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REVIEW PAPER

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STUDIES ON ELECTROCHEMICAL HYDROGEN STORAGE IN $MmNi_{5-x}M_x$ MULTICOMPONENT ALLOYS: A REVIEW

Ni-metal hydride (NMH) batteries, like Li-ion batteries, are considered as potential energy storage devices for portable applications. The most commonly used materials for the MH electrode so far are AB_2 (Mg-Ni) and AB_5 (La-Ni) type alloys. The Ni/MH battery as an electrochemical system is defined by its specific capacity, cycle lifetime, but principally by the exchange current density, equilibrium potential, dischargeability and self-discharge mechanisms. All of those electrochemical parameters permit that a specific electrochemical process takes place for absorbing/desorbing hydrogen in the bulk of the alloy. However, more research is in progress for improving the performance characteristics of the cell for a longer cycling lifetime, minimizing self-discharge and operation of the cell above 50 °C.

The movement towards serious consideration of H_2 fuel has been quite dramatic during the past years. While many individual scientists and national departments of energy have considered hydrogen fuel a worthwhile goal since the 1971 "energy crisis", we are now seeing strong interest from the industrial sector, in particular oil companies and automobile manufacturers. This trend seems to have at least three sources: 1) the commercial and technical successes of several new fuel-cell companies, 2) increasing movement towards efficient and clean vehicles, e.g., the Toyota Prius, and 3) a growing scientific and political realization that the long-suggested negative effects of greenhouse gases are likely real and pose very serious questions for our future.

Recently we have focused on storage R&D in new multicomponent alloys with the purpose of their application in Ni-Metal Hydride batteries. As discussed below, progress has been made in these two new areas. Alternatives to solid-state vehicular H_2 storage exist, such as high-pressure gas, cryogenic liquids and on-board reforming of conventional liquid hydrocarbon fuels. But well-known disadvantages can be cited for each. In view of recent progress with solid-state H_2 -storage in the form of conventional hydrides, it seems prudent that further R&D work in this area should be supported in the form of new electrochemical storage in multicomponent metal hydrides.

Metal Hydrides in Ni/MH batteries

Nickel/metal hydride batteries (MHB) offer a solution to the problems related to 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

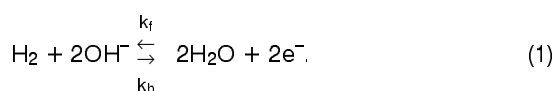
as negative electrodes. It is known that metal hydride alloys, based mainly on nickel and transition materials such as lanthanum [1], are less toxic materials than cadmium compounds.

In early years, the alloy $LaNi_5$ was considered as a promising material for use in electrochemical hydrogen storage systems. Another most important application is in the MHB as MHE. $LaNi_5$ and its derivative materials (multicomponent metal-hydride alloys) are very popular in commercial metal hydride systems. These types of multicomponent materials with complex stoichiometries and phase structures are being investigated and evaluated for commercial devices.

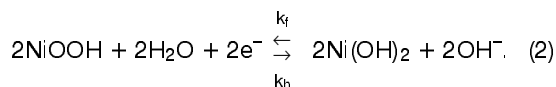
One of the most important problems to be solved for electrochemical hydrogen storage is the scarcity of negative electrode materials with suitable physico-chemical characteristics to be used in highly conducting alkaline electrolytes. Cadmium, iron and zinc are being considered as the most promising materials for this kind of devices. Each one of them has been investigated extensively in the last two decades, forming special cells in every case [2]. The experimental nickel-hydrogen battery is formed using nickel hydroxide as the positive electrode and a platinum-hydrogen negative electrode. This storage system was designed for space applications avoiding the use of Ni/Cd systems with less specific energy capacity. The good lifetime performance shown by the nickel-hydrogen battery for very high deep discharge is another reason to consider this kind of system involving hydrogen redox as promising energy storage devices.

The nickel-hydrogen (Ni/H_2) battery has been considered as one of the most efficient systems for energy storage. Its negative electrode, Pt/H_2 , is completely reversible for redox reactions and the voltage of the battery reaches around 1.25 V when a $Ni(OH)_2/NiOOH$ electrode is used as the positive electrode. The electrochemical reaction occurring at the negative electrode is:

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The reaction on the positive electrode is:



where, k_f and k_b represent the forward and backward reaction rates respectively. Ni/H₂ batteries can be overcharged and the product due to the oxygen evolution reaction is a recombination of the free gas in the negative electrode. This possibility permits the successful use of this battery in space applications.

The development of cheap nickel/metal hydride batteries allows their use in terrestrial applications. This kind of battery is very similar to Ni/H₂, but the use of novel absorbing alloys as the negative electrode with very high cycle lifetimes (charge/discharge), specific capacity and less La-Ni active absorbing alloy, ensures the possibility of decreasing the manufacturing cost of the cells. The performance of the nickel/metal hydride battery is based on the capacity of absorbing/desorbing hydrogen in metals using electrochemical methods. When this process occurs, the reversible transfer of one electron per hydrogen atom takes place via a first order charge transfer reaction. A La-Ni based hydrogen absorbing alloy is used as the negative electrode in a nickel/metal hydride battery. A standard nickel hydroxide electrode is used as the positive electrode. The use of aqueous or polymer (solid) alkaline electrolytes is being investigated for this kind of storage systems.

In the 1970s, the first work was reported using LaNi₅ as the negative electrode in an electrochemical cell. The possibility to store hydrogen in reversible form at room temperature and 1 bar pressure was proved. The absorption of hydrogen in LaNi₅ forms the alloy LaNi₅H₆ when the absorption is maximum. This alloy has a dissociation pressure of 0.98 bar at 15 °C. Actually, the interest for using new absorbing materials in commercial batteries is focused in two systems.

a) Multicomponent alloys based on a matrix of La-Ni with the substitution of La by the rare earth compound named *mischmetal*, associated with various transition metals to obtain a desired value of dissociation pressure and also with the possibility of protecting the active matrix forming a surface oxide, increasing the absorption/desorption cycle lifetime. This kind of multicomponent material corresponds to the AB₅ type alloy, where A is the *mischmetal* and B is a Ni based alloy [3-9].

b) Another complex system is the multicomponent alloy corresponding to the AB₂ type, where A can be Mg, Zr or Ti and B is Ni, V, Cr or Mn [10-18].

