

## THE THEORY OF STABILIZATION OF THE OUTPUT POWER OF A RECHARGEABLE FUEL CELL BATTERY UNDER CONDITIONS OF SIGNIFICANT CONCENTRATION POLARIZATION

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### Summary

A theory is developed for the output power stabilization of a rechargeable fuel cell battery in which the reactants and the electrochemical reaction products are in the electrolyte. Possible means of voltage stabilization are considered which employ continuous-flow and continuous flow-circulation supply of the working solution (electrolyte) to a fuel cell.

Expressions are derived for the effective stabilization time and the required electrolyte flow rate. For a battery with known output parameters, the means of stabilization have been optimized based on the electrolyte flow rate and time of stabilization. The optimum solution is shown to depend on the net energy losses in implementing the stabilization procedure.

### Zusammenfassung

Es wurde Theorie ausgearbeitet über Stabilisierung der Batterieausgangsleistung von Brennstoffzellen des wiederaufzuladenden Typs mit den sich in der Elektrolytlösung befindenden Reagenzien und Produkten der elektrochemischen Reaktion. Dazu wurden auch verschiedene Verfahren zur Stabilisierung der Spannung behandelt, die sich auf Nutzung der Durchfluss- und Durchfluss-Umlaufscheme der Erneuerung von Arbeitslösung (Elektrolyt) in Brennstoffzelle basieren.

Es sind Formeln für die Berechnung der effektiven Stabilisierungszeit und des dazu erforderlichen Elektrolytverbrauchs aufgestellt. Für die Batterie mit vorgegebenen Ausgangsparametern ist das Stabilisierungsverfahren an Verbrauch von Elektrolyt und Stabilisierungszeit optimiert. Es ist auch die Abhängigkeit der optimalen Lösung von der Verlustgrösse der Energie für Selbstverbrauch des Stabilisierungsverfahren gezeigt.

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### 1. Introduction

The proposed theory applies to such methods and conditions of fuel cell operation as involve changes in the composition of the free liquid

electrolyte which fills the cell and is not bound to the capillary membrane. These changes may occur either due to depletion of the amount of reactants, the accumulation of electrochemical reaction products (instead of continuous removal of these products in the process of cell operation it is sometimes more simple and effective, from the engineering point of view, to replace the whole electrolyte), or due to both reasons, as is the case in the so-called rechargeable fuel cells [1 - 4].

The term "rechargeable fuel cell" has been coined quite recently. Usually it refers to fuel cells with a certain reserve of reactants — fuel (reductant) as a rule — contained in the electrolyte solution, *i.e.*, cells with direct electrochemical oxidation of liquid hydrocarbon fuel in alkaline electrolyte [1 - 4].

This term can, with justification, be extended to a fuel cell with a consumable anode [5].

It is evident that long-term operation of such cells requires them to be "recharged" as their reactant reserve becomes consumed. This refers either to the reactant alone where the products of the current-forming reaction are continuously removed from the fuel cell when operating or to the reactant and the electrolyte in which the products accumulate. The operation of the fuel cell under the above conditions is characterised by the fall of power with time because of increasing polarization of the electrodes and intra-ohmic losses.

The earlier theory of the renewal (supply) of the working solution (electrolyte) in similar electrochemical apparatus [6] allows consideration of the problem of stabilization of the output power of a fuel cell, or a battery of such cells, provided that, with a given current loading on the cell, its voltage is determined only by the electrolyte composition.

The analysis of the galvanostatic operation of such fuel cells shows that the characteristic functions  $U(\tau)$  and  $c^j(\tau)$  (where  $U$  is the cell voltage and  $c^j$  is the concentration of the  $j$ th component of the electrolyte ( $j = r$  for the reactant or  $j = p$  for the product)) may, to a first approximation, be linearized\* to give

$$U = U_o - (U_o - U_{cr})\tau/\tau_{ic}^j, \quad (1)$$

$$c^j = c_o^j - (c_o^j - c_{cr}^j)\tau/\tau_{ic}^j. \quad (2)$$

Here,  $c_{cr}^j$ , in mol/l, is the critical concentration of either electrolyte component determined by the admissible working voltage,  $U_{cr}$ , or by any other parameter of the electrochemical system (for example, by the potential of anodic corrosion, etc.);

$$\tau_{ic}^j = V(c_o^j - c_{cr}^j)/\gamma_j I \quad (3)$$

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\*This assumption is not fundamental in character. It is only required for the development of the simplest analytical theory of voltage stabilization.

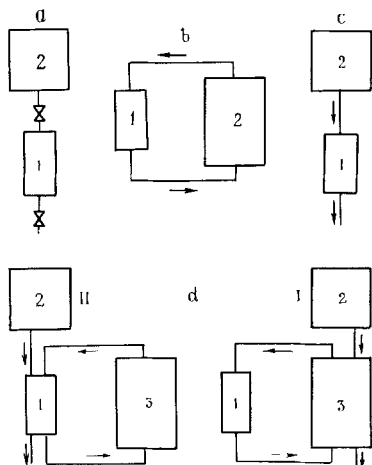


Fig. 1. Schemes of working solution (electrolyte) supply to a fuel cell: (a) periodic; (b) circulation; (c) continuous flow; (d) continuous flow-circulation. 1, Fuel cell; 2, working solution reserve; 3, auxiliary tank.

is the duration of the "interchange" cycle, *i.e.*, the time during which the cell parameters change from their initial ( $c_o^j, U_o$ ) to their final (critical) values ( $c_{cr}^j, U_{cr}$ ); the parameter  $\gamma_j$ , in mol/A h, represents the effective electrochemical equivalent based on the  $j$ th reaction component for a given load current,  $I$  ( $\gamma_j = \gamma_p, \gamma_j = -\gamma_r$ ), and  $V$  is the electrolyte volume in the fuel cell.

Eliminating time from eqns. (1) and (2) gives an expression which relates the cell voltage and concentration of one of the electrolyte components at any instant of time

$$U_\tau = U_o - (U_o - U_{cr}) \frac{c_o^j - c_\tau^j}{c_o^j - c_{cr}^j}. \quad (4)$$

Expression (4) holds not only for the simplest periodic scheme of electrolyte renewal ("recharging") (Fig. 1), but also for three other possible technological schemes, *viz.*, circulation, continuous flow [6], and their combination, referred to here as a continuous flow-circulation scheme, which is used, as may be expected from ref. 7, for fuel cells with a consumable anode [5].

