Electronic network modeling of rechargeable batteries. I: The nickel and cadmium electrodes

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Electronic Network Modeling of Rechargeable Batteries

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ABSTRACT

This work introduces electronic network modeling as a new way of simulating battery behavior. Mathematical descriptions are given for the Ni and Cd electrode charge/discharge reactions. These mathematical descriptions are subsequently introduced in the form of electronic components, combined in an electronic network. The advantage of this way of modeling is that it provides a compact electronic model of a battery, which can be used in any electronic-circuit simulation, providing a tool to develop new battery-management systems. In addition, due to the discretization of the electrochemical reactions into separate electronic components, local currents and overpotentials occurring in the system can be studied. This information can be used to investigate the origin of certain battery behavior.

Introduction

Battery models which can predict the behavior of batteries under a wide variety of operating conditions are of considerable importance, especially to battery manufacturers and manufacturers of battery-operated portable equipment. Both are confronted with a growing desire for lighter products with longer playing times. Much effort is therefore being directed toward the development of new battery technologies, on the one hand, and the development of advanced battery-management systems (BMS), on the other hand. The main tasks of advanced BMS are to realize faster and more efficient battery charging and full exploitation of the available battery capacity. Battery models can be used to study the impact of new materials on the battery characteristics and for designing BMS.

Mathematical models have been developed for separate electrodes, such as the Ni electrode and the metal hydride electrode, and for complete battery systems, such as sealed lead-acid, Ni/H₂, Li-polymer, and Li-ion batteries. The NiCd battery system has also been extensively studied, and several researchers have presented mathematical models to predict the battery performance. Fan and White have presented a model for a sealed NiCd battery including the oxygen reaction. Their model shows that the competition between the Ni and oxygen reactions is responsible for the lower charge efficiency toward the end of charge. Weidner and Timmerman have thereupon shown the importance of proton diffusion limitation on the discharge characteristics of the Ni electrode. As a next step, De Vids and White have developed a model for the NiCd battery which includes proton diffusion in the Ni electrode and the secondary oxygen reaction. Their calculations have shown that the discharge performance is determined mainly by the kinetics of the Ni electrode and the proton diffusion process.

To the best of our knowledge, none of these models considers the battery temperature and the internal gas pressure development during the operation of the battery and the interaction between these quantities. In fact, in a sealed battery system, the battery voltage, temperature, and internal cell pressure are closely linked, and the mutual influence is considerable. For example, the cell pressure determines the rate of the oxygen recombination reaction and thus influences the charge/discharge efficiency of the battery. Furthermore, all reactions and mass transport processes which are modeled are temperature dependent. Therefore, in order to obtain a more realistic battery behavior from simulations both temperature and pressure should be accounted for.

The present paper introduces a new way of modeling battery behavior based on the discipline called system dynamics, which is common in engineering and allows simultaneous simulation of coupled physical systems under dynamic conditions. The modeling procedure is as follows: the NiCd battery system is subdivided into three parts, the negative electrode, the positive electrode, and the electrolyte. For each part, the specific reactions, mass transport, and other physical phenomena are modeled mathematically. The mathematical equations are clustered and converted into equivalent circuit elements, using the principles of system dynamics. Finally, the equivalent circuit elements are combined in an electronic network, yielding a compact model of the battery, which is analyzed using an electronic circuit simulator.

This paper focuses on the modeling of the behavior of the main charge storage reactions of the Ni and Cd electrodes, including charge-transfer kinetics and ionic mass transport. Part II describes the complete NiCd battery system, including the various side reactions and the pressure and temperature buildup inside the battery. The main aim is to demonstrate the concept of electronic network modeling rather than to get full quantitative agreement with experiments. Experimental verification of the model will be presented in a future publication, as is also indicated in Part II.

Model

General.—The basic principle of system dynamics is that interacting physical systems must exchange power. This principle is used to establish a uniform description of different systems in terms of power and energy variables. In rechargeable batteries, electrical energy is converted into chemical and/or thermal energy and vice versa. All of these physical domains can be modeled by means of electronic networks due to the existing mathematical analogies between the effort and flow relationships in the mentioned domains. The interaction between two domains, for example electrical and chemical, can be modeled in an electronic network.

* Electrochemical Society Active Member.

References

network by means of an ideal transformer, as shown in
Fig. 1, which is ideal in the sense that power is conserved
between both ports, i.e., at every moment of time
\[ e_1 f_1 = e_2 f_2 \]  
where the subscripts 1 and 2 refer to the ports in the elec-
trical and chemical domains, respectively. In the electrical
domain, effort is voltage \( V \) and flow is current \( I \). In order
to satisfy Eq. 1 in the chemical domain, effort and flow
variables should be selected in such a way that their product
has the same unit as \( V J \) in the electrical domain, namely,
\( [W] = [J/s] \). This requirement is fulfilled by defining
chemical potential \( \mu \) as effort and flux \( J \) as flow. These
definitions are summarized in Table II. The ideal trans-
former is further defined by
\[ V = \frac{1}{nF} \mu \]  
with \( 1/(nF) \) as the transformer coefficient. In a similar
way, the displacement variable can be related in both
domains by means of the transformer coefficient. In electro-
cal systems the displacement variable is charge \( q \).
Therefore it follows that the displacement variable in the
chemical domain is molar amount \( m \), with \( m = q/nF \).
These relationships are summarized in Table I.

