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Ni-Doped Carbons as a Carbon Support for Metal Hydride Electrodes[†]

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In-lab synthesized Ni-doped carbon xerogels were used as a carbon support to study the possibility to improve the electrochemical behavior of AB_5-type alloy electrodes for nickel/metal hydride rechargeable batteries. The carbons used for this work were synthesized by polymerization of resorcinol and formaldehyde. These carbon supports were mixed with an AB_5-type alloy. For the electrochemical characterization of the electrodes, charge and discharge techniques, a high rate of discharge, and electrochemical impedance spectroscopy were used. Results show that this kind of carbon could be used as a support for hydrogen storage electrodes with good electrochemical behavior and kinetic response.

Introduction

Rechargeable nickel/metal hydride (Ni/MH) batteries have been popularly marketed since 1990. Ni/MH batteries are now extensively used in portable electronic devices and hybrid electric vehicles. In comparison to conventional Ni/Cd batteries of the same size, Ni/MH batteries have 30–40% higher gravimetric and volumetric energy densities. Ni/MH batteries employ this type of metal alloy electrode for advanced electricity storage systems in electric vehicles.[1–7] Electrochemical hydrogen storage, the entrapment of electrochemically generated hydrogen, such as in metal-hydride batteries, has been reviewed elsewhere.[8] The Ni/MH cells are encountering competition from Li-ion cells or Li-polymer cells in the applications of small electronic devices, such as mobile phones, lap-top computers, small power tools, etc. Therefore, how to reduce the cost of the rechargeable Ni/MH batteries and improve battery performance is significantly important.[9]

The performance of a Ni/MH battery, such as its capacity, charge–discharge cycling life, and rate capability, strongly depends upon 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 publications,[10,11] the capacities and cycle life of the electrodes containing AB_2 or AB_5 alloys were improved by the optimization of the composition and structures of electrodes using as a support electronic conductor-binder materials (additives), like different carbon materials, such as carbon blacks and a selection of commercial and in-lab synthesized carbon nanotubes and teflonized carbons.

The adhesive nature of these binder materials as well as their relative high electronic conductivities provide advantages for the fabrication of flexible three-dimensional networks with intimate and stable contacts between the active alloy particles. The effect of carbon on the properties of hydrogen alloys is complex depending upon various parameters, such as porosity, ordering, and electrical conductivity of the carbon material. However, there are few papers where the effect of the type of carbon material is studied and related

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to its different properties in the discharge capacity of the negative electrode in Ni/MH batteries.

Carbon gels are novel porous materials that have received considerable attention in the literature over the past decade.[12−17] The first carbon gel was synthesized by Pekala in 1989 from the polycondensation of resorcinol and formaldehyde in aqueous solution.[18] The main particularity of this type of material is that the textural (meso- and macroporosity) and density properties can be controlled using different synthesis protocols or different drying and pyrolisis conditions, making it possible to obtain a wide variety of materials with different properties. The size of the meso-/macropores is mainly regulated by the pH of the solution of the precursor. In addition, the chemical activation of these materials with metallic hydroxides makes it possible to increase and control the microporosity without modifying the meso-/macroporosity formed during the synthesis of the material. This is an important feature because of the suitability of microporous materials with a narrow micropore size distribution for hydrogen adsorption.[17−22] For this reason, this kind of carbon material could be used for a wide range of applications.[19] In addition, another advantage is that they are extremely pure materials and the conductivity is quite high, making possible their use as electrodes in different electrochemical applications. Finally, another attractive characteristic of these materials is that they can be prepared in different forms, i.e., as powder, monoliths, microbeads, etc., always with high packing densities.[23]

Recently, some works have shown that the presence of certain metals (Ni, Co, Pt, etc.) improves the hydrogen storage capacity of carbon materials via a spillover effect.[24−29] The spillover of hydrogen involves a transfer of electrons to acceptors within the support; this process not only modifies the chemical nature of the support but may also activate a previously inactive material and/or induce subsequent hydrogen physisorption.[30] Metal-doped carbon gels can be prepared by the impregnation method,[20] introducing the metal during the synthesis[21] and by ion-exchange processes.[22] These materials, therefore, also have a great potential as catalysts.[31,32] For all of this, they are suitable carbon materials to study the effect of Ni incorporation on the discharge capacity of the negative electrode in Ni/MH batteries.

