Metal hydride electrodes: The importance of surface area

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ABSTRACT

A large active specific surface area is a very efficient way to improve charge/discharge rate capabilities of metal hydride electrodes. This can be promoted by washing oxidized, pre-hydrided AB_5 alloy particles in a hot KOH solution. This leads to magnetization of the alloy powder, making it possible to lift the powder with a simple permanent magnet, indicating that nickel liberated in the surface layer is essential for the improved kinetics.

The overpotential of each step in the discharge process is analysed in detail using both half cells and sealed cells. The electrode polarisation depends inversely on the current density per active area. Untreated and treated alloy powders have similar current densities per active area, but treated powder exhibits superior kinetics due to its larger surface area. A NiMH cell with a surface-treated alloy has very good rate capability, only limited by the kinetics of the Ni electrode.

At low overpotential, the electrochemical reaction gives the main contribution to the electrode polarisation. If the discharge current is increased to give an overpotential of more than 0.1 V, concentration polarisation will become important and a limiting factor at high current densities.

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1. Introduction

Development of practical rechargeable battery chemistries has been much in focus during the last decades. But development has in spite of substantial efforts been surprisingly slow. Can this have some fundamental reasons? The lead acid battery came in the mid-nineteen century. We saw NiCd and Edison batteries (NiFe) about half a century later. The American space programme created long life Nickel—Hydrogen batteries (Ni—H$_2$) with gaseous hydrogen anodes and nickel hydroxide cathodes. In the last decade of the twenties century NiMH batteries arrived followed a few years later by Li-ion batteries. Both had a large impact on the consumer size battery market. Li-batteries now dominate in mobile phones and lap-tops while NiMH is so far the main choice for hybrid electric vehicles and in the lower end of consumer size batteries for electric razors, tooth brushes etc. Recently Toyota also selected NiMH batteries for its first commercial hydrogen fuel-cell car Mirai. One can question why not so many useful rechargeable battery chemistries have evolved over time. In practical batteries non-zero currents create various temperature-, concentration-, voltage- and current

gradients. These gradients further a variety of unwanted, complicated and badly understood interconnected parasitic side reactions. All reactions, including the side reactions, have to be exactly reversed when shifting from discharge to charge. The inability to fully reverse all parasitic reactions is a prerequisite for creating a chaotic system, and this will tend to make rechargeable batteries unstable with respect to charging and discharging. To slow down the chaotic development during charge/discharging, it is important that the electrodes are made to work under as ideal conditions as possible. This puts high demand on the production quality with emphasis on uniformity of electrodes and separators with respect to thickness, porosity, purity etc.

Interestingly all of the battery chemistries above are based on aqueous electrolytes except Li-batteries, where the high cell voltage makes it impossible. A high voltage is an advantage for increasing capacity but aggravates stability problems. In 2012 the major American Li-battery producers filed for protection under Chapter 11 of the Bankruptcy Code as the high cost for meeting the quality demands, lead to prices that car producers could not afford [1].

The advantage with aqueous systems is the very high electrolyte conductivity. This helps to smooth out gradients in the electrolyte, making reaction conditions more "ideal". It relaxes quality demands on electrodes and separators and facilitates the making of robust cells at low cost. The NiMH chemistry is especially simple as

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it involves two solid state intercalation reactions of hydrogen in each electrode, where water molecules transport the hydrogen atoms between the electrodes. The amount of electrolyte is, however, constant, when the batteries are cycled, as water is not included in the overall cell reaction. This facilitates battery cell construction.

To obtain suitable hydrogen-metal bond strength, electropositive metals (A) are alloyed with more electronegative metals. (B) The most common alloy is the AB_5 system based on $LaNi_5$, but with A being a mixture of rare earth elements and B combines Ni, Mn, Co and Al to reach desired electrochemical properties.

The surface properties of the metal hydride (MH) particles in the MH-anode are further very important for a functional electrode. The surface must create a layer that protects the inner hydrogen storing part from corroding in the strong alkaline electrolyte. The layer must be dense and firmly fixed to the inner alloy, that it is protecting, similar to the aluminium oxide layer that protects easily corroded aluminium in common cooking ware. The surface must further be electric conductive and thin to allow hydrogen atoms to pass in and out of the particles. This protective surface is essentially formed during the first activations cycles of the cells, when the alloy particles decrepitate into smaller sizes whereby fresh surfaces are exposed to the corroding electrolyte. The electropositive rare earth elements are oxidized and nickel containing clusters are formed within this passivated surface oxide/hydroxide layer. These nickel containing clusters have been attributed to the catalytic surface properties that promote the making and breaking of oxygen-hydrogen bonds in water molecules as well as hydroxide ions [2]. Different surface treatments and grinding methods will give rise to different Ni-containing cluster sizes, which can be characterised by their magnetic properties [3,4].

