

Self-buffered pH at carbon surfaces in aqueous supercapacitors

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ABSTRACT

This paper presents a unique strategy aiming at extending the operational voltage range in supercapacitor working in the neutral aqueous electrolyte. In-depth analysis of the equilibria formed at the carbon/electrolyte interface gives the possibility to reach 1.8 V with excellent reversibility during cycling. To reach the goal, the donor - acceptor nature of carbon electrode surface has been taken into consideration. Controlled oxidation of electrode materials coupled with ammonia adsorption have been realized in order to adjust the optimal equilibrium conditions. Nitric acid oxidation of carbon leads to the formation of electrochemically active acidic sites promoting adsorption of ammonia. Modification with ammonia results in the introduction of self-controlled pH gradient within the capacitor system and formation of protective layer on electrodes, responsible for higher overpotentials of solvent decomposition. This, in turn, allows capacitor operation at higher voltages. Furthermore, this configuration eliminates the need for physical separation of ions (such as an ion-exchange membrane) to decelerate their mixing and improves the power density of the device.

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1. Introduction

The area of energy storage devices is currently dominated by the batteries made of rechargeable cells, such as lead-acid, NiO(OH)-MH, NiO(OH)-Cd and Li-ion batteries. The latter are nowadays the most widely used in the growing market of portable electronics or hybrid electric vehicles [1]. On one hand, high specific energy is offered (>100 Wh/kg) at the nominal voltage of 3.6 V (4.2 V - 3.0 V, upper and lower voltage limits, respectively). On the other hand, many drawbacks such as relatively low power density (<200 W/kg) and limited cyclability (owing to faradaic nature of the energy storage process) can be listed as well [2]. Furthermore, Li-ion cells contain flammable, organic electrolyte and quite often the metallic lithium which may be explosive when exposed to moisture or oxygen (e.g. during incidental punctuation) [3]. An alternative solution developed during the last 50 years is a special type of capacitor operating in a medium containing ions as charge carriers, originally

called electrochemical capacitors. These are the devices for energy storage which utilize the electrical double-layer for charge storage phenomenon. It comprises physical attraction and repulsion of ions by the electrodes made of high surface area material, usually activated carbon. During charging, the positive electrode changes its potential towards more positive values, while the negative one - towards negative potential values. Unlike batteries, the electrochemical capacitors operate in variable voltage range [4]. The voltage of supercapacitor is proportional to the amount of charge stored on the electrodes. The maximum voltage, on the other hand, is dictated by the dielectric strength of insulator (electrical double-layer, EDL), which depends on the solvent used. Supercapacitors already commercialized and present on the market usually operate using an organic solvent (acetonitrile, propylene carbonate) for the electrolyte formulation, which allows reaching high voltage (2.7 V), but its toxicity and high price limits its further implementation [5]. Hence, supercapacitors operating in the aqueous medium is an interesting alternative [6]. Aqueous medium offers environmentally benign character but has the voltage limit relatively low, dictated by water decomposition (1.23 V).

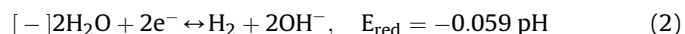
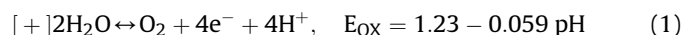
So far, many approaches have been made in order to extend the voltage limit above that value [7,8]; aqueous-based capacitor can

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operate even above 1.5 V, sustaining excellent cyclability. It has been elucidated by a phenomenon called hydrogen electrosorption, which takes place at negative electrode once the hydrogen evolution potential is reached. The product of water reduction is nascent hydrogen which is stored in the porosity of the electrode material. At the same time, the pH locally alkalizes owing to hydroxide ions release causing a change of equilibrium potential of di-hydrogen evolution. Considering the Pourbaix diagram, demonstrating the electrochemical stability window of water, it looks beneficial to increase and maintain pH gradient in supercapacitor system [9]. This strategy has already been reported and reaching higher voltage values by using different electrolytes for electrodes using inert separator made of glass fibre has been realized. However, the results of such treatment may be short-term due to the mixing of electrolytic solutions. It is worth to mention that the study is presented rather as a background theory, in oversized electrochemical vessel which impede commercialization [10]. The modification which allows using compact device includes the use of the ion-exchange membrane. However, in order to achieve good separation, the membrane must be sufficiently thick, which introduce additional mass-transfer resistance [11].

