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Short communication

## Influence of temperature on the electrochemical characteristics of $\text{MmNi}_{3.03}\text{Si}_{0.85}\text{Co}_{0.60}\text{Mn}_{0.31}\text{Al}_{0.08}$ hydrogen storage alloys

M. Raju<sup>a</sup>, M.V. Ananth<sup>a,\*</sup>, L. Vijayaraghavan<sup>b</sup><sup>a</sup> *Nickel–Metal Hydride Battery Section, Electrochemical Power Systems Division, Central Electrochemical Research Institute, Karaikudi 630006, India*<sup>b</sup> *Department of Mechanical Engineering, Indian Institute of Technology Madras, Chennai 600036, India*

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## ABSTRACT

The heat of hydride formation is a crucial parameter in characterizing a hydrogen storage alloy for battery applications. Novel  $\text{AB}_5$ -type, non-stoichiometric, lanthanum-rich  $\text{MmNi}_{3.03}\text{Si}_{0.85}\text{Co}_{0.60}\text{Mn}_{0.31}\text{Al}_{0.08}$  (Mm: Misch metal) hydrogen storage metal hydride alloy electrodes are prepared. Electrochemical hydrogen absorption/desorption and electrochemical impedance measurements are carried out at various temperatures in conjunction with sintered nickel hydroxide positive electrodes. The specific capacity of the prepared metal hydride electrodes decreases from  $283 \text{ mAh g}^{-1}$  at 303 K to  $213 \text{ mAh g}^{-1}$  at 328 K. Electrochemical pressure–composition–temperature (PCT) isotherms are constructed from galvanostatic discharge curves and the change in enthalpy ( $\Delta H_{\text{e}}$ ) and the change in entropy ( $\Delta S_{\text{e}}$ ) of the metal hydride alloy electrodes are evaluated as  $-41.74 \text{ kJ mol}^{-1}$  and  $146.28 \text{ J mol}^{-1} \text{ K}^{-1}$ , respectively. Kinetic parameters are obtained by fitting the electrochemical impedance spectrum performed at different temperatures. The charge-transfer resistance decreases with temperature, whereas exchange current density and diffusion coefficient parameters increase with temperature. It is concluded that the deterioration in capacity is due to enhanced surface activity at higher temperatures.

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## 1. Introduction

Nickel–metal hydride (Ni–MH) batteries have been the focus of attention since 1990 due to their inherent advantages of high specific energy, high-rate capability, and freedom from toxic materials. They find application in computers, cameras, camcorders, emergency lighting units, telecommunication systems, and hybrid electric vehicles. They are also serious contenders for electric vehicles. The performance of the system relies on the electrochemical activity of the metal hydride alloy negative electrode, which supplants the toxic cadmium electrode in the conventional nickel–cadmium (Ni–Cd) cell. The negative electrode can be prepared from a variety of intermetallic compounds, whose hydrogen absorption/desorption characteristics decide the performance of the Ni–MH cell. Hong [1] reported a semi-empirical method for the preparation of hydrogen-absorbing metal hydride alloys based on thermodynamic and electrochemical studies.

Metal hydrides for battery applications are characterized in terms of their hydrogen storage capacity at moderate hydride stability and approximately constant equilibrium pressure during hydride phase transformation. Data on these properties

can be obtained from pressure–composition–temperature (PCT) isotherms, which describe the dependence of the hydrogen equilibrium pressure on the amount of hydrogen absorbed or incorporated into the hydrogen storage material at various temperatures. Thermodynamic properties such as the change in enthalpy ( $\Delta H$ ) and the change in entropy ( $\Delta S$ ) can be calculated from PCT isotherms [2]. The PCT isotherms can also be used to identify different phases in metal hydride alloys. Hydrogen concentration at various stages such as in the  $\alpha$ -phase, during transition of  $\alpha$ -phase to  $\beta$ -phase, and in the  $\beta$ -phase in equilibrium with the  $\alpha$ -phase can also be obtained from PCT isotherms [3]. PCT diagrams can be constructed for metal hydride alloys in two ways, namely, a gas–solid PCT isotherm and an electrochemical PCT isotherm. In general, the plateau pressure for the metal hydride electrode at room temperature is lower than 1 atm, which calls for specially designed high-vacuum equipment as well as a long period for attaining hydrogen equilibrium pressure. If the plateau pressure is much lower than 1 atm, then it is impossible to attain the equilibrium pressure [4]. The electrochemical approach to construct PCT isotherms, therefore, is a simple and convenient alternative procedure. Despite the importance of the heat of hydride formation of metal hydrides for battery applications, sufficient studies have not appeared in the literature, especially by electrochemical methods.

