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Electronic Network Modeling of Rechargeable Batteries

I. The Nickel and Cadmium Electrodes

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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 electrode¹⁻⁴ and the metal hydride electrode,⁵ and for complete battery systems, such as sealed lead-acid,⁶ Ni/H₂,⁷ Li-polymer,⁸ and Li-ion⁹ 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^{10,11} 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 Timmerman¹² have thereupon shown the importance of proton diffusion limitation on the discharge characteristics of the Ni electrode. As a next step, De Vids and White¹³ 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,¹⁴ 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 II¹⁵ 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

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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

$$e_1 f_1 = e_2 f_2 \quad [1]$$

where the subscripts 1 and 2 refer to the ports in the electrical 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 $V \cdot I$ in the electrical domain, namely, $[W] = [J/s]$. This requirement is fulfilled by defining chemical potential μ as effort and flux J as flow. These definitions are summarized in Table II. The ideal transformer is further defined by

$$V = \frac{1}{nF} \mu \quad [2]$$

$$\frac{1}{nF} I = J \quad [3]$$

where $1/(nF)$ is the transformer coefficient. In a similar way, the displacement variable can be related in both domains by means of the transformer coefficient. In electrical 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/discharge reaction is given by

It is assumed that there are no volume changes in the active material during charging and discharging and that NiOOH and Ni(OH)₂ are the only species present within the Ni electrode. In other words, it is assumed that

$$x_{\text{NiOOH}} + x_{\text{Ni(OH)}_2} = 1 \quad [5]$$

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 .

Fig. 1. Schematic representation of an ideal transformer, coupling the electrical and chemical domains.

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

During charging, at the Ni electrode, divalent Ni Ni(OH)₂ is oxidized to the trivalent state (NiOOH). The change in ΔG_{Ni} for this reaction is given by

$$\Delta G_{\text{Ni}} = \mu_{\text{Ni(OH)}_2} + \bar{\mu}_{\text{OH}^-} - \mu_{\text{NiOOH}} - \mu_{\text{H}_2\text{O}} - \bar{\mu}_{\text{e}^-} \quad [6]$$

with μ_i the chemical potential of species i , according to

$$\mu_i = \mu_i^\circ + RT \ln \left(\frac{a_i}{a_i^{\text{ref}}} \right) \quad [7]$$

in which a_i^{ref} is the activity in the reference state. Furthermore, in Eq. 6 $\bar{\mu}_i$ is the electrochemical potential of species i , according to

$$\bar{\mu}_i = \mu_i + z_i F \phi \quad [8]$$

with ϕ the electrostatic potential of the phase containing the considered charged species and z_i is its charge with consideration of the sign. Combination of Eq. 6-8 and rearrangement of the terms yields

$$\Delta G_{\text{Ni}} = - \left\{ \Delta G_{\text{Ni}}^\circ + RT \ln \left(\frac{(a_{\text{NiOOH}}^s/a_{\text{NiOOH}}^{\text{ref}})(a_{\text{H}_2\text{O}}^s/a_{\text{H}_2\text{O}}^{\text{ref}})}{(a_{\text{Ni(OH)}_2}^s/a_{\text{Ni(OH)}_2}^{\text{ref}})(a_{\text{OH}^-}^s/a_{\text{OH}^-}^{\text{ref}})} \right) \right\} + n_{\text{Ni}} F (\phi_{\text{Ni}}^s - \phi^1) \quad [9]$$

with $a_{\text{e}^-}^s$ unity by definition and

$$\Delta G_{\text{Ni}}^\circ = \mu_{\text{NiOOH}}^\circ + \mu_{\text{H}_2\text{O}}^\circ + \mu_{\text{e}^-}^\circ - \mu_{\text{Ni(OH)}_2}^\circ - \mu_{\text{OH}^-}^\circ \quad [10]$$