Another source of pH gradient might originate from electrodes. Activated carbon is well known as being versatile for modifications [12–17]. We propose modifications of electrode materials by the adjustment of their acid-base character. It has been shown that surface acidity of carbon is strictly related to oxygenated functional groups which are characterized either by their electron acceptor or electron donor nature [18]. Reactions (1) and (2) present the half-reactions associated to electrolytic water decomposition in neutral medium [19]. Low pH value (high proton concentration) switch the equilibrium of reaction (1) towards substrates (water) according to Le Chatelier principle.



Considering Pourbaix diagram once again, water possesses highest electrochemical window specifically when oxidation takes place in an acidic environment (low pH), while the reduction occurs in an alkaline one (high pH). Consequently, the positive electrode material may be enriched in acidic surface groups (carboxyl, lactone, and phenol), while the negative one in basic functional groups (pyrone, chromene, ether, and carbonyl) [20]. The introduction of oxygen surface groups is often presented in the literature as treatment in nitric acid, hydrogen peroxide or ammonium persulfate [21]. Occasionally, the subsequent thermal treatment of the material may be used for selective removal of formed surface groups for adjusting acid-base properties of the carbon electrode [22]. A strategy to generate an alkaline character in the porosity of the electrode once contacted with aqueous electrolyte may be caused by previously adsorbed electron donating species, for example, ammonia. Dissolution of ammonia produces its soluble form of very weak acid (ammonium ion) and a strong base (hydroxide anion) (3).



Although ammonia is easily soluble in water, reaction (3) is an equilibrium reaction, meaning that some of the ammonia remains in the insoluble state, facilitated by its high affinity to porous carbon [23]. It is worth to add that oxidation of carbons prior to ammonia adsorption promotes the process [24], influencing the equilibrium of reaction (3). The equilibrium creates the self-buffering layer on the carbon by the attraction of OH^- ions

alkalizing the pH locally. The equilibrium of reaction (2) will be switched towards substrates owing to both ammonia and reversible hydrogen electrosorption. Ammonia, owing to its amphoteric properties, may act as an electron acceptor species in a reaction (4), producing hydronium cations which acidify the solution.



In order to take full advantage of capacitor asymmetry, it is necessary to account for the mutual operation of carbon electrodes with electrolyte. It seems to be important to ensure that the electrolyte operates in a non-buffered mode, which means that even slight change of hydronium ion concentration will result in dramatic pH changes.

In the paper, we present a novel strategy which aims at the introduction of intrinsic pH gradient to the electrochemical system (pH of both electrode/electrolyte interfaces differs by six units). Moreover, the susceptibility of the electrolyte to undergo pH fluctuation caused by diffusion current is taken into account. It is believed that proper adjustment of the acid-base properties of the electrode/electrolyte interfaces advantageously impact the lifetime of the capacitor, owing to the high stability of modified carbons. It allows extending the operating voltage of supercapacitor in an aqueous medium beyond theoretical decomposition voltage.

2. Experimental

2.1. Electrochemical measurements

The electrode active material is prepared using activated carbon Kuraray YP-50F (AC). The electrode composite is made of 97% of AC playing the role of active material and 3% of polytetrafluoroethylene (PTFE) as a polymeric binder. The ingredients are mixed and prepared as indicated elsewhere [25]. The circular pellets of 10 mm diameter and ~250 μm thickness playing the role of electrodes are cut from the resulting film. They are immersed in the electrolyte, 1 mol L^{-1} Li_2SO_4 , separated by glass fibre separator Whatman GF/A and placed in two-electrode cell configuration (Swagelok) equipped with reference electrode ($\text{Hg}/\text{Hg}_2\text{SO}_4$ - potential values recalculated versus Standard Hydrogen Electrode) for additional monitoring of the behaviour of positive and negative electrode separately.