Hong [1] reported that the heat of hydride formation for titanium/zirconium-based metal hydrides was in the range of

\* Corresponding author. Tel.: +91 4565 227555; fax: +91 4565 227713.  
E-mail address: [mvananth@rediffmail.com](mailto:mvananth@rediffmail.com) (M.V. Ananth).

–24.83 to –29.68 kJ mol<sup>-1</sup> and those of rare earth metal-based hydrides were –18.56 to –20.11 kJ mol<sup>-1</sup>. Kleperis et al. [5] and Ovshinsky et al. [6] found that alloys with  $\Delta H$  values between –25 and –50 kJ mol<sup>-1</sup> were suitable for battery applications. On the other hand, Hong [7] postulated that the heat of formation of hydrides should be between –15 and –40 kJ mol<sup>-1</sup>. A value lower than –15 kJ mol<sup>-1</sup> renders the alloy not sufficiently stable for charging at room temperature, whereas a  $\Delta H$  value exceeding –50 kJ mol<sup>-1</sup> should render it too stable for room temperature discharge. In practice,  $\Delta H$  is an index of the thermochemical stability of metal hydride electrodes. A high  $\Delta H$  value would signify a high degree of stability of the hydride and low dissociation pressures, which means that a high temperature is required to decompose the alloy to release the hydrogen. On the contrary, an alloy with a low  $\Delta H$  value would have characteristics opposite to those discussed above [8].

Bouten and Miedema [9], Oesterreicher [10], Griessen [11] and Shilov et al. [12] proposed models to determine the heat of formation of hydrides using different atomic parameters. Shuang et al. [13] constructed semi-empirical model for the heat of formation of hydrides and hydrogen concentration in LaNi<sub>5-x</sub>M<sub>x</sub> alloys. They used several atomic parameters such as atomic size, electronegativity, electron density and charge–radii ratio to construct the model via a stepwise regression method. The model has been used only for the ternary LaNi<sub>5</sub>-based alloy hydrides, however, and not for multi-component alloys and non-stoichiometric AB<sub>2</sub> alloys with different substitutions at the A and B sites. Recently, Mani et al. [14–17] and Kandavel et al. [18] systematically investigated the hydrogen storage properties of Zr-based C14 AB<sub>2</sub>-type alloys, Mm-based AB<sub>5</sub>-type alloys and Ti-substituted AB<sub>2</sub>-type alloys in order to assess the suitability of these materials for hydrogen storage devices. Since refined calculations of the heat of formation of hydrides require considerable computing efforts, only semi-empirical models have been investigated. It has been found that the amount of hydrogen absorbed in LaNi<sub>5-x</sub>M<sub>x</sub> alloys is controlled by electronegativity differences, atomic size, electron concentration and charge–radii ratio [13].

Ni–MH batteries give the best performance between 20 and 40 °C. The temperature at which the battery is discharged has a pronounced effect on its capacity and voltage characteristics. This is because discharge capacity and cell voltage are strongly dependent on the operating temperature. The rate of hydrogen diffusion within the bulk of the electrode and the processes occurring at the electrode–electrolyte interface are dependent upon temperature, and hence the present investigation becomes important. Previous efforts in this direction were mostly aimed at studies of kinetic parameters as a function of the state-of-charge of the electrode at ambient temperatures [19–21]. Only a few have concentrated on the temperature dependence of the hydrogen diffusion coefficient in metal hydride electrodes. This communication describes the preparation of a novel La-rich metal hydride electrode and its performance degradation at elevated temperatures. Generally, electrochemical kinetics can be described by electrode resistance, exchange current density and diffusion coefficient. The effect of temperature on these parameters as applied to an MmNi<sub>3.03</sub>Si<sub>0.85</sub>Co<sub>0.60</sub>Mn<sub>0.31</sub>Al<sub>0.08</sub> hydrogen storage alloy are reported.

