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A Comparison between Flow-through and
Flow-by Porous Electrodes for Redox Energy Storage

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Abstract

An a priori economic comparison is made between two electrode configurations for flow redox battery applications: (i) the flow-through configuration (current parallel to the fluid flow) and (ii) the flow-by configuration (current perpendicular to the fluid flow). Steady-state computer models are developed for each electrode system. These models are used to predict current density, cell voltage, and power density over a complete cycle (charge and discharge). The economic comparison is made by optimizing each configuration with respect to an objective function appropriate for this application. In this case, only the variable costs are considered. The results of the optimization show that the flow-by configuration is superior. The flow-through configuration not only yields a lower return on investment, but it is impractical due to a requirement of extremely low flow rates ($Re < 0.001$). Its failure is due to current flow (and ohmic potential drop) in the same direction as the fluid flow.

INTRODUCTION

In the post "energy crisis" years the ability of electric utilities to meet peak power demands economically has become increasingly acute. One answer to this problem is to store off-peak power and to recover this power during high demand periods (power load-leveling). Energy storage requirements for electric utilities may be met in several ways. The numerous advantages of flow-redox batteries (Thaller [1,2], Beccu [3], and Kangro [4,5] have been discussed by Yao and Birk [6], and Warshay and Wright [7]). Some particularly attractive features are listed below:

- 1) Unlimited cycle life regardless of the depth of discharge because redox reactions do not affect the morphology of the electrode material.
- 2) Simple electrode reactions.
- 3) High temperatures not required.
- 4) Minimal environmental impact.
- 5) Readily available reagents and materials of construction.

Preliminary capital cost estimates and size estimates for an iron/titanium $[\text{Ti(III)}|\text{Ti(IV)}||\text{Fe(III)}|\text{Fe(II)}]$ redox battery indicate economic viability for the system (Warshay and Wright [7]). Many other redox couples have been suggested (Thaller [1,2], Beccu [3], Giner, Swette, and Cahill [8], and Kangro [4,5]). Of these, the iron/chromium system $[\text{Cr(III)}|\text{Cr(II)}||\text{Fe(III)}|\text{Fe(II)}]$ appears to be the most promising. Recently, the NASA-Lewis Research Center, using an iron/chromium cell, has achieved a power density of approximately 915 W

per square meter of membrane separator (Gahn and Hagedorn [9]).

Two basic electrode configurations have been proposed for flow-redox batteries. Kangro [4,5] has suggested an electrode configuration where the current and fluid flow are in parallel (flow-through configuration, see Figure 1a and b). Thaller [1,2] and Beccu [3] have suggested a cell configuration where the current is perpendicular to the fluid flow and a separator is essential (flow-by configuration, see Figure 1c). The flow-through configuration (Figure 1a and b) has the advantage over the flow-by configuration (Figure 1c) that a separator is not required; however, a major disadvantage of this configuration can be seen in Figure 1b. Consider an iron/titanium cell. On discharge the unreacted Ti(III) and Fe(III) would be lost according to the reaction

when the streams are allowed to mix after flowing through the porous electrodes (Newman [10]).

The purpose of this paper is to compare, on an economic basis, the performance of the two configurations for redox-energy storage. As mentioned above, Warshay and Wright [7] have made preliminary capital cost estimates for the two-tank, flow-by configuration. The flow-by configuration is usually considered to be either a two-tank or a four-tank system. The flow-through configuration is primarily a three-tank system. The two-tank flow-by configuration can also be operated with a time varying superficial velocity, whereas, the other systems cannot due to their single-pass operation (Thaller [1]). (By single-pass operation

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Figure 1. Various configurations of electrode placement relative to the direction of fluid flow. a and b are the flow-through configuration on charge and discharge. c is the flow-by configuration.

we mean the reactants on each half cycle pass through the electrode only once.)

The perspective here is to compare the steady-state performance of two operational redox storage systems:

- 1) the flow-through configuration (current parallel to the fluid flow);
- 2) the flow-by configuration (current perpendicular to the fluid flow). The basis for comparison is the return on investment based on operating costs.

FLOW-THROUGH POROUS ELECTRODES

The analysis for a redox reaction is similar to that presented by Trainham and Newman [11,12] for a metal-deposition reaction. However, if the dimensional analysis also presented by Trainham and Newman [11,12] is to be used, separate analyses must be considered for both a cathodic limiting reactant and an anodic limiting reactant.

Cathodic reactant. The Butler-Volmer equation may be written as (Newman and Tiedemann [13] and Trainham and Newman [11])

$$i_{nR} = i_{oR,ref} \left\{ \frac{c_{Pw}}{c_{Pf}} \exp \left[\frac{\alpha a R F}{RT} (\Phi_1 - \Phi_2) \right] - \frac{c_{Rw}}{c_{Rf}} \exp \left[- \frac{\alpha c R F}{RT} (\Phi_1 - \Phi_2) \right] \right\}, \quad (2)$$

where $i_{oR,ref}$ is the value of the exchange current density at reference compositions $c_{R,ref}$ and $c_{P,ref}$. The reference electrode used in measuring Φ_2 is of the same kind as the redox reaction, and the

concentration of the reactant and product species in the reference electrode compartment, c_{Rr} and c_{Pr} , and the reference concentrations $c_{R,ref}$ and $c_{P,ref}$, have been set equal to c_{Rf} and c_{Pf} (the upstream feed concentration of the redox couple). It is also assumed that $s_R = -1$ and $s_P = 1$.

If axial diffusion is small compared to axial dispersion or if the diffusion coefficients of the reactant and product species are equal, the local concentration of the product species within the pores is simply related to the local reactant concentration within the pores and the feed concentration

$$c_P = c_{Rf} + c_{Pf} - c_R \quad (3)$$

Also, for a redox couple, the wall fluxes of the reactant and product species are equal and opposite

$$k_{mR}(c_R - c_{Rw}) = -k_{mP}(c_P - c_{Pw}) \quad (4)$$

One can now write c_{Pw} in terms of c_R and c_{Rw} with the use of equation 3 as

$$\frac{c_{Pw}}{c_{Pf}} = 1 + \frac{c_{Rf}}{c_{Pf}} - \frac{c_R}{c_{Pf}} \left(1 - \frac{k_{mR}}{k_{mP}} \right) - \frac{k_{mR}}{k_{mP}} \frac{c_{Rw}}{c_{Pf}} \quad (5)$$

This equation allows the explicit dependence of the product species concentration on the local reaction rate to be removed from equation 2 with the result:

$$i_{nR} = i_{oR,ref} \left\{ \left[1 + \frac{1}{c_{Pf}} \left(c_{Rf} - c_R \left(1 - \frac{k_{mR}}{k_{mP}} \right) - \frac{k_{mR}}{k_{mP}} c_{Rw} \right) \right] \exp \left(\frac{\alpha_{aR} F}{RT} \eta \right) - \frac{c_{Rw}}{c_{Rf}} \exp \left(- \frac{\alpha_{cR} F}{RT} \eta \right) \right\}, \quad (6)$$

where $\eta = \phi_1 - \phi_2$. Only one differential material balance is now required--that for the cathodic reactant. If the cathodic reactant R participates only in the primary reaction, then

$$i_{nR} = - \frac{nF}{s_R} j_{Rn} = \frac{nF}{s_R} k_m (c_R - c_{Rw}). \quad (7)$$

The elimination of c_{Rw} between equations 6 and 7 results in the equation

$$j_{Rn} = - \frac{\frac{c_R}{c_{Rf}} - \left(1 + \frac{c_{Rf} - c_R}{c_{Pf}} \right) \exp \left[\frac{(\alpha_{aR} + \alpha_{cR}) F}{RT} \eta \right]}{\frac{1}{k_{mR} c_{Rf}} - \frac{nF}{s_R i_{oR,ref}} \exp \left(\frac{\alpha_{cR} F}{RT} \eta \right) + \frac{1}{k_{mP} c_{Pf}} \exp \left[\frac{(\alpha_{aR} + \alpha_{cR}) F}{RT} \eta \right]} \quad (8)$$