2.2. Modifications of the electrodes

- The oxidation procedure involves the 1 h treatment of AC in concentrated HNO_3 at 90 °C, as presented elsewhere [22]. Selected oxidized ACs are subjected to heat treatment in the N_2 atmosphere at 300 °C or 500 °C for 2 h. Heating rate is 10 °C/min. The resulting carbons are denoted as k50ox, k50ox300, and k50ox500.
- Modification by ammonia is accomplished by placing the electrode films above the 25% ammonia solution for 3 h. It is carried out on composites prepared using unmodified AC (k50am), oxidized AC (k50oxam) and thermally treated carbons (k50ox300am and k50ox500am).

2.3. Physicochemical characterization

The textural parameters of activated carbons are determined from nitrogen adsorption/desorption isotherm measurement at 77 K (ASAP 2460, Micromeritics). The carbons are purged under helium flow at room temperature and placed under high vacuum for several hours prior to the analysis. Surface area is calculated

according to BET (Brunauer-Emmett-Teller) theory at relative pressure range from 0.01 to 0.05. Micro- and mesopore volume values are determined by 2D-NLDFT (Two Dimensional Non Local Density Functional Theory). Titration curves of the electrolytes are obtained using Metrohm Titrino 848. Thermoprogrammed desorption coupled with mass spectrometry measurements are carried out (TPD-MS, Netzsch). The monitored mass-to-charge ratios are 28 and 44, responsible for the detection of CO and CO₂. Ammonia and other N-containing species are identified by the quantitative analysis on TPD setup at 10 K min⁻¹ [26]. X-ray photoelectron spectroscopy (XPS) is performed with a VG Scienta SES 200-2 spectrometer equipped with a monochromatized Al K α X-ray source (1486.6 eV) and a hemispherical analyzer. The pass energy is 100 eV. The electrodes surface identities are characterized by titration method with 0.1 M NaOH or 0.1 M HCl, quantitatively determining total acidic and basic sites.

3. Results and discussion

3.1. Physicochemical characterization

The non-buffered condition of the electrolyte is found based on its titration curve. This mode of the electrolyte is positioned exactly at its equivalence point, which is accomplished by adjusting the initial pH to the value of electrolyte equivalence point of the salt resulting from a strong acid and strong base (e.g. Li₂SO₄) at high concentrations (>0.1 mol L⁻¹). High concentrations are demanded to ensure sufficient conductivity. Fig. 1 presents titration curves of Li₂SO₄ solutions of 0.5, 1 and 2 mol L⁻¹. It proves that at such concentrations, this parameter does not play an important role in the susceptibility for pH change. Based on the graph it is concluded that the electrolyte can easily change its pH by adding tiny amounts of strong acid/strong base in the region of ca. pH = 4–10. Calculating the equilibrium electrode potentials for oxygen and hydrogen evolution using Nernst equation, the electrochemical stability window is equal to 1.6 V. Considering the existence of considerable hydrogen evolution overpotential and small overpotential for oxygen evolution, the final cell should operate with high stability at the voltage higher than 1.8 V.

