

SELF-REGULATION OF THE WATER DRAIN IN A
HYDROGEN/OXYGEN FUEL CELL
COMMUNICATION II. WIDTH OF THE SELF-REGULATION ZONE

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Analyzed is the effect of various factors on the width of the self-regulation zone during a change in the rate of water drain and of water formation. The conditions are established under which a fuel cell with a capillary diaphragm should attain the maximum possible self-regulation after a change in current density.

In [1] we have analyzed the fundamental characteristics of water-drain self-regulation during the operation of hydrogen/oxygen fuel cells with capillary diaphragms. In the equilibrium state the rate of water formation by the electrochemical process (characterized by the current density) must be equal to the rate of water drain by evaporation from the surface of one electrode and by vapor transport to the condenser:

$$\frac{i}{2F} = k(P - \bar{P}). \quad (1)$$

When the balance is disturbed, the volume of electrolyte solution and, consequently, its concentration C as well as the vapor concentration P change: this change partially compensates the original perturbation. The system becomes self-regulatory, if these changes establish in it a new equilibrium state where the volume of solution does not exceed definite limits dependent on the operating capability of the cell: $V_{\min} \leq V \leq V_{\max}$. The vapor concentration and, consequently, the self-regulation are strongly affected by the gradient of electrolyte concentration, which appears in the diaphragm during the passage of current.

We will consider in detail the width of self-regulation zones when the variables in Eq. (1) deviate from their equilibrium values. The analysis can proceed both graphically and by simplified calculations. We will consider here a cell with an alkali electrolyte (KOH).

The mean electrolyte concentration in the diaphragm C_0 is determined by the initial concentration C_0^0 (when the volume of the solution in the cell is minimum V_{\min}) and by the depth of cell immersion x :

$$C_0 = C_0^0 \frac{V_{\min}}{V_{\min} + xQ}. \quad (2)$$

It has been shown in [2] that the KOH concentration near the anode (hydrogen electrode) surface drops almost linearly with increasing current density; the same applies to the rising concentration near the oxygen electrode:

$$C = C_0 \pm \delta\beta i. \quad (3)$$

Coefficient β increases somewhat with increasing mean concentration. Within the practical range of KOH concentrations, a change in the vapor concentration is accurately enough proportional to the change in electrolyte concentration:

$$\Delta P = -\gamma\Delta C. \quad (4)$$

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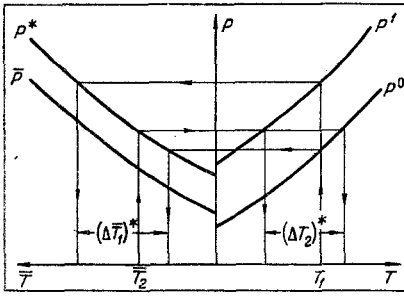


Fig. 1. Curves $P^0(T)$, $P^1(T)$, $\bar{P}(T)$, $P^*(T)$ for $\delta = 0.05$ cm, $Q = 0.024$ cm, $\varepsilon = 0.32$.

are respectively P_i^1 at $x = 1$ and P_i^0 at $x = 0$. The difference $(\Delta P)_i^* = P_i^1 - P_i^0$ characterizes the width of the self-regulation zone with respect to changes in the vapor concentration. According to (6), for the anode this zone is

$$(\Delta P)_{i,A}^* = \gamma C_0^0 \frac{Q}{Q + V_{\min}} - \gamma \delta (\beta_A^0 - \beta_A^1) i. \quad (7)$$

It follows from this equation that the self-regulation zone with respect to P widens with an increasing buffer volume Q or initial concentration, but narrows down with increasing current density. The diaphragm thickness δ affects V_{\min} . The $P_i^1(\delta)$ curve passes through a minimum at a definite diaphragm thickness; meanwhile, the self-regulation zone $(\Delta P)_i^*$ always narrows down with increasing diaphragm thickness. At some definite maximum thickness

$$\delta^{\max} = \frac{1}{2g} \sqrt{\frac{Q [(\beta_A^0 - \beta_A^1) Qi + 4gC_0^0]}{2g(\beta_A^0 - \beta_A^1) i}} \quad (8)$$

the cell completely loses its self-regulation with respect to P .

