EVALUATING THE EFFICIENCY OF ELECTROLYTE RESTORATION IN FUEL CELLS BY ELECTRODIALYSIS

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The electrodialytic method of restoring an alkaline electrolyte in a hydrogen–oxygen fuel cell during operation is considered here. Fundamental design equations are derived and analyzed, whereupon the efficiency of this method is evaluated.

During the operation of various fuel cells the electrolyte becomes diluted in water which has formed by the chemical reaction. For this reason, a long operation of a fuel cell at given energy levels requires a restoration of the electrolyte and this can be done by various methods, continuously or periodically – depending on the type and the design of such a cell.

In the case of fuel cells operating at higher temperatures (> 70°C), the obvious method of concentrating the electrolyte is by removing the water through evaporation with the heat released during the operation.

In the case of fuel cells operating at lower temperatures, this method would involve either a rather appreciable enlargement of the evaporation surface or a rather significant additional energy loss and, consequently, a reduction in the relative internal efficiency of the electrochemical generator.

In the case of the hydrogen–oxygen fuel cell, which operates with a liquid electrolyte at temperatures close to the ambient temperature, it would be of great interest to consider the apparently promising method of concentrating the electrolyte by "reverse" electrodialysis – distinct from conventional electrodialysis for water purification – as proposed and developed by E. Justi and associates [1].

The underlying idea here is to use two gas-diffusion electrodes connected through a gas channel as the anode and the cathode. Hydrogen generated at the vented cathode [2] combines with oxygen at the anode.

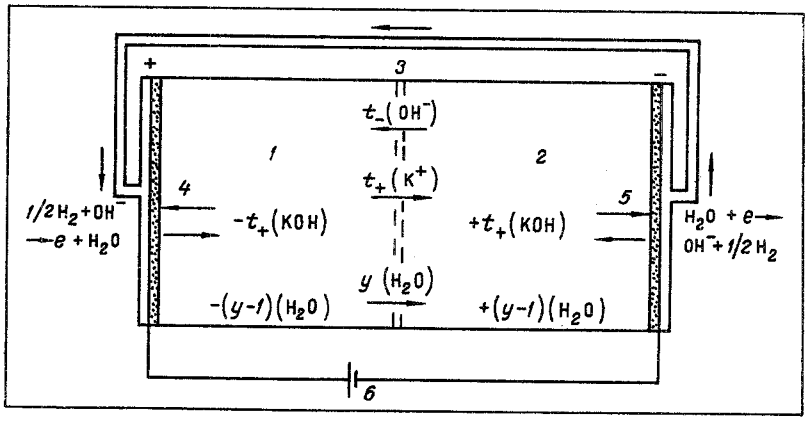

Fig. 1. Schematic diagram of a "reverse" electrodialyzer: 1) anolytic chamber; 2) catholytic chamber; 3) ion-exchange membrane; 4 and 5) electrodes; 6) voltage source.

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This arrangement eliminates any electrolysis of water and appreciably reduces the energy lost on electrodialysis, the latter process being now governed solely by the transport of ionic components in the solution, by the resistive losses in the electrolyte and in the ion-exchange membrane, and by the polarization of the electrodes. A schematic diagram of such a dialyzer together with the processes occurring in it is shown in Fig. 1.

An essential feature of electrodialysis for electrolyte restoration in a fuel cell, as distinguished from electrodialysis for water distillation, is that the ion-exchange membrane in our case operates in highly concentrated solutions and thus must satisfy certain definite requirements.