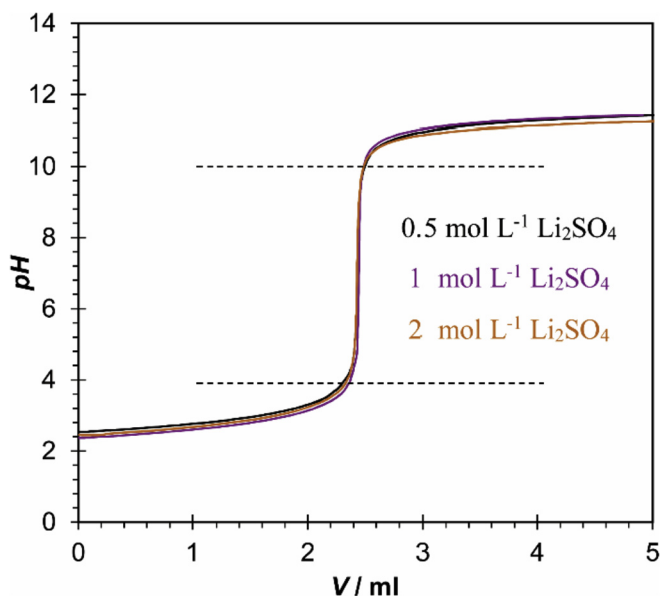


Fig. 1. Titration curves of 0.5, 1, 2 mol L⁻¹ Li₂SO₄ electrolytes. Colours indicate the concentration. (A colour version of this figure can be viewed online.)

The oxidation, as well as subsequent thermal treatment of carbon, preserves the dominant microporous character of the surface (Fig. 2a–b). The oxidation leads to the dramatic decrease in surface area by 20%, where both, micro and mesopore volumes are almost equally affected in non-ammoniated carbons (Table 1). It is probably caused by the formation of new oxygen functionalities which block the entrance to the pores. The subsequent treatment at 300 °C do not significantly impact the total surface area; rather it increases the micropore volume on the favour of mesopores. Treatment at 500 °C makes the carbon to approach the initial surface area (here it is reduced only by 11% with respect to k50). The surface area of carbon heat-treated at 500 °C is equal to 89% of the initial value. Microporosity increases by 10%, while the mesoporosity slightly falls. The results are dramatically changed for ammonia modified samples. For non-oxidized carbon, only the decrease by ca. 20 m² g⁻¹ is observed, what may be associated with permanent pore filling by ammonia groups. On the other hand, in oxidized and ammoniated samples the measured surface area is higher than in case when the carbon is only oxidized. The most appropriate explanation is that the adsorbed ammonia changes the oxygenated groups' nature, so that they do not block the pore entrance. It cannot be excluded that such groups are more easily evacuated during outgassing process before sorption measurements.

The variations in textural parameters are in agreement with TPD measurements (Fig. 3). The initial carbon k50 is characterized by the absence of desorption peaks below 600 °C, meaning that the carbon is relatively inert. A small desorption peak of CO₂ is observed above 600 °C up to 900 °C (Fig. 3a). It is related to oxygen functionalities, as lactones [27,28] strongly incorporated into carbon structure, and probably has a minor effect on its acid/base properties. The CO evolves significantly only at high temperatures. The oxidation in nitric acid causes weakening of C–O bonds in lactones, which makes the CO₂ evolving at a lower temperature – mainly situated on two peaks at 290 °C and 450 °C (Fig. 3b). They are responsible for increased acidity of the material caused by carboxyl groups and partially to anhydride groups. There is a tremendous increase of CO-evolving functionalities (740 °C and 830 °C) which correspond to phenol and carbonyl groups, respectively. Due to high binding energy, these groups might be less accessible and play a less important role in imposing the acid-base character of interface. Treatment at 300 °C selectively removes CO₂-evolving groups at 290 °C, being assigned as strongly acidic, as well as CO-evolving groups in close vicinity (300 °C and 450 °C), which are assigned to decomposition of R-substituted ketone or aldehyde. They are probably very unstable. CO-evolving groups at higher temperatures seem to remain unchanged. Further treatment at 500 °C removes the CO₂-evolving groups at 450 °C, assigned to less acidic ones. Strongly bonded CO groups (carbonyl/quinone) remain mostly unchanged. Consequently, acidity of carbons increases in the order k50 < k50ox500 < k50ox300 < k50ox.