Of all the above schemes, only the last two allow unrestricted control of the composition of the working solution (electrolyte) and, if necessary, its stabilization with time, thus, in accordance with eqn. (4), stabilizing the fuel cell voltage and finally its output power.

## 2. Means of stabilization and governing relationships

It is evident that fuel cells in the battery, while connected electrically in series, may electrolytically be connected either in series or in parallel. Both versions are encountered in practice [8, 9].

### 2.1 Stabilization using a continuous-flow scheme of electrolyte supply with electrolytically parallel cell connection

In accordance with ref. 6, the time dependence of the electrolyte composition of an operating fuel cell may be written as follows:

$$c_{\tau}^j = c_{\text{in}}^j + \frac{\gamma_j I}{u_{\text{con}}} - \left( \frac{\gamma_j I}{u_{\text{con}}} + c_{\text{in}}^j - c_{\text{o}}^j \right) \exp \left[ -\frac{u_{\text{con}}}{V} \tau \right], \quad (5)$$

where  $u_{\text{con}}$  (l/h) is the continuous electrolyte flow rate, and  $c_{\text{in}}^j$  (mol/l) is the concentration of the  $j$ th solution component at the fuel cell inlet.

Relationship (5) yields expressions for the steady-state reactant and the product concentrations established in the fuel cell ( $\tau \rightarrow \infty$ )

$$c_{\infty}^j = c_{\text{in}}^j + \gamma_j I / u_{\text{con}}. \quad (6)$$

Use of eqns. (6) and (4) allows determination of the electrolyte flow rate necessary to ensure stabilization of the voltage of a fuel cell (battery of  $N$  cells) at any level in the admissible range  $U_{\text{o}} - U_{\text{cr}}$  ( $NU_{\text{o}} - NU_{\text{cr}}$ ), depending on which of the solution components (either reactant or product) controls the potential

$$u_{\text{con}}^j = \gamma_j I / \left[ \frac{U_{\text{o}} - U_{\infty}}{U_{\text{o}} - U_{\text{cr}}} (c_{\text{cr}}^j - c_{\text{o}}^j) + c_{\text{o}}^j - c_{\text{in}}^j \right]. \quad (7)$$

It can be seen that the electrolyte flow rate increases as the stabilized voltage level is raised.

When the restrictions are due to several electrolyte components, the calculation is performed in terms of the one which is responsible for the highest electrolyte flow rate (hereafter the superscript  $j$  will be omitted).

The negative exponential time dependence of the fuel cell electrolyte composition (and, hence, of voltage) allows introduction of the concept of the effective time of voltage stabilization,  $\tau_{\text{st}}$ . This is defined as the time starting from which the voltage of the cell (battery) differs from the appropriate steady-state value ( $U_{\text{c,b}}^{\infty}$ ) by no more than any *a priori* assigned value of  $\epsilon$  which, in turn, is determined by the explicit relationship

$$\frac{100(U_{\text{c,b}}^{\tau} - U_{\text{c,b}}^{\infty})}{U_{\text{c,b}}^{\infty}} = \epsilon_{\text{c,b}}, \% \quad (8)$$

In the case considered it is evident that  $\epsilon_{\text{c}} = \epsilon_{\text{b}} = \epsilon$  (within the accuracy of voltage losses due to leakage currents).

Using relation (4) we may write

$$U_{\infty} = U_{\text{o}} - (U_{\text{o}} - U_{\text{cr}})(c_{\text{o}} - c_{\infty}) / (c_{\text{o}} - c_{\text{cr}}), \quad (9)$$

$$U_{\tau} = U_{\text{o}} - (U_{\text{o}} - U_{\text{cr}})(c_{\text{o}} - c_{\tau}) / (c_{\text{o}} - c_{\text{cr}}). \quad (10)$$

Substituting eqns. (9) and (10) into relation (8), we obtain

$$c_{\tau} = c_{\infty} + \frac{U_{cr}(c_o - c_{\infty}) + U_o(c_{\infty} - c_{cr})}{100(U_o - U_{cr})} \epsilon. \quad (11)$$

Now, the use of eqn. (5) and its substitution into eqn. (11) gives the required expression for the effective voltage stabilization time of the cell (or battery of such cells)

$$\tau_{st} = \frac{V}{u_{con}} \ln \frac{100(U_o - U_{cr})}{\epsilon \left( U_{cr} + U_o \frac{c_{\infty} - c_{cr}}{c_o - c_{\infty}} \right)}. \quad (12)$$

Substitution into eqn. (12) of the expression for  $c_{\infty}$  from eqn. (6) and for  $u_{con}$  from eqn. (7) yields the final expression for the effective time for cell (battery) voltage stabilization at any level of  $U_{\infty}$  ( $NU_{\infty}$ ) within an admissible range of values with a deviation not exceeding  $\epsilon\%$ .

$$\tau_{st} = \tau_c \ln \left[ \frac{100}{\epsilon} (U_o/U_{cr} - 1) \right], \quad (13)$$

where

$$\tau_c = V \left[ \frac{U_o - U_{\infty}}{U_o - U_{cr}} (c_{cr} - c_o) + c_o - c_{in} \right] / \gamma I \quad (14)$$

is the "time constant" of the fuel cell, since it represents the "rate" of electrolyte renewal.

## 2.2 Stabilization employing a continuous-flow electrolyte supply scheme with electrolytically series connection of the cells

By contrast with the scheme with electrolytically parallel cell connection (2.1), in the present arrangement all the fuel cells of the battery (other than the first) operate with time-dependent inlet concentrations of the electrolyte components. Then the following relationship holds

$$(c_{in})_n = c_{n-1}. \quad (15)$$

By solving the relevant problem (with the assumptions [6] of no electrolyte volume contraction with change in composition and absence of concentration gradients, which is almost certain due to natural electrolyte convection), one can write the following expression for the time dependence of the electrolyte component concentration in a chain of fuel cells connected electrolytically in series

$$c_n = c_{in} + n \frac{\gamma I}{u_{con}} + \exp \left[ -\frac{u_{con}}{V} \tau \right] \sum_{m=0}^{n-1} \frac{1}{m!} \left( \frac{u_{con}}{V} \tau \right)^m \left[ c_o - c_{in} - (n-m) \frac{\gamma I}{u_{con}} \right], \quad (16)$$

where  $n$  is the cell number.