Considering now an actual design of the fuel cell under specific thermal conditions and with a specific precision of the temperature regulator, it is necessary to characterize the self-regulation zone by the width of the allowable (from the point of view of cell performance) interval through which the temperature of the evaporation surface $(\Delta T)^*$ may change or by the analogous width of the interval through which the condenser temperature $(\Delta \bar{T})^*$ may change. The relation between $(\Delta T)^*$ and $(\Delta P)^*$ depends on the absolute values of P^0 and P^1 ; it can be determined only numerically. Such an evaluation has shown that ΔT increases with increasing Q or C_0^0 , and decreases with increasing δ . As temperature T rises, $(\Delta T)^*$ varies little while $(\Delta P)^*$ increases appreciably. This difference between the trends of $(\Delta T)^*$ and $(\Delta P)^*$ with rising T , as well as with a change in other parameters, is explained by the fact that the derivative dT/dP decreases with an increase in the absolute value of P .

The general case of water-drain self-regulation during excursions from the equilibrium level of T , \bar{T} , and k is most conveniently analyzed with the aid of nomograms, as those shown in Fig. 1. On the right-hand side we have curves of vapor concentrations P^0 and P^1 vs temperature T ; on the left-hand side we have curves of concentration \bar{P} ($\bar{P} = P_{H_2O}$) and of the equilibrium vapor concentration near the electrodes P^* vs condenser temperature \bar{T} , the vapor concentration P^* being necessary, according to Eq. (1), for water drain at given values of i and k . On the diagram is also indicated the procedure for graphically determining the allowable fluctuations of the condenser temperature $(\Delta \bar{T}_1)^*$ at a given electrode temperature T_1 or, conversely, for determining the allowable fluctuations of the electrode temperature $(\Delta T_2)^*$ at a given condenser temperature \bar{T}_2 . Such calculations can be made for any value of the current density. It is also possible, with the aid of such graphs, to find the allowable limit of coefficient k fluctuations. According to (1),

$$(1/k_{\min}) - (1/k_{\max}) = \frac{2F(\Delta P)_i^*}{i}, \quad (9)$$

where k_{\max} and k_{\min} are the maximum and the minimum allowable (from the point of view of cell performance) values of k . In this way, all factors contributing to an increase in $(\Delta P)_i^*$ also cause an increase in $(\Delta T)_i^*$, $(\Delta \bar{T})_i^*$, and $(\Delta(1/k))_i^*$.

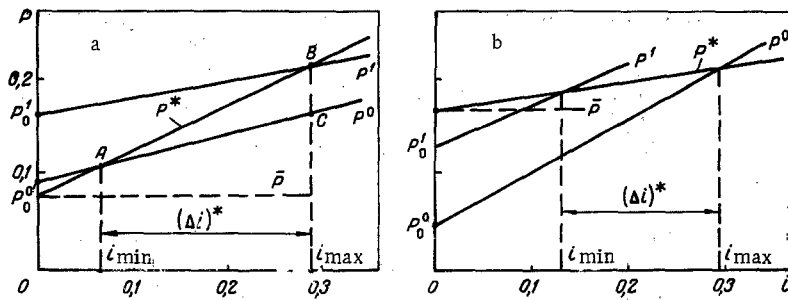


Fig. 2. Curves $P^1(i)$, $P^0(i)$, $P^*(i)$ for: a) $\delta\gamma\beta_A^0 < 1/2Fk$; b) $\delta\gamma\beta_A^1 > 1/2Fk$. Concentration P (kg/m^3), current density i (A/cm^2).

Let us now deal with the width of the self-regulation zone where the formation of water is concerned (i. e., during a change in current density); we will assume here that the drain parameters P and k are constant.