The presence of ammonia adsorbed by the carbon is confirmed by thermodesorption measurements, by showing the release of N-containing gaseous products (Fig. 4). NH₃, N₂, HCN, NO signals in ammoniated carbons clearly prove their origin from ammonia treatment. N₂ gas amount is the highest for k50oxam which has the highest tendency to adsorb ammonia, and then decreases for less oxidized samples. Along with that assumption, sample k50ox500am should be found slightly below k50ox300, however, it may be deduced that all this nitrogen is released mainly as HCN and NH₃ instead of N₂, meaning that it evolves from different functionalities. Exclusively high amount of NH₃ for k50ox500am informs about weak nature of bonding. Similar amount of HCN as for k50ox500am is also associated to k50oxam, which together with N₂ confirm strong bonding of nitrogen to carbon network as further

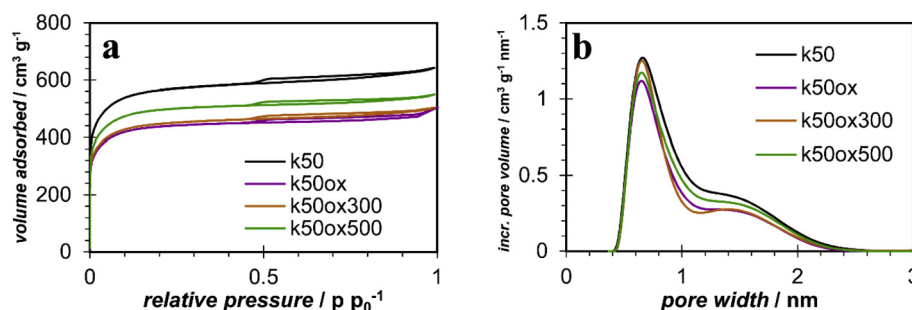


Fig. 2. Adsorption/desorption of nitrogen at 77 K measurement: a) isotherms, b) pore size distribution. (A colour version of this figure can be viewed online.)

Table 1

The values of specific surface area and volume adsorbed for carbon samples.

Name	Surface area [m²·g⁻¹]	V _{micro} < 2 nm [cm³·g⁻¹]	V _{meso} 2–50 nm [cm³·g⁻¹]
k50	2142	0.80	0.10
k50ox	1689	0.64	0.09
k50ox300	1724	0.64	0.07
k50ox500	1904	0.72	0.06
k50am	2118	0.79	0.09
k50oxam	1883	0.71	0.09
k50ox300am	1973	0.73	0.09
k50ox500am	1990	0.76	0.08

demonstrated also by XPS technique showing the existence of N-C bonds in quaternary nitrogen groups, known to be the most stable ones [27].

The considerations resulting from TPD are supported by elemental analysis, in which the non-modified sample do not exhibit any nitrogen content. The ammoniated sample (k50am) shows 0.45 wt% of N, while the sample oxidized and further ammoniated shows twice higher nitrogen content. In order to elucidate the nature of nitrogen functionalities, XPS measurements are carried out. Fig. 5 shows the XPS wide resolution survey spectra of non-modified and ammoniated carbon samples. The total nitrogen content resulting from XPS is 2.54 at% (Table 2). This is much

higher than the value from elemental analysis, therefore it confirms that nitrogen is adsorbed on the surface, rather than incorporated in the bulk. The deconvolution of N1s peak of k50am (Fig. 5b inset) reveals the presence of an intense peak at 399.5 eV which is assigned to N-C bonds in quaternary nitrogen groups [27]. Two other small contributions placed at 402 and 405 eV are detected as well and attributed to nitrogen oxides. These results match the TPD results showing the decomposition of these nitrogen groups as NH₃, NO_x and HCN groups.

3.2. Electrochemical characterization

Both carbon samples, without and with ammonia treatment, served as electrode materials for building electrochemical capacitor. Potential of electrodes is carefully monitored by using reference electrode (Fig. 6). The unmodified system is characterized by its discharge potential E_0 situated at 0.2 V vs. SHE, at the cell voltage of 1.8 V (Fig. 6a). The oxidation causes the dramatic shift of the electrode limiting potentials towards positive values. Most probably it is caused by the development of acidic surface groups. Thermal treatment at 300 °C causes that the limiting potentials of electrodes diminish by about 150 mV, while the E_0 potential remains almost unchanged. Relating this fact to TPD measurements, it can be stated that highly acidic CO₂-evolving functionalities at 290 °C are responsible for this effect. Thermal treatment at 500 °C diminishes the electrode limiting potentials in this case only by

