Hydrogen Measurement by Magnetic and Electronic Techniques in Ni-MH Battery and Hydrogen Storage Materials

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The ability of advanced hydrogen storage materials as well as nickel metal-hydride battery materials to absorb and desorb hydrogen has been measured using magnetic and electronic techniques. These techniques provide a unique sensing tool for available hydrogen in these materials. The ability of absorption and desorption of hydrogen has been correlated with the d-shell and f-shell electronic interactions with hydrogen as an electron donor. The tendency of the metallic materials, therefore, to dissolve hydrogen as well as to form hydride compounds has been established on the basis of donor and acceptor concepts. Experimental measurements include magnetic properties, electrical resistivity and thermoelectric [Seebeck] coefficient in different materials as a function of hydrogen content and temperature.

Ingress and egress diffusivities have been measured along with the thermal differential analyses of the uncharged and charged samples. Hydrogen Charging through gas phase at various temperatures for different lengths of time and at different pressures was accomplished. Cathodic charging was also used for bulk materials. Gas-chromatography was used to determine the content of hydrogen in samples as well as the weight change. The as-received samples were baked in argon environment at 400°C for 3 hours, before any charging of hydrogen gas. High temperature charging was avoided in these samples to prevent any structural change in the material.

Low temperature magnetic susceptibility measurements have been made on bulk and powdered samples in the baked and hydrogen charged conditions. The magnetic behavior of the material at 4.2K has been measured using a SQUID magnetometer. The observation of variation in magnetic properties as a function of temperature is indicative of the presence of diffusible untrapped hydrogen in the sample. The availability of diffusible hydrogen alters the ferromagnetic characteristics in the material. This study can, therefore, serve as a direct tool for the measurement of diffusible hydrogen (useful hydrogen in the battery for charging and discharging) availability as a function of temperature.

Magnetization hysteresis loops were measured with a transverse-field vibrating-sample magnetometer at room temperature with maximum applied fields of 6.0 T. Magnetization was computed as magnetic moment per unit mass of metal, not including hydrogen, and expressed in units of A m^2/kg (equivalent to emu/g). It was found that major hydrogen evolution peaks are at higher temperatures, indicating that some of the hydrogen is trapped even when the samples are charged at room temperature. The temperature for the major hydrogen release peak decreases as the charging pressure increases. A direct correlation was obtained between the amount of diffusible hydrogen and the measured ferromagnetic properties in the samples, as shown in Figure 1.

It has been shown that the presence of hydrogen can be detected in transition metal alloys by electrical resistivity change as well as the Seebeck Coefficient. The Seebeck coefficient decreases with an increase in hydrogen content. This phenomenon has also been explained on the basis of electronic interaction in these materials with hydrogen serving as an electron donor to the d-band. Figure 2 shows a typical plot of Seebeck measurement on a Ni-MH battery alloy. Compositionally, the effect of palladium on charging and discharging kinetics was also studied. The presence of diffusible hydrogen even at room temperature was observed by electronic measurements in Pd containing material.

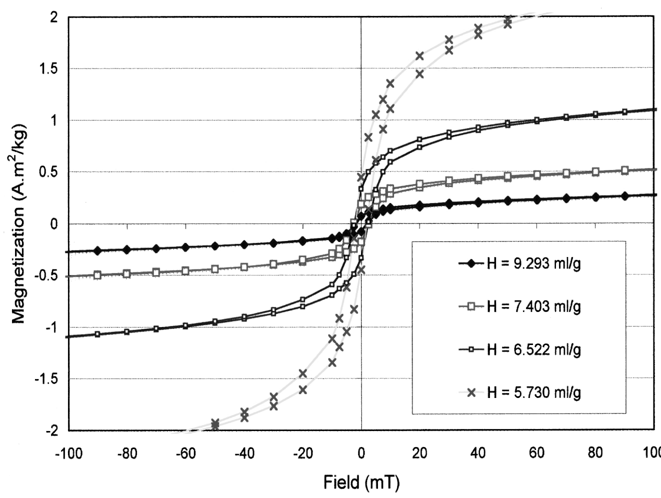

Figure 1: Evidence of ferromagnetism shown by the hysteresis in the magnetization curve for Alloy (La,Ce,Mg,Al)$(Ni,Mn)_5$.

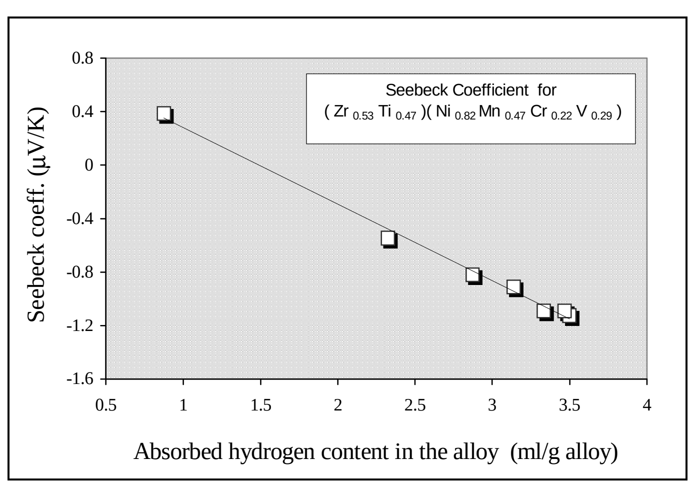

Figure 2: The variation of Seebeck coefficient with the amount of hydrogen stored in Alloy AB_2 $(Zr_{0.53}\ Ti_{0.47})$ $(Ni_{0.82}\ Mn_{0.47}\ Cr_{0.22}\ V_{0.29})$.