The concentrations P^0 , P^1 , and P^* above the surface of the hydrogen electrode are shown in Fig. 2 as functions of the current density. The slopes of these curves (straight lines, to the first approximation) are respectively equal to $\gamma\delta\beta_A^0$, $\gamma\delta\beta_A^1$, and $1/2Fk$. The case where

$$\delta\gamma\beta_A^0 < \frac{1}{2Fk} \quad (10)$$

is shown in Fig. 2a. Since the electrode is operative only so long as the vapor concentration above it remains within the limits P^0 and P^1 , hence the zone of allowable current densities $(\Delta i)^*$ is defined by the intersection of the P^* curve with the P^0 and P^1 curves (points A and B respectively); self-regulation will occur when the operating current density does not vary beyond the i_{\max} and i_{\min} limits. As i increases, the electrodes become more flooded: at a current density above i_{\max} there occurs overflowing ($x > 1$). At a current density below i_{\min} there occurs overdrying ($x < 0$).

For conventional diaphragms and electrodes, the time to reach the equilibrium flooding level τ_x (10-60 min) is longer than the time to reach a stable concentration gradient $\tau_{\Delta C}$ (1-2 min). Consequently, while the current density increases from i_{\min} to i_{\max} within the time $\tau_{\Delta C}$, for example, the vapor concentration increases from $P_{i_{\min}}^0$ to $P_{i_{\max}}^0$ (point C), i. e., almost the initial flooding level ($x = 0$) is reached. Subsequently, as a result of unbalance, the volume of electrolyte in the cell (i. e., x) and the vapor concentration P will both increase until a new equilibrium state has been established with the vapor concentration at $P_{i_{\max}}^1$ (point B).

For any $P < P_0^0$

$$(\Delta i)^* = \frac{(\Delta P)_{\max}^*}{1/2Fk - \gamma\delta\beta_A^0}, \quad (11)$$

i. e., the width of the self-regulation zone with respect to current density fluctuations is proportional to the width of the self-regulation zone with respect to vapor concentration fluctuations.

When

$$\gamma\delta\beta_A^1 > \frac{1}{2Fk} \quad (12)$$

(Fig. 2b), then an increase in current density causes the cell charge to diminish. This has to do with the increase in vapor concentration, following an increase in current density, due to a larger increase in the concentration gradient than necessary for maintaining equilibrium. At low current densities (when $P^1 < \bar{P}$) the vapor is transported to the electrode.

In both cases the position of the self-regulation zone depends on the selected value of \bar{P} . In the first case the optimum value is $\bar{P} = P_0^0$: then $(\Delta i)^*$ is maximum, $i_{\min} = 0$, and the electrode cannot become overdry. In the second case the optimum value is $\bar{P} = P_0^1$: then $(\Delta i)^*$ is also maximum, $i_{\min} = 0$, and the electrode cannot become overflowed.

Most interesting is the case where

$$\delta\gamma\beta_A^1 < \frac{1}{2Fk} < \delta\gamma\beta_A^0 \quad (13)$$

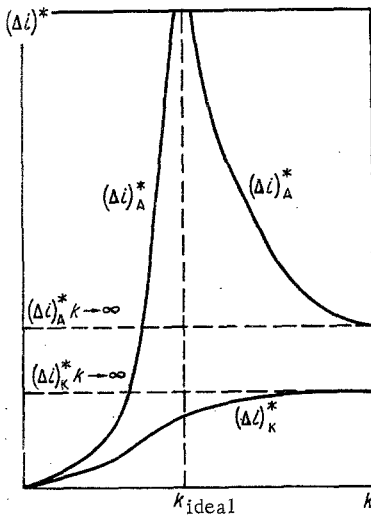


Fig. 3. Change in current densities $(\Delta i)_A^*$ and $(\Delta i)_K^*$ as a function of the water transport coefficient k .

at $P_0^0 < \bar{P} < P_0^1$. Here occurs ideal water-formation self-regulation, because $i_{\min} = 0$ and the maximum possible current density is very high (i. e., it is limited by other factors, not related to self-regulation). Ideal self-regulation means that the vapor concentration level established as a result of a change in the concentration gradient is exactly equal to the vapor concentration necessary for a balanced water drain at the new current density. The flooding level either does not change at all or changes very insignificantly. Conditions for ideal self-regulation are easily realized by the proper choice of values (expression (13)) for the parameters of the water drain system, i. e., for the coefficient of water transport $k = k_{\text{ideal}}$ and the temperature of the condenser surface \bar{T} . The width of the current-density self-regulation zone as a function of the water transport coefficient k is shown in Fig. 3.

