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An impedance model for electrode processes in metal hydride electrodes

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Abstract

A model for the impedance of granular metal hydride electrodes is presented. The model includes the rate of hydrogen exchange at the hydride–electrolyte interface and diffusion of hydrogen into the bulk of the hydride. The exchange reaction is assumed to occur in two steps: electrosorption of hydrogen at the interface and hydride formation. The subsequent transport process is approximated as spherical diffusion in the particles. The model was successfully fitted to experimental data for a misch metal/nickel based hydride forming compound ($MmNi_{3.5-3.7}Co_{0.7-0.8}Mn_{0.3-0.4}Al_{0.3-0.4}$) at different depths of discharge.

Keywords: Hydride; Impedance; Diffusion; Modelling; Kinetics

1. Introduction

The electrochemical properties of metal hydrides are interesting due to the possibility of using these as electrodes in secondary cells [1]. Knowledge of the charging and discharging processes and their rates is important for the development and optimization of electrode materials. Impedance measurements appear particularly promising for electrochemical in situ characterization [2]. Most of the attempts of impedance characterization of MH_x electrodes make use of equivalent circuits for interpretation of data [3,4] which at best remains semi-quantitative. Only the work of Zhang et al. [4] contains analytical expressions for the impedance derived based on the details of a proposed reaction mechanism. In that work, however, hydrogen diffusion in the electrode is neglected. The purpose of the present work, therefore, is to derive expressions for the impedance of a particulate metal hydride electrode, and compare these with impedance measurements on the metal hydride electrode.

2. Impedance model

We consider an assembly of metal hydride particles with dimensions of similar magnitude in all directions. All particles are electrically connected to a current collector and a major part of their surface is exposed to an aqueous solution with no processes competing with the hydride forming reaction. We assume that the electrode reactions at the metal hydride surface can be associated with three distinguishable processes. The first of these is a charge transfer reaction given by

$$H_2O + \square_M + e \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H_{ad} + OH^- \tag{1}$$

where $\square_M$ is an active site on the surface of the metal hydride forming alloy. The adsorbed hydrogen then reacts with the alloy to form interstitial hydrogen at the surface of the particle

$$H_{ad} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} H_i + \square_M \tag{2}$$

The interstitial hydrogen then forms a hydride phase

$$xH_{i,r_H} + M_{r_H} \rightarrow MH_{x,r_H} \tag{3}$$

where r_H is the radius of the reaction zone for the hydride formation. Parallel to this, hydrogen diffuses through both the hydride phase and the metal phase

$$H(MH_x)_{r=a} \rightarrow H(MH_x)_{r=r_H} \tag{4}$$

$$H_{i,r=r_H} \rightarrow H_{i,r<r_H} \tag{5}$$

Eqs. (3)–(5) are written for the charging of a hydride particle, with radius $r=a$, where the reaction zone for hydride formation is moving inward. In the further development we have assumed that Eq. (3) is in equilibrium and that the diffusion coefficient, D_H, is the same in the two phases. This means that formally the diffusion takes

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place in a continuum. The diffusion is further modelled by assuming particles with spherical symmetries. By defining $u_H(r) = c_{H_i}(r) \cdot r$ [5] the diffusion equation in spherical coordinates can be written

$$\frac{\partial u_H}{\partial t} = D_H \frac{\partial^2 u_H}{\partial r^2} \tag{6}$$

If the potential applied to the metal hydride electrode is the sum of a steady-state value and a harmonic contribution applied at time $t > 0$, we may split u_H into corresponding terms for $t > 0$

$$u_H(r, t) = u_H(r, 0) + \tilde{u}_H(r, t) \tag{7}$$

where $\tilde{u}_H$ will have the same frequency as the applied signal provided the amplitude of the latter is small enough that the system is in the linear range for such perturbations. The boundary condition at $r = 0$ is given by:

$$\tilde{u}_H = 0, r = 0 \tag{8}$$

The mass balance for the hydride particle at $r = a$ can be combined with the hydrogen concentration in the particle:

$$\left.\frac{d\tilde{c}_H}{dr}\right|_{r=a} = \frac{\tilde{v}_2}{D_H} \tag{9}$$

where $\tilde{c}_H$ and $\tilde{v}_2$ are the alternating components of hydrogen concentration and rate of reaction (2)

$$v_2 = (v_2)_{ss} + \tilde{v}_2 \tag{10}$$

Laplace-transforming Eqs. (6)–(10) and solving for the Laplace-transformed hydrogen concentration, $\mathscr{L}\{\tilde{c}_H\}$, gives

$$\mathscr{L}\{\tilde{c}_H\} = \frac{\mathscr{L}\{\tilde{v}_2\} \sinh(\alpha r)}{r D_H \left[\frac{\alpha}{a} \cosh(\alpha r) - \left(\frac{1}{a^2}\right) \sinh(\alpha r) \right]} = \mathscr{L}\{\tilde{v}_2\} \mathscr{L}\{G(s, r, a, D_H)\} \tag{11}$$

where $\alpha = \sqrt{\frac{s}{D_H}}$ and s is the Laplace variable. The reaction rate can be expanded

$$\tilde{v}_2 = \left(\frac{\partial v_2}{\partial \theta}\right)_{c_H} \tilde{\theta} + \left(\frac{\partial v_2}{\partial c_H}\right)_{\theta} \tilde{c}_H = C\tilde{\theta} + D\tilde{c}_H \tag{12}$$

With the use of Eq. (11) both sides of Eq. (12) can be Laplace transformed to give

$$\mathscr{L}\{\tilde{v}_2\} = \frac{C \mathscr{L}\{\tilde{\theta}\}}{1 - D\mathscr{L}\{G\}} \tag{13}$$

Laplace transforming the mass balance for the adsorbates gives

$$\Gamma s \mathscr{L}\{\tilde{\theta}\} = -\left[\frac{\mathscr{L}\{\bar{i}_f\}}{F} + \mathscr{L}\{\tilde{v}_2\} \right] \tag{14}$$

where i_f is the faradaic current density. If the concentrations of H_2O and OH^- are considered constant and the activity of the adsorbed hydrogen is proportional to the surface coverage, the alternating part of the current can be expressed by

$$\bar{i}_f = \left(\frac{\partial i_f}{\partial \theta}\right)_{\varphi} \tilde{\theta} + \left(\frac{\partial i_f}{\partial \varphi}\right)_{\theta} \tilde{\varphi} = A\tilde{\theta} + B\tilde{\varphi} \tag{15}$$

The faradaic impedance, Z_f, is now calculated as the ratio between the Laplace-transformed potential and current setting $s = j\omega$. Combining Eq. (13), Eq. (14) and the Laplace-transformed Eq. (15) gives

$$Z_f = \frac{\mathscr{L}\{\varphi\}}{\mathscr{L}\{\bar{i}_f\}} = \frac{1}{B} \left[1 + \frac{\frac{A}{F}}{\Gamma s + \frac{C}{[1 - D\mathscr{L}\{G\}]}} \right] \tag{16}$$

Eq. (16) may be represented by the circuit shown in Fig. 1 where a double-layer capacitance, C_{dl}, is included. The expressions for the circuit elements are:

$$R_{ct} = B^{-1} = \frac{1}{\left(\frac{\partial i_f}{\partial \varphi}\right)_{\theta}} \tag{17}$$

$$C_s = \frac{\Gamma F \left(\frac{\partial i_f}{\partial \varphi}\right)_{\theta}}{\left(\frac{\partial i_f}{\partial \theta}\right)_{\varphi}} \tag{18}$$

$$R_s = \frac{1}{F} \left(\frac{\partial i_f}{\partial \theta}\right)_{\varphi} \left(\frac{\partial v_2}{\partial \theta}\right)_{c_H}^{-1} \left(\frac{\partial i_f}{\partial \varphi}\right)_{\theta}^{-1} \tag{19}$$

