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Mathematical Model of a NiOOH/Metal Hydride Cell

Final Report

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by

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Summary

One of the objectives of our work on the nickel/metal hydride cell has been to develop a mathematical model of the performance of the cell. We have had three sources of funds for our work on the nickel/metal hydride system: ORD 93-F148100-100, LBL Contract DE-ACO3-78SF00098, Subcontract No 4614610 and BES DE-FGO5-93ER14382. This is a summary of our work to date based on these funding sources and is meant to be a Final Report for our BES project.

Mathematical model of the nickel/metal hydride cell depends on the kinetics, thermodynamics, and transport properties of the metal hydride electrode. Consequently, investigations were carried out to determine: (i) the exchange current density and the equilibrium potential as a function of hydrogen content in the electrode; (ii) the hydrogen diffusion coefficient in the bulk of the alloy; (iii) the hydrogen reaction rate order; (iv) the symmetry factor for hydrogen evolution reaction and (v) to determine the reaction mechanisms of the hydrogen charge and discharge processes including overcharge and overdischarge mechanism.

Investigations carried out at the Center of Electrochemical Engineering at USC have resulted in development of a mathematical model for the discharge performance of NiOOH-MH cell. The model can be used to study the effect of various parameters on predicted discharge curves. The solutions obtained using the model showed the expected decrease of charge utilization as the rate of discharge is increased. Increasing the particle size of the alloy and decreasing the diffusion coefficient of the hydrogen atoms in the hydride showed a similar effect on the discharge curves. The model simulations also show the critical role that the kinetic transport parameters play in the determining the overall shape of the predicted discharge curves for a metal-hydride electrode.¹

Porous electrode theory was applied to estimate the exchange current density, the polarization resistance, and symmetry factor for $\text{LaNi}_{4.27}\text{Sn}_{0.24}$ hydride electrode in alkaline solution.² It was found that conventional Tafel polarization method cannot be applied for the porous metal hydride system due to the presence of internal mass transfer effects and internal ohmic voltage drop of the electrode.

Potentiostatic and galvanostatic techniques were developed to determine the diffusion coefficient of hydrogen through MH electrodes in alkaline aqueous solutions.³ Using this technique the transport properties of $\text{La}_{0.65}\text{Ce}_{0.35}\text{Ni}_{3.55}\text{Co}_{0.75}\text{Mn}_{0.4}\text{Al}_{0.3}$ alloy were determined in alkaline solution.⁴

The electrochemical properties of MH electrodes such as the polarization resistance, exchange current density and electrode utilization were investigated at different alloy weights and binder contents using electrochemical techniques.⁵ It was found that at a low SOC the total resistance is independent of alloy weight while a high SOC is inversely proportional to the weight. An increase in binder content up to 5% reduces the polarization resistance. Further increase of the binder content resulted in increase of the resistance since the binder acted as an insulator. The sectorized utilization decreased by increasing the binder content and the electrode weight.

The objective of the project supported by LBL for the US DOE is to alleviate the problems associated with the pulverization, decomposition and passivation of the MH alloys. Investigations were carried out to optimize the metal hydride battery system by microencapsulating the alloy with thin coatings of palladium, copper or nickel using electroless plating technique. We also expected that microencapsulation of the alloy will increase the thermal conductivity of the alloy.

Electrochemical and transport properties of bare and copper plated $\text{LaNi}_{4.27}\text{Sn}_{0.24}$ electrodes were investigated in alkaline solutions.⁶ The exchange current density, polarization resistance, and equilibrium potential were determined as functions of the state of charge in the electrodes. By using a constant current discharge technique, the hydrogen diffusion coefficients in bare and coated $\text{LaNi}_{4.27}\text{Sn}_{0.24}$ were estimated. It was also found that copper coating on $\text{LaNi}_{4.27}\text{Sn}_{0.24}$ increases the exchange current density which is favorable for the battery operation. The copper coating was found to act as a microcurrent collector which facilitates the charge transfer reaction on the surface. Resistance of copper plated alloy was lower when compared with corresponding resistance estimated for the bare alloy for the same state of charge.

