

Modelling of rechargeable NiMH batteries

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Abstract

A new mathematical model has been developed for rechargeable NiMH batteries, which is based on the occurring physical–chemical processes inside. This model enables one to simultaneously simulate the battery voltage, internal gas pressures (both P_{O_2} and P_{H_2}) and temperature during battery operation. The model takes into account the thermodynamics, kinetics and diffusion processes occurring at/in both electrodes and in the electrolyte.

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1. Introduction

Nickel–metal hydride (NiMH) batteries are nowadays successfully applied in the field of consumer electronics and electrical vehicles and have several advantages over NiCd and Li-ion batteries. NiMH batteries have a high-energy storage density and can be operated at high current densities and low temperatures. Their chemical elements are nontoxic. The theoretical open-circuit potential of the NiMH battery is approximately 1.3 V, very similar to that of the NiCd battery [1,2]. This makes these two different battery systems very compatible.

Models, which can accurately predict the behaviour of batteries during operation are not only important for battery manufacturers to study the impact of new electrode materials on the battery characteristics but also for developers of advanced battery management systems allowing them, for example, to further optimise battery charging and state-of-charge algorithms [3–5].

Mathematical models have been developed for both Ni and MH electrodes [6,7], and for NiMH [8,9]. Unfortunately, these battery models do not predict the interactive behaviour of the battery voltage, temperature and internal pressure during operation. In the present work we introduce a new complete mathematical model for the NiMH batteries, considering all these aspects. We will restrict

ourselves here to a brief description of the MH electrode since the Ni electrode has been carefully described before [3,4].

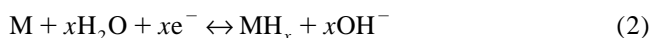
2. Theoretical model

2.1. General chemical description

The NiMH battery consists of two electrodes immersed in an alkaline electrolyte, which provides ionic conductivity between these electrodes. The electrodes are electrically insulated from each other by a separator. During charging divalent Ni is oxidized to the trivalent Ni state [1–6]



and water is reduced to hydrogen atoms at the MH electrode, which can subsequently be absorbed in the hydride-forming intermetallic compound [1], according to



Hydroxyl ions and water molecules are transported in the electrolyte from one electrode to the other. Hence no electrolyte consumption takes place during charging and discharging. The reverse reactions take place during discharging.

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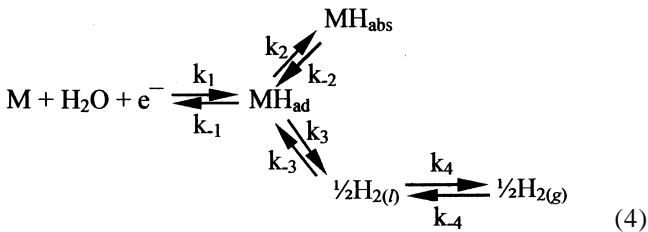
During overcharging hydroxyl ions are oxidized and oxygen evolution starts at the Ni electrode [1–5]



As a result, the partial oxygen pressure inside the battery will rise. Fortunately, oxygen can be transported to the MH electrode interface where it can be reduced to hydroxyl ions again. In the steady state, the amount of oxygen evolved at the Ni electrode is equal to the amount of oxygen recombined at the MH electrode, keeping the internal gas pressure constant.

2.2. MH electrode

The storage reaction at the MH electrode is more complex and consists in the simplest case of four reaction steps in alkaline solution [1,2]



The charge transfer reaction occurs at the electrode–electrolyte interface. As a result atomic hydrogen is chemically adsorbed at the surface. The adsorbed hydrogen atoms can subsequently be converted into the absorbed state by diffusing inside the electrode. Simultaneously recombination of two chemically adsorbed hydrogen atoms may take place at the electrode surface, leading to dissolved hydrogen in the electrolyte ($\text{H}_{2(\text{l})}$). Finally, $\text{H}_{2(\text{l})}$ is in equilibrium with that in the gas phase ($\text{H}_{2(\text{g})}$). Using this description of chemical reactions of the MH electrode, we define the corresponding chemical fluxes, and obtain a complete set of kinetic equations and flux balances.

A lattice gas model has been used to describe the thermodynamics of intercalated hydrogen. For simplicity, a mean field model has been adopted, which assumes a long-range interaction of intercalated hydrogen atoms [10]. The equilibrium potential of the MH electrode ($E_{\text{MH}}^{\text{eq}}$) is related to the Gibbs free energy (ΔG_{MH}), equilibrium hydrogen pressure ($P_{\text{H}_2}^{\text{eq}}$) and chemical potential [2,11,12], according to

$$\Delta G_{\text{MH}} = \sum v_i \mu_i = RT \ln \frac{P_{\text{H}_2}^{\text{eq}}}{P_{\text{ref}}} = -nFE_{\text{MH}}^{\text{eq}} \quad (5)$$

where R is the gas constant, T is the temperature, P_{ref} is the reference pressure of 1 bar, n is the number of electrons involved in Eq. (2) and F is the Faraday constant.

