



Electrochemical approaches used to evaluate the kinetic parameters of a multicomponent MH-electrode

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Abstract

In this paper we present a general panorama of views about the general considerations manifested in mathematical treatments, their basis, factors and general conclusions, permitting good electrochemical approaches between theoretical analysis correlated with experimental data. © 1999 International Association for Hydrogen Energy. Published by Elsevier Science Ltd. All rights reserved.

1. Introduction

Nickel/metal hydride batteries (MHB) offer a solution to the problems related with the production, use and disposal of nickel-cadmium batteries, principally, providing at the same time, similar levels of performance. MHB take their name due to the use of metal hydrides like negative electrodes, forming metal hydride electrodes (MHE). It is known that metal hydride alloys are less toxic materials than cadmium compounds, based mainly on nickel and transition metals like lanthanum [1].

In early days, the LaNi₅ alloy has been considered as a promising material for storing hydrogen electrochemically and one of the most important applications is in the MHB as MHE. Today, LaNi₅ and its derivatives (multicomponent metal-hydride alloys) are very popular in commercial metal hydride systems, these type of multicomponent materials with complex stoi-

chiometries and phase structures are being investigated and evaluated for commercial devices.

Kinetic processes that occur in the electrochemical absorption/desorption process of hydrogen, for some multicomponent metal-hydride material are not completely understood [2]. There are several electrochemical and thermodynamic treatments which focus on the determination of kinetic parameters and processes for the electrodesorption of hydrogen, principally using LaNi₅ or multicomponent hydriding alloys.

The study of kinetic processes occurring in a multicomponent metal-hydride alloy can be done in an electrochemical cell, supported on electrochemical models simulating the performance of a metal-hydride battery [3]. The models used to evaluate the kinetics of the absorption/desorption of hydrogen electrochemically in a MHE, involve some inter-related parameters such as the effect of particle size, porosity, polarization resistance of the electrode during desorption, electrolyte properties and conductivity. These models for the MHE have been presented in planar, cylindrical and spherical particle geometries, using porous electrode theory and strong electrolyte theory.

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2. Theoretical basis

The performance of a metal-hydride electrode is determined by the kinetics of the processes occurring at the metal–electrolyte interface and the hydrogen diffusion rate in the bulk of the alloy. Hydrogen diffusion rate can be affected by the surface-phase transfer reaction [4] limiting the mass transfer towards the bulk of the alloy. Electrochemical kinetic properties of an MHE such as the exchange current density, polarization resistance and symmetry factor are important variables, which help to characterize the performance of the electrode.

We expect that the double layer capacity, the exchange current density, and the equilibrium potential can be changed due to the hydrogen content in the multicomponent alloy. The following processes are considered to take place at the reduction reaction in a MHE [5].

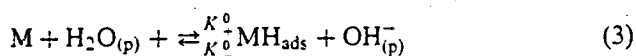
1. The interchange of water molecules from the bulk of the electrolyte (subscript b) to the electrode/electrolyte interface (subscript i) is given as:



2. The internal mass transfer of water molecules from the interface of electrode/electrolyte to the pores of the electrode (subscript p), must be:



3. Charge-transfer reaction occurring at the surface of each individual particle of the electrode, can be written as:



Where k_{-}^0 and k_{+}^0 are the reaction rate constants for the reduction and oxidation, respectively.

4. Interchange of OH^{-} in the system can be given as:



5. Hydrogen absorption process is related with the interchange between the hydrogen adsorption/absorption rate,



Previously considered points seem to be the basis for electrochemical approaches in the study of metal-hydride electrodes related to novel batteries. The hydrogen absorption process in a HME has been considered to take place in a multiphase system and based on Fick's law for the mass transport in an electrochemical solid/liquid medium.

3. General considerations

The principal problem related with the use of rare earth in nickel based electrodes, for example the case of LaNi_5 , is the degradation process presented in absorption/desorption cycles of hydrogen and its diffusion through the bulk of the alloy leading to an expansion of the lattice structure of the alloy and forming $\text{La}(\text{OH})_3$ by its contact with the electrolyte [6].

The treatment of hydrogen diffusion in the bulk of the alloy can help with the understanding of the principal processes affecting the performance in a MHE. It requires the solution of Fick's second diffusion equation for an appropriate case

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (6)$$

Fick's Law has been solved for thin plate electrode, cylindrical electrode and spherical electrode [7].

The hydrogen charging efficiency of an MHE under normal conditions without overcharge, can be high, even at high rates (0.5 C) [5]. When one observes a 100% charging efficiency of the MHE, it can be considered that the possibility of the hydrogen diffusion through the bulk of the alloy determines the complete process, and the hydrogen evolution reaction can be neglected.

The study of the hydrogen performance is related with the activity of H-atoms in the MHE by electrochemical or thermodynamic methods, this activity depends strongly on the concentration of hydrogen atoms present in the alloy, and they can be manifested in the C-P isotherm diagrams [8]. This treatment was given by Wicke and Brodowsky [9], defining a thermodynamic factor, associating the experimentally measured diffusion coefficient of hydrogen atoms in the metal, $D_{\text{H,measured}}(\theta_{\text{H}})$, with the diffusion coefficient of H-atoms, (D_{H}), and a thermodynamic factor, $g(\theta_{\text{H}})$, in the form

$$D_{\text{H,measured}}(\theta_{\text{H}}) = D_{\text{H}}g(\theta_{\text{H}}) \quad (7)$$

The thermodynamic factors can be expressed in terms of the activity of the H atoms and the diffusion of H_2 gas in equilibrium with the metal, getting a thermodynamic treatment for the transport of hydrogen in a metal/metal hydride system [8].

Mathematical models for metal hydride electrodes and nickel/metal hydride batteries [1,7,10–15] have been established in recent years. They have tried the problem associated with the electrochemical absorption of hydrogen in the negative electrode or simply in the hydriding alloy considering planar, spherical and cylindrical systems, using porous electrode theory, and strong electrolytes.

Depending on specific cases, those models have

helped to consider many factors that affect the performance of the MHE in MHB like dynamic systems related to the hydrogen diffusion in the alloys and the charge transfer at their surfaces.

In general, the mathematical models cited before have shown important considerations of mechanisms and processes occurring at the MHE/electrolyte system, by electrochemical reaction of hydrogen. Those models correlate experimental data with the theoretical electrode discharge model. Their results reveal some aspects for consideration, like exchange current density and equilibrium potential, which are functions of the electrode state of charge [14].

The use of porous electrode theory has found the importance of various factors like polarization resistance and symmetry factor [5] for evaluating the performance of MHE in alkaline solution. Internal mass transfer and internal ohmic drop of the electrode are factors that can be considered.

Particle size of the alloy and the hydrogen diffusion coefficient are considered as determining factors that affect the performance of the electrodes made with metal hydride particles when thermodynamic treatment is used [14].

The above discussion indicates the importance of considering a lot of factors that can affect the role of hydrogen absorption and diffusion through the MHE, and how they can contribute to the performance of a MHB, using a MHE like negative electrode.

4. Conclusion

The models referred to in this work have indicated, in general, that the performance of the MHE is controlled principally by the rate of hydrogen diffusion within the bulk and the particle size of the electrode. There are some factors that are being introduced into the models for more knowledge.

The exchange current density and the equilibrium potential have been presented as dynamic parameters

dependent of the state of charge of the electrode. The study of these parameters have permitted the partial understanding of the electrochemical processes occurring at the MHE, but it is important to continue studying phenomenologically the negative electrode of metal-hydride batteries.

Acknowledgements

The financial support for this work came through the project CONACYT 25519 A.

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