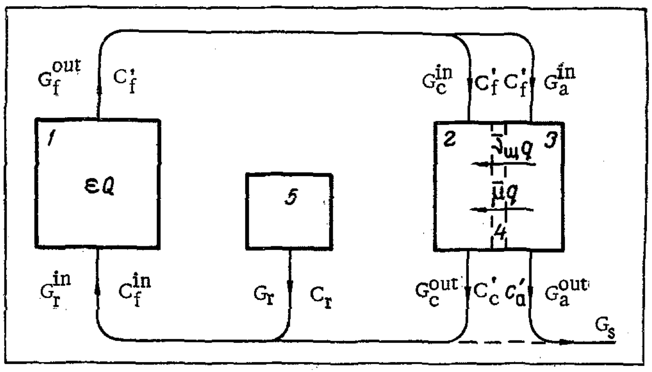

Fig. 2. Technological flow diagram of periodic (cyclic) electrolyte resoration in a hydrogen–oxygen fuel cell by electrodialysis: 1) fuel cell; 2) catholytic chamber; 3) anolytic chamber; 4) ion-exchange membrane; 5) reserve electrolyte.

We will analyze the electrodialytic method of electrolyte restoration, derive the fundamental design formulas, and then evaluate its efficiency on a typical example of a fuel cell with periodic restoration of an alkali metal (potassium) as the electrolyte.

Since this particular method of electrolyte restoration involves a certain loss of electrolyte (obviously, attaining a zero concentration of electrolyte in the anolytic chamber of the dialyzer is practically not feasible), hence an electrochemical generator must contain an appropriate reserve of electrolyte. The basic technological process of electrodialytic electrolyte restoration in a fuel cell is shown schematically in Fig. 2.

In the optimum operating mode, obviously, all the electrolyte removable from the anolytic chamber (bypassing the membrane) flows to a sink, i.e., $G_a^{out} = G_s$. When $G_a^{out} > G_s$ (dashed line in Fig. 1), on the other hand, the concentrated solution from the catholytic chamber of the dialyzer will be diluted with anolyte, i.e., there will be excess concentration here and, consequently, excess electric energy will be drawn for the dialytic process. In the opposite case ($G_a^{out} < G_s$), part of the concentrated solution from the catholytic chamber will be drained away and, consequently, excess alkali will be withdrawn from the reserve.

Therefore, we consider here only the optimum mode of electrolyte restoration. The cyclic process is described by the following system of balance equations:

solution balance

$$G_f^{out} = G_f^{in} + \varepsilon Q, \tag{1}$$

$$G_s = G_r + \varepsilon Q, \tag{2}$$

$$G_f^{out} = G_c^{in} + G_a, \tag{3}$$

$$G_c^{out} + G_s = G_c^{in} + G_a^{in}, \tag{4}$$

$$G_c^{out} = G_c^{in} + \bar{\mu} q; \tag{5}$$

alkali balance

$$G_f^{out} C_f' = G_f^{in} C_f^{in}, \tag{6}$$

$$G_s C_a = G_f C_f, \tag{7}$$

$$(G_c^{in} + G_a^{in}) C_f' = G_c^{out} C_c' + G_s C_a' \tag{8}$$

$$G_c^{out} C_c' = G_c^{in} C_f' + v_K q. \tag{9}$$

In (1), (2), (5), and (9) $\varepsilon = 0.337$ g/A·h is the electrochemical equivalent of the hydrogen oxidation reaction referred to the product (water) and $\bar{\mu} = \bar{\nu}_K + \bar{\nu}_{H_2O}$, with $\bar{\nu}_K$ and $\bar{\nu}_{H_2O} = \bar{\nu}_{H_2O}^m - 2\varepsilon$ denoting respectively the change in the quantity of alkali and of water in the catholyte or in the anolyte, per 1 A·h of electric charge passing through the dialyzer (in terms of the electrochemical reaction and in terms of transport across the ion-exchange membrane, $\bar{\nu}_{H_2O}$ representing the transport of water across that membrane).

