Electronic network modeling of rechargeable batteries: II: The NiCd system

Citation for published version (APA):

Notten, P. H. L., Kruijt, W. S., & Bergveld, H. J. (1998). Electronic network modeling of rechargeable batteries: II: The NiCd system. *Journal of the Electrochemical Society*, 145(11), 3774-3783.
<https://doi.org/10.1149/1.1838872>

DOI:

[10.1149/1.1838872](https://doi.org/10.1149/1.1838872)

Document status and date:

Published: 01/01/1998

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

www.tue.nl/taverne

Take down policy

If you believe that this document breaches copyright please contact us at:

openaccess@tue.nl

providing details and we will investigate your claim.

Electronic Network Modeling of Rechargeable Batteries

II. The NiCd System

P. H. L. Notten,* W. S. Kruijt, and H. J. Bergveld

Philips Research Laboratories, 5656 AA Eindhoven, The Netherlands

ABSTRACT

Based on the concept of a defined sealed rechargeable NiCd battery, the mathematics of the various electrochemical and physical processes occurring inside the battery are described. Subsequently, these sets of mathematical equations are clustered and converted into an electronic network model. Introducing the relevant electrochemical and physical parameters, the one-dimensional model is shown to be capable of simulating not only the development of the cell voltage during (over)charging and (over)discharging, but also of simultaneously calculating the development of the internal gas pressure. Considering the thermal dependencies of the various electrochemical reactions and those of the battery environment, the temperature development and the mutual interaction with the voltage and gas pressure can also be calculated. Since the electronic network approach gives access to all partial currents flowing through the different reaction paths inside the battery, it is easy to visualize what processes are occurring during battery operation. This is, for example, illustrated for the two-step overdischarge process, indicating that, respectively, the Cd and O₂ charge-transfer reactions play a dominant role under these conditions. Electronic network simulations are shown to be not only restricted to direct current applications but are also applicable to processes, like open-circuit voltage relaxation and self-discharge behavior.

Introduction

Electronic network modeling has been shown to be a very useful tool in the design of electronic circuits.¹ Complex structures consisting of, for example, capacitors, resistors, and transistors can nowadays easily be programmed and their mutual electronic interaction can be swiftly simulated by advantageously making use of both the predefined mathematical models of the individual electronic elements and the description of the interconnection between the elements within these electronic circuits.

It has been shown in general terms^{2,4} and in more detail in Part I of this series⁵ that, quite different from electronic circuit design, electronic network modeling can also be beneficially applied for simulating the thermodynamics and kinetics of electrochemical charge-transfer reactions and other physical processes, such as those occurring inside rechargeable batteries. This paves the way for simulating not only the electrochemical behavior of batteries but also the mutual interaction between these batteries and the surrounding electronics once accurate models are available. This in turn may lead, for example, to more efficient charging electronics and improved state-of-charge (SoC) indicators. On the other hand, materials research may benefit from this type of modeling as the impact of new materials on the overall battery behavior can be predicted at a very early stage.

Part I was devoted to the one-dimensional modeling of the thermodynamics and kinetics of the electrochemical storage reactions of the two individual electrodes of NiCd batteries, i.e., the Ni and Cd electrode.⁵ In the case of the Ni electrode the kinetics was modeled by considering a combined action of the charge-transfer reaction and mass transport of protons inside the solid.^{5,6} On the other hand, the Cd electrode has been modeled by the generally accepted precipitation/dissolution mechanism.^{5,7}

Apart from the main energy storage reactions it is essential that these batteries also operate under more severe conditions, such as those taking place during overcharging and overdischarging. Under these conditions side reactions, like gas formation and recombination reactions may occur, depending on the design of the battery. An important aspect of NiCd behavior is the close relationship between the voltage, the gas pressure inside the battery, and its temperature development. This not only determines the voltage dependence upon (over)charging and (over)discharging, but it is well known that this also affects cycle life of batteries in a negative sense. The main aim of our modeling activity is therefore not only to take into account the voltage dependence but also to consider the development of both the internal gas pressure and temperature and their mutual interactions.

The strategy adopted in the present work is as follows: (i) starting with an appropriate description of the concept of a NiCd battery the most important electrochemical reactions are identified. (ii) An appropriate mathematical description of the thermodynamics and kinetics of the relevant electrochemical and physical processes, including the pressure and temperature development, can then be given. (iii) Subsequently, these mathematical equations are clustered and converted into representing "electronic components," which are combined in an electronic network model. This leads to a "transparent" battery model, which enables one to designate the local thermodynamics, kinetics, and heat production of all individual processes occurring inside these batteries. (iv) Finally, introducing the relevant electrochemical and physical input parameters into the model, simulations can be performed. Some results, revealing the strength of this modeling method, are presented.

Concept of Sealed Rechargeable NiCd Batteries

Several concepts have been proposed and adopted for NiCd batteries in the past. They are, for example, optimized toward a high storage capacity cell or toward a more robust battery system. A schematic representation of a battery concept, which has proven its maturity, is shown in Fig. 1. The nickel and cadmium electrodes are electrically insulated from each other by a separator. In order to provide ionic conductivity between the two electrodes during current flow, both separator and electrodes are impregnated with a concentrated alkaline solution. The electrochemically active species involved in the energy storage reactions are indicated in Fig. 1. The white areas of both electrodes schematically represent the nominal storage capacity of the battery, which is dictated by the maximum reversible capacity of the Ni electrode, denoted by $Q_{\text{Ni}}^{\text{max}}$. The basic electrochemical charge-transfer reactions can, in their most simplified form, be represented by

During charging, divalent Ni(OH)₂ is oxidized into the trivalent NiOOH state and Cd(OH)₂ is reduced into metallic Cd. The reverse reactions take place during discharging. The mathematical description of these basic energy storage processes has been treated in detail in Part I of this series.⁵

To ensure the proper performance of sealed rechargeable NiCd batteries under all circumstances and to provide intrinsic safety, the battery is designed in a very specific way, in particular to prevent gas pressure buildup during overcharging and overdischarging. The various side reactions, taking place under these conditions are also indicated

* Electrochemical Society Active Member.

Fig. 1. Schematic representation of the concept of a sealed rechargeable NiCd battery, revealing the energy storage reactions (white areas) and the overcharging and overdischarging reactions (shaded areas).

ed in Fig. 1 (shaded areas). Since the Ni electrode is the capacity-determining electrode in a NiCd battery, oxidation of OH^- ions is forced to occur at the Ni electrode during overcharging, through which oxygen evolution starts, according to

Simultaneously, reduction of Cd(OH)_2 , in excess present in the Cd electrode, still continues according to reaction 2. As a result, the partial oxygen pressure within the cell starts to rise and induces electrochemical conversion of O_2 at the Cd electrode, according to

This recombination reaction thus competes with reduction of Cd(OH)_2 , represented by Eq. 2. Some investigators claim that O_2 can also chemically react with electrochemically formed Cd. However, the net effect is in both cases, the same, i.e., the recombination reaction limits the internal gas pressure.

It is shown in one of the following sections that, in particular, this oxygen recombination reaction produces a lot of heat. This implies that, depending on the competition between reactions 2 and 4, the gas pressure and/or temperature of the battery will rise during overcharging, which in turn will affect the battery voltage. The close interrelationship between the voltage, internal gas pressure, and battery temperature is clearly revealed in the result of a galvanostatic (over)charging experiment, depicted in Fig. 2. This figure shows that both the pressure and temperature remain essentially constant as long as the main storage reactions are involved in the charging process. This changes significantly when oxygen evolution starts at an almost fully charged battery, i.e., close to 100% SoC. The voltage increases upon overcharging, due to oxygen evolution and the increasing pressure induces the recombination reaction to take place and hence the temperature to rise. As a consequence, the cell voltage starts to level off and ultimately declines upon profound overcharging. This so-called $-\Delta V$ effect is often exploited to terminate galvanostatic charging in commercial battery chargers. This result shows that, in order to set up an appropriate model for NiCd batteries, it is essential to consider the interrelation of the three above-mentioned parameters.