## 2. Experimental

Non-stoichiometric, lanthanum-rich, AB<sub>5</sub>-type rare earth metal-based hydride alloy powder of MmNi<sub>3.03</sub>Si<sub>0.85</sub>Co<sub>0.60</sub>Mn<sub>0.31</sub>Al<sub>0.08</sub> was used to prepare the negative electrode of the nickel–metal hydride cell. The La:Ce ratio in Mm was 11.65. The

alloy was prepared by button arc melting followed by necessary treatment at the Defence Metallurgical Research Laboratory (DMRL), Hyderabad, India. The purity of the constituent metals (La, Ce, Ni) was at least 99.9%. In order to ensure homogeneity, ingots were turned over and melted twice. The ingots were mechanically pulverized into fine powders of sieve size less than 75 μm. The composition of the product was determined by X-ray fluorescence spectroscopy (Horiba XRF Analyzer, model XGT-2700).

Test electrodes for galvanostatic charge/discharge experiments were made from 1.00 g of the alloy and had a geometrical area of 3 cm × 2 cm. Electrodes for impedance measurements were made from 0.170 g of the alloy and had a geometrical area of 1 cm × 1 cm. A slurry of the alloy powder with appropriate amounts of conducting carbon powder and polytetrafluoroethylene binder was applied to both sides of a nickel foam substrate, dried and compacted under 75 MPa pressure, and finally heat-treated at 408 K for 1 h.

The test cell was comprised of the alloy as the working electrode, a sintered Ni(OH)<sub>2</sub> electrode (of higher capacity than the working electrode) as the counter electrode, and Hg|HgO in 6 M KOH as the reference electrode. Galvanostatic charge/discharge cycling was carried out at a current density of 60 mA g<sup>-1</sup> by means of a Bitrode LCN life cycle tester. Charging was undertaken for 7 h and discharging was continued until the potential of the alloy electrode reached –0.7 V with respect to the reference electrode. Up to 25 charge–discharge cycles were run at 303 K. Subsequently, cycling studies were carried out at 308, 318 and 328 K. Electrochemical impedance experiments were performed with an Auotolab 30 potentiostat/galvanostat between 100 kHz and 5 mHz at a signal amplitude of 5 mV at 100% state-of-charge. Before each measurement, sufficient time was allowed for the system to reach equilibrium conditions.

## 3. Results and discussion

Metal hydride alloy electrodes generally require more than 15 cycles to complete the activation process and to reach their maximum capacity. The variation of capacity of the MmNi<sub>3.03</sub>Si<sub>0.85</sub>Co<sub>0.60</sub>Mn<sub>0.31</sub>Al<sub>0.08</sub> alloy electrode as a function of cycle number over 100 cycles at C/5 rate and at 303 K is shown in Fig. 1. From an initial capacity of 111 mAh g<sup>-1</sup>, the capacity reaches 258 mAh g<sup>-1</sup> in the fourth cycle. Thereafter, the capacity stabilizes at around 275 mAh g<sup>-1</sup>. The maximum capacity obtained was 283 mAh g<sup>-1</sup>. Beyond 40 cycles, there is only a marginal decrease in capacity.

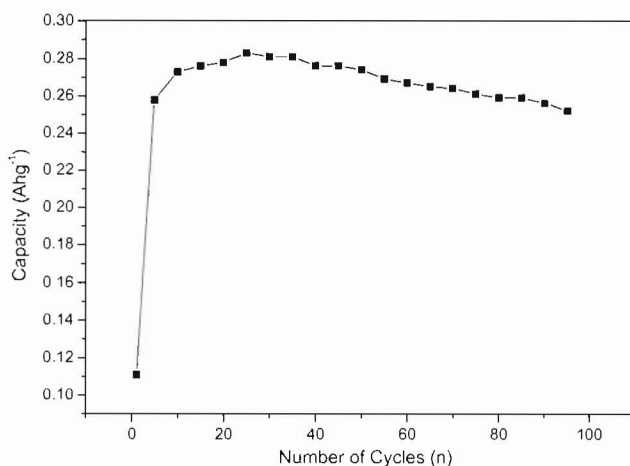


Fig. 1. Cycle-life performance of MmNi<sub>3.03</sub>Si<sub>0.85</sub>Co<sub>0.60</sub>Mn<sub>0.31</sub>Al<sub>0.08</sub> electrode at 303 K.