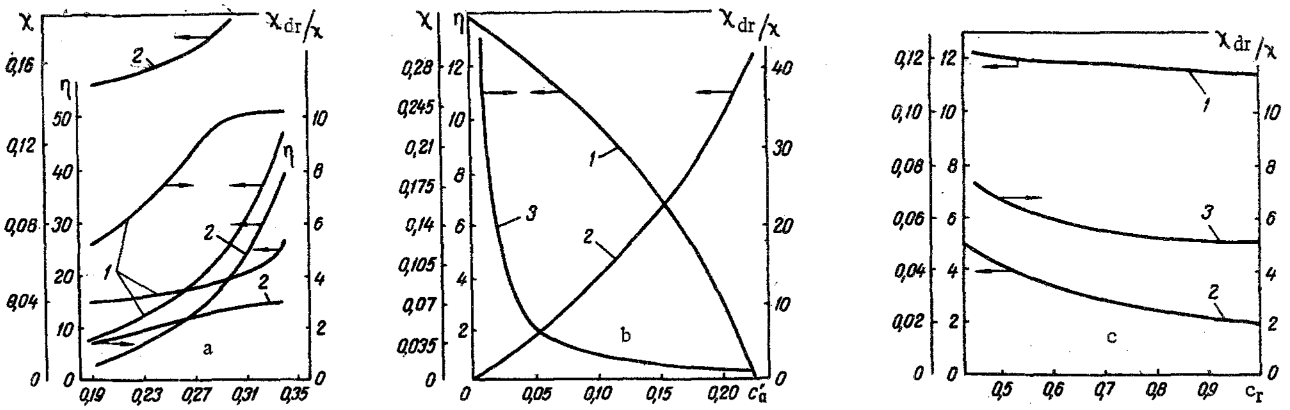

Fig. 3. Economic indicators for electrodialytic electrolyte restoration, as functions of (a) the final (per cycle) concentration of electrolyte in the fuel cell: 1) $c_r = 0.5$ and $c'_a = 0.05$; 2) $c_r = 0.5$ and $c'_a = 0.15$; of (b) the final concentration of anolyte in the dialyzer ($c_r = 0.5$ and $c'_f = 0.23$): 1) η,%; 2) χ, g/A·h; 3) χ_{dr}/χ; and (c) of the concentration of reserve electrolyte ($c'_f = 0.23$ and $c'_a = 0.05$): 1) η,%; 2) χ, g/A·h; 3) χ_{dr}/χ.

The experimentally determined coefficients $\bar{\nu}_K$ and $\bar{\nu}_{H_2O}$ characterize the effective transport of water and K$^+$ ions respectively across the membrane: $\bar{\nu}_K$ accounts for the transport of K$^+$ ions due to the electric current and also due to reverse diffusion, while ν_{H_2O} accounts for the transport of water due to hydration of the ionic components in the solution as well as due to osmosis. The values of these coefficients depend on c_c, c_a, and i_d [3], for a cycle with given parameters they represent average over the given interval changes in the concentration.

With given electrolyte concentrations c'_f (in the fuel cell, based on its operating conditions), c'_c and c'_a (catholyte and anolyte concentration, based on the dialyzer operating conditions: c'_a for instance, being determined by the properties of the anode and by the allowable energy loss on concentrating the electrolyte), and c_r (in the reservoir, based on the utility criteria of storing and transporting adequate quantities of electrolyte), also knowing the quantity of electric charge Q generated in the fuel cell during one cycle, one can easily determine the internal characteristics of the cell–dialyzer system.

From (2) and (7) follows

$$G_s = \frac{c_r}{c_r - c'_a}\,\varepsilon Q, \tag{10}$$

$$G_r = \frac{c'_a}{c_r - c'_a}\,\varepsilon Q. \tag{11}$$

Introducing $B = c_r/(c_r - c'_a)$, we have from (3), (4), (8), and (10)

$$G_f^{out} = B\,\frac{c'_K - c'_a}{c'_K - c'_f}\,\varepsilon Q, \tag{12}$$

$$G_c^{out} = B\,\frac{c'_{\text{э}} - c'_a}{c'_c - c'_f}\,\varepsilon Q. \tag{13}$$