Fig. 2. Experimentally measured voltage, pressure, and temperature development of an activated commercial NiCd (P60AA from Panasonic) battery during charging and overcharging with a constant current (0.6 A) at ambient temperature (298 K). The pressure ($10^5 \text{ Pa} \sim 1 \text{ bar}$) was measured through a hole by means of a pressure transducer (Transamerica Instruments, type no. 4702-10), which was drilled in the bottom of the battery. The temperature was monitored by means of a Pt-100 thermocouple placed on the battery.

Protection against overdischarging is also of considerable importance, especially when batteries, which inevitably reveal small differences in storage capacity, are used in series. Since a hydrogen recombination cycle has to be avoided, due to the poor electrocatalytic activity of the Cd electrode with respect to the H_2 oxidation reaction,⁸ battery manufacturers adopted another elegant approach.⁹ A significant amount of Cd(OH)_2 , generally denoted as depolarizer, is added to the Ni electrode and, to a lesser extent, some metallic Cd is added to the Cd electrode as discharge reserve (see also Fig. 1). During overdischarging the Cd(OH)_2 present in the Ni electrode ($Q_{\text{Cd(Ni)}}$) is reduced to metallic Cd (reaction 2), while the excess of metallic Cd at the Cd electrode ($Q_{\text{Cd(Cd)}}$) is still being oxidized. Under these conditions a battery voltage close to 0 V is to be expected.

As the amount of extra Cd in the Cd electrode is limited with respect to the amount of Cd(OH)_2 in the Ni electrode (see Fig. 1), a second overdischarge process will be established. An oxygen recombination cycle will again take place, now initiated at the cadmium electrode while recombination of oxygen occurs at the Ni electrode, according to Eq. 3 and 4, respectively (see Fig. 1). When O_2 is evolved at the Cd electrode at positive potentials and is converted again into OH^- at the Ni electrode at very negative potentials, a potential reversal of the battery is to be expected. This is in agreement with experimental observations. Evidently, under these overdischarge conditions it is also essential to consider the interaction between voltage, pressure, and temperature.

Theoretical Considerations

Thermodynamics of the oxygen reactions.—The electrochemical potential ($\bar{\mu}_i$) of species i involved in an electrochemical charge-transfer reaction can, in general terms, be represented by

$$\bar{\mu}_i = \mu_i^0 + RT \ln \frac{a_i^s}{a_i^{\text{ref}}} + z_i F \phi^{s/l} \quad [5]$$

where μ_i^0 gives the standard chemical potentials, R the gas constant, T the absolute temperature, a_i the activities of species i , a_i^{ref} the activities of these species in the reference state, z_i the charge of the reacting species involved, and F is the Faraday constant. The Galvani potential of either the electrode ($^{\circ}$) or the electrolyte (l) is represented by $\phi^{s/l}$ and indicates the electrostatic influence on the electrochemical potential of the charged reacting species, in the present case the electrons and OH^- ions.¹⁰ Applying this equation to the oxygen recombination reaction (Eq. 4), the change in free enthalpy (ΔG_{rec}) can be described by

$$\Delta G_{\text{rec}} = 4\mu_{\text{OH}^-}^\circ - \mu_{\text{O}_2}^\circ - 2\mu_{\text{H}_2\text{O}}^\circ - 4\mu_e^\circ + RT \ln \frac{(a_{\text{OH}^-}^s/a_{\text{OH}^-}^{\text{ref}})^4}{(a_{\text{O}_2}^s/a_{\text{O}_2}^{\text{ref}})(a_{\text{H}_2\text{O}}^s/a_{\text{H}_2\text{O}}^{\text{ref}})^2} + 4F(\phi^s - \phi^1) \quad [6]$$

in which a_e and a_e^{ref} are unity by definition. The coefficients are in accordance with Eq. 4. Under equilibrium conditions ΔG_{rec} is zero and Eq. 6 reduces to a relationship for the oxygen equilibrium potential ($E_{\text{O}_2}^{\text{eq}}$) and the surface activities turn into equilibrium activities ($\bar{a}_i$)

$$E_{\text{O}_2}^{\text{eq}} = (\phi^s - \phi^1) = \frac{\mu_{\text{O}_2}^\circ + 2\mu_{\text{H}_2\text{O}}^\circ + 4\mu_e^\circ - 4\mu_{\text{OH}^-}^\circ}{4F} + \frac{RT}{4F} \ln \frac{(\bar{a}_{\text{O}_2}/a_{\text{O}_2}^{\text{ref}})(\bar{a}_{\text{H}_2\text{O}}/a_{\text{H}_2\text{O}}^{\text{ref}})^2}{(\bar{a}_{\text{OH}^-}/a_{\text{OH}^-}^{\text{ref}})^4} \quad [7]$$

The same derivation can, of course, be given for the oxygen evolution reaction (Eq. 3).

There is a direct relationship between the partial oxygen pressure in the gas phase (g) and its activity in the electrolyte (l). The oxygen dissolution reaction can be represented by

where k_1 and k_2 are the corresponding reaction rate constants. For an ideal gas Henri's law applies, i.e.

$$a_{\text{O}_2} = K_{\text{O}_2} p_{\text{O}_2} \quad [9]$$

and

$$a_{\text{O}_2}^{\text{ref}} = K_{\text{O}_2} p_{\text{O}_2}^{\text{ref}} \quad [10]$$

in which the oxygen solubility constant (K_{O_2}) is given by k_2/k_1 . Advantageously, the reported solubility constant appears to be independent on the temperature in the strong alkaline solution present in NiCd batteries.¹¹ Introducing the pressure into Eq. 7 by means of Eq. 9 and 10 leads to the well-known Nernst equation

$$E_{\text{O}_2}^{\text{eq}} = E_{\text{O}_2}^\circ + \frac{RT}{4F} \ln \frac{p_{\text{O}_2}}{p_{\text{O}_2}^{\text{ref}}} \quad [11]$$

where the standard redox potential, $E_{\text{O}_2}^\circ$ is given by

$$E_{\text{O}_2}^\circ = \frac{\mu_{\text{O}_2}^\circ + 2\mu_{\text{H}_2\text{O}}^\circ + 4\mu_e^\circ - 4\mu_{\text{OH}^-}^\circ}{4F} + \frac{RT}{4F} \ln \frac{(a_{\text{H}_2\text{O}}/a_{\text{H}_2\text{O}}^{\text{ref}})^2}{(a_{\text{OH}^-}/a_{\text{OH}^-}^{\text{ref}})^4} \quad [12]$$

and includes the activities, which are considered to remain constant during battery operation. $p_{\text{O}_2}^{\text{ref}}$ is defined at a partial oxygen pressure of 1 atm ($\approx 10^5$ Pa) at 298 K.

One of the main aims of the present work is to model the close interaction between the voltage, pressure, and temperature. Since both the thermodynamics and kinetics are temperature dependent, these dependencies have to be considered as well. The temperature dependence of the standard redox potential $E_{\text{O}_2}^\circ$ is related to the entropy change involved in the electrochemical charge-transfer reaction (ΔS_{O_2}), according to

$$E_{\text{O}_2}^\circ(T) = E_{\text{O}_2}^\circ(298) + (T - 298) \frac{\Delta S_{\text{O}_2}}{4F} \quad [13]$$

in which T is expressed in kelvin. It is assumed that ΔS_{O_2} is constant within the limited temperature range batteries generally are operating. The ΔS_i values for the various electrochemical reactions considered in this work have been calculated from dE_i/dT values, reported in the literature,¹² according to $\Delta S_i = nF dE_i/dT$ where n gives the number of electrons involved in the charge-transfer reaction. The calculated values are listed in Table I. For the oxygen evolution reaction ΔS_{O_2} has a positive value. Evidently, for the oxygen recombination the same, but negative, value applies. The required temperature depen-

dencies for p_{O_2} in Eq. 11 are dealt with in the section on Pressure development.

