SELF-REGULATION OF WATER ELIMINATION IN AN H_2-O_2 FUEL CELL

I. PRINCIPAL CHARACTERISTICS OF THE OPERATION OF AN H_2-O_2 CELL WITH A CAPILLARY MEMBRANE

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The principal operating characteristics of a fuel cell with a capillary membrane are considered. Mechanisms for the self-regulation of water elimination are discussed.

In H_2-O_2 fuel cells with an aqueous solution of the electrolyte the reaction product (water) is originally formed in the liquid phase, from which it is then eliminated, generally by evaporation (excess water can also be removed from aqueous solutions in other ways, for example, by electrodialysis). In steady-state conditions the rate of elimination should be equal to the rate at which water is formed as a result of the electrochemical reaction. If the balance is temporarily disturbed, the total volume of electrolyte solution in the fuel cell changes and the concentration of the solution is correspondingly affected. In fuel cells with a liquid solution of the electrolyte there is usually quite a large electrolyte volume and, accordingly, if the disturbance does not last too long, the changes in concentration are only slight and have almost no effect on the efficiency of the cell.

In cells with a capillary membrane [1, 2] the total amount of electrolyte solution is usually small; moreover, the electrolyte is localized in a confined space – in the pore volume of the membrane and in part of the pore space of the electrodes. Since the membrane is more hydrophilic than the usual treated electrodes, when the water balance is disturbed, the degree of flooding of the electrodes X changes: if the imbalance is positive, it increases; if it is negative, it decreases. The operation of the gas-diffusion water-repellent electrodes in the variable flooding mode is the principal characteristic of fuel cells with a capillary membrane, whereas gas-diffusion electrodes in contact with free electrolyte always have an electrolyte content $X = X_{eq}$ corresponding to capillary equilibrium for a given pressure drop.

The equation for the water balance can be written in the following general form:

$$\varepsilon i = f(P[C,\ T] - \bar{P}[\bar{T}]). \tag{1}$$

Here the left side is equal to the rate of formation of water, and the right side to the rate of elimination of water in vapor form. In most cases the right side of this expression may be fairly accurately assumed to be linear in character:

$$\varepsilon i = k(P[C,\ T] - \bar{P}[\bar{T}]). \tag{2}$$

The water balance may be disturbed for various reasons: a) by a change in current load; b) by a deviation of P or $\bar{P}$ from the balance value owing to instability of the temperature T or $\bar{T}$; c) by a deviation of k from

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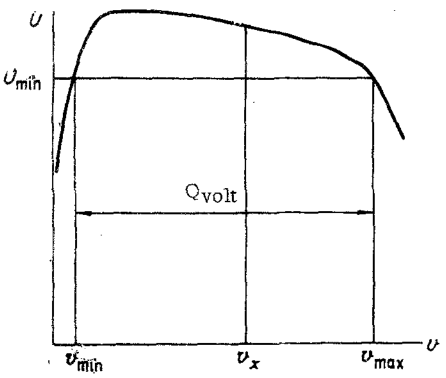

Fig. 1. Fuel-cell voltage as a function of the volume of electrolyte in the electrodes measured in the absence of water elimination.

the balance value. A disturbance of the water balance can be corrected by external means, but the possibilities are limited: such means are applicable only in the case of an imbalance due to a change of current, and not when the rate of elimination of water is disturbed by random fluctuations of the quantities T, $\bar{T}$, and k. External means of regulation are usually characterized by inertia and do not ensure the rapid establishment of a new balance. Moreover, they are not always capable of correcting considerable deviations of the parameters from the initial values.

The limitations of external regulating systems are not an obstacle to their use in connection with fuel cells with a liquid electrolyte, the buffer capacity of which is such that they are relatively insensitive to temporary disturbances of the water balance in one direction or the other. However, in the case of cells with a capillary membrane such devices are inadequate to ensure stable operation under actual conditions of current and temperature fluctuation.

