Influence of Plasma Treatment on Hydrogen Electrosorption Capacity by Carbon Electrodes

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This paper is reports on the effect of plasma treatment with various discharge regimes and plasma sources (Ar, O_2 and CO_2) on hydrogen capacity of carbon electrodes. Among various modifications of carbon materials being undertaken to increase hydrogen storage capacity, plasma treatment seems to be quite interesting one. Obtained results confirmed that surface properties modified by plasma treatment play an important role in hydrogen electrosorption process. The highest hydrogen capacity, i.e., 425 mAh g^{-1} (1.56 wt.%) was recorded for electrode after 15 seconds of Ar-plasma treatment, whereas the lowest value was observed also for electrode after Ar-plasma treatment but with longer time, i.e., 300 seconds. The results for samples with O_2 and CO_2 plasma source are rather comparable with the reference sample. Unfortunately, no direct dependency between plasma type, time of treatment and hydrogen capacity was found, however, an repeatable increase of hydrogen stored on the electrodes treated by Ar-plasma type was observed.

1. INTRODUCTION

Hydrogen as a fuel has advantageous non-pollutant character; its theoretical efficiency of combustion considered as Otto cycle (or Otto engine) is higher than for petroleum even by 8% and has the highest energy density, i.e., 142 MJ kg^{-1} because of its low weight. Unfortunately, the main obstacles aggravating hydrogen-based economy and development are related with storage methods [1].

Physicochemical methods of hydrogen storage mainly consist on its adsorption on porous materials like various forms of carbon. Among them, activated carbons play an important role today for hydrogen storage. Several works devoted also for carbon nanotubes did not give reproducible hydrogen uptake reported. Some extrapolations resulted in hydrogen storage capacity estimated as 10 wt% [2] or even 67 wt% of herringbone graphitic nanofibers [3-4]. Unfortunately, these results were never reproduced and reported by others.

On the other hand, it is also possible to store hydrogen on electrochemical manner. Electrosorption of hydrogen into carbon at ambient conditions (0.1013 MPa, 293 K) seems to be an attractive alternative for traditional high pressure or cryogenic method. Presently, intensive research is devoted to application of various form of activated carbons because they appeared to be the most promising materials in this application, due to their excellent conductivity, low charge transfer resistance, high specific surface area and well-developed microporosity [5-10]. Moreover, because of various textural and structural parameters [11], hydrogen capacity might be tailored by synthesis method [12], carbon source [13] and applied regime [14, 15].

The reversible process of hydrogen electrosorption is quite attractive also from the point of view of energy efficiency because this process arises in one-step hydrogen creation from water electrolysis; immediately after hydrogen reduction, there is simultaneous storage *in statu nascendi* in the carbon substrate [7,10,16]. Hydrogen produced by this way easily penetrates nanopores of the carbon matrix and is adsorbed due to the driving force of the negative polarization. The overall charge/discharge phenomenon can be summarized by reaction:

$$<C> + x\ H_2O + x\ e^- \rightarrow <CH_x> + x\ OH^- \qquad (1)$$
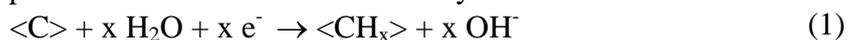
According to reaction, the hydrogen uptake can be recalculated from the Faraday law and the charge recovered during oxidation process; accordingly, 273 mAh g^{-1} corresponds to 1 wt.% of hydrogen stored in carbon material [7].

Although carbon materials have well-developed porosity and properties, the lack of surface functionalities (i.e., polar groups) in the structure makes their surface rather hydrophobic which significantly limits their application [17]. From this point of view, surface modification seems to be reasonable direction towards enhancement of their surface properties; hence, considerable efforts have been made to improve this parameter such as ammonia, steam or KOH treatment, plasma-enhanced chemical vapour deposition (PECVD), etc. [18-21]. Among various modification of carbon materials being undertaken to increase hydrogen storage capacity, plasma treatment seems to be quite interesting one. To the best knowledge of the authors, such an approach has never been applied for hydrogen electrosorption purposes.

