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Hydride-forming electrode materials seen from a kinetic perspective

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Abstract

A model is proposed which includes the charge transfer reaction and the formation of adsorbed hydrogen at the electrode/electrolyte interface, absorption of hydrogen into the solid-state MH electrode, recombination of adsorbed hydrogen atoms into molecular hydrogen dissolved in the electrolyte and hydrogen in the gas phase. It was found that the rate of the charge transfer reaction, as represented by the exchange current, is dependent on the partial hydrogen pressure (P_{H_2}) in a rather complex way: a positive linear dependence between $\log I_0$ and $\log P_{H_2}$ is found at relatively low partial pressures, which subsequently passes through a maximum, turning into a negative dependence at higher partial pressures. Both the slopes of the lines and the turning points are found to be strongly dependent on the rate constants of the various reactions. The theoretical model has been verified with both switchable mirror MH thin film electrodes and multicomponent MH electrode materials, nowadays widely applied in commercial NiMH batteries. The as-deduced theoretical relationship will form the basis for the modelling of complete NiMH batteries.

Keywords: Electrode materials; Hydrogen storage materials; Thin films; Electrochemical reactions

1. Introduction

Since the introduction in the late 1980s of corrosion-resistant AB_5-type hydride-forming electrode materials [1–3], rechargeable nickel–metal hydride (NiMH) batteries have become a tremendous success, not only from a technological point of view, but also from a commercial perspective. Nowadays, this type of battery is even more popular than NiCd and Li-ion batteries [4]. Areas of application include small portable electronic equipment, such as portable phones, camcorders, shavers, etc., and, more recently, large-scale applications such as, for example, hybrid electrical vehicles (HEV) [5]. Apart from their beneficial properties, such as corrosion stability, high-energy storage capacity and reliability, one of the key characteristics of NiMH batteries is the rate at which the battery can be discharged and recharged under various conditions. This is of special importance for high drain applications such as power tools and HEV, which should also operate properly under more extreme conditions, e.g. at low temperatures [6].

It has been observed that the kinetics of the electrochemical charge transfer reaction at the metal hydride (MH) electrode is strongly dependent on the physical-chemical characteristics of the hydride-forming material. More specifically, it is dependent on the partial hydrogen pressure of MH materials, which is in general quantified by the hydrogen absorption and desorption isotherm [7]. Although the charge transfer kinetics of MH electrodes have been extensively modelled by several groups [8–11], only little attention has been paid to the explanation for this phenomenon [3,12,13].

The aim of this contribution is to quantify the relationship between the electrochemical charge transfer kinetics and equilibrium hydrogen pressure of hydride-forming compounds. First, the theoretical relationship between these two characteristics is derived. Subsequently, this theoretical relationship is verified experimentally by means of two different classes of hydride-forming compounds. Both optically active rare-earth-type MH thin film elec-

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trodes and powder electrodes made of AB_5-type MH compounds were investigated and are reported and discussed.

2. Theoretical considerations

The electrochemical charge transfer reaction occurs at the interface of the hydride-forming electrode and the alkaline electrolyte. This reaction can, in its most simple form, be represented by

$$H_2O + e^- \underset{k_a}{\overset{k_c}{\leftrightarrow}} H_{ad} + OH^- \tag{1}$$

in which the formed atomic hydrogen will be adsorbed at the electrode surface (H_{ad}). Subsequently, H_{ad} can either be transported into the hydride-forming compound by means of diffusion, leading to absorbed hydrogen (H_{abs}):

$$H_{ad} \underset{k_{-2}}{\overset{k_2}{\leftrightarrow}} H_{abs} \tag{2}$$

or recombine to form hydrogen gas dissolved in the liquid electrolyte ($H_2(l)$):

$$2H_{ad} \underset{k_{-3}}{\overset{k_3}{\leftrightarrow}} H_2(l) \tag{3}$$

Obviously, an equilibrium exists between the molecular hydrogen dissolved in the electrolyte and that in the gas phase ($H_2(g)$):

$$H_2(l) \underset{k_{-4}}{\overset{k_4}{\leftrightarrow}} H_2(g) \tag{4}$$

Here, the so-called Heyrovsky reaction is not taken into account, as this reaction is reported to be insignificant [14]. The rates of the above overall reactions (r_i) can be represented by