The Ni electrode.—The Ni electrode overall charge/dis-
charge reaction is given by
\[ \text{charge} \quad \text{Ni(OH)}_2 + \text{OH}^- \rightarrow \text{NiOOH} + \text{H}_2\text{O} + e^- \]  
\[ \text{discharge} \quad \text{NiOOH} + \text{H}_2\text{O} + e^- \rightarrow \text{Ni(OH)}_2 + \text{OH}^- \]  
where \( x_i \) is the mole fraction of species \( i \), which is defined
as \( x_i = a_i/(a_{\text{NiOOH}} + a_{\text{Ni(OH)}_2}) \), with \( a_i \) the activity of species \( i \).

During charging, at the Ni electrode, divalent Ni \( \text{Ni(OH)}_2 \)
is oxidized to the trivalent state \( \text{NiOOH} \). The change in
\( \Delta G_{\text{Ni}} \) for this reaction is given by
\[ \Delta G_{\text{Ni}} = \mu_{\text{Ni(OH)}_2} + \mu_{\text{OH}^-} - \mu_{\text{NiOOH}} - \mu_{\text{e}} \]  
with \( \mu_i \), the chemical potential of species \( i \), according to
\[ \mu_i = \mu_i^o + RT \ln \left( \frac{a_i}{a_i^o} \right) \]  
in which \( a_i^o \) is the activity in the reference state. Fur-
thermore, in Eq. 6 \( \mu_i^o \) is the electrochemical potential of
species \( i \), according to
\[ \mu_i^o = \mu_i + z_i F \phi \]  
with \( \phi \) the electrostatic potential of the phase contain-
ing the considered charged species and \( z_i \) is its charge
with consideration of the sign. Combination of Eq. 6-8 and re-
arrangement of the terms yields
\[ \Delta G_{\text{Ni}} = -\left\{ \Delta G_{\text{Ni}}^o + RT \ln \left( \frac{(a_{\text{NiOOH}}/a_{\text{Ni(OH)}_2}) (a_{\text{OH}}/a_{\text{OH}}^o)}{(a_{\text{NiOOH}}/a_{\text{Ni(OH)}_2}) (a_{\text{OH}}/a_{\text{OH}}^o)} \right) \right\} + n_F F \phi \]  
where \( a_i^o \) symbolizes the activity in the reference state.

The activity is related to the concentration by means of the
dimensionless activity coefficient \( \gamma_i \), i.e., \( a_i = \gamma_i c_i \). In bat-
tery terms \( x_{\text{NiOOH}} \) corresponds to the state-of-charge of the
electrode.

In Eq. 9 the surface activities \( a_i \) are introduced because it
is assumed in this work that the electrode reaction takes
place at the electrode/electrolyte interface. Using the
transformation principle mentioned in the previous sec-
tion, the chemical potential terms in Eq. 9 are transformed
to electrical potentials by multiplying each term by the
transformer coefficient \( 1/nF \). This leads to the following
expression
\[ \psi_{\text{Ni}} = E_{\text{Ni}} - E_{\text{Ni}}^o F \]  
with \( \psi_{\text{Ni}} \) the reaction overpotential given by
\[ \psi_{\text{Ni}} = \Delta G_{\text{Ni}} / n_F F \]  
and \( E_{\text{Ni}}^o \) the “apparent” equilibrium potential in terms of
surface activities, given by
\[ E_{\text{Ni}}^o = E_{\text{Ni}} + RT \ln \left( \frac{(a_{\text{NiOOH}}/a_{\text{Ni(OH)}_2}) (a_{\text{OH}}/a_{\text{OH}}^o)}{(a_{\text{NiOOH}}/a_{\text{Ni(OH)}_2}) (a_{\text{OH}}/a_{\text{OH}}^o)} \right) \]  
with \( E_{\text{Ni}} \) the standard reaction potential, according to
\[ E_{\text{Ni}} = \Delta G_{\text{Ni}}^o / n_F F \]  
Note that in the absence of mass-transport limitations the
surface activities of all species are equal to the bulk activ-
ities. In that case \( E_{\text{Ni}}^o \) is equal to the true equilibrium
potential \( E_{\text{Ni}}^0 \), as defined by the Nernst equation for this
reaction, i.e.,
\[ E_{\text{Ni}}^o = E_{\text{Ni}}^0 + RT \ln \left( \frac{(a_{\text{NiOOH}}/a_{\text{Ni(OH)}_2}) (a_{\text{OH}}/a_{\text{OH}}^o)}{(a_{\text{NiOOH}}/a_{\text{Ni(OH)}_2}) (a_{\text{OH}}/a_{\text{OH}}^o)} \right) \]  
where the overlined activities refer to bulk activities. Mass-
transport limitation inside the Ni electrode are treated in a
later section. The dependence of \( E_{\text{Ni}}^o \) on \( x_{\text{NiOOH}} \) is given in
Fig. 2a. The natural log term in Eq. 14 leads to a sigmoidal
shape of the equilibrium potential, as Fig. 2a shows. This
typical shape is always recognized in the charge/discharge
characteristics of Ni-based battery types, like NiCd, NiMH, and Ni-H$_2$. As is shown later, the equilibrium potential of the Cd electrode is independent of state-of-charge. Therefore, the shape of the open-circuit potential of a NiCd battery is determined almost completely by the thermodynamics of the Ni electrode. At low and high states of charge, the equilibrium potential of the Ni electrode shows a strong dependence on state-of-charge. As a result of this, the electrode potential can change to a value at which secondary reactions take place. This is a common situation encountered in NiCd batteries upon overcharging or overdischarging, as is treated in Part II.  