Accordingly, plasma treated carbons with their further applications in electrochemical energy conversion and storage systems presently attract great attention because of convenience of such modification [22-29]. Plasma treatment (generally) does not affect typical textural properties [30-32] but strongly influences surface functionalities, significantly contributing in charge transfer and accumulation processes. Generally, due to oxidizing character of plasma, oxygen-based functional groups (phenolic, carbonyl or carboxylic) are generated [31,33]. Most extensive considerations of this matter can be found elsewhere [34-36].

In this paper, a special attention is focused on the effect of plasma treatment with various discharge regimes and plasma sources (Ar, O_2 and CO_2) on hydrogen capacity of carbon electrodes.

2. EXPERIMENTAL

2.1 Activated carbon samples

A commercial activated carbon tissue Kynol 2000 from Kynol® Germany (labelled as T0) was used as a raw material.

2.2 Plasma treatment

The process of plasma treatment was performed in a parallel plate reactor with a radio frequency (13.56 MHz) glow discharge. A scheme of the reactor is presented in Ref. [34]. Samples of activated carbon tissue were exposed to the plasma generated with three gases: O_2, CO_2 and Ar. The flow rate of reactive gases and their initial pressure in the reactor chamber were 8 sccm (standard cubic centimetres per minute) and 10 Pa, respectively. The power of the glow discharge and time of exposition is reported in Table 1. After treatment the pellets were turned on the other side and the process was repeated.

Table 1. Plasma treatment conditions.

Sample	Plasma type	Power, W	Treatment time, s
T0	REFERENCE		
T1	Argon	80	15
T2			60
T3			300
T4			600
T5	Oxygen		15
T6			60
T7			300
T8			600
T9	Carbon dioxide		15
T10			60
T11			300
T12			600

2.3 Physicochemical characterization of the samples

In order to evaluate the influence of plasma treatment on specific surface area, nitrogen adsorption/desorption isotherms were recorded on ASAP 2010 instrument (Micromeritics®, USA) for all investigated samples. Specific surface area calculated from isotherms are collected in Table 2.

Unfortunately, there is no direct tendency which can be extracted from obtained results. Generally, O_2-plasma enhanced the specific surface area ($+47$ m^2 g^{-1}, on average) and the discrepancy among the samples with various treatment time is the lowest. Oxidizing character of O_2-plasma type might result in novel functionalities on carbon surface, related also with some changes in micro/mesopore structure [37]. These results are in accordance to the present knowledge in the field; plasma might serve as a source of free radicals and these radicals might attack the surface even when the treatment seems to be finished. To date, there is no direct method to inhibit the activity of the radicals and to determine precisely the real treatment time.

Table 2. Specific surface area for samples after plasma treatment.

Sample	S_{BET} m^2 g^{-1}	S_{BET} change	Average S_{BET}	St. dev.
T0	1942	0	-	-
T1	1770	-172	1892	129
T2	1868	-74		
T3	1818	-124		
T4	2064	+122		
T5	2001	+59	1989	38
T6	2035	+93		
T7	1972	+30		
T8	1946	+4		
T9	1893	-49	1894	79
T10	1785	-157		
T11	1929	-13		
T12	1968	+26		

However, there is an optimal time for treatment observed; oxidizing character of O_2-plasma type, apart from functionalities development, might also block the entrance to the micropores by surface etching [38]. In case of Ar and CO_2-plasma types, generally, measured specific surface decreased, but for the longest time of treatment, i.e., 600 s, some development of this parameter can be observed. The higher value is observed for Ar-plasma type (i.e., $+122$ m^2 g^{-1} vs. $+26$ m^2 g^{-1} for CO_2-plasma type) followed by the highest discrepancy (by the meaning of standard deviation of specific surface area measured for treated samples). In both cases, rather destructive character of plasma is confirmed. It could be assumed, that rather inert character for functionality development of these kinds of plasma can only influence the micro/mesopore structure. Such a discrepancy in specific surface areas could be explained by surface degradation with time of treatment [33], blocked entrance to the micropores as well as by poly(tetrafluorethylene) deposition on carbon fibers [30]. Furthermore, precipitated species of PTFE could play a role of hydrophobizing agent and can limit the (aqueous) electrolyte penetration. On the other hand, one cannot neglect some influence of activation of sample impurities (precursor, etc.)