When water is drained from the oxygen electrode condition (10) is always satisfied by virtue of the negative derivative of vapor concentration (above the electrode surface) with respect to current density (6). In this case ideal self-regulation is impossible (Fig. 3). A more thorough analysis will show that under comparable conditions $(\Delta i)_K^* < (\Delta i)_A^*$, i. e., that the conditions of self-regulation during water drain from the oxygen electrode are worse than during water drain from the hydrogen electrode.

We will consider the transient process which leads to the establishment of a new equilibrium (steady state) after the current density has changed from i_1 to i_2 . The general equation of water balance is

$$\frac{i}{2F} - kP + k\bar{P} = Q\rho_{\text{H}_2\text{O}} \frac{dx}{d\tau} \quad (14)$$

If an unbalance has occurred as a result of a $i_1 \rightarrow i_2$ transition, then $i = i_2$ in this equation. Disregarding the insignificantly weak dependence of β on x and τ during the time $\tau_{\Delta C} \ll \tau_X$, we obtain for the extreme condition $x = x_1$ at $\tau = 0$ the following solution to Eq. (14):

$$\tau = \frac{Q\rho_{\text{H}_2\text{O}}}{L-N} \left[(x - x_1) - \frac{N}{\eta(L-N)} \ln \left| \frac{(L-N)\eta x - L}{(L-N)\eta x_1 + L} \right| \right] \quad (14')$$

The $x(\tau)$ curve has been plotted in Fig. 4 (curve 1).

From (14') we have at $x = x_1$

$$\frac{dx}{d\tau} = \frac{i_2 - i_1}{2FQ\rho_{\text{H}_2\text{O}}}, \quad (15)$$

while $dx/d\tau = 0$ at $x = x_2$.

Thus, the rate of electrode flooding or drying varies in proportion to the magnitude of the unbalance. Inasmuch as x approaches x_2 asymptotically, so instead of the exact transient time τ^{1-2} we prefer to use the characteristic time τ_{ch} :

$$\tau_{\text{ch}} = \left| \frac{x_2 - x_1}{i_2 - i_1} \right| 2Q\rho_{\text{H}_2\text{O}}F. \quad (16)$$

As the difference $(i_2 - i_1)$ increases, the ratio $\tau_X/\tau_{\Delta C}$ decreases because, to the first approximation, $\tau_{\Delta C}$ does not depend on τ while τ_X decreases appreciably with increasing $(i_2 - i_1)$. At some very large change in current density $\Delta i_{\text{max}} \approx 2Q\rho_{\text{H}_2\text{O}}F/\tau_{\Delta C}$ the self-regulation limit will be reached even when $k = k_{\text{ideal}}$, because during the time $\tau_{\Delta C}$ the fuel cell will be either flooded or dried beyond normal. At $\tau_{\Delta C} = 200$ sec and $Q = 0.024$ cm, for example, $\Delta i_{\text{max}} = 2.3$ A/cm².

When $k = k_{\text{ideal}}$, then $x_2 = x_1$, but even in this case x changes during the time $\tau_{\Delta C}$ (Fig. 4, curve 2). Initially x increases with time, as a result of a positive unbalance, but a rising concentration P due to the concentration gradient will increase the rate of water drain and, therefore, x will increase slower all the time because of self-regulation, and finally, after passing through its maximum, will decrease toward $x = x_2$. Other typical trends of the $x(\tau)$ curve are also shown schematically in Fig. 4.

