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Low temperature hydrogenation properties of platinum group metal treated, nickel metal hydride electrode alloy

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Abstract

Nickel metal hydride batteries are now an established technology, being used in a wide range of applications. One problem that has been identified with the technology is the poor high rate capability of these batteries, and therefore in a number of circumstances nickel cadmium batteries are still the preferred energy source. One option to resolve this problem has been to surface treat the materials with platinum group metals. This treatment produces cells that show great promise in applications such as the power tool, industrial and automotive markets. The current work describes the surface treatment of metal hydride electrode alloys with a wider variety of platinum metal combinations to assess the rate performance of these materials at ambient and near-zero temperatures. It is observed that the treatment improves the activity of the cells at low temperatures, supporting the view that the surface energy of the electrode alloy is a strong contender as the rate-determining feature of these materials. In addition to this conclusion, the data suggest that these cells would withstand the harsh constraints when used as an automotive starter battery.

Keywords: Electrodes; Platinum group metal; Low temperature; Kinetics

1. Introduction

Nickel metal hydride (NiMH) battery technology has the potential to enter the entire secondary battery market. The properties and cost of the technology enable NiMH cells to be used in a wide range of applications, from the standard size batteries for portable electronic equipment as well as mobile telephones to the higher value products such as power packs for portable powertools and automotive batteries [1]. The properties of the metal hydride electrode component are key to some of these technologies. Past work by the above authors has shown that surface treatment with a variety of platinum group metals (PGMs) produces electrodes with high efficiencies in charging and discharging, with the alloy being stable in oxidising environments for up to 6 weeks [2]. Further work has shown that the treatment can provide batteries suitable for high power applications [3].

Other methods of surface modification range from fluorination treatment, treatment with a variety of metal or metal oxides, or hot alkaline treatment [4–10]. Generally, none of these treatments are viable in a production environment as the cost/performance benefit of these technologies is too low. However, the use of PGMs may indeed give the desired properties at a reasonable industrial cost.

Automotive batteries are one such application for this technology as automotive companies are soon to increase the battery rating of most vehicles from 12 to 36 or 48 V. Therefore, the ability of the battery to charge and discharge at sub zero temperatures is an important property to quantify if this technology is to be useful in this market segment.

In the present paper the low temperature properties of these materials will be presented. In addition to the standard treatments, the effects of the surface treatment with platinum will be presented.

2. Experimental

The pseudo-mischmetal alloy was supplied by Honeywell (formerly Johnson Matthey Rare Earth Products) of the composition $La_{0.9}Pr_{0.05}Nd_{0.05}Al_{0.3}Mn_{0.4}Co_{0.65}Ni_{3.5}$. The alloy was pulverised by the hydrogen decrepitation

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Table 1
XPS data of the coated metal hydride powders (at%)

Element	Binding energy (eV)	Pd coated alloy	Ru coated alloy	Pt coated alloy	Pd/Ru coated alloy	Ru/Pd coated alloy	Pt/Ru coated alloy
Calcium	~347.5	0	0	0	0	0.6	0
Carbon	284.6–284.9	49.7	62.7	61.1	62.3	43.3	56.2
Lanthanum	835.0–835.6	1.1	0.47	0.8	0.6	0.6	0.6
Nickel	855.1–873.9	1.2	0.4	Trace	1.6	0.6	Trace
Oxygen	530.0–533.5	39.5	27.1	28.7	31.7	40.2	31.9
Palladium	334.9–337.1	8.6	0	0	3.3	0.6	0
Platinum	70.9–73.4	0	0	9.4	0	0	1.1
Ruthenium	280.2–283.3	0	9.4	0	0.6	14.1	10.1

process in preparation for the chemical deposition of the PGMs. The chemical coating process involved an aqueous solution of the PGM, reduced using hydrazine. Portions of the alloy were then coated with ~4 wt.% of platinum, palladium and ruthenium. In addition to the single coatings, combination coatings of palladium/ruthenium, ruthenium/palladium and platinum/ruthenium were prepared (~8 wt.% total).

The alloy was examined by a Phillips EM 400T TEM to assess the morphology and metal distribution of the deposited metals.

Portions of the uncoated and coated alloy were assessed at 298 K for hydrogen capacity and kinetic properties using a Hiden IGA-001 gravimetric balance. In addition to this the samples were cooled to 273 K and the tests repeated to examine the effect temperature has on these materials.

The samples were then prepared for electrochemical evaluation. The alloys were mixed with 30 wt.% nickel (99.99% purity, Aldrich) and 4 g of the alloy/nickel mix were pressed into an electrode of 26-mm diameter. The electrode was then pressed into nickel foam. These electrodes were used for cyclic voltammetry.

3. Results and discussion

After the preparation of the coated powders, the surface properties of the powders were examined by X-ray photon spectroscopy. The results of the studies are presented in Table 1. It was observed that the single coatings contain the precious metal, with oxygen, calcium and carbon being present as impurities. It is seen that all the precious metals are in their zero oxidation state — therefore metallic and that the platinum and the palladium appear to promote the reduction of the ruthenium during the reaction, as the concentrations of the initial deposited metal reduce when the second coating is assessed.