In Eq. 9 the surface activities a_i^s 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 section, 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

$$\eta_{\text{Ni}}^k = E_{\text{Ni}} - E_{\text{Ni}}^{\text{eq}'} \quad [11]$$

with η_{Ni}^k the reaction overpotential given by

$$\eta_{\text{Ni}}^k = \Delta G_{\text{Ni}}/n_{\text{Ni}} F \quad [12]$$

E_{Ni} is the interfacial potential difference between the electrode (s) and the electrolytic solution (l), given by

$$E_{\text{Ni}} = \phi_{\text{Ni}}^s - \phi^1 \quad [13]$$

and $E_{\text{Ni}}^{\text{eq}'}$ the "apparent" equilibrium potential in terms of surface activities, given by

$$E_{\text{Ni}}^{\text{eq}'} = E_{\text{Ni}}^\circ + \frac{RT}{n_{\text{Ni}} F} \ln \left(\frac{(a_{\text{NiOOH}}^s/a_{\text{NiOOH}}^{\text{ref}})(a_{\text{H}_2\text{O}}^s/a_{\text{H}_2\text{O}}^{\text{ref}})}{(a_{\text{Ni(OH)}_2}^s/a_{\text{Ni(OH)}_2}^{\text{ref}})(a_{\text{OH}^-}^s/a_{\text{OH}^-}^{\text{ref}})} \right) \quad [14]$$

with E_{Ni}° the standard reaction potential, according to

$$E_{\text{Ni}}^\circ = \Delta G_{\text{Ni}}^\circ/n_{\text{Ni}} F \quad [15]$$

Note that in the absence of mass-transport limitations the surface activities of all species are equal to the bulk activities. In that case $E_{\text{Ni}}^{\text{eq}'}$ is equal to the true equilibrium potential $E_{\text{Ni}}^{\text{eq}}$, as defined by the Nernst equation for this reaction, i.e.

$$E_{\text{Ni}}^{\text{eq}} = E_{\text{Ni}}^\circ + \frac{RT}{n_{\text{Ni}} F} \ln \left(\frac{(\bar{a}_{\text{NiOOH}}/\bar{a}_{\text{NiOOH}}^{\text{ref}})(\bar{a}_{\text{H}_2\text{O}}/\bar{a}_{\text{H}_2\text{O}}^{\text{ref}})}{(\bar{a}_{\text{Ni(OH)}_2}/\bar{a}_{\text{Ni(OH)}_2}^{\text{ref}})(\bar{a}_{\text{OH}^-}/\bar{a}_{\text{OH}^-}^{\text{ref}})} \right) \quad [16]$$

where the overlined activities refer to bulk activities. Mass-transport limitation inside the Ni electrode are treated in a later section. The dependence of $E_{\text{Ni}}^{\text{eq}}$ on x_{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

Table I. Relationships between electrical and chemical domains.

	Electrical domain	Chemical domain
Effort (e)	Voltage, V in [V]	Chemical potential, μ in [J/mol]
Flow (f)	Current, I in [A] = [C/s]	Flux, J in [mol/s]
Displacement (q)	Charge, $Q = \int I dt$ in [C]	Molar amount, $m = \int J dt$ in [mol]
Power (P)	$V \cdot I$ in [VA] = [J/s] = [W]	$\mu \cdot J$ in [J/s] = [W]

characteristics of Ni-based battery types, like NiCd, NiMH, and Ni-H₂.²¹ 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.¹⁵

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 II. List of parameters, parameter values, and constants used in the simulations.

