

Modeling Positive-Electrode Reaction Kinetics of a Sodium-Metal Chloride Cell

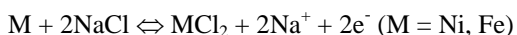
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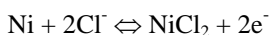
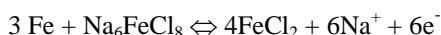
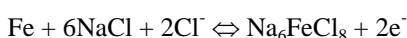
A model has been developed to investigate the reaction mechanism in a mixed-metal chloride (MCl₂, M=Ni & Fe) electrode; chemically similar to those found in sodium-metal chloride cells; during constant-current oxidation and reduction at 300° C. The proposed model is also used to predict open-circuit-voltage (OCV) relaxation data obtained at different states of oxidation and reduction during galvanostatic interrupt titration. The OCV relaxation data exhibit large transitions between Fe⁺⁺/Fe and Ni⁺⁺/Ni Nernst potentials, following interrupted reduction at Fe⁺⁺ reduction potentials. These transitions are simulated by assuming spontaneous redox between NiCl₂ and iron, confirming that residual NiCl₂ is present during FeCl₂ reduction.

A thin (~2 mm) coin-shaped working electrode, comprising a granulated mixture of common salt and solid metal powders (35% NaCl, 57% Ni, 8% Fe), is contained in, and separated from, the auxiliary electrode by a ceramic β"-alumina solid electrolyte/separators (BASE) tube that conducts Na⁺. The experiment is designed so that the ionic electric field is perpendicular to the flat bottom of the tube. The cathode materials are impregnated with molten NaAlCl₄ that functions as a second electrolyte. The reversible electrode reaction can be written as:



The reference electrode, an aluminum wire immersed in NaCl-saturated NaAlCl₄, is contained in a soda-containing, borosilicate tube that conducts Na⁺.

The electrochemical process in the electrode is modeled as 3 electrochemical reactions. Iron redox is modeled as two separate reactions where an intermediate solid compound, Na₆FeCl₈, participates in both reactions [1].



The Nernst potentials of the first and third reactions depend on Cl⁻ activity in the electrolyte; this dependence is seen in the OCV relaxation measurements. Solid-state, mass-transfer-limited kinetics; involving dissolution of NiCl₂ from a triclinic (Ni,Fe)Cl₂ solid solution [2]; governs the reduction of nickel chloride. This kinetics formulation allows us to predict electrode potential while NiCl₂ and FeCl₂ reduce simultaneously. NaCl and Na₆FeCl₈ dissolution/precipitation kinetics are modeled using free-energy change as the driving force.

The model equations include material balances for the solid compounds (Ni, Fe, NiCl₂, FeCl₂, NaCl, Na₆FeCl₈) and Cl⁻ in the electrolyte. The other molecular

and anionic electrolyte species (AlCl₃, Al₂Cl₆, AlCl₄⁻, Al₂Cl₇⁻) [3] are assumed to be saturated.

Material Balances :

$$\frac{dc_i^s}{dt} = \sum_{j=1}^{n_R} R_{ij}(c_i^s, c_G^e) + \sum_{j=1}^{n_J} J_{ij}(c_i^s, c_G^e, \eta_j)$$

$$\frac{dc_G^e}{dt} = \sum_{j=1}^{n_R} R_{Gj}(c_i^s, c_G^e) + \sum_{j=1}^{n_J} J_{Gj}(c_i^s, c_G^e, \eta_j) \quad (1)$$

n_R and n_J are the number of chemical and electrochemical reactions, respectively. c_i^s is the apparent solid concentration which is defined as the moles per electrode volume. Butler-Volmer kinetics is used to predict the electrochemical reaction rates where the overpotential for each reaction is given as:

$$\eta_j = \phi_s - \phi_e - U_j$$

Where φ_s, φ_e and U_j are the solid, electrolyte and Nernst potentials for each reaction, respectively. Cl⁻ concentration gradient and over-potential gradients are neglected. These assumptions are shown valid for moderate redox rates (≤ 0.2 A/cm³) for the present geometry. The charge balance is written as the equality of the sum of the electrochemical reaction rates and the total current density:

Charge Balance :

$$\frac{I_{app}}{V_p} = \sum_{j=1}^{n_J} j_j(c_i^s, c_G^e, \eta_j) \quad (2)$$

I_{app} and V_p are the applied current and electrode volume, respectively. Thus, a DAE system of 5 differential equations (Eq. (1), NiCl₂ and FeCl₂ are directly calculated using Fe and Ni balances) and one algebraic equation (Eq. (2)) is integrated through time to obtain cell potential (φ_s). Due to sharp φ_s transitions associated with nickel oxidation and iron reduction onsets, MATLAB's DAE solvers failed to converge. Thus, the equations are integrated by using a MATLAB stiff ode solver, and by solving the algebraic equation using a robust golden section search and parabolic interpolation method at each time step. Optimal kinetic parameters are found by training the model with oxidation and reduction data generated at 50 mA (~ 0.1 A/cm³) and 100 mA (~ 0.2 A/cm³) using MATLAB's Global Optimization Toolbox.

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References:

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