A material balance equation for the case of a cathodic limiting reactant is then obtained by substituting the above equation for j_{Rn} into the continuity equation (Newman and Tiedemann [13])

$$v \frac{dc_R}{dx} = \epsilon (D_R + D_a) \frac{d^2 c_R}{dx^2} + a j_{Rn}, \quad (9)$$

with the result

$$v \frac{dc_R}{dx} = \varepsilon(D_R + D_a) \frac{d^2 c_R}{dx^2}$$

$$-a \frac{\frac{c_R}{c_{Rf}} - \left(1 + \frac{c_{Rf} - c_R}{c_{Pf}}\right) \exp\left[\frac{(\alpha_{aR} + \alpha_{cR})F}{RT} \eta\right]}{\frac{1}{k_{mR}c_{Rf}} - \frac{nF}{s_{R^i oR, ref}} \exp\left[\frac{\alpha_{cR}F}{RT} \eta\right] + \frac{1}{k_{mP}c_{Pf}} \exp\left[\frac{(\alpha_{aR} + \alpha_{cR})F}{RT} \eta\right]} \cdot (10)$$

If the same assumptions are made about the side reaction as made by Trainham and Newman [11] (i.e., mass transfer resistance is unimportant and no explicit dependence of the rate on composition), an equation can be derived for the local overpotential:

$$\frac{d^2 \eta}{dx^2} = \left(\frac{1}{\kappa} + \frac{1}{\sigma}\right) a \left\{ i_{oS, ref} \left[\exp\left(\frac{\alpha_{aS}F}{RT} (\eta - \Delta U)\right) - \exp\left(-\frac{\alpha_{cS}F}{RT} (\eta - \Delta U)\right) \right] \right.$$

$$\left. - \left(-\frac{nF}{s_R}\right) \frac{\frac{c_R}{c_{Rf}} - \left(1 + \frac{c_{Rf} - c_R}{c_{Pf}}\right) \exp\left[\frac{(\alpha_{aR} + \alpha_{cR})F}{RT} \eta\right]}{\frac{1}{k_{mR}c_{Rf}} - \frac{nF}{s_{R^i oR, ref}} \exp\left[\frac{\alpha_{cR}F}{RT} \eta\right] + \frac{1}{k_{mP}c_{Pf}} \exp\left[\frac{(\alpha_{aR} + \alpha_{cR})F}{RT} \eta\right]} \right\} \cdot (11)$$

Equations 10 and 11 can be expressed in dimensionless form by introducing the dimensionless coordinate $y = ak_m x/v$, the dimensionless concentration $\theta = c_R/c_{Rf}$, and the dimensionless overpotential η' :

$$\exp(\eta') = - \frac{nFk_m c_{Rf}}{s_{R^i oR, ref}} \exp(\alpha_{cR} F \eta / RT): \quad (12)$$

Material balance

$$\frac{d\theta}{dy} = D' \frac{d^2\theta}{dy^2} - \frac{\theta - (1 + \frac{1-\theta}{\theta_{Pf}}) P_1 \exp[(1 + \alpha_{aR}/\alpha_{cR})\eta']}{1 + \exp(\eta') + P_1 P_7 / \theta_{Pf} \exp[(1 + \alpha_{aR}/\alpha_{cR})\eta']} \quad (13)$$

Charge balance

$$\begin{aligned} \frac{d^2\eta'}{dy^2} = P_2 \left\{ P_3 \exp(-\alpha_{cS}\eta'/\alpha_{cR}) \left[1 - P_4 \exp\left(\frac{\alpha_{aS} + \alpha_{cS}}{\alpha_{cR}} \eta'\right) \right] \right. \\ \left. + \frac{\theta - \left(1 + \frac{1-\theta}{\theta_{Pf}}\right) P_1 \exp[(1 + \alpha_{aR}/\alpha_{cR})\eta']}{1 + \exp(\eta') + P_1 P_7 / \theta_{Pf} \exp[(1 + \alpha_{aR}/\alpha_{cR})\eta']} \right\}. \quad (14) \end{aligned}$$

The dimensionless parameters D' , P_1 , P_2 , P_3 , and P_4 are the same as those defined by Trainham and Newman [11]. The additional parameters P_7 and θ_{Pf} are given by

$$P_7 = k_{mR}/k_{mP}, \quad (15)$$

$$\theta_{Pf} = c_{Pf}/c_{Rf}. \quad (16)$$

Anodic reactant. For an anodic reactant, equation 2 is expressed as

$$i_{nR} = i_{oR,ref} \left\{ \frac{c_{Rw}}{c_{Rf}} \exp\left[\frac{\alpha_{aR} F}{RT} (\Phi_1 - \Phi_2)\right] - \frac{c_{Pw}}{c_{Pf}} \exp\left[-\frac{\alpha_{cR} F}{RT} (\Phi_1 - \Phi_2)\right] \right\}. \quad (17)$$

Equation 5 can then be used to eliminate c_{pw}/c_{pf} in equation 17. By following the same procedures used in deriving equation 10, a material balance equation for an anodic limiting reactant is obtained:

$$v \frac{dc_R}{dx} = \varepsilon(D_a + D_R) \frac{d^2 c_R}{dx^2}$$

$$-a \frac{\frac{c_R}{c_{Rf}} - \left(1 + \frac{c_{Rf} - c_R}{c_{Pf}}\right) \exp \left[-\frac{(\alpha_{aR} + \alpha_{cR})F}{RT} \eta\right]}{\frac{nF}{s_{RoR,ref}} \exp \left[-\frac{\alpha_{aR}F}{RT} \eta\right] + \frac{1}{k_{mR}c_{Rf}} + \frac{1}{k_{mP}c_{Pf}} \exp \left[-\frac{(\alpha_{aR} + \alpha_{cR})F}{RT} \eta\right]} \quad (18)$$

Consequently, the charge balance equation becomes

$$\frac{d^2 \eta}{dx^2} = \left(\frac{1}{\kappa} + \frac{1}{\sigma}\right)_a \left\{ i_{oS,ref} \left[\exp \left(\frac{\alpha_{aS}F}{RT} (\eta - \Delta U) \right) - \exp \left(-\frac{\alpha_{cS}F}{RT} (\eta - \Delta U) \right) \right] \right.$$

$$\left. - \left(-\frac{F}{s_R} \right) \frac{\frac{c_R}{c_{Rf}} - \left(1 + \frac{c_{Rf} - c_R}{c_{Pf}}\right) \exp \left[-\frac{(\alpha_{aR} + \alpha_{cR})F}{RT} \eta\right]}{\frac{nF}{s_{RoR,ref}} \exp \left[-\frac{\alpha_{aR}F}{RT} \eta\right] + \frac{1}{k_{mR}c_{Rf}} + \frac{1}{k_{mP}c_{Pf}} \exp \left[-\frac{(\alpha_{aR} + \alpha_{cR})F}{RT} \eta\right]} \right\} \quad (19)$$

Equations 18 and 19 can now be put into forms identical to equations 13 and 14. This is accomplished by introducing into equations 18 and 19 a dimensionless local overpotential based on the anodic reactant (compare with equation 12 for the cathodic reactant):

$$\exp(\eta^{*'}) = -\frac{nFk_{mR}c_{Rf}}{s_{RoR,ref}} \exp(-\alpha_{aR}F\eta/RT), \quad (20)$$

along with the dimensionless coordinate y and the dimensionless concentration θ to yield

Material balance

$$\frac{d\theta}{dy} = D' \frac{d^2\theta}{dy^2} - \frac{\theta - (1 + \frac{1-\theta}{\theta_{Pf}})P'_1 \exp[(1 + \alpha_{aR}/\alpha_{cR})\eta^{*'}]}{1 + \exp(\eta^{*'}) + P'_1 P_7 / \theta_{Pf} \exp[(1 + \alpha_{aR}/\alpha_{cR})\eta^{*'}]} , \quad (21)$$

