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Kinetics of metal hydride electrodes when increasing the internal cell pressure

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Abstract

An external argon gas pressure was applied to an electrochemical system where metal hydride electrodes made of $LaNi_5$ and $MmNi_5$ were investigated at different pressures using various electrochemical techniques. One could expect that the distinctive properties of the same alloy were unchanged regardless of the external pressure, but the differences in various properties for $LaNi_5$ at different applied external pressures were notable. It is assumed that this is a result of an improved charge efficiency because of a reduced hydrogen evolution. An increase of the discharge capacity with increasing external pressure was observed. The results indicate that the overpotential for the discharge reaction increases as the hydrogen evolution rate during charging increases. This increase might either be a result of mechanical rearrangement of the surface during hydrogen evolution or blocking of electrode surface because of remaining hydrogen gas bubbles in the electrode structure after charging.

Keywords: Hydride; AB_5; Kinetics; High pressure

1. Introduction

Nickel metal hydride batteries are one of the most promising secondary batteries for extended automotive use. Understanding the processes governing the charge and discharge reactions in metal hydride electrodes is very important for improving the charge/discharge performance of such batteries.

1.1. Diffusion of hydrogen in metals

The diffusion in β-$LaNi_5$ is strongly dependent on the temperature and can be approximated by an Arrhenius type of equation [1]:

$$D = D_0 e^{-\frac{E_a}{RT}} \tag{1}$$

Here E_a is the activation energy for diffusion and D_0 is the diffusion coefficient of hydrogen at zero degrees (K). According to Buschow [2], the assumption of a single thermal activated diffusion process in the AB_5 type hydride is an oversimplification. The hydrogen motion in the $LaNi_5$ hydride is rather complicated and involves at least two different diffusion processes with activation energies differing by more than a factor of two. The diffusion process can be associated with the possible movement of hydrogen which involves the crossing of several potential wells of different depths. This is highlighted by the fact that in a $LaNi_5$ deuteride, the deuterium atoms occupy more than one interstitial lattice position. These lattice positions are interconnected by a multitude of different jump paths. Further experimental evidence suggest that the analysis of the diffusion related movements in terms of a simple Arrhenius type of activation is not sufficient and can be associated with the fact that for a number of hydrides, the activation energy, E_a, cannot be taken as temperature independent [2]. For a more detailed explanation, see also the paper by Richter et al. [3]. The activation energy for diffusion, i.e. diffusion energy barrier can furthermore be represented by:

$$E_{a,i} = E^* - E_\beta \tag{2}$$

Here E^* represents the absolute energy for the energy barrier and E_β the energy of the hydrogen site in the lattice. It can be assumed that in an alloy with a high plateau pressure, the hydrogen atom sites in the β phase lattice have a higher energy (E_β) than alloys with low plateau pressure.

If the absolute energy barrier for a diffusion mechanism is either constant or changing less than the energy of the hydrogen sites, the observed diffusion coefficient will increase when the plateau pressure is increased. This

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should give higher diffusion coefficients for the high plateau pressure A site substituted alloys, than for the low plateau pressure B site substituted alloys.

If the diffusion processes influence the overall reaction rates to a large extent, hydrogen will be depleted close to the surface of the metal hydride particle during discharge. This surface depletion is reflected by a more positive surface potential [4]. As a result, in the case of a potential cut off of the discharge process the potential during discharge will approach the cut off potential faster than the average hydrogen content indicates.

If n different thermally activated diffusion process mechanisms are assumed, the diffusion flux can then be described by [5]:

$$N_{\mathrm{H}} = \sum_{i=1}^{n} - D_i \nabla c_{\mathrm{H}} = - D_{\mathrm{e}} \nabla c_{\mathrm{H}} \qquad (3)$$

Here, D_{e} is the observed diffusion coefficient and c_{H} is the hydrogen concentration in the alloy. This indicates that an improvement of the diffusion rate for at least one of the rate contributing diffusion processes will improve the overall diffusion rate. The overall reaction rate may also be improved in the case of diffusion limitations in the system.

