Effect of carbon support on the kinetic behaviour of a metal hydride electrode

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ABSTRACT

The possibility to improve the electrochemical behaviour of AB_5-alloy commercial electrodes was studied using different carbons as support, such as carbon blacks and a selection of commercial and in-lab synthesised carbon nanotubes. The carbons selected for this work present different morphologies (i.e., spherical and tubular). Furthermore, they also present a variation of the porous structure and subsequent surface area, which are also going to influence their further electrochemical behaviour. Carbon samples were texturally characterised by the adsorption–desorption of N_2 and CO_2 at 77 and 273 K, respectively. The carbon structure was analysed by XRD, Raman, TEM, and the chemistry of the samples was also characterised by elemental analysis. The charge and discharge techniques, cyclic voltammetry, rate capability and linear polarisation were used for the electrochemical characterisation of the electrodes studied. The electrochemical behaviour of all the samples was related to their morphological, textural and chemical properties. The results show that there is a clear influence of the nature of the carbon support on the hydriding/dehydriding reaction of the alloy, and in the case of active carbons the kinetics decreases with the increase of the surface area of the carbon support.

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1. Introduction

As one of the most popular commercial rechargeable batteries, nickel–metal hydride (Ni/MH) batteries have been marketed in Japan since the 1990s and are currently applied extensively in many fields such as portable electronic devices, electric tools and electric vehicles/hybrid electric vehicles, etc. Ni/MH batteries have higher gravimetric and volumetric energy density than conventional Ni–Cd batteries by approximately 30–40% for cells of the same size and they are more environmentally friendly [1–6].

The performance of a Ni/MH battery, such as its capacity, charge–discharge cycling life and rate capability, strongly depends on the characteristics of the metal hydride anode. It is well known that many metals and alloys reversibly absorb large amounts of hydrogen to form metal hydrides, and the hydrogen volumetric density in some hydride phases is higher than that of liquid hydrogen. Most of the binary hydrides (metal–hydrogen phases) cannot be directly used for hydrogen storage because the forming hydrides are too stable to desorb hydrogen under the appropriate conditions. However, hydrogen reacts with some multi-component alloys easily and reversibly, and the thermodynamic properties of such systems allow them to be used in applications such as hydrogen reservoirs and energy systems.

In a previous paper [7], the capacities and cycle life of the electrodes containing AB_2 or AB_5 alloys were improved by the optimisation of the composition and structures of electrodes using electronic conductor–binder materials (additives), such as teflonised carbons and Cu powder. The adhesive nature of these binder materials, as well as their relatively high electronic conductivities, provides advantages for the fabrication of flexible three-dimensional networks with intimate and stable contacts between the active alloy particles. Aymard et al. [8] demonstrated that the addition of graphite to $LaNi_5$-based alloy during the ball-milling results in a composite electrode with improved electrochemical performance. This enhancement was mainly explained on the basis of a reduction of the alloy surface oxides with reactive graphite particles. These studies demonstrate that the effect of carbon on the properties of hydrogen alloys is complex depending on various parameters such a porosity, ordering and electrical conductivity of the carbon material.

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In recently published papers [9–10] using the same alloys as in this work, the authors showed the high capacity and good kinetics of AB$_5$-type alloys in the hydriding/dehydriding reactions. These reactions occur on the metal particle surfaces, but the influence of the structural properties of the electrode, such as porosity, active area and electrode length, affects the response of these electrodes. Their constant current discharge response was simulated by a physicochemical model based on the classical theory of flooded porous electrodes. The effect of structural parameters, determined by the compaction pressure during electrode preparation, on the discharge potential/time curves was analysed. Working electrodes were prepared with Carbon Vulcan, PTFE and AB$_5$-type alloy. Using a helium pycnometry method, the dependence of the electrode porosity and volume on pressure was derived. The dependence of the active area per unit volume on pressure was calculated by means of a model taking into account plastic deformation and fragmentation effects. This analysis predicts a maximum in active area and porosity at low pressures, leading to an improvement in discharge performance and rate capability with decreasing compaction pressure.

However, there are few papers where the effect of the type of carbon material is studied and related to its different properties in the discharge capacity of the negative electrode in Ni/MH batteries. In this work, the effect of the type, porosity and ordering of different carbon materials on the electrochemical performance of the negative electrode of Ni/MH batteries was studied.

2. Experimental

2.1. Materials

A commercial AB$_5$-type alloy with the nominal composition LmNi$_{4.1}$Co$_{0.4}$Mn$_{0.4}$Al$_{0.3}$ was used. A wide variety of carbon materials were employed as support: (i) commercially available carbon black, Vulcan XC72R; (ii) high specific surface area carbon commercially available from Chemopetrol (Czech Republic), Chezacarb A; (iii) commercially available high-grade single-wall carbon nanotubes, SWNT-N, and multi-wall carbon nanotubes, MWNT-N, from Nanoledge Europe; commercially available multi-wall carbon nanotubes from Ukrainian Advanced Technologies Ltd., MWNT-Ukr; and (iv) in-lab multi-wall carbon nanotubes synthesised in Argentina, MWNT-A.