Symbol	Value	Dimension	Description
A_{Cd}		m ²	Surface area Cd electrode
A_{Cd}^{max}	23.3	m ²	Maximum surface area Cd electrode
A_{Ni}	11.8	m ²	Surface area Ni electrode
a_i		mol/m ³	Activity of species i
$\bar{a}_i$		mol/m ³	Equilibrium activity of species i
a_i^s		mol/m ³	Surface activity of species i
a_i^{ref}		mol/m ³	Activity of species i in the reference state
C_{Cd}^{dl}	4.7	F	Double-layer capacitance Cd electrode
C_{Ni}^{dl}	2.4	F	Double-layer capacitance Ni electrode
C_e		mol ² /J	Electrochemical capacitance
c_i		mol/m ³	Concentration of species i
D_{H^+}	$5 \cdot 10^{-14}$	m ² /s	Diffusion coefficient of H ⁺ inside Ni at 298 K
D_{OH^-}	$5 \cdot 10^{-10}$	m ² /s	Diffusion coefficient of OH ⁻ at 298 K
d_{Cd}	10^{-6}	m	Diffusion layer thickness at Cd electrode
E_i^{red}		V	Equilibrium potential of redox reaction i
E_{Cd}^{red}	-0.808	V vs. SHE	Standard redox potential Cd electrode ²⁸
E_{Ni}^{red}	0.520	V vs. SHE	Standard redox potential Ni electrode ²⁸
E_i		V	Electrode potential of electrode i
e			Effort
F	96485	C/mol	Faraday's constant
f			Flow
ΔG		J/mol	Free energy change
ΔG_{Cd}^0	$-1.56 \cdot 10^5$	J/mol	Standard free energy change of cadmium electrode reaction ²⁸
ΔG_{Ni}^0	$5.02 \cdot 10^4$	J/mol	Standard free energy change of nickel electrode reaction ²⁸
I_{dif}		A	Diffusion controlled current
I_{kin}		A	Kinetically controlled current
I_i		A	Local current reaction path i
I_{Cd}^0	$2.3 \cdot 10^3$	A	Exchange current Cd reaction (value at 50% state of charge)
I_{Ni}^0	36	A	Exchange current Ni reaction (value at 50% state of charge)
J_i		mol/s	Flux of species i
k_i			Standard rate constant of reaction i at 298 K
L	$5.5 \cdot 10^{-6}$	m	Layer thickness Ni(OH) ₂ /NiOOH electrode
M_{Cd}	112.4	g/mol	Molecular weight Cd
m_i		mol	Molar amount species i
N	10^{14}	None	Number of nuclei
n_i		None	Number of electrons involved in reaction i
n	50	None	Number of spatial elements in Ni electrode
q		C	Charge
Q_{Cd}		C	Stored capacity Cd electrode
$Q_{Cd(Cd)}$	800	C	Initial storage capacity in Cd electrode
Q_{Cd}^{max}	5000	C	Maximum storage capacity Cd electrode
Q_{Cd}		C	Stored capacity Ni electrode
Q_{Ni}		C	Equilibrium stored capacity Ni electrode
Q_{Ni}^{max}	3060	C	Maximum storage capacity Ni electrode
Q_{Ni}^s		C	Stored surface capacity Ni electrode
R	8.314	J/mol·K	Gas constant
R^d		Js/mol ²	Mass-transport resistance
R_{ct}		Ω	Charge-transfer resistance
r		m	Radius
T	298	K	Temperature
t		s	Time
V		m ³	Volume
x_i		m	Mole fraction of species i
x			Space variable
α_i	0.5		Charge-transfer coefficient reaction i
γ_i	1	none	Activity coefficient species i
μ_i		J/mol	Electrochemical potential of species i
μ_i^o		J/mol	Chemical potential of species i
μ_i^s		J/mol	Standard chemical potential of species i
Φ_i^e		V	Electrostatic potential of electrode i
Φ_i		V	Electrostatic potential of electrolyte
Φ		V	Density of Cd
ρ_{Cd}	$8.64 \cdot 10^6$	g/m ³	Overpotential redox reaction i
η_i		V	Kinetic overpotential redox reaction i
η_i^k		V	Mass-transport overpotential redox reaction i
η_i^d		V	Extended surface area Cd electrode
θ_{ex}		m ²

