Two Dimensional Transport Modeling of an Aluminum/Air Cell   2 Nov/02

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Aluminum-air battery system has the potential to be used to produce power to operate cars and other vehicles [1]. A battery system may include multi-unit cells and auxiliary subsystems (CO_2 scrubber, temperature controller, crystallizer, etc.). To optimize the design and operation of the battery system, a mathematical modeling for analysis and prediction of the performance of the unit cell is required. The effects of design and operating parameters (such as cell gap, height, flow rate) and anode corrosion kinetics on the cell performance (voltage-current density curve, current distribution along the cell etc.) will be reported. MATLAB and FEMLAB software will be used.

Problem definition

The cell is made up of two plane, parallel electrodes with cell gap S and height H (H>>S). The electrolyte enters from the bottom in developing laminar flow. The electrochemical reactions occur only on the electrode surfaces. No crystallization reaction occurs in the cell. At the anode, the main reaction is $Al + 4OH^- \rightarrow Al(OH)_4^- + 3e^-$; the parasitic (undesired) reaction is $Al + 3H_2O + OH^- \rightarrow 3/2H_2 + Al(OH)_4^-$. At the Cathode, the reaction is $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$.

Model development

Following Newman [2], Brebbia [3] Chan et al. [4], We assume the electrolyte can be separated into two parts, the stagnant diffusion layer and the bulk layer.

1. *Bulk medium*

The bulk solution potential satisfies the following equation,

$$\nabla \cdot (\kappa \nabla \Phi) = 0 \qquad (1)$$

Where κ, the conductivity of the bulk solution, is a function of gas fraction. The boundary conditions just outside the diffusion layers for eq. (1) are:

$$\phi_1 = E_{eq} - V_{cell} - \eta_1 \qquad (2)$$

and

$$\phi_2 = -\eta_2 \qquad (3)$$

Where E_{eq} is cell equilibrium voltage; V_{cell} is cell voltage; η_1 and η_2 are the (concentration, activation) over-potentials of the anode and cathode. The activation overpotential can be expressed by a simple Butler-Volmer expression or an empirical equation.

2. *Diffusion layer*

In the diffusion layer, we need to relate the concentration profile to current density. A single electrode reaction can be written in symbolic form as

$$\sum_i s_{im} M_i^{z_i} \rightarrow n_m e^- \qquad (4)$$
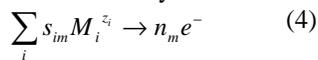
A parasitic reaction in the anode is expressed as

$$\sum_i s_{ip} M_i = 0 \qquad (5)$$

If the electron transfer number in reaction is n_p, then the flux of species i due to the parasitic reaction and main reaction is:

$$N_i = N_{im} + N_{ip} = -(\frac{s_{im}}{n_m F} + \frac{s_{ip}}{n_p FS_{m/p}})i_m, \qquad (6)$$

Where i_m is the current density of the main reaction; i_p is

current density of the parasitic reaction, $S_{m/p} = i_m / i_p$, is defined as selectivity.

In the diffusion layer, the flux of species i due to the migration and diffusion can be expressed as:

$$N_i = -z_i u_i F c_i \nabla \Phi - D_i \nabla c_i. \qquad (7)$$

For the first term of the RHS of eq. (7), we use average $\overline{c_i}$ in place of c_i, and combined with eq. 6, yields,

$$\frac{c_{i0}}{c_{ib}} = \frac{1 + \frac{-\nabla\phi\delta_i F}{2RT}}{1 - \frac{-\nabla\phi\delta_i F}{2RT}} \frac{(\frac{s_{im}}{n_m F} + \frac{s_{ip}}{n_p FS_{m/p}})i_m}{D_i \frac{c_{ib}}{\delta_i}(1 - \frac{-\nabla\phi\delta_i F}{2RT})} \qquad (8)$$

Where δi is the diffusion layer thickness for species i and is estimated by the convective electrolyte flow and the micro convection of gas evolution. δ_i is defined as the distance from the electrode where $c_i = c_{ib}$, by assuming linear concentration profile of species i . Note that eq. 8 is similar to Chan et al. (s_i/n is different). s_i/n is the stoichometric coefficient over the electronic transfer number ($s_{ip}/n_p = 1/3$ for OH- and -1/3 for Al(OH)$_4^-$; $s_{im}/n_m = 4/3$ for OH- and -1/3 for Al(OH)$_4^-$).

Modeling calculations

For a plane parallel geometric configuration, we used the improved anode data from our laboratory, and cathode data from Yardney [5] for our modeling calculation. We also analyzed cell performance for wedge-type cell configuration using our model.

Figure 1 shows $S_{m/p}$ as a function of i_m.

Figure 1. Selectivity as a fuction of current density
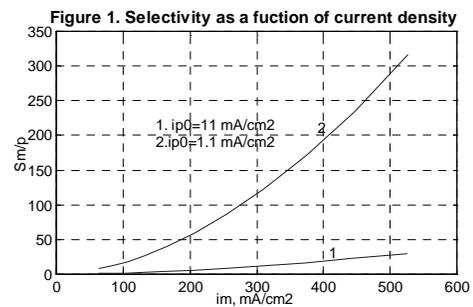
Figure 2 shows the potential distribution in a wedged-type Al /air cell.

Figure 2. Surface: electric potential (V)
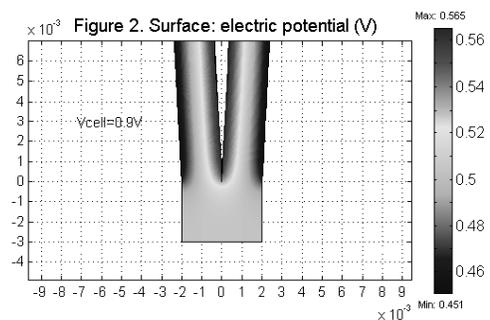
References
[1] S. Yang, H. Knickle, *J. Power Source,* 112 (1) (2002) 162-173.
[2] J. Newman, *Int. J. Heat Mass Transfer*, 10 (1967) 983-997.
[3] C.A. Brebbia, (ed.), *Leture Notes in Engineering*, 75, J. Deconinck, *Current Distributions and Electrode Shape Changes in Electrochemical Systems*, 1992.
[4] K.Y. Chan et al, *J. Electrochem. Soc.*, 138 (7) (1991) 1976-1984.
[5] http://www.yardney.com/alupower/products.htm.