

HIGHLY EFFECTIVE HYDROGEN SORPTION ON GRAPHENE EDGE PLANES THROUGH ELECTROREDUCTION OF AQUEOUS ELECTROLYTES

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Introduction

Hydrogen can be sorbed on activated carbons (AC) in aqueous medium when the electrode potential is lower than the equilibrium value for water reduction [1]. The amount of reversibly stored hydrogen has been determined in alkaline and acidic medium [2] and the activation energy of about 110 kJ mol⁻¹ confirms the chemical character of the hydrogen bonding [3]. The texture of nanoporous carbons plays an important role, especially for template carbons where the amount of hydrogen is proportional to the ultramicropore volume (0.6-0.7 nm) [4]. More recently, galvanostatic charge/discharge experiments carried out in alkaline medium on a series of ACs with similar porosity but with various surface chemistries showed that the amount of hydrogen electroadsorbed reversibly decreases with the increase of the oxygenated surface functionalities [5].

In this work, the hydrogen storage process is studied in neutral medium and is compared with alkaline medium. The effect of temperature on the performances and on the desorption energy is evaluated. For the first time, we demonstrate that the sorption capacity can reach the order of 2.5 wt% at 50°C.

Experimental

A high purity commercial activated carbon (AC, MWV-E510A from MeadWestvaco, USA) was used. The porous texture of AC was analysed by nitrogen and CO₂ adsorption at 77 K and 273 K, respectively (Autosorb-1, Quantachrome Instruments). Before analysis, the sample was degassed (Flo Vac Degasser, Quantachrome Instruments) overnight at 200 °C. The specific surface area was calculated from the N₂ adsorption isotherm by applying the BET equation. The micropore volume was calculated from the application of the Dubinin-Radushkevich equation to the adsorption data up to P/P₀ ≤ 0.015 for N₂ and P/P₀ < 0.1 for CO₂. X-ray photoelectron spectra (XPS) were recorded on the powder with a VG ESCALAB 250 spectrometer using an Al K α monochromatic source (15 kV, 15 mA) and a multidetection analyzer, under 10⁻⁸ Pa residual pressure.

A paste was prepared by mixing the AC (80%), acetylene black (10%) and PTFE (10%) as a binder, and was rolled up in order to obtain films. Electrodes were made by punching pellets in the AC composite based paste, and dried overnight at 120 °C before building the cells.

Electrochemical measurements were carried out at ambient pressure in a special Teflon three-electrode cell with a gold current collector and a sintered glass separator. The auxiliary and reference electrodes were a graphite rod and Hg/Hg₂SO₄ in 0.5 mol L⁻¹ Na₂SO₄, and nickel and Hg/HgO in 6 mol L⁻¹ KOH. All potentials are further expressed versus the normal hydrogen electrode (NHE). Galvanostatic cycling was realized using a VMP2 (Biologic) multichannel potentiostat/galvanostat. The cells were thermostated in a VT 4002 chamber (Vötsch Industrietechnik, Germany).

The AC powder (alone, e.g., without binder and percolator) was electrochemically charged in 0.5 mol L⁻¹ Na₂SO₄ at -2 A g⁻¹ during 3 hours at 50°C and further analyzed by thermoprogrammed desorption (TPD), e.g., TGA (Netzsch STA 449 C) coupled to mass spectrometry (Netzsch QMS 403 C), in order to measure di-hydrogen evolution with temperature.

Results and Discussion

Table 1 presents adsorption and XPS data recorded for AC. Oxygen was the only element detected on the surface of AC, in small amount, indicating the high purity of the material, what is interesting for the hydrogen storage process [5]. The adsorption data demonstrate a microporous material with a well-developed porosity and some amount of mesopores favorable for ions-transportation [6].

Table 1. Specific surface area, pore volume and oxygen content (XPS) of AC.

	S _{BET}	V _{ultramicro}	V _{micro}	V _{meso}	O%
	(m ² g ⁻¹)	(cm ³ g ⁻¹)	(cm ³ g ⁻¹)	(cm ³ g ⁻¹)	At. %
AC	2244	0.83	0.79	0.45	2.4

The best conditions to reach the highest amount of reversibly stored hydrogen with AC were determined in alkaline medium at 20°C. The optimal paste composition consisted of a mixture of AC 80%, acetylene black 10% and PTFE 10%. We also noticed that a highly negative load is necessary to strain the hydrogen storage process. For a charge of -6 Ah g⁻¹, the best performance was obtained by applying a negative current of 2 A g⁻¹ during 3 hours.

Fig. 1 compares the galvanostatic charge/discharge curves obtained with AC in alkaline and in neutral medium. In KOH (green curve), the plateau at -0.6 V vs. NHE is characteristic for a porous carbon material in this medium [2]. By contrast, in neutral medium (red curve), the curve exhibits two different slopes, a first part where the stored hydrogen is oxidized at potentials lower than 0.1 V vs. NHE, and a plateau at higher potentials corresponding to highly bonded hydrogen. It also has to be noted that the reduction over-potential is more important in neutral than in alkaline medium. The amount of stored hydrogen is 1.5 wt% and 1.4 wt% in neutral and alkaline medium, respectively.

