MECHANISMS OF ELECTROCHEMICAL ENERGY STORAGE IN ACTIVATED CARBONS USING AN AQUEOUS ELECTROLYTE

Krzysztof Jurewicz[1], Elzbieta Frackowiak[1], François Béguin[2]
[1]ICTE, Poznan University of Technology, ul. Piotrowo 3, 60-965 Poznan, Poland
[2]CRMD, CNRS-University, 1b rue de la Férollerie, 45071 Orléans Cedex 2, France

Corresponding author e-mail address: beguin@cnrs-orleans.fr

Introduction

Electrochemical energy storage is an important challenge for the development of electric vehicles during the next decades. Therefore, an important research effort is devoted to the development of high energy density nickel/metal hydride (Ni-MH) or lithium-ion batteries. The performance of Ni-MH batteries is limited by the hydrogen capacity of the anodic material, which does not exceed ca. 1.5 wt.% at room temperature for the most popular $LaNi_5$-based alloy. Cheap materials giving a higher reversible capacity are presently under investigation. Carbon nanotubes materials have been extensively investigated for the electrochemical storage of hydrogen through the electrodecomposition of aqueous 6M KOH electrolyte at ambient pressure and temperature, giving very scarce values ranging from 0.2 wt% to 3.7 wt% of stored hydrogen [1-4]. However, the storage capacity does not exceed 0.2-0.4 wt% when high purity single wall and multiwalled nanotubes are investigated [5]. Using microporous activated carbons for the cathodic electrodecomposition of water, we observed values of reversible storage capacity up to 2 wt.% [6,7], confirming that nanotructured carbons might be more efficient than carbon nanotubes for this application. On the other hand, the storage capacity of the same materials under di-hydrogen pressure of 70 bar at 0°C, does not exceed 0.4 wt% [6]. Hence, the driving forces that exist during electrochemical polarization allow a very efficient trapping of hydrogen.

In order to optimise the process, the objective of this paper is to contribute to a better understanding of the electrochemical hydrogen storage mechanism in nanoporous activated carbons [8].

Experimental

For our experiments we selected an activated carbon cloth which can be used as self-standing electrode without any kind of binder or additive for conductivity improvement, that is an advantage for investigating only the electrochemical properties of the sample. The activated carbon cloth, noted as AC, was prepared by viscose pyrolysis at 1000°C, followed by CO_2 activation at 1000°C.

The nitrogen adsorption/desorption isotherm has been determined at 77 K using a Micromeritics ASAP 2010 after outgassing AC at 350°C until the pressure reached 10^{-6} mbar. For a detailed estimation of narrow micropores, CO_2 adsorption was also performed at 25°C.

The hydrogen sorption ability has been evaluated electrochemically in a three-electrode cell, where AC (10 to 20 mg in the dried state) is used as the working electrode. The electrolytic medium is aqueous KOH (3M and 6M) medium, with

nickel and Hg/HgO/6M KOH as counter and reference electrodes (+ 0.052 V *vs* NHE), respectively. In the galvanostatic mode, hydrogen is stored spontaneously in AC during the decomposition of the electrolytic solution using a current load of -500 mA/g. Then, the system is allowed to relax for half to one hour, and the amount of hydrogen reversibly stored in the carbon sample is quantitatively evaluated by measuring the time of galvanostatic discharge at current loads from 10 to 25 mA/g. Taking into account the Faraday law, 1 wt. % of hydrogen corresponds to a charge of 270 mAh/g. Potentiodynamic cycling at a scan rate of 5 mV/s is also used to obtain information on the mechanism and kinetics of the reversible hydrogen storage. All the experiments have been performed at ambient temperature and atmospheric pressure, using VMP (Biologic, France) and ARBIN - BT2000 (USA) multichannel galvanostat/potentiostats.
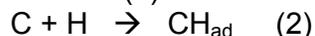
Results and discussion

The sample AC displays a type I nitrogen adsorption isotherm, with an important uptake at low relative pressure, characteristic of an essentially microporous carbon. The data calculated from this curve are S_{BET} = 1390 m^2/g and V_{total} = 0.522 cm^3/g. The pore distribution is as follows: 94 % of pores below 2 nm (0.49 cm^3/g); 3% in the range 2-3 nm (0.014 cm^3/g); 2% in the range 3-5 nm (0.005 cm^3/g). CO_2 adsorption at 25°C gives a volume V_{CO2} = 0.291 cm^3/g and a surface area of 765 m^2/g, demonstrating that AC contains a noticeable amount of ultramicropores (smaller than 0.7 nm) which are generally supposed to be highly efficient for hydrogen sorption.

Figure 1a presents the voltammetry characteristics of the AC electrode in 3M KOH at a constant scan rate of potential (5 mV/s), however, with a stepwise (100 mV) shift of potential cut-off to more negative values, it means towards hydrogen evolution. The almost rectangular shape of the curves down to a potential cut-off of -0.8 V *vs* Hg/HgO, with comparable values of positive and negative current, proves entirely a pure capacitive and reversible behaviour of AC in this potential range. The Faradaic reactions begin gradually to take place from the third loop when the potential cut-off is lower than the equilibrium potential (The theoretical value of the equilibrium potential in 3M KOH is -0.856 V vs NHE, i.e. –0.908 V *vs* Hg/HgO). The increase of positive current is a clear proof that water decomposition starts and produces hydrogen which is immediately adsorbed on the surface as H_{ad}, being then electro-oxidised during the anodic sweep if the potential is higher than the equilibrium value.

In the alkaline solution, water itself is the proton source leading to OH^- as the conjugated-base product after electron transfer according to reaction (1):

$$H_2O + e^- \rightarrow H + OH^- \quad (1)$$
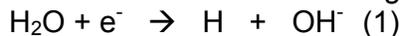
The nascent hydrogen formed in reaction (1) can adsorb onto the carbon surface:

$$C + H \rightarrow CH_{ad} \quad (2)$$

and/or recombine to H_2 molecules as follows:

$$CH_{ad} + H_2O + e^- \rightarrow H_2 + OH^- + C \quad (3)$$

$$2H \rightarrow H_2 \quad (4)$$

$$CH_{ad} + CH_{ad} \rightarrow H_2 + 2C \quad (5)$$

The steps above are often distinguished as Volmer (1), Heyrovsky (3) and Tafel (4) reactions. If the hydrogen adsorption energy is smaller than the energy released in the Tafel or Heyrovsky reactions, and if the activation barrier for one of these processes is enough low, then the recombination of H_{ad} takes place and molecular

hydrogen evolves by chemical or electrochemical way, respectively. If not, the adsorbed hydrogen can further diffuse in the bulk of the carbon host occupying sites with higher adsorbing energy.

The detailed analysis of the voltammograms in figure 1a allows to distinguish three fundamental regions of potential: 1/ from +0.05 V to –0.8 V *vs* Hg/HgO where only a typical charging of the electrical double layer takes place; 2/ from –0.8 V to –1.5 V *vs* Hg/HgO the Faradaic formation of hydrogen (1) and its adsorption onto carbon (2) giving CH_{ad} proceeds. The Tafel recombination does not occur in this region because of not high enough polarization; 3/ the recombination into molecular H_2 and its evolution takes place below –1.5 V until –2.0 V *vs* Hg/HgO. When the hydrogen evolution becomes significant, the gas bubbling provokes fluctuations of the active carbon surface area that causes an important noise for the potential values lower than –1.5 V *vs* Hg/HgO.

During the oxidation step, the above reactions run in opposite direction. When the value of the cut-off potential is below –0.8 V *vs* Hg/HgO, the hydrogen oxidation is well visible on the anodic part of the voltammetry characteristics. The positive current due to hydrogen oxidation increases with the decrease of potential cut-off and a more and more pronounced hump shifts towards more positive values of potential. When the negative potential cut-off reaches –2 V *vs* Hg/HgO, the hump is located ca. 0 V *vs* Hg/HgO, i.e. +0.052 V *vs* NHE. The latter value is very high compared to the equilibrium potential for reaction (1) in 3M KOH medium, i.e. –0.856 *vs* NHE. This high overvoltage (i.e. high energy) required for hydrogen oxidation is a clear proof that hydrogen stored at very negative values of potential is strongly adsorbed in the porous carbon bulk. It must be noticed that for a quantitative estimation of the hump shift, a slower scan rate of potential should probably be used to eliminate the polarization connected with the excessive ohmic drop in the electrolyte.

Quite interesting results were obtained when the positive side potential cut-off was shifted up to 0.55 V *vs* Hg/HgO, ca. 0.60 V *vs* NHE (Figure 1b). The hump which prolongs beyond 0 V *vs* Hg/HgO in the anodic part of the curve indicates that a part of inserted hydrogen is oxidised at potential even higher than 0 V *vs* Hg/HgO, confirming the presence of sites with strongly bonding character. However, when the positive cut-off potential reaches 0.55 V *vs* Hg/HgO, AC is oxidised, that is clearly demonstrated by the small hump at about –0.5 V *vs* Hg/HgO in the cathodic part of the voltammetry characteristics.

Table 1 shows the reversible capacity and the efficiency of hydrogen storage depending on the charge capacity in 6M KOH medium. The maximum reversible capacity reaches ca. 500 mAh/g, what is quite interesting for battery application by comparison to metallic hydrides. If one wants to keep a good efficiency of the process, an effective sorption of hydrogen is observed only up to a charge of ca. 1000 mAh/g, which gives values of reversible capacity in the range 300-400 mAh/g. A further increase of the supplied charge leads to a saturated state with almost no increase of hydrogen uptake. However, when the charging time is increased, the galvanostatic oxidation plateau is better defined [7].

Conclusion

Hydrogen could be stored in a nanoporous activated carbon by cathodic decomposition of water in KOH aqueous solutions. Applying a negative polarization to the activated carbon electrode, hydrated K^+ cations are adsorbed, forming the

electrical double layer. Once the electrode potential becomes lower than the equilibrium redox potential, hydrogen in the zero oxidation state is formed by the reduction of water. In a next step, hydrogen is adsorbed physically onto the carbon surface giving rise to H_{ad}. The total amount of hydrogen adsorbed, and consequently the storage capacity, depends essentially on the kinetics of hydrogen diffusion and incorporation into the nanopores. At low overvoltage, the diffusion of H_{ad} proceeds slower than the reduction step of water, then H_{ad} participate in chemical (Tafel) or electrochemical (Heyrovsky) recombination reactions that result in evolution of di-hydrogen. In KOH electrolyte, due to the high value of polarization, the carbon AC demonstrates a noticeable hydrogen capacity with a well defined discharge plateau. Hence, the electro-reduction of water in basic medium allows higher internal hydrogen pressure than in the conventional gas phase technique to be reached. Taking into account the quite interesting characteristics of this process for battery application, further investigation of electrochemical hydrogen storage in nanostructured activated carbons is necessary, paying a peculiar attention to the micropores size and to the use of other electrolytic media.

References

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Charge (mAh/g)	Discharge (mAh/g)	Efficiency (%)
211	194	92
423	312	74
846	376	45
1690	429	25
3383	466	14
7166	488	7
14333	476	3

Table 1. Discharge hydrogen capacity (at 25 mA/g) of AC in 6M KOH medium for various values of charge capacity at a current load of -500 mA/g.
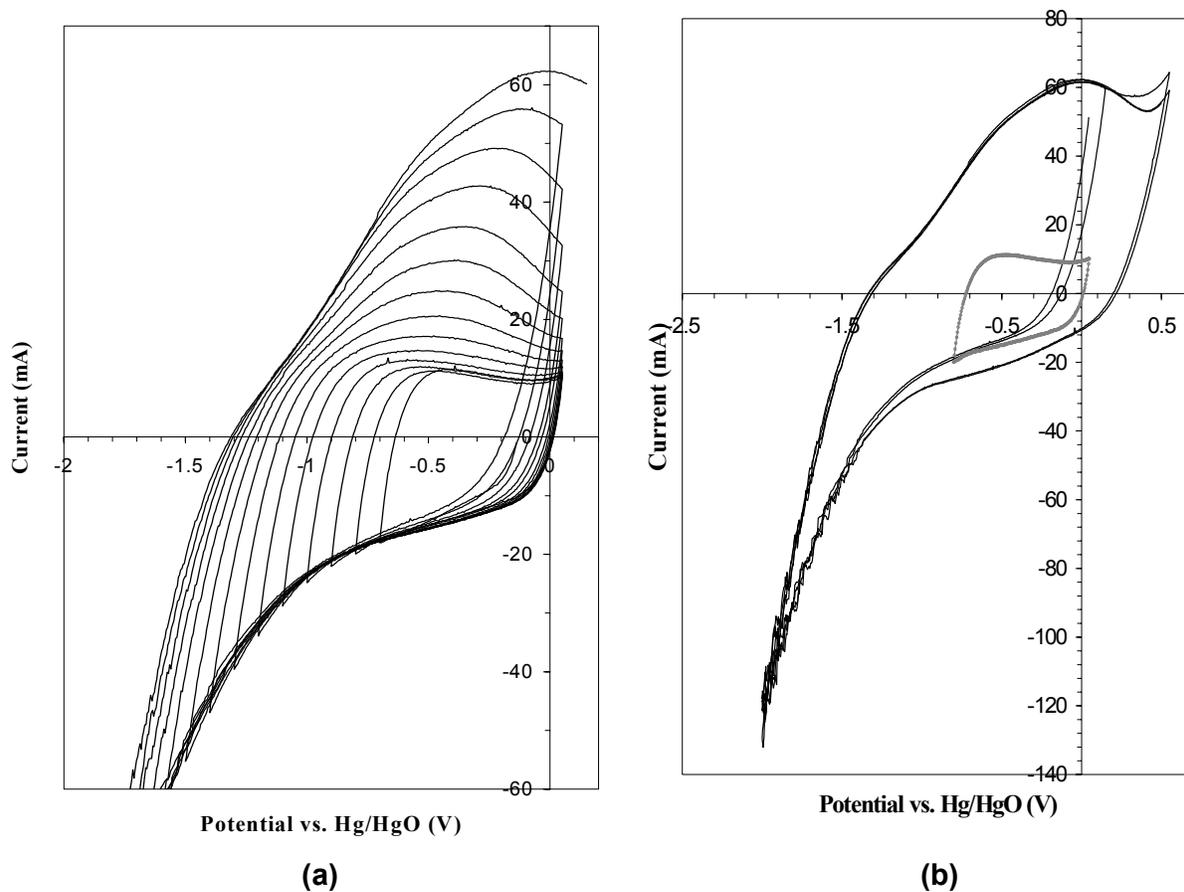
(a)

(b)

Figure 1. (a) Voltammetry characteristics of AC (15.2 mg) for different values of negative potential cut-off. Electrolyte: 3 M KOH. Scan rate of potential: 5 mV/s. The various loops are obtained by stepwise (100 mV) shifting the potential cut-off to more negative values;

(b) Voltammetry characteristics of AC (15.2 mg) for different values of positive potential cut-off. Electrolyte: 3 M KOH. Scan rate of potential: 5 mV/s. The values of positive potential cut-off are successively 0.05 V, 0.15V, 0.55V *vs* Hg/HgO.