Electronic network modeling of Ni electrode for the case of pure kinetic control.—The Ni electrode is modeled as an electronic network consisting of a separate electrical and

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Value</th>
<th>Dimension</th>
<th>Description</th>
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</thead>
<tbody>
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<td>$A_{Ni}$</td>
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<td>Activity of species i</td>
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<td>$a_i^0$</td>
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</tr>
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<td>$C_{Cd}$</td>
<td>2.4</td>
<td>F</td>
<td>Double-layer capacitance Ni electrode</td>
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<td>m$^2$/s</td>
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<tr>
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<td>Standard free energy change of cadmium electrode reaction</td>
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<td>Number of nuclei</td>
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<td>Number of electrons involved in reaction i</td>
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<td>Number of spatial elements in Ni electrode</td>
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<td>C</td>
<td>Charge</td>
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<td>C</td>
<td>Initial storage capacity in Cd electrode</td>
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<td>Stored capacity Ni electrode</td>
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<td>Stored surface capacity Ni electrode</td>
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<td>Volume</td>
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<td>$Q_{Ni}$</td>
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<td>Charge-transfer coefficient reaction i</td>
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<td>Activity coefficient species i</td>
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<td>Standard chemical potential of species i</td>
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<td>Mass transport overpotential redox reaction i</td>
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<tr>
<td>$Q_{Ni}$</td>
<td>C</td>
<td>Extended surface area Cd electrode</td>
<td></td>
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</table>
This total chemical potential is transformed to the electrical domain through the ideal transformer. Thus, the electrical potential $V_{Ni}^\text{chem}$ across the electrical port of the transformer corresponds to $V_{Ni}^\text{chem} = V_{Ni}^\text{chem}/nNF = E_{N} - \eta_{N}^\text{Ni} = E_{N}^\text{Ni}$, in accordance with Eq. 11.

The electrical domain is connected to the upper port of the transformer. If an external current or voltage source is connected between terminals a and b, a current I will flow, which is the sum of two partial currents: $I_{N}$, the current required to charge the electrical double-layer and $I_{Ni}$, the reaction current. Therefore in the electrical domain two parallel paths are introduced, the upper representing the double-layer capacitance ($C_{dl}$) and the lower the electrochemical reaction. It is assumed that the double-layer capacitance does not change significantly in the considered potential range, hence, an average value is used. The reaction kinetics of reaction 4 are described by the Butler-Volmer equation according to

$$I_{Ni} = I_{N}^e \left[ \exp \left( \frac{\alpha_{Ni} n_{F} F \phi_{Ni}^\text{chem}}{R T} \right) - \exp \left( -\left(1 - \alpha_{Ni} \right) \frac{n_{F} F \eta_{Ni}^\text{chem}}{R T} \right) \right]; \text{[19]}$$

where $I_{N}^e$ is the exchange current given by

$$I_{N}^e = n_{Ni} F A_{Ni} \rho_{Ni}^{\text{NiOH}} (\rho_{Ni}^{\text{NiOH}})^{1/2} (\rho_{Ni}^{\text{OH}})^{1/2} \rho_{Ni}^{\text{H}^2}; \text{[20]}$$

In Eq. 20 is $\rho_{Ni}$ refers to the equilibrium activity of species i, $A_{Ni}$ denotes the electrode surface area, $k_{Ni}$ is the standard rate constant, and $\alpha_{Ni}$ is the charge-transfer coefficient. Figure 2b shows that the exchange current displays a parabolic dependence on $X_{NOOH}$ with the position of the maximum determined by $\alpha$. At the state-of-charge corresponding to the maximum exchange current, the reaction kinetics is fastest, and the overpotential required to charge or discharge the electrode has a minimum value. At states of-charge both lower and higher than this point, the reaction kinetics decreases, and thus the overpotential rises. This implies that it is more difficult to charge or discharge a nearly empty or nearly full electrode than a partially charged electrode.

