Correlation of hydrogen capacity in carbon material with the parameters of electrosorption

Invited Paper

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Abstract: Electrochemical storage of hydrogen in activated carbon material has been investigated using different parameters of cathodic polarization. It has been proven that application of short galvanostatic pulses could be efficient for hydrogen storage in microporous carbon material. Charging current loads from 50 mA g\(^{-1}\) to 32 A g\(^{-1}\) have been used showing correlation between hydrogen capacity, time of charging and electrical efficiency. The anodic charge equivalent to electrooxidation of 1.0 wt% of hydrogen can be already reached after 90 s of cathodic polarization. Temperature effect has been also evaluated and a gradual increase of hydrogen capacity with a better pronounced oxidation plateau was obtained at higher temperatures.

Reversible electrosorption of hydrogen is a useful reaction in supercapacitor performance and it might have a potential application for a negative electrode of supercapacitor as well as reversibly operating electrode in the secondary cell.

Keywords: Hydrogen storage • Activated carbon electrode • Electrosorption • Pulse mode charging • Effect of temperature

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1. Introduction

Storage of hydrogen in carbon by electrosorption in ambient conditions is an attractive alternative for traditional high pressure or cryogenic storage methods. Hence, intensive research is presently devoted to application of nanotextured carbons because they seem to be the most promising materials. The reversible process of hydrogen electrosorption is attractive from the point of view of energy efficiency, since, in one step, it allows the hydrogen production from water electrolysis and its simultaneous storage in statu nascendi in the carbon substrate [1-12]. Hydrogen produced this way easily penetrates into the nanopores of the activated carbon where it is then adsorbed due to the driving force of the negative polarization. The charge/discharge phenomenon can be represented by the following general reaction:

\[ C + x H_2O + x e^- \leftrightarrow <CH_x^> + x OH^- \]

where \(<CH_x^>\) stands for the atomic hydrogen in a chemisorbed state inserted into the nanostructured carbon during charging and oxidized during discharging. It was assumed that the adsorbed hydrogen diffuses in the bulk of the carbon material occupying sites with high adsorbing energy [1-4]. Lately, it has been proven that, apart from physisorption being controlled by weak van der Waals forces, some part of hydrogen adatoms interact with carbon much stronger. The energy of hydrogen desorption evaluated by thermal programmed desorption (TPD) has a value of ca. 110 kJ mol\(^{-1}\) which suggests weak chemical bonds [5]. The type of bonding is affected by a microtexture of carbon material [6]. However, the role of surface functionality in carbon material is also important for hydrogen storage and cannot be neglected [7,8].

Hydrogen capacity is strongly determined by the physicochemical properties of carbon materials (texture, ultramicropore volume, elemental composition, etc.) but also by the parameters of the charging process (applied charging and discharging current density, time, and the total charge), temperature and the type of electrolytic medium. Detailed studies performed with different electrolytic solutions showed that alkaline medium seemed to be the most appropriate because
of the highest polarization occurring during cathodic process [3]. Some research has been devoted to study different conditions of discharge (oxidation) process [11-12], however, various parameters of charging process, especially with a pulse mode, were not considered.

In this paper, special attention will be devoted to the effect of cathodic polarization, with various current regimes, pulse mode charging and different temperatures during the sorption/desorption process, on hydrogen capacity.

2. Experimental Procedure

Hydrogen electrosorption was performed using an activated carbon obtained by carbonization and CO$_2$ activation of a viscose cloth. The activated cloth (AC) is a microporous material characterized by type I isotherm with narrow pore size distribution, estimated from nitrogen sorption at 77 K (Fig. 1). Specific surface area from N$_2$ sorption reaches value of 1390 m$^2$ g$^{-1}$, while micropore volume is 0.49 cm$^3$ g$^{-1}$ and total pore volume is 0.522 cm$^3$ g$^{-1}$. The ultramicropores (below 0.7 nm) were investigated by carbon dioxide sorption at 25$^\circ$C giving a volume of 0.291 cm$^3$ g$^{-1}$ and surface area of 765 m$^2$ g$^{-1}$.

