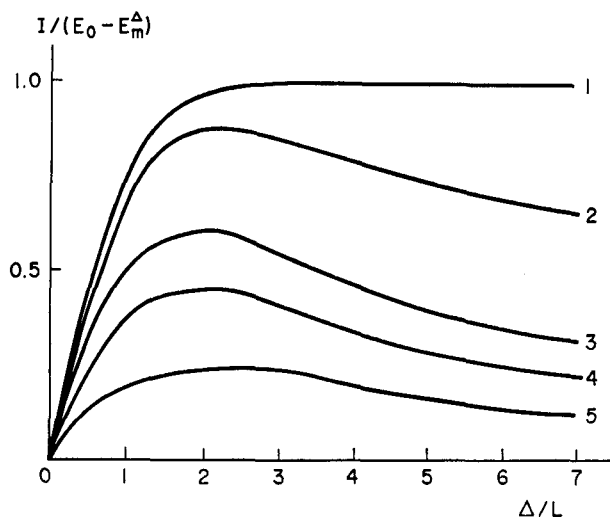


Fig. 5. Dependence of the electrochemical activity of a porous electrode on its thickness at α : 1-0, 2-0.1, 3-0.5, 4-1, 5-3.

with $\alpha = 0$ is of a conventional shape: it forms a plateau because the electrode thickness Δ becomes larger than the current generation zone localized on the front side of the electrode. At $\alpha \neq 0$, the shape of the curves is different. Here the ohmic losses are present not only in electrolyte but also in catalyst, being localized at opposite electrode sides. At a same difference $E_0 - E_m$ increased electrode thickness hinders "transport" of electrons and ions into the current generation zone and therefore the electrochemical activity of the electrode has an optimum at a certain thickness equal to approximately two characteristic ohmic lengths.

Let us evaluate for the case of low polarizations ($\gamma \sim 1$) the most important characteristics of porous electrodes with SPE: the electrode activity I , the current generation zone length L and the parameter LS which is the ratio of the working inner surface of a porous electrode to the unit surface of a smooth electrode. The obtained value shows how reasonable it is to use a porous electrode in the case in question. Since in system with SPE the electrochemical process is localized at the sites of direct contact of catalyst particles with ion-exchange membrane grains it can be assumed that the specific surface on which the reaction occurs is the same that surface of SPE grains. Then, assuming SPE grains to be spherical and to have the diameter d , we obtain

$$L = \left[\frac{RTd}{6\alpha F i_0 (\beta + \beta_m)} \right]^{1/2} \quad (11)$$

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$$LS = \left[\frac{6RT}{\alpha F i_0 d (\tilde{\rho} + \tilde{\rho}_m)} \right]^{1/2} \quad (12)$$

$$y = i_0 LS = \left[\frac{6RT i_0}{\alpha F d (\tilde{\rho} + \tilde{\rho}_m)} \right]^{1/2} \quad (13)$$

The above formulas show that the main parameters determining the course of the processes in electrodes with SPE are the exchange current i_0 and the average size of polymer electrolyte grains d . Numerical values of these parameters for $\alpha=0,5$ are in table 1.

TABLE 1. Numerical values of the main parameters characterizing porous electrodes with SPE ($\rho=50$ ohm.cm)

i_0 A·cm ⁻² d_{SPE}	Parameter	10 ⁻⁶	10 ⁻⁴	10 ⁻²
1	I, mA·cm ⁻²	8, 5	85	850
	L, mm	8, 5	0, 85	0, 085
	LS	8, 5·10 ³	8, 5·10 ²	85
10	I, mA·cm ⁻²	2, 7	27	270
	L, mm	27	2, 7	0, 27
	LS	2, 7·10 ³		
100	I, mA·cm ⁻²	0, 85	8, 5	85
	L, mm	85	8, 5	0, 85
	LS	850	85	8, 5

As would be expected, use of porous electrodes gives the greatest effect in the case of low-activity catalysts. Here development of the working surface leads to increase of the total current. For platinum catalysts with a high activity, use of porous electrodes may prove ineffective, especially when the surface of the ion-exchange membrane grains is not large ($d \sim 100 \mu\text{m}$). The thickness of electrodes with active catalysts can be small, of the order of tens of microns. A high electrode activity can be achieved by increasing the dispersion of polymer particles in the catalyst-SPE mixture ($d < 1 \mu\text{m}$).