Scanning Electron Microscopy (SEM) characterisation made using Quanta FEG – FEI, confirms mentioned assumptions. The SEM images of original tissue and after Ar-plasma treatment are shown in Fig. 1. The surface of carbon fibres seems to be rather smooth, however, some defects can be observed at higher magnifications. After 15 seconds of Ar-plasma treatment, the surface is more smoothed than for raw material. The number of defects observed is lower which reflects in specific surface area S_{BET} value reported (-172 $m^2 g^{-1}$ vs. raw material).
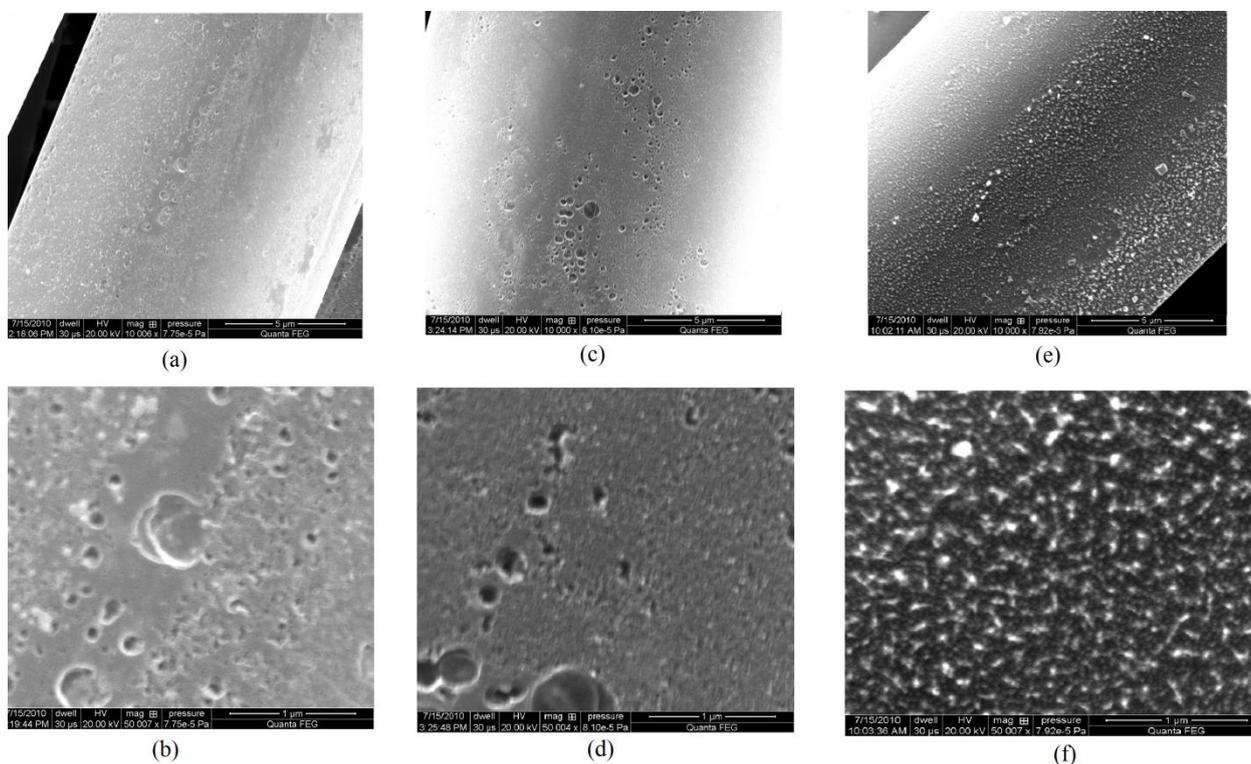

Figure 1. SEM images of: activated carbon tissue (T0 sample) before plasma treatment (a,b); after 15 s of Ar-plasma treatment (T1 sample) (c,d) and after 600 s of Ar-plasma treatment (T4 sample) (e,f).