The experiments were done in a three-electrode cell in which disk-shaped AC carbon and nickel foil were the working and the auxiliary electrodes, respectively. The mass of carbon electrode was in the range of 8 to 14 mg and a geometric surface area of one electrode was 0.8 cm$^2$. Most of the experiments were undertaken in 6 mol L$^{-1}$ KOH. The reference electrode was Hg/HgO in 6 mol L$^{-1}$ KOH. A wide range of current loads, i.e., from 50 mA g$^{-1}$ to 32 A g$^{-1}$ for charging and from 10 mA g$^{-1}$ to 1 A g$^{-1}$ for discharging process, have been applied.

For galvanostatic tests and potentiodynamic cycling at different voltage scan rates the following apparatus were used: ARBIN Instruments BT2000 – USA, VMP2/Z Biologic - France and AUTOLAB 30 FRA2 - Netherlands potentiostat-galvanostats. Some electrochemical characterization was performed at enhanced temperatures from 25$^\circ$C to 60$^\circ$C.

3. Results and Discussion

Voltammetry is a very valuable technique to study the kinetics of hydrogen electrosorption/desorption. A gradual 100 mV shift of potential limit in the negative directions allows to separate faradaic processes from charging the electrical double layer as has already been reported [3-6]. Obviously, there is a region where both processes overlap. After reaching the equilibrium potential of hydrogen evolution which is −0.924 vs. Hg/HgO in 6 mol L$^{-1}$ KOH, hydrogen is stored in the carbon nanotexture oxidized during anodic sweep. An example of such a voltammery curve with a 5 mV s$^{-1}$ scan rate for AC carbon electrode in 6 mol L$^{-1}$ KOH is presented in Fig. 2. The maximum anodic current is in the potential range from −0.9 V to −0.2 V vs. Hg/HgO. But extraction of hydrogen is strongly determined by oxidation parameters and cannot be excluded at −0.1 V vs. Hg/HgO. Obviously, over 0 V vs. Hg/HgO the simultaneous carbon oxidation can take place, hence, for efficient and long-term use of carbon electrode it is important.
to limit the potential of anodic hydrogen oxidation. It is noteworthy that the oxidation peak (hump) in the region of hydrogen desorption area has a tendency to split in the case of higher hydrogen capacity (last loop) assuming that carbon/hydrogen binding points out various energy sites of chemical character. It proves that for extraction of strongly bonded hydrogen the higher over-potential is compulsory.

Voltammetry supplies qualitative, rather than quantitative information on hydrogen sorption/desorption, which are processes very sensitive to scan rate. In some cases, it allows to observe underpotential hydrogen evolution (deposition) UPD as well as overpotential OPD process [13]. From theoretical predictions UPD seems to be responsible for stronger bonds of higher energy. On the other hand, galvanostatic charging/discharging is more adapted for a quantitative estimation of hydrogen capacity by a precise evaluation of time for H oxidation.

Generally, a high current load (0.5 to 1 A g\(^{-1}\)) is used for the charging process with a great excess of charge. Our target was to study more precisely the effect of cathodic polarization on hydrogen storage. Fig. 3 shows the effect of different charge capacity at constant current load of 32 A g\(^{-1}\) on electrical efficiency. It appears that with an electrical efficiency of 38%, 1 wt% of hydrogen can be loaded and it takes only 90 s whereas over 1.3 wt% of hydrogen can be reached with 50% efficiency during 340 s charging. It can be clearly seen that prolongation of charging definitively aggravates electrical efficiency and does not significantly improve the hydrogen capacity.

