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The electrochemical impedance of metal hydride electrodes

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Abstract

Electrochemical impedance spectroscopy (EIS) and other characterization methods combined with modelling are very useful tools to gain an understanding of the processes governing the charge and discharge reactions in metal hydride electrodes. Impedance measurements were performed in the range from 10 kHz to 0.1 mHz. The proposed model simulated the experimental data better than previously presented models by a smooth fit for all frequencies. Especially the fit at the lower frequencies (diffusion) was notable. The diffusion was modelled using spherical diffusion geometry. To fit the experimental data, equations describing the current distribution in porous electrodes were needed. The different sub-processes taking place during the charge/discharge reaction were identified. The following parameters were found to be of significant importance in order to describe the overall process: charge transfer resistance, double layer capacitance and impedance resulting from diffusion. A continuous improvement of the catalytic properties during electrochemical cycling of the metal hydride electrode was found to take place. This improvement in the catalytic properties was found to be a result of a decrease in the charge transfer resistance. The results confirmed the usefulness of the impedance method for in situ characterization of hydride electrodes. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Metal hydride batteries are one of the most promising secondary batteries for a range of applications. Understanding the processes governing the charge and discharge reactions in metal hydride electrodes is very important for improving the performance of such batteries.

Electrochemical impedance spectroscopy (EIS) and other electrochemical characterization methods combined with modelling, are very useful tools to gain mechanistic understanding of electrochemical processes. Impedance characterization can be used to provide information on the overall reaction rate as well as the rate and significance of sub-processes. This provides important information about the kinetics and reaction mechanism.

Impedance analysis of metal hydride electrodes is an established characterization technique. Furthermore, the EIS technique provides a non-destructive method for investigating the electrochemical properties of the electrode, as all data are obtained with a minimum polarization (i.e. change in the state of charge) of the electrode. EIS is one of the most sensitive electrochemical techniques, but it is usually not sufficient to solve all the questions which exist with regards to the kinetics. Like any other electrochemical technique, impedance spectroscopy can not be regarded as a ‘stand-alone’ method for model identification because the response of a system to a periodic perturbation does not provide a direct measure of the governing physical phenomena [1].

Impedance characterization of metal hydride electrodes generally makes use of equivalent circuits for interpretation of data, but modelling has also been carried out. Harrington and Conway [2] modelled the ac impedance of faradaic reactions involving electrosorbed intermediates. This model was extended by the present authors to also include spherical diffusion of hydrogen within the metal hydride particles [3]. Several other authors have also contributed to the interpretation of impedance response in metal hydride electrodes. Kuriyama et al. [4–6] assigned different segments of the impedance spectra to different sub-processes. These authors proposed that the following parameters need to be taken into account: hydrogen content, rates of electrode reactions on alloy particles, double-layer capacitance, and contact resistance and capacitance between alloy particles in the electrode.

Impedance measurements have been used to obtain variations of the polarization resistance as a function of depth of discharge (DOD) [7–13] and temperature [14]. It was stated in these papers that for electrodes of AB_5 type

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alloys, the reaction impedance was highest for charged electrodes.

The scope of the present paper is to show that electrochemical impedance spectroscopy can be utilised in combination with other characterization methods to obtain a more thorough understanding of the change in kinetic properties of metal hydride electrodes with charge/discharge cycling.

2. Theory

Gas phase and electrochemical absorption of hydrogen in metals have similar, but yet slightly different reaction paths. In the case of hydrogen gas absorption, the hydrogen molecule must be accommodated at the surface and atomic hydrogen is absorbed into the alloy. The electrochemical absorption and desorption of hydrogen by a metal involves a number of steps. For the charging (absorption) process these include:

- Transport of H_2O molecules to the electrode surface:

  $$H_2O_{Bulk} \rightleftharpoons H_2O_{Surface} \tag{1}$$

- Charge transfer and adsorption of hydrogen atoms at an active site (Volmer step), $\square_M$, at the surface:

  $$H_2O_{Surface} + \square_M + e \underset{k_{(-2)}}{\overset{k_2}{\rightleftharpoons}} H_{ad} + OH^-_{Surface} \tag{2}$$

  Here H_{ad} is adsorbed hydrogen and $\square_M$ is an active site at the surface of the hydrogen storage alloy. The OH^- ions are then transported away from the surface:

  $$OH^-_{Surface} \rightleftharpoons OH^-_{Bulk} \tag{3}$$

  The charge transfer reaction can either be uniform or catalytically enhanced. In the latter case the reaction takes place on designated active surface sites.