$$r_1 = k_c A_0 (1-\theta) a^z_{H_2O} \left[\exp\left\{ \frac{-(1-\alpha)FE}{RT} \right\} \right] - k_a A_0 \theta^x a^y_{OH^-} \left[\exp\left\{ \frac{\alpha FE}{RT} \right\} \right] \tag{5}$$

$$r_2 = k_2 A_0 \theta - k_{-2} A_0 (1-\theta) a_{H_{abs}} \tag{6}$$

$$r_3 = k_3 A_0 \theta^2 - k_{-3} A_0 (1-\theta) a_{H_2(l)} \tag{7}$$

$$r_4 = k_4 a_{H_2(l)} - k_{-4} a_{H_2(g)} \tag{8}$$

where k_i are the rate constants of both the electrochemical charge transfer reaction and the various chemical reactions (i), A_0 is the electrode surface area; θ is the surface coverage of H_{ad}, a_{OH^-} and a_{H_2O} are the activities of the indicated electrolyte species at the electrode interface for which x, y, z are the reaction orders, α is the charge transfer coefficient, F is the Faraday constant, R the gas constant, T the absolute temperature and E the electrode potential [3]. The surface activity of H_{ad} ($a_{H_{ad}}$) is dependent on the maximum surface activity $a^{max}_{H_{ad}}$ and θ via $a_{H_{ad}} = \theta a^{max}_{H_{ad}}$; for simplicity, a constant value of $a^{max}_{H_{ad}}$ is included in the relevant rate constants.

The exchange current is generally accepted as an important parameter describing the kinetics of the electrochemical charge transfer reaction (1). The relationship for I_0 has been derived [3,12] and can be represented by

$$I_0 = FA_0 k_a^{(1-\alpha)} k_c^{\alpha} \theta^{x(1-\alpha)} (1-\theta)^{\alpha} a_{OH^-}^{y(1-\alpha)} a_{H_2O}^{\alpha z} \tag{9}$$

where the surface coverage plays an important role. Assuming that the diffusion limitations of both OH^- and H_2O in the electrolyte are negligible, which is reasonable due to the high concentrations in 6 M KOH, these activities can be considered as constant. Consequently, I_0 depends, according to Eq. (9), on A_0, k_i, α and θ. In order to unravel the implications of Eq. (9) an expression for θ is required.

If it is assumed that the formed molecular hydrogen (see Eqs. (3) and (4)) will immediately be removed from the electrode surface, only H_{ad} is responsible for electrode blocking. Considering Eqs. (1)–(3), a change in θ as a function of time can be represented by

$$\begin{aligned} \frac{d\theta}{dt} = {} & k_c A_0 (1-\theta) a^z_{H_2O} \left[\exp\left\{ \frac{-(1-\alpha)FE}{RT} \right\} \right] \\ & - k_a A_0 \theta^x a^y_{OH^-} \left[\exp\left\{ \frac{\alpha FE}{RT} \right\} \right] - k_2 A_0 \theta \\ & + k_{-2} A_0 (1-\theta) a_{H_{abs}} - k_3 A_0 \theta^2 + k_{-3} A_0 (1-\theta) a_{H_2(l)} \end{aligned} \tag{10}$$

which equals 0 under equilibrium conditions. In addition, no external current is flowing under these conditions, i.e. $de/dt = 0$ and Eq. (5) equals 0. As a result, Eq. (10) can be simplified to

$$\begin{aligned} \frac{d\theta}{dt} = {} & -k_2 A_0 \theta + k_{-2} A_0 (1-\theta) a_{H_{abs}} - k_3 A_0 \theta^2 \\ & + k_{-3} A_0 (1-\theta) a_{H_2(l)} = 0 \end{aligned} \tag{11}$$

