Estimation of Thermal Losses of Regenerative Fuel Cells from Cycling Data

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MUCH USEFUL information can be deduced about the performance of a regenerative fuel cell from a simple thermodynamic analysis of the cycling data. This article describes a simple, approximate method to estimate thermal energy losses from fuel cell cycling data. Cycling data for a regenerative hydrogen-oxygen, ion-exchange membrane fuel cell are used to illustrate the method. A brief description of this fuel cell, previously described in detail *(1-6)*, follows.

FUEL CELL

This fuel cell is primarily being developed as a component for space power systems. Its feasibility for operation in the environment of outer space has already been demonstrated.

The electrolyte is an anionic membrane which is saturated with 30% aqueous KOH. Platinum black electrodes on each side of the membrane are held in place by nickel screens which also serve as the current collectors.

The over-all anode and cathode reactions during discharge are given, respectively, by Reactions 1 and 2.

$$H_2 + 2OH^- \rightarrow 2H_2O + 2e \qquad (1)$$

$$\tfrac{1}{2}O_2 + H_2O + 2e \rightarrow 2OH^- \qquad (2)$$

The over-all cell reactions during discharge and charge are summarized in Reaction 3.

$$H_2 + \tfrac{1}{2}O_2 \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftharpoons}} H_2O(1) + \text{energy} \qquad (3)$$

As in most chemical batteries, the discharge reaction is exothermic, and most of the heat will be generated during the discharge portion of the charge-discharge cycle.

CYCLING DATA

Some typical cycling data which were obtained with small single cells are given in Table I. These data represent two different sets of cycling conditions. The electrochemical and and energy efficiencies were about 100 and 50%, respectively, in Experiment 1. The electrochemical efficiency in Experimental 2 was about 90%; the energy efficiency decreased sharply with time.

These test cells contained membranes and electrodes that were each 4 inches in diameter. The hydrogen and oxygen pressures were about 100 p.s.i.g. at the beginning of discharge and 60 p.s.i.g. at the end of discharge. These fuel cells can be discharged to atmospheric pressure without any serious decreases in performance. They were operated at room temperature during these experiments. The ambient temperature was about 25° C., and the internal temperature of the cells was only slightly higher than this value. The thermal design of this type of cell is sufficient to maintain the internal cell temperature reasonably constant.

THERMODYNAMIC ANALYSIS

Two thermodynamic relations that are important to fuel cells are

$$\Delta F = \Delta H - T\Delta S \qquad (4)$$

$$-\Delta F = n_e f E_r \qquad (5)$$

The change in enthalpy represents the total energy change that occurs during a chemical reaction. The change in free energy is the maximum energy from the reaction that is available as electrical energy. $T\Delta S$ is that portion of the enthalpy that cannot be converted to electrical energy and is the minimum amount of heat that is released during discharge. The theoretical thermal efficiency, $\Delta F/\Delta H$, of the hydrogen-oxygen fuel cell at room temperature is 0.83 (based on Reaction 3).

Equation 5 relates the free energy and the reversible electromotive force. The reversible electromotive force of the hydrogen-oxygen fuel cell at room temperature is 1.23 volts.

The electrical energy losses that occur in a single cell during charge (L_c) and discharge (L_d) are given, respectively, by Equations 6 and 7.

$$L_c = W_c - n_c\Delta H \qquad (6)$$

$$L_d = n_d\Delta F - W_d \qquad (7)$$

These losses are due to polarization effects, side reactions, internal resistances, and other factors. The electrical energy put into the fuel cell during charge (W_c) and the electrical energy taken out during discharge (W_d) are related to the cycling parameters by Equations 8 and 9, respectively.

$$W_c = E_c I_c t_c \qquad (8)$$

$$W_d = E_d I_d t_d \qquad (9)$$

Table I. Cycling Data

			Charge			Discharge				
Expt.	Exptl. Cell	Cycle	Voltage, v.	Current, amp.	Time, hr.	Voltage, v.	Current, amp.	Time, hr.	El. Eff.,[a] %	E. Eff.,[b] %
1	12-A-8	20	1.59	1.20	0.65	0.85	1.26	0.62	100	54
		99	1.56	1.20	0.58	0.82	1.20	0.57	98	50
		175	1.62	1.20	0.62	0.84	1.20	0.58	96	49
2	12-A-11	13	1.60	0.25	4.17	0.83	0.95	1.00	91	47
		246	1.62	0.25	3.83	0.69	0.85	1.00	89	38
		664	1.70	0.26	3.17	0.60	0.73	1.00	90	31

[a] Electrochemical efficiency = $(I_d t_d / I_c t_c)$. [b] Energy efficiency = $(E_d I_d t_d / E_c I_c t_c)$.