- Transfer of atomic hydrogen through the interface forming interstitial hydrogen in the crystal lattice in a surface film:

  $$\square_i + H_{ad} \underset{k_{(-4)}}{\overset{k_4}{\rightleftharpoons}} H_i + \square_M \tag{4}$$

  Here $\square_i$ is an empty interstitial hydrogen position. In the further development, it is assumed that the electrode has a shell of β phase hydride. The thickness of this shell is very dependent on the state of charge for the electrode and varies between zero and a, where a is the radius of the particle.

- The interstitial hydrogen then diffuses through the hydride (β) phase and to the interface between the β and metal (α) phase where the new β phase hydride phase forms and expands inwards:

  $$H(MH_x)_{r=a} \rightarrow H(MH_x)_{r=r_H} \tag{5}$$

  $$H_{i,r=r_H} \rightarrow H_{i,r<r_H} \tag{6}$$

  Here r_H is radius of the reaction zone for hydride formation and a is the radius of the metal hydride particles.

- Nucleation and growth of the hydride phase in the bulk is the next step:

  $$xH_{i,r_H} + M_{r_H} \rightarrow MH_{x,r_H} \tag{7}$$

  During formation of the hydride β phase, there is a hybridization between the electron orbitals of the hydrogen atom going in and the electron orbitals of the metal atoms. New electronic states below the Fermi level are also formed and according to Switendick [15], a partial transfer of the s electron is taking place.

In Fig. 1, an equivalent circuit for a metal hydride electrode, mathematically modelled by the authors [3], is given. The shaded area represents the processes in the metal hydride electrode.

The charge transfer resistance, R_{ct}, is directly related to the catalytic activity of the electrode. The double layer capacitance, C_{dl}, is resulting from the non faradaic current response in the electrical double layer on the electrode surface. The parallel capacitance, C_p, can be recognized as a pseudo capacitance dependent on the the surface coverage of hydrogen and the kinetics of the surface reaction. R_1 may be related to a product of partial derivatives of the rates of different reaction steps with respect to surface coverage and potential, i.e. a resistance. The diffusion impedance, Z_{Ds}, is dependent on both frequency, particle radius and the diffusion coefficient of hydrogen in the alloy. Z_{Ds} may therefore be interpreted as a diffusion impedance resulting from spherical diffusion.

In order to be able to utilise the EIS technique, however, the impedance response from auxiliary processes needs to be taken into account. This is even more important for low

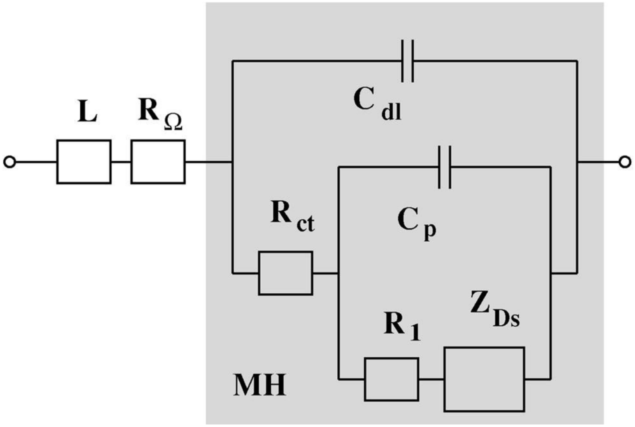

Fig. 1. Equivalent circuit model for a planar metal hydride electrode. The shaded area represents the modelled processes in the metal hydride electrode.

impedance battery electrode applications as the auxiliary processes may contribute significantly to the total impedance measured.

The inductance in the wires connecting the metal hydride electrode and the impedance system, L, may contribute to the total impedance, and so does the electrolyte resistance, R_Ω. The electrolyte resistance is largely dependent on the distance between the electrodes and it will in the case of an electrochemical setup with the electrodes placed very close to each other, be very dependent also on the porosity of the electrodes. The case of electrodes having channel formed pores was developed by De Levie [16]. To account for porosity in the pressed powder electrodes, the pores can be approximated as cylindrical. In an electrode with channel formed pores, the total equation for the impedance is given by [17]:

$$\hat{Z} = R_\Omega + \frac{R_{\Omega,\mathrm{p}}}{\sqrt{\Lambda}} \coth(\sqrt{\Lambda}) \qquad (8)$$

Here Λ is the dimensionless electrode admittance for a corresponding planar electrode. Consequently, a semicircle in the complex plane plot becomes deformed [18]. It is worthwhile to mention that this approach does not account for the electrolytic diffusion of species in the pores in the electrode, but it takes into account the potential drop in the pores. It can also be noted that a model for an electrode process including porous morphology can not be represented using an equivalent circuit, but a mathematical approach is needed.