Fig. 2. (a, top) The equilibrium potential ($E_{\text{Ni}}^{\text{eq}}$) vs. SHE as a function of state-of-charge (x_{NiOOH}) and (b, bottom) the exchange current (I_{Ni}^0) of the Ni reaction as a function of the state-of-charge (x_{NiOOH}) of the electrode for different values of the charge transfer coefficient α . The curves are calculated using the parameter values listed in Table II.

chemical domain. In the electrical domain the electrical potentials and currents are modeled, whereas in the chemical domain the (electro-)chemical potentials and fluxes are modeled. Both domains are coupled by means of an ideal transformer with a transformer coefficient of $1/n_{\text{Ni}}F$, as is indicated in Fig. 3. In the chemical domain, nonlinear, variable capacitances are used to model each chemical species. Each capacitance is defined such that the voltage across the capacitance corresponds to μ_i , according to Eq. 7, while the charge on the capacitance corresponds to m_i . The capacitances are placed in series with the polarities as indicated in Fig. 3, such that during charging a molar amount is extracted from $C_{\text{Ni(OH)}_2}^s$ and $C_{\text{OH}^-}^s$ and stored on C_{NiOOH}^s and $C_{\text{H}_2\text{O}}^s$. The total chemical potential $V_{\text{Ni}}^{\text{chem}}$ is the sum of the chemical potentials, with consideration of the sign, across the capacitances and is given by

$$V_{\text{Ni}}^{\text{chem}} = \sum_i \pm \mu_i = \Delta G_{\text{Ni}}^{\circ} + RT \ln \left(\frac{(a_{\text{NiOOH}}^s/a_{\text{NiOOH}}^{\text{ref}})(a_{\text{H}_2\text{O}}^s/a_{\text{H}_2\text{O}}^{\text{ref}})}{(a_{\text{Ni(OH)}_2}^s/a_{\text{Ni(OH)}_2}^{\text{ref}})(a_{\text{OH}^-}^s/a_{\text{OH}^-}^{\text{ref}})} \right) \quad [17]$$

The chemical port of the transformer is placed in parallel to the series of capacitances, such that, in accordance with Eq. 9 the chemical potential across the chemical port is equal to

$$V_{\text{Ni}}^{\text{chem}} = n_{\text{Ni}}F(\phi_{\text{Ni}}^s - \phi^l) - \Delta G_{\text{Ni}} \quad [18]$$

This total chemical potential is transformed to the electrical domain through the ideal transformer. Thus, the elec-

Fig. 3. Electronic network model of the Ni electrode in the case of a purely charge-transfer-controlled reaction.

trical potential $V_{\text{Ni}}^{\text{el}}$ across the electrical port of the transformer corresponds to $V_{\text{Ni}}^{\text{el}} = V_{\text{Ni}}^{\text{chem}}/n_{\text{Ni}}F = E_{\text{Ni}} - \eta_{\text{Ni}}^k = E_{\text{Ni}}^{\text{eq}}$, 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: $I_{\text{Ni}}^{\text{dl}}$, 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 ($C_{\text{Ni}}^{\text{dl}}$) 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

$$I_{\text{Ni}} = I_{\text{Ni}}^0 \left\{ \exp \left[\alpha_{\text{Ni}} \frac{n_{\text{Ni}}F}{RT} \eta_{\text{Ni}}^k \right] - \exp \left[-(1 - \alpha_{\text{Ni}}) \frac{n_{\text{Ni}}F}{RT} \eta_{\text{Ni}}^k \right] \right\} \quad [19]$$

where I_{Ni}^0 is the exchange current given by

$$I_{\text{Ni}}^0 = n_{\text{Ni}}FA_{\text{Ni}}k_{\text{Ni}}(\bar{a}_{\text{NiOOH}})^{\alpha}(\bar{a}_{\text{Ni(OH)}_2})^{1-\alpha}(\bar{a}_{\text{H}_2\text{O}})^{\alpha}(\bar{a}_{\text{OH}^-})^{1-\alpha} \quad [20]$$