Assuming in eqn. (16) that  $\tau = \infty$ , we obtain the expression for the steady-state concentrations of the electrolyte components in the sequence of cells through which the electrolyte is pumped.

$$(c_n)_\infty = c_{in} + n \frac{\gamma I}{u_{con}}. \quad (17)$$

The above expression and relation (4) give the formula for the steady-state voltage of a battery of  $n$  fuel cells connected in series both electrically and electrolytically

$$U_b^\infty = nU_o - n(U_o - U_{cr}) \frac{c_{in} - c_o}{c_{cr} - c_o} - \frac{n(n+1)\gamma I}{2u_{con}} \cdot \frac{U_o - U_{cr}}{c_{cr} - c_o}. \quad (18)$$

Equation (18) easily provides an expression for calculating the electrolyte flow rate which ensures voltage stability for the battery of  $n$  series connected fuel cells at any level in the range  $nU_o - nU_{cr}$

$$u_{con} = n(n+1)\gamma I/2 \left[ \frac{nU_o - U_b^\infty}{U_o - U_{cr}} (c_{cr} - c_o) + n(c_o - c_{in}) \right]. \quad (19)$$

With obviously monotonic variation of electrolyte component concentrations in the considered sequence of fuel cells, it is natural to set their values in the last cell as equal to the critical concentrations. Then, by setting the steady-state concentrations in eqn. (17) equal to the appropriate critical values, we obtain the expressions for the number,  $N$ , of series-connected fuel cells at any given electrolyte flow rate,  $u_{con}$ , or, conversely, for the flow rate for any given number,  $N$ , of cells which ensure the validity of the equality  $c_N^\infty = c_{cr}$

$$N = \frac{c_{cr} - c_{in}}{\gamma I} u_{con}, \quad (20)$$

$$u_{con}^* = \frac{N\gamma I}{c_{cr} - c_{in}}. \quad (21)$$

The steady-state voltages consistent with these battery parameters ( $N$  and  $u_{con}^*$ ) may be calculated by the following formulae obtained from eqn. (18)

$$U_b^\infty = u_{\text{con}} \frac{c_{\text{cr}} - c_{\text{in}}}{\gamma I} \left[ U_o - (U_o - U_{\text{cr}}) \frac{c_{\text{cr}} + c_{\text{in}} - 2c_o}{2(c_{\text{cr}} - c_o)} \right] - (U_o - U_{\text{cr}}) \frac{c_{\text{cr}} - c_{\text{in}}}{2(c_{\text{cr}} - c_o)}, \quad (22)$$

$$U_b^\infty = N \left[ U_o - (U_o - U_{\text{cr}}) \frac{c_{\text{cr}} + c_{\text{in}} - 2c_o}{2(c_{\text{cr}} - c_o)} \right] - (U_o - U_{\text{cr}}) \frac{c_{\text{cr}} - c_{\text{in}}}{2(c_{\text{cr}} - c_o)}. \quad (23)$$

In the particular case of  $c_{\text{in}} = c_o$ , eqns. (22) and (23) are simplified to give

$$U_b^\infty = u_{\text{con}} U_m \frac{c_{\text{cr}} - c_{\text{in}}}{\gamma I} - \frac{U_o - U_{\text{cr}}}{2}, \quad (22')$$

$$U_b^\infty = N U_m - \frac{U_o - U_{\text{cr}}}{2} \approx N U_m, \quad (23')$$

where  $U_m = (U_o + U_{\text{cr}})/2$  is the arithmetic mean voltage in a cycle of cell operation with no replacement of electrolyte.

Thus, it is seen that for the adopted scheme of electrolyte supply, the voltage of a battery of fuel cells, connected in series electrically and electrolytically, is stabilized at the voltage level which is the mean for the interchange cycle, provided that in the last cell the electrolyte concentration is the same as the critical concentration of the components.

To determine the effective time of battery voltage stabilization in accordance with the above approach, it is necessary to consider possible assumptions that would simplify the system of eqn. (16). The assumptions imply consideration of two time intervals after the battery has been loaded. These are: the *initial period*, which is a short time interval that allows substitution of  $\exp[(u_{\text{con}}/V)\tau]$  for the finite sum in eqn. (16), and the *period somewhat removed* from the start of battery operation which, firstly permits use of the quasi-stationary approximation, from which the solution of the above problem can be written in a form differing from eqn. (16), i.e.,

$$c_n \approx c_{\text{in}} + n \frac{\gamma I}{u_{\text{con}}} - n \left( \frac{\gamma I}{u_{\text{con}}} + c_{\text{in}} - c_o \right) \exp \left[ -\frac{u_{\text{con}}}{V} \tau \right] - \frac{n(n-1)}{2} \cdot \frac{\gamma I}{u_{\text{con}}} \exp \left[ -\frac{u_{\text{con}}}{V} \tau \right] + \frac{n(n-1)}{2} \left( \frac{\gamma I}{u_{\text{con}}} + c_{\text{in}} - c_o \right) \exp \left[ -2 \frac{u_{\text{con}}}{V} \tau \right] - \dots - (-1)^n \frac{\gamma I}{u_{\text{con}}} \exp \left[ -(n-1) \frac{u_{\text{con}}}{V} \tau \right] - \dots - (-1)^{n-1} \left( \frac{\gamma I}{u_{\text{con}}} + c_{\text{in}} - c_o \right) \exp \left[ -n \frac{u_{\text{con}}}{V} \tau \right], \quad (16')$$

and, secondly allows the terms of the second and higher orders of smallness (*i.e.*, the terms  $\propto \exp[-n(u_{\text{con}}/V)\tau]$  where  $n \geq 2$ ) in this solution to be neglected.

These time periods depend on the electrolyte flow rate: with increasing  $u_{\text{con}}$  the first period decreases, while the second increases.