AB₂ alloys can store higher amounts of hydrogen than AB₅ alloys, showing better corrosion resistance

characteristics and are considered to be cheaper depending on the preparation technique. The electrokinetic characteristics of AB₅ and AB₂ type multicomponent hydrogen absorbing alloys are being considered for their use in commercial batteries. The Ni/MH battery as an electrochemical system is defined for its specific capacity, cycle lifetime, but principally for the exchange current density, equilibrium potential, dischargeability and self-discharge mechanisms. All of those electrochemical parameters permit that a specific electrochemical process take place for absorbing/desorbing hydrogen in the bulk of the alloy.

However, more research is in progress for improving the performance characteristics of the cell for longer cycling lifetime, minimizing self-discharge and operation of the cell above 50 °C.

The performance of a Ni/MH battery is very similar to that of the Ni/Cd system, about 1.2-1.3 V nominal voltage. It makes it possible to directly substitute Ni/Cd batteries by Ni/MH. The specific energy of Ni/MH batteries is almost 2 times higher than Cd based batteries. The state of the art of Ni/MH batteries indicates that this kind of system can be used under overcharge and overdischarge conditions for a long time, without modifying the performance of the battery.

Commercial rechargeable Ni/MH batteries are being designed as cylindrical and prismatic structures, for many sizes and capacities. Small batteries are used in portable electronic devices such as mobile phones, laptops, GPS, portable music systems, etc. Instead, 100 AH capacity prismatic batteries (12-14 V) are available for module uses, which can substitute Pb/acid batteries in traction systems of electric vehicles [19] or in solar-photovoltaic systems as non-breaking power systems in series, parallel or both configurations. The most modern technology in Ni/MH batteries is associated with the knowledge and improvement of the metal hydride negative electrode performance.

The dissociation pressure of hydrogen from a metal hydride needs to be between 0.1 and 1 atm at room temperature to guarantee the absorption of hydrogen instead of the hydrogen evolution reaction according to the electrokinetics of the alloy. In other words, it is also important to note that the hydrogen can be released completely from the bulk of the alloy and this easily happens at pressures lower than 1 atm. The quantity of hydrogen absorbed in multicomponent alloys by electrochemical methods describes the specific capacity of the negative electrode of the battery and the energy storage capacity of the system. The absorption of hydrogen is a function of the bonding potential between the atoms in the La-Ni matrix for AB₅ alloys [20]. The phenomenon of absorbing/desorbing hydrogen can be detected in the phase diagram [21]. The metal-H or alloy-H system can be considered as a binary or pseudobinary system in the phase rule.

The characteristics shown by practical hydrogen absorbing alloys, from a phase diagram study can be summarized as: 1) the quantity of absorbed hydrogen per unit weight of absorbing alloy must be as high as possible, 2) the absorption/desorption process must occur below 100 °C; 3) the absorption/desorption cycle must occur at below 10 atm for solid/gas systems and below 1 atm for solid/liquid systems, 4) the alloys must be quite inexpensive, 5) the heat of reaction and the reaction rate for the absorption/desorption process should be reasonable and 6) the materials used as metal hydrides must be stable under working conditions. Typical examples of hydrogen absorbing materials for practical use are the transition metal alloys such as Fe-Ti, V-Nb, Zr-Mn, Mg-Ni-Co and La-Ni systems. La-Ni systems show a CaCu₅ type structure. This structure has a hexagonal symmetry with the space group P6/*mmm*, and consists of alternate (Ca+Cu) planes (*z*=0) and only Cu planes (*z*=1/2) stacked along the *c*-axis. For the system LaNi₅H_x (*x* ≤ 6), the phase transition occurs from P6/*mmm* to P31*m* at a fixed composition of hydrogen [22–24]. Multicomponent hydrogen absorbing alloys related to the LaNi₅ system are thought to lead that phase transition.

The equilibrium potential of a metal hydride electrode in an electrochemical system corresponds to the desorption pressure of the same electrode. As we have discussed before, for an optimal hydrogen desorption pressure from 0.1 to 1 bar, the desorption pressure must be as high as the equilibrium potential on the negative electrode for absorbing large amounts of hydrogen. A typical value for a maximum content of hydrogen absorbed in a MmNi_{5-x}M_x alloy corresponds to about -0.932 V/Hg/HgO [25] just below the hydrogen evolution reaction above -1.0 V/Hg/HgO [26].

The kinetic processes that occur in the electrochemical absorption/desorption for some multicomponent metal-hydride materials are not completely understood [26]. There are several electrochemical and thermodynamic treatments focused on the determination of the kinetic parameters and processes for the electrodesorption of hydrogen, principally using LaNi₅ or multicomponent hydriding alloys.

The study of the kinetic processes occurring in a multicomponent metal-hydride electrode can be carried out in an electrochemical cell and explained by electrochemical models, simulating the performance of a metal-hydride battery [1, 27–29].

The models used to explain the kinetics of the electrochemical absorption/desorption of hydrogen in a MHE involve some interrelated 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 sizes, using porous electrode theory and strong electrolyte theory.

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. The hydrogen diffusion rate can be affected by the surface-phase transfer reaction [28] limiting the mass transfer towards the bulk of the alloy.

The electrochemical kinetic properties of a MHE such as the exchange current density, polarization resistance and symmetry factor are important parameters 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 during the reduction reaction in a MHE [29].

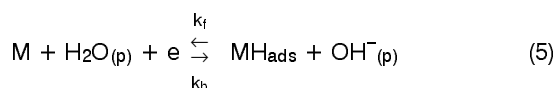
1. The interchange of water molecules from the bulk of the electrolyte (subscript *b*) to the electrode/electrolyte interface (subscript *i*) is given as



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

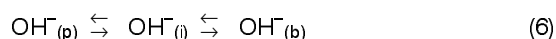


3. The charge-transfer reaction occurring at the surface of each individual particle of the electrode, can be written as

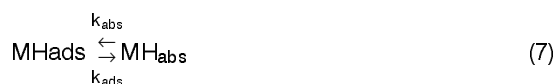


where *k_f* and *k_b* are the reaction rate constants for the reduction and oxidation, respectively.

4. The interchange of OH⁻ in the system can be given as



5. The hydrogen absorption process is related with the change between the hydrogen adsorption/absorption rate,



The previously considered points seem to be the basis for the electrochemical approaches in the study of metal-hydride electrodes related to novel batteries.

The hydrogen absorption process in a MHE has been considered to take place in a multiphase system

and is based on Ficks law for mass transport in an electrochemical solid/liquid medium.

General Considerations

The principal problem related with the use of rare earth elements in nickel based electrodes, in the case of LaNi₅ for example, is the degradation process presented in the 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 La(OH)₃ by its contact with the electrolyte [30].