2.2. Support characterisation

The textural characterisation of the samples was performed by the physical adsorption of N$_2$ at 77 K and CO$_2$ at 273 K in a TriStar 3000 from Micromeritics. The use of carbon dioxide adsorption at 273 K for the textural characterisation of narrow micropores has already been established as an effective procedure [11] because carbon dioxide adsorption occurs in pores smaller than 0.7 nm, and nitrogen does not easily enter such small pores. Thus, a combination of nitrogen and carbon dioxide adsorption isotherm data provides complementary and relevant information about the full micropore range. The Dubinin–Radushkevich (DR) method [12] was applied to the carbon dioxide and nitrogen adsorption isotherms in order to obtain the narrow micropore volume, $V_{\text{DUB-CO}_2}$, and the wider micropore volume, $V_{\text{DUB-N}_2}$, respectively. By taking these micropore volumes and the mean pore size (L) from the Stoeckli equation [13], the micropore surface can be calculated ($S_{\text{mic}} = (2V_{\text{mic}})/L$). The BET surface area was also evaluated from the nitrogen adsorption isotherms [14].

The morphology and structure of the samples was evaluated by X-ray diffraction (XRD), Raman spectroscopy and transmission
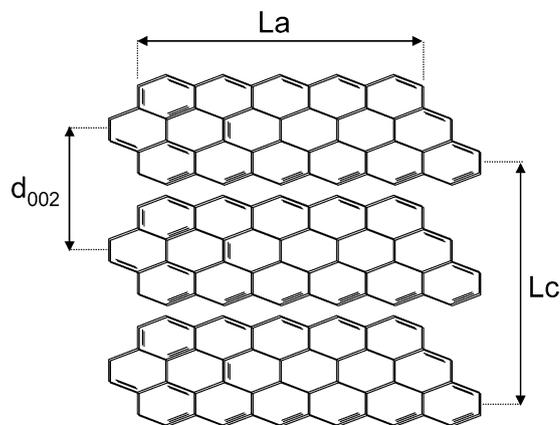

Fig. 1. Model of local graphite structure and structural parameters determined by XRD.

electron microscopy (TEM). The X-ray diffractograms were collected by a Bruker D8 Advance diffractometer equipped with a Göbel mirror and a Cu Kα radiation tube ($\lambda = 0.15406$ nm). Scherrer equation [15] was used to calculate different crystallographic parameters (i.e., L_c, d_{002} and L_a). L_c, the layer dimension perpendicular to the carbon basal plane, and d_{002}, the interlayer distance (see Fig. 1) were obtained from the (0 0 2) diffraction. L_a, the layer dimension parallel to the basal plane, was calculated by the (1 0 1) diffraction. Raman characterisation was performed with a labRam HRUV from JYV-Jobin Yvon, using an Ar laser CDPS532M-DPSS at 24.3 mW; and TEM evaluations were performed in a JEOL JEM-2000 EX II.

2.3. Electrochemical testing

In order to study their electrochemical behaviour, the metal hydride electrodes were made by mixing 75 mg of alloy powder with 75 mg of different carbon samples teflonised with 33 wt% PTFE. The mixture was then pressed onto nickel mesh under a pressure of 2000 kg/cm^2 inside a 1 cm^2-section cylindrical die. A three-electrode cell containing 6 M KOH at 298 K was used to determine the electrochemical characteristics of the alloy electrodes. The working electrode was placed between two counter-electrodes of large surface area made of sintered NiOOH. The electric potentials were measured against a Hg/HgO reference electrode. The discharge capacity was determined as a function of the charge–discharge cycling number. To do this, a fixed cathodic current of 10 mA was applied for 8000 s in order to ensure the full charge of the electrode. The discharge was conducted at 5 mA until the cut-off potential (−0.6 V versus Hg/HgO) was reached. The high rate discharge (HRD) was evaluated by measuring the discharge capacity for increasing discharge currents up to 1.5 until 45 mA.

The exchange current was determined by the linear polarisation method by taking the electrode to different states of charge (25%, 50%, 75% and 100% SOC). The potential was allowed to stabilise for 10 min at open circuit and then a potential scan at ±10 mV was performed at a rate of 0.1 mV/s. For cyclic voltammetry a scan rate of 1 mV/s between −0.6 and −1.2 V was used.

3. Results and discussion

3.1. Support characterisation

Differences in the morphologies and structures of the series of samples evaluated can be easily observed in the TEM images presented in Fig. 2. It can be observed that the three samples of