The charge-transfer reaction is modeled in the electrical domain by two antiparallel diodes, $D_{Ni}$. The upper diode refers to the oxidation reaction, whereas the lower diode refers to the reduction reaction. Note that this particular representation is purely illustrative and has been chosen because of the mathematical analogy between the exponential form of the current-voltage relationship of the electrochemical reaction (Eq. 19) and an electrical diode. In the actual electronic network the antiparallel diodes are a user-defined element, having a current/voltage relationship according to Eq. 19 and 20. The voltage across $D_{Ni}$ corresponds to $\eta_{Ni}^\text{Ni}$ whereas the voltage across the double-layer capacitance corresponds to the electrode potential $E_{N}^\text{Ni}$.

**Electronic network modeling of Ni electrode including diffusion limitations.**—Reaction 4 is generally assumed to proceed through diffusion of protons through the active
electrode material to the electrode/electrolyte boundary where they recombine with OH⁻ to form H₂O, according to

\[
\text{Ni(OH)}_2 + \text{OH}^- + \text{H}^+ + e^- \rightleftharpoons \text{NiOOH} + \text{H}_2\text{O} \quad [21]
\]

charge

\[
\text{H}^+ + \text{OH}^- \rightleftharpoons \text{H}_2\text{O} \quad [22]
\]

discharge

A schematic representation of the Ni electrode is given in Fig. 4. It is assumed that the position of the Ni atoms is fixed and that charge and mass transport occurs only by means of electrons and protons, where the movement of protons is assumed to be rate-limiting. It is further assumed that the Ni electrode is a perfect conductor, meaning that there is no electric field inside the electrode, so that mass transport due to migration can be neglected. Convection is also neglected, thus, only diffusion is considered. During charging at the electrode/electrolyte surface, an electron is removed from the lattice, and Ni(OH)₂ is oxidized to NiOOH, accompanied by the simultaneous release of a proton (see reaction 21). The proton moves through the lattice from one nickel site to the other. This leads to an apparent flux of Ni(OH)₂ and NiOOH species. Concentration gradients of both species appear when the reaction kinetics is fast in comparison to the mass-transport rate of protons. For simplicity linear diffusion is considered in the direction perpendicular to the electrode surface.

The driving force for diffusion of species i is a chemical potential difference \( \Delta \mu_i \), or

\[
J_i = \frac{1}{R_i} \Delta \mu_i \quad [23]
\]

where \( J_i \) is the flux and \( R_i \) is a proportionality constant. The subscript i refers to either Ni(OH)₂ or NiOOH. The diffusion flux can also be written as

\[
J_i = A_{ni} D_{hi} \nabla a_i \quad [24]
\]

although, strictly speaking, this equation is only valid for dilute solutions. Note that, in line with the reasoning stated above, the proton diffusion coefficient \( D_{hi} \) is entered in Eq. 24, while concentration and flux refer to either Ni(OH)₂ or NiOOH. The initial and boundary conditions for the considered system are

(i) At time \( t = 0 \) the activity of each species is uniform throughout the electrode and is equal to the equilibrium activity, i.e., \( a_0 = \bar{a}_i \).

(ii) At the electrode/electrolyte interface the activity gradient is determined by the electrical current due to the charge/discharge reaction according to Eq. 19, i.e., \( A_{ni} D_{hi} \nabla a_i = I_{ni}/(n_{ni} F) \).

(iii) At the electrode/current collector interface (\( x = L \)) the activity gradient is equal to zero, i.e., \( \nabla a_i = 0 \), since ions cannot pass the interface.

Diffusion can be modeled by means of electrical RC-ladder networks by making use of the mathematical analogies between the equations for electrical and chemical fluxes (Eq. 16-20). A schematic diagram of such an RC-ladder network describing linear diffusion is presented in Fig. 5. The electrode is discretized into \( n \) spatial elements with thickness \( \Delta x \). Each spatial element is represented by a combination of a nonlinear variable capacitance \( C_i \) and a nonlinear variable resistance \( R_{di} \). The capacitances are defined in the same way as described in the previous section, and the potential across each capacitor corresponds to the chemical potential given by \( \mu = \mu^0 + RT \ln a(x, t)/[\bar{a}(x, t)] \) where \( a(x, t) \) is the activity at position \( x \) and time \( t \), while the charge on the capacitors corresponds to the local molar amount of the species \( m(x, t) = a(x, t)\bar{a}\Delta x \). Thus, the capacitances are given by

\[
C_i = \frac{dm}{d\mu} = \frac{m(x, t)}{RT} \quad [25]
\]