Overcharging kinetics.—During overcharging, oxygen evolution occurs at a fully charged Ni electrode, i.e., at NiOOH ($E_{\text{Ni}}^\circ = 0.520$ V vs. standard hydrogen electrode, SHE), according to Eq. 3. Since this reaction generally takes place at relatively positive potentials with respect to the redox potential for the O_2 reaction ($E_{\text{O}_2}^\circ = 0.401$ V vs. SHE), the kinetics of this reaction, expressed by the partial O_2 evolution current (I_{O_2}), can simply be described by the anodic branch of the Butler-Volmer relationship,¹⁰ according to

$$I_{\text{O}_2} = I_{\text{O}_2}^\circ \exp \left\{ \frac{\alpha_{\text{O}_2} n F \eta_{\text{O}_2}}{RT} \right\} \quad [14]$$

in which the exchange current ($I_{\text{O}_2}^\circ$) is given by

$$I_{\text{O}_2}^\circ = nFA_{\text{Ni}} k_a^{(1-\alpha_{\text{O}_2})} k_c^{\alpha_{\text{O}_2}} a_{\text{O}_2}^{\alpha_{\text{O}_2}} a_{\text{H}_2\text{O}}^{\alpha_{\text{O}_2}} a_{\text{OH}^-}^{(1-\alpha_{\text{O}_2})z_{\text{O}_2}} \quad [15]$$

and A_{Ni} the Ni electrode surface area, k_a and k_c the anodic and cathodic reaction rate constant, respectively, x_i , y_i , z_i the reaction orders of the various electroactive species involved, α_{O_2} the charge-transfer coefficient, and η_{O_2} , the overpotential, is defined as the difference between the Ni electrode potential (E_{Ni}) and the oxygen equilibrium potential ($E_{\text{O}_2}^{\text{eq}}$)

$$\eta_{\text{O}_2} = E_{\text{Ni}} - E_{\text{O}_2}^{\text{eq}} \quad [16]$$

In order to reduce the complexity of the mathematical treatment, it is assumed in Eq. 14 that the surface coverage by oxygen molecules remains negligibly low ($\theta_{\text{O}_2} \sim 0$) and that the concentrated alkaline electrolyte behaves like an ideal solution.

The temperature dependence of the charge-transfer reactions is revealed not only by the direct influence of T in the given kinetic Eq. 14, but also by the dependence of the rate constants in Eq. 15. In general terms this dependence can be described by the Arrhenius equation

$$k_a, k_c = k_{\text{O}_2}^\circ \exp \left(\frac{-E_{k_{\text{O}_2}}}{RT} \right) \quad [17]$$

where $k_{\text{O}_2}^\circ$ is the pre-exponential factor and $E_{k_{\text{O}_2}}$ is the activation energy. The values for k_a and k_c are considered to be equal in this work for each reaction. The various values for $I_{\text{O}_2}^\circ$, listed in Table I, refer to standard conditions at 298 K.

Fortunately, O_2 evolved at the Ni electrode will recombine at the Cd electrode. Therefore, it has to be transported from the Ni to the Cd electrode either via the gas phase or via the electrolyte. Since the oxygen solubility in alkaline electrolyte is relatively low it is most likely that O_2 will mainly be transported via the free volume (V_g) of the battery.¹¹ According to Eq. 4, the availability of water is essential for O_2 reduction to occur. Redissolution of O_2 into the electrolyte and diffusion toward the electrode/electrolyte interface is therefore an essential step. For a purely kinetically controlled reaction, for which no transport limitations are considered, the partial recombination current (I_{kin}) can be expressed by the cathodic branch of the Butler-Volmer equation

$$I_{\text{kin}} = I_{\text{rec}}^\circ \exp \left\{ \frac{-(1 - \alpha_{\text{rec}}) n F \eta_{\text{rec}}}{RT} \right\} \quad [18]$$

where I_{rec}° , the exchange current for the recombination reaction, is given by

$$I_{\text{rec}}^\circ = nFA_{\text{Cd}} k_a^{(1-\alpha_{\text{rec}})} k_c^{\alpha_{\text{rec}}} a_{\text{rec}}^{\alpha_{\text{rec}}} a_{\text{H}_2\text{O}}^{\alpha_{\text{rec}}} a_{\text{OH}^-}^{(1-\alpha_{\text{rec}})z_{\text{rec}}} \quad [19]$$

It should, however, be noted that k_a and k_c do not necessarily need to be the same as those for the oxygen evolution reaction in Eq. 15.

Since the oxygen reduction reaction takes place at very high overpotentials, i.e., at very negative potentials with respect to $E_{\text{O}_2}^\circ$, it is reasonable to assume that transportation of O_2 toward the electrode interface might become a

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

Symbol	Value	Dimension	Description
A_{bat}	$2.7 \cdot 10^{-3}$	m^2	Battery surface area
A_{Cd}		m^2	Surface area Cd electrode
$A_{\text{Cd}}^{\text{max}}$	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
a_i^{ref}		mol/m^3	Activities of species i in the reference state
a_i^s		mol/m^3	Surface activity of species i
a_i^e		mol/m^3	Equilibrium activity of species i
C_{amb}	∞	J/K	Heat capacitance environment
C_{bat}	14	J/K	Heat capacitance battery
C_{KOH}	$8 \cdot 10^3$	mol/m^3	Electrolyte KOH concentration
$C_{\text{Cd}}^{\text{dl}}$	0.2	F/m^2	Double-layer capacitance Cd electrode
$C_{\text{Ni}}^{\text{dl}}$	0.2	F/m^2	Double-layer capacitance Ni electrode
D_i		m^2/s	Diffusion coefficient of species i
$D_{\text{H}^+}^0$	$5 \cdot 10^{-14}$	m^2/s	Diffusion coefficient protons in Ni at 298 K ²¹
$D_{\text{OH}^-}^0$	$5 \cdot 10^{-10}$	m^2/s	Diffusion coefficient OH ⁻ at 298 K ²⁰
$D_{\text{O}_2}^0$	$5 \cdot 10^{-10}$	m^2/s	Diffusion coefficient O ₂ in 8 M KOH at 298 K ²²
d_{Cd}	$1 \cdot 10^{-6}$	m	Diffusion layer thickness at Cd electrode
d_{O_2}	$3 \cdot 10^{-7}$	m	Diffusion layer thickness for oxygen transport
E_i		V	Potential redox reaction i
E_i^{eq}		V	Equilibrium potential redox reaction i
E_{Cd}^a	$40 \cdot 10^3$	J/mol	Activation energy Cd reaction
$E_{\text{OH}^-}^a$	$14 \cdot 10^3$	J/mol	Activation energy OH ⁻ diffusion ²⁰
$E_{\text{D}_{\text{O}_2}}^a$	$14 \cdot 10^3$	J/mol	Activation energy diffusion coefficient O ₂ ²²
$E_{\text{H}^+}^a$	$9.62 \cdot 10^3$	J/mol	Activation energy proton diffusion ²³
E_{Ni}^a	$40 \cdot 10^3$	J/mol	Activation energy Ni(OH) ₂ reaction
$E_{\text{O}_2}^a$	$40 \cdot 10^3$	J/mol	Activation energy O ₂ reaction at Ni
$E_{\text{K}_{\text{O}_2}(\text{Cd})}^a$	$40 \cdot 10^3$	J/mol	Activation energy O ₂ reaction at Cd
$E_{\text{K}_{\text{rec}}}^a$	$40 \cdot 10^3$	J/mol	Activation energy O ₂ recombination at Ni
$E_{\text{K}_{\text{rec}}(\text{Cd})}^a$	$40 \cdot 10^3$	J/mol	Activation energy O ₂ recombination at Cd
E_{Cd}^0	-0.808	V vs. SHE	Standard redox potential Cd electrode ¹²
E_{Ni}^0	+0.520	V vs. SHE	Standard redox potential Ni electrode ¹²
$E_{\text{O}_2}^0$	+0.401	V vs. SHE	Standard redox potential O ₂ reaction ¹²
F	96485	C/eq	Faraday constant
ΔG_i		J/mol	Free energy change for reaction i
ΔG_i^0		J/mol	Standard free energy change for reaction i
I_{dif}		A	Diffusion-controlled current
I_{kin}		A	Kinetically controlled current
I_i		A	Local current in reaction path i
I_{Cd}^0	$2.3 \cdot 10^3$	A	Exchange current Cd electrode at 50% SoC
I_{Ni}^0	36	A	Exchange current Ni electrode at 50% SoC
$I_{\text{O}_2}^0$	$117.6 \cdot 10^{-9}$	A	Exchange current O ₂ evolution at Ni electrode
$I_{\text{O}_2(\text{Cd})}^0$	$23 \cdot 10^{-3}$	A	Exchange current O ₂ evolution at Cd electrode
I_{rec}^0	$2.3 \cdot 10^{-3}$	A	Exchange current O ₂ recombination at Cd
$I_{\text{rec}(\text{Ni})}^0$	$0.5 \cdot 10^{-3}$	A	Exchange current O ₂ recombination at Ni
J_i		mol/s	Flux of species i
$J_{\text{in/out}}$		W	Heat flux in/out the battery
K_{O_2}	$0.51 \cdot 10^{-6}$	$\text{mol/m}^3 \cdot \text{Pa}$	Solubility constant O ₂ in KOH ¹¹
k_i			Rate constant of reaction i at 298 K
L	$5.5 \cdot 10^{-6}$	m	Layer thickness Ni electrode
M_{Cd}	112.4	g/mol	Molecular weight, Cd
n_i		mol	Molar amount species i
N	10^{14}		Number of nuclei
n	50		Number of spatial elements in Ni electrode
n_i			Number of electrons involved in reaction i
p_{O_2}		Pa	Partial oxygen pressure
$p_{\text{O}_2}^{\text{ref}}$	10^5	Pa	Reference partial oxygen pressure
Q_{Cd}		C	Stored capacity Cd electrode
$Q_{\text{Cd}}^{\text{max}}$	5000	C	Maximum storage capacity Cd electrode
$Q_{\text{Cd}(\text{Cd})}$	800	C	Overdischarge capacity Cd in Cd electrode
Q_{Ni}		C	Stored capacity Ni electrode
$Q_{\text{Ni}}^{\text{max}}$	3060	C	Equilibrium stored capacity Ni electrode
$Q_{\text{Ni}}^{\text{max}}$		C	Maximum storage capacity Ni electrode, (nominal capacity NiCd battery)
Q_{Ni}		C	Stored surface capacity Ni electrode
$Q_{\text{Cd}(\text{Ni})}$	1000	C	Overdischarge capacity Cd in Ni electrode
R	8.314	J/mol K	Gas constant
R_e	$10 \cdot 10^{-3}$	A	Ohmic resistance electrolyte
R_{Cd}	$2 \cdot 10^{-3}$	A	Ohmic resistance Cd electrode
R_{Ni}	$2 \cdot 10^{-3}$	A	Ohmic resistance Ni electrode
r		m	Radius
ΔS_{Cd}	-204	J/mol K	Entropy change Cd(OH) ₂ reduction ¹²
ΔS_{Ni}	+130	J/mol K	Entropy change Ni(OH) ₂ oxidation ¹²
ΔS_{O_2}	+649	J/mol K	Entropy change O ₂ evolution ¹²
T		K	Battery temperature
T_{amb}		K	Ambient temperature
t		s	Time
V		m^3	Volume
V_g	$1.5 \cdot 10^{-6}$	m^3	Battery void gas volume
x_i			Mole fraction of species i
x_i, y_i, z_i	1		Reaction orders various species i
z_i			Charge of charged species i
α_i	0.5		Charge transfer coefficients reaction i
α_{th}	14.9	W/m ² K	Heat-transfer coefficient
ϕ^s		V	Galvani potential of the electrode
ϕ^l		V	Galvani potential of the electrolyte
γ_i			Activity coefficient species i
μ_i		J/mol	Chemical potential for species i
μ_i^0		J/mol	Standard chemical potential for species i
μ_i		J/mol	Electrochemical potential for species i
ρ_{Cd}	$8.64 \cdot 10^6$	g/m ³	Density of Cd
η_i		V	Overpotential redox reaction i
η_i^k		V	Diffusion overpotential redox reaction i
η_i^k		V	Kinetic overpotential redox reaction i
θ_{ex}		m^2	Extended surface area Cd electrode