At low hydrogen concentrations a solid solution is formed in the MH electrode, which is generally denoted by the α phase. After the hydrogen activity in the MH

electrode reaches a certain critical value (x_α), the formation of a new β phase starts and a two-phase coexistence region is formed. After reaching the critical value x_β , phase transformation is completed and a solid solution region is again formed now denoted by the β phase. The following set of equations for the equilibrium potential of the MH electrode has been derived

$$E_{\text{MH}}^0 = \begin{cases} E_i^0 + (T - T_{\text{ref}}) \frac{\Delta S_{298}^0}{nF} + \frac{RT}{nF} \left(\ln \left[\frac{1-x}{x} \right] - U_\alpha x \right), & x < x_\alpha \\ k_E x + C, & x_\alpha \leq x \leq x_\beta \\ E_i^0 + (T - T_{\text{ref}}) \frac{\Delta S_{298}^0}{nF} + \frac{RT}{nF} \left(\ln \left[\frac{1-x}{x} \right] - U_\beta x \right), & x > x_\beta \end{cases} \quad (6)$$

where E_i^0 is the standard electrode potential of phase i , T_{ref} is the reference temperature at 298 K, ΔS_{298}^0 the standard entropy, x the molar fraction of hydrogen intercalated in the MH electrode, k_E and C are coefficients that are depending on the interaction energies and standard electrode potentials of each phase.

The charge transfer kinetics of the electrochemical storage reaction is described by a Butler–Volmer equation. This equation expresses the dependence of the reaction current on the overpotential (η_{MH}), exchange current (I_{MH}^0) and charge transfer coefficient (α_{MH}):

$$I_{\text{MH}} = I_{\text{MH}}^0 \left\{ \exp \left[\frac{\alpha_{\text{MH}} nF}{RT} \eta_{\text{MH}} \right] - \exp \left[\frac{-(1 - \alpha_{\text{MH}}) nF}{RT} \eta_{\text{MH}} \right] \right\} \quad (7)$$

Diffusion of hydrogen inside the solid is treated in a conventional way by adopting Fick’s laws [3,6,7].

Oxygen evolution takes place during overcharging at the Ni electrode (Eq. (3)). In order to recombine O_2 it has to be transported to the MH electrode. Considering a mixed kinetics–diffusion process for the oxygen recombination reaction at the MH electrode one obtains the following equation for the reaction current [4,5]

$$I_{\text{rec}} = \frac{I_{\text{rec}}^{\text{kin}} I_{\text{rec}}^{\text{dif}}}{I_{\text{rec}}^{\text{kin}} + I_{\text{rec}}^{\text{dif}}} \quad (8)$$

where $I_{\text{rec}}^{\text{kin}}$ is the kinetics current given by a Butler–Volmer equation, $I_{\text{rec}}^{\text{dif}}$ is the diffusion current which depends on the electrode surface area and the average diffusion layer thickness through which O_2 must be transported.

Since the oxygen reduction reaction takes place at very high overpotentials it is allowed to conclude that diffusion of oxygen is the limiting stage of the hydrogen recombination process [4,5].

2.3. Battery pressure development

The partial oxygen gas pressure is related to the amount of oxygen produced at the Ni electrode minus the amount of oxygen consumed at the MH electrode. The partial

hydrogen pressure consists of the thermodynamically determined equilibrium pressure that can be obtained from Eq. (5) and a kinetically controlled part ($P_{\text{H}_2}^{\text{kin}}$), which can be obtained from considering the various fluxes in the scheme of Eq. (4). The total partial hydrogen pressure is then composed of $P_{\text{H}_2}^{\text{tot}} = P_{\text{H}_2}^{\text{eq}} + P_{\text{H}_2}^{\text{kin}}$. Obviously, the total battery pressure is the sum of partial oxygen and hydrogen pressures.

2.4. Temperature development

The temperature of the battery depends on the heat flux generated by the battery (J_{in}) and heat dissipation to the environment (J_{out})

$$\frac{dT}{dt} = \frac{J_{\text{in}} - J_{\text{out}}}{C_{\text{bat}}} \quad (9)$$

where C_{bat} is the heat capacitance of the battery [4,5].

The Ni electrode has been modelled in an analogous way, i.e. by considering the electrochemical storage reaction, the side reactions and transport properties [3–5]. Evidently, the total battery voltage is given by E_{Ni} and E_{MH} .

