Journal of Energy Storage 27 (2020) 101067

Contents lists available at ScienceDirect

Journal of Energy Storage

journal homepage: www.elsevier.com/locate/est

EIS study on metal hydride electrodes using a porous model: Fitting methodology and SOC effects.

Marcos Martínez[a], Erika Teliz[b], Carlos F. Zinola[b], Verónica Díaz[a,*]

[a] University of the Republic, School of Engineering, Chemical Engineering Institute, Electrochemical Engineering Interdisciplinary Group, J.Herrera y Reissig 565, CP 11300, Montevideo, Uruguay

[b] University of the Republic, School of Science, Fundamental Electrochemistry Lab, Electrochemical Engineering Interdisciplinary Group, Igua 4225, CP 11400, Montevideo, Uruguay

ARTICLE INFO

Keywords:
EIS
Hydrides
Batteries
Electrochemical energy storage

ABSTRACT

In order to understand and improve the performance of Metal Hydride (MH) materials for Ni-MH battery's applications, Electrochemical Impedance Spectroscopy is used to provide interfacial information. However, it still offers significant challenges regarding methodology practices and results' interpretation due to the multiple interpretations arising from equivalent circuit fittings. The use of physicochemical models expresses in a better way the functionalities of charge/discharge mechanisms in MH. Moreover, for the impedance of MH porous electrodes there is little information from previous models, so the physical meaning of parametric figures and time constants is here emphasized. A complete fitting methodology is detailed and implemented *via* a specifically designed *Octave* program. An AB_2 alloy of $Zr_{0.3}Ti_{0.7}Cr_{0.7}Mo_{0.3}Ni$ composition is used to construct a porous electrode. Impedance spectra of the activated electrode are recorded and standard deviations of data are experimentally estimated. Validity of both the model and the methodology are thoroughly assessed. Changes in the system response when varying its state of charge are fully analyzed.

1. Introduction

It is well known that in our modern societies the worldwide energy consumption keeps a clear growing tendency [1,2]. On top of that, fossil fuels from finite sources exhibit negative impacts on the environment; so many alternatives to those feedings are being examined. In this context, research and development in both generation and storage of renewable energy acquires the highest importance [3–8]. In light of this situation, investigation on metal hydrides (alloys capable of store hydrogen and form a metal hydride phase) is of great relevance [9–16]. These materials are studied to use them in nickel-metal hydrides (Ni-MH) batteries (electrochemical hydrogen storage) and for gas phase hydrogen storage. It is worthwhile noticing that other more innovative applications are also being considered [17,18].

Ni-MH batteries became a consolidated technology for diverse mobile applications or low power consumption devices [19–21], showing interesting characteristics regarding technical requirements, costs and environmental impacts. Besides that, MH constitutes one of the safest choices for storing gaseous hydrogen [22–25]. However, with the aim of spreading this technology out to other applications with higher performances, continuous research for materials with better mechanical and electrochemical properties is mandatory.

Electrochemical Impedance Spectroscopy (EIS) is an electrochemical technique which provides valuable information about interfacial properties of dynamic systems, such as in MH electrodes. EIS has already been used to study this type of electrodes through the application and development of different models and methodologies [26–30].

The basis of EIS is to measure the response of a system when it is perturbed with a low amplitude sinusoidal potential signal (potentiostatic EIS) or current (galvanostatic EIS) with continue change in the frequency in order to obtain an impedance spectrum. One of its biggest advantages is that it provides qualitative and quantitative information regarding pathway's contributions to the involved mechanism. However, it still offers various experimental and methodological challenges, many of them regarding interpretation of the results. When the technique is not used in the best way, there is a loss on quality and quantity of the obtained information. If it is not well understood, it can easily lead to misinterpretation of the results [31,32].

This work is related –continuing the line of research of our Group– to the study of the composition and electrochemical properties of Zr-based alloys (AB_2 metal hydrides) in order to understand their behavior

---

* Corresponding author.
E-mail address: verodiaz@fing.edu.uy (V. Díaz).

https://doi.org/10.1016/j.est.2019.101067
Received 18 September 2019; Received in revised form 6 November 2019; Accepted 6 November 2019

and then, to improve their electrochemical energy storage performance [12–16]. With the aim of improving the quality of the analysis of EIS results, it was sought to conduct a new work methodology including a formal support without losing physical meanings. In this respect, EIS data are able to be compared with results obtained from other studies on the same alloys.

Besides consolidating the work methodology, it was decided to develop a model which takes into account the porosity of the electrode. One of the aims was to study the frequency range where porous effects are negligible, and other zones where they are imperative. While many models already exist that describe porous intercalation electrodes [33–35] (and the developed model is based on them), it was considered as obligatory to advance a model that clearly enables to fit the data with simple, intuitive and physically meaningful parameters.

A fitting program was created using *Octave* programming language in order to test the different choices in fitting methodology and to customize the used model in a well understood manner. The adequacy of the selected model and fitting choices could be assessed.

Changes in the system response when varying the electrode *State Of Charge* (SOC) are also studied, since it was found that this parameter was relevant to EIS results.

In order to focus the attention into this methodology and modeling, it was decided to narrow the study to a single alloy, ($Zr_{0.3}Ti_{0.7}Cr_{0.7}Mo_{0.3}Ni$, named ``Ti7″) which was characterized in previous studies with useful kinetic properties for electrochemical hydrogen storage [16].