limiting factor. In the extreme case when the recombination rate is completely dominated by mass transport a linear concentration gradient is established across the diffusion layer thickness under steady-state conditions. The diffusion controlled recombination current (I_{dif}) can then be expressed by

$$I_{\text{dif}} = \frac{nFA_{\text{Cd}}D_{\text{O}_2}a_{\text{O}_2}}{d_{\text{O}_2}} \quad [20]$$

where D_{O_2} is the diffusion coefficient for O_2 in the electrolyte, d_{O_2} the average diffusion layer thickness through which O_2 must be transported. Considering a mixed kinetic/diffusion controlled reduction reaction it can be easily shown¹⁰ that the overall recombination current (I_{rec}) can be represented by

$$I_{\text{rec}} = \frac{I_{\text{kin}} I_{\text{dif}}}{I_{\text{kin}} + I_{\text{dif}}} \quad [21]$$

Obviously, the temperature dependence of $E_{\text{O}_2}^0$ is equal to that of the O_2 evolution reaction given by Eq. 13. The temperature dependencies of the recombination rate constants in Eq. 19 are similar to that described by Eq. 17, although it should be noted that the activation energy for these reaction rate constants (E_{rec}^a) does not necessarily need to have the same value as $E_{\text{K}_{\text{O}_2}}^a$. The temperature dependence of the diffusion coefficient in Eq. 20 can be represented by

$$D_{\text{O}_2} = D_{\text{O}_2}^0 \exp\left(\frac{-E_{\text{D}_{\text{O}_2}}^a}{RT}\right) \quad [22]$$

where $D_{\text{O}_2}^0$ is the pre-exponential factor, and $E_{\text{D}_{\text{O}_2}}^a$ is the activation energy of the diffusion coefficient of oxygen in alkaline solution.

It can be concluded that the set of Eq. 14-17 describes the kinetically controlled O_2 evolution rate at the Ni electrode, whereas the set of Eq. 17-22 gives a description of the mixed kinetic/diffusion controlled recombination rate at the Cd electrode as a function of both pressure and temperature during overcharging.

Overdischarging kinetics.—As pointed out in the previous section, two different processes have to be distinguished during overdischarging (Fig. 1). During the initial stages of overdischarging Cd species are converted at both electrodes, according to Eq. 2. The thermodynamics and kinetics of these reactions and its dependence on the temperature are identical to those of the main electrochemical storage reactions, which have been described in detail in Part I of this series.⁵

When the excess of Cd species in the Cd electrode decreases during prolonged overdischarging, O_2 will be evolved at this electrode, according to Eq. 3, in competition with Cd conversion. The kinetics of the O_2 evolution reaction can be described in a similar way as shown above by Eq. 14-17, using the same parameters (see Table I). It should, however, be emphasized that some parameter values at the Cd electrode, like $I_{\text{O}_2(\text{Cd})}^0$, are rather different from those at the Ni electrode ($I_{\text{O}_2}^0$).

Similarly, O_2 reduction will take place at the Ni electrode, according to Eq. 4, in competition with $\text{Cd}(\text{OH})_2$ reduction. Since the overpotentials for O_2 reduction are again very high under these overdischarging conditions (electrode potential is now dominated by the Cd species in the Ni electrode), a mixed kinetic/diffusion reaction rate seems to be appropriate in this case also. Equations 17-22 are therefore also applicable during overdischarging when the appropriate parameter values are taken into account.

Pressure development.—The relationship between the partial O_2 pressure, the battery temperature (T), and the free gas volume (V_g) inside the battery is given by

$$p_{\text{O}_2} = \frac{RTm_{\text{O}_2}}{V_g} \quad [23]$$

where m_{O_2} is the molar amount of O_2 in the gas phase. As the solubility of O_2 in strong alkaline solutions is very low

in comparison to that stored in the gas phase, the contribution of the electrolyte phase to m_{O_2} is neglected.¹¹ Using Faraday's law,¹⁰ m_{O_2} can then simply be calculated from the amount of O_2 produced at the Ni (I_{O_2}) and Cd electrode ($I_{\text{O}_2(\text{Cd})}$) and the amount of O_2 consumed at the Cd (I_{rec}) and Ni electrode ($I_{\text{rec}(\text{Ni})}$) during overcharging and overdischarging, respectively

$$\frac{dm_{\text{O}_2}}{dt} = \frac{I_{\text{O}_2} + I_{\text{O}_2(\text{Cd})} + I_{\text{rec}} + I_{\text{rec}(\text{Ni})}}{nF} \quad [24]$$

Note that the oxidation and reduction currents are defined as positive and negative, respectively. Combining Eq. 23 and 24 leads to a general expression for the pressure development of the battery in time

$$\frac{dp_{\text{O}_2}}{dt} = \frac{RT}{nFV_g}(I_{\text{O}_2} + I_{\text{O}_2(\text{Cd})} + I_{\text{rec}} + I_{\text{rec}(\text{Ni})}) \quad [25]$$

Integrating Eq. 25 gives the pressure-time dependence. Using the circuit simulator this can easily be accomplished, as shown later. Obviously, Eq. 25 not only holds for overcharging but also for the overdischarging reaction sequence in which an oxygen recombination cycle is operative (see Fig. 1).