According to Eq. (8) a direct relationship exists between the activity of hydrogen dissolved in the electrolyte and that in the gas phase. Introducing the fugacity constant ($\gamma_{H_2(g)}$), $a_{H_2(l)}$ can be related to the partial hydrogen pressure (P_{H_2}) according to

$$a_{H_2(l)} = \frac{k_{-4}}{k_4} \gamma_{H_2(g)} P_{H_2} \tag{12}$$

which can be recognized as Henry's law for ideal gases. When, in addition, the activity constant $\gamma_{H_{abs}}$ for H_{abs} is considered ($a_{H_{abs}} = \gamma_{H_{abs}} C_{H_{abs}}$), an expression for θ is obtained which relates θ to the concentration of absorbed hydrogen in the hydride-forming compound ($C_{H_{abs}}$) and P_{H_2}:

$$\theta=\frac{-k_2-k_{-2}\gamma_{\mathrm{H_{abs}}}C_{\mathrm{H_{abs}}}-(k_{-3}k_{-4}/k_4)\gamma_{\mathrm{H_{2(g)}}}P_{\mathrm{H_2}}}{2k_3}+\frac{\sqrt{[k_2+k_{-2}\gamma_{\mathrm{H_{abs}}}C_{\mathrm{H_{abs}}}+(k_{-3}k_{-4}/k_4)\gamma_{\mathrm{H_{2(g)}}}P_{\mathrm{H_2}}]^2+4k_3[k_{-2}\gamma_{\mathrm{H_{abs}}}C_{\mathrm{H_{abs}}}+(k_{-3}k_{-4}/k_4)\gamma H_{\mathrm{H_{2(g)}}}P_{\mathrm{H_2}}]}}{2k_3} \tag{13}$$

Eliminating θ in Eq. (9) by means of Eq. (13) ultimately yields the desired relationship between the exchange current and the partial hydrogen pressure. This complex relationship has been simulated numerically. Typical results of these analyses are shown in Fig. 1. Plotting the exchange current versus the hydrogen pressure shows that both a positive and a negative correlation may exist separated by an intermediate region, revealing a maximum value for I_0. Both the slopes of these linear dependencies and the location of the maxima are found to be dependent on the values for the various rate constants.

3. Experimental

Two different hydride-forming electrode systems were investigated to test the above-derived relationship: (i) switchable mirror electrode materials, revealing interesting optical properties [15,16]; and (ii) multicomponent compounds widely applied in commercial NiMH batteries; these multicomponent materials have the composition $\mathrm{MmNi_{3.9-x}Mn_{0.4}Al_xCo_{0.7}}$, in which the Al content (x) varies within the range between 0 and 0.8 [13].

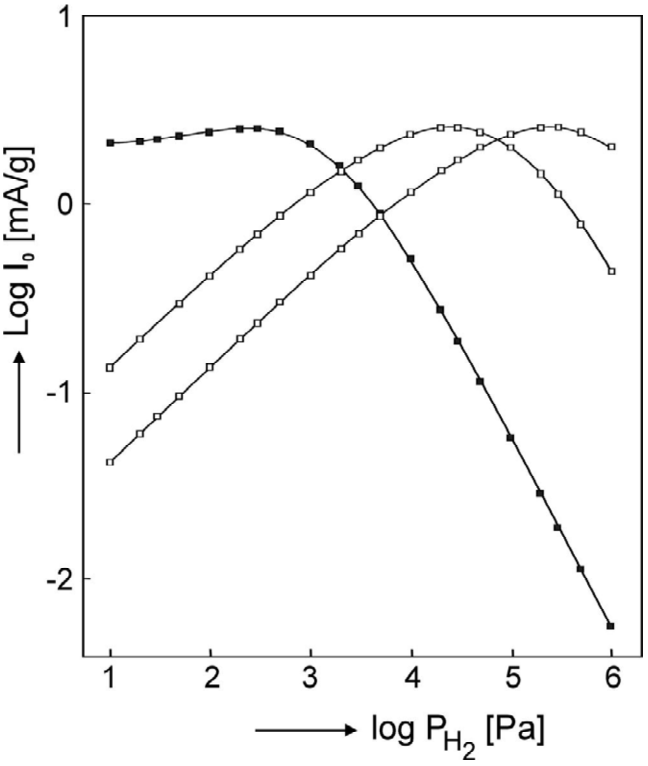

Fig. 1. Typical examples of numerical simulations of the relationship between the exchange current (I_0) and the partial hydrogen pressure ($P_{\mathrm{H_2}}$).