Combination of Eq. 23 and 25 leads to the following expression for \( R_{di} \)

\[
R_{di} = \frac{RT(\Delta x)^2}{D_{hi} m(x, t)} \quad [26]
\]

Note that \( C_i \) and \( R_{di} \) are variable due to the variation of \( m(x, t) \). A difference in molar amount between adjacent capacitances results in a chemical potential difference across the nonlinear resistances and thus leads to a diffusion flux \( J_m \). The condition of mass continuity is also fulfilled in this RC combination. This is understood by realizing that the mass continuity equation, i.e.,

\[
\frac{da_i}{dt} = D_{hi} \nabla a_i = \frac{1}{A_{ni}} \nabla J_i \quad [27]
\]

may be rewritten as

\[
\frac{dm_i}{dt} = \Delta J_i \quad [28]
\]

using \( \nabla J_i = \Delta J_i/\Delta x \). Equation 28 is equivalent to the electrical equation for charging of a capacitor. Figure 5 clearly shows that Eq. 28 is fulfilled since the difference between the fluxes flowing into and out of a spatial element is stored as molar amount on \( C_i \).

In the case of the Ni electrode, two RC ladder networks are combined, one for the NiOOH and the other for the Ni(OH)₂ species, as is indicated in Fig. 6. Both networks are connected by means of the reference line in the middle. The capacitances denoted with the superscript \( s \) correspond to the surface species, while the other capacitances refer to species within the electrode. The current flowing through the electrochemical port is given by \( I_{ni}/n_{ni} F \) (see Eq. 3), which satisfies the boundary conditions of the mass-transport problem at the electrode/electrolyte interface. The boundary condition at \( x = L \) is automatically fulfilled because no current can enter or leave the network at the other end of the transmission line. The initial condition of the mass-transport problem is met by applying an initial charge on the capacitances corresponding to the initial molar amount of the considered species within each spatial element. When mass-transport limitations play a role, the molar amount on the surface capacitances and those in the interior of the RC ladder network differ, leading to a difference between \( E_{ni}^{0} \) and \( E_{ni} \) in the electrical

![Fig. 4. Schematic representation of the Ni electrode during charging.](image)

![Fig. 5. Schematic representation of RC ladder network describing linear diffusion.](image)
domain. This difference is also referred to as the diffusion overpotential \( \eta_{\text{diff}} \).

The Cd electrode.—The Cd electrode is modeled as a heterogeneous system composed of two separate phases: metallic Cd and an oxide layer consisting of Cd(OH)\(_2\). The overall charge/discharge reaction is represented by

\[
\text{Cd(OH)}_2 + 2e^- \rightarrow \text{Cd} + 2 \text{OH}^- \quad [29]
\]

The reaction rate is considered to be determined by the kinetics of the charge-transfer reaction and mass transport of OH\(^-\) species. It is further assumed that the charge-transfer reaction takes place only at the free metallic Cd surface, since Cd(OH)\(_2\) is a poor electronic conductor.\(^{25}\) The change in free enthalpy for reaction 29 is given by

\[
\Delta G_{\text{Cd}} = \mu_{\text{Cd}} + 2\mu_{\text{OH}} - \mu_{\text{Cd(OH)2}} - 2\mu_e \quad [30]
\]

which, combined with Eq. 8 and 9, gives

\[
\Delta G_{\text{Cd}}^o = \left\{ \Delta G_{\text{Cd}}^o + RT \ln \left( \frac{(a_{\text{Cd(OH)2}}/a_{\text{Cd}})(a_{\text{OH}}/a_{\text{OH}})^2}{(a_{\text{Cd}}/a_{\text{Cd(OH)2}})(a_{\text{OH}}/a_{\text{OH}})^2} \right) \right\} + n_{\text{Cd}}F(\psi_e - \phi) \quad [31]
\]

where

\[
\Delta G_{\text{Cd}}^o = \mu_{\text{Cd(OH)2}} + 2\mu_e - \mu_{\text{Cd}} - 2\mu_{\text{OH}} \quad [32]
\]

Like the Ni electrode, this electrode is also modeled in an electronic network by separate chemical and electrical domains, which are coupled by means of an ideal transformer having a transformer coefficient of \( 1/n_{\text{Cd}}F \), as is shown in Fig. 7. The chemical domain consists of a series of capacitances which are placed such that during charging a molar amount is extracted from Cd(OH)\(_2\) and stored on Cd and \( \text{CH}^- \). The capacitances are defined in the same way as mentioned before. The chemical port is placed in parallel to the series of capacitances, with the potential across the chemical port corresponding to

\[
V_{\text{Cd}} = n_{\text{Cd}}F(\phi^*_{\text{Cd}} - \psi_e) - \Delta G_{\text{Cd}} - \Delta G_{\text{Cd}}^o + RT \ln \left( \frac{(a_{\text{Cd(OH)2}}/a_{\text{Cd}})(a_{\text{OH}}/a_{\text{OH}})^2}{(a_{\text{Cd}}/a_{\text{Cd(OH)2}})(a_{\text{OH}}/a_{\text{OH}})^2} \right) \quad [33]
\]