For the first period we have

$$c_n \approx c_o + \frac{\gamma I}{V} \tau. \quad (24)$$

For the second

$$c_n \approx c_{\text{in}} + n \frac{\gamma I}{u_{\text{con}}} - n \left( \frac{n+1}{2} \cdot \frac{\gamma I}{u_{\text{con}}} + c_{\text{in}} - c_o \right) \exp \left[ -\frac{u_{\text{con}}}{V} \tau \right]. \quad (25)$$

By contrast with the scheme with electrolytically parallel fuel cell connection, in this case each of the cells will have its own effective time of stabilization. The prescribed relative deviation of the battery voltage,  $\epsilon_b$ , at a given time instant and appropriate voltage deviation of each cell,  $\epsilon_n$ , is related in accordance with eqn. (8) as follows

$$\epsilon_b = \frac{\sum_1^n \epsilon_m (U_\infty)_m}{U_b^\infty}. \quad (26)$$

Substituting expressions (24) and (25) into the appropriate analog of eqn. (11) provides the required relationship between the time,  $\tau$ , and the relative voltage deviation,  $\epsilon_n$ , of an individual cell for the initial period:

$$\epsilon_n = \frac{100(U_o - U_{\text{cr}}) \left( c_o - c_{\text{in}} - n \frac{\gamma I}{u_{\text{con}}} + \frac{\gamma I}{V} \tau \right)}{(U_o - U_{\text{cr}}) \left( c_{\text{in}} + n \frac{\gamma I}{u_{\text{con}}} \right) + U_{\text{cr}} c_o - U_o c_{\text{cr}}}, \quad (27)$$

and for the later period:

$$\epsilon_n = \frac{100(U_o - U_{\text{cr}}) n \left( c_o - c_{\text{in}} - \frac{n+1}{2} \frac{\gamma I}{u_{\text{con}}} \right) \exp \left[ -\frac{u_{\text{con}}}{V} \tau \right]}{(U_o - U_{\text{cr}}) \left( c_{\text{in}} + n \frac{\gamma I}{u_{\text{con}}} \right) + U_{\text{cr}} c_o - U_o c_{\text{cr}}}. \quad (28)$$

In accordance with eqns. (26) and (18), by estimation of the voltage deviation of the fuel cell battery at a particular time,  $\tau$ , and from its steady-state value  $U_b^\infty$ , we may obtain all the parameters of interest.



The maximum deviation of the battery voltage will naturally occur at the initial time (upon loading) and in a particular case (with the given number,  $N$ , of cells and  $c_{in} = c_o$ ) will be

$$(\epsilon_b)_{\max} = 100(U_o - U_{cr}) \frac{N + 1}{(N - 1)U_o + (N + 1)U_{cr}} \approx 100 \frac{U_o/U_{cr} - 1}{U_o/U_{cr} + 1},$$

$$N \gg 1. \quad (29)$$

For the general case, the effective time of voltage stabilization is found from the expression

$$\tau_{st} = \frac{V}{u_{con}} \ln \frac{100(U_o - U_{cr})[c_{in} - c_o + (n + 2)\gamma I/3u_{con}](n + 1)}{2\epsilon_b \left[ U_o(c_{cr} - c_o) + (U_o - U_{cr})(c_{in} - c_o) - (U_o - U_{cr}) \frac{\gamma I(n + 1)}{2u_{con}} \right]}$$

$$(30)$$

where the electrolyte flow rate,  $u_{con}$ , is given by eqn. (19).

For a particular case (where the parameters  $u_{con}$  and  $N$  are related by the condition  $c_N^\infty = c_{cr}$ ), with a known electrolyte flow rate,  $u_{con}$ , the stabilization time will be

$$\tau_{st} = \frac{V}{u_{con}} \ln \frac{100(U_o - U_{cr})(c_{cr} - c_{in} + 2\gamma I/u_{con}) [1 + u_{con}(c_{cr} - c_{in})/\gamma I]}{3\epsilon_b [(U_o + U_{cr})(c_{cr} - c_{in}) - \gamma I(U_o - U_{cr})/u_{con}]}$$

$$(31)$$

For a known number,  $N$ , of cells

$$\tau_{st} = \frac{\tau_{ic}}{N} \ln \frac{100(U_o - U_{cr})[c_{cr} + 2c_{in} - 3c_o + 2(c_{cr} - c_{in})/N](N + 1)}{3\epsilon_b [U_{cr}(c_{cr} + c_{in} - 2c_o) + U_o(c_{cr} - c_{in}) - (U_o - U_{cr})(c_{cr} - c_{in})/N]}$$

$$(32)$$

For the case where  $c_{in} = c_o$

$$\tau_{st} = \frac{\tau_{ic}}{N} \ln \frac{100(N + 1)(N + 2)(U_o/U_{cr} - 1)}{3\epsilon_b [N(U_o/U_{cr} + 1) - (U_o/U_{cr} - 1)]} \approx$$

$$\approx \frac{\tau_{ic}}{N} \ln \frac{100(N + 2)(U_o/U_{cr} - 1)}{3\epsilon_b (U_o/U_{cr} + 1)} \quad (32')$$

Figure 2 shows the effect of parameters  $U_o/U_{cr}$ ,  $N$ , and  $\epsilon_b$ , entering into expression (32'), on the dimensionless effective time of battery voltage stabilization ( $\tau_{st}/\tau_{ic}$ ) at the mean voltage level for a cell operation cycle without electrolyte replacement. The explanation for the decreasing character of the function  $\tau_{st}(N)$  lies in the fact that in the case considered the electrolyte flow rate (the rate of pumping) is, according to eqn. (21), directly proportional to the number of cells, and it is the increase in the

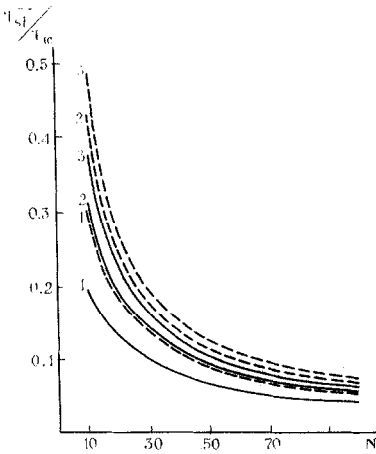


Fig. 2. Effective voltage stabilization time *vs.* the number of fuel cells in the battery (continuous flow scheme of electrolyte supply with electrolytically in-series connection of cells): 1,  $U_o/U_{cr} = 1.11$ ; 2, 1.43; 3, 2.0; —,  $\epsilon_b = 3\%$ ; ---,  $\epsilon_b = 1\%$ .

number of cells which results in this kind of dependence and which is contrary to expectation.

### 2.3 Stabilization employing a continuous flow-circulation scheme of electrolyte supply

In general, with a continuous flow-circulation scheme, as well as with a continuous flow scheme of electrolyte supply, a fuel battery voltage may be stabilized by two methods. First by electrolytically-parallel battery cell connection using one circulation path; second by series connection. In the latter case, the circulation paths cover separate battery sections connected electrolytically in series. In the following, only the first stabilization method is considered for two (of the four possible) versions of the continuous flow-circulation supply scheme which differ in the points of electrolyte input and output (Fig. 1(d)). Consideration of the second method (possible in principle) involves considerable mathematical effort since the pertinent governing relations are very complex.

