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Effect of measurement parameters on thermodynamic properties of La-based metal hydrides

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ABSTRACT

Pressure–concentration isotherms (PCIs) of $LaNi_{5-x}Al_x$ ($x = 0.3$ and 0.4) hydrides were measured using a volumetric method. Two important thermodynamic properties, enthalpy of formation (ΔH) and entropy of formation (ΔS), were calculated using the van't Hoff equation. The effects of the Al content on the hydrogen storage capacity, plateau pressure and thermodynamic properties were studied. Additionally, the effects of the charging/discharging pressure difference (ΔP_s) during each step of the absorption/desorption PCI measurement on the hydrogen storage capacity (wt%), equilibrium pressure (P_e), plateau slope, reaction enthalpy (ΔH) and entropy (ΔS) were studied for $LaNi_{4.6}Al_{0.4}$ hydride. All of these properties (P_e, ΔH, ΔS, etc.) showed a significant variation with ΔP_s. The effect of the temperature range on the estimation of the enthalpy of formation was investigated. It was observed that ΔH depends on the experimental temperature range.

1. Introduction

$LaNi_5$-based hydrides have been widely investigated as hydrogen storage materials because of their favourable hydrogen absorption/desorption characteristics under near-atmospheric conditions and their excellent kinetics [1]. The pressure–concentration isotherms (PCIs) of these materials exhibit a nearly flat plateau and low hysteresis. These materials find applications in many thermodynamic devices, such as heat pumps, heat transformers, air conditioners, and metal hydride compressors. The performance of these thermodynamic devices largely depends on the properties of the metal hydrides employed (hydrogen storage capacity, enthalpy of formation, reaction kinetics, equilibrium pressure, plateau slope, hysteresis, thermal conductivity, specific heat, etc.) as well as the operating conditions (supply pressure, temperature range, pressure ratio: $P_{delivery}/P_{supplied}$, etc.) [2]. Many studies [3–5] have been conducted to improve the thermodynamic, structural and kinetic properties of $LaNi_5$ hydrides by the partial substitution of one or more metals for nickel. Ni is typically replaced with Al, Cu, Cr, Sn, Fe, Mn, Co, Ga, Zn, etc. Among these elements Al, Co and Mn are commonly substituted for Ni, as they lead to a wide range of thermodynamic properties. The partial substitution of Al for Ni in $LaNi_5$ improves cycling performance and significantly reduces the plateau pressure. The plateau pressure decreases as the unit cell volume increases with an increase in Al content [3]. It has also been reported that the substitution of Al in $LaNi_5$ increases hydride stability [6]. The partial substitution of Mn for

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Ni reduces the plateau pressure without affecting the hydrogen storage capacity [7], and the partial substitution of Co for Ni improves cycling performance and enhances the anti-electro-oxidation ability of the final material. The unit cell volume increases with the partial substitution of M (M = Al, Mn and Co) in $LaNi_{4.7}M_{0.3}$ in the order of Co < Mn < Al, which is due to the increase in the atomic radii of the elements in the same order: 1.25 Å (Co) < 1.37 Å (Mn) < 1.43 Å (Al) [4].

The hydrogen diffusion behaviour of $LaNi_{5-x}Al_x$ (x = 0–1.5) hydride was studied using nuclear magnetic resonance [8], and the results showed that the activation energy increases with increasing aluminium content, with an analogous reduction in the apparent diffusion constant. The enthalpy of formation associated with aluminium substitution increases from −31.6 kJ/mol for $LaNi_5$ to −46 kJ/mol for $LaNi_4Al$ [9]. Muthukumar et al. [10] discussed the dependence of ΔH and ΔS on hydrogen concentration for $LaNi_5$ and $LaNi_{4.7}Al_{0.3}$ hydrides and developed a correlation between ΔH and hydrogen concentration.