As it was mentioned above, the longer time of plasma treatment can result in precipitation of PTFE from plasma installation. Presented SEM images (Fig. 1 e, f) after 600 seconds of treatment confirm these assumptions. Obviously, their presence on the carbon surface can enhance the specific surface area (+122 $m^2 g^{-1}$), but they are rather useless for hydrogen storage due to poor porosity, hydrophobic character and lack of the active sites for adsorption. Additionally, longer time of treatment might deteriorate peculiar porous structure of carbon material. Similar results were obtained for other samples. Unfortunately, we did not remark some significant increase of active surface area (ASA) [8].

2.4 Electrochemical characterisation

Hydrogen storage properties of plasma treated carbons were investigated by its electrosorption from alkaline electrolyte. The experiments were done in a three-electrode cell with a pellet of carbon tissue and nickel foil as the working and the counter electrodes, respectively. The mass of carbon electrode was in the range of 16 to 19 mg and a geometric surface area of one electrode was 0.8 cm^2. All experiments were carried out in 6 mol L^{-1} KOH. The reference electrode was Hg|HgO in 6 mol L^{-1} KOH (+0.052 V vs. NHE). The current regime was -1 A g^{-1} for charging (hydrogen storage) and +50 mA g^{-1} for discharging process (hydrogen oxidation). VMP3 multipotentiostat/galvanostat from BioLogic$^®$, France, was used for all electrochemical measurements.

3. RESULTS AND DISCUSSION
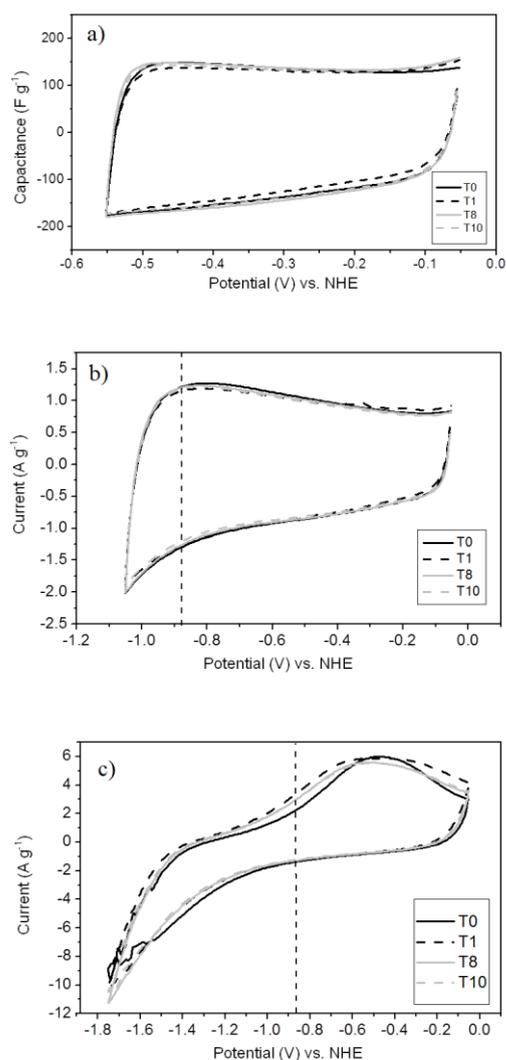
Figure 2. Cyclic voltammograms of activated carbon electrodes after: Ar (15 s), O$_2$ (600 s) and CO$_2$ (60 s) - plasma treatment, operating in 6 mol L^{-1} KOH solution, recorded at 5 mV s^{-1} scan rate; (a) electrical double layer charging/discharging area, (b) potential range near to hydrogen evolution potential and (c) far from hydrogen evolution potential with hydrogen reduction and oxidation peaks.