The derivations of the so-called Kramers Krönig transforms are based on the fulfilment of some general conditions of the system: causality, stability, finiteness, and linearity [17,19]. Rapidly corroding alloys and alloys with a very flat plateau region will as such not be suited for EIS studies, as the state of charge and consequently the kinetic properties of these alloys will be altered during impedance measurements. Alloys should also exhibit a minimum hysteresis to satisfy the Kramers Krönig criteria. It is furthermore very important that the measurements are carried out under steady state conditions.

Performing the impedance measurements with a low amplitude is important, and according to Lasia [17], the maximum amplitude, ΔE should be lower than $8/n_\mathrm{e}$ mV, peak to peak, where n_e is the number of electrons exchanged in the reaction. A particularly low amplitude is desired for metal hydride electrochemical systems to prevent the state of charge of the electrode from being changed as the measurement is taken.

3. Experimental

AB_5 type 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) powder with fine copper powder and cold-pressing this mixture at 4×10^8 Pa. The electrolyte was 6 M KOH (Merck, p.a.) in deionized water deaerated by N_2-bubbling. Unless otherwise noted, before any measurements were taken, the electrodes were activated during 20 charge/discharge cycles.

The average initial particle size was measured to be around 50 μm using a Coulter LS Particle Size Analyser. The particle size was assumed to decrease because of cracking of the particles during charge/discharge cycling.

A three compartment cell with separate compartments for the hydride electrode, the platinum counter electrode and the Hg/HgO reference electrode was used. Impedance measurements were carried out after discharging the electrode to the actual depth of discharge (DOD). An amplitude of 5 mV was applied in the whole frequency range from 10 kHz to 0.1 mHz. The electrodes were kept at the open circuit potential during the impedance measurements, so that the net DC current was approximately zero.

4. Results and discussion

In Fig. 2, complex plane plots for an electrode discharged to 90% depth of discharge is given. The 1st run is after 48 cycles and 7 impedance measurements and the 2nd run is after 73 cycles and 18 impedance measurements, respectively. The impedance simulation is based on the circuit given in Fig. 1 including porous electrode morphology (Eq. (8)).

From Fig. 2 it can be observed that the simulation of the impedance response fitted the experimental data very well in the whole frequency range. From the impedance simulations it was found that the resistance R_1 was small

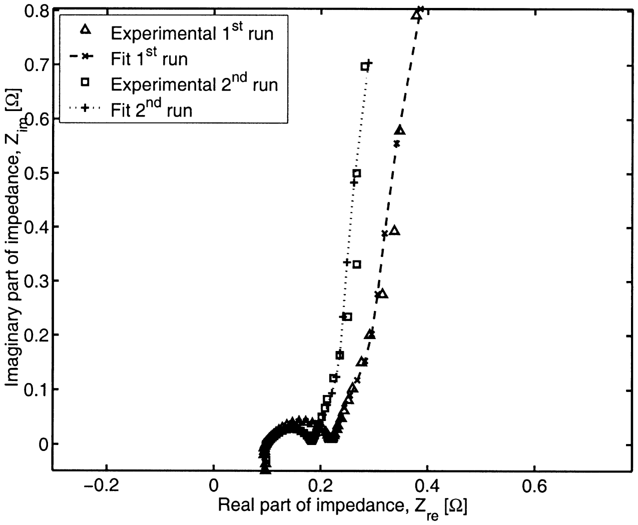

Fig. 2. Complex plane plots for an electrode discharged to 90% depth of discharge. 1st run is after 48 cycles, 7 impedance measurements, and 2nd run is after 73 cycles and 18 impedance measurements respectively. The parameters in Fig. 1 except C_p and R_1 as well as porous electrode morphology are included in the fit.

compared to the diffusion contribution. The parallel capacitance, C_p, was impossible to separate from the double layer capacitance. Including these two elements in the simulation equations did therefore not improve the fit to the experimental data. Therefore, both R_1 and C_p were assumed not to play any significant role in the impedance response and therefore omitted in the impedance simulation fit.

It was, however, found that adding a resistance in parallel to the charge transfer significantly improved the fit, both for charged electrodes (hydrogen evolution side reaction) and discharged electrodes (redox processes involving corrosion products in the electrolyte). From Fig. 2, it is also worthwhile to comment that the low frequency part is not a vertical line parallel to the imaginary axis. The reason for this is assumed to be that in an aqueous solution containing corrosion products, several side reactions can take place. For instance, both hexavalent and heptavalent manganese ions are stable in the electrolyte during the conditions exhibited in the electrolyte during measurements [20].

