Modeling of Nickel Hydroxide Electrode Containing Multiple Phases

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ABSTRACT

Mathematical models of alkaline rechargeable nickel cell systems (e.g., Ni-Cd, Ni-112 and Ni-MH) have so far been developed based on the assumption that the active material at Ni electrode exists primarily in a single phase as \( \beta-\text{Ni(OH)}_2 \), despite enough experimental evidence for the second phase, i.e., \( \gamma-\text{Ni(OH)}_2 \), especially under conditions of extended overcharge. Here, we have incorporated the additional couple of \( \gamma-\text{Ni(OH)}_2 - \alpha\text{-Ni(OH)}_2 \), into the modeling, of the Ni electrode. The reaction scheme includes an electrochemical redox reaction of \( \beta-\text{Ni(OH)}_2 \) - \( \beta-\text{Ni(OH)}_2 \), unidirectional conversion of \( \beta-\text{Ni(OH)}_2 \) to \( \gamma-\text{Ni(OH)}_2 \), electrochemical redox reaction \( \alpha-\text{Ni(OH)}_2 \) - \( \gamma-\text{Ni(OH)}_2 \) and a chemical conversion of \( \alpha-\text{Ni(OH)}_2 \) to \( \beta-\text{Ni(OH)}_2 \). Changes in the electronic conductivities, proton concentrations, and the states of charge are monitored individually and coupled appropriately to obtain the response of the nickel electrode under variety of simulated test conditions. The multi-phase model has provided simulations of Ni electrode behavior with improved accuracy and agreement with the experimental data.

INTRODUCTION

Mathematical models would be greatly helpful in predicting the performance of batteries and providing guidelines for a proper management of power subsystem on spacecraft. In spacecraft, nickel-based rechargeable batteries are being used almost exclusively. JPL has been involved for the past few years in the development of first-principles mathematical models for aerospace, scaled Ni-Cd and Ni-112 rechargeable batteries. The earlier versions of these models were built around the cell models developed by White et al.,\textsuperscript{1,4} utilizing the macrohomogeneous approach of Newman\textsuperscript{1} for a description of porous electrodes. The more recent battery models at JPL\textsuperscript{11}, utilize relatively simplified treatments with respect to mass transport processes in electrolyte. Realizing that the concentration changes in liquid phase are relatively less prominent compared to gradients in solid phase electrodes, the porous electrode treatment has been simplified.
assuming a planar electrode geometry, with a homogeneous reaction on the electrode. Under these conditions, a semi-analytical solution can be obtained for the diffusion of protons across the positive active material layer. This modification has resulted in considerable simplification with respect to computational needs, enabling them to be operational on portable computers. Furthermore, the predictions from the simplified model are generally consistent with the results from the complex porous electrode models, except at very high rates of discharge, where the mass transport processes in the liquid phase should be treated more thoroughly. This approach is the basis of the current work, and has allowed an extensive modeling of Ni electrode model by incorporating a treatment of multiple phases of active material.

**REACTION SCHEME**

Our earlier studies on the Ni-Cd boiler plate cell, indicate that the shape of discharge curve changes appreciably on cycling. The discharge profiles in the beginning of cycling are rather flat, whereas those after cycling are distinctly sloping. The sloping nature of cycled Ni oxide electrode may be explained by a possible generation of a different phase of nickel oxhydroxide during extensive cycling and/or overcharge. Nickel hydroxide or oxhydroxide exists in multiple phases, i.e., α and β forms of Ni(OH)₂ and γ forms of NiOOH. In the normal course of cycling, β-Ni(OH)₂ gets converted to β-NiOOH on charge and vice versa on discharge. On prolonged charging or on overcharge, β-NiOOH is converted to γ-NiOOH. A larger number of electrons (about 1.5-1.75) are exchanged per Ni atom during the α ↔ γ redox cycling. However, α-Ni(OH)₂ is unstable and transforms to its β-analogue on stand. Delahaye-Vidal et al. suggested that α-Ni(OH)₂ contains the same sheets of Ni(OH)₂ in the lattice as the β-form, but in a disoriented manner along the c axis (hence termed as turbostratic) and with larger interlamellar spacing due to incorporation of electrolyte species. Furthermore, the α-form converts by dissolution-precipitation mechanism into thin platelets of β-Ni(OH)₂, which eventually grow to the usual thick platelets. The reversible potentials of these two phases are not known accurately, though the γ couple has reportedly a lower potential than the β-β couple. Values of 0.39 and 0.44 V vs. Hg/HgO for the reversible potentials of α-γ and β-β couples, respectively, have been reported. To add to this complexity, considerable hysteresis of 60-80 mV has been reported between oxidation and reduction potentials.