For the scheme considered, when

$$c_{c,t,in}^p|_{\tau=0} = 0, \quad c_c^r|_{\tau=0} = c_t^r|_{\tau=0} = c_{in}^r,$$

the time dependence of the electrolyte composition of the operating cell may be approximated by:

*for the first version* (input and output of electrolyte through an auxiliary tank)

$$c_{\tau} \approx c_{in} + N \frac{\gamma I}{u_{con}} \left( 1 + \frac{1}{K} \right) + \frac{2K\gamma I \{1 + 2/V_t [\sqrt{(a^2 - 4b)} - a]\}}{Nu_{con} V^2 \sqrt{(a^2 - 4b)} [a - \sqrt{(a^2 - 4b)}]} \exp \left[ \frac{\sqrt{(a^2 - 4b)} - a}{2} u_{con} \tau \right], \quad (33)$$

where  $a = K(1/NV + 1/V_t) + 1/V_t$ ;  $b = K/NVV_t$ ;  $K = u_c/u_{con}$  is the circulation number,  $V$  and  $V_t$  the volumes of electrolyte in the fuel cell and the auxiliary tank, respectively,  $N$  the number of cells in the battery,  $u_{con}$  the electrolyte flow rate through the battery and  $u_c$  the circulation rate.

For the second version (electrolyte input and output through the battery)

$$c_{\tau} \approx c_{in} + N \frac{\gamma I}{u_{con}} - \frac{\gamma I \{2K/V_t [a - \sqrt{(a^2 - 4b)}] - 1\}}{u_{con} V \sqrt{(a^2 - 4b)}} \exp \left[ \frac{\sqrt{(a^2 - 4b)} - a}{2} u_{con} \tau \right], \quad (34)$$

where  $a = K(1/NV + 1/V_t) + 1/NV$ .

Equations (33) and (34) provide the expressions\* for the steady-state concentrations of the reactant and the product established in fuel cells with  $\tau \rightarrow \infty$ :

version I

$$c_{\infty} = c_{in} + N \frac{\gamma I}{u_{con}} (1 + 1/K), \quad (35)$$

version II

$$c_{\infty} = c_{in} + N \frac{\gamma I}{u_{con}}. \quad (36)$$

From this, using relation (4) we straightaway obtain the expressions for the electrolyte flow rate which ensures battery voltage stabilization at any level in the admissible range  $NU_o - NU_{cr}$ :

version I

$$u_{con} = \frac{N\gamma I}{c_{cr} - c_{in}} \cdot \frac{U_o - U_{cr}}{U_o - U_b^{\infty}/N} (1 + 1/K), \quad (37)$$

\*It should be noted that these expressions are exact because they are identical with those obtained from accurate equations for electrolyte composition with the above limited transition.

## version II

$$u_{\text{con}} = \frac{N\gamma I}{c_{\text{cr}} - c_{\text{in}}} \cdot \frac{U_o - U_{\text{cr}}}{U_o - U_b^\infty/N} \quad (38)$$

Again, the negative-exponential time dependence of the electrolyte composition (and, hence, of the cell voltage), which is typical of the method of electrolyte supply under consideration, allows estimation of the effective time of voltage stabilization as:

## version I

$$\tau_{\text{st}} = \tau_b \ln \frac{200K^2(U_o/U_b^\infty/N - 1)\{2/V_t[a - \sqrt{(a^2 - 4b)}] - 1\}}{\epsilon_b(1 + K)(NV)^2\sqrt{(a^2 - 4b)}[a - \sqrt{(a^2 - 4b)}]}, \quad (39)$$

where the time constant of the joint system "battery-auxiliary tank" is

$$\tau_b = \frac{2K(c_{\text{cr}} - c_{\text{in}})(U_o - U_b^\infty/N)}{N\gamma I(1 + K)[a - \sqrt{(a^2 - 4b)}](U_o - U_{\text{cr}})}; \quad (40)$$

## version II

$$\tau_{\text{st}} = \tau_b \ln \frac{100(U_o/U_b^\infty/N - 1)\{2K/V_t[a - \sqrt{(a^2 - 4b)}] - 1\}}{\epsilon_b NV\sqrt{(a^2 - 4b)}}, \quad (41)$$

where

$$\tau_b = \frac{2(c_{\text{cr}} - c_{\text{in}})(U_o - U_b^\infty/N)}{N\gamma I[a - \sqrt{(a^2 - 4b)}](U_o - U_{\text{cr}})}. \quad (42)$$

As expected, the method of fuel cell voltage stabilization considered with version II of the continuous flow-circulation scheme of electrolyte supply yielded a flow rate value which is identical with that obtained for the continuous flow scheme (with electrolytically parallel cell connection) (see expressions (38) and (7)). The methods differ only in the effective time of voltage stabilization: with the continuous flow-circulation scheme it is higher because of the auxiliary tank which increases the system time lag.

The difference becomes appreciable when employing version I of the scheme. In this case the electrolyte flow rate necessary for voltage stabilization increases to  $(1 + 1/K)$ -times that of the continuous flow scheme and version II of the scheme considered.

It should be borne in mind that the above relations are valid for the so-called "pouring-in" or "pool-type" of fuel cell design. In the case of a filter-press battery design with a moderate amount of electrolyte in the inter-electrode space and a rather high rate of electrolyte pumping, one may speak of the "piston" flow mode (the approximation often used to describe chemical reactors [10]). With this mode, after a time lapse of  $V/u_{\text{con}}$ , the concentrations of the solution components at the cell outlet are as follows

$$c_{\text{ou}} = c_{\text{in}} + \frac{\gamma I}{u_{\text{con}}}, \quad (43)$$

which may be related to the voltage of the fuel cell since the cell exhibits monotonic distribution of concentrations down the electrolyte flow.

The identity of expressions (43) and (6) allows use of the present relations for the filter-press battery design. The exception is the expressions for the effective time of voltage stabilization which are replaced by the explicit formula

$$\tau_{\text{st}} = \frac{V}{u_{\text{con}}}. \quad (44)$$

### 3. Optimization of the stabilizing method

It is evident that a multifactor system such as a battery of fuel cells involves a number of optimization problems. Among them, the following seem to be of practical interest.

For a battery of known useful power,  $P$ , voltage,  $U_b$ , and admissible deviation,  $\epsilon_b$ , the method of stabilization is optimized by the electrolyte flow rate and the effective stabilization time.