The real part of impedance versus frequency for two completely charged electrodes is given in Fig. 3. One is cycled 5 times and the other is cycled 15 times. The difference in the total impedance between the two measurements is also indicated in the figure.

From the figure it is seen that the activation processes mainly change the real part of the impedance response in a very narrow frequency range from 0.1 to 1 Hz. The imaginary part of the impedance was practically unchanged, indicating a relatively small change in the capacitive part of the impedance response. The auxiliary processes such as the electrolyte resistance and the wire inductance, as well as the porous resistance, all influence the high frequency impedance response. In the low frequency range, the diffusion processes are assumed to dominate the impedance response. And as seen from the figure, the change in the diffusion response is negligible compared to the change in the medium frequency range. This small difference indicates that cracking of the metal hydride particles in the electrode was not a major contributor to the activation process. The charge transfer resistance, however, is assumed to be more important in the frequency window with the most pronounced change in the impedance response.

In Fig. 4, the charge transfer resistance versus number of impedance measurements without prior activation for an electrode at approximately 15% depth of discharge is given.

The electrode was here polarized to a potential corresponding to a 15% depth of discharge and impedance measurements were carried out continuously with a 2 h break between each measurement. From Fig. 4, it is clearly observed that the charge transfer resistance of the electrode is changing significantly during impedance measurements for an electrode which is not fully activated. This result also confirms that all electrochemical charge/discharge cycling will decrease the overpotential caused by the charge transfer resistance.

The hydrogen evolution reaction has a common charge transfer step with the hydriding reaction. A significant decrease in the closed circuit hydrogen evolution potential on a metal hydride electrode with increasing cycle number should therefore be possible to observe. In Fig. 5, the hydrogen evolution potential at the end of the charging period for $LaNi_{3.4}Co_{1.2}Mn_{0.1}Al_{0.3}$ is shown. The electrode is overcharged to 400 mAh/g using currents of 100 mA/g.

The figure shows that the hydrogen evolution potential

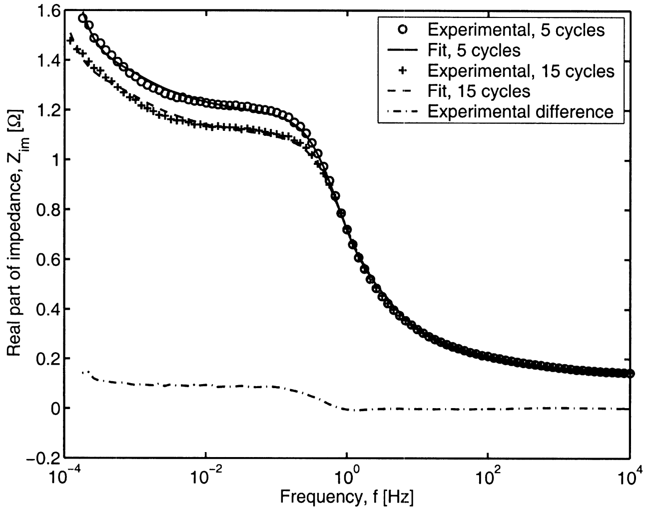

Fig. 3. Real part of impedance versus frequency for two completely charged electrodes. Same parameters as in Fig. 2 are included in the fit. One is cycled 5 times and the other is cycled 15 times. The difference in the impedance between the two measurements are also indicated.

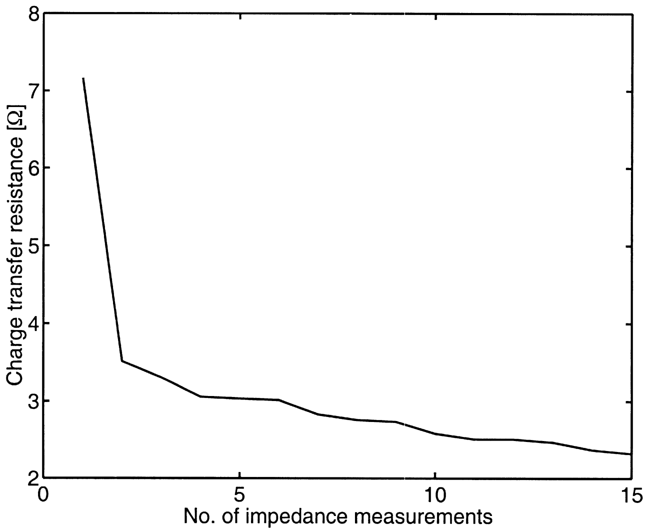

Fig. 4. Charge transfer resistance versus number of impedance measurements without prior activation for a $LaNi_{3.4}Co_{1.2}Mn_{0.1}Al_{0.3}$ electrode at 15% depth of discharge.