The treatment of hydrogen diffusion in the bulk of the alloy can help the understanding of the principal processes affecting the performance in a MHE. It requires the solution of Ficks diffusion equation for the appropriate case

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (8)$$

Ficks law has been solved for a thin plate electrode, cylindrical electrode and spherical electrode [31].

The hydrogen charging efficiency of a MHE under normal conditions without overcharge, can be high, even at high rates (0.5 C). When 100% charging efficiency of the MHE is reached, it can be considered that 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 the H-atoms in the MHE by electrochemical or thermodynamic methods, this activity depends strongly on the concentration of hydrogen atoms present in the alloy, which can be manifested in the C-P isotherm diagrams [32]. This treatment was given by Wicke and Brodowsky (1978) [36], defining a thermodynamic factor, associating the experimentally measured diffusion coefficient of hydrogen atoms in the metal, $D_{H,measured}(\theta_H)$, with the diffusion coefficient of H-atoms, (D_H), and a thermodynamic factor, $g(\theta_H)$, in the form

$$D_{H,measured}(\theta_H) = D_H g(\theta_H) \quad (9)$$

The thermodynamic factor can be expressed in terms of the activity of the H atoms and the concentration of H₂ gas in equilibrium with the metal, obtaining a thermodynamic treatment for the transport of hydrogen in a metal/metal hydride system [32].

Mathematical models for metal hydride electrodes and nickel/metal hydride batteries [1,31,33-39] 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 the porous electrode theory and strong electrolytes. For specific cases, these models have helped to consider many factors that affect the performance of the MHE in MHB such as dynamic

systems related with 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 the electrochemical reaction of hydrogen. Those models correlate experimental data with the theoretical electrode discharge model. Their results reveal some aspects to consider such as the exchange current density and equilibrium potential being a function of the electrode state of charge [38].

The use of the porous electrode theory has found the importance of various factors such as the polarization resistance and symmetry factor [34] for solving the performance of MHE in alkaline solution. Internal mass transfer and internal ohmic drop of the electrode are factors that can be considered.

The 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 [38].

The above commented results show the importance of considering numerous 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 as a negative electrode.

The use of new hydrogen absorbing alloys as negative electrodes in rechargeable batteries has allowed the consideration of Ni/MH batteries performing as traditional batteries based on cadmium or lead materials [40-44]. Although Ni/MH batteries have more specific energy than the other two aqueous electrolyte systems (lead-acid and Cd/Ni batteries), they are less efficient than rechargeable lithium (Li-ion) batteries. However, lithium batteries are much more expensive to produce [45]. In addition, lithium batteries cannot be operated without electronic control of each individual cell.

The use of *mischmetal* (Mm = La, Ce, Pr, Nd) and transition metals (M) as components of the matrix $Mm_xLa_{1-x}(Ni,M)_5$ in hydrogen absorbing alloys has been extensively investigated [46-51]. As a result of these investigations, it can be noted that a *mischmetal* based predominantly on La (>50 wt%) and the substitution of nickel elements (M) such as Al, Co and Mn, greatly improve the intrinsic characteristics of the alloys for absorbing hydrogen electrochemically and the performance of the Ni/MH batteries. The cycle lifetime, high discharge capability, thermal stability and specific capacity characterize the performance of a rechargeable battery. The kinetic parameters involved in the exchange current density that permit the absorption/desorption of hydrogen in the electrochemical system, such as the polarization resistance and potentials are being investigated to understand the performance and

characteristics of the electrode/electrolyte interface between metal-hydride electrodes and very strong alkaline electrolytes (5 to 6M KOH) [52,53]. Cyclic voltammetry (CV) is a useful electrochemical technique to investigate electrode/electrolyte interfaces and superficial charge distribution under potentiodynamic conditions farther from equilibrium [26, 54-58].

MmNi_{5-x}M_x : Promising Hydrogen Absorbing Alloys for Battery Applications

For battery applications it is important to consider hydrogen absorbing alloys with good electrochemical properties. That has been found in multicomponent alloys based on MmNi_{5-x}M_x related to the AB₅ type, where their stoichiometry can be adjusted by controlling the preparation conditions. The final MmNi_{5-x}M_x hydrogen absorbing alloy can have a multiphase structure [59, 60]. In the multiphase AB₅ related alloy, there is a hydride solid phase involved and a second or third phase with catalytic or protective properties [61]. In practical terms, it is possible to consider the H₂ absorbing alloys as quasi-stoichiometric AB₅ materials for electrochemical characterizations, however, for thermodynamic investigations they are treated as non stoichiometric compounds [20].

Normally, MmNi_{5-x}M_x alloys are obtained by a combined procedure of melting and rapid cooling of a mixture of rare earth chemical elements and transition metals, to form ingots and powders of selected particle size by mechanical pulverization. The grain homogeneity of the obtained alloy must be quantified by spectroscopic methods such as EPMA and EDS. It is normal to use post-preparation treatments related with annealing processes to obtain more homogeneous particles that form the alloy powder [62]. The experimental conditions for annealing these kinds of alloys have been investigated extensively, obtaining structural improvement; however, it is possible not to obtain it, due to the physical properties of the alloy constituents [63, 64]. An optimal experimental technique used for preparing hydrogen absorbing alloys permits the obtaining of MmNi_{5-x}M_x materials showing good structural, morphological, electrochemical and thermodynamic quality. The problems associated with the experimental techniques used for some MmNi_{5-x}M_x related alloys have been technically discussed previously [65-67]. Rhodia Inc. has developed an experimental technique to prepare MmNi_{5-x}M_x related alloys with very good structural quality, purity and electrochemical properties and the alloys have been used to prepare MHE for battery applications [26, 68]. There have been many studies to improve the electrochemical characteristics such as cycle lifetime and dischargeability in MmNi_{5-x}M_x alloys when they are used as metal-hydride electrodes. The intrinsic

composition of the hydrogen absorbing alloys plays an important role in electrochemical responses [69].

One important advantage shown for MmNi_{5-x}M_x alloys is their high anti-corrosion capacity due to the use of the *mischmetal*, Co and Al principally. This capacity can be associated with the formation of an active surface oxide or hydroxide involving transition metals, and the other thing is the possibility to reduce lattice expansion in the hydride phase to lower than 25% [70].