For the above problems, equal energy losses due to leakage currents *via* electrolyte ducts in the battery are assumed, and neglect of the net energy losses due to the use of a particular method of voltage stabilization is accepted.

#### 3.1 Electrolyte flow rate optimization

Obviously, with increasing dependence of the electrolyte flow rate and decreasing (under the conditions considered) dependence of the number of battery cells on the stabilized voltage, there must be an optimum number of cells to minimize the total flow rate of the working solution (electrolyte). To determine this, we will enumerate the expressions for the required electrolyte flow rate which are consistent with the considered methods of voltage stabilization and, using a familiar technique, find the optimum number of cells.

##### 3.1.1 Stabilization employing the continuous flow scheme of electrolyte supply with electrolytically parallel connection of cells

Based on expression (7), the volumetric flow rate per hour of the working solution through a battery of  $N$  fuel cells can be written as

$$q^{\bar{}} = N\gamma I / [c_o - c_{\text{in}} + (c_{\text{cr}} - c_o)(U_o - P/NI)/(U_o - U_{\text{cr}})]. \quad (45)$$

Minimizing the above, the number of cells is

$$N_{\text{opt}} = 2P(c_{\text{cr}} - c_o) / I[U_o(c_{\text{cr}} - c_{\text{in}}) + U_{\text{cr}}(c_{\text{in}} - c_o)]; \quad (46)$$

in the case when  $c_{\text{in}} = c_o$

$$N_{\text{opt}} = 2P/IU_o. \quad (46')$$

The values of the fuel cell voltages to be stabilized, consistent with eqns. (46) and (46'), are

$$U_{\text{opt}} = [U_o(c_{\text{cr}} - c_{\text{in}}) + U_{\text{cr}}(c_{\text{in}} - c_o)] / 2(c_{\text{cr}} - c_o) \quad (47)$$

and

$$U_{\text{opt}} = U_o/2. \quad (47')$$

The explicit constraint,  $U_{\text{opt}} \geq U_{\text{cr}}$ , is satisfied by the following initial to critical cell voltage ratios, consistent with expressions (47) and (47')

$$U_o/U_{\text{cr}} \geq [2(c_{\text{cr}} - c_o) - (c_{\text{in}} - c_o)] / (c_{\text{in}} - c_o) \quad (48)$$

and

$$U_o/U_{\text{cr}} \geq 2. \quad (48')$$

If these inequalities are not satisfied, then

$$N_{\text{opt}} = P/IU_{\text{cr}}. \quad (49)$$

The expressions for the total electrolyte flow rate corresponding to the optimum numbers of eqns. (46), (46'), and (49) are

$$q_{\text{opt}}^{\bar{}} = \frac{4\gamma P(c_{\text{cr}} - c_o)(U_o - U_{\text{cr}})}{[U_o(c_{\text{cr}} - c_{\text{in}}) + U_{\text{cr}}(c_{\text{in}} - c_o)]^2}, \quad (50)$$

$$q_{\text{opt}}^{\bar{}} = 4\gamma P(U_o - U_{\text{cr}}) / (U_o)^2 (c_{\text{cr}} - c_{\text{in}}), \quad (51)$$

$$q_{\text{opt}}^{\bar{}} = \gamma P / U_o (c_{\text{cr}} - c_{\text{in}}). \quad (52)$$

### 3.1.2 Stabilization employing the continuous flow scheme of electrolyte supply with electrolytically series connection of cells

According to expression (20), the electrolyte flow rate per hour, which allows voltage stabilization in a battery of  $N$  cells connected electrolytically in series, is determined by the expression

$$q^{\bar{}} = \frac{\gamma IN(N+1)(U_o - U_{\text{cr}})}{2[(NU_o - P/I)(c_{\text{cr}} - c_o) + N(U_o - U_{\text{cr}})(c_o - c_{\text{in}})]}. \quad (53)$$

The optimum number of cells for the particular case  $c_{\text{in}} = c_o$  is

$$N_{\text{opt}} = P[1 + \sqrt{(1 + IU_o/P)}] / IU_o \approx 2P/IU_o \quad (54)$$

(when solving the appropriate square-root equation we take the "+" sign,

since the “—” sign leads to  $N_{\text{opt}} < N_{\text{min}} = P/IU_o$ , which has no physical meaning since it requires the maximum electrolyte flow rate).

Analysis of expression (54) shows that the voltage of one cell in such a battery (with  $N_{\text{opt}}$ ) is, on average,  $P/IN_{\text{opt}} \approx U_o/2$  which, in turn, means that some cells (the last ones down the electrolyte flow) operate with voltages less than the admissible ( $U_{\text{cr}}$ ), and the final cell operates with  $U_N \approx 0$ . This can be easily demonstrated by direct calculation using present formulae.

Therefore, for the method of voltage stabilization in question, the optimum electrolyte flow rate and the corresponding number of cells must be determined from the operating condition of the final cell having a voltage of  $U_N = U_{\text{cr}}$ . The number of cells follows directly from expression (23):

$$N_{\text{opt}} = \frac{P/I + (U_o - U_{\text{cr}})(c_{\text{cr}} - c_{\text{in}})/2(c_{\text{cr}} - c_o)}{U_o - (U_o - U_{\text{cr}})(c_{\text{cr}} + c_{\text{in}} - 2c_o)/2(c_{\text{cr}} - c_o)} \quad (55)$$

which, in the particular case of  $c_{\text{in}} = c_o$ , is considerably simplified to

$$N_{\text{opt}} = (2P/I + U_o - U_{\text{cr}})/(U_o + U_{\text{cr}}) \approx 2P/I(U_o + U_{\text{cr}}). \quad (55')$$

A comparison of expressions (54) and (55') shows that in the latter case the optimum number of cells is less than in the former where cell voltage limitations were neglected.

The expressions for the electrolyte flow rate per hour corresponding to  $N_{\text{opt}}$  are determined by substitution of eqns. (55) and (55') into formula (53)

$$q_{\text{opt}} = \frac{\gamma P + \gamma I(U_o - U_{\text{cr}})(c_{\text{cr}} - c_{\text{in}})/2(c_{\text{cr}} - c_o)}{(c_{\text{cr}} - c_{\text{in}})[U_o - (U_o - U_{\text{cr}})(c_{\text{cr}} + c_{\text{in}} - 2c_o)/2(c_{\text{cr}} - c_o)]}, \quad (56)$$

$$q_{\text{opt}} = \frac{\gamma[2P + I(U_o - U_{\text{cr}})]}{(U_o + U_{\text{cr}})(c_{\text{cr}} - c_{\text{in}})} \approx 2\gamma P/(U_o + U_{\text{cr}})(c_{\text{cr}} - c_{\text{in}}). \quad (56')$$

### 3.1.3 Stabilization employing the continuous flow-circulation scheme of electrolyte supply

For this stabilization method, expressions (46'), (47'), (48'), (49), (51) and (52) hold, with the factor  $(1 + 1/K)$  introduced into formulae (51) and (52) for the first version.

