



Electrochemical characteristics of AB₅-type hydrogen storage alloys

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ABSTRACT

The kinetic behaviour of the LaNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.4}Fe_{0.35} metal hydride, used as a negative electrode in the nickel/metal-hydride (Ni/MH) batteries, was investigated using electrochemical impedance spectroscopy (EIS) at different state of charge (SOC). Impedance measurements were performed in the frequency range from 50 kHz to 1 mHz. Electrochemical impedance spectrum of the metal hydride electrode was interpreted by an equivalent circuit including the different electrochemical processes taking place on the interface between the MH electrode and the electrolyte. Electrochemical kinetic parameters such as the charge-transfer resistance R_{tc} , the exchange current density I_0 and the hydrogen diffusion coefficient D_H were determined at different state of charge. The results of EIS measurements indicate that the electrochemical reaction activity of the LaNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.4}Fe_{0.35} metal hydride electrode was markedly improved with increasing state of charge (SOC). The transformation α - β is probably a limiting step in the mechanisms of hydrogenation of metal hydride electrode.

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1. Introduction

Recently, nickel–metal hydride (Ni–MH) batteries have been developed and commercialized because of their higher energy density, high rate dischargeability, long cycle life, no memory effect and environment cleanness compared with nickel–cadmium (Ni–Cd) batteries. AB₅ hydrogen storage alloys have now been widely used as negative electrode (anode) materials for Ni–MH rechargeable batteries. Much research has been performed in order to improve the overall properties of the AB₅ alloys and to develop new types of alloy electrodes, used as the negative electrode materials of the Ni/MH battery [1–11]. The performance of these electrodes is determined by both the kinetics of the processes occurring at the metal/solution interface and the rate of hydrogen diffusion within the bulk of the metal alloy particles. Different electrochemical methods have been used to study the kinetics process in the hydrogen storage alloys [12–15]. Electrochemical impedance spectroscopy (EIS) is a powerful analysis technique, which can provide a wealth of information on the corrosion reactions, the mass transport and the electrical charge transfer characteristics of the electrode/solution interface.

In this paper, the electrochemical impedance characteristics of the LaNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.4}Fe_{0.35} metal hydride electrode with different state of charge are extensively investigated. The relationship between the parameters of the equivalent circuit elements and the state of charge is discussed.

2. Experimental

The intermetallic compound LaNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.4}Fe_{0.35} was prepared, by the induction melting of the pure elements followed by an appropriate annealing to ensure a good homogeneity, as reported in Ref. [16]. The LaNi_{3.55}Mn_{0.4}Al_{0.3}Co_{0.4}Fe_{0.35} obtained alloy was first ground and sieved (to less than 63 μ m) in a glove box under an argon atmosphere. The so-called “latex” technology has been used for the electrode preparation [17]. Ninety percent of this powder has been mixed with 5% of the polytetrafluorethylene (PTFE) and 5% of the carbon black. The mixture (~0.06 g) was compressed on the two faces of a nickel grid ($S=0.5$ cm²), playing the role of a current collector. The thickness of this electrode is 0.5 mm. The electrochemical measurements were performed at a room temperature in a three-electrode open cell using a Voltalab 40 system (Radiometer Analytical) constituted by a Potentiostat–Galvanostat PGZ301. The MH electrode used as the working electrode, a wire of gold and a Hg/HgO electrode were used as the counter electrode and reference electrode, respectively. The electrolyte consisted of a 7 M KOH solution in which a continuous flow of Ar is kept through the cell.

Electrochemical impedance spectroscopy (EIS) studies were conducted at different state of charge (SOC). Before EIS measurements, the electrode was first completely activated by charging/discharging for 25 cycles. The EIS spectra of the electrode were measured in the frequency range from 50 kHz to 5 mHz with an ac amplitude perturbation of 5 mV under the open-circuit conditions. The EIS measurements were performed only after the open-circuit potential (i.e. equilibrium potential) was stabilized (i.e. a variation in the potential was less than 1 mV for a period of 1 h). EIS spectra were fitted to equivalent circuit using the software ZSimpWin 3.1.

3. Results and discussion

The electrochemical reactions taking place at the electrode/electrolyte interface inside each electrode during charging and discharging can be represented as follows:



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where M is the hydrogen storage alloy, H_{ads} the adsorbed hydrogen on the surface of the alloy, H_{abs} the absorbed hydrogen in the bulk, and H_{hyd} is the metal hydride [18,19]. Reaction (1) reflects the charge-transfer process at the interface between the MH alloy powder and the electrolyte, Reaction (2) is transfer from adsorbed to absorbed state and Reaction (3) represents the diffusion of hydrogen from the surface to the bulk. The performance of the negative electrode is mainly controlled by the kinetics of the hydrogen diffusion process and/or the reactions taking place on the alloy surface. Electrochemical impedance spectroscopy (EIS) is a powerful tool in such a context as it allows to get an understanding of the different processes if their time constants are well separated.