\( V_{\text{Cd}}^\text{chem} \) is transformed to the electrical domain through the ideal transformer to yield the following electrical potential \( V_{\text{Cd}}^e \) across the electrical port

\[
V_{\text{Cd}}^e = E_{\text{Cd}} - \eta_{\text{Cd}} = E_{\text{Cd}}^o \quad [34]
\]

with \( E_{\text{Cd}} \) the Cd electrode potential, \( \eta_{\text{Cd}} \) the reaction overpotential, and \( E_{\text{Cd}}^o \) the “apparent” equilibrium potential, which is defined as

\[
E_{\text{Cd}}^o = E_{\text{Cd}} - \eta_{\text{Cd}} = \frac{RT}{n_{\text{Cd}}F} \ln \left( \frac{(a_{\text{Cd(OH)2}}/a_{\text{Cd}})(a_{\text{OH}}/a_{\text{OH}})^2}{(a_{\text{Cd}}/a_{\text{Cd(OH)2}})(a_{\text{OH}}/a_{\text{OH}})^2} \right) \quad [35]
\]

with \( E_{\text{Cd}} = \Delta G_{\text{Cd}}/(n_{\text{Cd}}F) \). The activities of the solids Cd(OH)\(_2\) and Cd and \( \text{OH}^- \) are defined by unity. The true equilibrium potential \( E_{\text{Cd}}^o \) of reaction 29 is therefore given by

\[
E_{\text{Cd}}^o = E_{\text{Cd}} - \frac{RT}{n_{\text{Cd}}F} \ln(a_{\text{OH}})^2 \quad [36]
\]

with \( a_{\text{OH}}^\text{bulk} \) the bulk equilibrium activity of \( \text{OH}^- \). It is assumed that this quantity is constant throughout the charging and discharging process. Therefore, \( E_{\text{Cd}}^o \) is considered as constant, as was mentioned before. If the surface and bulk activities of \( \text{OH}^- \) differ, a diffusion overpotential arises, which is equal to the difference between \( E_{\text{Cd}}^o \) and \( E_{\text{Cd}} \). The \( \text{OH}^- \) diffusion problem is defined by the following diffusion and mass-continuity equations

\[
J_{\text{OH}^-} = \bar{A}_{\text{OH}^-}D_{\text{OH}^-} \nabla a_{\text{OH}^-} \quad [37]
\]

\[
\frac{da_{\text{OH}^-}}{dt} = D_{\text{OH}^-} \nabla^2 a_{\text{OH}^-} \quad [38]
\]

with \( J_{\text{OH}^-} \) and \( D_{\text{OH}^-} \) being the flux and diffusion coefficient of \( \text{OH}^- \), respectively. The initial and boundary conditions of this system are given by

\[
a_{\text{OH}^-} = a_{\text{OH}^-}^\text{eq} \quad \text{at } t = 0, \text{ for all } x \quad [39]
\]

\[
a_{\text{OH}^-} = a_{\text{OH}^-}^\text{bulk} \quad \text{at } x >> 0, \text{ for all } t \quad [40]
\]
The diffusion problem can be modeled by a similar RC ladder network as described for the Ni electrode. In the present model, however, a simplification has been made by considering stationary mass transport of OH⁻. This is justified because the time required to build a diffusion layer dCd between both electrodes inside a battery is much less than the typical charge/discharge time. The solution of the steady-state mass-transport problem under the mentioned initial and boundary conditions is given by

\[ J_{\text{OH}} = \frac{I_{\text{Cd}} D_{\text{Cd}}}{\sigma_{\text{Cd}} (\sigma_{\text{OH}} - \sigma_{\text{ac}})} \]  

(42)

The flux is also described by Eq. 23, which, combined with Eq. 42, yields the following expression of the "diffusion" resistance R:\(_\text{OH}^*\):

\[ R_{\text{OH}}^* = \frac{R T d_{\text{Cd}}^2}{D_{\text{OH}} m_{\text{OH}}} \]  

(43)

The electrical domain consists of a double-layer capacitance C\(_\text{Cd}\) placed in parallel to the series combination of which grow at a rate controlled by both diffusion and time \(t_0\). Furthermore, hemispherical nuclei are assumed, being instantaneous, meaning that all nuclei are formed at sufficiently small to consider the nucleation process as the time interval during which the nuclei are formed is eventually merge to form a layer. It is further assumed that these grow further to form small metallic particles, which metal phase starts with the formation of single nuclei.

\[ \theta_{\text{ex}} = \pi N r^2 \left( \frac{4}{3} \pi r^3 \right)^{1/3} \]  

(47)

where \(m_{\text{Cd(OH)2}}\) is the initial molar amount of Cd. When the growing particles merge, the actual surface area covered by metallic Cd is smaller than the extended surface \(\theta_{\text{ex}}\). Therefore, a correction should be made for the overlapping areas (see Fig. 8). The relation between the actual covered and the extended surface is given by Avrami's theorem²⁶:

\[ A_{\text{Cd}} = A_{\text{Cd}}^{\text{ext}} \left( 1 - \exp(-\theta_{\text{ex}}) \right) \]  

(48)

where \(A_{\text{Cd}}^{\text{ext}}\) refers to the maximum surface area of the Cd electrode.