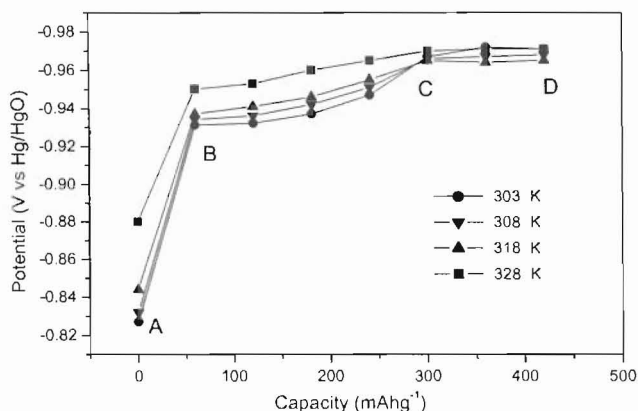
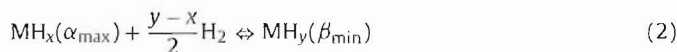


Fig. 2. Charging performance of  $\text{MnNi}_{3.03}\text{Si}_{0.85}\text{Co}_{0.60}\text{Mn}_{0.31}\text{Al}_{0.08}$  electrode at various temperatures.

The charging curves of the alloy electrode at 303, 308, 318 and 328 K at C/5 rate are shown in Fig. 2. It is seen that the potential profile increases suddenly and reaches almost a plateau region beyond  $60 \text{ mAhg}^{-1}$ . Furthermore, an increase in the potential plateau is observed with increase in temperature. The charging profiles are evidence for the phase transformations that accompany the charging processes. The region A to B represents the  $\alpha$ -phase, in which the hydrogen content is low,  $x < 0.1$  H/M (H/M: Hydrogen to metal ratio). The hydrogen absorption–desorption in this single-phase solid solution can be described by the reaction



The region B to C represents the transformation of  $\alpha$ -phase to  $\beta$ -phase. The region C to D represents hydrogen evolution. Hydrogen absorption reaches a saturation value at C. Any further charging leads to evolution of hydrogen at the negative electrode. The hydrogen may take part in a recombination reaction with oxygen liberated at the positive electrode. For  $0.1 < x < 0.8$  H/M, there is a two-phase domain. Here, the saturated  $\alpha$ -phase ( $x = \alpha_{\max}$ ) transforms into the  $\beta$ -phase ( $x = \beta_{\min}$ ). It corresponds to a plateau pressure, the composition range of which extends as long as the following equilibrium reaction takes place:



A solid–solution, single-phase domain also occurs at  $x > 0.8$  H/M, which is the region corresponding to the  $\beta$ -phase. This can be described according to Eq. (1). The discharge performance of the alloy electrode at various temperatures is shown in Fig. 3. Variation in temperature significantly affects the performance of the metal hydride electrode. The performance curve shows that the specific capacity decreases as the temperature is raised. The capacity falls from  $283 \text{ mAhg}^{-1}$  at 303 K to  $213 \text{ mAhg}^{-1}$  at 328 K. It is also seen that at the highest temperature studied (328 K), the electrode potential reaches a maximum value and exhibits the highest capacity fade. At elevated temperatures, some amount of hydrogen or oxygen could be liberated and this could adversely affect battery performance, e.g., reduced cycleability, battery swelling, and/or thermal runaway.