Cyclic voltammetry as a great qualitative technique was used to evaluate electrochemical behaviour of carbon electrodes before and after plasma treatment. 5 mV s^{-1} scan rate in wide potential range was applied in order to examine both double layer charging/discharging and hydrogen storage processes. The results are presented in Figure 2. Changing of potential limits in the negative directions permits to extract the electrical double layer charging/discharging area from the faradic reactions connected with hydrogen reduction and oxidation. After exceeding the equilibrium potential of hydrogen evolution (-0.826 V vs. NHE in 6 mol L^{-1} KOH solution) hydrogen reduction and oxidation peaks are visible [15].
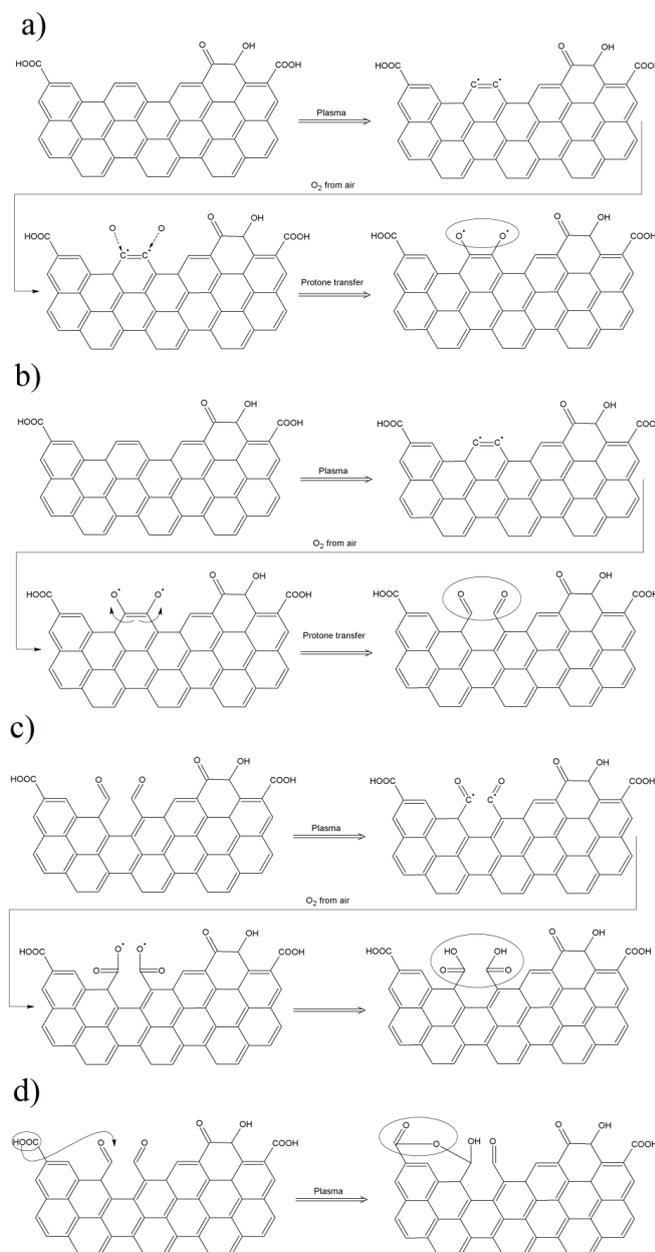
Figure 3. C-O type (a), C=O type (b), -OC=O (c) and lactone-like (d) functionals generation during electrode exposition on air after plasma treatment.

As it can be seen in Fig 2, there is no significant change in qualitative response of electrodes after plasma treatment, whatever plasma type. However, the higher oxidation current can be observed for electrodes subjected to Ar-plasma treatment. It might suggest that this type of plasma does not affect and does not develop significantly surface functionalities; quite inert type of plasma could only influence the porous structure but no significant influence of plasma treatment on hydrogen evolution overpotential is observed.

As it was mentioned earlier, carbon functional group (especially with high oxygen content such as carboxylic, ester or epoxy type) might deteriorate the hydrogen storage process. Generally, the presence of surface oxygen groups in the activated carbons affects the amount of electrochemically stored hydrogen not only in alkaline but also in neutral medium [39,40]. It is worth to note that such functionalities are not created only during plasma treatment but also during the sample exposition on air after treatment. Free radicals present on carbon matrix after treatment can create various types of functionals, as it is presented in Fig. 3.