In this work, the effect of in-lab synthesized Ni-doped carbons (i.e., carbon xerogels) were used as a carbon support to study the possibility to improve the electrochemical behavior of AB_5-type alloy electrodes for Ni/MH rechargeable batteries.

Experimental Section

Aqueous organic gels were synthesized by polycondensation of resorcinol (R) with formaldehyde (F) in water (W) with NaOH as the alkaline agent, whose role is to settle the starting pH of the solution of the precursor. All of the gels were synthesized in the following conditions: the R/F molar ratio was chosen equal to the stoichiometric value (0.5), and the dilution ratio, D (i.e., the total solvent/reactants molar ratio), was fixed at 5.7. Note that the "total solvent" includes added deionized water and water and methanol contained in the formaldehyde solution, while "reactants" refer to resorcinol and formaldehyde. Methanol is a stabilizer that prevents the formaldehyde molecules from undergoing polymerization during storage. The starting pH of the solution was adjusted to 6.8. Resorcinol (VWR International, 99%), R, and sodium carbonate (UCB, 99.5%), C, were first solubilized in deionized water in a sealable flask under magnetic stirring. Two different R/C molar ratio were used: 300 and 1000. After dissolution, formaldehyde (Aldrich, 37 wt % in water, stabilized by 10−15 wt % methanol) was added and the mixture was stirred until a homogeneous solution was obtained. The solution was then placed in an oven at 85 °C for 72 h for gelation and aging.

Afterward, the obtained aqueous gels were dried by vacuum evaporation without any pretreatment. The unsealed flasks were kept at 60 °C, and the pressure was progressively reduced from 10^5 to 1200 Pa. The drying procedure was performed over 20 h. The samples were then heated to 150 °C (1200 Pa) and kept overnight in these conditions.

After drying, the gels were pyrolyzed at 800 °C under nitrogen flow in a tubular oven; the procedure was the same as that used in previous works.[33,34] The following heating program was used: (i) ramp at 1.7 °C min^{-1} to 150 °C and hold for 15 min, (ii) ramp at 5 °C min^{-1} to 400 °C and hold for 60 min, (iii) ramp at 5 °C min^{-1} to 800 °C and hold for 120 min, and (iv) cool slowly to room temperature.

Both organic and carbon xerogels were activated chemically with KOH. The activating agent/carbonaceous precursor mass ratio (A/P) used was 3:1 in all cases. The mixture of activating agent and carbonaceous precursor was performed by the wet impregnation method. The mixtures were continually stirred at 85 °C until the elimination of water and then pyrolyzed at 750 °C under nitrogen flow. The heating rate was chosen equal to 5 °C min^{-1}, and the flow rate was fixed at 0.60 mmol s^{-1}. The samples were maintained at the maximum temperature for 2 h and then cooled slowly by natural convection. The samples were then washed repeatedly with a 5 M solution of HCl, followed by distilled water, until the pH of the drained solution reached 6. Finally, the samples were dried at 110 °C overnight.

The carbon xerogels were doped with Ni using an excess solution impregnation technique. In all cases, hexahydrated nickel nitrate was used as the nickel precursor and a different percentage of Ni was incorporated into different carbon xerogels:

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25 and 50 wt %. For that, the corresponding amount of hexahydrated nickel nitrate to have 25 or 50 wt % metallic Ni on the final Ni-doped samples was calculated. The doping procedure was described elsewhere.[35]

Final supports were texturally characterized by adsorption–desorption of N_2 and CO_2 at −196 and 0 °C, respectively. The carbon structure was analyzed by X-ray diffraction (XRD). The sample composition was also characterized by elemental analysis using a combustion process followed by infrared detection of the elements (i.e., C, H, N, S, and O). Commercial analyzers LECO CHNS-932 and VTF-900 were used for this aim. Structural and chemical data from the supports employed are shown in Table1.