The charge–discharge curves under galvanostatic conditions are electrochemical equivalents of the PCT isotherms of the gas–solid phase reaction. In fact, there is a thermodynamic correlation between the equilibrium pressure measured in the gas phase reaction and the electrode potential measured in an electrochemical cell. The potential of the metal hydride electrode in alkaline solution, as measured with respect to a Hg/HgO reference electrode,

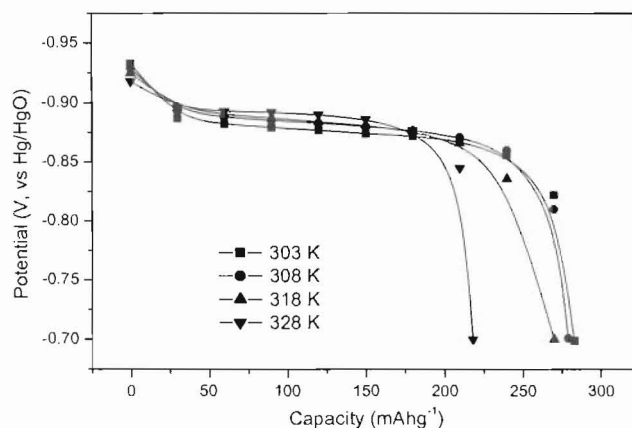


Fig. 3. Discharge performance of  $\text{MnNi}_{3.03}\text{Si}_{0.85}\text{Co}_{0.60}\text{Mn}_{0.31}\text{Al}_{0.08}$  electrode at various temperatures.

is converted to the hydrogen equilibrium pressure based on the Nernst equation corresponding to the reversible reaction in Eq. (1):

$$E(\text{V vs. Hg|HgO}) = -0.932 - 0.0296 \ln P(\text{H}_2) \quad (3)$$

where  $E$  is the potential of the metal hydride alloy electrode and  $P(\text{H}_2)$  is the equilibrium hydrogen pressure [3]. A completely charged electrode was discharged at  $60 \text{ mAhg}^{-1}$  for 30 min and allowed to stabilize for 30 min under open-circuit conditions, during which the potential was monitored. After 30 min of open-circuit conditions, it was discharged at the same rate and this cycling was repeated until the potential reached  $-0.7 \text{ V}$  with respect to Hg/HgO. The potential of the metal hydride alloy electrode was converted into the equilibrium pressure of hydrogen using the Nernst equation. An electrochemical PCT isotherm was constructed by plotting the logarithmic equilibrium pressure of hydrogen versus electrochemical absorption capacity according to the van't Hoff relation:

$$\ln \left[ \frac{P(\text{H}_2)}{P^0} \right] = \frac{\Delta H}{RT} - \frac{\Delta S}{R} \quad (4)$$

where  $P^0$  is the standard pressure,  $R$  is gas constant and  $T$  is the absolute temperature. The variation of the equilibrium potential under open-circuit conditions after complete charging as a function of temperature is shown in Fig. 4. It can be seen that the equilibrium potential is shifted in a positive direction, which suggests that the hydride alloy is of good quality with low equilibrium hydrogen pressure in the plateau region.

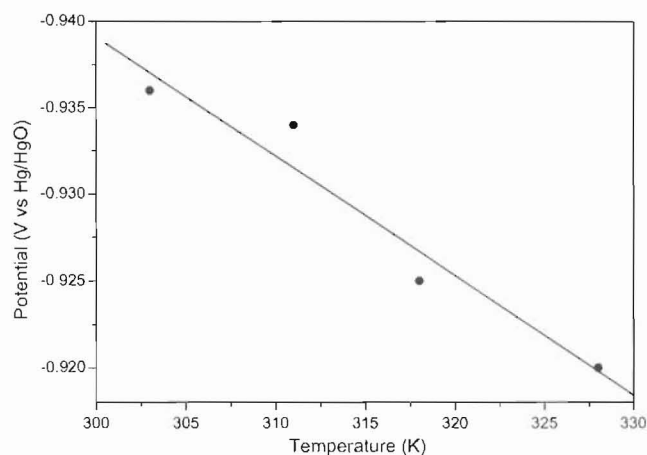


Fig. 4. Relationship between equilibrium potential and temperature.