2. Experimental

Two alloys, $\mathrm{LaNi_5}$ and $\mathrm{La_{0.60}Ce_{0.04}Nd_{0.18}Pr_{0.18}Ni_5}$, were prepared by arc-melting using a water-cooled copper crucible, and using elements of high purity (La 99.99%, Johnson Matthey; Ce 99.12%, Treibacher; Pr 99.12%, Treibacher; Nd $<$99.7, Treibacher; Ni 99.95+, Johnson Matthey). The alloys were melted under argon for at least five times to ensure homogeneity. Both compositions were checked by X-ray diffraction (XRD) using a Nicolet-Stoe powder diffractometer (Cu Kα radiation). Pressure–composition isotherms (P–C–T) were measured at 298 K using a volumetric Sievert’s type apparatus. The absorption plateau pressures for $\mathrm{LaNi_5}$ and $\mathrm{La_{0.60}Ce_{0.04}Nd_{0.18}Pr_{0.18}Ni_5}$ were 3.4 and 9.0 bar whereas the desorption plateau pressures were 1.7 and 5.4 bar, respectively. For comparison a commercial type alloy with composition $\mathrm{LaNi_{3.4}Co_{1.2}Mn_{0.1}Al_{0.3}}$ (Shin Etsu) with a plateau pressure well below 1 bar at room temperature was also included in some measurements. Electrochemical results using arc melted alloys $\mathrm{La_{0.60}Ce_{0.18}Nd_{0.18}Pr_{0.04}Ni_5}$ and $\mathrm{La_{0.74}Ce_{0.04}Nd_{0.04}Pr_{0.18}Ni_{4.2}Al_{0.8}}$ were also included in some of the electrochemical measurements.

Electrodes were made using the hydrogen absorption alloy pressed together with fine copper particles to form an electrode. The active layer in the electrode was 0.20 g of hydrogen absorption alloy sieved to a distribution of sizes between 32 and 50 μm, mixed with 0.80 g of copper ($<$3 μm).

The electrolyte was 6 M KOH (Merck, p.a.) in deionized water. Charging was performed using currents of 300 mA/g, and discharging was carried out at the same rate to a cutoff voltage of −600 mV versus Hg/HgO. None of the electrodes were subject to any activation procedure or chemical pretreatment. For electrochemical cycling, the electrodes were unless otherwise noted charged with 300 mAh $\mathrm{g^{-1}}$. This is below the maximum storage capacity for $\mathrm{LaNi_5}$. For safety reasons the overcharging and consequently the hydrogen evolution reaction was minimized during charging. A three compartment cell with separate compartments for the hydride electrode, the platinum counter electrode and the Hg/HgO reference electrode was used. Simultaneous hydrogen evolution from the metal hydride electrode and oxygen evolution from the platinum counter electrode could in the presence of platinum be a possible security hazard especially at elevated pressures. A small flow of inert gas through the autoclave was maintained continuously during all measurements to remove hydrogen from the autoclave atmosphere.

3. Results and discussion

3.1. Cycle life

In Fig. 1 it is illustrated how the cycling properties are improved when a metal hydride electrode is pressurized during charge/discharge cycling.

From Fig. 1, it is seen that the discharge capacity is increasing with increasing external pressure. This can as such enhance the practical cycle life of the electrode. It is, however, important to note that this result is more significant for hydrogen storage alloys with a plateau pressure of more than one bar.

From the figure it is also observed that activation takes place faster when the external pressure is increased. The

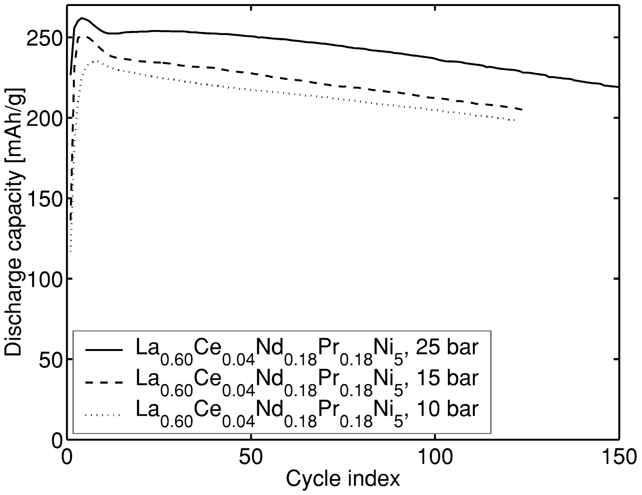

Fig. 1. Discharge capacity versus cycle index for different applied pressures for $\mathrm{La_{0.60}Ce_{0.04}Nd_{0.18}Pr_{0.18}Ni_5}$.

reason for this is assumed to be that the parasitic hydrogen evolution reaction during charge of the electrode is suppressed, resulting in a better charge efficiency.