To study their electrochemical behavior, the metal hydride electrodes were made by mixing 75 mg of these carbon samples with 75 mg of the lanthanide mischmetal-based (Lm) alloy with nominal composition $LmNi_{4.1}Co_{0.4}Mn_{0.4}Al_{0.5}$ and 75 mg of Vulcan XC72R teflonized with 33 wt % polytetrafluoroethylene (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.

In this work, data arising from three different supports and two different amounts of nickel are presented. The samples were labeled as follows. The first two letters refer to the type of precursor (CX for carbon xerogel and OX for organic xerogel). These letters are followed by the R/C used in the xerogel synthesis. The activated samples incorporate the A/P mass ratio used during the chemical activation with KOH (A/P of 3 in all cases). Finally, the nickel content in the samples is mentioned. Therefore, the sample CX3003Ni25% indicates the carbon xerogel synthesized with R/C of 300 and activated with A/P of 3 with 25 wt % nickel.

Electrochemical measurements were made in a three-compartment cell with the corresponding working electrode (metal hydride electrode), counter electrode (sintered NiOOH), and reference electrode (Hg/HgO electrode). In this work, potentials are referred to the Hg/HgO reference electrode. The electrolyte, 6 M KOH solution, was prepared from reagent-grade KOH and deionized water. The experiments were carried out at 298 K. 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 9000 s to ensure the full charge of the electrode. The discharge was conducted at a constant anodic current of 5 mA until the cutoff potential (−0.6 V versus Hg/HgO). The high rate discharge (HRD) was evaluated by measuring the discharge capacity for increasing discharge currents from 1.5 to 45 mA.

Before the electrochemical impedance spectroscopy (EIS) measurements, the electrodes were charge–discharge-cycled at a constant current for 25 cycles. After cycling, the electrodes were discharged to a state of charge (SOC) of 50% and left at open circuit potential (E_o) for 15 min. The EIS spectra were recorded, at E_o, in the 10 kHz to 1 mHz frequency range, with a 5 mV amplitude.

Results and Discussion

Table 2 shows the textural properties of carbon xerogels used as a support for Ni incorporation. It is possible to see that they present different surface area, total pore volume, medium pore size, and micropore volume, which were obtained from both N_2 and CO_2 desorption isotherms. Therefore, it is possible to study, besides the effect of the presence of different amounts of Ni, also the effect of the mesoporosity, surface area, and micropore volume on the final electrode behavior of the samples.

The electrochemical results show that the Ni content has a direct influence on the electrode behavior. Figure 1 shows that the electrodes with 50% Ni have better capacities during the cycling than the electrodes with 25% Ni.

Table 1. Structural and Chemical Data of the Carbon Xerogels Used as a Support

	elemental analysis (wt %, db[a])					XRD		
sample	C	H	O	N	S	d_{002} (Å)	L_c (Å)	L_a (Å)
CX300	96.9	0.8	2.2	nd[b]	nd[b]	3.89	10.84	40.66
CX3003	94.1	0.5	5.2	nd[b]	nd[b]	3.85	10.70	39.80
OX10003	92.8	0.4	7.1	nd[b]	nd[b]	3.87	10.04	47.43

[a] Dry basis. [b] Not detected.

Table 2. Textural Properties of Carbon Xerogels Used as a Support

	N_2 adsorption at −196 °C				CO_2 adsorption at 0 °C
sample	S_{BET} (m^2 g^{-1})	W_0[a] (cm^3 g^{-1})	V_T (cm^3 g^{-1})	$d_{p,max}$ (nm)	W_0 (cm^3 g^{-1})
CX300	636	0.26	0.58	10	0.26
CX3003	1540	0.69	0.94	11	0.43
OX10003	1850	0.82	0.81	3	0.36

[a] Obtained applying the Dubinin–Raduskevich equation.