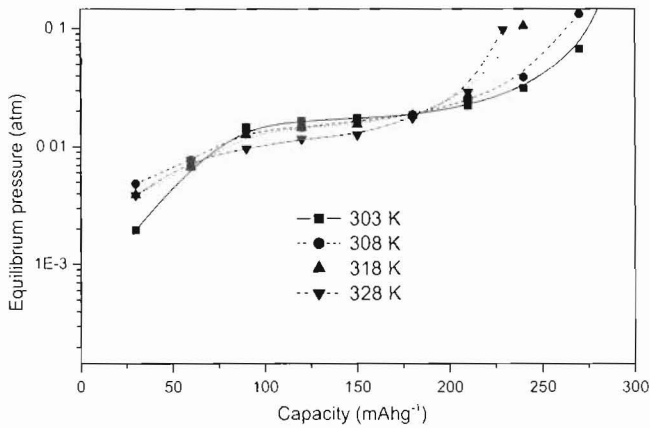


Fig. 5. Electrochemical hydrogen desorption isotherms at various temperatures.

The electrochemical hydrogen desorption isotherms at 303, 308, 318 and 328 K is presented in Fig. 5. The plateau of the hydrogen desorption isotherm decreases with increase in temperature. The van't Hoff plot (logarithm of the equilibrium plateau pressure vs. reciprocal of temperature) for the electrode is given in Fig. 6. The values of  $\Delta H$  ( $-41.74 \text{ kJ mol}^{-1}$ ) and  $\Delta S$  ( $146.28 \text{ J mol}^{-1} \text{ K}^{-1}$ ) were evaluated from the slope and the intercept of van't Hoff plot, respectively. The values are in agreement with those available in the literature [3]. It is noteworthy that the coulombic efficiency of the electrode even after 100 cycles is 97%, which shows that the alloy performs well. The apparent activation energy ( $\Delta_r H^*$ ) of the charge-transfer reaction occurring on the metal hydride electrode surface can be obtained from:

$$\log \left( \frac{T}{R_{ct}} \right) = -\frac{\Delta_r H^*}{2.3RT} + A \quad (5)$$

where  $A$  is a constant. In Fig. 7  $\log(T/R_{ct})$  is plotted against  $1000/T$ , from which the apparent activation energy at 100% state-of-charge is calculated as  $49.01 \text{ kJ mol}^{-1}$ . This value is higher than that reported by Yuan and Xu [22]. The high value indicates high surface activity at the interface. On the other hand, the plot also shows that the catalytic activity of the negative electrode decreases with increase in temperature.

The main electrochemical reactions that occur at the metal hydride electrode are

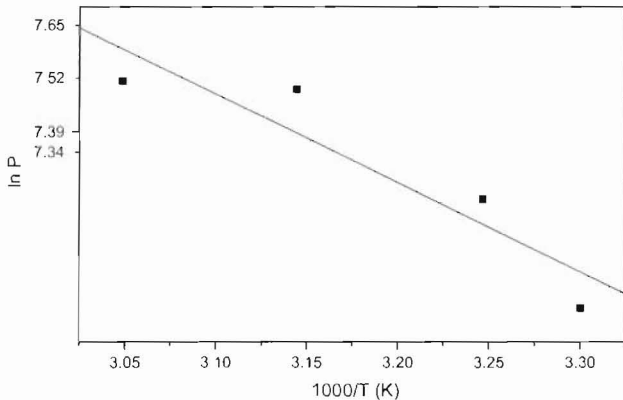
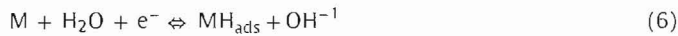


Fig. 6. van't Hoff plot for  $MmNi_{3.03}Si_{0.85}Co_{0.60}Mn_{0.31}Al_{0.08}$  electrode.

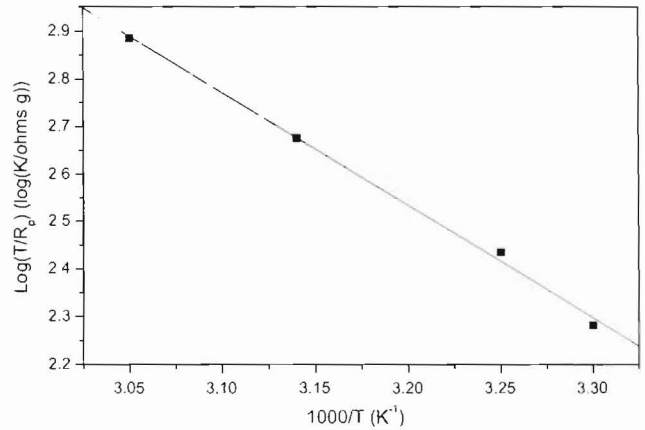


Fig. 7. Relationship between  $\log(T/R_p)$  and  $1/T$  for prepared metal hydride electrode.