Let us compare the results obtained in the theoretical treatment of the current generation process in the catalyst-membrane system with experimental data. We used in our study the cation-exchange membranes on the basis of sulfonated fluoroplastic⁹⁾ to which a mixture of catalyst and disperse polymer membrane particles had been applied by hot pressing.⁹⁾

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Figs. 6 and 7 show the polarization characteristics of electrodes in the oxygen (Fig. 6) and hydrogen (Fig. 7) evolution reactions measured for mixtures containing platinum black and polymer particles of different dispersion degree in the ratio 1:1. Simultaneously in our experiments the catalyst surface available to electrochemical process was measured by means of the charging curves. The measurements were made in water and in 2 N sul-

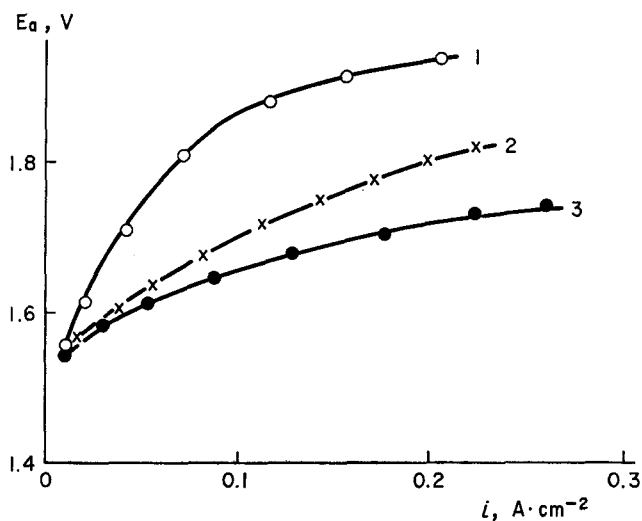


Fig. 6. Polarization characteristics of anodes from a catalyst-membrane composition at average size of polymer particles (μm): 1-25, 2-10, 3-3.

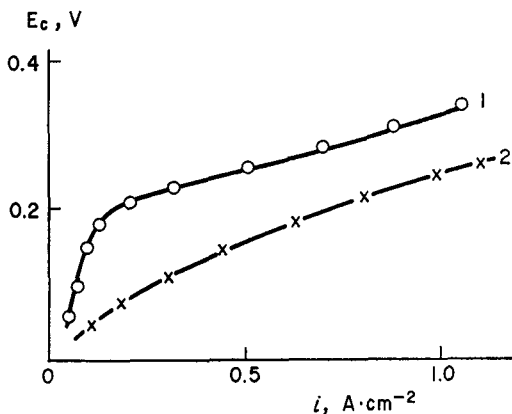


Fig. 7. Polarization characteristics of cathodes with the active mass from platinum-palladium black and membrane powder with the average size of polymer particles (μm): 1-25, 2-10.

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furic acid solution by ordinary sweep potential method at the rate of potential change 1 mV/sec. From the difference in the amounts of electricity expended in ionization of the hydrogen adsorbed on platinum catalyst surface in the potential range 0.05~0.35 V (for H₂O and H₂SO₄) was evaluated the catalyst efficiency in the system with SPE. As a reference electrode in this system were used a specially designed sulfate-mercury electrode, a strip of ion-exchange membrane wetted by water being used as an electrolytical bridge.