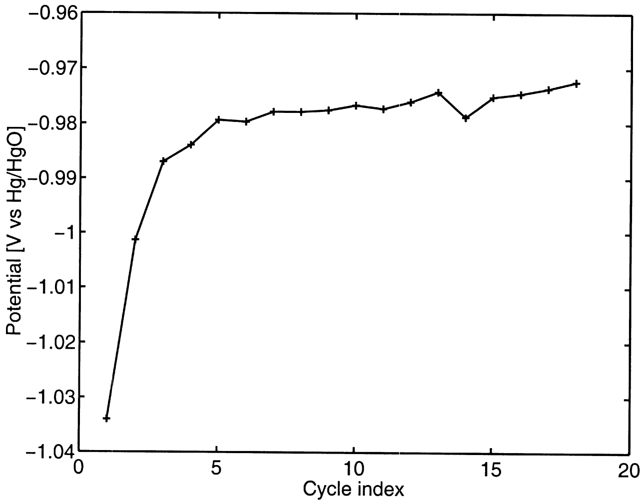

Fig. 5. End of charge (hydrogen evolution) potential for $LaNi_{3.4}Co_{1.2}Mn_{0.1}Al_{0.3}$. The electrode is overcharged using 400 mAh/g, using currents of 100 mA/g.

became less negative (i.e. less overpotential) as the charge/discharge cycling proceeded. The kinetic measurements displayed in Fig. 5 together with the impedance measurements show that the kinetics of the alloy was very dependent on the number of charge/discharge cycles performed. The first charge/discharge cycle possesses special challenges and should be treated separately. However, there is a significant change in the electrocatalytic activity for the subsequent cycles as well, even after the initial activation. It is known that the surface of AB_5 type metal hydride electrodes will change during cycling, with a resulting nickel enrichment [21,22], as well as a rare earth oxide rearrangement [21]. Keeping in mind that the change in the impedance response occurs in a very narrow frequency range, the enhanced catalytic activity is very likely to be caused by the surface nickel enrichment and the rare earth oxide rearrangement.

From the observed experimental data it is clear that very useful kinetic information on the charge transfer reaction can be obtained using EIS. The low frequency response can be assumed to be originating from some diffusion process. An exact prediction of the diffusion coefficient from the data is not attainable without knowing the exact diffusion length. From the impedance fitting routine, values for the diffusion coefficient divided by the diffusion length in the range of 10^{-9}–10^{-8} m/s were obtained, depending of the depth of discharge. By assuming an average diffusion length of 10 μm, diffusion coefficients in the range of 10^{-14}–10^{-13} m^2/s were calculated from simulation of the impedance response to the experimental data. This is comparable with literature data for diffusion coefficients for AB_5 type metal hydrides given by Richter et al. [23]. The magnitude of the obtained diffusion coefficients (yet uncertain because of uncertainties in the diffusion length) indicates that the observed diffusion response originated from diffusion of hydrogen within the metal lattice. The response from the hydride forming reaction would be in the low frequency range, and it should contain a reaction resistance in parallel to a reaction capacitance. The only response observed in this frequency range was the response from the hydrogen evolution side reaction and in the case of discharged electrodes, a response in parallel to the charge transfer step, presumably a competing redox reaction [24]. The results indicate that the diffusion process is very slow compared to the hydride forming reaction. To confirm this, measurements were carried out on alloys with a very flat plateau region allowing for a significant change in the state of charge during impedance measurements. The impedance response for these alloys resemble the impedance response for electrodes exhibiting a charge storage [25], namely a significantly more pronounced frequency dependence of the imaginary part of the impedance at medium low frequencies. The results therefore indicate that EIS is a useful tool to study the kinetics of metal hydride electrodes for battery purposes. In the case of more fundamental studies, the slow hydrogen diffusion will limit the study of the absorption and phase transformation phenomena as the rate of these reactions are high compared to the rate of the charge transfer reaction and the hydrogen diffusion within the metal lattice.

5. Conclusions

The proposed model fits the experimental data for different metal hydride electrodes very well for all frequencies in the range from 10 kHz to 0.1 mHz. The EIS technique, when used properly and in combination with other characterization techniques, is very useful in determining the significance of the different sub-processes in the overall process. The charge transfer resistance is found to be a very important kinetic parameter. The double layer capacitance, spherical hydrogen diffusion in the metal phase, as well as porous electrode morphology are required parameters in the model. The charge transfer resistance was found to decrease substantially as the electrode was undergoing electrochemical charge/discharge.

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