3. Results and discussion

Using the battery model briefly presented in this paper one can simultaneously simulate the battery voltage, gas pressure and temperature. The simulation of charging and overcharging process is shown in Fig. 1. The voltage increased during charging and decreased during overcharging. Battery pressure and temperature are sharply increased as soon as the oxygen formation starts. During prolonged overcharging the voltage decreases again due to the

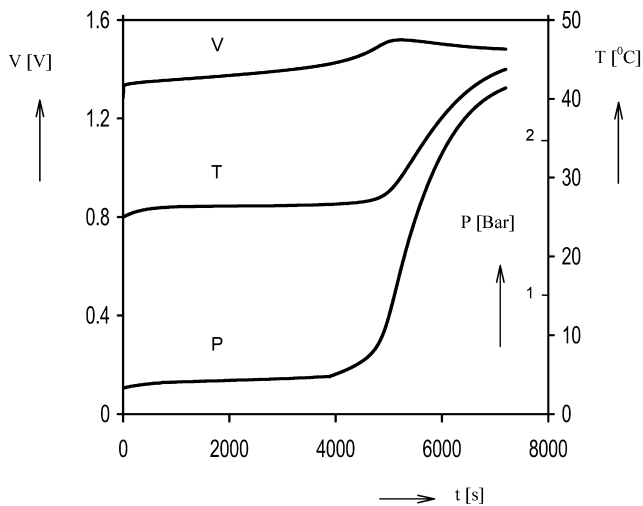


Fig. 1. Simulation results of battery voltage, internal gas pressure and temperature during battery operation.

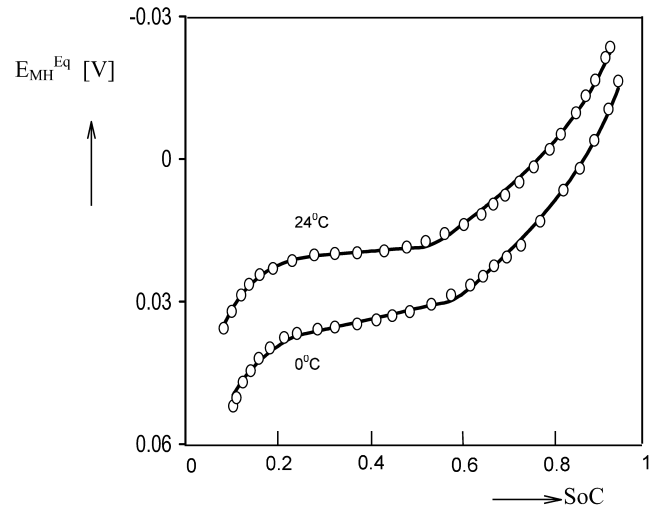


Fig. 2. Equilibrium potential of the MH electrode ($E_{\text{MH}}^{\text{eq}}$) as a function of state-of-charge at 0 and 24 °C.

temperature rise resulting from the extensive heat generation of the oxygen recombination reaction. These effects have also been observed experimentally [13].

Fig. 2 shows the equilibrium potential of the MH electrode and reveals that the experimental data as obtained from gas absorption isotherms (data points from Matsushita [14]) and our theoretical results obtained from the lattice gas model (lines) are in good agreement.

The splitting of the applied charge current into the hydrogen related reactions [reaction scheme (4)] and the oxygen recombination reaction are represented in Fig. 3. As expected, the recombination reaction current increases sharply during overcharging. The proposed model allows simulations of various battery characteristics such as voltage, pressure and temperature. Although a good agree-

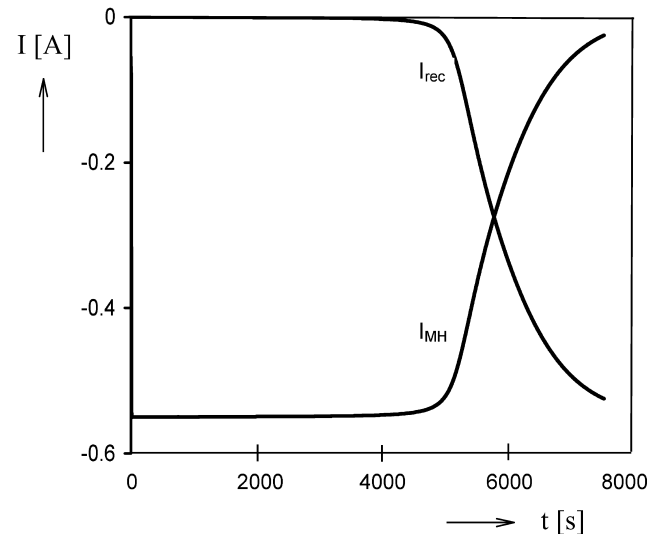


Fig. 3. Simulated hydrogen related reaction current (I_{MH}) and oxygen recombination current (I_{rec}) as a function of charging time (t).

ment is found with the experiments further optimisation of the input model parameters is required.

4. Conclusions

In the present work we introduce a new mathematical model for the NiMH rechargeable batteries, which describes various physical–chemical processes occurring in the battery. This enables one to simultaneously simulate the battery voltage, internal gas pressures (both P_{O_2} and P_{H_2}) and temperature during battery operation. The model takes into account the relevant thermodynamics, kinetics and diffusion processes occurring at/in both electrodes and in the electrolyte. Suitable computer software has been developed and reveals a good agreement between simulation and experiments.

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