A representative TEM image of the coated powders is shown in Fig. 1. The metals are present in a discontinuous coating over the whole particle, but show preferential deposition on some of the faces of each particle.

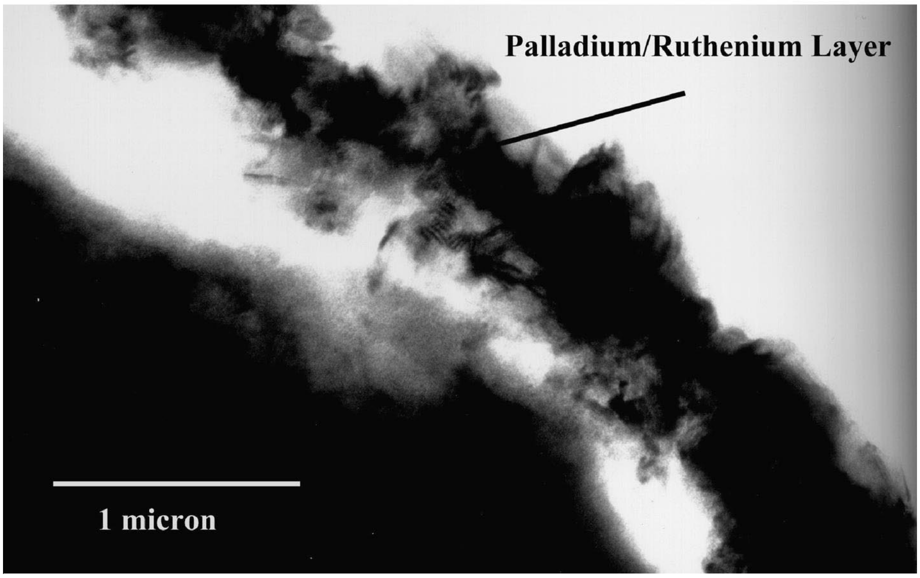

Fig. 1. TEM image of a palladium/ruthenium coated lanthanum nickel alloy.

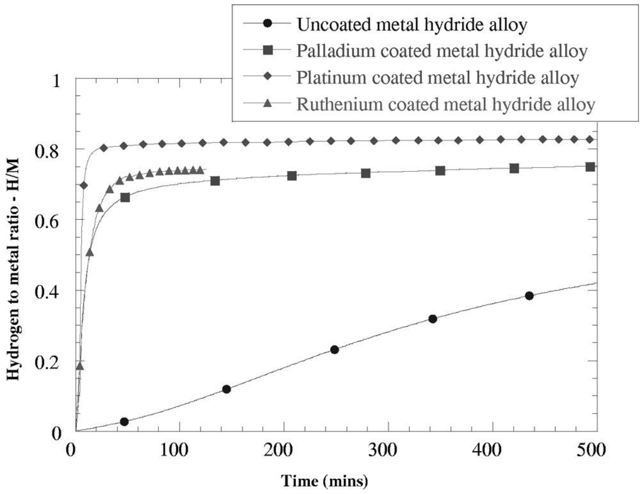

Fig. 2. Gravimetric analysis of the single PGM coated alloys, 1 bar hydrogen, 298 K.

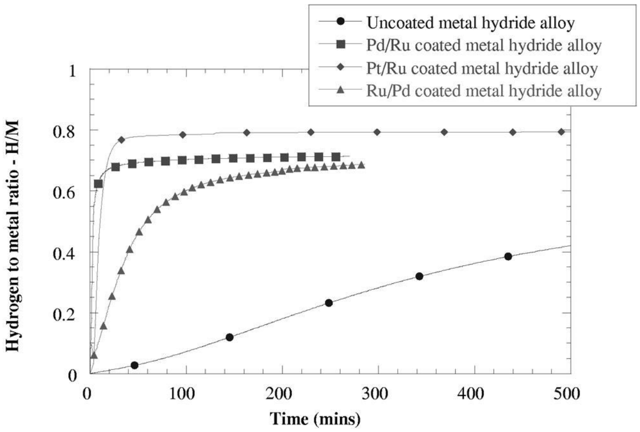

Fig. 4. Gravimetric analysis of the combination PGM coated alloys, 1 bar hydrogen, 298 K.

The powders were then assessed by gravimetric analysis for hydrogenation properties. The powders were assessed at room temperature, nominally 298 K, and subsequently at 273 K. The absorption kinetics were measured using a constant pressure of 1 bar hydrogen, and the desorption kinetics were measured when the powders were put under vacuum. The average mass of each sample under test was ~50 mg. Fig. 2 shows the room temperature absorption kinetics of the single coated powders, including a trace of the uncoated alloy as reference. It is observed that the rates of hydrogenation for the coated powders are very rapid under these test conditions; with the platinum coated powders being the best of the PGM coated alloys. Also confirmed (as shown in past work) is that surface coatings of ruthenium produce excellent absorption kinetics. Fig. 3 shows the low temperature absorption kinetics of the single coated powders. It is observed that the drop in temperature has a large impact on the kinetics of the platinum coated alloy, while the ruthenium maintains the best kinetic properties.