The use of chemical elements such as Li, C, Mg, Al, Si, Ti, Cr, Mn, Co, Ni, Cu, Y, Nb, Mo, La, Pr, Ce, Nd, in MmNi_{5-x}M_x based electrodes, influences their electrochemical performance. The contribution of each element mentioned above to the final electrochemical response of a MHE, is still not completely understood. These elements, used in optimal proportions, can increase:

- The number of hydrogen atoms absorbed per unit cell of the alloy,
- The active surface area showing high electrocatalytic properties, and
- The corrosion resistance of the alloy in alkaline medium, producing an improvement in electronic and ionic conductivities when an MHE is performing as a negative electrode in a MHB.

The advanced study of these chemical elements in electrode/electrolyte systems will help to design better metal-hydride batteries.

MmNi_{5-x}M_x alloys imply the partial substitution of Ni by Mn, Cu, Cr, Al, Co, etc, improving cycle lifetime and dischargeability when they are placed at optimum Ni_{5-x}M_x composition [69]. The presence of Co has shown excellent results due to its electrocatalytic properties. Co is considered to be able to reduce volume cell expansion in the hydride solid phase. Co can also protect the active La-Ni matrix from corrosion in alkaline medium, but it has been found in electrochemical characterizations that Co on the particle surface reacts at potentials close to -0.65 V/Hg/HgO/1M KOH, to form Co(OH)₂ via $\text{Co} + 2\text{OH}^- = \text{Co(OH)}_2 + 2\text{e}^-$, followed by oxidation producing the irreversible formation of CoOOH at more positive potentials [71-74], promoting a decrease in the specific capacity of the electrode.

Mm(Ni_{0.71}Co_{0.14}Al_{0.08}Mn_{0.06})_{5.02} : A Case Study

As an example of a MmNi_{5-x}M_x alloy, a La-Ni based hydrogen absorbing alloy powder was used as the negative electrode material of an experimental cell. The electrochemical, morphological and thermodynamic characteristics of this material have been mentioned in previous works [26, 68]. The charge transfer reaction at the electrode/electrolyte interface and hydrogen surface coverage capacity were investigated using the CV technique.

EXPERIMENTAL

A hydrogen storage alloy (MH) of nominal composition $Mm(Ni_{0.71}Co_{0.14}Al_{0.08}Mn_{0.06})_{5.02}$ (where Mm denotes Mischmetal, comprising 55 at.% La, 30 at.% Ce, 4 at.% Pr and 11 at.%Nd) was prepared by induction melting and rapid cooling. The average particle size of the alloy for this study was 30 μm . The MH alloy was mixed with nickel powder in a weight ratio of 1:1 together with a small amount (3wt.%) of polytetrafluoroethylene (PTFE) aqueous solution as a binder and then pressed at a pressure of 500MPa. The positive electrode in this cell, a sintered $Ni(OH)_2/NiOOH$ plate, was obtained from a commercial supplier.

The experimental set-up consisted of a three compartment cell. The negative electrode was placed in the central compartment and two $Ni(OH)_2/NiOOH$ electrodes were placed on either side. The electrolyte in the cell was a 6M KOH aqueous solution.

The charge/discharge and polarization tests of the experimental cell were carried out using a Solartron 1285 Potentiostat with CorrWare software for Windows. The testing resolution of the potential, current and time was 0.1mV, 0.1mA and 0.1s respectively. The charge and discharge regimes were conducted in an air-conditioned room at controlled temperatures. The experimental electrode was activated electrochemically and charged at a current of 100 mA g^{-1} for 3.2 hrs. and then discharged at controlled current densities to an end-of-discharge potential of -0.6 V/Hg/HgO . An interruption of the electrode current was used to compensate for the IR potential drop errors.

RESULTS AND DISCUSSION

Electrochemical Characterization

Figure 1 shows the weight percent composition of the $MmNi_5$ -based alloy powder, measured by the EDS and EPMA techniques. The nominal composition of the alloy is also shown in Fig. 1. EDS and EPMA studies were carried out on the same sample. The composition of each element, obtained using EDS, is very close to the nominal composition. EPMA results differ from the stoichiometric composition shown for this AB_5 type alloy. The accuracy in the composition measurements allows a better understanding of the electrochemical performance for $MmNi_5$ -based electrodes due to the complex chemistry of these alloys. The difference in composition, observed between EDS and EPMA studies in Fig. 1, may be related to impurity at the powder surface. These kinds of compositional studies can be used for evaluating $MmNi_5$ -related alloys. From Fig. 1, the preparation technique used for this metal-hydride alloy permits the preparation of very close stoichiometric alloys from the nominal composition. The EPMA technique is used to measure the metallic composition at the surface layer of the alloy powder. It is shown in Fig.1 that the composition of rare earth elements is a

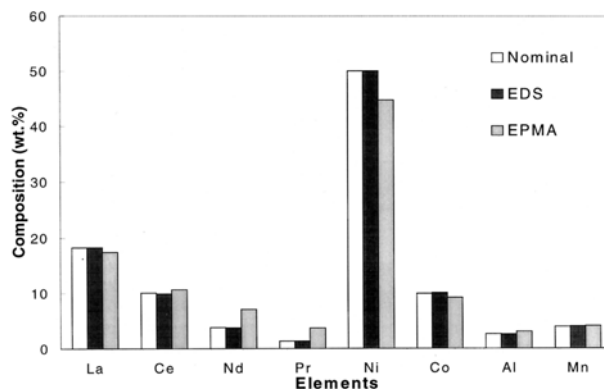


Figure 1. Elemental composition of the $Mm(Ni,Co,Al,Mn)_{5.02}$ alloy obtained from the nominal composition, EDS and EPMA measurement

little higher than the nominal composition. This reflects that the rare earth elements are segregated at the surface layer of the alloy powder. The rare earth elements are easily oxidized to form a passive phase.

Fig. 2 shows the discharge capacity of the $Mm(Ni_{0.71}Co_{0.14}Al_{0.08}Mn_{0.06})_{5.02}$ alloy electrode at different discharge currents. The discharge capacity of the alloy powder at 100 mA g^{-1} discharge current reaches 290 mA h g^{-1} . The specific discharge capacity at 600 mA g^{-1} discharge current reaches a saturated value of 248 mA h g^{-1} . The MH electrode was charged/discharged over 200 cycles. The specific discharge capacity remains at 255 mA h g^{-1} at 298K. The manufacturing of the electrode, additives and bonding materials also influences the measurement of the specific discharge capacity.