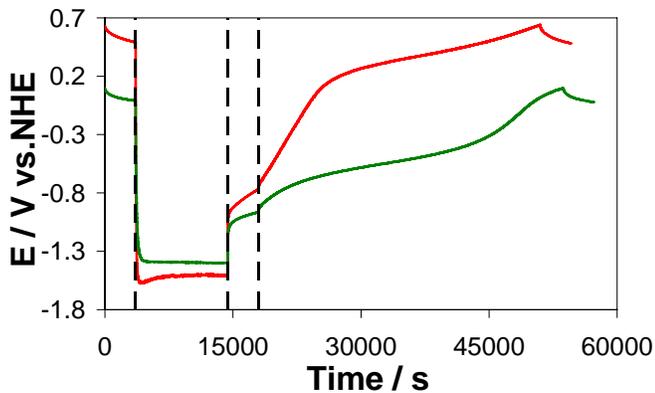


Fig. 1 Galvanostatic charge/discharge of AC in 6 mol L^{-1} KOH (green) and 0.5 mol L^{-1} Na_2SO_4 (red). After one hour relaxation, a negative current of -2 A g^{-1} is applied during 3 hours. Then, after 1 hour relaxation, a positive current of $+50 \text{ mA g}^{-1}$ is applied in order to oxidize the sorbed hydrogen.

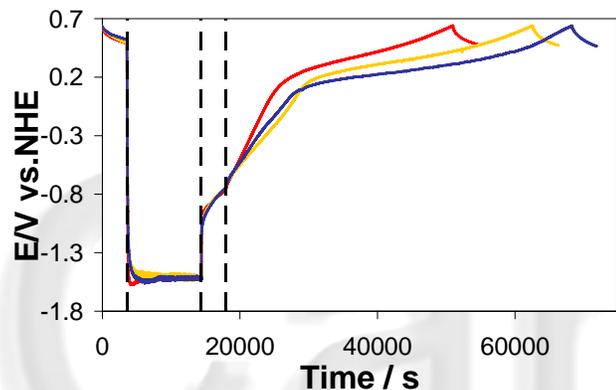


Fig. 2 Galvanostatic charge/discharge of AC in 0.5 mol L^{-1} Na_2SO_4 at 20°C (red), 40°C (yellow) and 50°C (blue).

The effect of temperature on the electrochemical performance has been evaluated. As shown on fig. 2, when temperature increases, the curves during charging and subsequent 1 hour relaxation are superimposed. By contrast, the oxidation time is higher (higher amount of stored hydrogen) when the temperature increases, while the potential is lower due to a better conductivity of the electrolytic medium [3]. Finally, while the amount of stored hydrogen is only 1.5 wt% at 20°C , it reaches 2.1 wt% at 40°C and 2.4 wt% at 50°C .

Fig. 3 presents the di-hydrogen evolution during TPD on the AC powder charged at 50°C in neutral medium. Two main peaks corresponding to di-hydrogen desorption are observable at 125°C and 430°C . The desorption activation energies calculated following the equation given in ref. 3 are 110 and 205 kJ mol^{-1} , respectively. These two values fit well with the two oxidation branches in fig. 2. The highest value demonstrates that a part of nascent hydrogen is strongly bonded to the graphene edges in 0.5 mol L^{-1} Na_2SO_4 .

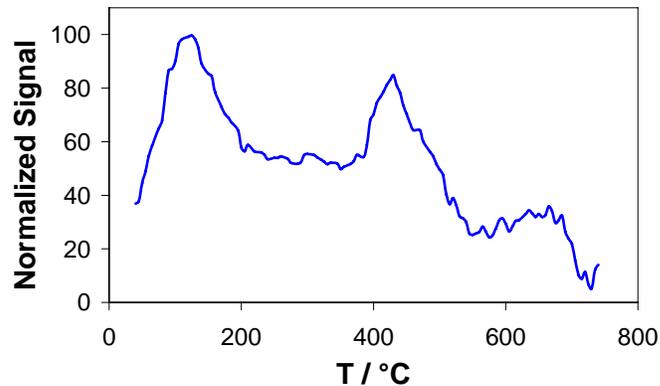


Fig. 3 TPD analysis of hydrogen evolved from AC powder charged at -2 A g^{-1} during 3 hours at 50°C in neutral medium.

Conclusions

This study demonstrates the effectiveness of a neutral medium for electrochemical hydrogen bonding to graphene edges. Particularly, the amount of hydrogen reversibly stored reaches 2.4 wt% at 50°C . These promising results indicate that this electrolytic medium is adapted for applications such as supercapacitors, batteries and solid hydrogen storage.

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References

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