From (5), (9), and (13) follows

$$G_c^{in} = B\,\frac{c'_f - c'_a}{c'_c - c'_f}\cdot\frac{\bar{\nu}_K - \bar{\mu} c'_c}{\bar{\nu}_K - \bar{\mu} c'_f}\,\varepsilon Q, \tag{14}$$

$$q = B\,\frac{c'_f - c'_a}{\bar{\nu}_K - \bar{\mu} c'_f}\,\varepsilon Q. \tag{15}$$

From (3), (12), and (14) follows

$$G_a^{in} = B\,\frac{\bar{\nu}_K - \bar{\mu} c'_a}{\bar{\nu}_K - \bar{\mu} c'_f}\,\varepsilon Q. \tag{16}$$

From (1) and (12) follows

$$G_f^{in} = \frac{c_r(c'_f - c'_a) + c'_a(c'_c - c'_f)}{(c_r - c'_a)(c'_c - c'_f)}\,\varepsilon Q, \tag{17}$$

From (6), (7), and (12) follows

$$c_f^{in} = \frac{c_r c_f' (c_c' - c_a')}{c_r (c_f' - c_a') + c_a' (c_c' - c_f')}. \tag{18}$$

The internal characteristics of the fuel cell and the dialyzer include the initial and the final solution of electrolyte (G_i^0 and G_i') and, for given initial and final concentration of electrolyte (c_i^0 and c_i') based on the operating conditions, the obviously applicable equation of solution balance

$$G_i' - G_i^0 = G_i^{out} - G_i^{in}, \tag{19}$$

and of alkali balance

$$G_i^0 c_i^0 = (G_i - G_i^{out}) c_i' + G_i^{in} c_i^{in}, \tag{20}$$

yield the following expressions:

for the characteristics of the fuel cell

$$G_f^0 = \frac{c_f'}{c_f^0 - c_f'} \varepsilon Q, \tag{21}$$

$$G_f' = G_f^0 + \varepsilon Q = \frac{c_f^0}{c_f^0 - c_f'} \varepsilon Q; \tag{22}$$

for the characteristics of the catholytic chamber in the dialyzer

$$G_c^0 = B \frac{c_f' - c_a'}{c_c' - c_c^0} \cdot \frac{\bar{\nu}_K - \bar{\mu} c_c'}{\bar{\nu}_K - \bar{\mu} c_f'} \varepsilon Q, \tag{23}$$

$$G_c' = B \frac{c_f' - c_a'}{c_c' - c_c^0} \cdot \frac{\bar{\nu}_K - \bar{\mu} c_c^0}{\bar{\nu}_K - \bar{\mu} c_f'} \varepsilon Q; \tag{24}$$

and for the characteristics of the anolytic chamber in the dialyzer

$$G_a^0 = B \frac{c_f' - c_a'}{c_a^0 - c_a'} \cdot \frac{\bar{\nu}_K - \bar{\mu} c_a'}{\bar{\nu}_K - \bar{\mu} c_f'} \varepsilon Q, \tag{25}$$

$$G_a' = B \frac{c_f' - c_a}{c_a^0 - c_a'} \cdot \frac{\bar{\nu}_K - \bar{\mu} c_a^0}{\bar{\nu}_K - \bar{\mu} c_f'} \varepsilon Q. \tag{26}$$