For optimization of the charging process some experiments have been performed with lower current loads, e.g. 5 A g\(^{-1}\) but with enhanced temperatures. In this case the total cathodic charge was fixed at 500 mAh g\(^{-1}\) (6 min. charging); electrical efficiency increased from 55 to 62% for 25°C and 50°C, respectively. Fig. 4 presents galvanostatic oxidation (discharge) of electrosorbed hydrogen using anodic current of 200 mA g\(^{-1}\). Both processes (charging and discharging) were performed at enhanced temperatures from 25°C to 60°C. Discharge capacity is strongly affected by the potential which is selected as a final one for calculating
discharging time. It was proved that the limit of +0.1 V vs. Hg/HgO is too high because efficiency exceeds 100%, e.g. at 50°C it is equal to 102% (charge is consumed for carbon oxidation). It seems that the most appropriate value for cut-off potential is an inclination of characteristic. The characteristics shown in Fig. 4 proved that process of electrosorption proceeds with a higher efficiency at enhanced temperatures; desorption plateau is better defined with a temperature increase, discharge capacity gradually increases from 274 mAh g⁻¹ for 25°C until 311 mAh g⁻¹ for 50°C, however, over this temperature the capacity has a constant value. A slight recombination (Tafel reaction) could be a competitive chemical reaction to faradaic process at the elevated temperature. Irreversible overoxidation of carbon must be taking place at higher voltage, accelerated especially at 60°C. The value of efficiency Qa/Qc (ratio of anodic charge to cathodic charge) over 100% at this temperature clearly supports this conclusion. The next method tried to modify the charging process was application of galvanostatic cathodic pulses with a pause step (Fig. 5). Instead of great excess of cathodic charge, as it was previously done in our research, the limited charge (500 mAh g⁻¹) was supplied in these experiments. The goal was to minimize time of charging with a simultaneous maintenance of high efficiency of hydrogen storage. Various charging current loads from 0.5 A g⁻¹ to 10 A g⁻¹ were used with different pulse mode, while selected charging time and pause varied from a few seconds to 0.1 s. By using optimal parameters (1 s pulse of 5 A g⁻¹ and 0.5 s pause) a total charging time of 9 minutes (6 min. charging + 3 min. pauses) was established to be enough to load carbon electrode with 1.08 wt% of hydrogen with 59% electrical efficiency. However, a pulse mode gave only moderate improvement with the slight increase of hydrogen capacity in comparison to the constant current without pulses (Fig. 6). The results showed that hydrogen sorption/desorption process on carbon electrode can proceed at high current loads and can have interesting application for the negative electrode of electrochemical capacitors, i.e., supercapacitors [9]. Quick faradaic processes are extremely useful for efficient charge propagation in these power devices. It is noteworthy that the pure double layer charging takes place on a short time scale, in micro to milliseconds, while hydrogen pseudocapacitance rises on time scales 10 to thousand times longer. Both processes can be easily distinguished. All the experiments were performed on the same AC cloth; hence, a further improvement is possible by selecting optimal carbon material with more adapted ultramicroporosity, mesopore fraction, surface functionality, conductivity, number of defects etc. Investigations performed on the carbon with controlled
hierarchical micro/mesoporosity [10-12] have shown that hydrogen capacity can be significantly increased.

4. Conclusions

Nanoporous carbon is a promising material for hydrogen electrosorption. Charging with high current loads of 5 A g\(^{-1}\) to 32 A g\(^{-1}\) (with or without pulse mode) is a quick and an efficient method for storage of hydrogen in the carbon electrode. Enhancement due to the temperature improves the hydrogen capacity and better defines oxidation plateau. Cyclability of carbon electrode for hydrogen storage was proven (over 50 cycles) and only moderate loss of hydrogen capacity was observed. It is important to limit potential for anodic hydrogen oxidation for an efficient and long-term use of carbon electrode.

Interesting properties of carbon with electrosorbed hydrogen have useful applications in supercapacitors (negative electrode) and as reversible anodes operating in the secondary cell.

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