Oxygen-based functionalities play an important role with potential distribution and can significantly change the pH (towards acidic one) near to the electrode/electrolyte interface because of oxygen electronegativity. Additionally, the reactions between electrode material and electrolyte (on the interface) might be competitive with hydrogen sorption and can decrease hydrogen capacity. Such assumption was confirmed by Lee et al. [41]; chemically treated multi-walled carbon nanotubes showed decreasing or increasing hydrogen storage capacity dependently on the kind of treatment (basic or acidic). Increase of hydrogen capacity was observed due to the acceptor-donor interaction at specific sites on the surface of modified carbon materials.

In order to determine hydrogen storage capacity quantitatively, galvanostatic charging discharging method was applied. The results are presented in Fig. 4. The results of galvanostatic charging/discharging method are in great accordance with cyclic voltammetry in double layer charging/discharging area, however, more significant changes in hydrogen capacity can be observed. The hydrogen capacity of non-treated carbon electrode was 395 mAh g^{-1} (1.44 wt.%). The highest hydrogen capacity, i.e., 425 mAh g^{-1} (1.56 wt.%) was recorded for electrode after 15 seconds of Ar-plasma treatment, whereas the lowest value was observed also for electrode after Ar-plasma treatment but with longer time, i.e., 300 seconds; The value of 210 mAh g^{-1} (0.77 wt.%) is reported. Slight increase of hydrogen capacity is observed for 600 seconds of Ar-plasma treatment; it might be related with some increase of electrode specific surface area, but the value reported (275 mAh g^{-1}, 1.01 wt.%) is still lower than for the raw material.

The results for other samples with O_2 and CO_2 plasma source are rather comparable with the reference sample. Similar course of the discharging curves in case of O_2-plasma type treated electrodes prove that not only specific surface area is important factor for hydrogen storage. We assume, that created oxygen-based functionalities aggravate the hydrogen electrosorption and for this reason there is no reflection of specific surface area development in hydrogen storage capacity (ca. 325 mAh g^{-1}, 1.19 wt.%). In case of CO_2-plasma type, similar courses of discharging curves were recorded which suggest rather inert character of this treatment; however, the specific surface area is lower than for raw material; it suggests that plasma treatment can slightly change the porous structure but rather in the area of macro- and mesopores. For both cases, surface etching cannot be neglected.

