

Modeling the Impedance Response of Porous Metal Hydride Electrodes

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INTRODUCTION

Electrochemical impedance is a powerful tool for characterization of actual metal hydride electrodes. Here, a mathematical model for the impedance response of a porous metal hydride electrode was derived based on a model for porous intercalation electrodes (1). The effect of a continuous particle size distribution and porosity (i.e. finite conductivities of the electrolyte phase and the solid phase) is taken into account.

THEORY

The starting point is the derivation of the impedance response of a single particle (1):

$$Z_f = R_{ct} + \frac{R_{part}}{Y_s(\Omega_s)} \quad [1]$$

$$\text{where } R_{part} = \left(-\frac{\partial U^{ocp}}{\partial c_H} \right) \frac{r_p}{FD_H}$$

$$\text{and } \Omega_s = \omega r_p^2 / D_H$$

U^{ocp} is the open circuit voltage, c_H is the surface concentration of hydrogen, r_p the particle radius, and D_H the diffusion coefficient for hydrogen in the metal hydride. The overall, specific admittance, $[aY]$, is then obtained by integration over a lognormal particle size distribution of width Ψ (1). By application of the porous electrode theory, the following solution is obtained for the impedance of the electrode of thickness L (1):

$$Z_{el} = \frac{L}{\kappa + \sigma} \left(1 + \frac{2 + \left(\frac{\sigma}{\kappa} + \frac{\kappa}{\sigma} \right) \cosh \nu}{\nu \sinh \nu} \right) \quad [2]$$

where

$$L / \nu = \left(\frac{\kappa \sigma}{\kappa + \sigma} \right)^{1/2} (aY)^{-1/2}$$

EXPERIMENTAL

AB₅ type electrodes were made by mixing powder of MnNi_{3.5-3.7}Mn_{0.3-0.4}Al_{0.3} with fine Cu powder and cold-pressing this mixture at 4·10⁸Pa. The measurements were conducted in a three-compartment cell with separate compartments for the hydride electrode, the Pt counter electrode and the Hg/HgO reference electrode. The electrolyte was 6M KOH. Prior to the measurements, the electrodes were activated/deactivated during 20 charge/discharge cycles. Impedance measurements were taken after discharging the electrode to the actual depth of discharge (DOD). Further details are given in Ref. 2.

RESULTS

The model was fitted to the experimental impedance spectra by a least square fitting routine (LEVM 7.0 (4)). The simulated curves agree very well with the experimental results for DODs around 50%, where the diffusion process dominates the impedance response, as shown in Fig. 1. The relative residuals lie within ±2.5% for all frequencies except for the highest, where the relative residuals are around 8%. The estimated diffusion coefficient for hydrogen in the alloy was in the order of 10⁻¹⁰ cm² s⁻¹. It can be shown that including both particle size distribution and finite conductivities of the electrolyte phase as well as the solid metal hydride phase is essential for the interpretation of the impedance spectra. A similar conclusion was reached in Ref. 3, but in this work, results for the lowest frequencies are not shown. At very high or very low DODs, a more sophisticated treatment of the surface reactions (i.e. including chemical reactions at the surface, like hydrogen evolution at low DODs) is required (2). The model offers the possibility to assess kinetic and material parameters under realistic operating conditions. Fig. 2 shows simulated impedance spectra for various average particle sizes. The width of the distribution, Ψ , is kept constant.

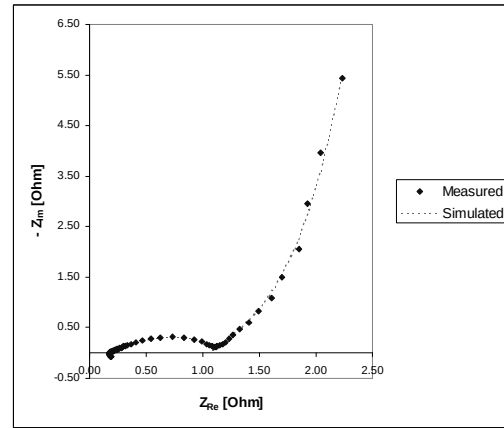


Fig. 1. Comparison of measured and simulated (least square fitting) results for an AB₅ electrode discharged to 50 % DOD.

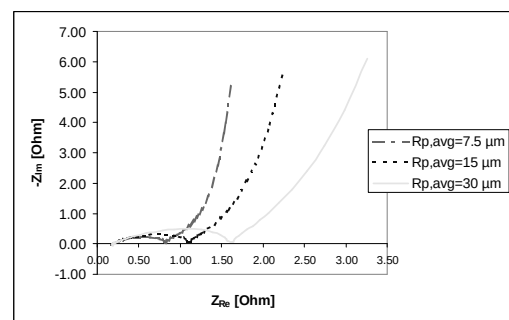


Fig. 2. Predicted impedance spectra for various average particle sizes.

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