3.2. High rate dischargeability

In Fig. 2, relative capacity discharged versus discharge current density for different alloy systems (Mm = $La_{0.60}Ce_{0.04}Nd_{0.18}Pr_{0.18}$) at different external pressures after 30 charge/discharge cycles are shown. A commercial AB_5 type alloy ($LaNi_{3.4}Co_{1.2}Mn_{0.1}Al_{0.3}$) is shown for reference. All electrodes were subjected to the same charge/discharge treatment prior to the measurements.

It is clearly observed from Fig. 2 that the high rate dischargeability increases considerably as the external pressure is increased. It is reasonable to assume that the rate of the hydrogen evolution was quite different for the different external pressures applied. For a fractured electrode surface formed by selective oxidation of elements (such as lanthanides) in the hydride forming alloy, even a small increase in the hydrogen evolution rate could mechanically rearrange the surface structure. Such a rearrangement would most likely smoothen the electrode surface, giving a smaller effective surface area. Hydrogen bubbles remaining in the electrode structure after charging could also block parts of the electrode surface. A smaller effective surface would give a higher overpotential for the same current, thus lowering the discharge capacity. The main reason for the increased discharge capacity is, however, assumed to be an increase of the charging efficiency because the hydrogen bubble formation is suppressed as the external pressure is increased.

An elevated battery pressure will also enable the use of metal hydride alloys with a high equivalent hydrogen pressure. These alloys will be less expensive since the cobalt content can be reduced substantially. Operating the battery under elevated pressure has as such the potential of lowering the total cost of the battery.

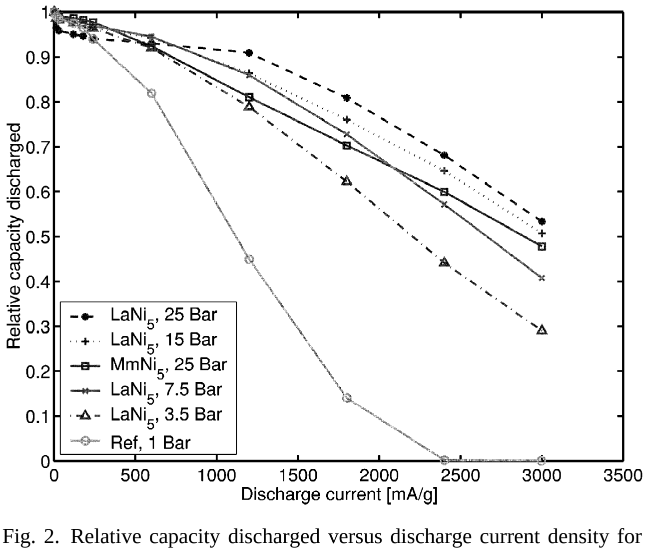

Fig. 2. Relative capacity discharged versus discharge current density for different alloy systems at different external pressures after 30 charge/discharge cycles. A commercial AB_5-type alloy ($LaNi_{3.4}Co_{1.2}Mn_{0.1}Al_{0.3}$) is shown for reference.

In addition, alloys with a high equivalent hydrogen pressure has a corresponding high open circuit voltage [4]. A high open circuit voltage is desirable for most applications. In a car propulsion battery, a higher open circuit voltage will give a better acceleration. The case is similar for electrical power tools.

3.3. Diffusion gradients

After the electrodes were discharged to the cutoff potential, there was a break with no external circuit current flow where the electrode rested unpolarized, equalizing of the hydrogen concentration in the electrode before the next charging. In Fig. 3 a plot of the potential versus time during this break is shown for different alloys after 50 charge/discharge cycles.