Due to the fact, that hydrogen electrosorption on carbon materials depends on porous structure, surface chemistry and electrical properties of the materials, the linear influence on the efficiency is relatively doubtful. It was confirmed by Babel et al. [13] – activated carbons produced from natural precursors (with changing the carbonization and KOH activation parameters of processes) showed completely various hydrogen storage capacity.
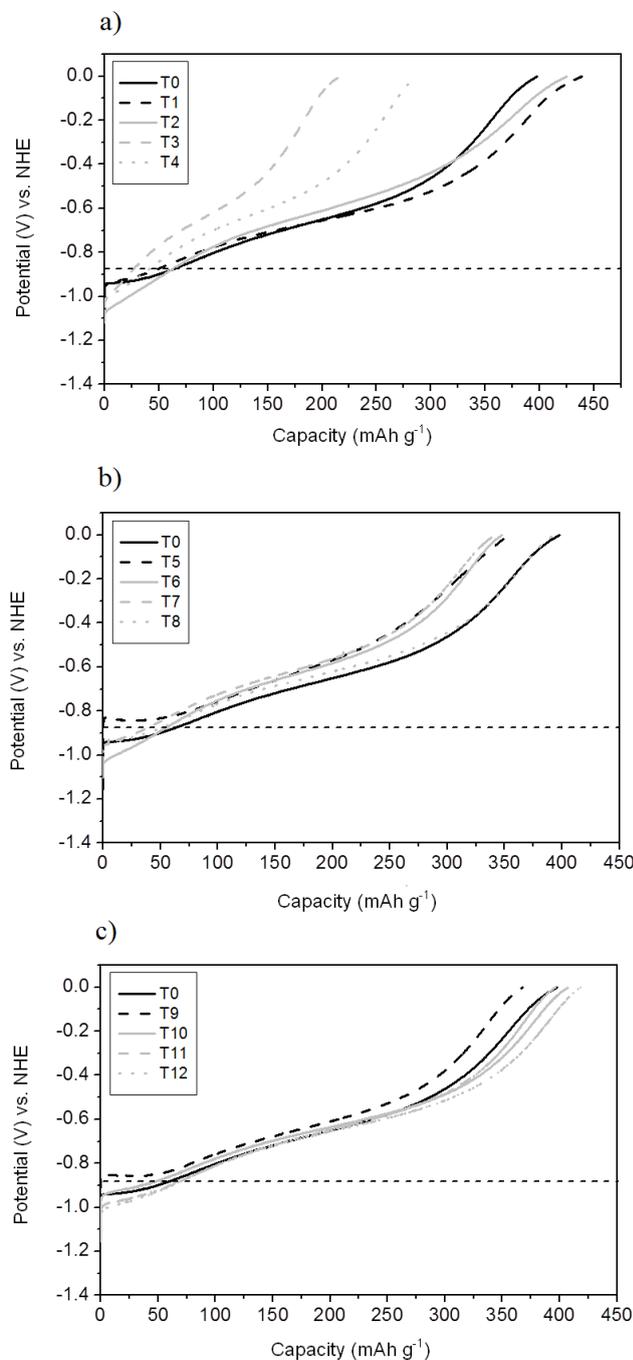
Figure 4. Galvanostatic discharging (50 mA g^{-1}) curves for carbon electrodes after: Ar-plasma treatment (a), O$_2$-plasma treatment (b), CO$_2$-plasma treatment (c) and 6 hours of hydrogen loading at 1 A g^{-1} cathodic current density .
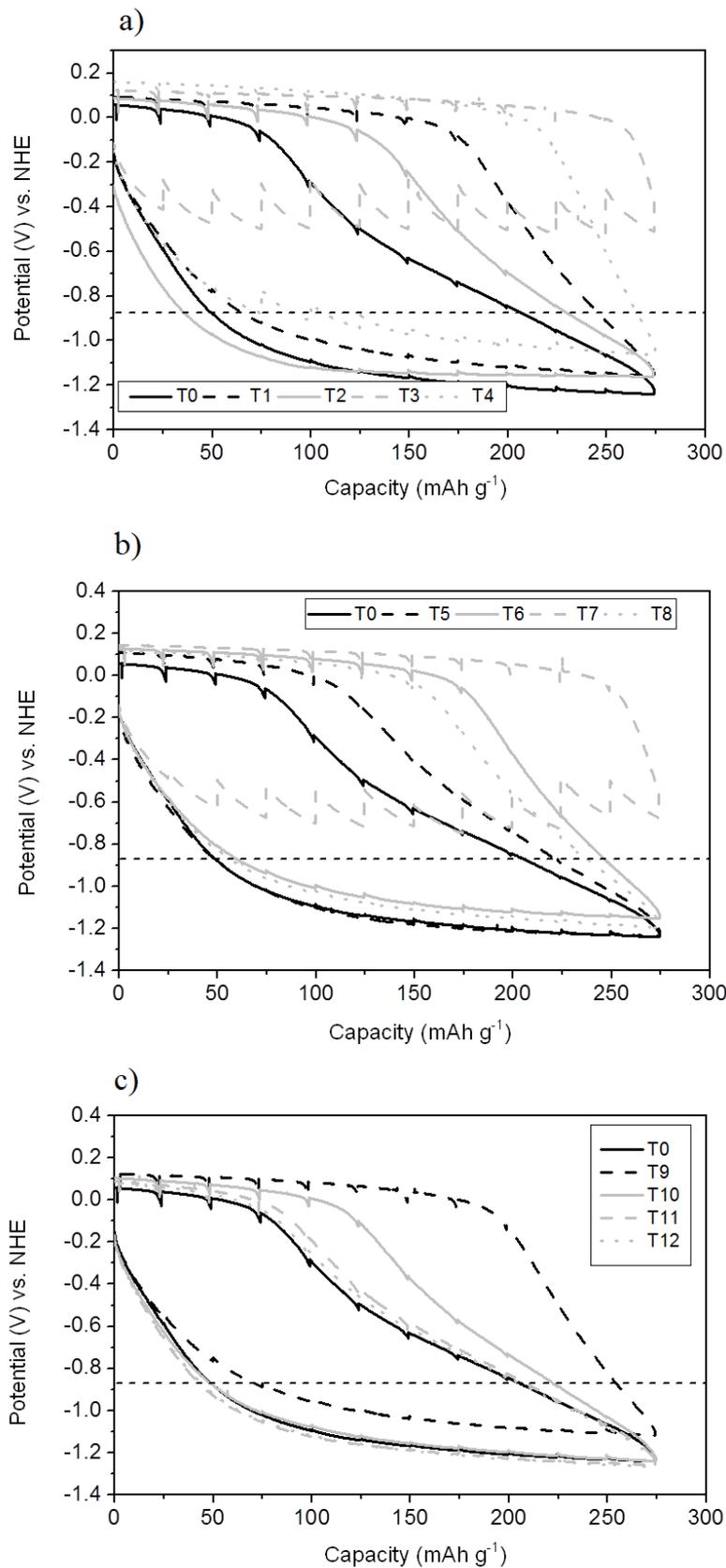
Figure 5. Galvanostatic Intermittent Titration Technique (GITT) curves for carbon electrodes after: Ar-plasma treatment (a), O_2-plasma treatment (b) and CO_2-plasma treatment (c).