In Eq. 20 $\bar{a}_i$ refers to the equilibrium activity of species i , A_{Ni} denotes the electrode surface area, k_{Ni} is the standard rate constant, and α_{Ni} is the charge-transfer coefficient. Figure 2b shows that the exchange current displays a parabolic dependence on x_{NiOOH} , with the position of the maximum determined by α . 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 η_{Ni}^k , whereas the voltage across the double-layer capacitance corresponds to the electrode potential E_{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 H_2O , according to

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

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

where J_i is the flux and R_d is a proportionality constant. The subscript i refers to either Ni(OH)_2 or NiOOH . The diffusion flux can also be written as

$$J_i = A_{\text{Ni}} D_{\text{H}^+} \nabla a_i \quad [24]$$

although, strictly speaking, this equation is only valid for dilute solutions.²² Note that, in line with the reasoning stated above, the proton diffusion coefficient D_{H^+} 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., $a_i = \bar{a}_i$.

(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., $A_{\text{Ni}} D_{\text{H}^+} \nabla a_i^s = I_{\text{Ni}} / (n_{\text{Ni}} F)$.

(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

Fig. 4. Schematic representation of the Ni electrode during charging.

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 Δx . Each spatial element is represented by a combination of a nonlinear variable capacitance C_i and a nonlinear variable resistance $R_{d,i}$. The capacitances are defined in the same way as described in the previous section, i.e., the potential across each capacitor corresponds to the chemical potential given by $\mu = \mu^0 + RT \ln a(x, t) / [a^{\text{ref}}(x, t)]$ 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 $m(x, t) = a(x, t) A_{\text{Ni}} \Delta x$. 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 $R_{d,i}$

$$R_{d,i} = \frac{RT(\Delta x)^2}{D_{\text{H}^+} m(x, t)} \quad [26]$$

Note that C_i and $R_{d,i}$ 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_d . The condition of mass continuity is also fulfilled in this RC combination. This is understood by realizing that the mass continuity equation, i.e.

$$\frac{da_i}{dt} = D_{\text{H}^+} \nabla^2 a_i = \frac{1}{A_{\text{Ni}}} \nabla J_i \quad [27]$$

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 $I_{\text{Ni}} / n_{\text{Ni}} F$ (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 $E_{\text{Ni}}^{\text{ref}}$ and $E_{\text{Ni}}^{\text{eq}}$ in the electrical

Fig. 5. Schematic representation of RC ladder network describing linear diffusion.

domain. This difference is also referred to as the diffusion overpotential η_{Ni}^d .

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 $\text{Cd}(\text{OH})_2$. The overall charge/discharge reaction is represented by

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 $\text{Cd}(\text{OH})_2$ is a poor electronic conductor.²⁵ The change in free enthalpy for reaction 29 is given by

$$\Delta G_{\text{Cd}} = \mu_{\text{Cd}} + 2\bar{\mu}_{\text{OH}^-} - \mu_{\text{Cd}(\text{OH})_2} - 2\bar{\mu}_{e^-} \quad [30]$$

which, combined with Eq. 8 and 9, gives

$$\Delta G_{\text{Cd}} = - \left\{ \Delta G_{\text{Cd}}^0 + RT \ln \left(\frac{(a_{\text{Cd}(\text{OH})_2}^s / a_{\text{Cd}(\text{OH})_2}^{\text{ref}})}{(a_{\text{Cd}}^s / a_{\text{Cd}}^{\text{ref}})(a_{\text{OH}^-}^s / a_{\text{OH}^-}^{\text{ref}})^2} \right) \right\} + n_{\text{Cd}}F(\phi^s - \phi^1) \quad [31]$$

where

$$\Delta G_{\text{Cd}}^0 = \mu_{\text{Cd}(\text{OH})_2}^0 + 2\mu_{e^-}^0 - \mu_{\text{Cd}}^0 - 2\mu_{\text{OH}^-}^0 \quad [32]$$