Temperature development.—The temperature development of a battery is determined by the heat flow generated by the battery during operation (J_{in}) and heat dissipation to the environment (J_{out}) by means of either conduction, radiation, convection, or a combination of these. J_{in} can be represented by¹³

$$J_{\text{in}} = \sum_i I_i \frac{-T\Delta S_i}{n_i F} + \sum_i I_i \eta_i + I_{\text{bat}}^2 \sum_i R_i \quad [26]$$

The factors, which contribute to the heat evolution during current flow, can easily be recognized in Eq. 26. The first term refers to the entropy change (ΔS_i) brought about by each electrochemical reaction (i). This term is proportional to the relevant partial currents (I_i) and can be either positive or negative, dependent on whether the considered reactions are exothermic or endothermic. The second summation term reveals the kinetic contribution of all electrochemical charge-transfer reactions taking place. Obviously, both the rate of each reaction, expressed by I_i , and the corresponding overpotential η_i play an important role in the heat production. It should be noted that this term has a positive value under all conditions, as both η_i and the partial currents, I_i , have the same sign in this work by definition. The third term relates to the heat dissipated by the battery current (I_{bat}) flowing through the internal ohmic resistances (R_i). Herewith R_i considers the summation of the ohmic resistance of the electrolyte (R_e) and that of both electrodes (R_{Ni} and R_{Cd}). Whether the battery is heating up or cooling down depends on the relative contribution of the individual terms in Eq. 26. This may even continuously change during, for example, charging and discharging as the partial currents as well as the corresponding local overpotentials may change continuously. The advantage of the use of an electronic network simulator now becomes very pronounced as both the local overpotentials and the partial currents, needed for the determination of the heat evolution, are already continuously calculated during the self-consistent simulations.

The heat dissipation flow to the environment (J_{out}) is given by Fourier's law

$$J_{\text{out}} = \alpha_{\text{th}} A_{\text{bat}} (T - T_{\text{amb}}) \quad [27]$$

in which α_{th} is the combined heat-transfer coefficient, A_{bat} the battery surface area, and T and T_{amb} are the battery and ambient temperatures, respectively. The net heat flow (J_{tot}) can then be calculated, according to

$$J_{\text{tot}} = J_{\text{in}} - J_{\text{out}} \quad [28]$$

Integration of Eq. 28 yields the heating or cooling down effect (Q_{bat}) of the battery or battery pack

Fig. 3. Overall electronic network model of the considered NiCd battery. Two subcircuits can be distinguished: (a) the electrical domain of the NiCd battery, including several chemical domains, which are separated from the electrical domain by ideal transformers and (b) the temperature domain. The symbols are defined in the text and in Table I.

$$Q_{bat} = \int J_{tot} dt = C_{bat} T \quad [29]$$

where C_{bat} is the heat capacitance of the battery or battery pack. It is assumed in the present simulations that the heat capacitance of the environment (C_{amb}) is very large. The whole set of Eq. 26–29 describes the development of the battery temperature.

Electronic Network Model

The complete electronic network model of the sealed rechargeable NiCd battery under consideration is shown in Fig. 3. The network consists of an electrical domain, including several chemical domains (a) and a temperature domain (b). As has been pointed out in Part I of this series there exists a close resemblance between, on the one hand, the effort and flow for electrical systems (voltage V and current I , respectively) and, on the other hand, the “chemical effort,” expressed by the chemical potential (μ), and the “chemical flow” expressed by the molar flux (J) for

(electro)chemical systems.⁵ The thermodynamics and kinetics of (electro)chemical reactions can therefore be treated in a similar way as electrical systems. In order to separate the electrical domain from the various chemical domains, ideal transformers are used in the equivalent circuit of Fig. 3a. Also in the case of thermal systems there is a close resemblance between electrical systems and thermal systems and the latter can therefore also be treated in a similar way (see Fig. 3b).¹⁵ An overview of the used similarities between the electrical, (electro)chemical, and thermal domains are listed in Table II. The gradual construction of the total network is outlined below.

The structure of the battery, revealing the two electrodes separated by the electrolyte, can be easily identified in the electronic network of Fig. 3a. It is assumed that no transport limitations occur in the bulk of the strong alkaline electrolyte (>7 M KOH) of the considered NiCd battery. As a result, the ionic conductivity in this model is assumed to be constant during battery operation and can therefore be represented by a fixed ohmic resistance (R_e) in the electrical domain. In the present simulations R_e was set at $10^{-2} \Omega$, which is a common value for aqueous rechargeable batteries. Besides the electrolyte resistivity, the conductivity properties of both electrodes have to be considered as well. These are related to, for example, the contact resistance between the metallic conductor and the electroactive species, and the poor electronic conductivity of the solids themselves.¹⁴ These solid-state properties are combined in the series resistances R_{Ni} and R_{Cd} and are set at a fixed value of $2 \cdot 10^{-3} \Omega$ each.

As described in Part I, in order to model the main electrochemical storage reactions, two electrical double-layer capacitances (C_{Ni}^{dl} and C_{Cd}^{dl}) have to be considered in parallel to the two pairs of antiparallel diodes (D_{Ni} and D_{Cd} in Fig. 3a) in the electrical domain, representing the mathematics of the charging (upper diodes) and discharging (lower diodes) kinetics at both electrodes.⁵ The transformers represent the conversion of chemical potentials in both chemical domains into electrical potentials in the corresponding electrical domains, using the transformation coefficient $1/nF$ (see also Table I). The chemical potential of the overall (electro)chemical reactions is composed of the individual chemical potential contributions (μ_i) of all species involved. In Part I it was pointed out that this can be modeled by many variable capacitances. In accordance with Eq. 1 and 2, this implies that five and four capacitances for the Ni and Cd electrode, respectively, have to be taken into account.⁵ In order to reduce the complexity, a somewhat simplified approach is adopted here, tailored to the individual electrode reactions, as is outlined below.

Starting with the Ni electrode the chemical potential of this reaction is composed of a constant part and a variable part. The constant part is represented by the standard free energy change, ΔG_{Ni}^0 in Fig. 3a, and includes the standard chemical potentials of all involved species ($\Sigma \mu_i^0$) together with the activities, which are considered to remain constant at the Ni electrode during battery operation, i.e., $a_i^s = \bar{a}_i$ for these species, implying that

$$\Delta G_{Ni}^0 = \Sigma \mu_i^0 + RT \ln \frac{(\bar{a}_{H_2O}/a_{H_2O}^{ref})(\bar{a}_e/a_e^{ref})}{(\bar{a}_{OH^-}/a_{OH^-}^{ref})} \quad [30]$$

Table II. List of parameters and dimensions used in the electrical, chemical, and thermal domains. Note the analogy between the electrical and both the chemical and temperature domains. Transformation coefficient for both the electrochemical potential-to-voltage and flux-to-current conversion is $1/nF$.