All the above suggested procedures of stabilizing the voltage of a fuel cell battery with a known useful power are compared as regards optimum electrolyte flow rates per hour for the case most frequently encountered in practice where  $c_{\text{in}} = c_o$ .

A comparison of expressions (51), (52), and (56') shows absolute advantage for the voltage stabilization method employing the continuous flow scheme with electrolytically series connection of cells. This advantage quantitatively depends on the ratio of the initial to the ultimate (critical) voltages of a cell

at  $1 < U_o/U_{cr} \leq 2$

$$q_{opt}^-/q_{opt}^{--} = (U_o/U_{cr} + 1)/2, \quad (57)$$

at  $U_o/U_{cr} \geq 2$

$$q_{opt}^-/q_{opt}^{--} = 2[(U_o/U_{cr})^2 - 1]/(U_o/U_{cr})^2, \quad (58)$$

and ranges from 1 to 2. As compared with the first version of the method employing the continuous flow-circulation scheme of electrolyte supply, this advantage increases still more by a factor of  $(1 + 1/K)$ .

### 3.2 Effective stabilizing time optimization

The above expressions give the effective voltage stabilization time under the conditions of optimized electrolyte flow rate. For the stabilization method employing continuous flow of electrolyte supply with electrolytically parallel connection of cells, the effective voltage stabilization time appears to be

at  $1 < U_o/U_{cr} \leq 2$

$$\tau_{st}^- = \tau_{ic} \ln [100(U_o/U_{cr} - 1)/\epsilon_b], \quad (59)$$

at  $U_o/U_{cr} \geq 2$

$$\tau_{st}^- = \frac{\tau_{ic}}{2} \cdot \frac{U_o/U_{cr}}{U_o/U_{cr} - 1} \ln \frac{100}{\epsilon_b}. \quad (60)$$

Here and below,  $c_{in} = c_o$ .

For the continuous flow scheme with electrolytically series connection of cells, the unknown voltage stabilization time is found from expression (32'), with  $N_{opt}$ , determined from formula (55'), substituted for  $N$ .

A comparison of the above voltage stabilization times gives:

at  $1 < U_o/U_{cr} \leq 2$

$$\tau_{st}^-/\tau_{st}^{--} \approx N_{opt} \frac{\ln [100(U_o/U_{cr} - 1)/\epsilon_b]}{\ln [100(N_{opt} + 2)(U_o/U_{cr} - 1)/3\epsilon_b(U_o/U_{cr} + 1)]}, \quad (61)$$

at  $U_o/U_{cr} \geq 2$

$$\tau_{st}^-/\tau_{st}^{--} \approx \frac{N_{opt} U_o/U_{cr}}{2(U_o/U_{cr} - 1)} \frac{\ln(100/\epsilon_b)}{\ln [100(N_{opt} + 2)(U_o/U_{cr} - 1)/3\epsilon_b(U_o/U_{cr} + 1)]}, \quad (62)$$

where  $N_{opt}$  is found from formula (55').

Figure 3 illustrates relations (61) and (62). It is seen that, with increasing power (number of constituent fuel cells) of the battery, the difference in the voltage stabilization time greatly increases. This dependence of  $\tau_{st}^-/\tau_{st}^{--}$  on the number of cells in the battery, as well as the fact that voltage stabilization in the case of electrolytically series connection of cells requires less time



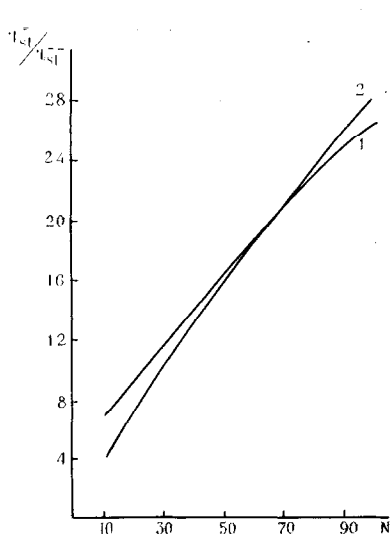


Fig. 3. Ratio of effective battery voltage stabilization times with known output parameters for two versions of the continuous flow electrolyte supply scheme *vs.* the optimum number of fuel cells connected electrolytically in series at minimum electrolyte flow rate ( $\epsilon_b = 1\%$ ): 1,  $U_o/U_{cr} = 1.027$ ; 2,  $U_o/U_{cr} \gg 1$ .

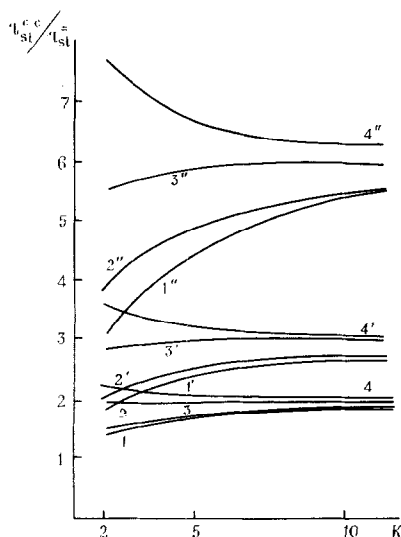


Fig. 4. Ratio of effective battery voltage stabilization times with known output parameters for the continuous flow-circulation and continuous flow (with parallel connection of the cells) schemes *vs.* the circulation number at minimum electrolyte flow rate ( $\epsilon_b = 1\%$ ): 1, version I of c.-c. scheme,  $U_o/U_{cr} = 1.027$ ,  $k = 1$ ; 2, version I of c.-c. scheme,  $U_o/U_{cr} > 2$ ,  $k = 1$ ; 3, version II of c.-c. scheme,  $U_o/U_{cr} = 1.027$ ,  $k = 1$ ; 4, version II of c.-c. scheme,  $U_o/U_{cr} > 2$ ,  $k = 1$ ; ',  $k = 2$ ; ",  $k = 5$ .

than in the case of parallel connection at smaller total electrolyte flow rate, is conceivable when one considers that the voltage stabilization time of an individual cell depends on the velocity of the electrolyte passing through it. In the scheme with parallel connection of cells this velocity (total flow rate divided by the number of elements) is considerably lower than with series connection (where it is equal to the total flow rate).

