On the kinetics of the electrochemical charging reaction of hydridable alloys

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New applications for Ni-MH batteries such as emergency lighting units and photovoltaic energy storage require the development of new materials for the negative electrode. Hydrogen absorbing alloys with increased specific capacity and enhanced life duration have been the subject of numerous studies [1]. The optimum alloy composition has to be a compromise between the capacity of the material, its corrosion resistance, its charge acceptance and its cost. It is thus necessary to study the mechanisms that limit the electrochemical kinetics during the charge reaction of the alloys, taking into account the influence of corrosion products that are formed with time. In this work, the electrochemical kinetics properties of Ni-MH negative electrodes were investigated with a cavity microelectrode (CME). This technique is a powerful tool in electroanalytical studies of powder materials due to a high mass transfer, a small ohmic drop and a negligible double layer capacitance. Moreover, it is possible to study the intrinsic properties of conductive powder materials without any adjunction of electronic conductor or binder [2].

Electrochemical measurements were carried out in a classical three-electrode cell. The working electrode was a cavity microelectrode, which consisted in a platinum wire of 50 µm diameter embedded in a glass capillary. A small cavity was performed by controlled electrodissolution of the Pt wire. The cavity was filled up with material particles using the electrode as a pestle. No electronic conductor was added to the material. The reference electrode was a Hg/HgO electrode and the counter electrode was a nickel wire. Both cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were used to characterize the cycle-life evolution and the processes involved in the hydrogen insertion reaction.

Figure 1 shows the general shape of voltammograms which were recorded with the CME at 50 mV s^{-1}. Reproductible voltammograms were obtained during cycling. An anodic peak is observed between -0.7 and -0.3 V/Hg/HgO. It is attributed to hydrogen desorption. The measurement of this peak area allows evaluating the exchange charge associated to the anodic current through the relationships:

$$Q = \frac{A}{v}$$

Where v is the scan rate. After 20 cycles, the exchange charge is constant indicating that the number of accessible sites in the material which are implicated in the electrochemical reactions is constant.

Figure 2 shows impedance diagrams obtained after 92 cycles at three different potentials. These diagrams show the porous behavior of the metal hydride electrode. Each EIS spectrum consisted of a small semicircle in the high-frequency region, which is ascribed to the contact resistance between the alloy and the current collector and between the alloys particles themselves. The flattened semicircle in the 10 kHz - 100 Hz frequency domain is ascribed to the charge transfer process whereas the linear domain with a phase angle close to 45° is characteristic of a Warburg's impedance corresponding to diffusion process in material grains [3]. Finally, a large semicircle in the low frequency region (1 - 0.01 Hz) is observed. It can also be seen that the HF and LF time constants are potential dependent. For more cathodic potential, the impedance presents a slower charge transfer process.

The deterioration behavior of metal hydride during the cycling was also studied using Raman spectrometry.

A specific attention will be paid in this presentation to the description of the kinetics through the analysis and the fitting of the impedance spectra, and to the description of the corrosion products.
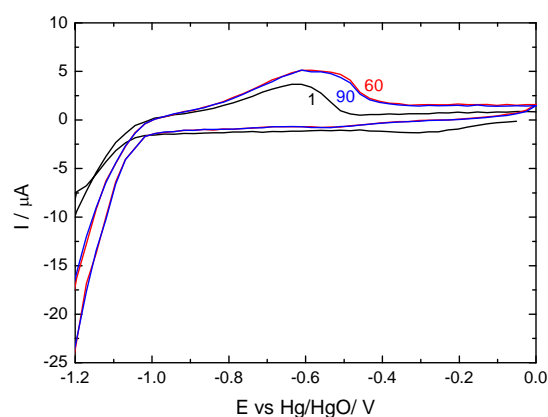

Figure 1. Evolution of the CV curves for different number of cycles recorded with a 50 µm in diameter CME at 50 mV s^{-1} in 7 M KOH solution. Each curve is labeled by its cycle number.
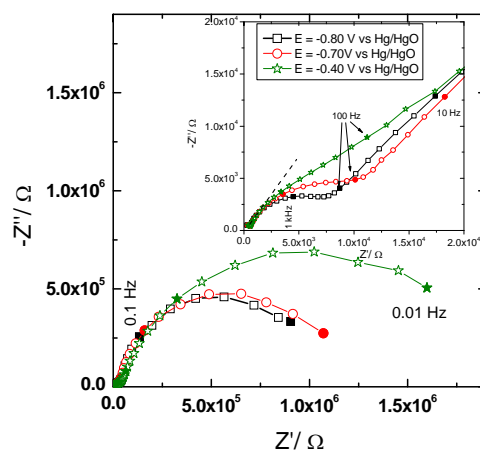

Figure 2. Electrochemical impedance spectra for the Ni-MH electrode at different potentials after 92 cycles.

References

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