

STORAGE OF HYDROGEN IN CARBON NANOSTRUCTURES THROUGH ELECTROCHEMICAL DECOMPOSITION OF WATER

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Introduction

Safe storage, easy and low cost delivery of hydrogen are essential requirements to make successful the application of fuel cells for electric vehicles. Among the various power supplies, the hydrogen-oxygen (air) fuel cell has been considered for developing all-electric or hybrid vehicles [1, 2]. However, feeding such a device for 500 km range requires to store about 3.1 kg of hydrogen safely and at a reasonable cost. The present technologies using high pressure or cryogenic vessels cannot fulfil these conditions, therefore there is a strong requirement for other solutions. Actually, most of the vehicles available on the market in the next ten years should be mainly based on lithium-ion or nickel-metal hydride (Ni-MH) batteries. In the case of Ni-MH batteries the performance is limited by the hydrogen capacity of the anodic material, which does not exceed 1.4 wt.% at room temperature for the most popular LaNi₅-based alloys [3].

Recent works seem to indicate that nanostructured carbon materials could be promising for the storage of hydrogen. Besides the great controversy between the results published, high pressure (~ 100 bars) looks to be needed for getting remarkable results, however there is not a clear statement on the amount of hydrogen which could be sorbed. In the case of single wall nanotubes, theoretical computations indicate that H₂ molecules are rather sorbed in the canal and that the storage capacity increases linearly with the tube diameter, exceeding 14 wt %, i.e. 160 kg H₂/m³ [4]. Experimentally, the hydrogen storage capacity reached only 4.2 wt % at 300 K under a high pressure of 100 bar for a sample of single-wall nanotubes with a large mean diameter of about 1.85 nm [5].

Storage of hydrogen by electrochemical decomposition of water has been studied by Nützenadel et al. for carbon samples containing nanotubes [6]. For a material based on single-wall nanotubes, they noticed a discharge capacity which corresponds to 0.39 wt % of hydrogen, claiming that no other form of carbon absorbs comparable amounts of hydrogen [6]. Even bigger adsorption values up to about 2.9 wt % were found after screening a number of single-wall carbon nanotubes samples with different degrees of purity [7, 8]. However, if one looks carefully at the data published in reference [7], there is not a systematic relationship between the indicated purity and the maximum discharge capacity. This suggests that single-wall carbon

nanotubes are probably not responsible for the values of sorption observed. Indeed, whatever the method of preparation, besides nanotubes the materials always contain other forms of carbon, mainly strongly disordered, on which electrochemical decomposition of water is probably more efficient than on nanotubes. On the other hand, the use of nanotubular materials for this application is quite doubtful because of the cost, of limited scale production and uncertain purity. Therefore, we decided to check hydrogen adsorption at ambient temperature by electrolysis of water on an activated carbon electrode. We selected activated carbon fabrics, because they can be readily available in quite large amount and no binding substance or enhancing conductivity additive is necessary for the manufacture of the electrode.

Experimental

The activated carbon samples (AC) were prepared by pyrolysis of viscose fabrics at 1000°C followed by CO₂ activation at 1000°C. Additional treatment either by 69 % nitric acid during 4h at 80°C (ACox1) or by NaOCl (available chlorine 2-5 %) during 20 h at room temperature (ACox2) were performed in order to modify the surface functionality. Concentration of the surface groups determined accordingly to the Boëhm method of back titration is given in Tab. 1. As-prepared AC sample has a poor surface functionality. On the other hand, oxidative treatments allow to increase strongly the concentration of surface groups, especially using NaOCl which produces a high total amount of acidic groups. Nitrogen adsorption/desorption isotherms at 77 K (Micromeritics ASAP 2010) show that the samples are essentially microporous and their specific surface area ranges from about 1100 to 1500 m²/g.