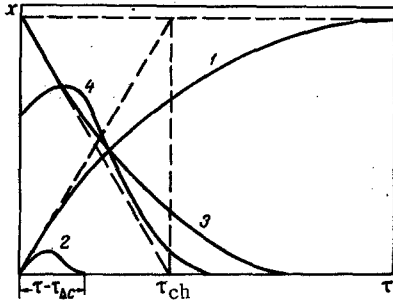


Fig. 4

Fig. 4. Curves of x vs τ for $i_2 > i_1$: 1) $\tau_{\Delta C} \ll \tau_x$ and $\delta\gamma\beta_A^0 < 1/2Fk$; 2) $\tau_{\Delta C} \approx \tau_x$ and $\delta\gamma\beta_A^1 < 1/2Fk < \delta\gamma\beta_A^0$; 3) $\tau_{\Delta C} \ll \tau_x$ and $\delta\gamma\beta_A^1 > 1/2Fk$; 4) $\tau_{\Delta C} \approx \tau_x$ and $\delta\gamma\beta_A^1 > 1/2Fk$.

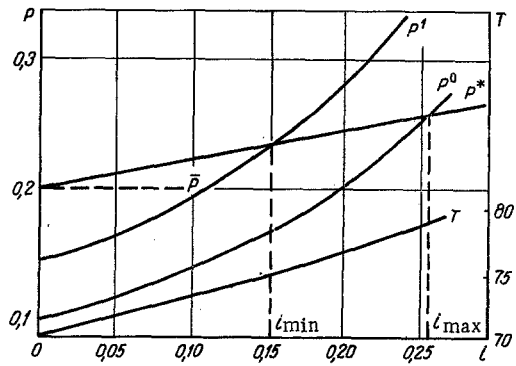


Fig. 5

Fig. 5. Curves of P^0 , P^1 , P^* , and T vs i for a fuel cell with a single heat-transfer circuit. Concentration P (kg/m^3), temperature T ($^{\circ}\text{C}$), current density i (A/cm^2).

Sometimes several parameters affecting the rate of water formation and drain change simultaneously during the operation of a fuel cell. Most often the cell temperature rises following an increase in current density, which in turn causes both the vapor concentration above the electrode and the rate of water drain to increase. In the preceding analysis of current-density self-regulation we assumed that all other parameters, including the electrode temperature, remain constant. This was equivalent to assuming the existence of two thermal circuits in the fuel cell: one for thermostatizing the cell and one for thermostatizing the condenser. In the case of a single-circuit scheme (thermostatizing the condenser only), the cell temperature is a function of the current density, which depends on the design characteristics, on the ohmic and the polarization losses in the cell, and on other factors. The T - i relation can be established by test or by calculation. The self-regulation zones in this case are determined from graphs analogous to those in Fig. 2, but it is necessary to account for the simultaneous changes in the electrode temperature when P^0 and P^1 as functions of the current density are calculated. Evidently, a temperature change makes the slopes of the $P^0(i)$ and $P^1(i)$ curves much greater than slopes $\gamma\delta\beta_A^0$ and $\gamma\delta\beta_A^1$ of the respective isothermal curves. An example of such calculations is shown in Fig. 5. Obviously, $\bar{P} > P_0^1$ without the second circuit (the electrode temperature and the condenser temperature are the same when $i = 0$); the single-circuit system is not suitable at very low current densities, therefore, because of cell flooding which then occurs.

If the two-circuit system is used, but with inadequate electrode thermostatization, then the electrode temperature will rise during operation, although less than without the second circuit. In this case, one may select a condenser temperature at which $P_0^0 < \bar{P} < P_0^1$. By modifying the trend of the $T(i)$ curve with appropriately matched heat transmission parameters, it is possible to obtain a situation where the slopes of the $P^0(i)$ and $P^1(i)$ curves approach the slope of the $P^*(i)$ curve. The current-density self-regulation zone can then become very wide, i.e., the system can approach the conditions of ideal self-regulation. In comparison with the earlier scheme for ideal self-regulation under isothermal conditions, a small controllable temperature gradient can lower the value of k_{ideal} at which ideal self-regulation occurs. This may be the value, for example, when water vapor is removed from the electrode surface by gas (e.g., hydrogen) circulation and when a too fast circulation for the purpose of attaining k_{ideal} under isothermal conditions requires too much energy.