2. Experimental Section

2.1. Experimental Design

A $Zr_{0.3}Ti_{0.7}Cr_{0.7}Mo_{0.3}Ni$ (called Ti7) alloy was synthesized by arc melting under high purity argon from pure metallic ingots of each component. The resulting alloy ``button'' was re-melted twice to ensure the sample homogeneity and it was mechanically pulverized and sieved for the electrode formation. The latter was prepared by mixing and compacting 100 mg of sample powders –with an initial particle size of 63–125 µm– with equal amounts of powder teflonized carbon (Vulcan XC-72). The mixture was pressed under 250-MPa at room temperature and a nickel wire was used as current collector.

The electrochemical single compartment cell was mounted placing the working electrode (metal hydride electrode), counter electrode (nickel mesh) and reference electrode (Hg/HgO electrodes). All the experiments were carried out at room temperature and all potentials referred to the Hg/HgO electrode. The electrolyte, 6 M KOH solution, was prepared from reagent-grade potassium hydroxide and Millipore^{R} MilliQ Plus water.

The electrode was cycled by a charge–discharge process at constant density currents of 80 mA g^{-1} and 26 mA g^{-1}, respectively, with a charge time of 5 h and cut-off potential of −0.60 V during discharge. Potentiostatic EIS measurements were performed once the alloy had reached its maximum capacity after the activation.

Prior to each EIS experiment, the electrode was completely charged and partially discharged, until reaching the desired SOC, then left at open circuit potential (E_{OCP}) during 90 min in order to minimize the system drift. EIS spectra were recorded, at E_{OCP}, in the 5.00E+04 – 1.00E-04 Hz frequency range, with a 5 mV amplitude, ten points per decade. After this, the electrode was completely discharged (until reaching a cut-off potential of −0.60 V) and the SOC was recalculated, considering both discharge times (after and before recording the EIS spectrum) and discharge capacity of the electrode. EIS spectra were recorded at SOCs (recalculated) of 92%, 77%, 73%, 62%, 57%, 46% and 30%.

Multiple consecutive impedance spectra ($n = 6$) of the same electrode were recorded at SOC = 73%, with the objective of determining the standard deviation behavior for a given state of the system, especially its frequency dependence.

Electrode activation was performed in a four-channel cycler device. Potentiostatic EIS measurements were performed using a Gamry Interface 1000™ Potentiostat/Galvanostat.

2.2. Physicochemical model

A physicochemical model of the porous electrode is proposed here to obtain the equations describing the impedance of the system.

Metal hydride electrodes store energy through the electrochemical adsorption and subsequent absorption of hydrogen into metallic particles. The charging process on the alloy begins with hydrogen adsorption on the metal surface (Volmer reaction). In alkaline medium, it can be depicted as follows:

$$\mathrm{H}_2O + \mathrm{e}^- + \mathrm{M}_s \rightleftharpoons MH_{ads} + OH^- \tag{1}$$

where M_s is a free adsorption site at the surface. Under certain conditions, adsorbed hydrogen may give rise to Hydrogen Evolution Reaction (HER), following either Heyrovsky or Tafel mechanisms;

$$MH_{ads} + H_2O + \mathrm{e}^- \rightleftharpoons H_2 + \mathrm{M}_s + OH^- \tag{2}$$

$$2MH_{ads} \rightleftharpoons 2\mathrm{M}_s + H_2 \tag{3}$$

In the charged or discharged alloy, adsorbed hydrogen has to follow absorption and diffusion steps:

$$MH_{ads} + \mathrm{M}_{ss} \rightleftharpoons \mathrm{M}_s + MH_{abs,R_0} \tag{4}$$

$$MH_{abs,R_0} \rightleftharpoons MH_{abs,r} \tag{5}$$

where M_{ss} is a free interstitial subsurface site, $MH_{abs,R0}$ is an absorbed hydrogen atom in $r = R_0$ (surface of the alloy particle), and $MH_{abs,r}$ is an absorbed hydrogen atom in $r < R_0$ (bulk of the particle).

Inside the bulk of the particle, nucleation and growth of one or various hydride phases are known to happen. Alloys to be studied with this model are complex multiphasic alloys, but in order to simplify the approach, the bulk of the particle is assumed to be composed of a single phase with a given hydrogen saturation concentration $C_{H,max}$ and a fixed apparent diffusion coefficient D_H.

The electrode under study consists of alloy powder particles, mixed and compacted with a conductive carbon powder. As a result, a porous conductive matrix is formed, in which the solution remains in intimate contact with alloy particles.

To account for the porous nature of the electrode we introduce volumetric expressions for impedances (Ω cm^3). The volumetric interfacial impedance Z_i can be expressed by the following equation:

$$Z_i^{-1} = Z_{dl}^{-1} + Z_F^{-1} \tag{6}$$

where Z_{dl} is the volumetric impedance of the double-layer and Z_F is the volumetric faradaic impedance. Both of these elements arise from surface processes. Consequently, parameters that relate area to volume ratios (cm^2/cm^3) must be considered.

2.2.1. Faradaic impedance

Faradaic impedance is related to the electron transference occurring at the surface of metallic particles. The faradaic impedance per unit of interfacial active area Z_f (Ω cm^2) follows the following relation (demonstrated and detailed in references [30] and [32]):

$$Z_f = R_{ct} + \frac{1}{j\omega C_p + \frac{1}{R_{ev}} + \frac{1}{R_{ab} + Z_w}} \tag{7}$$

where R_{ct} is the charge transfer resistance (related to the Volmer step), C_p is the adsorption pseudocapacitance (related to the surface capability of storing adsorbed hydrogen), R_{ev} is a HER resistance (related to the Heyrovsky step), R_{ab} is an absorption resistance and Z_w is the Warburg impedance (related to the hydrogen diffusion inside the alloy). Fig. 1 depicts the equivalent circuit for the faradaic impedance

Under certain conditions, this equation can be simplified: