

Study of the mechanism of electrochemical hydrogen storage in nanoporous carbons

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An efficient method of hydrogen storage in nanoporous carbons is its reversible sorption by electrochemical decomposition of a KOH water solution [1-3] according to the following equation: $C + x H_2O + x e^- \rightleftharpoons <CH_x> + x OH^-$ where $<CH_x>$ stands for the hydrogen inserted into the nanoporous carbon during charging and oxidized during discharging.

Although various carbon materials have been investigated as hydrogen adsorbents, the information about the storage mechanism as well as the nature of the hydrogen/carbon interaction is still not sufficient. In order to extend the understanding of the process, carbon samples charged electrochemically were investigated by temperature programmed desorption (TPD). The nature of the hydrogen/carbon interaction was studied by electrochemical analysis at different temperatures.

The TPD experiments consist of heating the samples from room temperature to 950°C and of quantitative analysis by on-line mass spectrometry, the di-hydrogen evolved from the carbon material. Fig. 1 shows the desorption rate of hydrogen during the TPD experiment carried out on an activated carbon cloth loaded at -500 mA/g during 12 hours. The first peak below 300°C corresponds to the desorption of hydrogen fixed on the carbon surface during the charging process. The shape and the position of this peak suggests that the gas is released from sites of different and relatively high energies. The second hydrogen peak results from the reaction between the carbon material and KOH as already mentioned in literature [4]. Carbon materials were also loaded at -500 mA/g during different times (3, 6, 12 and 24 hours), and then analysed by TPD, showing that the intensity of the peak below 300°C increases with the charging time. Hence TPD gives the direct proof that hydrogen is really stored in nanoporous carbons by this electrochemical process. Moreover, the position of the desorption peaks demonstrates that at least a part of hydrogen presents stronger interactions than in the state of physisorption.

In order to confirm the latter interpretation, galvanostatic cycling and cyclic voltammetry experiments were realized in 6 mol.L⁻¹ KOH at various temperatures ranging from 20 to 60°C. The results obtained show that, as temperature increases, both cathodic and anodic processes are accelerated (Fig. 2) by reducing the kinetic barriers, and in consequence the hydrogen uptake efficiency is enhanced. On the basis of the electrochemical data, an Arrhenius plot was created, and the activation energy related to the hydrogen reaction was estimated.

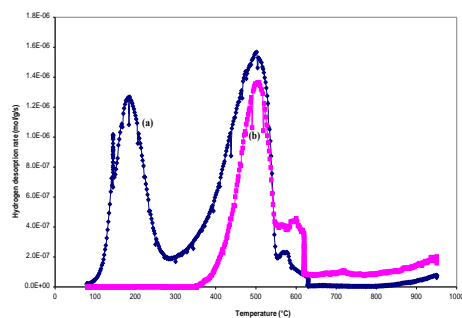


Fig. 1. Hydrogen desorption rate during the TPD analysis of (a) carbon cloth charged at -500 mA/g during 12 hours; (b) carbon cloth charged at -500 mA/g during 15 minutes.

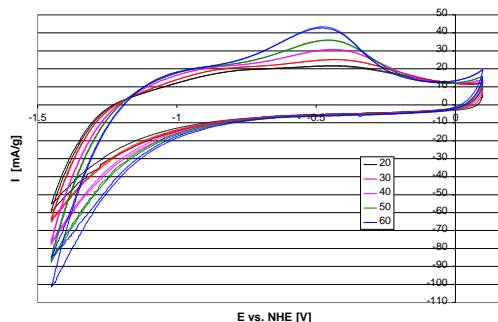


Fig. 2. Cyclic voltammograms performed on an activated carbon cloth at different temperatures in 6 mol.L⁻¹ KOH. Scan rate of potential 1 mV/s, mass of sample 20 mg.

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