Self-regulation may be important also under a nonuniform process distribution across the electrode surface as, for example, during a nonuniform water formation because of a nonuniform distribution of catalyst across the electrode surface, or during a nonuniform water drain because of different effective values of coefficient k at different surface segments. If λ_s denotes the distribution factor (ratio of current density at a given surface segment s to the mean-integral current density) in the case of a nonuniform current density distribution across the electrode, then the maximum change in current density Δi_s due to a change in the mean-integral current density from i_1 to i_2 is

$$\Delta i_s = \lambda_{\text{max}} i_2 - \lambda_{\text{min}} i_1. \quad (17)$$

When condition (10) applies, then the more active surface segments are more flooded than the less active ones; when condition (12) applies, then the pattern reverses; when condition (13) applies, then x is the same across the entire surface. The general condition for remaining operative (without overdrying or overflowing the cell) is

$$(\Delta i_s) \leq \frac{\Delta P_{i_{\max}}^*}{1/2Fk - \delta\gamma\beta_A^0} \quad (18)$$

From this equation we derive an expression for the maximum allowable, under these conditions, change in the mean-integral current density:

$$(\Delta i)^* = \frac{1}{\lambda_{\max}} \left[\frac{(\Delta P)_{i_{\max}}^*}{1/2Fk - \gamma\delta\beta^0} - i_{\max}(\lambda_{\max} - \lambda_{\min}) \right] \quad (19)$$

It is necessary to remember, however, that under a nonuniform process distribution across the electrode surface the operating conditions are somewhat better than according to Eq. (19), owing to the equalizing effect of electrolyte filtration inside the cell and of vapor flow over the electrode surface.

This analysis of mass and heat transfer in a hydrogen/oxygen fuel cell with a capillary diaphragm indicates that this type of fuel cell will, under specific conditions, be very suitable for self-regulation, which is necessary for a stable and reliable performance.

NOTATION

P, \bar{P}	are the concentrations of water vapor above the evaporation surface and above the condenser surface, respectively;
$P_{\text{H}_2\text{O}}$	is the concentration of water vapor above the water surface;
i	is the current density;
F	is the Faraday number;
k	is the water transport coefficient;
c	is the electrolyte concentration in an electrode;
Q	is the buffer volume;
C_0	is the mean electrolyte concentration in the cell;
$C_0^0 = C_0$ at $x = 0$;	
C_i^x, P_i^x	are the electrolyte concentration and the vapor concentration at certain values of x and i ;
T_i^x	is the temperature of the outside electrode surface at certain values of x and i ;
$P^* = \bar{P} - i/2Fk$;	
δ	is the thickness of the diaphragm;
g	is the porosity of the diaphragm;
ε	is the coefficient of the diffusion attenuation inside the porous space of the diaphragm;
\bar{T}	is the condenser temperature;
$(\Delta T)^* = T^0 - T^1$;	
$(\Delta \bar{T})^* = \bar{T}^0 - \bar{T}^1$;	
i_{\max}, i_{\min}	are the limiting maximum and minimum current density at which the fuel cell is still operative;
$(\Delta i)^* = i_{\max} - i_{\min}$;	
τ	is the time;
$L = i/2F - kP_0^0 - k\gamma\delta\beta i$;	
$N = k\gamma C_0^0$;	
$(\Delta P)_i^* = P_i^1 - P_i^0$;	
$\rho_{\text{H}_2\text{O}}$	is the weight of water per 1 cm ³ of solution;
λ_s	is the coefficient of the current density distribution in a microregion;
$\lambda_{\max}, \lambda_{\min}$	are the values of λ_s for the most active and least active segments on the electrode surface.

Subscripts

A denotes the hydrogen electrode (anode);
 K denotes the oxygen electrode (cathode);
 Other symbols are as in [1].

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