Charge balance

$$\begin{aligned} \frac{d^2\eta^{*'}}{dy^2} = P'_2 \left\{ P'_3 \exp(-\alpha_{cS}\eta^{*'} / \alpha_{aR}) \left[1 - P'_4 \exp\left(\frac{\alpha_{aS} + \alpha_{cS}}{\alpha_{cR}} \eta^{*'}\right) \right] \right. \\ \left. + \frac{\theta - \left(1 + \frac{1-\theta}{\theta_{Pf}}\right) P'_1 \exp[(1 + \alpha_{cR}/\alpha_{aR})\eta^{*'}]}{1 + \exp(\eta^{*'}) + P'_1 P_7 / \theta_{Pf} \exp[(1 + \alpha_{cR}/\alpha_{aR})\eta^{*'}]} \right\} , \quad (22) \end{aligned}$$

where the dimensionless parameters are defined as

$$P'_1 = \left(\frac{s_{R\ oR,ref}^{i}}{nFk_{mR}c_{Rf}} \right)^{1+\alpha_{cR}/\alpha_{aR}} , \quad (23)$$

$$P'_2 = - \frac{\alpha_{aR} nF^2 v^2 c_{Rf}}{s_{R\ ak\ mR} RT} \left(\frac{1}{\kappa} + \frac{1}{\sigma} \right) , \quad (24)$$

$$P'_3 = \frac{s_{R\ oS,ref}^{i}}{nFk_{mR}c_{Rf}} e^{-\alpha_{aS} F \Delta U / RT} \left(\frac{nFk_{mR}c_{Rf}}{s_{R\ oR,ref}^{i}} \right)^{\alpha_{aS}/\alpha_{aR}} , \quad (25)$$

$$P'_4 = \left(\frac{s_{R,ref}^i}{nFk_{mR}c_{Rf}} \right)^{\frac{\alpha_{aS} + \alpha_{cS}}{\alpha_{aR}}} \exp[(\alpha_{aS} + \alpha_{cS})F\Delta U/RT] . \quad (26)$$

These parameters correspond to the dimensionless variables defined previously by Trainham and Newman [11] for the cathodic reactant (e.g. P_1 for the cathodic reactant corresponds to P'_1 for the anodic reactant).

Boundary conditions. Before equations 13 and 14 or equations 21 and 22 can be solved simultaneously for θ and η' , or θ and η^{*} , respectively, four boundary conditions are required for each electrode configuration shown in Figure 2. For θ , the following conditions are applicable

$$\theta - D' \frac{d\theta}{dy} = 0 \quad \text{at } y = 0 \quad (27)$$

and

$$\frac{d\theta}{dy} = 0 \quad \text{at } y = \alpha L \quad (28)$$

which are the Danckwerts [14], Wehner-Wilhelm [15] conditions when axial diffusion and dispersion are included. The conditions on η' and η^{*} depend on electrode configuration and may be determined from Ohm's Law

$$\frac{d\eta}{dx} = \frac{d(\Phi_1 - \Phi_2)}{dx} = -\frac{i_1}{\sigma} + \frac{i_2}{\kappa} , \quad (29)$$

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Figure 2. Various configurations of counter-electrode placement and current collector placement relative to the direction of the fluid flow: (i) upstream counter-electrode, downstream current collector (UD), (ii) downstream counter-electrode, upstream current collector (DU), (iii) upstream counter-electrode, upstream current collector (UU), (iv) downstream counter-electrode, downstream current collector (DD). UD and UU are charging configurations, whereas DU and DD are discharge configurations. (See Trainham and Newman [12].)

and are tabulated in Table 1. On charge, the conditions for either the UD configuration or the UU configuration are applicable. On discharge, the conditions for either the DU configuration or the DD configuration apply [12]. The dimensionless parameters P_5 and P_6 for a cathodic reactant which arise in the analysis are related to P_2

$$P_5 = - \frac{\sigma P_2}{\sigma + \kappa} \quad (30)$$

and

$$P_6 = - \frac{\kappa P_2}{\sigma + \kappa} \quad (31)$$

so that

$$-P_2 = P_5 + P_6 . \quad (32)$$

For an anodic reactant, the conditions on $\eta^{*'}$ are of the same form as those given in Table 1 for η' , except that P_5 and P_6 should be replaced by P'_5 and P'_6 , which are defined as

$$P'_5 = - \frac{\sigma P'_2}{\sigma + \kappa} , \quad (33)$$

and

$$P'_6 = - \frac{\kappa P'_2}{\sigma + \kappa} , \quad (34)$$

so that

$$-P'_2 = P'_5 + P'_6 . \quad (35)$$

Table 1. Current and potential boundary conditions for various electrode configurations.

Electrode Configuration	$i_1(0)$	$i_1(L)$	$i_2(0)$	$i_2(L)$	$d\eta/dx _{x=0}$	$d\eta/dx _{x=L}$	$d\eta'/dy _{y=0}$	$d\eta'/dy _{y=\alpha L}$
UD	0	-i	-i	0	$-i/\kappa$	i/σ	$P_5 I^*$	$-P_6 I^*$
DU	i	0	0	i	$-i/\sigma$	i/κ	$P_6 I^*$	$-P_5 I^*$
UU	i	0	-i	0	$-i\left(\frac{1}{\sigma} + \frac{1}{\kappa}\right)$	0	$-P_2 I^*$	0
DD	0	-i	0	i	0	$i\left(\frac{1}{\sigma} + \frac{1}{\kappa}\right)$	0	$P_2 I^*$

Cycling procedure. A calculation procedure is needed so that system behavior can be predicted over a complete cycle (i.e., charge and discharge). The following procedure was used for the flow-through configuration.

1. The variables listed in Table 2 were set;
2. Equations 21 and 22 were solved for the positive electrode (subject to the UD configuration boundary conditions);
3. Equations 13 and 14 were then solved for the negative electrode (subject to the UD configuration boundary conditions);
4. The cell voltage on charge was then evaluated from the results of 2 and 3, which includes the ohmic drop in the gap between the electrodes given by $\Delta\Phi_{\text{gap}} = I_c L_{\text{gap}} / \kappa$;
5. Equations 21 and 22 and then equations 13 and 14 were solved for the positive electrode and the negative electrode, respectively; subject to the DU configuration and the following restrictions:
 - a. The feed concentrations for each electrode on charge and discharge are the same as the product concentrations on charge;
 - b. The superficial velocity on discharge $v_d = v_c t_c / t_d$, where $v_{d+} = v_{d-}$ and $t_c / t_d = 1$ in the calculations which follow;
 - c. The discharge current density was arbitrarily set at $I_d = 0.95 I_c$. (Note that I_d and I_c are negative for the cathode and positive for the anode);
6. The cell voltage on discharge is then calculated from the results of 5, which again includes the ohmic drop in the gap between the electrodes.

Table 2. Variables set on charge and conditions used in the calculations. + = positive electrode, - = negative electrode, c = charge, d = discharge

Variables set on charge		Conditions used in calculations
L_+ , L_-	electrode lengths for the positive electrode and the negative electrode	$L_+ = L_-$
v_{+c} , v_{-c}	superficial velocities for the positive electrode and the negative electrode	$v_+ = v_{-c}$
I_c	current density on charge	$I_c < 0$ for cathode
c_{+c} , c_{-c}	concentration of reactants on charge in the feed tank	$c_{+c} = c_{-c}$
c_{+d} , c_{-d}	concentration of products on charge in the feed tank	$c_{+d} = c_{-d}$ at equilibrium with c_{+c} and c_{-c}

From the above results the power on charge and discharge are calculated: $P_c = I_c V_c$ and $P_d = I_d V_d$. In the optimization procedure which follows in a later section I_c , I_d , and v are optimized with respect to an objective function appropriate for this system. I_d is optimized with the condition that cell operation on discharge is at the power maximum. This choice follows from the optimization because energy is lost due to mixing in the gap between the electrodes by equation 1.

FLOW-BY POROUS ELECTRODES

A flow-redox battery using flow-by porous electrodes (perpendicular current to fluid flow) can be modeled to include the following characteristics:

1. Each electrode exhibits linear polarization behavior; this is typical of a "practical" redox system because the exchange current densities are large.

2. The positive electrode and the negative electrode are both of length L (in the direction of fluid flow) with isotropic porosities ϵ_+ and ϵ_- and specific surface areas a_+ and a_- which remain constant in time; for a redox system no morphological changes occur in the electrode material.