Reliable thermodynamic property (PCI, ΔH, ΔS) data for metal hydrides are essential for the design and performance evaluation of thermodynamic devices. Although many investigations have been performed regarding the measurement of PCIs and thermodynamic properties of various metal hydrides, the effects of measurement parameters such as the charging/discharging pressure difference (ΔP_s) and applied temperature range on the estimation of thermodynamic properties have not been addressed in the literature. Two well-known La-based hydrides ($LaNi_{4.7}Al_{0.3}$ and $LaNi_{4.6}Al_{0.4}$) that are widely used in metal hydride-based engineering applications [11–14] were chosen as the focus of the present study. The PCIs of these materials were measured using the Sieverts method. The effects of the charging/discharging pressure difference and temperature range on the thermodynamic properties of $LaNi_{4.6}Al_{0.4}$ hydride during absorption and desorption were investigated.

2. Details of experimental setup

The experimental setup used to measure the PCIs of metal hydrides is illustrated in Fig. 1. The setup consists of pipelines for gas flow, which were fabricated using 1/4-inch seamless stainless steel tubes, medium-pressure bellow sealed valves (working pressure upto 100 bar) at different locations to control gas flow and stainless steel calibrated cylinders for storage of hydrogen gas. Piezoresistive pressure transducers P_1 and P_2 with an operating range of 0–100 bar were used to measure the supply pressure, and transducer P_3, with the same operating pressure range, was used to measure the metal hydride equilibrium pressure in the reactor. A differential pressure transducer (DP) with an operating range of 0–5 bar was installed to measure the pressure difference between a reference volume and the supply volume. A thermostatic bath with an operating temperature range of −50 to 250 °C (stability: ±0.01 °C) was used to maintain the reactor at constant temperature during absorption/desorption. 'K'-type thermocouples with an accuracy of ±0.1 °C and a time constant of 0.2 s were used to measure the temperature of hydrogen gas at different locations in the experimental setup (Fig. 1) and reaction bed (Fig. 2). Hydrogen gas of 99.99% purity was used for PCI measurements, and argon of 99.99% purity was used for volume measurement and in leak tests of the entire experimental setup. A vacuum pump was used to evacuate the system to a final pressure of 5×10^{-4} mbar, and a digital Pirani gauge with an accuracy of ±0.5% was used to measure the vacuum level.

For the measurement of PCIs, a perfectly sealed reactor was fabricated (Fig. 2). The reactor was composed of an SS-316 tube with an inner diameter of 12 mm and wall thickness of 2 mm. The reactor was designed to measure the PCIs of 10–20 g of metal hydride. Only 50–70% of the reactor volume was filled with metal hydride through the threaded end during PCI measurements. A PTFE washer with a threaded end cap was used to seal the reactor and make it leak-proof. There was a provision for connecting thermocouple at the top of the reactor. A 'K'-type thermocouple was connected through that provision, which continuously monitored the bed temperature. An SS tube was welded to allow for the supply of hydrogen with a filter assembly, which prevented the drawing-off of the metal hydride powder during desorption and evacuation. The tube ensured that the hydrogen was supplied from top of the reactor so that hydrogen could flow through the entire void volume of the reactor and diffuse uniformly throughout the volume. The gas pressure and temperature at different locations in the system were recorded continuously (every 2 second) using a data acquisition system. The experimental setup was divided into nine volumes as shown in Fig. 1. All of the volumes were accurately calculated and are listed in Fig. 1.

3. Experimental procedure

Before starting the PCI measurements, activation of the sample material was required for the vaporisation of the liquid and removal of gaseous substances and to weaken the oxide film from the surface of metal hydride particles. Hydride samples, each with a mass of 20 g, were used for PCI measurement. During activation, the sample material ($LaNi_{4.6}Al_{0.4}$/$LaNi_{4.7}Al_{0.3}$) was degassed at 10^{-3} mbar and 80 °C for several hours to avoid any obstruction in the activation of the material by environmental adsorbates. Then, $LaNi_{4.7}Al_{0.3}$ alloy was exposed to hydrogen at 30 bar and 80 °C (30 bar and 70 °C for $LaNi_{4.6}Al_{0.4}$) for 1 hour, allowed to cool to 20 °C and held in that state for 5 hours. The hydride temperature was then increased to 80 °C to desorb hydrogen. The activation process was repeated until the maximum hydrogen storage capacity and absorption/desorption rates were reached. Approximately 10–15 cycles were required for the complete activation of these materials.

3.1. *Absorption PCI measurement*

During the absorption PCI measurements, hydrogen was added to the metal powder in steps. At least one of the volumes V_6 and V_7 was used for this purpose by operating valves