The efficiency of such cells is chiefly determined by the fact that they are to some extent self-regulating as far as the elimination of water is concerned [2].

Operating the electrodes of a fuel cell with a capillary membrane (henceforth referred to as the electrochemical group (ECGr) of the cell) over a broad range of electrode electrolyte contents leads to a series of effects, the more important of which are considered below.

1. In the absence of water elimination the dependence of electrode polarization and, moreover, cell voltage on the volume of electrolyte in the electrodes at a given current has a dome-like form [1, 2]. Such dependences can easily be measured in cells without water elimination, where the increase in electrolyte volume is uniquely related to the amount of electricity transmitted. A flooding curve of this kind is shown in Fig. 1 in $U(v_x)$ coordinates. At small v_x the effective electrical conductivity $\varkappa_{eff}$ is small, and the porous electrodes operate in the internal activation-resistance mode, which explains the left branch of the flooding curve. At large values of v_x the reaction rate at the electrodes is limited by the diffusion of hydrogen and oxygen to the reaction surface, which explains the right branch of the curve. The minimum permissible cell voltage U_{min} determines the values v_{min} and v_{max}. The voltage buffer capacity (or more precisely the capacity with respect to the fall of the electrical characteristics of the cell) Q_{volt} is equal to the maximum possible change of electrolyte volume in the fuel cell $v_{max}-v_{min}$ at $U \geq U_{min}$. It should be noted that the voltage buffer capacity may be determined not only by the degree of flooding X (electrolyte content buffer capacity) but also by the electrolyte concentration field in the ECGr (electrolyte concentration buffer capacity), since the reaction kinetics at both electrodes and the electrical conductivity of the electrolyte depend on its concentration C.

2. At $X < X_{eq}$, as X increases, ever larger hydrophilic pores and subcritical hydrophobic pores are filled with electrolyte. Once a state of capillary equilibrium is reached ($X = X_{eq}$), with further increase in the amount of electrolyte in the ECGr, electrolyte begins to force its way into ever more hydrophobic pores. However, starting with a certain $v_x = v_d$, when only the highly hydrophobic pores remain unfilled, electrolyte begins to be discharged from the hydrophilic pores into the gas chamber. Escape of the electrolyte solution from the ECGr cannot be allowed, since this would result in the irreversible loss of electrolyte (but not water), might interfere with the normal supply of gas to the electrodes, cause a leakage of current, etc. Consequently, it is possible to speak of an electrolyte discharge buffer capacity $Q = v_d - v_{min}$. The actual buffer capacity of the ECGr is the least of the above three forms of buffer capacity. This may be one buffer capacity or the other, depending on the circumstances. For example, for a highly water-repellent electrode, $Q = Q_d$.

3. To a considerable extent H_2–O_2 fuel cells with a capillary membrane are self-regulating as far as the elimination of water is concerned. The basic principle of self-regulation consists in that, when an imbalance develops, under the influence of that imbalance there is a change in the electrolyte content X, and hence in the mean electrolyte concentration C_0 in the ECGr [2]. The change of C_0 causes a change in the electrolyte concentration C at the evaporation surface and hence a change in the water vapor concentration P above the evaporation surface. In the event of a positive imbalance the electrolyte is gradually diluted and P and the rate of elimination of water increase [2]. If, as a result of this change, the rate of elimination

of water increases after a certain time to the point at which it is equal to the rate of water formation, i.e., if a new state of balance is established, then the system is self-regulating. If, however, in order to establish a new state of balance the quantity v_x would have to be greater than v_{max} or v_d, then the system ceases to be self-regulating. In the event of a negative imbalance the electrolyte concentration increases, P decreases, and the rate of elimination of water correspondingly decreases (Eq. (2)). If in order to establish a new state of balance it is not necessary for v_x to fall below v_{min}, then self-regulation could take care of the imbalance, and conversely.