3. The concentration variations in the direction of current flow are negligible.

4. The variation of potential in direction of fluid flow is negligible; this will be a good approximation except near the fluid inlet.

5. The hydrodynamics are characterized by superficial velocities v_+ and v_- and average mass-transfer coefficients k_{m+} and k_{m-} .
6. Only one electrode reaction occurs at each electrode.

It should be noted that the only other modeling work completed for this configuration is that done by Alkire and Ng [16,17]. Their model, which was applied specifically to metal-ion removal, included two-dimensional concentration variations and complete Butler-Volmer kinetics with a side reaction.

Analysis. The emphasis is on a simplified model which includes only the pertinent features of flow-by porous batteries. The results obtained illustrate the important features that would be observed with a more sophisticated approach.

Figure 3 shows a schematic of the flow-by configuration to be modeled. The cell potential V is defined to be the difference between the positive and negative current collectors

$$V = \phi_{1+}(d+) - \phi_{1-}(d-) , \quad (36)$$

which may be decomposed:

$$V = U_+^{\theta} - U_-^{\theta} + \frac{RT}{n_+ F} \ln \frac{c_{Ow}^+}{c_{Rw}^+} - \frac{RT}{n_- F} \ln \frac{c_{Ow}^-}{c_{Rw}^-}$$

open-circuit potential

Flow-by porous electrode configuration

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Figure 3. Flow redox cell with current flow perpendicular to the fluid flow.

$$\begin{aligned}
 & -i \left\{ \frac{d_+}{\kappa_+ + \sigma_+} \left[1 + \frac{2 + \left(\frac{\sigma_+}{\kappa_+} + \frac{\kappa_+}{\sigma_+} \right) \cosh v_+}{v_+ \sinh v_+} \right] \right. \\
 & \left. + \frac{d_-}{\kappa_- + \sigma_-} \left[1 + \frac{2 + \left(\frac{\sigma_-}{\kappa_-} + \frac{\kappa_-}{\sigma_-} \right) \cosh v_-}{v_- \sinh v_-} \right] + \frac{L_s}{\kappa_s} \right\}, \quad (37)
 \end{aligned}$$

surface overpotential and ohmic-potential drop

where 0 and R are the oxidized and reduced species of the redox couple and subscripts + and - denote the positive and negative electrode.

Equation 37 has been written for a positive value of i on discharge and a negative value of i on charge. The first term and the second term in brackets represent the total potential loss in each electrode in the direction of current flow, a combination of surface overpotential for linear kinetics and ohmic potential drop (Newman and Tiedemann [13]). The last term in brackets represents the ohmic potential drop across the separator.

In equation 37, v^2 is the dimensionless exchange current density for an electrode (Newman and Tiedemann [13])

$$v^2 = (\alpha_a + \alpha_c) \frac{aFd^2}{RT} \left(\frac{1}{\kappa} + \frac{1}{\sigma} \right) i_o. \quad (38)$$

It is assumed to have a composition dependence of the form

$$i_o = i_{o,ref} \prod_i \left(\frac{c_{iw}}{c_{i,ref}} \right)^{\gamma_i}, \quad (39)$$

where $i_{o,ref}$ is the value of the exchange current density at a reference composition $c_{i,ref}$. It is further assumed that the transfer coefficients α_a and α_c sum to n (in this case $n = 1$) for an electrode reaction of the form

and that the exponents γ_i have the dependence

$$\gamma_i = q_i + \frac{\alpha_c}{n} s_i \quad (41)$$

such that $q_i = -s_i = 1$ for a cathodic reactant and zero otherwise.

For $\alpha_a = \alpha_c = 0.5$, equation 38 becomes

$$v^2 = \frac{aFd^2}{RT} \left(\frac{1}{\kappa} + \frac{1}{\sigma} \right) i_{o,ref} \sqrt{\frac{c_{Ow} c_{Rw}}{c_{Of} c_{Rf}}}, \quad (42)$$

where $c_{i,ref}$ have been set equal to c_{if} (the upstream feed concentration of the oxidized and reduced species of a redox couple).

Material balances. Continuity equations for reactant and product species can be used to describe the variation of concentration and current density through the porous electrode. In addition, the electrode length may be calculated for set values of the cell voltage and utilization of the reactants. From these results, the power

densities on charge and discharge can be obtained.

To do this, the unknown wall concentration in equations 37 and 38 must be related to the bulk concentration of the oxidized species for the positive electrode. The wall concentrations c_{iw} and the bulk concentrations c_i are linked through the limiting current density relationship

$$c_{iw} = c_i (1 - i/i_L) , \quad (43)$$

where

$$i_L = F a d k_m c_i \quad (44)$$

is the limiting current density in the direction of current flow, which follows from Faraday's law (Newman and Tiedemann [13]):

$$a j_{in} = - \frac{s_i}{nF} \nabla \cdot \underline{i}_2 = \frac{s_i}{nF} \nabla \cdot \underline{i}_1 \quad (45)$$

or

$$F a k_m c_i = \overset{\text{neglect}}{\frac{\partial i_{1x}}{\partial x}} + \frac{\partial i_{1y}}{\partial y} \quad (46)$$

with $i_{1y}(d) = i_L$, $i_{1y}(0) = 0$, and $s_i = -1$.

The bulk and wall concentrations of the reduced and oxidized species in each electrode can be related through the pore-wall fluxes, since these fluxes are equal and opposite for a redox reaction:

$$k_{m0}(c_0 - c_{0w}) = - k_{mR}(c_R - c_{Rw}) . \quad (47)$$

Equations 43 and 47 can be combined to yield the reactant-wall concentrations in terms of the bulk concentrations and the limiting current

$$c_{Rw} = c_R + \frac{k_{m0}}{k_{mR}} \frac{i}{i_{L0}} c_0 . \quad (48)$$

The local bulk concentration of the reduced species is given by

$$c_R = c_{Of} + c_{Rf} - c_0 , \quad (49)$$

provided that diffusion in the x-direction is neglected (or $D_R = D_0$).

Equations 47, 48, and 49 relate the wall concentrations of the reduced and oxidized species to the bulk concentration of the oxidized species in each electrode.

The differential material balance for a species i may be simplified (owing to the assumptions stated previously):

$$v \left(\frac{\partial c_i}{\partial x} + \overset{\text{neglect}}{\frac{\partial c_i}{\partial y}} \right) = \frac{s_i}{nF} \left(\overset{\text{neglect}}{\frac{\partial i_{lx}}{\partial x}} + \frac{\partial i_{ly}}{\partial y} \right) . \quad (50)$$

An integration over y with $i_{ly}(d) = -i$ and $i_{ly}(0) = 0$, gives

$$vd \frac{dc_i}{dx} = - \frac{s_i}{nF} i . \quad (51)$$

It follows that for each electrode on discharge

$$d_+ v_+ F \frac{dc_{0+}}{dx} = - d_- v_- F \frac{dc_{R-}}{dx} = i , \quad (52)$$

or

$$c_{R-} = c_{Rf-} + \frac{d_+ v_+}{d_- v_-} (c_{0f+} - c_{0+}) \quad (53)$$

With the use of equations 43, 44, 48, 49, and 53, all the unknown compositions in equations 37 and 42 can be related to the differential material balance for the oxidized species in the positive electrode (equation 51). Either the electrode length can be calculated for a set superficial velocity and reactant utilization or the superficial velocity for a set electrode length and reactant utilization:

$$L = d_+ v_+ F \int_{c_{0+}}^{c_{0f+}} \frac{dc'_{0+}}{i} \quad (54)$$

or

$$v_+ = \frac{L}{d_+ F \int_{c_{0+}}^{c_{0f+}} \frac{dc'_{0+}}{i}} \quad (55)$$

COST ANALYSIS

An objective function must be specified in order to compare the performance of the flow-by and flow-through configuration on a sound economic basis. This objective function should relate the overall costs (capital, fixed, and variable costs) for an entire system to local variables, such as current density, cell voltage, and flow rate. However, for the comparison considered here, only the costs and system variables related to the net specific power of a particular configuration

are important. In this case, the objective function will be based solely on the variable costs. The terminology "net specific power" refers to the amount of power in watts per square meter recovered during the day, over and above that required to pay for the nighttime power. In general, the objective function should be constructed in terms of intensive variables, that is, independent of the separator or gap area (membrane area for the flow-by configuration; superficial-flow area for the flow-through configuration).