The simulated development of \(A_{\text{Cd}}\), normalized to \(A_{\text{Cd}}^{\text{ext}}\) during charging of a Cd electrode is shown in Fig. 9 for different values of the number of nuclei \(N\). All other parameters values are as listed in Table II. It is seen that, for high values of \(N\), the electrode is at once completely covered by metallic Cd. In that case the reaction rate is fastest since \(I_{\text{Cd}}\) obtains a maximum value from the beginning and remains unchanged during charging. For lower

\[ V = \frac{2}{3} \pi N r^3 \]  

(46)

In Eq. 46 \(M_{\text{Cd}}\) represents the molecular weight of the Cd species, and \(p_{\text{Cd}}\) its density. Furthermore, \(V_c\) corresponds to the volume of the formation of Cd. \(V_c\) consists of both the volume of the initial amount of material present at the electrode and the volume of the metallic clusters formed during the nucleation stage. The integral in Eq. 46 is equivalent to the state-of-charge \(Q_{\text{Cd}}\) of the electrode.
values of $N$, $A_{C}$ starts at a low value and slowly increases during charging, according to Eq. 48. Since $E_{q}$ is linearly related to $A_{C}$, in that case, the reaction rate starts at a lower rate and increases during charging. If the electrode is charged/discharged with a constant current, the lower reaction rate can be noticed in the electrode characteristics by a higher overpotential and thus to a lower performance of the electrode.

Simulation results.—The electronic-circuit simulator PSTAR® was used for all described simulations. Other circuit simulators, such as SPICE®, can also be used as long as they allow the introduction of large sets of coupled nonlinear equations. Simulations of the Ni electrode behavior were performed with the electronic network presented in Fig. 6. All simulations were performed at constant ambient temperature of 298 K. Figures 10 to 13 show the simulation results of galvanostatic charging, resting, and discharging with low and high currents. The parameters used in the simulations are given in Table II. Figure 10a shows the development of $E_{M}$ and $E_{Mq}$ as a function of state-of-charge, obtained when the electrode is successively charged and discharged with 0.1 A, which corresponds to 0.12 C based on the electrode capacity given in Table II. It is seen that $E_{Mq}$ lies exactly midway between the charge and discharge curves. During charging $E_{Mq}$ is higher than during discharging, as is to be expected, since during charging the overpotential is positive, while during discharging it is negative. The corresponding overpotentials during charging and discharging are shown in Fig. 10b. It is seen that $\eta_{Mq}$ is much smaller than $\eta_{M}$, showing the importance of mass-transport limitations in the electrode. The parabolic shape of the exchange current can be recognized in the overpotential characteristic by realizing that the overpotential is inversely related to the exchange current. However, the effect of the parabolic shape of $E_{q}$ has a less significant effect on the total overpotential than the contribution of $\eta_{M}$. The latter also shows an inverse parabolic shape, as a result of the logarithmic term in the expression for $\eta_{M}$. i.e.

$$\eta_{M} = E_{Mq} - E_{M} = \frac{RT}{n_{M} F} \ln \left( \frac{a_{NiOOH}^{\infty}}{a_{NiOOH}^{0}} \right)$$

For $0.2 < x_{NiOOH} < 0.8$, the total overpotential is relatively small, so that the electrode potential $E_{M}$ nearly coincides with $E_{Mq}$. Outside these ranges, a deviation between $E_{M}$ and $E_{Mq}$ is noticeable, which is mainly due to $\eta_{M}$. Figure 11a shows that, in the case of charging and discharging with 1 A, a relatively large difference exists between $E_{Mq}$ and $E_{M}$. The corresponding overpotentials in Fig. 11b show that this is again mainly caused by mass-transport limitations, i.e., $\eta_{Mq}$ is significantly higher than $\eta_{M}$.