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 $C_{\text{Cd}(\text{OH})_2}^s$ and stored on C_{Cd}^s and $C_{\text{OH}^-}^s$. The capacitances are defined in the same way as mentioned before. The chemical port is placed in

Fig. 7. Electronic network model of the Cd electrode.

parallel to the series of capacitances, with the potential across the chemical port corresponding to

$$V_{\text{Cd}}^{\text{chem}} = n_{\text{Cd}}F(\phi_{\text{Cd}}^s - \phi^1) - \Delta G_{\text{Cd}} = \Delta G_{\text{Cd}}^0 + RT \ln \left(\frac{(a_{\text{Cd}(\text{OH})_2}^s / a_{\text{Cd}(\text{OH})_2}^{\text{ref}})}{(a_{\text{Cd}}^s / a_{\text{Cd}}^{\text{ref}})(a_{\text{OH}^-}^s / a_{\text{OH}^-}^{\text{ref}})^2} \right) \quad [33]$$

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

$$V_{\text{Cd}}^{\text{el}} = E_{\text{Cd}} - \eta_{\text{Cd}}^k = E_{\text{Cd}}^{\text{eq}'} \quad [34]$$

with E_{Cd} the Cd electrode potential, η_{Cd}^k the reaction overpotential, and $E_{\text{Cd}}^{\text{eq}'}$ the “apparent” equilibrium potential, which is defined as

$$E_{\text{Cd}}^{\text{eq}'} = E_{\text{Cd}}^0 + \frac{RT}{n_{\text{Cd}}F} \ln \left(\frac{(a_{\text{Cd}(\text{OH})_2}^s / a_{\text{Cd}(\text{OH})_2}^{\text{ref}})}{(a_{\text{Cd}}^s / a_{\text{Cd}}^{\text{ref}})(a_{\text{OH}^-}^s / a_{\text{OH}^-}^{\text{ref}})^2} \right) \quad [35]$$

with $E_{\text{Cd}}^0 = \Delta G_{\text{Cd}}^0 / (n_{\text{Cd}}F)$. The activities of the solids $\text{Cd}(\text{OH})_2$ and Cd are unity by definition. The true equilibrium potential $E_{\text{Cd}}^{\text{eq}}$ of reaction 29 is therefore given by

$$E_{\text{Cd}}^{\text{eq}} = E_{\text{Cd}}^0 - \frac{RT}{n_{\text{Cd}}F} \ln(\bar{a}_{\text{OH}^-})^2 \quad [36]$$

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

$$J_{\text{OH}^-} = A_{\text{Cd}} D_{\text{OH}^-} \nabla a_{\text{OH}^-} \quad [37]$$

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

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

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

$$a_{\text{OH}^-} = \bar{a}_{\text{OH}^-} \quad \text{at } x \gg 0, \text{ for all } t \quad [40]$$

Fig. 6. Electronic network model of the Ni electrode in the case of combined charge-transfer and diffusion-controlled reaction.

$$\nabla a_{\text{OH}^-} = \frac{I_{\text{Cd}}}{n_{\text{Cd}} F A_{\text{Cd}} D_{\text{OH}^-}}$$

at $x = 0$ (electrode/electrolyte interface) [41]

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 d_{Cd} 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

$$J_{\text{OH}^-} = \frac{A_{\text{Cd}} D_{\text{OH}^-}}{d_{\text{Cd}}} (\bar{a}_{\text{OH}^-} - a_{\text{OH}^-}^s) \quad [42]$$

The flux is also described by Eq. 23, which, combined with Eq. 42, yields the following expression of the "diffusion" resistance $R_{\text{OH}^-}^d$

$$R_{\text{OH}^-}^d = \frac{RT(d_{\text{Cd}})^2}{D_{\text{OH}^-} m_{\text{OH}^-}} \quad [43]$$