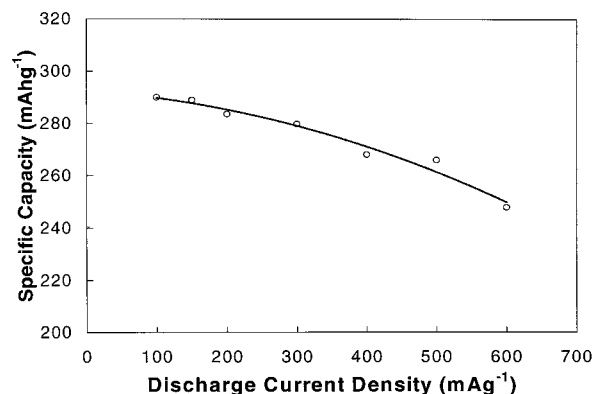


Figure 2. Plot of the specific capacity of $Mm(Ni,Co,Al,Mn)_{5.02}$ the vs discharge current density.

Fig. 3 shows the specific discharge capacity vs. temperature. The discharge capacity was measured at 100 mA g^{-1} discharge current. The specific capacity of the MH electrode has a maximum value of 290 mA h g^{-1} at 298K. The discharge capacity decreased to 252 mA h g^{-1} at 273K and 246 mA h g^{-1} at 335K. The electrochemical reaction at the surface of the MH alloy powder is controlled by the charge transfer process at the MH

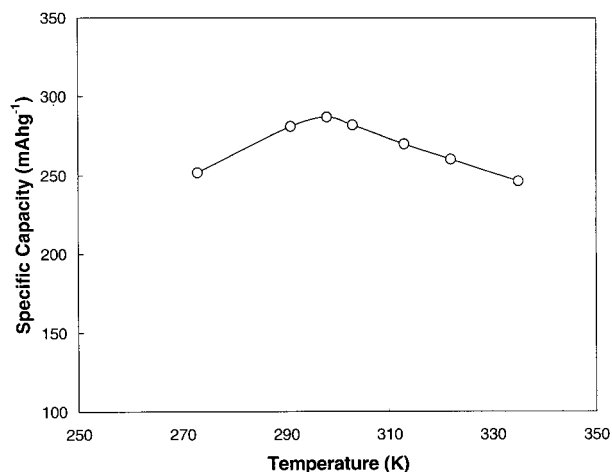


Figure 3. Plot of specific capacity of $Mm(Ni,Co,Al,Mn)_{5.02}$ vs temperature.

electrode/electrolyte interface and the mass transfer process in the bulk MH alloy. The higher temperature leads to an increase in the charge transfer and mass transfer reactions. However, the higher temperature leads to a decrease in the hydrogen storage capacity in the MH alloy.

Fig. 4 shows cyclic voltammograms at the scan rates ranging from $100\text{mV}\cdot\text{s}^{-1}$ to $800\text{mV}\cdot\text{s}^{-1}$. The value of the anodic peak current density, observed in Fig. 4, is influenced by the hydrogen concentration in the alloy powder at a small scan rate. The hydrogen desorption can be observed at potentials lower than -0.8 V vs. Hg/HgO in the anodic direction. The redox couple of hydrogen adsorption/desorption is strongly influenced by the hydrogen evolution reaction (HER) potential at -1.1 V . The presence of a maximum peak around -0.6 V , is associated with charge transfer mechanisms and the desorption of hydrogen species. Due to the complex chemistry of the polycrystalline electrode-based alloy and its porosity morphology, some electrochemical processes can be occurring at that potential forming a thick peak around -0.6 V .

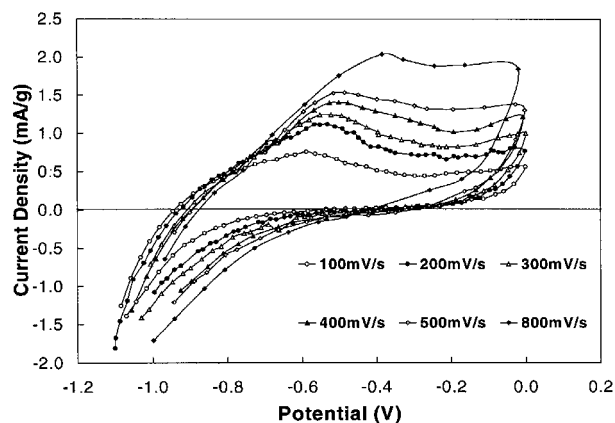


Figure 4. Cyclic voltammograms of the $Mm(Ni,Co,Al,Mn)_{5.02}$ alloy electrode at scan rates ranging from $100\text{mV}\cdot\text{s}^{-1}$ to $800\text{mV}\cdot\text{s}^{-1}$

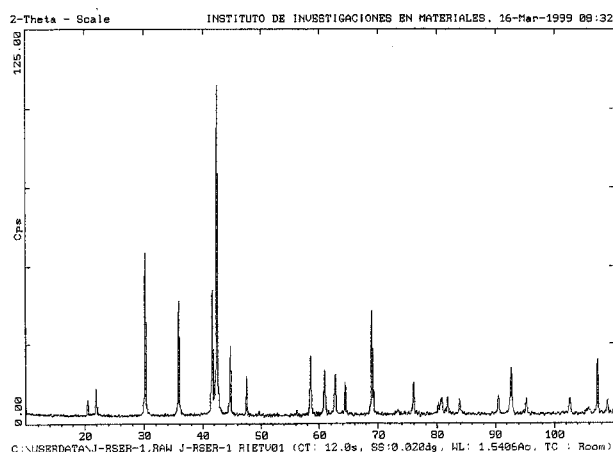


Figure 5. The XRD picture for the $Mm(Ni,Co,Al,Mn)_{5.02}$ alloy

A metal hydride can be crystalline or amorphous in nature. So, for determining the structure of $MmNi_{5-x}M_x$, the XRD technique was used. Figure 5 shows the XRD picture for the compound, which indicates preferential reflection peaks related to the CaCu_5 space group in the same form as LaNi_5 based alloys [8]. It is possible to find stable phases in the crystallographic matrix associated with interstitial centers with correlated potentials for fixing hydrogen adatoms. The $MmNi_{5-x}M_x$ alloy has a similar XRD pattern to LaNi_5 and related alloys.

Morphological Characterization

$MmNi_{5-x}M_x$ particle size and composition were examined using scanning electron microscopy and a microprobe analyzer (EDS) coupled to SEM. Fig. 6a) shows the micrograph of the selected $MmNi_{5-x}M_x$ by secondary electron detection. Fig. 6b) shows the micrograph of the alloy using backscattering electron detection. The multicomponent metal-hydride alloy was estimated to have a mean particle size of $30\text{ }\mu\text{m}$, with a standard deviation of $20\text{ }\mu\text{m}$. The calculated particle size of this alloy allows optimization of the active surface area via electrochemical activation and the use of nickel foam as a substrate for the $MmNi_{5-x}M_x$ based electrodes. The nickel foam used in this study has a pore size greater than $500\text{ }\mu\text{m}$ permitting the consideration of a uniform electron transfer mechanism and minimization of the internal resistance effect in the metal-hydride electrode.