Another, more complex self-regulation mechanism is also possible. This is the case when a change in X leads to a certain change in the operating parameters of the electrodes, for example, the current density at a given voltage. Thus, for example, in the presence of a positive imbalance and an increase in the volume of liquid in the pores, the local current density, i.e., the rate of formation of water, may be reduced; this process also could eventually lead to a new state of balance. This means of self-regulation is of only limited applicability, but it could be used, for example, to compensate for the nonuniform removal of water over the surface of the electrode. In this case, when the current is kept constant, it is possible to observe a certain redistribution of current density along the ECGr that ensures the preservation of a state of balance in all parts.

A third possibility of self-regulation is associated with the increase in the temperature of the evaporation surface with increase in current density, i.e., with increase in the rate of formation of water.

As noted above, self-regulation is effective only within the limits set by the quantities v_{min} and v_{max} (or v_d), i.e., the width of the region of self-regulation is related with Q.

The width of the region of self-regulation can also be characterized by the ratio:

$$\gamma = \frac{\nu_m + v_{max}}{\nu_m + v_{min}} \tag{3}$$

(in the case of discharge v_d is always substituted for v_{max}), which expresses the relative change in mean concentration corresponding to the maximum permissible change of electrolyte content in the ECGr. For most real ECGr $v_{min} \ll v_{max}$ and $v_{min} \ll v_m$. Then

$$\gamma = \frac{\nu_m + Q}{\nu_m} = 1 + \eta. \tag{3a}$$

Depending on what parameters vary relative to their balance values it is necessary to consider separately the possibilities of self-regulation with respect to the elimination of water (when the quantities P, $\bar{P}$, and k vary) and the possibilities of self-regulation with respect to the formation of water (when i varies). Cases of joint variation of the rates of formation and elimination of water are possible.

4. In calculating the regions of self-regulation, in addition to the change in the mean electrolyte concentration C_0 in the ECGr due to the change in electrolyte content associated with imbalance it is also necessary to take into account the electrolyte concentration gradient in the ECGr when current flows [2-4], since the rate of elimination of water is determined not by the mean concentration C_0 but by the concentration C at the evaporation surface. The presence of this concentration gradient is determined by the slowness of the transport processes in the electrolyte over the thickness of the ECGr. The concentration gradient over the thickness of the membrane, which constitutes a considerable part of the total gradient over the thickness of the ECGr, is determined by the thickness of the membrane, the degree to which the membrane interferes with transport (i.e., the structure of the membrane), the current density, the mean electrolyte concentration in the membrane, temperature, and the anion transport number. Thus all these factors affect the width of the region of self-regulation of the elimination of water.

NOTATION

v_{max}, v_{min}	are the maximum and minimum permissible (from the standpoint of fuel cell efficiency) volumes of electrolyte in the electrode pores;
v_x	is the variable volume of electrolyte in the electrode pores;
v_d	is the volume of electrolyte in the electrodes at which electrolyte begins to be discharged into the gas chamber;
v_m	is the volume of electrolyte in the membrane pore space;
X	is the degree of flooding of the electrodes by electrolyte, $X \equiv v_x - v_{min}/v_{max} - v_{min}$;

X_{eq}	is the degree of flooding of the electrodes by electrolyte in the state of capillary equilibrium;
U	is the cell voltage;
U_{min}	is the minimum permissible cell voltage;
Q_{volt}	is the voltage buffer capacity of the electrodes;
Q_d	is the discharge buffer capacity of the electrodes;
Q	is the actual buffer capacity;
C	is the electrolyte concentration at the evaporation surface;
C_0	is the mean electrolyte concentration in the electrochemical group;
$\varkappa_{eff}$	is the effective electrical conductivity of electrolyte in the porous electrode;
i	is the current density;
ε	is the electrochemical equivalent of water;
P and $\bar{P}$	are the water vapor concentrations over the evaporation and condensation surfaces;
T and $\bar{T}$	are the electrode and condenser temperatures;
k	is the water-transfer coefficient (given by Eq. (2));
$\eta = Q/v_m$	is the relative buffer capacity of ECGr.

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