The electrical domain consists of a double-layer capacitance $C_{\text{Cd}}^{\text{dl}}$ placed in parallel to the series combination of two reaction diodes, represented by D_{Cd} , and the electrical port of the ideal transformer. According to Eq. 34, and by applying Kirchhoff's voltage law, the potential across $C_{\text{Cd}}^{\text{dl}}$ is E_{Cd} , the potential across D_{Cd} is η_{Cd}^k , and the potential across the electrical transformer port is $E_{\text{Cd}}^{\text{eq}}$. The current I_{Cd} through D_{Cd} is determined by the following current-voltage relationship

$$I_{\text{Cd}} = I_{\text{Cd}}^0 \left\{ \exp \left[\alpha_{\text{Cd}} \frac{n_{\text{Cd}} F}{RT} \eta_{\text{Cd}}^k \right] - \exp \left[-(1 - \alpha_{\text{Cd}}) \frac{n_{\text{Cd}} F}{RT} \eta_{\text{Cd}}^k \right] \right\} \quad [44]$$

with the exchange current I_{Cd}^0 is given by

$$I_{\text{Cd}}^0 = n_{\text{Cd}} F A_{\text{Cd}} k_{\text{Cd}} \bar{a}_{\text{Cd}}(\text{OH})_2 \bar{a}_{\text{OH}^-} \bar{a}_{\text{Cd}} \quad [45]$$

where A_{Cd} refers to the metallic Cd surface area and k_{Cd} is the potential-independent standard rate constant. Since it is assumed that the reaction takes place only at the free metallic Cd surface A_{Cd} , I_{Cd}^0 is a function of state-of-charge. The development of A_{Cd} on the state-of-charge of the electrode is derived in the next section.

Cd electrode surface-area dependence on the state-of-charge.—To model the way in which A_{Cd} depends on the state-of-charge of the electrode, it is assumed that the metal phase starts with the formation of single nuclei. These grow further to form small metallic particles, which eventually merge to form a layer. It is further assumed that the time interval during which the nuclei are formed is sufficiently small to consider the nucleation process as being instantaneous, meaning that all nuclei are formed at time t_0 . Furthermore, hemispherical nuclei are assumed, which grow at a rate controlled by both diffusion and charge transfer, as was shown in the previous section. The "extended" electrode surface, θ_{ex} , covered by N separate hemispherical particles is given by $\theta_{\text{ex}} = \pi N r^2$, with the radius r following from the volumetric amount of deposited material according to

$$V = \frac{2}{3} \pi N r^3 = V_0 + \frac{M_{\text{Cd}}}{\rho_{\text{Cd}}} \int_{t_0} J_{\text{Cd}}(t) dt \quad [46]$$

In Eq. 46 M_{Cd} represents the molecular weight of the Cd species, and ρ_{Cd} its density. Furthermore, V_0 corresponds to the volume of the deposit at time t_0 , and J_{Cd} is the flux resulting from the formation of Cd. V_0 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_{Cd} of the electrode,

Fig. 8. Overlapping metal nuclei growing on a surface.

since Cd is formed during charging (see Eq. 29). From Eq. 46 it follows that the extended surface is given by

$$\theta_{\text{ex}} = \pi N r^2(t) = (\pi N)^{1/3} \left(\frac{3M_{\text{Cd}}}{2\rho_{\text{Cd}}} (m_{\text{Cd}(\text{Cd})} + m_{\text{Cd}}) \right)^{2/3} \quad [47]$$

where $m_{\text{Cd}(\text{Cd})}$ 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 θ_{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

$$A_{\text{Cd}} = A_{\text{Cd}}^{\text{max}} (1 - \exp\{-\theta_{\text{ex}}\}) \quad [48]$$

where $A_{\text{Cd}}^{\text{max}}$ refers to the maximum surface area of the Cd electrode.