As it follows from the data given in Figs. 6 and 7, increase in the

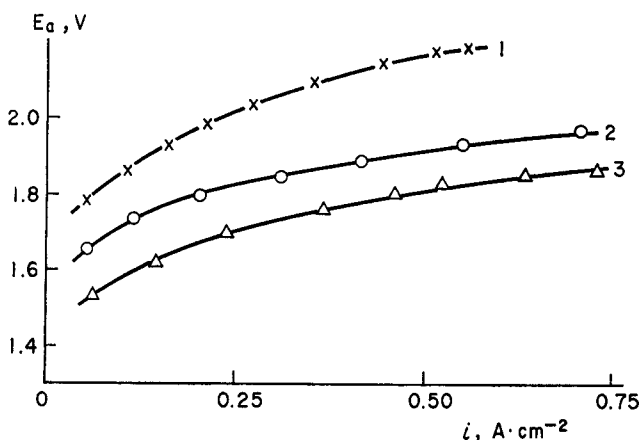


Fig. 8. Polarization curves of oxygen evolution on electrode with catalysts: 1-platinum, 2-platinum-palladium, 3-platinum-iridium (20°C).

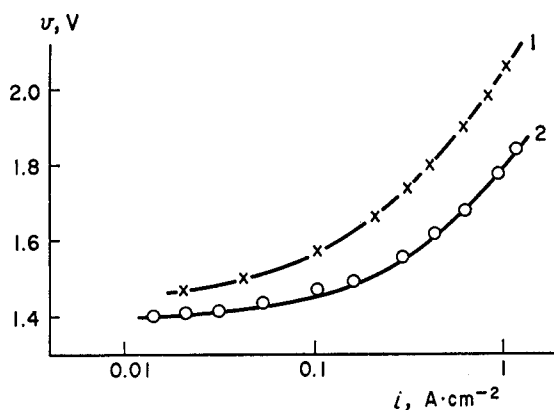


Fig. 9. Current-voltage characteristics of electrolytic cells with SPE and electrodes from platinum (cathode) and platinum-iridium (anode) catalysts at temperatures (°C): 1-20, 2-80.

degree of dispersion of the ion-exchange membrane particles in the active electrode layer leads to a marked increase of the current density of cathodic and anodic reactions, the catalyst surface efficiency determined from the charging curves increasing in this case from 30% to 85%.

Fig. 8 shows the influence of the catalyst nature on the polarization characteristics of the anode. It is clear from the figure that for an anodic reaction it is expedient to use a mixed platinum-iridium catalyst. For cathodic reaction of hydrogen evolution an active catalyst is platinum black.

Fig. 9 gives the current-voltage characteristics of electrolytic cells with electrodes on the basis of the above-mentioned catalysts, measured at 20 and 80°C. The voltage across the cell with a current collector from platinum gauze is 1.8 V at 80°C and the current density 1 A/cm².

In studying the polarization characteristics of electrolytic cells it is also important to know the value of ohmic losses in the electrolyte-polymer membrane, separating cathode and anode since the contribution of these losses increases with current density. The voltage across the cell electrodes can be written as

$$V = (E_A - E_C) + IR_{e1} \quad (14)$$

where R_{e1} is the resistance of the interelectrode space, or, considering that in the working current density range the polarization characteristics obey the Tafel plots:

$$V = b_A \ln I + b_C \ln I + IR_{e1} = (b_A + b_C) \ln I + IR_{e1} \quad (15)$$

Differentiating (15) with respect to I , we obtain:

$$\frac{dV}{dI} = (b_A + b_C) \frac{1}{I} + R_{e1} \quad (16)$$

This function when plotted as the coordinates dV/dI , $1/I$ should be a straight line the slope equal to the sum of Tafel slopes and forming on the ordinate axis an intercept corresponding to R_{e1} . The membrane resistivity values determined from these data are close to the results from direct measurements of the ohmic voltage drop across the membrane when current flows through it and equal to 10~12 and 5~6 ohm.cm at 20 and 80°C respectively, which points to negligible losses at the catalyst-solid polymer electrolyte interface.

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