Table 1 BET specific surface area (m²/g) and surface groups concentration (meq/g) of the carbon materials

	AC	ACox1	ACox2
S _{BET} (m ² /g)	1500	1140	1320
Carboxylic	0	1.3	2.7
Lactones	0.1	1.0	0.6
Phenols	0.2	1.1	2.0
Carbonyl	0.4	1.1	3.1
Basic	0.5	0.5	-

The electrolysis of water was carried out in 6 mol.l^{-1} KOH electrolytic medium at room temperature and at atmospheric pressure using a three electrode cell in which disk shape activated carbon (10 to 20 mg) and glassy carbon were the working and the auxiliary electrodes, respectively. The reference electrode was Hg/HgO. Platinum net was used as additional current collector for the working electrode. A Wenking 70HC3 potentiostat together with Wenking EVI80 integrator (Bank, Germany) and a VMP multichannel galvanostat/potentiostat (Biologic, France) were applied.

For a comparison, high pressure adsorption experiments were performed at 273 K. The samples were introduced in a stainless steel cell and outgassed under secondary vacuum at 150°C for 12 hours. Stepwise introduction of dihydrogen was performed from a calibrated reservoir thermostated at 273 K. Dihydrogen uptake was measured at 273 K and different pressures up to 70 bar, after reaching the equilibrium.

Results and Discussion

The amount of hydrogen able to be stored electrochemically in the carbon samples was estimated by galvanostatic experiments with a current load of 500 mA/g for charging (negative current) and 100 mA/g for discharging (positive current). In all cases, the charging capacity strongly exceeded the storage hydrogen capacity of the material. Decreasing of the rest potential of the working electrode in the order of a few hundreds mV was a proof of hydrogen insertion in the host carbon. Hydrogen was released by reversing current until the system reached the initial rest potential.

Typically, two regions were detected during oxidation (Fig. 1, curve I): one up to ca. the value of initial potential attributed to hydrogen release and the other exponential above this value which could be attributed to capacitance effects together with a possible oxidative modification of the carbon surface. The plateau of potential (at ca. -0.6 V vs Hg/HgO) observed for the pristine material AC in the first region of curve I, although not so flat as for hydride electrode materials, is a good proof for a true faradaic hydrogen oxidation. During the second cycle, significant changes are remarkable. The charge curve (II) proceeds at a lower overpotential than curve (I) with a longer time for reaching the plateau of hydrogen evolution. The second discharge curve (II) is more sloppy and the value of capacity for reaching the rest potential is ca. 13% smaller. This unprofitable changes could be connected with a surface oxidation provoked by a prolonged application of a positive current at the end of the first cycle.

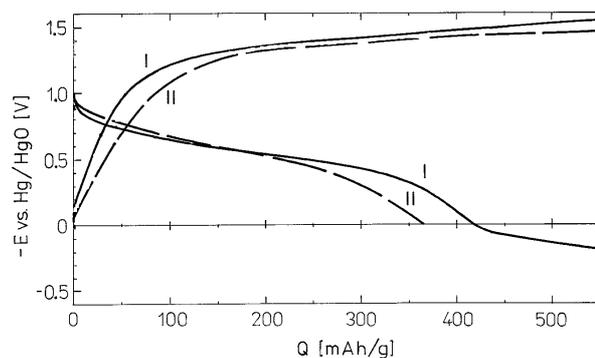


Figure 1: Galvanostatic charge (-500 mA/g) / discharge ($+100 \text{ mA/g}$) of an AC carbon electrode.

Curves I and II represent respectively first and second reduction/oxidation processes. Electrolytic solution: 6 mol.l^{-1} KOH.

In order to confirm this assumption, a new sample of the electrode material was deeply oxidised (Fig.2 curve 1) prior to its reduction (Fig. 2, curve 2), the corresponding discharge curve (3) is then quite sloppy and the capacity for reaching the initial rest potential was definitively smaller than for the pristine material. Hence, an oxidised carbon surface definitively aggravates the hydrogen storage ability.