In Figure 1, it is possible to see that, independently on the used carbon support, samples with higher Ni content improve the capacity of the electrode. Electrodes composed by carbon xerogels with 50 wt % Ni always present a higher capacity in comparison to the counterparts with 25 wt % Ni. Therefore, it can be concluded that the presence of Ni in carbon samples increases the capacity of the electrochemical system, and the higher the amount of Ni, the more beneficial the effect. The textural properties of the carbon support used to prepare the electrode also have relevance. First, it can be observed that, in the case of samples with high Ni content, the presence of bigger mesopores in carbon supports produce a higher increase of the capacity. In this case, it seems that the mesopores present more influence than micropores because CX300Ni50% presents bigger mesopore but lower micropore sizes than OX10003Ni50%. However, the first sample exhibits a higher capacity. On the other hand, in the case of samples with lower Ni content, both types of pores (micro- and mesopores) present influence on the performance. The samples CX3003Ni25% with bigger mesopore size than OX10003Ni25% and higher micropore size than CX300-Ni25% present the best results. Probably, in the samples with higher Ni content, the effect of the microporosity is hidden because of the blockage of this type of porosity. In the case of samples with 25 wt % Ni, probably the blockage of the porosity is lower, and as a consequence, the microporosity has a higher influence than in 50 wt % doped samples.

Figure 2 shows that, independent of the carbon xerogel used as a support when the Ni content increases, the electrodes present smaller overpotentials. As observed in the charge–discharge experiments, the effect of the textural properties on the overpotentials depends upon the amount of Ni in the samples. As mentioned above, when carbon xerogels with a higher Ni amount are used to prepare the electrode, the presence of bigger mesopores is the most important characteristic, with the effect of micropores being minimized. As a consequence, the samples CX300Ni25% and CX300Ni50% present the best behavior. However, if samples with 25 wt % Ni are compared, the presence of micropores are more beneficial.

In the case of using high Ni content samples in the preparation of the electrodes, the decrease of the capacity with the

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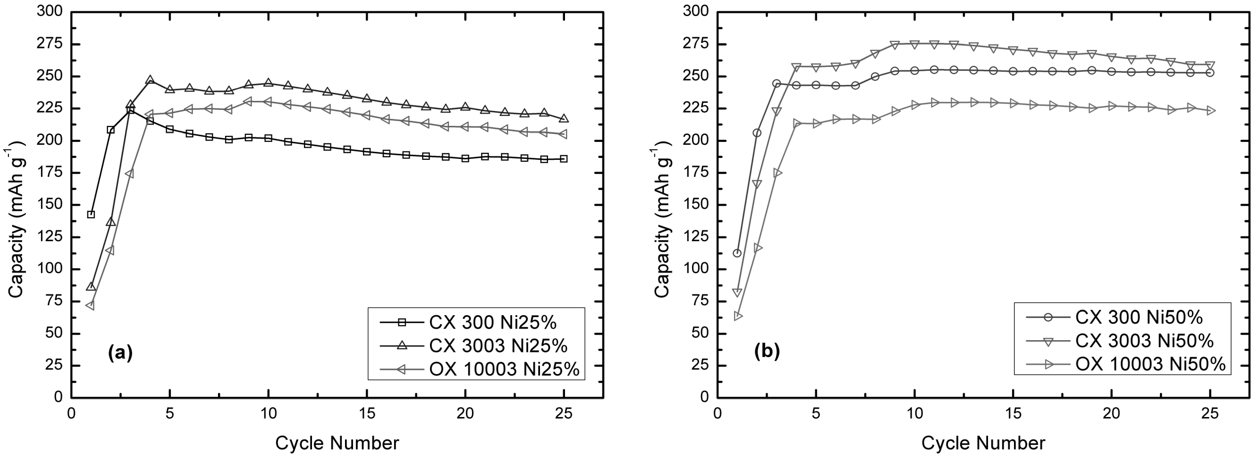

Figure 1. Discharge capacity versus cycles for carbon xerogel supports with (a) 25 wt % Ni and (b) 50 wt % Ni.