Table II. Analysis of Cycling Data

	Charge				Discharge						
Cycle	W_c, watt-hr.	$n_c\Delta H$, watt-hr.	L_c, watt-hr.	$\frac{L_c}{W_c}$, %	W_d, watt-hr.	$n_d\Delta F$, watt-hr.	L_d, watt-hr.	$\frac{L_d}{n_d\Delta F}$, %	$n_d\Delta H$, watt-hr.	$\frac{L_d}{n_d\Delta H}$, %	$\frac{L_d + n_dT\Delta S}{n_d\Delta H}$ %
					Cell 12-A-8						
20	1.24	1.15	0.09	7	0.664	0.962	0.298	31	1.16	26	43
99	1.09	1.03	0.06	6	0.562	0.836	0.274	33	1.01	27	44
175	1.21	1.08	0.13	11	0.584	0.848	0.264	31	1.02	26	43
					Cell 12-A-11						
13	1.67	1.53	0.14	8	0.788	1.17	0.38	32	1.40	27	44
246	1.55	1.41	0.14	9	0.567	1.04	0.45	43	1.25	36	53
664	1.40	1.22	0.18	13	0.438	0.897	0.459	51	1.08	42	59

The total energy loss (W_t) that occurs during a complete cycle is

$$W_t = W_c - W_d = L_d + L_c + n_dT\Delta S \qquad (10)$$

This equation is derived on the assumption that n_c and n_d are equal. Since the electrochemical efficiencies are 90 to 100%, this is a reasonable assumption.

Analysis of the cycling data is summarized in Table II. W_c is calculated from the data in Table I with Equation 8. $n_c\Delta H$ is readily calculated by Equation 11.

$$n_c\Delta H = \frac{79.2\ I_ct_c}{53.7} = 1.47\ I_ct_c \qquad (11)$$

The molar enthalpy of Reaction 3 at room temperature is 79.2 watt-hours and 1 mole of water is electrolyzed by the passage of 53.7 ampere hours of electricity. L_c is readily obtained from Equation 6. The discharge calculations are made in a similar manner. W_d is calculated from Equation 9 and $n_d\Delta F$ from Equation 12.

$$n_d\Delta F = \frac{65.8\ I_dt_d}{53.7} = 1.23\ I_dt_d \qquad (12)$$

The molar free energy of Reaction 3 is 65.8 watt-hours at room temperature. L_d is calculated from Equation 7; $n_d\Delta H$ and $n_dT\Delta S$ are calculated by Equations 13 and 14, respectively.

$$n_d\Delta H = 1.47\ I_dt_d \qquad (13)$$

$$n_dT\Delta S = \frac{13.5\ I_dt_d}{53.7} = 0.251\ I_dt_d \qquad (14)$$

The molar value of $T\Delta S$ for Reaction 3 at room temperature is 13.5 watt-hours.

During charge, the energy losses are about 10% of the total electrical energy put into the fuel cell. These losses are probably associated with the high polarization of the oxygen electrode during the electrolysis of water. Only about 70% of the free energy is converted to electrical energy during discharge. The total energy losses ($L_d + n_dT\Delta S$) during discharge are about 50% of total energy ($n_d\Delta H$) of the reaction. A large portion of these losses are due to the exothermic nature of the discharge reaction.

The internal resistance of this type of ion-exchange membrane fuel cell is relatively high. The resistivities of the membranes saturated with aqueous KOH are about twice that of the free electrolyte.

The analytical method described in this article provides a simple and rapid means to calculate the energy losses of a regenerative hydrogen-oxygen fuel cell from cycling data. These losses generally show up as heat: the quantitative thermal information is useful in the design of this type of fuel cell.

The illustrative data given in this article are for a particular regenerative hydrogen-oxygen fuel cell and the specific conclusions are applicable only to that fuel cell. The analytical method, however, is valid for many types of regenerative fuel cells and batteries.

NOMENCLATURE

E_c = charge voltage
E_d = discharge voltage
E_r = reversible e.m.f. of cell
ΔF = change in free energy
f = faraday
ΔH = change in enthalpy
I_c = charge current
I_d = discharge current
L_c = energy losses during charge
L_d = energy losses during discharge
n_e = numerical constant ($n = 2$ for Reaction 3)
n_c = moles of H_2 produced during charge
n_d = moles of H_2 consumed during discharge
ΔS = change in entropy
T = absolute temperature
t_c = charge time
t_d = discharge time
W_c = electrical energy consumed during charge
W_d = electrical energy produced during discharge

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RECEIVED for review April 2, 1962. Accepted July 10, 1962.