The simplified cost analysis presented here allows a quick evaluation of the two different electrode configurations. However, it must be emphasized that construction of large scale systems should be based on more detailed cost and performance evaluations.

Capital costs and fixed costs. In this particular study, the exact functional form for these costs is not important because it is assumed that the energy storage facilities are built and are operational. However, for the sake of completeness an approximate formulation will be given (see Newman [18]) for the case of variable, capital, and fixed costs.

The capital costs and the fixed costs in \$/year - m² for each configuration are assumed to have one value:

Flow-by

$$C'_{CF} = [(C_{A+} + C_{B+}^{d+}) + (C_{A-} + C_{B-}^{d-})]r + C'_F, \quad (56)$$

Flow-through

$$C'_{CF} = [(C_{A+} + C_{B+}^{L+}) + (C_{A-} + C_{B-}^{L-})]r + C'_F, \quad (57)$$

where C_{Bi} and C_{Ai} are the total costs per unit volume ($\$/m^3$) and total costs per superficial-electrode area ($\$/m^2$), respectively. The factor r (year^{-1}) represents the effect of interest, depreciation, and taxes. This factor should reflect the average lifetime of the components in the system. If the expected lifetime of the components depends significantly on the current density or cell voltage, this simplified treatment of capital costs would have to be modified.

The terms C'_F in equations 56 and 57 represent the fixed costs (i.e., labor, materials, and maintenance). This term is sometimes taken to be a fraction of the total capital investment plus the cost of labor. This assumes that the labor costs can be scaled with the superficial-electrode area.

Variable costs. The costs to be emphasized here are the power costs on charge and discharge, and the pumping costs. The variable costs also include materials makeup plus waste treatment, which may or may not be functions of the operating conditions. In any case, the relationships are not known, and it will therefore be assumed that these additional costs are negligible.

The variable costs ($\$/\text{year} - m^2$) are given by

Flow-by

$$C'_V S = \underbrace{I_c V_c t_c SC_{pN}}_{\text{charge}} - \underbrace{I_d V_d t_d SC_{pD}}_{\text{discharge}}$$

$$\begin{aligned}
 & + \frac{4.2 S}{\xi_p} \left[\frac{\mu_{+d+a+}^2}{\epsilon_+^3} (v_{+c}^2 t_c C_{pN} + v_{+d}^2 t_d C_{pD}) \right. \\
 & \quad \left. + \frac{\mu_{-d-a-}^2}{\epsilon_-^3} (v_{-c}^2 t_c C_{pN} + v_{-d}^2 t_d C_{pD}) \right] , \quad (58)
 \end{aligned}$$

pressure drop

Flow-through

$$\begin{aligned}
 C'_V S &= I_c V_c t_c SC_{pN} - I_d V_d t_d SC_{pD} \\
 & + \frac{4.2 S}{\xi_p} \left[\begin{array}{cc} \text{charge} & \text{discharge} \\ \frac{\mu_{+L+a+}^2}{\epsilon_+^3} (v_{+c}^2 t_c C_{pN} + v_{+d}^2 t_d C_{pD}) & \\ \\ \frac{\mu_{-L-a-}^2}{\epsilon_-^3} (v_{-c}^2 t_c C_{pN} + v_{-d}^2 t_d C_{pD}) & \end{array} \right] . \quad (59)
 \end{aligned}$$

pressure drop

The only difference between equations 58 and 59 is that the length of electrode over which the pressure drop occurs is explicit for the flow-through configuration and implicit for the flow-by configuration.

In equation 58, the electrode thicknesses (perpendicular to the direction of fluid flow) d_+ and d_- account for the fact that the

volumetric flow rate may be different for each electrode.

The factor S is the on-stream factor (either days operating per 365 days or operating cycles per year).

In equations 58 and 59, the pressure drop correlation used is for $Re = v/av < 1$ (see Bird et al. [19]). This is typical of the flow rates encountered in the cell stacks at NASA-Lewis for the flow-by configuration [9] and, as will be seen later, the optimum flow rates for the flow-through configuration typically give $Re < 0.001$.

As can be seen in equations 56 through 59, there is no optimum value for electrode length. An order of magnitude analysis of the terms in these equations indicates that practical systems can be built so that the pressure drop terms are small compared to the remaining terms. In the case of the flow-by configuration, the electrode length is determined by the desired conversion and the minimum flow rate which can be easily controlled in practice. Therefore, the variable costs for either configuration can be expressed as

$$C'_V S = P_c t_c SC_{pN} - P_d t_d SC_{pD}, \quad (60)$$

where $P_c = V_c I_c$ and $P_d = V_d I_d$.

The total cost of a redox system can now be given by

$$\frac{\text{cost}}{\text{year}} = [C'_{CF} + P_c t_c SC_{pN} - P_d t_d SC_{pD}] A_{\text{tot}}, \quad (61)$$

where A_{tot} is the total superficial electrode area of the system.

For the comparison considered here, only the variable costs C_{pN}

and C_{pD} , and the system variables related to these costs P_c , P_d , t_c , and t_d are important. The capital and fixed costs per unit superficial area can be optimized separately, and will not be considered further in this analysis.

Dimensional considerations indicate that only ratios of costs are needed to determine the optimum design and operating conditions. In this comparison only the ratio of the cost of daytime and nighttime power is important. Consequently, the objective function to be maximized can now be expressed as

$$NSP(W/m^2) = P_d - \frac{t_c}{t_d} CP_c, \quad (62)$$

where $C = C_{pN}/C_{pD}$.

OPTIMIZATION PROCEDURES AND RESULTS

To simplify the optimization, only the case where $v_c = v_d$ and $t_c = t_d$ will be considered. It is also convenient to equate the superficial velocities in each electrode $v_{+c} = v_{-c}$. With these assumptions, equation 62 becomes

$$NSP(W/m^2) = P_d - CP_c. \quad (63)$$

The method of optimization is different for each configuration. For the flow-through configuration, the net specific power is maximized over discharge current, charging current, and flow rate. For the flow-by configuration, it was only necessary to optimize the net specific

power with respect to the cell voltage on discharge in order to obtain a valid comparison with the results obtained for the flow-through configuration.

It was not necessary to optimize the flow-by configuration with respect to flow rate because the pressure drop is ignored in the objective function. Furthermore, this configuration can operate at any velocity with a corresponding change in electrode length. Also, because the effluent is isolated and side reactions are ignored, the number of coulombs passed on charge and discharge must balance, whereas with the flow-through configuration, extra charge is lost according to equation 1.

Chemical system. The results presented are for the Fe/Ti redox system. This chemical system was chosen because data on fundamental parameters, such as exchange current densities, solution conductivities, and viscosities were available (Giner et al. [8] and Miller [20], see Table 2). However, the values of the exchange current densities were not available on the electrode materials used in the cells at NASA-Lewis for which a power density of approximately 237 W/m^2 [9] was achieved for the Fe/Ti system.

The primary electrochemical reactions were assumed to be

and

The species assumed in these reactions are based on stability data (Baes and Mesmer [21], experimental measurements of open-circuit potentials (Reid and Gahn [22]), and secondary reference state quantities (Wagman [23]). For Ti(IV) the hydrolyzed species is expressed Ti(OH)_2^{2+} , as there is no strong evidence supporting the commonly written "titanyl" ion, TiO^{2+} (Baes and Mesmer [21]).

The flow-through model has provision for side reactions, and these were assumed to be evolution of hydrogen and chlorine

and

Flow-through configuration. As mentioned previously, this configuration was optimized with respect to discharge current density, charging current density, and flow rate, with equation 63 as a criterion. To simplify this procedure, and also to reduce computer costs, the charging current density I_c was set and the value of C (cost of night-time to daytime power) was eventually calculated for which this value of I_c was an optimum. This has the advantage, first of all, that the discharge current density can be optimized separately--operation is to be at the power maximum independent of the value of C . For this reason, the search is one-dimensional rather than three-dimensional.