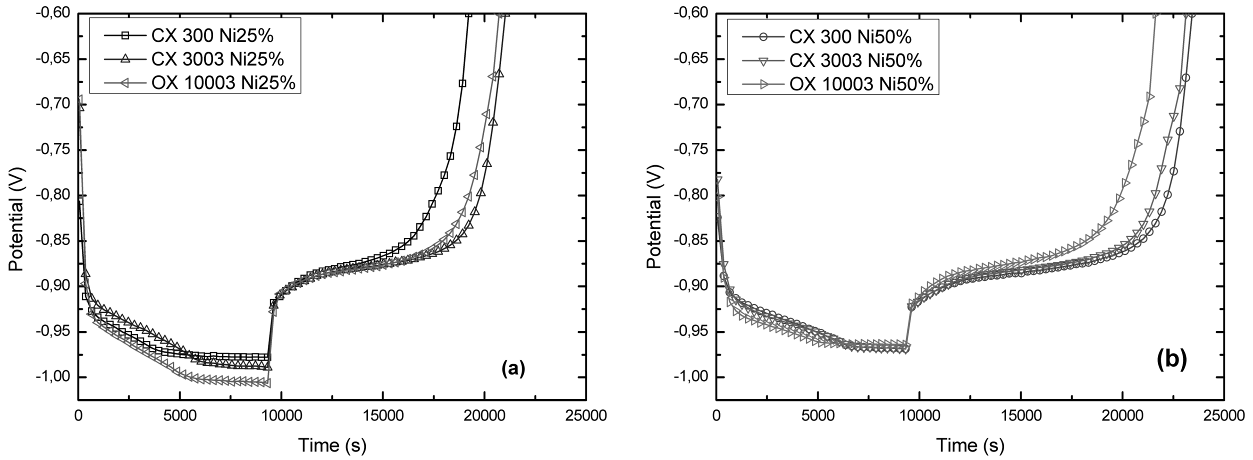

Figure 2. Potential response during the 25th charge−discharge cycle for carbon xerogel supports with (a) 25 wt % Ni and (b) 50 wt % Ni.

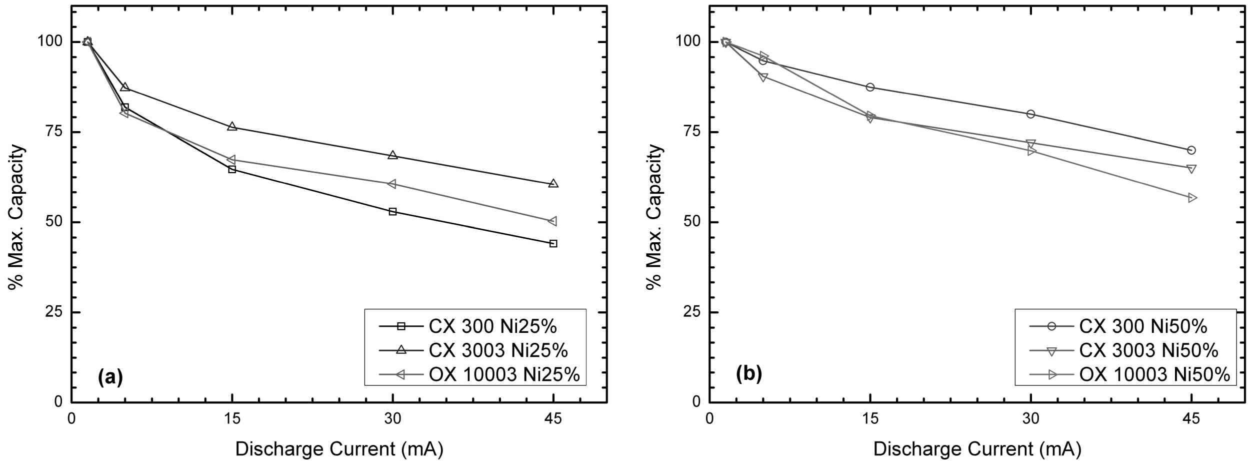

Figure 3. High rate discharge for carbon xerogel supports with (a) 25 wt % Ni and (b) 50 wt % Ni.

increase of the discharge current is lower (high rate capability), indicating that carbon samples with high Ni content are more suitable for this application, as shown in Figure 3. Concerning to the effect of the textural properties, the tendency is the same as that observed in overpotential and charge−discharge experiments (see Figures 1 and 2).

