Hydrogen diffusion in AB5 type metal hydride anodes by potentiostatic intermittent titration technique

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Abstract. Metal hydrides are widely used for hydrogen-related energy storage applications due to their high volumetric capacity, safety, and selectivity to absorb hydrogen. One of the main applications of metal hydrides is their use as electrode material in Ni-MH batteries. Metal hydride electrodes provide high energy density, high rate capability, tolerance to overcharge and over-discharge, and no electrolyte consumption during the charge/discharge cycle. One of the key factors of metal hydride electrode performance is a hydrogen diffusion from the electrolyte to the bulk of metal hydride material. In the present study, effective hydrogen diffusion coefficients in AB5 type metal hydride electrodes during the charging process are investigated employing potentiostatic intermittent titration technique.

1. Introduction
Metal hydrides (MH) are widely used for hydrogen-related energy storage applications due to their high volumetric capacity, safety, and selectivity to absorb hydrogen. A wide class of materials recognized as metal hydrides include elemental metals, intermetallic compounds, alloys, and solid solutions, which are available to reversible hydrogen absorption onto their crystal structure. Intermetallic compounds with general formula A,B propose enhanced hydrogen sorption properties at near ambient conditions. Generally, they consist of two types of metals: hydride-forming metal in A-site (La, Ce, Ti, Zr, Mg, etc.) and hydride non-forming metal in B-site (transition metals, Al, Sn, Zn, Cu, etc.) [1].

One of the most popular applications of metal hydrides is their use as anode material in commercialized Ni-MH batteries [2]. At that, MH electrodes provide high energy density, high rate capability, tolerance to overcharge and over-discharge, and no electrolyte consumption during the charge/discharge cycle. Currently, LaNi5-based AB5 type compounds as anode material are used in commercial Ni-MH batteries [3]. They have good surface catalytic activity, easy activation performance, and cycle stability; however, their capacity is restricted to 300 – 320 mAh/g because of their crystal structure. From the point of maximum electrochemical capacity, AB5 based Laves type alloys [4] and newly developed Rare Earth-Mg-Ni alloys (AB3 – AB4 type) [5, 6] look better; unfortunately, low cycle stability reduces widespread use of such materials. In terms of overall metal hydride electrochemical performance, AB5 type alloys still stay the most effective material. Partial substitution [7-9], annealing and surface modification [10-12] can significantly improve their electrochemical properties.
The hydrogen absorption/desorption reactions in alkaline aqueous solutions for metal hydrides involve the following steps: charge transfer step, adsorption, and absorption of electroactive species and mass transfer from the surface to the bulk of metal hydride. In parallel to the hydrogen diffusion reaction, recombination processes described by the Tafel and the Heyrovski reactions are also occurred on the metal hydride surface [13, 14].

The above-mentioned reactions show a complex combination of different processes on the metal hydride electrode during the electrochemical reaction. Thus, the estimation of hydrogen diffusion by traditional non-steady state methods is quite difficult. However, diffusion kinetics affect greatly the electrode’s rate capability and accurate determination of diffusion constants are of great interest from both practical viewpoint and understanding of the mechanisms of insertion processes. In comparison with traditional techniques used to estimate hydrogen diffusion in metal hydride electrodes, such as constant potential step methods [10, 15, 16], and electrochemical impedance spectroscopy [14, 17, 18], potentiostatic intermittent titration technique (PITT) has two major advantages: (i) applying of small potential steps makes it possible to linearize the electrochemical system responses to the potential perturbation, and (ii) the potential dependence of the diffusion coefficients of intercalated species can be evaluated continuously in the entire potential domain of interest [19].

The present study is aimed to investigate activation performance and hydrogen diffusion kinetics during the charge process of metal hydride electrodes based on AB\textsubscript{5} type alloys in an alkaline electrolyte solution.