Electrical domain			Chemical domain			Thermal domain		
Voltage	V	[V]	Chemical potential	μ	[J/mol]	Temperature	T	[K]
Current	I	[A]	Flux	J_{th}	[mol/s]	Heat flow	J_{th}	[W]
Power	$P = VI$	[W]	Chemical power	$P_{ch} = \mu J_{ch}$	[W]	Thermal power	$P_{th} = T J_{th}$	[WK]
Charge	$Q = It$	[As]	Molar amount	$m = J_{ch} t$	[mol]	Heat amount	$Q_{th} = J_{th} t$	[J]
Energy	$E = Pt$	[J]	Chemical energy	$E_{ch} = P_{ch} t$	[J]	Thermal energy	$E_{th} = P_{th} t$	[JK]
Capacitance	$C = Q/V$	[As/V]	Chemical capacitance	$C_{ch} = m/\mu$	[mol ² /J]	Thermal capacitance	$C_{th} = Q_{th}/T$	[J/K]
Resistance	$R = V/I$	[V/A]	Diffusion resistance	$R_{ch} = \mu/J_{ch}$	[Js/mol ²]	Heat resistance	$R_{th} = T/J_{th}$	[K/W]

where the various equilibrium activities again refer to the corresponding reference states (a_i^{ref}). The variable contribution to the chemical potential is determined by the molar amounts of $\text{Ni}(\text{OH})_2$ and NiOOH species at the electrode surface, which are subject to continuous change. According to Table I these molar amounts can be calculated by means of the variable capacitances $C_{\text{Ni}(\text{OH})_2}^s$ and C_{NiOOH}^s in Fig. 3a. Transport of protons within the Ni electrode plays an important role and directly influences the surface activities of both electroactive Ni species.⁵ Proton transport is included in the network by means of the ladder networks, one network for NiOOH and the other for $\text{Ni}(\text{OH})_2$. In these networks, R_i represents the chemical diffusion "resistance" and the charge on C_i corresponds with the molar amount of chemical energy (m_i) stored within each compartment (i). Under current flowing conditions the voltage across the transformer represents the summation of the thermodynamically determined equilibrium potential and the diffusion overpotential.⁵ The voltages across the diodes correspond to the kinetically controlled overpotentials. Under equilibrium conditions, on the other hand, when no current is flowing through the Ni reaction path, the voltage across the transformers represents the equilibrium potential only since no concentration gradient will be present inside the Ni electrode and the diffusion overpotential will be reduced to zero. Obviously, the kinetic overpotential across the antiparallel diodes is also zero under these conditions.

In the case of the Cd electrode it has been shown that mass transport of OH^- near the electrode surface determines the kinetics of the charge-transfer reaction. It was, however, argued that a steady-state situation was quickly established, leading to the assumption of a linear concentration gradient. This allows a more simplified treatment for the Cd electrode than that for the Ni electrode.⁵ On the analogy of the description of the oxygen recombination kinetics outlined above, the mixed controlled kinetics (see Eq. 21) is combined in the antiparallel diodes. Consequently, the voltage across the Cd diodes corresponds in this case with the summation of the kinetic and diffusion overpotential. The voltage across the Cd transformer then corresponds with the equilibrium potential of the Cd electrode. It should, however, be noted that more complex diffusion problems, as shown for the Ni electrode, can be dealt easily within the network model.

The advantage of electrical network modeling is that it is, in principle, very easy to expand the model to other reactions. Since the oxygen evolution and recombination reactions at both electrodes are competing reactions with respect to the main electrochemical storage reactions during both overcharging and overdischarging, they can be modeled as reaction paths in parallel to both the Ni and Cd main storage reaction paths (Fig. 3a). The upper diodes correspond to the kinetics of the oxygen evolution reaction at the Ni electrode and the recombination reaction at the Cd electrode during overcharging and are covered by Eq. 14-17 and Eq. 17-22, respectively. The lower diodes correspond to the recombination reaction at the Ni electrode and the evolution reaction at the Cd electrode during the second overdischarge step. These diodes (D_{O_2}) reflect the kinetics covered by Eq. 17-22 and Eq. 14-17, respectively. The voltages across these diodes represent the overpotentials of the O_2 reaction, including both the kinetic and diffusion overpotentials. As pointed out in the previous section the battery pressure is determined by the amount of gas produced and consumed at both electrodes. The molar amounts involved in all oxygen reaction paths are stored in the variable "chemical" capacitance C_{O_2} , "connecting" both electrodes via the gas phase, which is identical to the physical situation. Using Eq. 23, the calculated molar amount stored on this capacitance yields the partial oxygen pressure. In addition, using the dependence of the equilibrium potential on both the partial oxygen pressure and temperature, as described by Eq. 11 and 13, respectively, the voltage across both O_2 transformers represents $E_{\text{O}_2}^{\text{eq}}$ for the two O_2/OH^- redox systems.

In order to complete the overdischarge behavior of the present NiCd battery, an additional Cd reaction path is

included at the Ni electrode (see Fig. 1). The corresponding mathematics has been described in Part I.⁵

Finally, the temperature behavior is calculated by means of subcircuit (b). Here, the close mathematical analogy between electrical current fluxes and heat fluxes is exploited. As described previously, the heat generated or consumed by the battery can be described in Eq. 26. The three terms of this equation can, for each individual reaction, be treated mathematically as three different heat generating/consuming current sources, denoted by J_{th} in Fig. 3b. The integrated amount of heat generated by all electrochemical reactions flows into the heat capacitance, C_{bat} , of the battery. Equation 27 gives an expression for the heat transfer to the environment and can in the simplest case be treated as a fixed resistance R_{th} , where R_{th} is defined as $1/\alpha_{\text{th}}A_{\text{bat}}$. The heat stored at C_{bat} is dissipated into C_{amb} , the heat capacitance of the environment. Following the analogy between an electrical capacitance and heat capacitance expressed by Eq. 29, obviously the voltage across C_{bat} and the amount of charge stored on C_{bat} is equivalent with the T and Q_{bat} , respectively (see Table II). In this consideration, heat transport within the battery is assumed to be very fast so that no heat gradients occur inside the battery. It should furthermore be emphasized that the present thermal modeling of the environment is kept rather simple, but that it can easily be extended to more complex systems with other heat producing or heat consuming components with mutual thermal interferences, as will be shown in a separate paper.¹⁶

Simulation Results

A wide variety of electronic network simulators is nowadays available, such as SPICE® and PSTAR®. In order to perform battery simulations with the described model, it is essential to have a network simulator available, which is able to deal with user-defined nonlinear mathematical equations. PSTAR is very well equipped for this purpose. In the present work all battery simulations are therefore performed with this simulation tool but, obviously, other tools might also be successfully applied. An additional advantage of the simulation tool used is that the calculation time of the complete battery model is generally limited to a typical value of only 10 s.

The simulated galvanostatic charging behavior (constant current of 1 A) of a NiCd battery is shown in Fig. 4. A comparison of the simulated voltage, pressure, and temperature dependencies (Fig. 4) and those experimentally measured (Fig. 2) show a good qualitative agreement, as is highlighted below. The simulated voltage curve reveals that the voltage increases rapidly in the initial stages of charging ($0 < t < 2$ min). This is related to the fact that the equilibrium potential of the Ni electrode is very sensitive at low SoC, in accordance with the Nernst equation. In addition, it was ana-

Fig. 4. Simulation of voltage, pressure, and temperature during galvanostatic charging and overcharging a NiCd battery under ambient temperature conditions, using the input parameters as listed in Table I. The charging current is 1 A and charging is interrupted after 60 min.

lyzed in Fig. 10 of Part I⁵ that the diffusion overpotential also significantly contributes to this behavior in the beginning of charging. After longer charging times the steep voltage increase levels off. During this normal charging procedure all electrical energy is consumed by the Ni and Cd electrochemical storage reactions. Hence no side reactions occur. Consequently, the gas pressure remains low. A careful examination of the temperature curve reveals that the battery initially cools down. Inspection of the various heat sources in the temperature network of Fig. 3b reveals that in this region the negative entropical heat contribution of the Ni reaction is more dominant than the other heat producing contributions in Eq. 26, resulting from the kinetics of the individual reactions and ohmic losses.

After 30 min charging, the cell voltage increases more rapidly as a result of the initiated oxygen recombination cycle. This can be recognized on both the pressure and temperature increase in Fig. 4. The sharp increase in temperature is mainly due to the large overpotential that accompanies the oxygen recombination at the Cd electrode. This overpotential can be easily monitored in the simulations and amounts more than 1.2 V, explaining the pronounced heat production under these recombination conditions. Furthermore, the simulation reveals that the higher temperature is also responsible for the voltage decrease after prolonged overcharging at $t > 40$ min. This $-\Delta V$ effect is also in agreement with the experiments (see Fig. 2) and is mainly due to the temperature dependencies of the involved standard redox potentials. The charging current is interrupted in the simulation after 60 min and the simulated voltage, pressure and temperature relax toward new steady-state values.