Thermodynamic Properties

The changes in the solid phases due to hydrogen absorption in $MmNi_{5-x}M_x$ alloys and the possibility of using electrochemical methods for absorbing/desorbing hydrogen, can be observed in T-C-P curves. Fig. 7a) shows the absorption/desorption plots for a sample of $MmNi_{5-x}M_x$ at room temperature (25°C). Fig. 7b) shows the T-C-P plots at 50°C . In Figure 7 a) we can identify a plateau pressure of 2.7 psi for hydrogen absorption

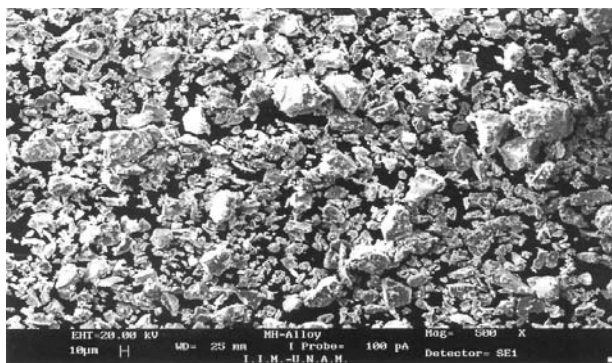


Figure 6a. The SEM of $Mm(Ni,Co,Al,Mn)_{5.02}$ alloy in the secondary electron detection mode

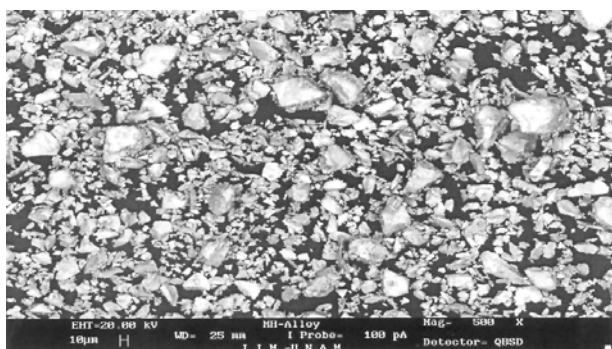


Figure 6b. The SEM of $Mm(Ni,Co,Al,Mn)_{5.02}$ alloy in the backscattering electron detection mode

process, and 1.2 psi for content desorption. When the temperature increases to 50 °C, the alloy modifies its plateau values changing to 6.0 and 3.4 psi for absorption and desorption processes, respectively. The metal-hydride alloys must have a plateau pressure lower than 15 psi for electrochemical applications. This examined $MmNi_{5-x}M_x$ has adequate T-C-P characteristics for these purposes, so the stability and electrochemical performance of the alloy in alkaline medium must be investigated. The theoretical capacity of the alloy at 15 psi was calculated as 286 mAh/g @ 25°C.

Determination of the active surface of the $MmNi_{5-x}M_x$

The BET technique was used for determining the active area of the metal-hydride alloy for electrochemical applications. The active area of a metal-hydride alloy based electrode depends on the manufacturing methods for obtaining the metal-hydride, experimental techniques used for developing metal-hydride electrodes and the conditions for activating the electrodes formed. The specific surface areas of the powders at different treatment conditions are 0.183 m²/g for the fresh alloy, 1.92 m²/g for the sample annealed in an argon atmosphere at 900 °C for 10 minutes. After that, the sample annealed was activated electrochemically showing a specific surface area of 3.92 m²/g. The combined process, annealing plus electrochemical activation showed the best results

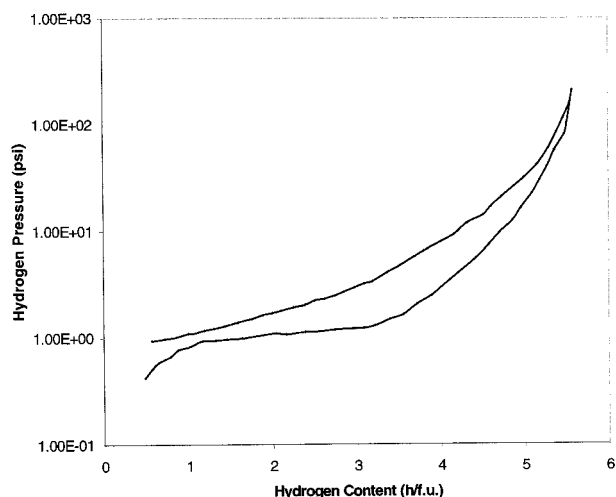


Figure 7a. The T-C-P plot at 25 °C for the $Mm(Ni,Co,Al,Mn)_{5.02}$ alloy

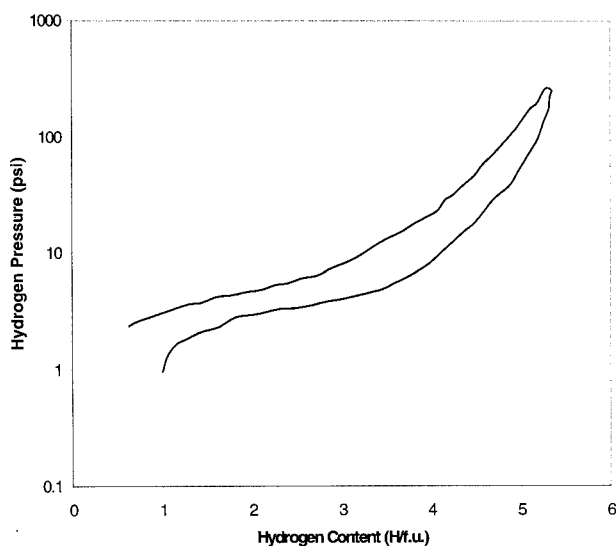


Figure 7b. The T-C-P plot at 50 °C for the $Mm(Ni,Co,Al,Mn)_{5.02}$ alloy

for improving the surface area. A greater active area permits the absorption of more hydrogen through the metal alloy system.

CONCLUSIONS

The principal problem related with the use of rare earth elements in nickel based electrodes in the case of $LaNi_5$, for example, is the degradation process presented in the 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 $La(OH)_3$ by its contact with the electrolyte.