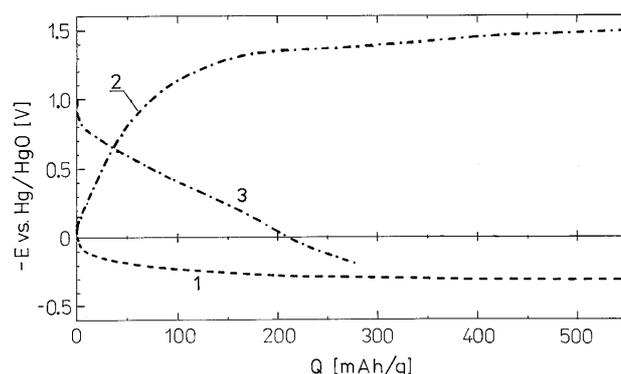


Figure 2: Galvanostatic charge (-500 mA/g)/discharge ($+100 \text{ mA/g}$) of an AC electrode. The sample was first oxidised (curve 1) and then reduced (curve 2) and oxidised (curve 3). Electrolytic solution: 6 mol.l^{-1} KOH.

The influence of oxidising surface modification of carbon on hydrogen sorption ability is shown in Fig. 3. For a complete removal of hydrogen from the carbon material without its harmful oxidation, the process was continued with a current load I_H of 10 mA/g after finishing the main discharge step at high current ($I_1 = 100 \text{ mA/g}$) until the rest potential. Moderately oxidised sample ACox1 appears to be the most efficient (Fig. 3, curve 2) with an increase of capacity of about 10% as compared to AC (Fig. 3, curve 1), keeping a good shape of discharge curve with a typical faradaic plateau.

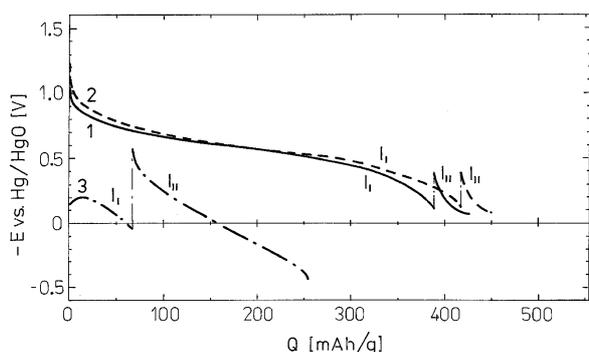


Figure 3: Galvanostatic discharge of three carbon electrodes (1: AC; 2: ACox1; 3: ACox2) at two subsequent current loads ($I_I = +100$ mA/g and $I_{II} = +10$ mA/g). Electrolytic solution: 6 mol.l^{-1} KOH.

However, for sample ACox2 with a very rich surface functionality (Tab. 1), the discharge curve is shifted toward more positive potential due to an important ohmic drop. In this case, the electrical conductivity has been strongly depressed by the deep oxidation of carbon and the discharge capacity was approximately two times smaller than in pristine AC.

The reversible hydrogen storage capacity of the activated carbons AC and ACox1 is ca. 1.5 wt % that is much more than the values which we got for the adsorption under a gas pressure of 70 bar at 273 K (Tab. 2). Taking into account that a part of hydrogen inserted under high pressure remains probably chemisorbed [10], performance is definitively better using electrochemical decomposition of water. This enhancement is interpreted by the formation of nascent hydrogen during water reduction which penetrates easily in the carbon nanostructure.

Table 2 : Values of hydrogen electrochemically released (% wt) compared to the amount adsorbed under a high pressure for the three carbon samples.

	Electro-decomposition	High pressure
AC	1.4	0.4
ACox1	1.6	0.4
ACox2	0.9	0.4

Conclusion

Electrochemical decomposition of water is a very simple method for a reversible hydrogen sorption in nanostructured carbon materials. Compared to carbon nanotubes, activated carbons, due to their low cost and easy handling, should be more carefully considered for this application. Their storage capacity is comparable to that of

metallic alloys used as anodic material in Ni-MH accumulators, that opens new insights for improving the performance and understanding better the hydrogen insertion mechanism.

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