Fig. 1 shows the equilibrium potential of the $\text{LaNi}_{3.55}\text{Mn}_{0.4}\text{Al}_{0.3}\text{Co}_{0.4}\text{Fe}_{0.35}$ metal hydride alloy electrode at different state of charge. Two regions could be distinguished on this figure. It can be seen when the state of charge of the electrode is less than 40%, the equilibrium potential depends strongly on the hydrogen content. This region corresponds to the single-phase solid solution, called α -phase. Increasing the hydrogen content

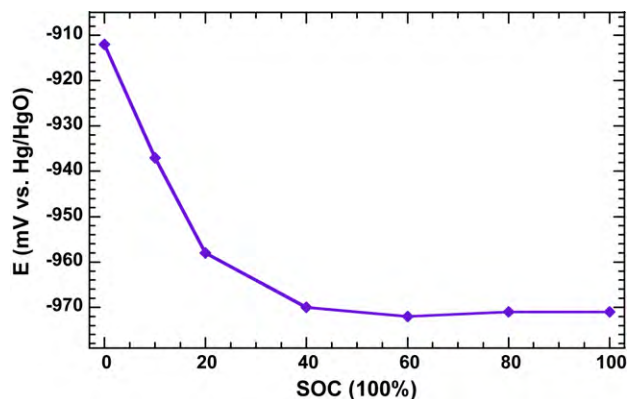


Fig. 1. The equilibrium potential of the $\text{LaNi}_{3.55}\text{Mn}_{0.4}\text{Al}_{0.3}\text{Co}_{0.4}\text{Fe}_{0.35}$ alloy electrode as a function of the state of charge.

in the electrode, the equilibrium potential reaches a plateau. This plateau region indicates the formation of β -phase (hydride phase) and at this region two phases (α and β) coexist.

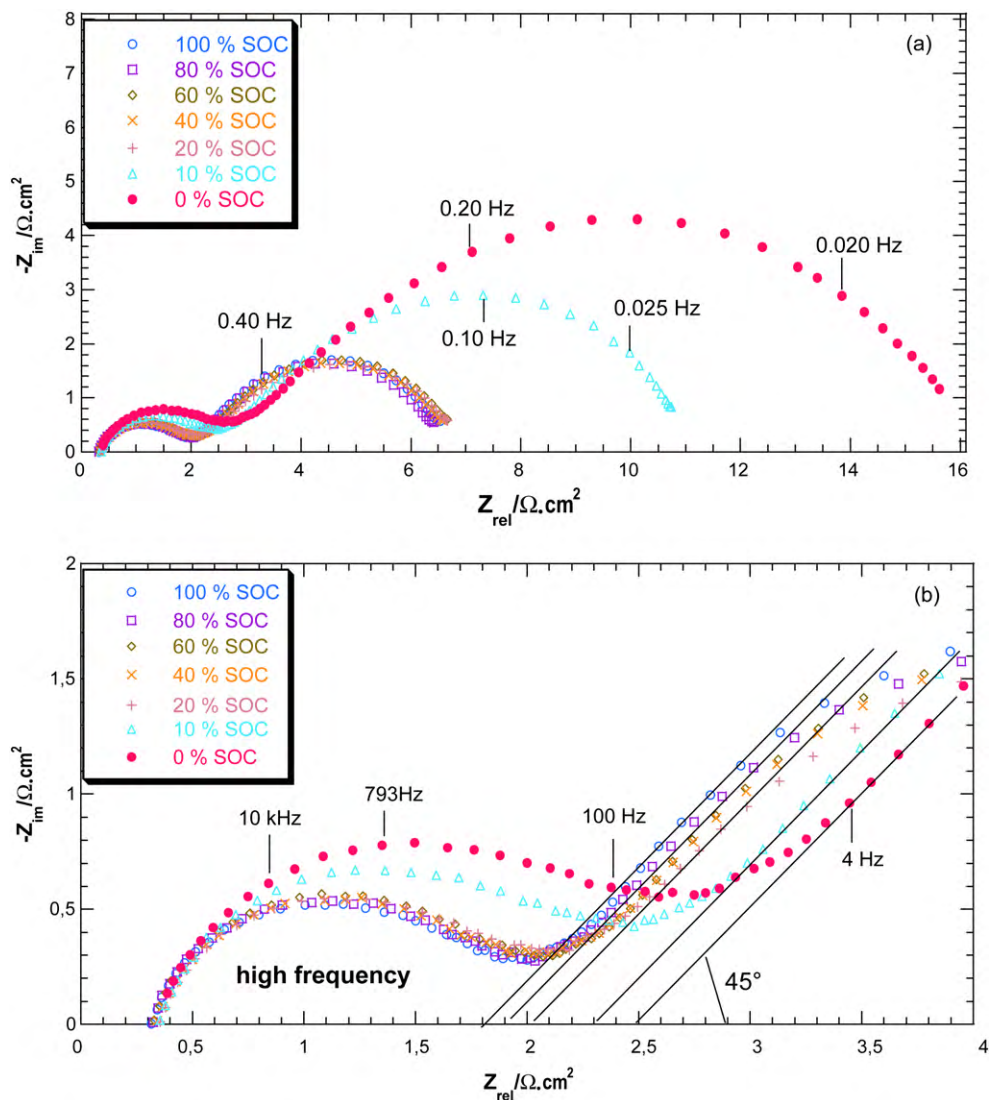


Fig. 2. (a) Nyquist plots of the $\text{LaNi}_{3.55}\text{Mn}_{0.4}\text{Al}_{0.3}\text{Co}_{0.4}\text{Fe}_{0.35}$ electrode at different state of charge. (b) Enlarged view of the smaller semicircle in the high-frequency region for the $\text{LaNi}_{3.55}\text{Mn}_{0.4}\text{Al}_{0.3}\text{Co}_{0.4}\text{Fe}_{0.35}$ metal hydride electrode at different state of charge.

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