The use of *mischmetal* ($Mm = La, Ce, Pr, Nd$) and transition metals (M) as components of the matrix $Mm_xLa_{1-x}(Ni,M)_5$ in hydrogen absorbing alloys has been extensively investigated. As a result of these investigations, it can be noted that a mischmetal based

predominantly on La (>50 wt%), and the use of substituting nickel elements (M) such as Al, Co, and Mn, greatly improve the intrinsic characteristics of the alloys for absorbing hydrogen electrochemically and the performance of the Ni/MH batteries. Cycle lifetime, high discharge capability, thermal stability and specific capacity characterize the performance of a rechargeable battery. The kinetic parameters involved in the exchange current density that permit the absorption/desorption of hydrogen in the electrochemical system, such as the polarization resistance and potentials are being investigated to understand the performance and characteristics of the electrode/electrolyte interface between metal-hydride electrodes and very strong alkaline electrolytes (5 to 6M KOH). Cyclic voltammetry (CV) is a useful electrochemical technique to investigate electrode/electrolyte interfaces and superficial charge distribution under potentiodynamic conditions further from equilibrium.

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REFERENCES

- [1] B. Paxton and J. Newman, *J. Electrochem. Soc.*, **144** (1997) 3818.
- [2] R.; Dell, *Solid State Ionics*, **134** (2000) 139.
- [3] P.H.L. Notten, M. Latroche and A. Percheron-Guégan, *J. Electrochem. Soc.*, **146** (1999) 3181.
- [4] F. Feng, J. Han, M. Shen, M. Geng, Z. Zhou and D.O. Northwood, *J. New Mater. Electrochem. Sys.* **2** (1999) 45.
- [5] M. Geng, J. Han, F. Feng and D.O. Northwood, *J. Electrochem. Soc.*, **146** (1999) 3591.
- [6] J. Han, F. Feng, M. Geng, R. Buxbaum and D.O. Northwood, *J. Power Sources*, **80** (1999) 39.
- [7] M. Geng, J. Han, F. Feng and D.O. Northwood, *J. Electrochem. Soc.*, **146** (1999) 2371.
- [8] F. Feng, X. Ping, Z. Zhou, M. Geng, J. Han and D.O. Northwood, *Int. J. Hydrogen Energy*, **23** (1999) 599.
- [9] T. Sakai, H. Miyamura, N. Kuriyama, A. Kato, K. Oguro and H. Ishikawa, *J. Electrochem. Soc.*, **137** (1990) 795.
- [10] H. Sawa, S. Wakao, *Mater. Trans. JIM*, **31** (1990) 487.
- [11] X.G. Yang, W.K. Zhang, Y.Q. Lei and Q.D. Wang, *J. Electrochem. Soc.*, **146** (1999) 1245.
- [12] H. Lee, S.M. Lee, J.Y. Lee, *J. Electrochem. Soc.*, **146** (1999) 3666.
- [13] J.S. Yu, H. Li, S.M. Lee, J.Y. Lee, *J. Electrochem. Soc.*, **146** (1999) 4366.
- [14] W. Choi, K. Yamataka, S. Zhang, H. Inoue, C. Iwakura, *J. Electrochem. Soc.*, **146** (1999) 46.
- [15] B. Knosp, C. Jordy, P. Blanchard, T. Berlureau, *J. Electrochem. Soc.*, **145** (1998) 1478.
- [16] X.G. Yang, Y.Q. Lei, W.K. Zhang, G.M. Zhu, Q.D. Wang, *J. Alloys and Comp.*, **243** (1996) 151.
- [17] A. Züttel, F. Meli, L. Schlapbach, *J. Alloys and Comp.*, **206** (1994) 31.
- [18] A. Züttel, F. Meli, L. Schlapbach, *J. Alloys and Comp.*, **200** (1993) 151.
- [19] G. Benczur-ÜrmÖssy, D. Berthold and K. Wiesener, in Holmes CF, Landgrebe AR editors. Batteries for portable applications and electric vehicles, PV 97-18, The Electrochemical Society Proceeding series. NJ, Pennington, 1997
- [20] K. Kosuge, *Chemistry of Non-stoichiometric Compounds*, Oxford University Press, NY, 1993.
- [21] H. Bruning and A. Sieverts, *Z. Physik. Chem.*, **163** (1933) 409.
- [22] T.B. Flanagan and W.A. Oates, *Ber. Bunsenges, Phys. Chem.*, **76** (1972) 706.
- [23] P. Fisher, A. Furrer, G. Busch and L. Schlapbach, *Helv. Phys. Acta*, **50** (1977) 421.
- [24] J.F. Lakner, F.S. Uribe and S.A. Steward, *J. Less-Comm Met.*, **72** (1980) 87.
- [25] F. Feng, M. Geng and D.O. Northwood, *Int. J. Hydrogen Energy*, **26** (2001) 725.
- [26] S.A. Gamboa and P.J. Sebastian, *Int. J. Hydrogen Energy*, **26** (2001) 117.
- [27] W. Metzger, R. Westfall and A. Hermann, *Int. Journal of Hydrogen Energy*, **23** (1998) 1179.
- [28] J.J. Willems and H.J. Buschow, *J. Less-Common Metals*, **129** (1987) 13.
- [29] S. Cheng, J. Zhang, M. Zhao and C. Cao, *J. Alloys and Compounds*, **293-295** (1999) 814.
- [30] M. Viitanen, *J. Electrochem. Soc.*, **140** (1993) 963.
- [31] D.A. King and D.P. Woodruff, Eds., *The Chemical Physics of Solid Surfaces and Heterogeneous Catalysis*, vol. 3, Chemisorption Systems, Part A, Elsevier, p.5 (1990).
- [32] G. Zheng, B.N. Popov and R.E. White, *J. Electrochem. Soc.*, **143** (1996) 435.
- [33] M. Geng, *J. Alloys and Compounds*, **217** (1995) 90.
- [34] Q.M. Yang, M. Ciureanu, D.H. Ryan and J.O. Ström-Olsen, *J. Electrochem. Soc.*, **141** (1994) 2108.
- [35] S.W. Feldberg and J.J. Reilly, *J. Electrochem. Soc.*, **144**, (1997) 4260.
- [36] E. Wicke and H. Brodowsky, *Topics in Applied Physics*, Vol. 29, Alefeld and J. Völkl, editors, Springer-Verlag, pp. 73-155, (1978).
- [37] J. Newman, and W. Tiedemann, *AIChE J.*, **21** (1975) 25.
- [38] Z. Du, D. Wang and W. Zhang, *J. Alloy and Compounds*, **264**, 209(1998).
- [39] C. Wang, *J. Electrochem. Soc.*, **145** (1998) 1801.
- [40] J. Heikonen, K. Vuorilehto, and T. Noponen, *J. Electrochem. Soc.*, **143** (1996) 3972.
- [41] B.S. Haran, B.N. Popov, and R.E. White, *J. Electrochem. Soc.*, **145** (1998) 4082.
- [42] M. Viitanen, *J. Electrochem Soc.*, **140** (1993) 936.
- [43] T. Sakai, H. Miyamura, N. Kuriyama, H. Ishikawa and I. Uehara, *Z. Phys. Chem.*, **183** (1994) 333.
- [44] S.R. Kim and J.Y. Lee, *J. Alloys Comp.*, **210** (1994) 109.
- [45] J.S. Yu, S.M. Lee, K. Cho and J.Y. Lee, *J. Electrochem. Soc.*, **147** (2000) 2013.
- [46] M. Ikoma, Y. Hoshina and I. Matsumoto, *J. Electrochem. Soc.*, **143** (1996) 1904.
- [47] V. Badri and A.M. Hermann, *Int. J. Hydrogen Energy*, **25**, (2000) 249.
- [48] P. Ruetschi, F. Meli, and J. Desilvestro, *J. Power Sources*, **57** (1995) 85.
- [49] J.J.G. Willems, *Philips J. Res.*, **39**, Suppl. No. 11(1984).
- [50] H. Senoh, K. Morimoto, H. Inoue, C. Iwakura and P.H.L. Notten, *J. Electrochem. Soc.*, **147** (2000) 2451.
- [51] G. Zheng, B.N. Popov and R.E. White, *J. Electrochem. Soc.*, **143** (1996) 435.
- [52] M. Geng, *J. Alloys Comp.*, **217** (1995) 90.
- [53] X. Wang, B. Liu, J. Yan, H. Yuan, D. Song and Y. Zhang, *J. Alloys Comp.*, **293-295** (1999) 788.
- [54] T. Sakai, K. Oguro, H. Miyamura, N. Kuriyama, A. Kato and H. Ishikawa, *J. Less-Common Met.*, **161** (1990) 193.
- [55] P.H.L. Notten and P. Hokkelling, *J. Electrochem. Soc.*, **138** (1991) 1877.
- [56] M. Geng, J. Han, F. Feng and D.O. Northwood, *J. Electrochem. Soc.*, **146** (1999) 3591.
- [57] H.S. Kim, M. Nishizawa and I. Uchida, *Electrochim. Acta*, **45** (1999) 483.