In the incorporation of the above multiple phases of active material at Ni electrode, we have employed a similar reaction scheme. Accordingly, two phases of NiOOH/Ni(OH)₂ react independently as

\[ \beta \rightarrow NiOOH + H_2O + e^- \quad <\rightarrow \beta' \rightarrow Ni(OH)_2 + OH^- \]  

(1)
\[
\gamma - \text{NiOOH} + 1.5H_2O + 1.5e^- \leftrightarrow \gamma - \text{Ni(OH)}_2 + 1.5OH^- \quad (2)
\]
In addition, \(\beta\)-NiOOH is converted to \(\gamma\)-NiOOH upon overcharge (electrochemically) as:

\[
\beta - \text{NiOOH} + 0.5e^- \rightarrow \gamma - \text{NiOOH} \quad (3)
\]

It should be noted that the above reaction is irreversible. The conversion of \(\beta\)-NiOOH to \(\gamma\)-NiOOH involves co-intercalation of electrolyte species into the lattice of \(\gamma\)-NiOOH, but is not included in this treatment.

Finally, \(\alpha\)-Ni(OH)$_2$ undergoes a chemical transformation into a more stable \(\beta\)-Ni(OH)$_2$ by Ostwald’s ripening, i.e., a morphological transition from thin platelets to thick plates by dissolution-precipitation process;

\[
\alpha - \text{Ni(OH)}_2 \rightarrow \beta - \text{Ni(OH)}_2 \quad (4)
\]

Apart from the above reactions, there are several parasitic reactions involving electrolyte. For example, oxygen evolution occurs during charge and during self-discharge at the Ni-electrode as:

\[
O_2 + 4e^- + 2H_2O \leftrightarrow 4OH^- \quad (5)
\]

The above reaction is assumed to occur independently, similar to the reactions (1) and (2), at \(\alpha\)-Ni(OH)$_2$ and \(\beta\)-Ni(OH)$_2$. Recombination of oxygen, which is a reverse of the above reaction occurs at the negative electrode, either Cd,II,(for the present case of Ni-III model), or metalhydride, along with the main reaction:

\[
H_2 + 2OH^- \leftrightarrow 2H_2O + 2e^- \quad (6)
\]

The self-discharge of Ni-electrode induced by hydrogen is similar to the cell discharge reactions, except that both the reactions occur on the positive electrode.

**MODEL IMPLEMENTATION**

In order to compute cell current (or potential) on applying a potential (current) perturbation, a set of differential equations have been formulated based on the application of principles of mass balance for each of the species in the above reactions, current balance, energy balance, mass transport, thermodynamics, and kinetics. In this model, the mass transport of protons through solid phase is treated by a semi-analytical solution.
of Fick’s second law. The resulting solution requires the numerical solution of an integral for determining the proton diffusion gradients. The primary equations are solved using a Gaussian elimination method.

**Proton Diffusion**

It has been long realized that slow diffusion of protons in the lattice of the positive electrode material might contribute to mass transfer polarization which in turn affects the utilization of the positive electrode at high discharge rates. Proton concentration in the Ni oxide is calculated by solving, Fick’s second law as:

\[
C(x, \tau) = \frac{1}{D(1 - \Theta)} \int_0^\infty \left[ 1 + 2 \sum_{k=1}^{\infty} \cos \left( k \pi x \right) \right] l(Z) dZ
\]

where \( \tau \) is the time and \( x \) is the distance in dimensionless form. Proton concentration is thus monitored in the \( \alpha-\gamma \) and \( \beta-\beta \) phases independently.