The simulated (over)discharging curves are shown in Fig. 5. A constant discharge current of 1 A is used in the simulations. The voltage curve shows that its level remains more or less constant for a long period of time at about 1.2 V. Such a flat voltage plateau is in agreement with experimentally determined discharge curves. At the end of the discharge process ($t \sim 40$ min) the voltage drops sharply, due to a strong decrease of available NiOOH at the surface. Inspection of the concentration gradient, as calculated in the RC ladder network of Fig. 3a, indeed proves that this concentration decreases drastically at the end of discharging, as expected. Under normal discharging conditions the simulations reveal that the pressure remains extremely low and that the temperature increases only slightly, indicating that the kinetics of the discharge reactions are relatively fast and that reactions, which produce a lot of heat like the O_2 recombination reaction, do not occur under these conditions.

When the battery is forced to deliver current even beyond a cell voltage, which generally is accepted as cutoff voltage at which the discharge process is terminated, the battery enters the overdischarge mode. This mode is characterized by a two-step process, as the voltage curve of Fig. 5 shows.

Fig. 5. Simulation of voltage, pressure, and temperature during galvanostatic discharge and overdischarging a NiCd battery under ambient temperature conditions with 1 A.

The first overdischarge voltage plateau ($40 < t < 45$ min) is found close to 0 V. This is due to the small overpotentials involved with the $Cd/Cd(OH)_2$ reactions, which now simultaneously take place at both electrodes.

The partial currents of both Cd reactions paths at the two electrodes are shown in Fig. 6a. Oxidation of the excess Cd, available in the Cd electrode ($I_{Cd(Cd)}$), continues till the transition of the first to the second overdischarge plateau at ~ 45 min (see Fig. 5). Reduction of Cd species, present in the Ni electrode ($I_{Cd(Ni)}$), starts at the beginning of the first voltage plateau after ~ 40 min as soon as the surface concentration of NiOOH becomes extremely low. But there is still some significant competition between $Cd(OH)_2$ and NiOOH after 40 min, as both partial cathodic currents, $I_{Cd(Ni)}$ and I_{Ni} , respectively, indicate in Fig. 6a. This is due to the fact that NiOOH reduction can continue in time as this reaction is controlled by proton diffusion in the Ni electrode. The surface concentration of NiOOH remains, however, very low under these diffusion-controlled conditions. The total reduction current ($I_{Ni} + I_{Cd(Ni)}$) is, of course, equal to the partial anodic Cd current and is dictated by the applied current of 1 A. The pressure and temperature rise is still very limited in this first voltage plateau region (see Fig. 5).

Consuming the excess of Cd species in the Cd electrode, the competition with the oxygen evolution reaction at this electrode becomes very pronounced, as the calculated anodic oxygen evolution current at the Cd electrode ($I_{O_2(Cd)}$) in Fig. 6b shows. At the beginning of the second discharge plateau (see Fig. 5 at $t \sim 45$ min) the two partial oxygen cur-

Fig. 6. (a, top) Partial Cd and Ni currents flowing through both electrodes upon overdischarging. The positive partial current ($I_{Cd(Cd)}$) flows through the Cd electrode while both partial negative currents (I_{Ni} and $I_{Cd(Ni)}$, respectively) are flowing through the Ni electrode. The considered time interval mainly corresponds to the first overdischarge voltage plateau in Fig. 5. (b, bottom) Partial oxygen evolution ($I_{O_2(Cd)}$) and oxygen recombination ($I_{rec(Ni)}$) currents upon overdischarging. The time interval of these reactions corresponds to the second overdischarge voltage plateau in Fig. 5.

rents, i.e., the partial oxygen evolution current at the Cd electrode ($I_{O_2(Cd)}$) and the partial recombination current at the Ni electrode ($I_{rec(Ni)}$), are not yet exactly balanced, as some NiOOH and Cd(OH)₂ are still reduced under these conditions, as can be deduced from Fig. 6a and b. Consequently, the internal gas pressure starts to rise at the beginning of the second overdischarge process (after ~45 min; see Fig. 5). In line with this oxygen recombination onset, the voltage decreases toward more negative values and a second voltage plateau is established in Fig. 5: the Cd electrode potential is now very positive due to oxygen evolution whereas the Ni electrode has a rather negative potential due to the oxygen reduction reaction, leading to the calculated cell voltage reversal. The temperature rise in this region can again be attributed to the large overpotentials which accompany the oxygen recombination reaction now at the Ni electrode, as has been verified by inspecting the local heat sources in the network model of Fig. 3b. At higher temperatures the recombination kinetics improve, as can be concluded from the local overpotentials in the electronic network. At a certain moment a steady-state situation is reached where the voltage, pressure, and temperature (Fig. 5), and all partial currents (Fig. 6) do not change anymore.

From practical battery use it is well known that fully charged batteries slowly lose their stored energy upon storage. This so-called self-discharge process can easily be simulated using the present network model. The simulation results are shown in Fig. 7 and reveal that the decay rate is strongly dependent on storage time. The origin of this self-discharge process must be sought in the thermodynamic instability of the Ni electrode as $E_{Ni}^0 > E_{O_2}^0$. This can simply be deduced from the local currents flowing through the network model of Fig. 3. Focusing on the partial currents of both the Ni and O₂ paths at the Ni electrode indicates that the chemical energy stored at the variable NiOOH capacitances is lost under open-circuit conditions. A small Ni current is "leaking" through the lower Ni diode toward the upper O₂ diode and is converted into O₂ gas. As a result, chemical energy stored at the NiOOH capacitances is lost at the benefit of "oxygen stored" at the O₂ capacitance, resulting in an increase of the internal gas pressure. This in turn induces the oxygen recombination reaction sequence at the Cd electrode to initiate. This simultaneously reduces the energy stored at the Cd capacitance (see Fig. 3a) under open-circuit conditions, keeping the internal gas pressure low.

Furthermore, Fig. 7 shows, in agreement with reported experimental results,¹⁷ that the self-discharge rate increases with increasing temperatures. This is in line with the fact that the kinetics of charge-transfer reactions in general, and those of the Ni and O₂ reactions at the Ni

electrode in this specific case, are improved at higher temperatures. It should, however, be emphasized that other mechanisms than that presently simulated also may contribute to the overall self-discharge rate.¹⁸

The above simulation results focus on the battery response under dc conditions. However, ac analyses can also simply be applied with the used circuit simulator. More detailed simulation results and an extensive description of how electronic network models can be exploited in the field of applications will be presented in a forthcoming paper.¹⁶

Conclusions

It has been shown that electronic network modeling is a very useful tool to study the electrochemical and physical properties of rechargeable batteries under a wide variety of (over)charging, (over)discharging, and open-circuit conditions. Essential steps in the setup of such a model are identified to be (i) an appropriate electrochemical/physical description of all relevant processes occurring inside the battery system under study, (ii) a proper mathematical description of all these processes, (iii) clustering the mathematical equations and converting them into an electronic network, and (iv) finally, after introduction of all relevant electrochemical and physical parameters simulations can be performed. This approach has been successfully applied to the rechargeable NiCd battery system.

By using an electronic network simulator, it has been shown that the close interaction of voltage, internal gas pressure, and battery temperature, which is so characteristic for aqueous battery systems, can be simultaneously simulated during (over)charging, (over)discharging, and open-circuit conditions. The advantage of using an electronic network model is that the battery effectively has been made "transparent," so that all partial currents and local (over)potentials can be monitored during battery simulation, as has been shown for the overdischarge process. This leads to a better understanding of the sometimes complex battery behavior and may improve future battery performance. Furthermore, it is very easy to simulate several cells in series or in parallel, so that both the electrical properties of battery packs and the thermal interaction with the surrounding electronics can be investigated.¹⁶

The aim of the present series of papers was to outline the basic ideas of electronic network modeling rather than to strive for a perfect quantitative agreement of the simulations with the experimental battery characteristics. In order to set up more quantitative models it is essential to experimentally determine the values of the most important electrochemical parameters and to investigate the multidimensional space very accurately. These subjects are in progress and will be treated in future papers.^{24,25}

The present work was focusing on a one-dimensional NiCd model. It is, however, evident that the electronic network approach is not restricted to this simplified case but allows more complex models to be constructed. The battery model can therefore easily be extended with other interesting phenomena. It is, however, essential that a proper mathematical description of the included processes is available. It is therefore conceivable that aging phenomena or cycle life reduction of aqueous battery systems can be simulated as well, once the origin of this process is known and the kinetics are described in mathematical terms.

