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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 (MCl, 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/separator (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:

M + 2NaCl ⇌ MCl₂ + 2Na⁺ + 2e⁻ (M = Ni, Fe)

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, Na₆FeCl₁₇, participates in both reactions [1].

Fe + 6NaCl + 2Cl⁻ ⇌ Na₆FeCl₁₇ + 2e⁻ (3)

3Fe + Na₆FeCl₁₇ ⇌ 4FeCl₂ + 6Na⁺ + 6e⁻ (4)

Ni + 2Cl⁻ ⇌ NiCl₂ + 2e⁻ (5)

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 Na₆FeCl₁₇ 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, Na₆FeCl₁₇) and Cl⁻ in the electrolyte. The other molecular and anionic electrolyte species (AlCl₃, Al₂Cl₆, AlCl₄⁻, Al₃Cl₇⁻) [3] are assumed to be saturated.

Material Balances:

\[
\frac{dM}{dt} = \sum_{j} R_{M_j} \left( c_{M_j} - c_{M_j}^{\infty} \right)
\]

\[
\frac{dNaCl}{dt} = \sum_{j} R_{NaCl_j} \left( c_{NaCl_j} - c_{NaCl_j}^{\infty} \right)
\]

\[
\frac{dFeCl_2}{dt} = \sum_{j} R_{FeCl_2_j} \left( c_{FeCl_2_j} - c_{FeCl_2_j}^{\infty} \right)
\]

\[
\frac{dNiCl_2}{dt} = \sum_{j} R_{NiCl_2_j} \left( c_{NiCl_2_j} - c_{NiCl_2_j}^{\infty} \right)
\]

Where \( c_{M_j} \) and \( c_{M_j}^{\infty} \) are the number of chemical and electrochemical reactions, respectively. \( c_i \) 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:

\[ \eta_i = \phi_i - \phi - U_i \]

Due to sharp \( \phi \) 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/cm²) and 100 mA (~ 0.2 A/cm²) using MATLAB’s Global Optimization Toolbox.

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