**Electronic Conductivity of the Active Material**

The conductivity of the positive electrode is a strong function of the state of charge of the electrode; the conductivity of reduced phase is orders of magnitude lower than the conductivity of oxidized phase. A modified empirical expression, similar to that used in the nickel-hydrogen model is used to define the conductivity, i.e.,

\[
\sigma = A \cdot e^{-\left( \frac{1}{\Theta} \right)^c}
\]

where \( A \) is the conductivity of the oxidized phase, \( \Theta \) is the state of charge and \( B \) and \( C \) are constants characterizing the change in the conductivity of Ni electrode during discharge. The gradient of protons through the active material is used to calculate the conductivity at each point, and the resistance across the film thickness is expressed as an integral. Application of Ohm’s law across the solid phase yields:

\[
\phi_{ionic} = \frac{(J_{Na, \beta} + J_{\alpha, \beta}) I_{\beta} \rho_{\beta}}{e_{\alpha} - e_{\alpha, \beta}}
\]

Similar expressions have been used for both the \( \alpha-\gamma \) and \( \beta-\beta \) phases. Since, the two phases are assumed to be situated parallel to each other along the electrode surface, the effective transfer resistance are intercombined of irreducible base mass transport of protons through the film.
Schottky Barrier Potential

At the Ni electrode the Ni substrate current collector is separated from hydroxide/oxyhydroxide active material by a semi-conducting barrier termed as Schottky layer.\textsuperscript{14} A junction potential, termed as Schottky junction potential, is thus created at the cathode/metal oxide interface. The Schottky junction potential consists of a relaxation term to control the on-set of the overpotential during charge/discharge and a second term quantifying the overpotential as shown below:

\[
\phi_{\text{Junction}} = \phi_{\text{Substrate}} - \left( 1 - \exp^\frac{-t}{\tau_{\text{cell}} * \tau_{\text{ff}}(t)} \right) \times \text{Scale} \times \text{Tanh} (I_{\text{cell}} * kT/\text{Thk}I) \times \text{Scale} \times \text{Bias}
\]

11 is assumed here, as a first approximation, that the Schottky junction characteristics of both \(\alpha\)-\(\gamma\) and \(\beta\)-\(\beta\) phases are identical, as may be expected from the identical values for their (electronic) conductivities in the oxidized as well as reduced state. A single Schottky layer thus separates the Ni substrate from the active material in \(\alpha\)-\(\gamma\) and \(\beta\)-\(\beta\) phases.

Mass balance

The general expression for the mass balance of a species in the electrolyte is

\[
n_i \sum_{n_i} J_i \times D_i \nabla C_i = \frac{dC_{\text{out}}}{dt} \text{THIK1} \times \text{THIK2}
\]

where the first term is the consumption/generation of \(C_i\) due to electrochemical reaction, \(J_i\), the second corresponds to the diffusion of the species due to concentration gradient \(\nabla C_i(D_i\text{ is the diffusion coefficient})\) and the third term describes the transport through migration under a potential gradient of \(\nabla \phi_{\text{Solution}}(Z_i\text{ is the charge and}\mu_i\text{ is the mobility}).\) Specific equations for the mass balance of hydroxide ions, oxygen and proton are

\[
\frac{dC_{\text{out}}}{dt} \text{THIK1} - \text{THIK2} = \frac{dC_{\text{out}}}{dt} \text{THIK1} + \frac{dC_{\text{out}}}{dt} \text{THIK2}
\]
\[
\frac{dC_{\text{H}_2\text{O}}}{dt} = -THK1 \left( J_{\text{H}_2\text{O},pp} \right) + D_{\text{H}_2\text{O}} \frac{dC_{\text{H}_2\text{O}}}{THK2}
\]

and

\[
\eta_p = \frac{1}{L \rho} \left[ \frac{f D_{\text{H}_2\text{O}} \left( \text{H}_2\text{O} \text{H}_2\text{O}^+ \right) \left( \text{H}_2\text{O} \text{H}_2\text{O}^+ \right) \left( 1 - \gamma \right) \right] \left( B_{\gamma,2,20} \right) \left( J_{\text{H}_2\text{O},pp} \right) \text{CurSum}
\]

respectively. The B coefficients are numerically evaluated parameters as described earlier. Similar expressions have been used for the mass balance of the proton in the \( \alpha-\gamma \) phase as well.