Figure 4 shows the EIS results and presents a clear contribution of Ni on the reduction of the transference resistance value, and this fact is a clear kinetic contribution to the behavior of the electrodes. Independent of the carbon xerogel used as a support, the samples with a higher amount of Ni present a lower charge-transfer resistance, indicating the strong effect of Ni.

However, not only the amount of Ni influences the kinetics of electrodes, but also a strong effect of the textural properties can be observed. Samples with a lower surface area and lower

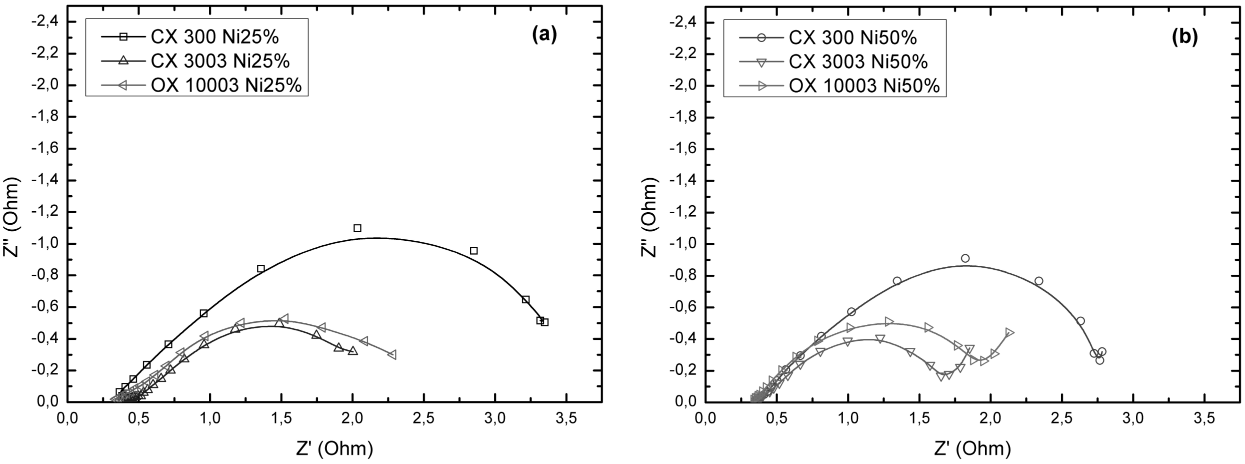

Figure 4. Nyquist plot of EIS electrode response for carbon xerogel supports with (a) 25 wt % Ni and (b) 50 wt % Ni.

micropore volume present higher resistance, independent of the amount of Ni in the samples (i.e., CX300Ni25% and CX300Ni50%). This indicates that the presence of micropores in carbon samples benefits the kinetic behavior of the electrode. Concerning the effect of the mesopore size, there is not a high contribution of this type of pore, because carbon xerogels with the same amount of Ni, similar micropore volume, and different mesopore size present similar resistivity (CX3003Ni25% and OX10003Ni25%). As a result, carbon samples with high Ni content, high surface area, and high micropore volume are the most suitable to reduce the resistance of the electrode.

Conclusions

Results showed that both textural properties and Ni content have a strong influence on the electrochemical performance of electrodes. According to the results obtained and at least up to 50 wt % Ni, it seams that the higher the Ni content, the lower the overpotentials during charge−discharge cycles. On the other hand, an increase in the capacity performance is observed in electrodes with higher Ni content and electrodes with higher surface area carbons. Ni content also has a positive influence on the kinetics of the process. EIS results showed that the charge-transfer resistance of the electrodes decreases with the increase of Ni in the carbons used.

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