Comparison of this parameter for the stabilization schemes employing continuous flow-circulation and continuous flow with parallel connection of cells is illustrated in Fig. 4 (to save space, the appropriate relations that can be simply obtained from eqns. (39) and (41) are not given).

As would be expected, the use of an auxiliary tank containing working solution for the continuous flow-circulation scheme increases the voltage stabilization time as compared with stabilization by the continuous flow scheme. This difference becomes more pronounced as the volume of the tank increases, while with increase in the circulation number it becomes less pronounced, approaching at the limit ( $K \gg 1$ ) a constant value. (Thus for  $k = V_t/N_{opt}$ ,  $V = 1$ , the ratio of the quantities compared in each version of the continuous flow-circulation scheme approaches 2.) However, while for the first version of the continuous flow-circulation scheme, in the whole

range of possible ratios,  $U_o/U_{cr}$ , and for the second version at  $U_o/U_{cr} < 2$ , this function is increasing, for the second version at  $U_o/U_{cr} > 2$  it is decreasing.

So, as far as the optimized parameters (electrolyte flow rate and effective voltage stabilization time) are concerned, the procedure employing the continuous flow scheme with electrolytically series connection of cells is superior to that using the continuous flow scheme with parallel connection of cells, followed by the one with the continuous flow-circulation scheme of electrolyte supply.

#### 4. Conclusions

Finally, we shall attempt to determine the net energy losses relating to a particular method of voltage stabilization. In a general form (ignoring the design of a cell or battery) such an estimation is possible only on certain assumptions, it is comparative and, hence, cannot pretend to be exhaustive.

Net power losses for electrolyte pumping through the battery of fuel cells may be calculated as

$$P_b^1 = q \sum_i \Delta p_i, \quad (63)$$

where  $\Delta p_i$  is the pressure drop along the  $i$ th section of the electrolyte duct.

Basic assumptions used below are:

- (1) Pressure losses in a cell depend only on local resistances (inlet, outlet, and relevant expansion and contraction of the electrolyte flow);
- (2) pressure losses due to local resistances at junctions between the cells or between the cells and the input and output collectors are neglected because of uncertainty concerning their values. However, it should be remembered that, with uniform electrolyte supply over the cells, these losses may be appreciable.

With these assumptions, power losses for electrolyte pumping through an individual cell will be

$$P^1 = u_{con} \zeta \rho v^2 / 2 = u_{con} \zeta \rho (u_{con} / S_{cq})^2 = \zeta^* u_{con}^3, \quad (64)$$

where  $\zeta^*$  is the generalized coefficient of local cell resistance and  $u_{con}$  is the volumetric flow rate of the electrolyte through the cell.

Then, the power losses for a battery of fuel cells with voltage stabilized using the suggested methods are determined by the following explicit expressions:

$$(P_b^1)^- = \zeta^* (q^-)^3 / N^2 \quad (65)$$

and

$$(P_b^1)^{--} = N \zeta^* (q^{--})^3. \quad (66)$$

Substituting expressions (46') and (51), (49) and (52), (55') and (56'), respectively, into eqns. (65) and (66) and comparing them gives

at  $1 < U_o/U_{cr} < 2$

$$(P_b^1)^{-}/(P_b^1)^{-} = 16(P/IIU_{cr})^3/(U_o/U_{cr} + 1)^4, \quad (67)$$

at  $U_o/U_{cr} \geq 2$

$$(P_b^1)^{-}/(P_b^1)^{-} = (U_o/U_{cr})^4(P/IIU_{cr})^3/(U_o/U_{cr} + 1)^4(U_o/U_{cr} - 1)^3. \quad (68)$$

The analysis of these relations shows that for the whole range of possible ratios of the initial to ultimate cell voltages, the power losses to provide battery voltage stabilization with the continuous flow scheme (with electrolytically series connection of cells) exceed the corresponding losses when using the same scheme but with parallel connection of the cells. With increasing voltage ratio this excess decreases from  $(P/IIU_{cr})^3$  to  $(P/IIU_o)^3$ .

Thus, within the accuracy of the above assumptions, and depending on the absolute values of the net power losses considered, it may turn out that, contrary to the conclusion arrived at above, the method employing the continuous flow scheme with electrolytically parallel cell connections will be the best in respect of the electrolyte flow rate. Therefore, a final choice of the voltage (power) stabilization method must take into account the net power losses for its implementation.

### List of symbols

$\tau$	Time.
$\tau_{ic}^i$	Duration of the "interchange cycle".
$\tau_{st}$	Effective time of voltage stabilization.
$\tau_b$	Time constant of battery and auxiliary tank.
$\tau_c$	Time constant of cell.
$U(\tau)$	Characteristic function of cell voltage, $U$ .
$U_{cr}$	Admissible working voltage.
$U_c^\infty$	Steady state cell voltage.
$U_b^\infty$	Steady state battery voltage.
$c^j(\tau)$	Characteristic function of the concentration of the $j$ th component of the electrolyte. $j$ equals $r$ for reactant and $p$ for product.
$c_{cr}^j$	Critical concentration of either electrolyte component (mol/l).
$c_{in}^j$	Concentration of the $j$ th solution component at the fuel cell inlet (mol/l).
$\gamma_j$	Effective electrochemical equivalent in mol/A h, subscript $r$ for reactant, subscript $p$ for product.
$V$	Volume of electrolyte in a fuel cell.
$V_t$	Volume of electrolyte in auxiliary tank.
$I$	Load current.
$P$	Battery power.

$N$	Number of cells in the battery.
$n$	Cell number.
$\epsilon\%$	Difference of cell voltage from steady state value.
$U_m$	Arithmetic mean of initial and critical voltages.
$u_{con}$	Continuous electrolyte flow rate (l/h).
$u_c$	Rate of circulation.
$K$	Circulation number, $u_c/u_{con}$ .
$q^=$	Volumetric flow rate/hour, electrolytically parallel connection.
$q^{--}$	Volumetric flow rate/hour, electrolytically series connection.
$\Delta p_i$	Pressure drop along the $i$ th section of the electrolyte duct.
$\xi^*$	Generalised coefficient of local resistance.
	Subscript o initial value, subscript cr admissible or critical value, subscript or superscript $\infty$ steady state value.

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