2. Experimental details

Three AB\textsubscript{5} type alloys based on La\textsubscript{0.8}Ce\textsubscript{0.2}Ni\textsubscript{2}Co\textsubscript{0.4}Mn\textsubscript{0.6}Al\textsubscript{0.3} composition with the partial replacement of La by Nd, Ni, and Co by Al, Cr with a mass approximately 50 g were prepared by arc melting on a water-cooled copper crucible under argon atmosphere and remelted three times to improve their homogeneity. The purity of each element constituent was not less than 99.5%. To compensate for the partial evaporation at high melting temperatures, 2 wt.% of the excess of Mn, Al was added to the mixture of the components prepared for the arc melting preparation as compared to the aimed stoichiometric composition. After the melting, the as-cast alloy ingots were crushed and sealed into stainless-steel tube sample holders filled with Ar and then transferred into an annealing furnace. These alloys were annealed at 1223 K for 20 h and then quenched into cold water resulting in their homogenization.

XRD patterns of the annealed alloys were obtained from X-ray diffractometry (Bruker’s D8 ADVANCE diffractometer). Samples for XRD analysis were prepared by mechanical grinding to a fine powder. The step size was 0.02° and the exposition time was 1 s. The 20 angles scanned were within the range from 15 to 80. Crystal structure and phase composition were performed using Jana2006 and Crystal Impact Match software using JCPDS PDF-2 Data Base.

MH powders with a particle size of 40 – 60 µm were formed in pellet type electrode, consisting of 20wt.% of MH powder and 80 wt.% of carbonyl Ni and having a total mass of 0.5 g. The mean particle size of MH powder is assumed to be 50 µm. The pellet electrodes with a diameter of 10 mm and a thickness of about 1 mm were fabricated by cold-pressing under a pressure of 25 MPa for 3 min. Then fabricated pellet was pressed between two Ni foam plates connected to the current collector.

Electrochemical activation performance and hydrogen diffusion into MH electrode were studied in an open three-electrode cell with a 6 M aqueous KOH electrolyte solution at room temperature. Sintered Ni(OH)\textsubscript{2}/NiOOH plate was used as a counter electrode and Hg/HgO electrode was used as a reference electrode, respectively. The experiments were performed using a multichannel potentiostat P-20X8 from ElectroChemical Instruments. MH electrodes were activated for 10 cycles by fully charging them at a current density of 100 mA/g for 4.5 h and then discharged at 100 mA/g to the cut-off voltage of 0.6 V. After the activation, hydrogen diffusion was measured by PITT. The method of potentiostatic intermittent titration consisted in sequentially applying a step of the potential ∆E -20 mV within the range from -0.84 to -0.98 V, followed by fixing the current change in time until the minimum current value was reached at each step.
3. Results and discussion

3.1. Structural characterization
All investigated alloys had sharp well-defined peaks on XRD patterns. The alloys were single-phase and no impurity phases were detected. The refinement of obtained crystallographic data showed small changes in unit cell parameters. Partial Nd substitution in A-site slightly decreases unit cell parameters and volume, while additional Cr substitution in B-site increases crystal lattice.

3.2. Electrochemical activation performance
Metal hydride electrode activation performance of parent AB$_5$ type alloy with composition La$_{0.8}$Ce$_{0.2}$Ni$_4$Co$_{0.4}$Mn$_{0.3}$Al$_{0.3}$ is shown in Figure 1. The other two alloys demonstrate similar behavior. It is noted that the alloys are easily activated within 2-3 cycles, indicating good activation performance of the prepared alloys. Charge – discharge potential reaches its equilibrium at 6-7$^{th}$ cycle.

![Figure 1. Activation charge-discharge performance of parent La$_{0.8}$Ce$_{0.2}$Ni$_4$Co$_{0.4}$Mn$_{0.3}$Al$_{0.3}$ metal hydride electrode.](image)

![Figure 2. Maximum discharge capacity and activation performance of AB$_5$ metal hydride electrodes.](image)
During activation, potential hysteresis between charge and discharge significantly decreased to a value within a range of 0.03 – 0.06 V to the 10th cycle. Nearly at a potential of 0.91 V, β-hydride phase formation starts. The coexistence of α-solid solution and β-hydride phase is observed in the potential range of 0.91 – 0.94 V. Maximum charge capacity is reached at a potential of 0.98 V and equals approximately 375 mAh/g, which corresponds to a maximum theoretical capacity for AB5 type alloys [20]. At potentials higher than 0.98 V, overcharge occurs. The maximum discharge capacity reaches 290 – 320 mAh/g at a current density of 100 mA/g (Figure 2).