where  $H_{ads}$ ,  $H_{abs}$ , and  $H_{hyd}$  represent hydrogen adsorbed on the surface, adsorbed on the surface, and in hydride form, respectively [23]. During charging, hydrogen is adsorbed on the electrode surface, which is subsequently absorbed into the bulk by diffusion and is converted into metal hydride according to Eqs. (6)–(8). Generally, the relative rate of individual reactions and especially the coulombic efficiency of hydrogen entry and withdrawal in metal hydride systems strongly depend on the magnitude of the metal–hydrogen interactive energy which, in turn, depends on temperature. The electro-reduction of water molecules becomes slower whereas the rate of hydrogen evolution increases. The hydrogen diffusion in a charge–discharge reaction is influenced by both the micro- and the macro-structure of the alloy. The diffusion coefficient of atomic hydrogen in the solid phase was shown to depend on the strength of the metal–hydrogen interaction and the hydrogen concentration in the bulk since this is a characteristic of mass transport in metal hydride electrodes [23]. The hydrogen diffusion coefficient ( $D$ ) under galvanostatic discharge conditions was calculated as proposed by Zheng et al. [23]:

$$D = \frac{i_d r^2}{15(Q_0 - \tau i_d)} \quad (9)$$

where  $i_d$  = discharge current density ( $A g^{-1}$ );  $r$  is average radius of the alloy particle (cm);  $Q_0$  is the initial specific capacity ( $C g^{-1}$ );  $\tau$  is transient time (s), which is the time required for the sur-

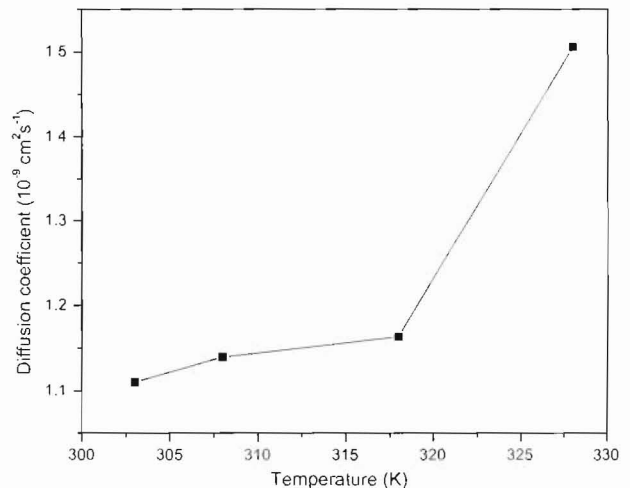
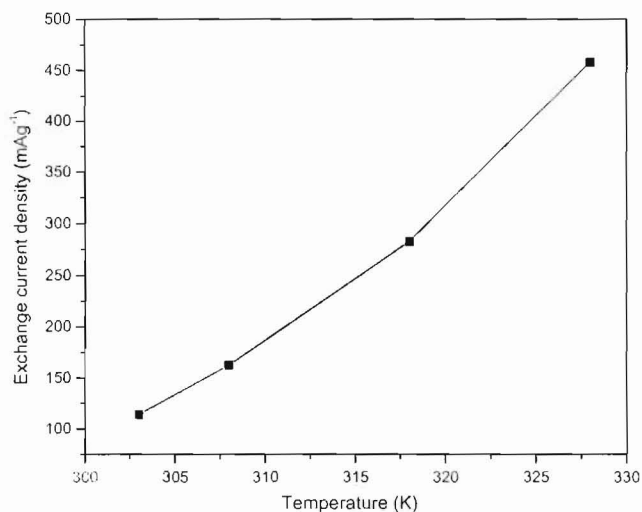


Fig. 8. Diffusion coefficient values at various temperatures for  $MmNi_{3.03}Si_{0.85}Co_{0.60}Mn_{0.31}Al_{0.08}$  electrode.