**Electrochemical kinetics**

The kinetics of electrochemical process are governed by Butler-Volmer equation which is generally expressed as:

\[
i = i_{0,j,0} \left[ \exp \left( \frac{\alpha_j F}{RT} \eta_j \right) - \exp \left( - \frac{\alpha_j F}{RT} \eta_j \right) \right]
\]

where the overpotential is given by:

\[
\eta_j = \phi_s - \phi - U_{i,0}
\]

and the exchange current density is given by:

\[
i_{0,j,0} = i_{0,j,\text{ref}} \left( \frac{a_{i,j}}{a_{i,\text{ref}}} \right)^n
\]

Expressing the reversible potential in terms of 0, the mole fraction of reduced NiOOH 1 (or concentration of proton):

\[
\phi_{eq} = \phi_{eq}^0 + \frac{RT}{nF} \ln \left( \frac{\Theta}{1 - \Theta} \right) + \frac{RT}{nF} \ln \left( \frac{a_{\text{Ni}^{2+}}}{a_{\text{Ni}^{3+}}} \right) + K (\Theta - 1)
\]

The last term in the above equation is incorporated to explain the non-Nernstian behavior in the intercalation potentials of proton in nickel oxides. In other words, it is an empirical fit to the observed electrode potential.
incorporation equations (15), (16) and (17) into equation (14) gives the expression for the electrokinetics of the redox reactions involving Ni oxides as:

\[
J_{\text{g}} = 2 \alpha_{\text{g}} \left[ C_{(\text{g})}^{(\text{0})} \left( \frac{C_{(\text{g})}^{(\text{0})}}{C_{(\text{g})}^{(\text{0})}} \right)^{1/2} \right] \left[ e^{\frac{\alpha_{\text{g}}}{C_{(\text{g})}^{(\text{0})}}} \right]
\]

and

\[
J_{\text{h}} = 2 \alpha_{\text{h}} \left[ C_{(\text{h})}^{(\text{0})} \left( \frac{C_{(\text{h})}^{(\text{0})}}{C_{(\text{h})}^{(\text{0})}} \right)^{1/2} \right] \left[ e^{\frac{\alpha_{\text{h}}}{C_{(\text{h})}^{(\text{0})}}} \right]
\]

The corresponding equations for oxygen and hydrogen reactions are:

\[
J_{\text{oxygen}} = a_{\text{oxygen}} \left[ \left( \frac{C_{(\text{0})}^{(\text{1})}}{C_{(\text{0})}^{(\text{1})}} \right)^{1/2} \right] \left[ e^{\frac{\alpha_{\text{oxygen}}}{C_{(\text{0})}^{(\text{1})}}} \right]
\]

and

\[
J_{\text{hydrogen}} = a_{\text{hydrogen}} \left[ \left( \frac{C_{(\text{1})}^{(\text{0})}}{C_{(\text{1})}^{(\text{0})}} \right)^{1/2} \right] \left[ e^{\frac{\alpha_{\text{hydrogen}}}{C_{(\text{1})}^{(\text{0})}}} \right]
\]

Similar expressions have been used to describe the reactions of gaseous species at both the \( \alpha \)-\( \gamma \) and \( \beta \)-\( \beta \) phases. The rate of the electrochemical conversion of \( \beta \)-NiOOH into \( \gamma \)-NiOOH on overcharge is expressed as:

\[
J_{\text{overcharge}} = a_{\text{overcharge}} \left[ \left( \frac{C_{(\text{overcharge})}^{(\text{0})}}{C_{(\text{overcharge})}^{(\text{0})}} \right)^{1/2} \right] \left[ e^{\frac{\alpha_{\text{overcharge}}}{C_{(\text{overcharge})}^{(\text{0})}}} \right]
\]

The above is unidirectional; there is no conversion of the gamma phase to the beta unless through the reduced form of \( \alpha \)-Ni(OH)\(_2\). Finally, the kinetics of the chemical conversion process of \( \alpha \)-Ni(OH)\(_2\) to \( \beta \)-Ni(OH)\(_2\) are expressed by a first order Arrhenius-type rate equation as:

\[
\text{RATF}_{\text{alpha}} = K_{\text{alpha}} \times X_{\gamma} \times (H_{\alpha\gamma})_{\text{surf}} \times (1 - \theta_{\alpha\gamma}) \times e^{\left( \frac{1}{T} - \frac{1}{T_0} \right) F_{\text{overcharge}}}
\]

where \( X_{\gamma} \) is the phase fraction of the \( \alpha \)-\( \gamma \) phase.
Other Governing Equations