A small reduction of equilibrium potential for Cr-substituted alloy was observed. It is known that the discharge potential of the alloy electrode is associated with the surface activity, the electrolyte concentration, and the internal resistance of the alloy electrode [21]. Ni is an excellent catalyst due to the formation of metallic clusters during activation, thus, the reduction of Ni in alloy composition could result in a decrease of the surface catalytic ability. It appears that the substitution of Cr in the alloy deteriorates the surface activity of the electrode and thereby results in a lower value of the discharge potential. Besides, Cr substitution slightly reduces activation performance and maximum discharge capacity.

3.3. Hydrogen diffusion properties
Current transients at low amplitude (20mV) were measured within the potential range from -0.84 to 0.98 V (Figure 3). Each potential was applied until the constant current was achieved.

![Figure 3. Time dependence of currents as related to applied potentials for La0.8Ce0.2Ni4Co0.4Mn0.3Al0.3 metal hydride electrode.](image)

Experimental curves plotted \( I^{1/2} vs \log t \) coordinates are time-invariant and should provide a horizontal section at short time domains, which corresponds to a typical Cottrellian behavior of diffusion [22].

To calculate the effective hydrogen diffusion coefficient, we used a modified Cottrellian equation (1) [4, 23]:

\[
\frac{1}{I^{1/2}} = \frac{R_S}{\Delta Q \sqrt{t}} + \frac{I^{1/2}}{\Delta Q \sqrt{D}}
\]

where \( R_S \) is the sum of all non-diffusion resistances, \( \Delta Q \) is the integral capacity of the electrode at given potential, \( D \) is the diffusion coefficient, \( l \) is the diffusion path length.

The linear dependence of experimental data on \( I^{1/2} vs 1/\sqrt{t} \) plot makes it possible to calculate the hydrogen diffusion coefficient for each potential step using equation (1). As shown in Figure 2, there is a negligible charge capacity change at low potentials under 0.86 V, which corresponds to less than 1% of the total charge. On the other hand, potential step 0.98 V relates to the overcharge process. To the
accurate calculation of the hydrogen diffusion coefficient, we excluded the first and last potential steps from fitting analysis.

Hydrogen diffusion coefficients calculated from plots corresponding to equation (1) are shown in Figure 4.

![Figure 4. Effective hydrogen diffusion coefficients vs state of charge for AB₅ type metal hydride electrodes](image)

Highest hydrogen diffusion coefficient values equal approximately to $10^{-9}$ cm$^2$/s were obtained at minimum studied state of charge 2-4% and belong to α-solid solution formation in metal hydride electrodes. As the state of charge increases, hydrogen diffusion coefficients become lower decreasing to $2.4 - 6.9 \times 10^{-13}$ cm$^2$/s, because of saturation of β-hydride phase. Such behavior of hydrogen diffusion also noted for AB₃ [6, 23] and AB₂ [4] type metal hydride electrodes and assumed to be typical for hydride forming alloys [24]. Cr-substituted alloy with lower surface catalytic activity shows lower hydrogen diffusion kinetics through hydrogen sorption.

**Conclusions**

The AB₅ type alloys based on La₀.₈Ce₀.₂Ni₄Co₀.₄Mn₀.₃Al₀.₃ alloy were investigated in terms of activation performance, maximum discharge capacity, and effective hydrogen diffusion coefficient. All MH electrodes show high activation performance, fully activated within 2-3 cycles up to their maximum discharge capacities within the range of 290 - 320 mAh/g. The reduction of highly catalytic Ni for Cr substituted alloy decreases both activation performance and hydrogen diffusion kinetics. Hydrogen diffusion coefficients measured by PITT reach approximately $10^{-9}$ cm$^2$/s at α-solid solution formation, then drastically decrease during saturation of β-hydride phase.

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