and

$$Z_{Ds} = -\left(\frac{\partial i_f}{\partial \theta}\right)_{\varphi} \left(\frac{\partial v_2}{\partial c_H}\right)_{\theta} \left(\frac{\partial v_2}{\partial \theta}\right)_{c_H}^{-1} \left(\frac{\partial i_f}{\partial \varphi}\right)_{\theta}^{-1} F^{-1} \cdot G(j\omega) \tag{20}$$

where $G(j\omega)$ is given by

$$G(j\omega) = \frac{\sinh\left(a\sqrt{\frac{j\omega}{D_H}}\right)}{a D_H \left[\frac{1}{a}\sqrt{\frac{j\omega}{D_H}} \cosh\left(a\sqrt{\frac{j\omega}{D_H}}\right) - \frac{1}{a^2} \sinh\left(a\sqrt{\frac{j\omega}{D_H}}\right) \right]} \tag{21}$$

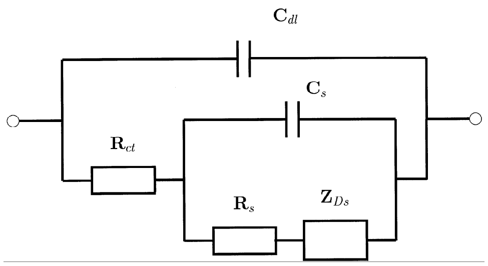

Fig. 1. Equivalent circuit representation of Eq. (16) with a double-layer capacitance, C_{dl}, included.

The use of regular chemical and electrochemical kinetics [6] renders all circuit elements positive.

3. Experimental

Electrodes were made by mixing $MmNi_{3.5-3.7}Co_{0.7-0.8}Mn_{0.3-0.4}Al_{0.3-0.4}$, (GfE) with fine copper powder (Merck, p.a., 64 μm) and cold-pressing this mixture at $4 \cdot 10^8$ Pa [1]. The mixture was pressed together with a layer of copper powder and a copper plate in a sandwich construction. The compressed powder layer containing hydride was approximately 650 μm thick. An isolated wire was soldered to the copper plate and the back side of the electrode was mounted in epoxy to prevent corrosion. The electrolyte was 6 M KOH (Merck, p.a.) in deionized water deaerated by N_2-bubbling at 25 °C. Charging was carried out at the 1.25 C rate with 10% overcharge, while discharging was carried out at the 0.5 C rate to a cutoff voltage of −600 mV vs. Hg/HgO. Before measurements, the electrodes were activated during 20 charge/discharge cycles. The electrodes were kept at the open circuit potential during the impedance measurements, so that the DC current was approximately zero. Impedance measurements were carried out after discharging the electrode to the actual depth of discharge (DOD), in a frequency range from 10 kHz to 0.1 mHz with an amplitude of 5 mV, using a computer-controlled Solartron 1250 frequency response analyzer coupled directly to a Princeton EGG 273 potentiostat.

4. Results and discussion

The measured impedance of a 10% discharged electrode is shown as crosses in Fig. 2. The fit to the equivalent circuit of Fig. 1 in series with a circuit consisting of a resistor and a capacitor in parallel is shown as a continuous line. This series circuit is included to take into account the contact to the backing plate, whereas the interparticle contact-impedance is neglected [3]. A corresponding simulation using planar diffusion is showed as a dotted line, giving an inferior fit to the low frequency values. Fig. 3 exhibits a complex plane plot of the impedance for a hydride electrode with 50% DOD, compared with the model including spherical diffusion. Simulated values for the circuit elements are given in Figs. 2 and 3. The value of the obtained diffusion coefficient varies between 10^{-10} and 10^{-9} $cm^2\ s^{-1}$ depending on the state of charge of the electrode.

As seen from the figures, the model fits the experimental data reasonably well for two different DOD. The curves also have the same shape in the low and medium frequency region as the impedance data presented by Kuriyama et al. [3], although there are some differences in the high frequency region due to different electrode construction.