The distribution of NiOOH species inside the electrode during charging, resting, and discharging with a current of 0.1 A is shown in Fig. 12. Under this condition the distribution is found to be uniform. Comparison with Fig. 13 shows that charging and discharging with 2 A (2.4 C) leads to a spatial distribution of NiOOH. This is caused by mass-transport limitation of protons. It is seen that during charging, at each moment of time, the state-of-charge at the electrode surface ($x = 0 \mu m$) is higher than at other ($x > 0 \mu m$) positions within the electrode. If the electrode is allowed to rest under open-circuit conditions, the distribution relaxes toward the bulk equilibrium value, as can be seen in Fig. 13 during the rest period. If the current is reversed, i.e., during discharging, an opposite state-of-charge gradient develops, and a depletion of NiOOH is found at the electrode surface. According to Eq. 19 the

![Fig. 10. Simulated state-of-charge dependences of (a, top) the Ni electrode voltage ($E_{M}$ vs. SHE) and the equilibrium voltage ($E_{Mq}$ vs. SHE), and (b, bottom) the charge transfer ($\eta_{M}$) and diffusion ($\eta_{Mq}$) overpotential, using the parameter values listed in Table II, with a charge/discharge current of 0.1 A.](image1.png)

![Fig. 11. Simulated state-of-charge dependences of (a, top) the Ni electrode voltage ($E_{M}$ vs. SHE) and the equilibrium voltage ($E_{Mq}$ vs. SHE), and (b, bottom) the charge transfer ($\eta_{M}$) and diffusion ($\eta_{Mq}$) overpotential, using the parameter values listed in Table II, with a charge/discharge current of 2 A.](image2.png)
charging and discharging processes stop when the state-of-charge at the electrode/electrolyte surface attains the maximum value or becomes zero, respectively. Figure 13 shows that, when the electrode is charged with a high current, the state-of-charge at the electrode surface differs significantly from the state-of-charge within the electrode. Likewise, if the electrode is discharged with a high current, the state-of-charge at the electrode surface becomes zero while there is still active material (NiOOH) within the electrode. In both cases the electrode cannot be utilized completely, which has a negative effect on both charge and discharge efficiency.

Improvement of the charge and discharge performance of the electrode can be expected by reducing the diffusion length of the protons, which can be achieved by reducing the layer thickness of NiOOH/Ni(OH)$_2$. Figure 14 shows the simulated effect of the layer thickness on the charge efficiency, which is defined as $Q_{Ni}/Q_0$, of the Ni electrode using the tabulated $D_{Ni}$ and a current of 2 A (2.4 C). It is found that the charge efficiency drops rapidly for layer thickness values larger than 5 μm and is close to 100% for layer thickness values less than 1 μm. In that case diffusion is no longer a limiting factor.

Besides studying the dc behavior, the network model can also be applied to study the response to more complex perturbations, such as in impedance spectroscopy. Some simulated impedance spectra for the Ni electrode at various states-of-charge are presented in Fig. 15 using the parameter values listed in Table II and in the frequency range of 0.1 Hz to 10 kHz. The semicircle seen in the figure is due to the parallel combination of the double-layer capacitance $C_{Dl}$ and the reaction element $D_{Ni}$. The impedance of the reaction element $D_{Ni}$ is the charge-transfer resistance $R_{Ni}$, which is equal to the derivative $d\eta_{Ni}/dF$ of Eq. 19. In the impedance spectrum $R_{Ni}$ can be recognized as the semicircle diameter. For low amplitude perturbations, Eq. 19 can be linearized, which leads to the following known expression for $R_{Ni}$:

$$R_{Ni} = \frac{RT}{n_{Ni}F}$$

From Eq. 50 it follows that the charge-transfer resistance is determined solely by $R_{Ni}$, which shows a dependence on the state-of-charge according to Eq. 20. Figure 2b shows that for $\alpha = 0.5$, $R_{Ni}$ is symmetrical around 50% state-of-charge; therefore also the semicircles in the impedance plots are symmetric around 50% state-of-charge, i.e., the impedance plots of 25 and 75% state-of-charge coincide, as do the plots of 10 and 90% state-of-charge. At lower frequencies mass-transport limitations start to play a role, which is recognized in the impedance plots as a 45° line in the lower frequency range, due to the RC transmission line.

**Conclusions**

It has been shown that electronic network modeling can be used to simulate the electrochemical reactions and transport phenomena inside batteries. The attention has
been focused on the main charging and discharging reactions of the Ni and Cd electrodes in a NiCd battery. However, the principles shown here also can be used to model other reactions which occur inside a NiCd battery. This is shown in Part II,15 where the model is extended with the addition of oxygen production and recombination cycles. Part II also shows how the battery pressure and temperature can be simulated simultaneously with the cell voltage.

An important advantage of this type of modeling is that the network representation allows one to focus on the local overpotentials across or partial currents flowing through the electronic elements. This is helpful in investigating the origin of certain battery behavior. Moreover, the electronic network representation allows simulation of a total system in such a way that the interaction between a battery and its surrounding electronics can be studied. Some examples of this are shown elsewhere.16

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29. PSTAR® is a trademark of Philips Electronics N.V., Eindhoven, The Netherlands.