The simulated development of A_{Cd} , normalized to $A_{\text{Cd}}^{\text{max}}$, 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_{Cd}^0 obtains a maximum value from the beginning and remains unchanged during charging. For lower

Fig. 9. Simulated development of the normalized metallic Cd electrode surface area ($A_{\text{Cd}}/A_{\text{Cd}}^{\text{max}}$) as a function of state-of-charge for different numbers of nuclei N . The simulation is performed using the parameter values listed in the Table II, at a charge current of 0.1 A.

values of N , A_{Cd} starts at a low value and slowly increases during charging, according to Eq. 48. Since I_{Cd}^0 is linearly related to A_{Cd} , 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_{Ni} and E_{Ni}^{eq} 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_{Ni}^{eq} lies exactly midway between the charge and discharge curves. During charging E_{Ni} 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 η_{Ni}^k is much smaller than η_{Ni}^d , 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 cur-

rent. However, the effect of the parabolic shape of I_{Ni}^0 has a less significant effect on the total overpotential than the contribution of η_{Ni}^d . The latter also shows an inverse parabolic shape, as a result of the logarithmic term in the expression for η_{Ni}^d ,³⁰ i.e.

$$\eta_{Ni}^d = E_{Ni}^{eq'} - E_{Ni}^{eq} = \frac{RT}{n_{Ni}F} \ln \left(\frac{a_{NiOOH}^s \bar{a}_{Ni(OH)_2}}{\bar{a}_{NiOOH} a_{Ni(OH)_2}^s} \right) \quad [49]$$

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

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_{Ni} vs. SHE) and the equilibrium voltage (E_{Ni}^{eq} vs. SHE), and (b, bottom) the charge transfer (η_{Ni}^k) and diffusion (η_{Ni}^d) overpotential, using the parameter values listed in Table II, with a charge/discharge current of 0.1 A.

Fig. 11. Simulated state-of-charge dependences of (a, top) the Ni electrode voltage (E_{Ni} vs. SHE) and the equilibrium voltage (E_{Ni}^{eq} vs. SHE), and (b, bottom) the charge transfer (η_{Ni}^k) and diffusion (η_{Ni}^d) overpotential, using the parameter values listed in the Table II, with a charge/discharge current of 2 A.

Fig. 12. State-of-charge (x_{NiOOH}) development as a function of time within the electrode during charging, resting, and discharging with 0.1 A, using the parameter values listed in Table II.

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 $Q_{\text{Ni}}/Q_{\text{Ni}}^{\text{max}}$, of the Ni electrode using the tabulated D_{H^+} 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 $C_{\text{Ni}}^{\text{dl}}$ and the reaction element D_{Ni} . The impedance of the

Fig. 13. State-of-charge (x_{NiOOH}) development as a function of time within the electrode during charging, resting, and discharging with 2 A, using the parameter values listed in Table II.

Fig. 14. Simulated charge efficiency ($Q_{\text{Ni}}/Q_{\text{Ni}}^{\text{max}}$) as a function of the NiOOH/Ni(OH)₂ electrode thickness, using the parameter values of Table II.

reaction element D_{Ni} is the charge-transfer resistance R_{ct} , which is equal to the derivative $d\eta_{\text{Ni}}^k/dI_{\text{Ni}}$ of Eq. 19. In the impedance spectrum R_{ct} 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_{ct}

$$R_{\text{ct}} = \frac{RT}{n_{\text{Ni}} F I_{\text{Ni}}} \quad [50]$$

From Eq. 50 it follows that the charge-transfer resistance is determined solely by I_{Ni} , which shows a dependence on the state-of-charge according to Eq. 20. Figure 2b shows that for $\alpha = 0.5$, I_{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

Fig. 15. Simulated impedance plots of the Ni electrode at 1, 10, 25, 50, 75, and 90% state-of-charge (SoC) in the frequency range of 0.1 Hz to 10 kHz, using the parameter values listed in Table II.

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.³¹

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