As described in detail elsewhere, thin film electrodes (high-vacuum e-beam evaporation deposited) were prepared in the case of mirror materials [16–18] and powder electrodes [13] in the case of battery materials. All measurements were performed on activated electrodes in 6 M KOH electrolyte at 25 °C. The hydrogen content was controlled by a constant charge/discharge current and time.

The equilibrium electrode potential was obtained as a function of the hydrogen content by intermittent constant current charging/discharging and resting. The thermodynamically controlled partial hydrogen pressure can be calculated from the following relationship [3]:

$$E_{\mathrm{MH}}^{\mathrm{eq}}=-0.926-\frac{RT}{nF}\ln\frac{P_{\mathrm{H_2}}}{P_{\mathrm{ref}}} \tag{14}$$

where the equilibrium potential is measured against a Hg/HgO reference electrode (6 M KOH) and the partial hydrogen pressure is referred to 1 bar (≈10^5 Pa). It has been shown that electrochemical measurements are excellently suited to obtain the thermodynamic characteristics of materials [3,13].

Values for the exchange currents were obtained by means of micro-polarisation and impedance spectroscopy. In the latter case, an ac voltage signal was applied to the electrode under open-circuit equilibrium voltage conditions. The amplitude of the voltage signal was 5 mV and the frequency was in the range 1–50 kHz.

4. Results and discussion

A typical example of an intermittent charging experiment with a thin film switchable mirror electrode is shown in Fig. 2 [18]. During constant current charging the current was periodically interrupted. The electrode potential at the end of each current (I) flowing period is represented by the curve E_{MH}^{I}. After interruption of the current the electrode was allowed to equilibrate. The resulting equilibrium voltages are given by the curve $E_{\mathrm{MH}}^{\mathrm{eq}}$. Obviously, the difference between the two curves corresponds to the driving force of the charge transfer reaction, i.e. the electrochemical overpotential. Two rather flat regions can be distinguished in both curves, which are separated by a much more steep voltage region. It is generally accepted

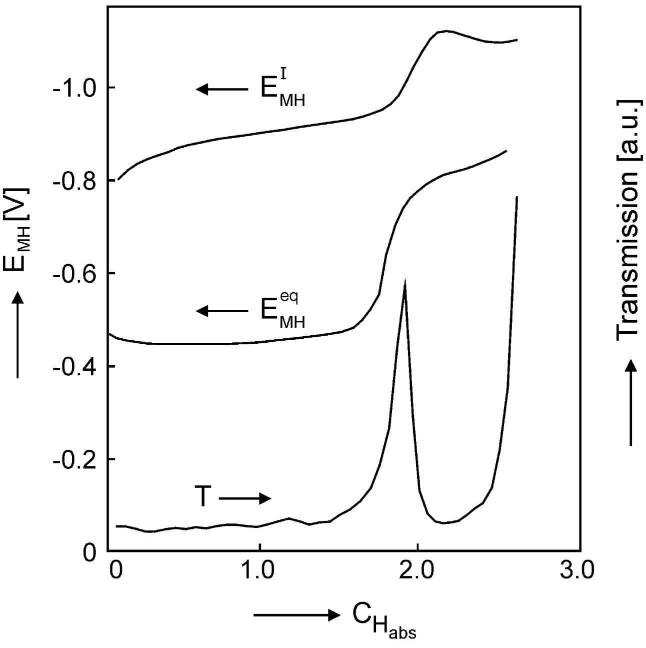

Fig. 2. Typical example of an intermittent charging (1 mA/cm^2) experiment of a thin film yttrium electrode (500 nm), which was covered with a 200 nm thick Pd layer, acting as a catalyst; the transparent glass substrate was covered with an electronic conducting transparent SnO_2 layer. The corresponding electrode transmissions (T in arbitrary units) obtained at the equilibrium potential are also indicated.

that a phase transformation occurs in the plateau regions, while the more steep part corresponds to a solid solution region, which is characteristic for a single-phase process [3]. This transition region is also accompanied by a small transmission window (see curve T), which has been reported and discussed previously [16–19]. The electrode fully opens at higher hydrogen contents, i.e. close to the hydrogen evolution region (not shown in Fig. 2). In order to study the impact of the partial hydrogen pressure on the exchange current the solid solution phase is of special interest as the partial pressure varies here over almost 10 orders of magnitude. In addition, because phase transformations are not included in the present model the theory is expected to hold for single-phase systems only.