To be more specific, two equations result for the cost ratio C when equation 63 is differentiated with respect to v at constant I_c and then with respect to I_c at constant v , setting the results equal

to zero

$$\frac{\partial P_d / \partial v}{\partial P_c / \partial v} = C, \quad (68)$$

$$\frac{\partial P_d / \partial I_c}{\partial P_c / \partial I_c} = C. \quad (69)$$

The procedure is to set I_c and guess a value for v ; calculate the derivatives in equations 68 and 69; while simultaneously adjusting the current density on discharge so that cell operation is at the power maximum. The procedure is repeated at a set I_c adjusting v until a plot can be made of equations 68 and 69 versus $I_c^* = I_c / nFvc_{Rf}$ (the current density on charge made dimensionless with the limiting current density that would exist for fluid velocity v if all the reactant in the feed were completely reacted) as shown in Figure 4. I_c^* is really a dimensionless substitute for v because I_c , n , F , and c_{Rf} are set. In Figure 4, the point of intersection of the two curves represents the value of the cost ratio for which I_c , I_d , and v are optimum. Figure 4 also shows that equation 68 is more dependent on v than equation 69.

Figure 5 shows that for an increase in optimum flow rate by a factor of 8.1, I_c increases by a factor of 20. This implies a greater utilization of the reactant species on charge at higher current densities. It should be noted that the optimum superficial velocity varied from $(0.961 \text{ to } 7.78) \cdot 10^{-5} \text{ cm/s}$ over the charging range

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Figure 4. Computer-aided graphical optimization procedure.

XBL 796-10068

Figure 5. Effect of charging current density on the reciprocal of the superficial velocity.

considered. However, these low velocities would probably be difficult to attain in practice.

Figure 6 shows that the cost ratio decreases with current density. Therefore, the higher the cost of daytime power relative to nighttime power, the higher the current density at which the system can be economically charged.

As might be expected from the previous graphs, Figure 7 shows that the ratio of the optimum current density recovered on discharge to that of the required charging current density, decreases with charging current density. Thus, the current efficiency is low. Also, a low value of C results in a low energy efficiency.

The decrease in the energy efficiency with current density on charge is clearly shown in Figure 8. At $I_c = 1 \text{ mA/cm}^2$, P_d/P_c is 0.6, whereas at $I_c = 20 \text{ mA/cm}^2$, P_d/P_c drops to 0.27.

The NSP (W/m^2) is shown in Figure 9 as a function of C . The NSP is much higher at low values of C .

Flow-by configuration. As mentioned previously, this configuration was optimized only with respect to the cell voltage on discharge. Again, optimization of the flow rate is unnecessary because the pressure drop contribution to the objective function is not included.

In order to compare the net specific power of the two systems, similar results as were obtained in Figure 9 are required. The values of V_d , v , and c_{OL} are set, and the electrode length is calculated from equations 37 and 54. Once L is known, a value of V_c that will recharge the cell to the initial concentrations can be calculated. The

XBL 796-10069

Figure 6. Effect of the charging current density on the cost ratio (nighttime to daytime power costs).

XBL 796-10067

Figure 7. Ratio of the optimum discharge current density to the charging current density versus the charging current density.

XBL 796-10066

Figure 8. Dependence of the power required on charge and power recovered on discharge as a function of the charging current density.

XBL 796-10065

Figure 9. Net specific power recovered by the flow-through configuration versus the cost ratio (nighttime to daytime power).

total current density, and consequently the power, for either charge or discharge can be obtained from

$$I_c = n_+ F v_d (c_{Rf} - c_{RL})_+ / L , \quad (70)$$

and

$$I_d = n_+ F v_d (c_{Of} - c_{OL})_+ / L . \quad (71)$$

A value for C is then determined for which V_d is an optimum from the equation

$$C = (\partial P_d / \partial V_d) / (\partial P_c / \partial V_d) , \quad (72)$$

and finally the net specific power is calculated with equation 63.

Equation 72 is analogous to equations 68 and 69 used for optimization of the flow-through reactor.

Figure 10 shows a comparison between the flow-through and flow-by configurations. Except for very high reactant utilization on discharge (< 90%), the flow-by configuration yields the greater return on investment.

In Figure 11, the effect of increasing the specific interfacial area and decreasing the electrode thickness is shown for the flow-by reactor. An increase in a by a factor of ten yields an increase in the performance by a factor of three. Similar results can be expected for the flow-through configuration.

XBL 796-10073

Figure 10. A comparison between the flow-by configuration and the flow-through configuration based on the net specific power recovered. The curve for the flow-through configuration is the same as that shown in Figure 9. The flow-by results are for the discharge feed compositions shown at various utilizations of reactant.

XBL 796-10072

Figure 11. Dependence of the net specific power on the cost ratio for the flow-by configuration with the specific interfacial area and the electrode thickness as parameters.

DISCUSSION

The results of the optimization have shown several important differences between the two configurations. However, these results have raised several pertinent questions:

1. Were the parameters used in the calculations equivalent for both systems, and if so, were values representative of actual systems?
2. Why is the performance of the flow-through configurations so much poorer?
3. Why is the optimum flow rate for the flow-through configuration so small?
4. Is there perhaps a better configuration coupled with a different chemical system for which the flow-through electrodes would yield competitive results?

We will endeavor to answer these questions in this section.

Parameters. In order to obtain a valid comparison between the two configurations, the parameter values were shared whenever possible (see Table 3). However, the differences need some clarification. The total iron concentration and titanium concentration were each 3.00 M for the flow-through configuration and 2.97 M for the flow-by configuration.

In the flow-through case, the concentrations of Ti^{3+} and FeCl_2^+ in the feed (set equal to 3.2942×10^{-4} M, see Table 3) were determined from the equilibrium for the reaction which occurs in the gap between the electrodes on mixing after passing through the electrodes on discharge

Table 3. Values of the parameters used in generating the results in Figures 4 through 11.

Parameters used in both electrode systems

$$a = 25 \text{ cm}^{-1}, \epsilon = 0.3 \quad D_{O, Ti^{3+}} = D_{O, Ti(OH)_2^{2+}} = 5 \times 10^{-6} \text{ cm}^2/\text{s}$$

$$n = 1, T = 298.15 \text{ K}, D_{O, FeCl_2} = 5.5 \times 10^{-6} \text{ cm}^2/\text{s} \text{ (a)}$$

$$D_{O, FeCl_2^+} = 5.7 \times 10^{-6} \text{ cm}^2/\text{s} \text{ (a)}, \alpha_a = \alpha_c = 0.5 \text{ (b)}$$

$$U_{FeCl_2/FeCl_2^+}^\theta = 0.6513 \text{ V} \text{ (c)}, U_{Ti^{3+}/Ti(OH)_2^{2+}}^\theta = 0.1 \text{ V} \text{ (d)}$$

$$i_{oR} = 10 \left(c_{FeCl_2, f} c_{FeCl_2^+, f} \right)^{1/2} \text{ (e)}, i_{oR} = \left(c_{Ti^{3+}, f} c_{Ti(OH)_2^{2+}, f} \right)^{1/2}$$

Flow-through configuration

$$\kappa_o = 0.25 \text{ mho/cm}, \sigma = 2 \times 10^{14} \text{ mho/cm}, L = 3 \text{ cm}, L_{gap} = 1 \text{ cm}$$

on charge:

$$c_{H^+} = 5 \text{ M}$$

$$c_{Ti(OH)_2^{2+}, f} = c_{FeCl_2, f} = 3 \text{ M}$$

$$c_{Ti^{3+}, f} = c_{FeCl_2^+, f} = 3.2942 \times 10^{-4} \text{ M}$$

$$2Cl^- \rightarrow Cl_2(g) + 2e^- : i_{oS} = 10^{-3} c_{Cl^-}, \text{ (f)} \quad \alpha_{aS} = 0.38, \text{ (f)}$$

$$\alpha_{cS} = 0.69 \text{ (f)}$$

(Table 3 continued)

$$c_{\text{Cl}^-,f} = 20 \text{ M}, U_{\text{Cl}_2/\text{Cl}^-}^\theta = 1.3595 \text{ (g)}$$

$$\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^- : i_{\text{OS}} = 6.708 \times 10^{-13} \text{ A/cm}^2, \text{ (f)}$$

$$\alpha_{\text{aS}} = \alpha_{\text{cS}} = 0.5 \text{ (f)}$$

$$\frac{\epsilon k_m}{aD_o} = 0.07054 \left(\frac{v}{aD_o} \right)^{0.5454} \text{ (h)}$$