**Table 1**  
Kinetic parameters of  $\text{MmNi}_{3.03}\text{Si}_{0.85}\text{Co}_{0.60}\text{Mn}_{0.31}\text{Al}_{0.08}$  alloy electrode obtained by fitting the electrochemical impedance spectrum at different temperatures

Parameters	Temperature (K)			
	303	308	318	328
$R_s$ ( $\Omega \text{ cm}^2$ )	0.337	0.339	0.252	0.256
$R_1$ ( $\text{m} \Omega \text{ cm}^2$ )	91.5	87.2	60.9	61.7
$C_1$ (mF)	1.054	1.237	1.050	0.983
$R_2$ ( $\text{m} \Omega \text{ cm}^2$ )	190.9	165.7	110.9	90.0
$C_2$ (mF)	22.46	16.88	14.69	12.24
$R_{ct}$ ( $\Omega \text{ cm}^2$ )	1.581	1.129	0.670	0.427
$C_{dl}$ (mF)	113.7	84.7	66.3	63.9
$Z_d$	0.1074	0.1520	0.1688	0.2252



**Fig. 12.** Exchange current density of  $\text{MmNi}_{3.03}\text{Si}_{0.85}\text{Co}_{0.60}\text{Mn}_{0.31}\text{Al}_{0.08}$  electrode at various temperatures.

decreases as the temperature is raised. The charge-transfer resistance decreases from  $1.581 \Omega \text{ cm}^2$  at 303 K to  $0.427 \Omega \text{ cm}^2$  at 328 K. This observation suggests that hydrogen evolution reaction proceeds more readily at higher temperatures, which may be due to the greater electrocatalytic activity of hydride-forming electrodes at higher temperatures.

Apart from thermodynamic properties, an important criterion for the selection of a metal hydride system is the kinetics of hydrogen electroadsorption-desorption. This may be deduced from the value of the apparent exchange current density and polarization resistance, which are measures of the alloy's catalytic activity. The ohmic resistance,  $R_o$  is calculated by adding  $R_s$ ,  $R_1$  and  $R_2$ .  $R_{ct}$  and  $R_o$  decrease with increasing temperature. The decrease in  $R_{ct}$  implies a faster reaction rate at higher temperatures. This is reflected in the value of the exchange current density at different temperatures, as calculated by

$$i_o = \frac{RT}{nF} \left( \frac{1}{R_{ct}} \right) \quad (10)$$

where  $F$  is the Faraday constant. The exchange current densities vary between  $114.23 \text{ mA g}^{-1}$  at 303 K and  $458.00 \text{ mA g}^{-1}$  at 328 K (Fig. 12). The decrease of  $R_o$  may be explained by considering the conductivity of the electrolyte, which decreases with increasing temperature. It can be seen from Fig. 12 that the exchange current density increases with increasing temperature, which suggests

that the electrode reaction becomes more reversible at higher temperatures. Both exchange current density and diffusivity increase with temperature, which implies that the discharge capacity and charge-discharge efficiency should increase with increasing temperature. At high temperatures, however, metallic phases become oxidized, which decreases the hydrogen evolution reaction, discharge capacity and the charge-discharge efficiency. Raising the temperature also increases the activation enthalpy of the charge-transfer reaction.

#### 4. Conclusions

A lanthanum-rich metal hydride alloy  $\text{MmNi}_{3.03}\text{Si}_{0.85}\text{Co}_{0.60}\text{Mn}_{0.31}\text{Al}_{0.08}$  has been prepared as a hydrogen storage electrode and its electrochemical hydrogen absorption/desorption characteristics have been investigated. Changes in enthalpy and entropy associated with the reactions are calculated as  $-41.74 \text{ kJ mol}^{-1}$  and  $146.28 \text{ J mol}^{-1} \text{ K}^{-1}$ , respectively. It is found that the charge-transfer resistance decreases with increase in temperature. The exchange current density and diffusion coefficient are also shown to increase with temperature. It is concluded that capacity deterioration at elevated temperatures is associated with higher surface activity.

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