The inset of Fig. 3 shows the results of impedance measurements obtained in the solid solution region at different values of E^{eq}_{MH}. Semi-circles are obtained in all cases, revealing a clear monotonic decrease of the diameter with increasing hydrogen content. The semi-circles can be correlated with the electrical double layer and the charge transfer resistance (R_{ct}) [20]. I_0 can then be calculated from R_{ct} (diameter of the semi-circles) according to

$$I_0 = \frac{RT}{F} \cdot \frac{1}{R_{ct}} \tag{15}$$

The as-obtained values for I_0 are plotted on a logarithmic scale as a function of the partial hydrogen pressure, according to Eqs. (9) and (13), where P_{H_2} is calculated from E^{eq}_{MH}. A linear dependence is found, indicating that the kinetics of the charge transfer reaction are improved with increasing partial hydrogen pressures. It should be noted, however, that the pressure dependence is rather weak. This indeed corresponds to the situation at the left-hand part of the upper curve in Fig. 1.

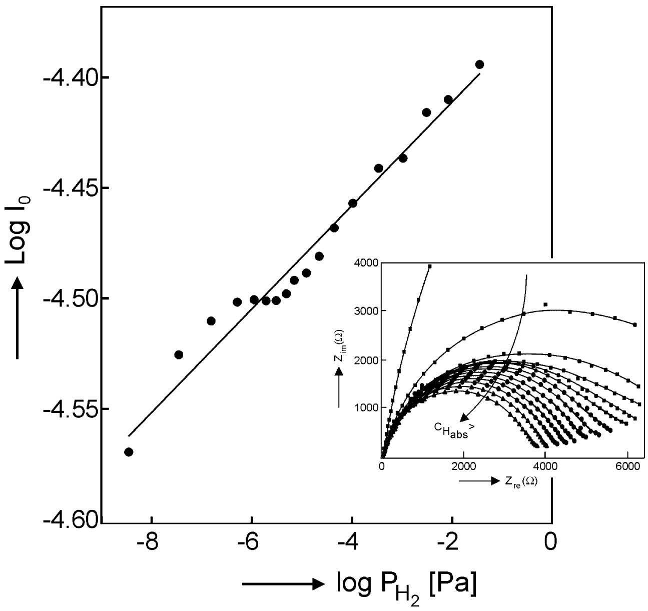

Fig. 3. Exchange current as a function of the hydrogen content, as obtained by impedance spectroscopy under equilibrium open-circuit conditions at Pd-coated thin film yttrium electrodes. The impedance spectra are shown in the inset.

Impedance measurements and micro-polarisation were also carried out at multicomponent powder electrodes as a function of $C_{H_{abs}}$, by charging towards different levels of depth-of-charge (DOC) [13]. Typical examples are shown in the inset of Fig. 4 and again reveal a dependence on the stored hydrogen concentration. The calculated values for I_0 are plotted versus the calculated hydrogen pressure (Eq. (14)) and reveal that the kinetics of these materials pass through a maximum, as expected from theory (Fig. 1). This contrasts, however, with the situation for thin film electrodes. Only at higher partial hydrogen pressures are deviations from the theoretical curves found.