Figs. 4 and 5 show the absorption properties of the combination-coated powders. Both palladium/ruthenium and platinum/ruthenium show good absorption kinetics, while the ruthenium/palladium coated alloy has significantly slower kinetics. It appears that during the deposition process the palladium and platinum nucleated on active absorption sites, with the ruthenium nucleating on these sites, while ruthenium seems to deposit differently under the plating conditions employed.

It is clear that PGMs enhance the kinetic properties of metal hydrides and that hydrogen sorption of these materials can occur at low temperatures with high rate charging/discharging capabilities. The best material is the palladium/ruthenium coated material.

The electrochemical response of the powders when formed into an electrode was assessed. The charging currents of the electrodes were measured at 298 and 273 K, as the electrodes were held at voltages approaching and

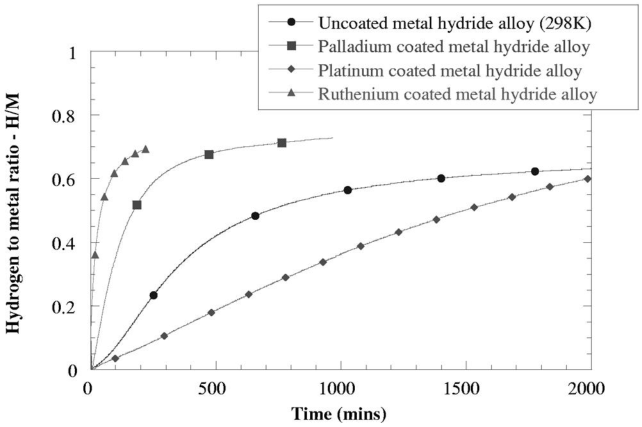

Fig. 3. Gravimetric analysis of the single PGM coated alloys, 1 bar hydrogen, 273 K.

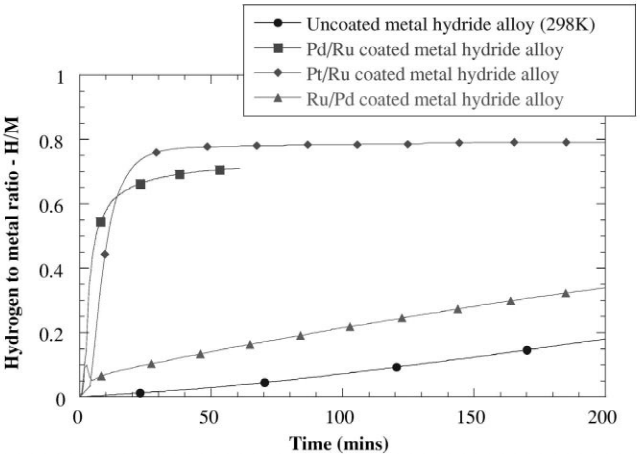

Fig. 5. Gravimetric analysis of the combination PGM coated alloys, 1 bar hydrogen, 273 K.

Table 2
Electrochemical charging of PGM coated electrodes at 298 and 273 K (current in mA)

Temperature (K)	Charging voltage (mV) versus Hg/HgO reference electrode	Uncoated alloy	Pd coated alloy	Ru coated alloy	Pt coated alloy	Pd/Ru coated alloy	Ru/Pd coated alloy	Pt/Ru coated alloy
298	−1000	30	141	162	265	221	200	267
	−1100	162	260	298	452	380	330	449
	−1200	315	396	465	630	558	472	628
	−1300	510	555	625	770	721	589	798
273	−1000	16	107	116	200	142	151	164
	−1100	100	194	230	377	225	241	283
	−1200	220	300	309	492	348	324	403
	−1300	340	500	410	612	486	364	510

past the hydrogen evolution potential. Table 2 shows the charging currents of the alloy electrodes at 298 and 273 K, respectively. It is observed that the platinum coated electrode evolves the highest currents over the ruthenium, palladium and uncoated alloy electrodes. For the combination-coated electrodes, it is observed that the platinum/ruthenium electrode again shows the highest current.

The difference in the response of these materials between the solid–gas reactions and the electrochemistry can possibly be explained in that palladium/ruthenium has the best hydrogen transfer properties while the hydrogen oxidation reaction is improved using the platinum/ruthenium combination. Although more work is required to investigate the difference between the solid–gas and electrochemical reaction, both modes of measurement show enhanced kinetic properties.

4. Conclusions

The PGM coated metal hydride powders have been shown to enhance the kinetics of the metal hydride powders. At low temperatures where the performance of such materials is usually affected, it is observed that the activity is maintained, with the best coating being palladium/ruthenium. The electrochemical measurements show that platinum is better than palladium.

Therefore the use of PGM coated metal hydrides in storage, fuel cell, heat pump and battery applications has the potential of improving these systems for efficient use.

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