Flow-by configuration

$$\kappa_{\text{o}+} = 0.176 \text{ mho/cm} \text{ (i)}, \kappa_{\text{o}-} = 0.207 \text{ mho/cm} \text{ (i)}$$

$$d_+ = d_- = 3 \text{ cm}, d_+ = d_- = 0.5 \text{ cm} \text{ (j)}, L_s = 0.047 \text{ cm} \text{ (k)}$$

$$v = 1.7 \times 10^{-3} \text{ cm/s}, \quad 1/\kappa_s = 25 \text{ mho/cm} \text{ (k)}$$

on discharge:

$$c_{\text{Ti}^{3+},f} = c_{\text{FeCl}_2^{2+},f} = 2.7 \text{ M}$$

$$c_{\text{Ti(OH)}_2^{2+},f} = c_{\text{FeCl}_2,f} = 0.27 \text{ M}$$

$$\frac{\epsilon k_m}{aD_o} = 0.91 \epsilon \left(\frac{v}{a v \psi} \right)^{0.49} \psi^2 \left(\frac{v}{D_o} \right)^{1/3} \text{ (l)}$$

$$\psi = 0.86, v = 0.0251 \text{ cm}^2/\text{s}$$

- (a) Ateya and Austin (1973)
- (b) All primary reactions
- (c) Reid and Gahn (1977) and Wagman et al. (1968)

(Table 3 continued)

- (d) Dean (1973) and Baes and Mesmer (1976)
- (e) Miller (1977)
- (f) Erdey-Gruz (1972)
- (g) Newman (1973)
- (h) Trainham and Newman (1978)
- (i) Giner et al. (1976)
- (j) Figure 11 only
- (k) Alexander and Hodgdon (1978)
- (l) Bird et al. (1960)

which has an equilibrium constant

$$\frac{c_{\text{Ti}^{3+}} c_{\text{FeCl}_2^+}}{c_{\text{Ti(OH)}_2^{2+}} c_{\text{FeCl}_2}^2 c_{\text{H}^+}^2} = 4.823 \times 10^{-10} \left(\frac{\ell}{\text{mole}} \right)^2. \quad (74)$$

In equation 74, the activity coefficients and the activity of water have been set equal to unity.

The results of the optimization show that the charge imbalance due to incomplete conversion of FeCl_2^+ on discharge is very small. In fact, the percent of charge (stored on discharge) required to restore the system to the initial state of charge (i.e., all FeCl_2^+ converted to FeCl_2), was always less than 0.05%. Therefore, the side reactions on charge are extremely small. This is due to the optimization procedure, which forces the system to operate at nearly 100% current efficiency on charge.

The correlation used in predicting the mass transfer coefficient for the flow-through configuration is the same on that determined by Trainham and Newman [11]. For the flow-by configuration, a mass transfer correlation appropriate for the Reynolds numbers encountered was used [19].

Other variations in the parameters are due to the inherent differences between the two systems. For example, the superficial

velocity was arbitrarily set for the flow-by system ($v = 1.7 \times 10^{-3}$ cm/s), whereas, an optimum value was determined on charge for the other system. Experimental conductivity and viscosity data were available for the mixtures $\text{FeCl}_2/\text{FeCl}_2^+$ and $\text{Ti}^{3+}/\text{Ti}(\text{OH})_2^{3+}$ encountered in typical flow-by systems [8], but were not available for the Fe/Ti mixtures of the flow-through system. In the latter case, a value of 0.25 mho/cm was assumed (see Table 3). Experimental data for the membrane separator thickness and resistivity were also known for the flow-by system (Alexander and Hodgdon [24]), where a 1 cm gap was assumed in the flow-through calculations.

It can be concluded from the above discussion that the differences between the parameters used in each system are minor and, therefore, will not account for the discrepancy in performance.

As mentioned previously, values for the kinetic parameters and the specific interfacial area were not available for the system at NASA-Lewis for which a discharge power density of 237 W/m^2 [9] was achieved. This compares with a calculated maximum power density of 170 W/m^2 (top curve Figure 11). A value of 25 cm^{-1} for the specific interfacial area was used in most of the calculations. However, Figure 11 has shown that for a tenfold increase in the value of a , the NSP increases by a factor of three. Even a value of a equal to 250 cm^{-1} could be conservative by a factor of two or three, and this would account for most of the discrepancy. In addition, the values of the exchange current densities used in the calculations (see Table 3) could easily be low by an order of magnitude. At the present time, there is no way to tell how well the

models predict reality, because there are no steady-state data available.

Superficial velocity. In Figure 5, the optimum superficial velocity for the flow-through system varied from (0.961 to 7.78) 10^{-5} cm/s over the charging range of 1 mA/cm^2 to 20 mA/cm^2 . Again, these velocities would be extremely difficult to achieve in practice.

The optimum velocity is low for several reasons:

1. The conversion is moderate on both charge ($0.11 < c_{RL}/c_{RF} < 0.64$) and discharge ($0.15 < c_{RL}/c_{Rf} < 0.6$) for the charging current density range of 1 mA/cm^2 to 20 mA/cm^2 . A low conversion, which would allow a much higher flow rate, is not possible due to the single pass operation.

2. The feed composition of the reactants on charge is 3 M. This is 300 times the feed composition of the copper removal process of Bennion and Newman [25]. This contributed substantially to the two-orders of magnitude difference in flow rate.

3. A comparison of Figure 8 with Figures 9 and 10 shows that the system cannot be run economically at high current densities.

An estimate of the maximum allowable velocity on charge can be obtained from the limiting current design equations of Bennion and Newman [25]. The difference in the standard electrode potentials for the system is $\Delta U^\theta = 0.5513 \text{ V}$ (see Table 3). If we assume 0.0513 V is lost to the separator, then there is approximately 0.2 V available for ohmic losses in each electrode. If we combine the equation for the mass transfer coefficient given in Table 3 for the flow-through configuration [11] with the expression for the ohmic drop across an electrode [25]

$$\Delta\phi'_2 = \frac{nFv^2 c_{Rf}}{ak_m s_R \kappa} , \quad (76)$$

an expression for the velocity results

$$v^{1.4546} = 0.07054 \frac{s_R \kappa \Delta\phi'_2}{enFc_{Rf}} a^{1.4546} D^{0.4546} . \quad (77)$$

Using the values of the parameters in Table 3 and $\Delta\phi'_2 = 0.2$ V, we obtain $v = 2.1 \times 10^{-5}$ cm/s. This estimate is the same order of magnitude as the velocities obtained by the optimization procedure.

As mentioned previously, the results for the flow-by configuration operating at a fixed conversion are essentially independent of velocity. For a desired conversion, the electrode length is set, and the velocity can be calculated or vice versa. This operational flexibility makes the flow-by configuration superior.

Effects of electrode thickness. For the flow-by configuration, results were obtained for electrodes of thickness 3 cm and 0.5 cm in the direction of current flow. Figure 11 shows that there is only a small improvement in the performance of the 3 cm thick electrode over the 0.5 cm thick electrode. The electrode length of the 3 cm thick varied from approximately 5.2 to 5.5 times that of the 0.5 cm thick electrode over the discharge range considered.

Other systems. It should be kept in mind that the Fe/Ti chemical system has been used for a relative comparison between two electrode configurations. Other chemical systems offer larger open-circuit

potentials and reaction rates per unit volume (ai_0). However, the mathematical models and the optimization procedures developed here can be used directly or modified accordingly, so that other systems can be compared.

SUMMARY AND CONCLUSIONS

Theoretical models have been developed for two electrode configurations for redox battery applications: 1) flow-through porous electrodes and 2) flow-by porous electrodes. These models were used to determine which system yields the greater return on investment. To do this, both systems were optimized with respect to an objective function appropriate for the application.