Plasma treatment less influences textural properties and surface functionalities than KOH activation, therefore the hydrogen capacities obtained are not so high as 2.31 wt.% as it was in case of activated carbon obtained from blackthorn stones [13].

Obtained results imply that type of hydrogen bonding is quite different for investigated samples. In order to evaluate the strength of carbon/hydrogen bonds, Galvanostatic Intermittent Titration Technique (GITT) was applied. Each sample was subjected to 25 mA g^{-1} of cathodic current 11 times with 1 hour relaxation period between each polarisation step and after that 25 mA g^{-1} of anodic current with the same manner. The results are presented in Fig. 5.

Significant overpotential observed for samples T3 and T4 after Ar-plasma treatment suggests rather weak hydrogen bonding and probably significant change of carbon functionality. It could be also related with hydrophobic character of the electrode. On the other hand, for T1 and T2 samples, coarse of GITT curve is almost the same as for reference one. It means that the hydrogen is bonded strongly and after polarisation there is no evolution or recombination of gaseous hydrogen (H_2) during relaxation time. It concerns also the samples treated with other plasma type with similar time of the treatment. Additionally, for samples subjected to Ar- and O_2-plasma treatment for 300 seconds, the electrodes did not reach the hydrogen evolution potential (dashed lines), hence, hydrogen storage cannot be considered. It seems that applied current density (25 mA g^{-1}) is too low to overcome the barrier of the hydrogen evolution reaction energy.

4. CONCLUSIONS

It has been proved that various type of plasma treatment, dependently on time and plasma source can influence on electrochemical response of carbon electrodes and hydrogen electrosorption capacity. Obtained results confirmed that surface properties modified by plasma treatment play an important role in hydrogen electrosorption process. These results confirmed a general assumption that hydrogen should be stored in microporous carbons with rather low oxygen content. Unfortunately, no direct dependency between plasma type, time of treatment and hydrogen capacity was found, however, slight increase of hydrogen stored on the electrodes treated by Ar-plasma type was observed. It might be caused by aggressive character of free radicals and uncontrolled damage of the carbon surface during treatment as well as blockage of the pores serving as active sites for hydrogen storage. Finally, we experimentally proved an important influence of functionalities and surface area parameters on electrosorption of hydrogen in carbon materials.

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