- [58] M. Geng, F. Feng, P.J. Sebastian, A.J. Matchett and D.O. Northwood, *Int. J. Hydrogen Energy*, **26** (2001) 165.
- [59] S.R. Ovshinsky, M.A. Fetcenko and J. Ross, *J. Science*, **260** (1993) 176.
- [60] M.A. Gutjahr, H. Buchner, K.D. Beccu and H. Saufferer, *J. Power Sources*, **4** (1973) 79.
- [61] P.H.L. Notten, P. Hokkelling, *J. Electrochem. Soc.*, **138** (1991) 1877.
- [62] A. Percheron.Guegan and J. Welter, in L. Schlapbach, editor. *Hydrogen Intermetallic Compounds I*, Berlin, Springer, 1988.
- [63] T. Sakai, H. Miyamura, N. Kuriyama, H. Ishikawa and I. Uehara, *Zeitschrift für Physikalische Chemie*, **183** (1994) 333.
- [64] T. Sakai, T. Hazama, H. Miyamura, N. Kuriyama, A. Kato and H. Ishikawa, *J. Less-Common Met.*, **172-174** (1991) 1175.
- [65] A. Percheron.Guegan and J. Welter, in L. Schlapbach, editor. *Hydrogen Intermetallic Compounds I*, Berlin, Springer, 1988.
- [66] S. Fujitani, S. Yasuyama, A. Furukawa, T. Yonesaki, K. Nasako, I. Yonezu and T. Saito, *J. Japan Inst. Metals*, **56** (1992) 965.
- [67] Y. Nakamura, H. Nakamura, S. Fujitani and I. Yonezu, *J. Alloys and Comp.*, **221** (1995) 284.
- [68] S.A. Gamboa, P.J. Sebastian, M. Geng and D.O. Northwood, *Int. J. Hydrogen Energy*, **26** (2001) 1319.
- [69] M. Geng, J. Han, F. Feng and D.O. Northwood, *Int. J. Hydrogen Energy*, **23** (1998) 1055.
- [70] J.J. Willems, *Philips J. Res.*, **39**, Suppl. 1 (1984) 1.
- [71] H.S. Kim, M. Nishizawa, I. Uchida, *Electrochim. Acta*, **45**, (1999) 483.
- [72] B.S. Haran, B.N. Popov and R.E. White, *J. Electrochem. Soc.*, **145** (1998) 3000.
- [73] B. Popov, Z. Koneska, J. Ivshin and D.M. Dražić, *J. Serb. Chem. Soc.*, **54** (1989) 435.
- [74] M. Oshitani, H. Yufu, K. Takashima, S. Tsuji and Y. Matsu-
maru, *J. Electrochem. Soc.*, **136** (1989) 1590.

IZVOD

PROČAVANJE ELEKTROHEMIJSKOG AKUMULIRANJA VODONIKA PRIMENOM VIŠEKOMPONENTNIH LEGURA $MmNi_{5-x}M_x$: Pregled

(Pregledni rad)

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Ni–metal hidridne baterije (NMH), kao i Li–jonske baterije se razmatraju kao budući potencijalni uređaji za akumuliranje energije i primenu kod pokretnih sistema. Najčešće korišćeni materijali za MH elektrode su legure tipa AB_2 (Mg–Ni) i AB_5 (La–Ni). Ni/MH baterije kao elektrohemijski sistemi su definisane po: specifičnom kapacitetu, veku trajanja, povoljnoj gustini struje, ravnotežnom potencijalu, pražnjenju i mehanizmu samo–pražnjenja. Sve navedene karakteristike odnosno elektrohemijski parametri omogućavaju da se elektrohemijski proces adsorpcije i desorpcije vodonika odigrava u masi legure. Međutim, trenutno je veliki broj istraživanja u cilju poboljšanja osobina i karakteristika ćelija kako bi se obezbedio njen duži vek trajanja, smanjio efekat samo–pražnjenja i omogućio rad na temperaturi iznad 50°C .

Ključne reči: Skladištenje vodonika •
Baterije • Metalni hidridi •
Key words: Hydrogen storage •
Batteries • Metal hydride •