Fig. 5 shows so-called Sieverts' plots (calculated square root of the hydrogen pressure vs. $C_{H_{abs}}$) for the multicomponent powder electrodes. As expected for solid solutions, straight lines are found in all cases passing through the origin. Sieverts' constants can be derived from the slope. Deviations of these straight lines can be found at higher hydrogen concentrations and these have been attributed to phase transformations. These deviations coincide with the deviations found in Fig. 4, indicating that the presented theory only applies for solid solutions. Furthermore, it can be seen from Fig. 4 that the kinetics improve with higher Al contents. When the Al content is increased beyond the 0.3 level, the curves decrease again,

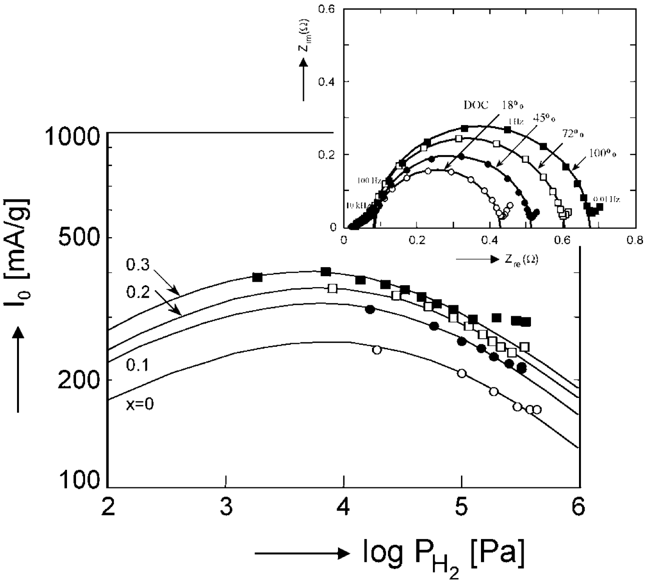

Fig. 4. Relationship between the exchange current and the partial hydrogen pressure for various multicomponent battery electrode materials ($MmNi_{3.9-x}Mn_{0.4}Al_xCo_{0.7}$; Al content x is indicated). Both the I_0 values and the partial hydrogen pressures were obtained from electrochemical measurements [3]. The inset shows the impedance spectroscopic results for the $x = 0.3$ electrode [13].

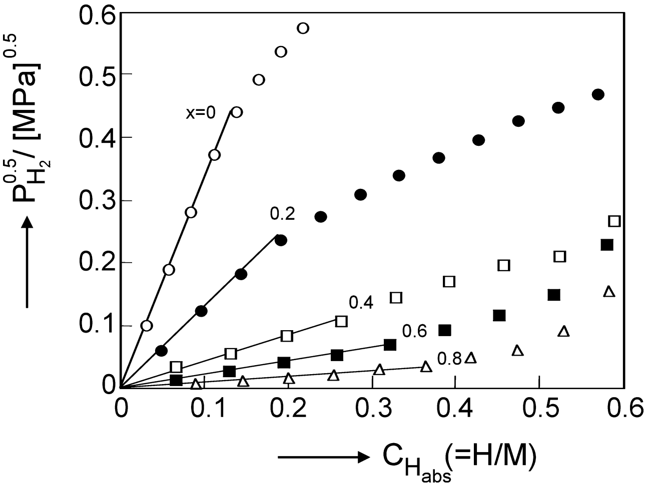

Fig. 5. Square root of the partial hydrogen pressure as a function of the hydrogen content of the same electrodes as shown in Fig. 4. The material's composition is $MmNi_{3.9-x}Mn_{0.4}Al_xCo_{0.7}$ with the Al content in the range $0 < x < 0.8$.

indicating diminishing kinetics [13]. This shows that an Al content of 0.3 can indeed be considered as the optimum composition with respect to the electrochemical charge transfer kinetics.

5. Conclusions

A model has been proposed which relates the kinetics of the electrochemical charge transfer reaction and the partial hydrogen pressure of hydride-forming compounds. Simulations reveal that different regions can be distinguished: the exchange current is found to increase with low partial hydrogen pressures P_{H_2}, and subsequently passes through a maximum, followed by a decrease at higher P_{H_2}. This relationship has been verified experimentally by applying optically active thin film electrodes and commercial battery electrode materials of the AB_5 type. An interesting impact of this theoretical relationship is that a positive dependency of the exchange current on the hydrogen pressure is, a priori, not necessary. Under certain conditions it is desirable to design catalysts which exhibit a negative dependence. Evidently, this is of interest for the design of new, highly electro-catalytic, hydride-forming compounds. The derived theoretical relationship will form the basis for the modelling of complete Ni–MH batteries [11].

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