So far have, however, only AB_5 and $AB_{3.3}$ systems containing at least some rare earth elements been able to reach acceptable properties in commercial production. The reason for this limitation is still unclear. In the present paper we want to describe how a surface treatment can lead to more "ideal reaction conditions" as it significantly enlarges the active surface and thus improves battery performance. NiMH batteries are usually made as sealed cells, with an often significant MH-electrode overcapacity to allow for the overcharge and overdischarge reactions in the gas phase to work properly at high currents. With a larger active surface the MH-overcapacity can be reduced, which is an effective way to reduce weight and increase total cell capacity. We have limited the study to the AB_5 system, but hopefully the results can be extended to other systems. Young and Nei recently reviewed a large number of possible battery alloys. Some use very available metals, making more sustainable solutions possible [5].

Electrochemical charge and discharge kinetics can vary greatly, depending on alloy composition and electrode fabrication method, but it is always considerably slower than the gas-phase hydrogen absorption and desorption kinetics, indicating that surface and not bulk properties dominate the reaction kinetics under electrochemical conditions. Efforts to improve its electrochemical charge and discharge kinetics, for example by surface treatments [6–9] or A- and B-element substitution [10–13] and by varying the stoichiometry [14,15] have been attempted by many groups.

2. Experimental

A standard "Hydralloy F" supplied by GfE, Nuernberg with composition $MmNi_{3.6}Co_{0.7}Mn_{0.4}Al_{0.3}$ was investigated in detail, both in half cells and in sub-C size cells over a wide temperature range and during extensive charge and discharge cycling.

This conventionally cast and heat treated alloy was further pulverized from an average particle size ≤ 85 micron by both

mechanical grinding and by a hydriding/dehydriding (HDH) procedure. This decrepitated the alloy was into a very fine powder with a particle size of a few microns. This was done by heating the alloy under hydrogen in a steel autoclave to 150 °C, thereafter the pressure was cycled between 50 bar and ambient for 20 times. A steel encapsulated thermocouple inserted into the powder bed was used to follow the reaction by recording the temperature swing caused by the HDH reaction. The fine powder was subsequently surface treated by carefully oxidizing a hydrided sample. The oxidized powder was then poured into a hot 90 °C, 6 M KOH solution for 1.5 h followed by washing in water and drying in vacuum. A pre-oxidation was made by cooling the autoclave to room temperature, thereafter air was admitted into the autoclave. By recording the temperature with the inserted thermocouple runaway reactions could be mitigated by stopping the air supply. This pre-oxidation reduced the risk of igniting the powder as it was further oxidized by carefully spreading it in fine layer on a steel plate, where it was kept exposed to air for about one week.

The active very fine powder was finally stored in a protective argon atmosphere. We interpreted that the surface treatment created a nickel enriched surface, as the powder became so magnetic, that it could be lifted by a permanent magnet.

The development of this pre-treatment of the alloy powder was inspired by a preliminary investigation of the possibility to recover battery alloys from spent batteries, which had been cycled with 600 deep discharge cycles. In a post mortem analysis by making new half-cell electrodes of the old MH-electrodes, we found a capacity drop of about 30%. To find out if the capacity decrease was due to surface poisoning or loss of alloy due to corrosion, we tried to recover the surface by boiling the spent hydride in a 6 M KOH solution. This has been suggested to be an effective surface treatment to enhance cycle life of alloy powders in batteries [6]. This resulted in marginally recovering some capacity, but more surprisingly we found a dramatic increase of the charge/discharge kinetics.

To obtain this increase also with pristine alloy we tried to oxidize and boil alloy powder that had been finely ground or decrepitated by hydriding and dehydriding cycles. None of these attempts were successful until we tried to oxidize and boil pre-hydrided alloy samples. What role the presence of hydrogen has in the process is still unclear.

Half-cell tests of the electrodes were made by mixing one part of alloy powder (0.15 g) with three parts of copper powder (200 mesh). The mixture was compacted in a tablet press at 4 tons to pellets with 1 cm diameter. Pellets were folded in a nickel net (100 mesh) and pressed again at 4 tons. A nickel wire was spot-welded to the nickel net for electric connection. A 6 M KOH electrolyte was used in the half-cell test. After 20 charge/discharge activation cycles, the discharge capacity at different currents was measured for a fully charged electrode. The cut-off potential of the hydride electrode was set to −0.6 V with respect to a Hg/HgO reference electrode. In order to study changes in rate capability during cycling, this measurement was repeated after each 50 cycles for a selected numbers of electrodes. During cycle-life testing, the electrodes were cycled by charging for 90 min at 200 mA g^{-1} and discharging for 70 min at 200 mA g^{-1}. The discharge rate capability of an electrode with surface-treated alloy was tested at different temperatures. The charge rate capability was characterised by charging the electrode, at different currents, to 100% and 90% of maximum capacity. Then the discharge capacity was measured at a 100 mA/g rate.

The alloy was also evaluated in sub-C sized cells, where both electrodes were made by a dry powder method [16]. The batteries contained about 15 g of alloy powder and 6 g of a 6 M KOH + 1 M LiOH electrolyte. The nominal capacity of the cells was about 2.3 Ah. The cells were activated by 0.1 C charging for 15 h and 0.2 C