Obviously, other battery systems, such as NiMH and Li-ion batteries, but also nonrechargeable batteries, can be modeled in a similar way, since the electrochemistry of all these systems is based on the same underlying principles. In addition, this modeling activity is not only restricted to simulate energy storage devices but it can easily be expanded to, for example, electrochromic devices, which are nowadays widely studied.¹⁹ This enables one to simulate simultaneously electrical and optical properties under both steady-state and dynamic conditions.

Acknowledgments

The authors thank S. Onneweer and B. van den Akker for their indispensable help in constructing the PSTAR

Fig. 7. Simulated storage capacities as a function of time at various temperatures of an initially fully charged NiCd battery. Charging was simulated in all cases at 25°C, using a constant current of 1 A up to a charging level of 150% depth-of-charge (DoC). Self-discharge simulations are performed in the temperature range of 0 and 60°C, as indicated.

software, J. van Beek for providing the experimental V , P , T curves of the investigated NiCd battery and P. Blanken for stimulating discussions.

Manuscript submitted February 4, 1998; revised manuscript received May 19, 1998. This was in part Paper 96 presented at the Montreal, Quebec, Canada, Meeting of the Society, May 4-9, 1997.

Philips Research Laboratories assisted in meeting the publication costs of this article.

REFERENCES

1. L. O. Chua and P. M. Lin, *Computer-Aided Analysis of Electronic Circuits*, Prentice Hall, Englewood Cliffs, NJ (1975).
2. P. H. L. Notten, W. S. Kruijt, and H. J. Bergveld, Extended Abstract I-5-05, 46th ISE Meeting, Xiamen, China (1995).
3. P. H. L. Notten, W. S. Kruijt, and H. J. Bergveld, Abstract 96, p. 110, The Electrochemical Society Meeting Abstracts, Vol. 97-1, Montreal, Quebec, Canada, May 4-9, 1997.
4. W. S. Kruijt, E. de Beer, P. H. L. Notten, and H. J. Bergveld, Abstract 104, p. 114, The Electrochemical Society Meeting Abstracts, Vol. 97-2, Paris, France, Aug 31-Sept 5, 1997.
5. W. S. Kruijt, H. J. Bergveld, and P. H. L. Notten, *J. Electrochem. Soc.*, **145**, 3764 (1998).
6. Z. Mao, P. Vidts, and R. E. White, *J. Electrochem. Soc.*, **141**, 54 (1994).
7. R. Barnard, *J. Appl. Electrochem.*, **11**, 217 (1981).
8. S. Trassati, *J. Electroanal. Chem.*, **39**, 163 (1972).
9. *Gasdichte Nickel-Cadmium Akkumulatoren*, W. Rand-szus and H. A. Kiehne, Editors, Varta Batterie AG, Hannover, Germany (1978).
10. A. J. Bard and L. R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, John Wiley & Sons, New York (1980).
11. S. U. Falk and A. J. Salkind, *Alkaline Storage Batteries*, John Wiley & Sons, New York (1969).
12. S. G. Bratsch, *J. Phys. Ref. Data*, **18**, 1 (1989).
13. C. H. Hamann and W. Vielstich, *Electrochemie II*, Verlag Chemie, Weinheim (1981).
14. J. McBreen, *Mod. Aspects Electrochem.*, **21**, 29 (1990).
15. D. Karnopp and R. Rosenberg, *System Dynamics: A Unified Approach*, John Wiley & Sons, New York (1975).
16. H. J. Bergveld, W. S. Kruijt, and P. H. L. Notten, *J. Power Sources*, Submitted (1998).
17. *Handbook of Batteries*, D. Linden, Editor, McGraw-Hill, New York (1995).
18. P. H. L. Notten, in *Interstitial Intermetallic Alloys*, NATO ASI Series E: Applied Science, Vol. 281, F. Grandjean, J. T. Long, and K. H. J. Buschow, Editors, Chap. 7, p. 151, Kluwer Academic Publ., London (1995).
19. C. G. Granqvist, *Handbook of Inorganic Electrochromic Materials*, Elsevier, Amsterdam (1995).
20. Y. Okinaka, *J. Electrochem. Soc.*, **117**, 289 (1970).
21. S. Motupally, C. C. Streinz, and J. W. Weidner, *J. Electrochem. Soc.*, **142**, 1401 (1995).
22. R. E. Davis, G. L. Horvath, and C. W. Tobias, *Electrochim. Acta*, **12**, 287 (1967).
23. D. M. MacArthur, *J. Electrochem. Soc.*, **117**, 729 (1970).
24. P. H. L. Notten, A. A. Jansen van Rosendaal, W. S. Kruijt, and H. J. Bergveld, In preparation.
25. H. J. Bergveld, W. J. J. Rey, R. Du Cloux, W. S. Kruijt, and P. H. L. Notten, In preparation.

A Methanol Sensor for Portable Direct Methanol Fuel Cells

Scott A. Calabrese Barton,^{*a} Bryan L. Murach,^b Thomas F. Fuller,^{**b} and Alan C. West^{***a}

^aDepartment of Chemical Engineering and Applied Chemistry, Columbia University, New York, New York 10027, USA

^bInternational Fuel Cells, South Windsor, Connecticut 06074, USA

ABSTRACT

An aqueous methanol sensor for portable direct methanol fuel cell applications is demonstrated. The design is based on current output limited by methanol diffusion through a Nafion 117 perfluorosulfonic acid membrane. Steady-state polarization measurements demonstrate sensitivity to concentrations of 0 to 4 M over a temperature range of 40 to 80°C. Furthermore, a correlation that is first order in concentration and temperature is demonstrated for concentrations of 0 to 3 M, with an accuracy of ± 0.1 M. Measurements of transient response to step concentration change indicate a response time of about 10 to 50 s, depending primarily on temperature.

Introduction

The need for high energy density electrochemical energy sources has brought about the development of direct methanol fuel cell (DMFC) systems, in which methanol is oxidized at the anode to form carbon dioxide. Such systems are under development as electrical power sources for transportation and portable applications.

Van Dine and Maricle describe one DMFC concept,¹ in which fuel is stored as neat methanol and supplied to the fuel cell stack as an aqueous solution. To achieve acceptable fuel efficiencies, the methanol concentration in contact with the anode must be maintained near 1 M. Because the DMFC anode consumes only a fraction of the methanol in the feed stream, recirculation and the controlled addition of concentrated methanol are required to maintain a constant inlet concentration. In laboratory demonstrations, a methanol sensor has proven to be critical to the operation of such a system, to continuously monitor the inlet methanol concentration and provide feedback for the control of pure methanol injection. This was the motivation for the present work.

Methanol sensors have previously been developed for flexible-fuel engine and chemical process applications, achieving selectivity by exploitation of electrical, optical, or other properties.^{2,3} Fuel cell sensors, which operate by galvanic oxidation of the measured species, have previously been applied to a methanol fuel cell system.^{4,5}

Amperometric concentration sensors rely on a diffusion-limited electrochemical reaction involving the measured species. The diffusion limitation is often realized using a semipermeable membrane, but can also be obtained through fluid-flow boundary layers. Aqueous amperometric sensors are currently used to measure oxygen concentration in natural waters and wastewater toxicity. A thorough review of amperometric techniques is available.⁶

The present design relies on a Nafion membrane to limit methanol diffusion. Other workers have studied diffusion of methanol through Nafion in the context of methanol crossover in a DMFC. Verbrugge⁷ measured the concentration transients in two compartments separated by a perfluorinated ion-exchange membrane and developed a mathematical model by which the room-temperature diffusion and partition coefficients of methanol were obtained. Ren et al.⁸ studied methanol crossover in direct methanol fuel cells using

* Electrochemical Society Student Member.

** Electrochemical Society Active Member.