From the figure, it appears that the concentration gradients of hydrogen in the electrode are higher for B site substituted alloys in general. The B site substituted alloy containing cobalt had a markedly higher concentration gradient of hydrogen than all the other alloys. As reported previously in literature, alloys with high contents of especially cobalt, were reported to exhibit lower diffusion rates, and showed as such increased concentration gradients in the hydride alloy [6,7]. Cobalt prevents AB_5 type alloys from cracking during cycling. Alloys containing cobalt will therefore have a lower surface to volume ratio compared to alloys not containing cobalt and hence have a longer diffusion path for hydrogen in the metal hydride particles in the electrode assuming the same starting particle size. Since the surface to volume ratio is lower for alloys exhibiting less cracking, the current density during both charge and discharge will also be higher for the cobalt containing alloys. The surface overpotential both during charge and discharge will therefore be higher since the surface overpotential is proportional to the logarithm of the current density [5]. In addition, cobalt lowers the plateau pressure, lowering the energy of the hydrogen sites in the metal lattice. This can as such lower the hydrogen mobility in the system, indicating that the absolute energy barrier for the diffusion of hydrogen in the alloys is changing less than the energy of the hydrogen sites as the plateau pressure is increased.

Consequently, there are several processes giving the same effects, but it seems clear that high plateau pressure alloys are more efficiently discharged and with less hydrogen left in the electrode after discharge at constant current than low plateau pressure alloys. From Fig. 3, it can be observed that the difference in the hydrogen content in the alloys is equivalent to approximately 100 mV, which corresponds to roughly 30 times of equivalent hydrogen pressure [4].

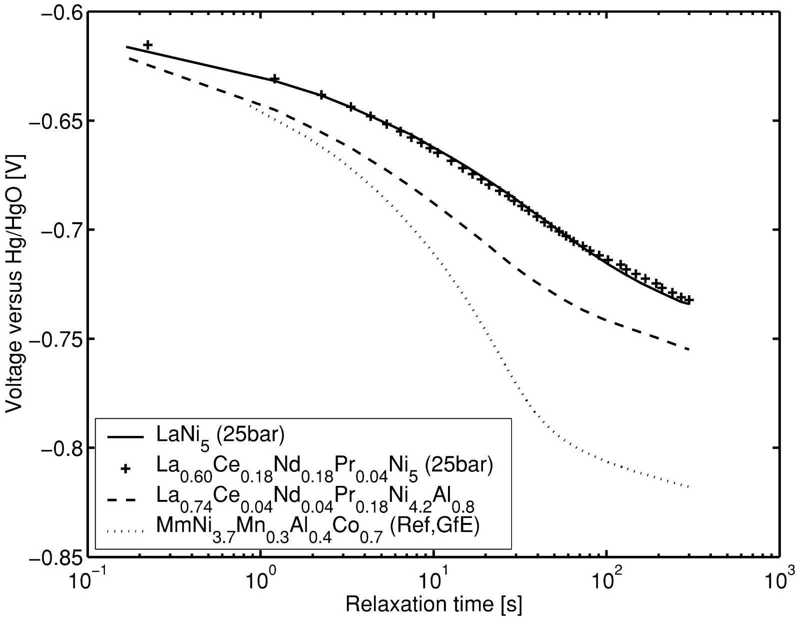

Fig. 3. Plot of the surface potential versus time during the break after discharge for three different arc-melted alloys and a commercial reference alloy (GfE) after 50 charge/discharge cycles.

4. Conclusions

An increase of the discharge capacity with increasing external pressure was observed. The main reason for the observed increase in the discharge capacity were assumed to be a better charge efficiency because of a reduction in the hydrogen evolution rate during charge as the external pressure was increased.

The results also indicate that nickel is a better catalyst than the mixture of B elements used in commercial nickel metal hydride batteries based on the AB_5-type hydrogen storage alloys. The results also indicated a higher rate of the hydrogen diffusion in AB_5-type alloys with pure nickel on B site than B site substituted alloys. Pressurized battery systems with a metal hydride electrode made of an alloy with a high plateau pressure are promising candidates for power applications requiring a high discharge capacity at high current densities.

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