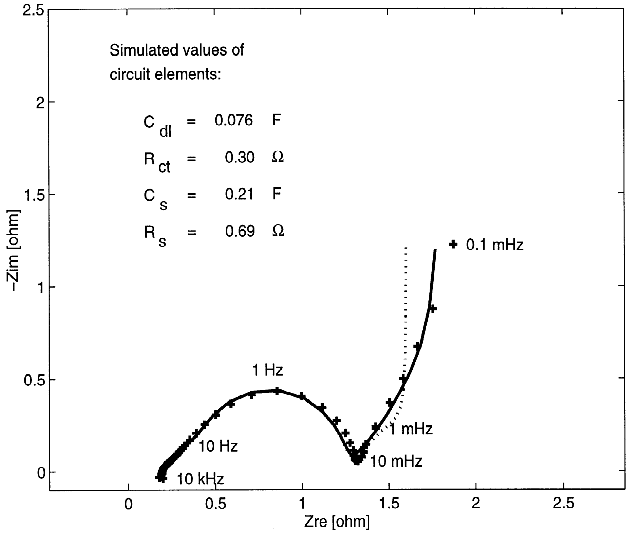

Fig. 2. Complex plane plot, hydride electrode, 10% DOD. Measured values (+) compared with models including spherical diffusion (–) and planar diffusion (···).

If the diffusion impedance is zero, i.e. diffusion is fast relative to all other processes, the model described by Fig. 1 yields the same equivalent circuit as proposed for faradaic reactions involving one electrosorbed intermediate, developed by Harrington and Conway [7] for the hydrogen evolution process.

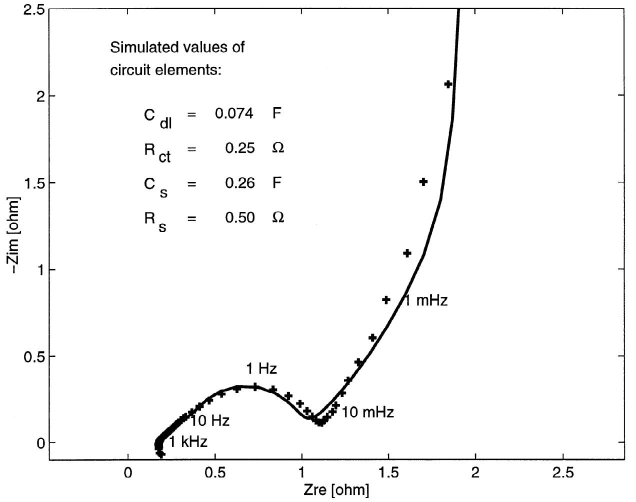

Fig. 3. Complex plane plot, hydride electrode, 50% DOD. Measured values (+) compared with model including spherical diffusion (–).

5. Conclusion

The proposed impedance model agrees fairly well with the experimental curves. The results suggest that hydrogen diffusion in the hydride particles must be taken into account for a proper description of the impedance of metal hydride electrodes, and that the total process is best described using spherical geometry.

Acknowledgments

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References

[1] J.J.G. Willems, *Philips J. Res. Suppl., 39(1)* (1984).

[2] P. Agarwal, M.E. Orazem and A. Hiser, in *Hydrogen storage materials, batteries and electrochemistry, vol. 92–5*, D.A. Corrigan and S. Srinivasan (Eds.) pp 120–137, The Electrochemical Society, 1992.

[3] N. Kuriyama, T. Sakai, H. Miyamura, I. Uehara, H. Ishikawa and T. Iwasaki, *J. Alloys and Compounds, 202* (1993) 183–197.

[4] W. Zhang, M.P. Sridar Kumar, S. Srinivasan and H.J. Plohen, *J. Electrochem. Soc., 142(9)* (1995) 2935–2943.

[5] J. Crank, *The Mathematics of Diffusion*. Oxford, 2 Edn., 1975.

[6] J.S. Newman, *Electrochemical Systems*. Prentice Hall, Englewood Cliffs, 2 Edn., 1991.

[7] D.A. Harrington and B.E. Conway, *Electrochim. Acta, 32(12)* (1987) 1703–1712.