Experimental results showed that coating MH particles with Pd significantly decreases the electrode resistance and increases the electrode discharge capacity.⁷ The electrochemical impedance spectroscopy technique was used to determine various resistive components in the electrodes and electrolyte by fitting an equivalent circuit to the experimental data. The results indicated that the electrode made from the Pd-coated alloy had much less ohmic resistance (particle to particle resistance and current collector to electrode pellet resistance) when compared to the electrodes made from bare alloy. The discharge experiments indicated that Pd coating increases the discharge capacity of the bare alloy from 125 to 290 mAh/g.

The observed increase of the capacity of palladium coated alloy resulted from the fact that (i) the palladium coating serves as a barrier which protects the alloy from oxidation and (ii) the hydrogen entry efficiency in the bare alloy (defined as the ratio of the amount of hydrogen entering in bulk of the alloy to form hydride vs. the amount hydrogen produced) is much smaller compared with the hydrogen entry efficiency of palladium coated alloy. In other words, the hydrogen atoms on the bare surface tend to recombine and to form hydrogen molecules rather than to diffuse into the alloy and form hydrides.

The effect of temperature on the performance of $\text{LaNi}_{4.27}\text{Sn}_{0.24}$ was investigated in the temperature range of 0 to 50°C.⁸ The discharge capacities were measured for different discharge rates as a function of temperature. Linear polarization and electrochemical impedance spectroscopy were used to determine the total resistance, polarization and ohmic resistance of the electrodes. The apparent activation enthalpies were determined as a function of state of charge of the electrodes. The discharge capacity decreased by 6% when the temperature was increased from 25 to 50°C at 0.1C rate. At lower temperatures the effect was more significant as seen by the 25% decrease in capacity on lowering the temperature from 25 to 0°C. The loss in capacity at low temperatures is due to the high internal resistance of the electrode. At high temperatures the high equilibrium pressure of hydrogen results in lowering the capacity of the electrode. Further, the apparent activation enthalpy determined from the polarization resistance is an indicator of the relative rate of hydrogen absorption and reaction at the hydride alloy surface and electrolyte interface.

The investigations carried out at the Center of Electrochemical Engineering at USC have resulted in development of a relatively simple mathematical model for the discharge performance of NiOOH-MH cell.⁹ The model can be used to predict the electrode potential and the utilization of the electrodes at various discharge rates, electrode thicknesses and different alloy particle sizes.

As shown in Table 1, microencapsulation of the hydrogen storage alloys with electroless copper and palladium coatings has been found to improve the performance of the negative electrode. Electroless Pd, Cu and Ni plated on MH alloy powder increase the capacity and decrease the particle to particle resistance during cycling. Most important, our preliminary studies carried out to reduce the increase of the surface area during cycling of the electrode indicated a feasibility to develop an alloy pretreatment which will decrease the pulverization and prevent

corrosion of the alloy.

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Table 1. Summary of kinetic and diffusion parameters for different alloys

	symmetry factor, β		hydrogen reaction order	exchange current density, mA/g		$D/a^2 \times 10^5$, s^{-1}	Capacity, mAh/g	Percentage of theoretical capacity, mAh/g
	Tafel	Linear polarization		Linear polarization	AC impedance			
LaNi _{4.25} Al _{0.75}	0.38	0.54	0.3	4.39-18.0	25-560	1.10-1.47	122	122/394 =31%
Pd coated LaNi _{4.25} Al _{0.75}	0.35	0.53	0.2	19.5-22.7	70-100	—	295	295/394 =75%
LaNi _{4.27} Sn _{0.24}	0.34	0.53	0	4.90-19.8	6.8-86	0.82-2.40	270	270/351 =77%
Cu coated LaNi _{4.27} Sn _{0.24}	0.34	0.51	0.5	15.7-23.7	—	—	275	275/351 =78%
Ni coated LaNi _{4.27} Sn _{0.24}	0.20	0.50	—	8.4-17.6	—	6.3-9.6	334	316/351 =90%
La _{0.65} Ce _{0.35} Ni _{3.55} Co _{0.75} Mn _{0.4} Al _{0.3}	0.36	0.55	—	19.6-45.5	—	1.34	278	278/381 =73%

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