Other ancillary collisions utilized in the model are

\[
I_{\text{cell}} = THK1 \times \sum_j J_{Ni,j} \tag{24}
\]

\[
\text{Gamma Phase Fraction Balance: } X_y = X_{Y,0} + \int_{t_0}^{t} J_{Ni,y} \, dt - \int_{t_0}^{t} K_{off} \, dt \tag{25}
\]

\[
\text{State of charge: } SOC_t = SOC_{t,0} - \sum_j J_{Ni,j} \, dt \times MW_i / (\text{Loading} \times n \times \gamma \times X_i) \tag{26}
\]

\[
\text{Efficiency: } \eta_{Ni} = \sum_j J_{Ni,j} / I_{\text{cell}} \tag{27}
\]

RESULTS

Discharge behavior of Ni-Cd and Ni-H₂ cells

Simulations have been performed with the above two-phase model under discharge and charge conditions. Figs. 3 and 4 show the discharge curves of Ni-Cd and Ni-H₂ cells from models compared with the experimental data. These simulations were carried out with a marginally slower kinetics for the α-γ couple compared to the β-β couple (\sim 80 and 200" μA/cm², respectively). The rest of the model parameters in the model are described in our earlier publication.\(^{14}\) As is clear from the figures, the agreement between the experimental data and the simulations has significantly improved, upon the incorporation of the second couple at the Ni electrode.

Charging

Regarding the charge process, it has been observed from our testing of a 50 Ah Eagle Picher aerospace Ni-H₂ cell that at low temperatures (\textless -20°C), the charge profile consists of an additional plateau, before the roll-over (Fig. 3). This may be attributed to the conversion of \(\beta\)-NiOOH to \(\gamma\)-NiOOH, which is not as prominent at higher temperatures due to the interfering oxygen evolution reaction. We have demonstrated this trend with simulations, using the two-phase model (Fig. 4). The individual partial-current densities under these conditions, i.e., corresponding to the main reaction and oxygen evolution at both the phases, \(\beta\)-NiOOH to \(\gamma\)-NiOOH conversion and \(\alpha\)-Ni(OH)\(_2\) to β-
Ni(OI)₂ transformation support the above deduction. Apparently, the kinetics of oxygen evolution process are relatively sluggish such that the electrochemical conversion of β-NiOOI₁ to γ-NiOOI₁ is facilitated at low temperatures. This would result in an increase in the capacity of the Ni-112 cell due to a higher specific capacity of γ-NiOOI₁.

Cyclic Voltammetry

Finally, in an effort to further validate the two phase reaction scheme, the existing models of the nickel electrode were modified to simulate cyclic voltammetric behavior, by solving for the current at a time-dependent voltage. Any form of voltage sweep such as linear, triangular etc. can be adopted, with selected scan rates and number of cycles. Fig. 5 shows the typical cyclic voltammogram obtained from the model. Studies are underway to corroborate these voltammograms with experimental observations, especially under conditions favorable to both the phases.

CONCLUSIONS

The model incorporating the multiple phases of the active material at the Ni electrode in Ni rechargeable cells provides simulations with improved accuracy and closer to the experimental data, especially under favorable conditions such as extensive cycling, overcharge and low temperature charging. The reaction scheme includes two redox couples of β-NiOOI₁/β-Ni(OII)₁ and γ-NiOOI₁/α-Ni(OI)₁, and electrochemical, unidirectional conversion of β-NiOOI₁ to γ-NiOOI₁ and a chemical transformation of /α-Ni(OII)₁ to β-Ni(OI)₁.

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REFERENCES


Fig. 1: Comparison of 1) simulated discharge curve (boldline) of a 50 Ah [TOP]:X cell with 2) experimental data (dashedline) at C/2 and 25°C.
Fig. 2: Comparison of 1) simulated discharge curve (bold line) of a 5 Ah HEP cell with 2) experimental data (dashed line) at C/2 and 25°C.

Fig. 3: Experimental charge curves of a Ni-111 cell at C/10 and at various temperatures of 1) 35, 2) 20, 3) 10, 4) 0, and 5) -10 and 6) -2°C, respectively.
Fig. 4: Simulated charge curves of a Ni-I_2 cell at C/1 and at various temperatures.

Fig. 5: Typical simulated DC cyclic voltammetric curve of Ni oxide electrode in 7 M KOH.