The results show that the flow-by configuration is superior. Not only does this system yield a greater return on investment, but it also offers the operational flexibility of variable flow rate and conversion. Its limitations compared to the flow-through system will be associated with the maintenance and reliability of the membrane separator.

The flow-through configuration in addition to yielding a lower return on investment, offers an impractical superficial velocity (the optimum superficial velocity was of order 10^{-5} cm/s). Its failure is due to current flow (and ohmic potential drop) in the same direction as the fluid flow.

The perspective here has been to use a simplified optimization procedure to obtain a valid comparison between two electrode systems.

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Notation

a	specific interfacial area, cm^{-1}
c_R	concentration of the reactant species, in the flow-by analysis it is referred to as the reduced species, mole/cm^3
c_0	concentration of the oxidized species in a redox reaction, mole/cm^3
c_P	concentration of the product species in a redox reaction, mole/cm^3
c_S	reactant species concentration in the side reaction, mole/cm^3
$c_{i,L}$	concentration at electrode exit, mole/cm^3
C_{Ai}	cost per unit volume, $\$/\text{m}^3$
C_{Bi}	cost per superficial-electrode area, $\$/\text{m}^2$
C'_{CF}	capital and fixed costs, $\$/\text{year-m}^2$
C'_F	fixed costs, $\$/\text{year-m}^2$
C'_V	variable costs, $\$/\text{year-m}^2$
C_{pD}	daytime power costs, $\$/W$
C_{pN}	nighttime power costs, $\$/W$
DD	downstream counterelectrode, downstream current collector
DU	downstream counterelectrode, upstream current collector
D_a	axial dispersion coefficient of the reactant species, cm^2/s
D_o	molecular diffusion coefficient of the reactant species, cm^2/s
D_R	effective diffusion coefficient of the reactant species, cm^2/s
D'	$= (D_R + D_a)ak_m/v^2$, dimensionless parameter describing the relative importance of axial diffusion and dispersion

F	Faraday's constant, 96487 C/equiv
i	superficial current density to an electrode, A/cm^2
i_{oj}	exchange current density for reaction j , A/cm^2
$i_{oj,ref}$	exchange current density for reaction j at a reference composition $c_{i,ref}$, A/cm^2
i_1	superficial current density in the matrix, A/cm^2
i_2	superficial current density in pore-solution phase, A/cm^2
i_{nj}	transfer current for reaction j per unit interfacial area, A/cm^2
I^*	$= s_R i/nF v c_{RF}$, dimensionless superficial current density to an electrode
i_R	total current density to an electrode due to metal-deposition reaction, A/cm^2
I	total current to an electrode, A
I_c	current density on charge, A/cm^2
I_d	current density on discharge, A/cm^2
j_{in}	pore-wall flux of species i , mole/ cm^2 -s
k_m	average mass-transfer coefficient between flowing solution and electrode surface, cm/s
L	thickness of porous electrode, cm
L_s	separator thickness in flow-by porous electrode, cm
L_{gap}	gap thickness of flow-through porous electrode, cm
M_i	symbol for the chemical formula of species i
n	number of electrons transferred in an electrochemical reaction
n_j	number of electrons transferred in reaction j

- P_S hydrogen or chlorine partial pressure, atm
- Pe Péclet number, v/aD_o
- P_1 $= (-s_R i_{oR,ref}/nF k_m c_{Rf})^{1+\alpha_{AR}/\alpha_{CR}}$, dimensionless parameter describing the relative importance of the anodic term in a metal deposition reaction, and a redox reaction
- P_2 $= \alpha_{cR} nF^2 v^2 c_{Rf}/s_R a k_m RT (\frac{\kappa+\sigma}{\kappa\sigma})$, dimensionless parameter describing the relative importance of the ohmic potential drop
- P_3 $= -s_R i_{os,ref}/nF k_m c_{Rf} e^{\alpha_{cS} F \Delta U/RT} (-nF k_m c_{Rf}/s_R i_{oR,ref})^{\alpha_{cS}/\alpha_{cR}}$, dimensionless parameter describing the relative importance of the forward term in the side reaction
- P_4 $= (-s_R i_{oR,ref}/nF k_m c_{Rf}) \exp[-(\alpha_{aS} + \alpha_{cS}) \Delta U_F/RT]$, dimensionless parameter describing the relative rate of the backward term in the side reaction
- P_5 dimensionless parameter which characterizes the ohmic potential drop in the pore-solution phase, see equation 30
- P_6 dimensionless parameter which characterizes the ohmic potential drop in the matrix phase, see equation 31
- P_7 $= k_{mR}/k_{mP}$, ratio of mass transfer coefficients for reactant and product series in a redox reaction
- P_1 dimensionless parameter describing the relative importance of the cathodic term in a metal deposition reaction and a redox reaction, see equation 23
- P_2 same physical significance as P_2 only for an anodic reactant, see equation 24

P_3	same physical significance as P_3 , see equation 25
P_4	same physical significance as P_4 , see equation 26
P_5	same physical significance as P_5 , see equation 33
P_6	same physical significance as P_6 , see equation 34
q_{ij}	cathodic reaction order
r	the effect of interest, depreciation and taxes, yr^{-1}
R	universal gas constant, 8.3143 J/mole-K
Re	$= v/\nu$ or $v/\psi\nu$, Reynolds number
S	on-stream factor, days operating/365 days or operating cycles/year
s_{ij}	stoichiometric coefficient of species i in electrode reaction j
s_R	stoichiometric coefficient of reactant species
s_P	stoichiometric coefficient of product species
T	absolute temperature, K
t_c	charging time, s
t_d	discharge time, s
U	open-circuit cell potential, V
UD	upstream counterelectrode, downstream current collector
UU	upstream counterelectrode, upstream current collector
U_{jw}	open-circuit potential for reaction j at local wall composition relative to a reference electrode of a given kind, V
U_j^θ	standard electrode potential for reaction j , V

U_k^θ	standard electrode potential for reaction k , V
U_r^θ	standard electrode potential of reference electrode, V
ΔU	$= U_S - U_R$, difference in open-circuit cell potentials of the side reaction and primary reaction at the reference composition, V
v	superficial fluid velocity, cm/s
VOP	potential of the cathode current collector relative to a saturated calomel reference electrode placed in the dilute product stream, V
$(VOP)_{\max}$	maximum value of VOP at which appreciable side reaction does not occur, V
ΔV_k	$VOP - U_k^\theta + V_{\text{cal}}^\theta$, V
x	distance through porous electrode, cm
y	$x a_{\text{m}}/v$ dimensionless distance through porous electrode, in the flow-by analysis it is the distance in the direction of current flow, cm
z_i	valance or charge number of species i

Greek Letters

α	$= a k_{\text{m}}/v$, reciprocal of penetration depth at the limiting current, cm^{-1}
α_{aj}	anodic transfer coefficient for reaction j
α_{cj}	cathodic transfer coefficient for reaction j

γ_{ij}	exponent in composition dependence of exchange current density
ϵ	porosity or void volume
ϕ	quasi-electrostatic potential, V
ϕ_1	electrostatic potential in matrix phase, V
ϕ_2	quasi-electrostatic potential in the pore solution phase, V
$\Delta\phi_2$	ohmic potential drop across porous electrode, V
$\Delta\phi_2'$	estimate of ohmic potential across porous electrode at the limiting current, V
$\Delta\phi_{\text{gap}}$	$I_c L_{\text{gap}} / \kappa_o$, ohmic drop across gap in flow-through porous electrode, V
η_{sj}	$= \phi_1 - \phi_2 - U_{jw}$ surface overpotential for reaction j, V
η	$= \phi_1 - \phi_2$ local overpotential, V
η'	dimensionless local overpotential for the cathodic reactant
η^*	dimensionless local potential for the anodic reactant
κ	effective conductivity of solution, mho/cm
κ_o	intrinsic conductivity of solution, mho/cm
κ_s	effective conductivity of the separator, mho/cm
μ	viscosity, g/cm-s

Subscripts

f	upstream feed
w	wall or surface
R	reactant or reduced species
P	product species
O	oxidized species

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