The most significant economic efficiency indicators for the electrodialytic method of electrolyte restoration are the relative quantity of electric charge used for restoration

$$\eta = q/Q \tag{27}$$

and the specific weight consumption of electrolyte

$$\chi = G_r/Q. \tag{28}$$

For a valid comparison with other methods of electrolyte restoration in a fuel cell, the second of these indicators must be recalculated per unit electric charge supplied to the user network, namely:

$$\chi = G_r/Q(1 - \eta). \tag{28'}$$

In the optimum mode of electrodialytic electrolyte restoration considered here these indicators can be described by the following expressions:

$$\eta = B \frac{c_f' - c_a'}{\bar{\nu}_K - \bar{\mu} c_f'} \varepsilon, \tag{29}$$

$$\chi = \frac{\varepsilon}{1 - \eta} (B - 1). \tag{30}$$

In the case of nondialytic electrolyte restoration in a fuel cell (from the reserve), the second of these indicators can be determined from the expression

$$\chi_{dr} = \frac{c_f'}{c_v - c_f'} \varepsilon, \tag{31}$$

which follows directly from the respective equation of solution balance

$$G_f^{out} = G_r + \varepsilon Q, \tag{32}$$

and of alkali balance

$$G_r C_r = G_f^{out} C_f'. \tag{33}$$

The efficiency of the electrodialytic method, as compared to the efficiency of the direct method (by replacement), can be defined in terms of the alkali economy as the ratio of two respective indicators:

$$\frac{\chi_{dr}}{\chi} = \frac{c_f' (c_r - c_a')}{c_a' (c_r - c_f')} (1 - \eta). \tag{34}$$

An analysis of these relations shows that the geometry (volume) of all system components here is uniquely determined by the allowable limits within which the electrolyte concentration in the fuel cell and in the dialyzer may change during an operating cycle and by the concentration of reserve electrolyte as well as by the quantity of electric charge generated.

An analysis of the economic indicators for electrodialytic electrolyte restoration (η and χ) shows that they are determined primarily by the final concentration of electrolyte in the fuel cell and in the anolytic chamber as well as by the concentration of reserve electrolyte. The effect of the other electrolyte concentrations in the dialyzer (c_a^0, c_c^0, and c_c'), in terms of the effective parameters of transport across the ion-exchange membrane $\bar{\nu}_K$ and $\bar{\nu}_{H_2O}$, may be neglected on the basis of an analysis of published data [3].

The results of calculations illustrating the relations derived here are shown in Fig. 3. Their reliability is determined quantitatively by the deviation from constant transport characteristics $\bar{\nu}_K = 1.25$ g/A·h and $\bar{\nu}_{H_2O} = 1.75$ g/A·h assumed in the calculation, the values in Fig. 3 being based on an analysis of the data in [3].

According to these curves, our efficiency indicators for the electrodialytic method depend in different ways on the governing electrolyte concentrations. Thus, the fraction of electric charge used for dialysis depends strongly on the final concentration of electrolyte in the fuel cell (Fig. 3a, curves 1 and 2), much less on the final concentration of anolyte (Fig. 3b), and almost not at all on the concentration of reserve electrolyte (Fig. 3c). It is to be noted, by the way, that the fraction of electric energy used for electrodialysis is smaller than the fraction of electric charge, because the voltage across the dialyzer is usually lower than the voltage across the fuel cell.

As to the specific weight consumption of electrolyte, it depends very strongly on the final concentration of anolyte (Fig. 3b) and rather weakly on the other two concentrations (c_f' and c_r).

The relative efficiency of the electrodialytic method depends very strongly on the final concentration of anolyte in the dialyzer, varying from ∞ at zero concentration to 1 at $c_a' = c_f'$ (Fig. 3b).

NOTATION

G	is the weight of the solution, g;
c	is the weight concentration, $g_{alkali}/g_{solution}$;
Q, q	are the quantity of electric charge per cycle in the fuel cell and in the dialyzer respectively, A·h;
i_d	is the electric current through the dialyzer, A;
F	is the Faraday's constant.

Subscripts and Superscripts

f	refers to the fuel cell;
d	refers to the dializer;
a	refers to anolyte;
c	refers to catholyte;
s	refers to sink;
r	refers to reserve;
K	refers to alkali metal (potassium);
H_2O	refers to water;
in	refers to inlet;

out refers to outlet;
0 refers to initial state;
' refers to final state.

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