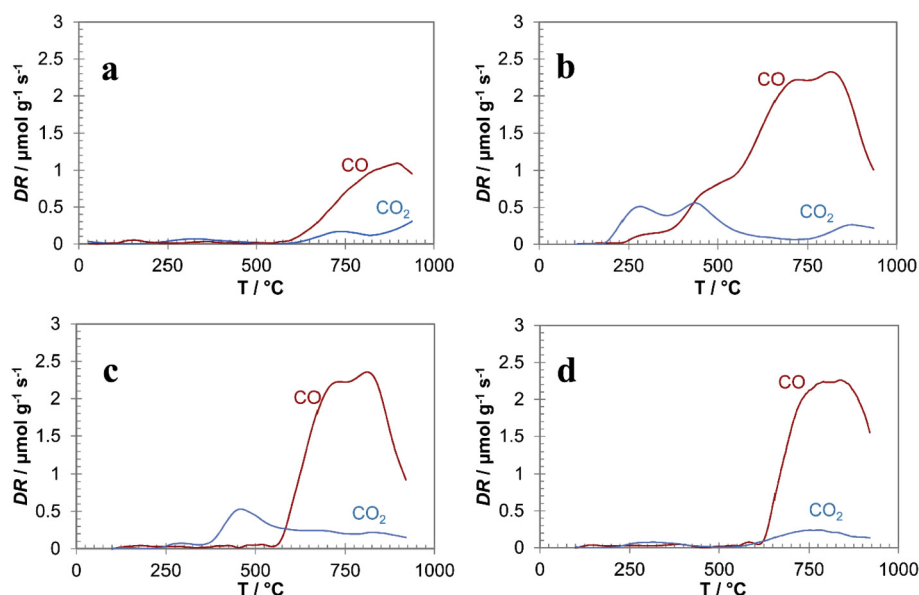


Fig. 3. TPD-MS desorption profiles on non-ammoniated carbons, a) k50, b) k50ox, c) k50ox300 and d) k50ox500. (A colour version of this figure can be viewed online.)

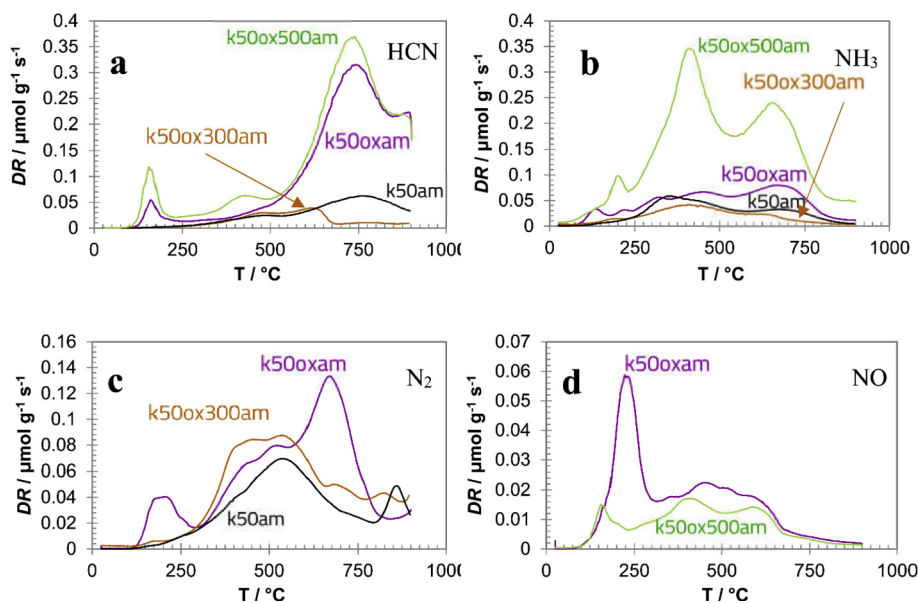


Fig. 4. TPD-MS desorption profiles on ammoniated carbons, a) HCN, b) NH₃, c) N₂, d) NO. The colours represent different carbons. (A colour version of this figure can be viewed online.)

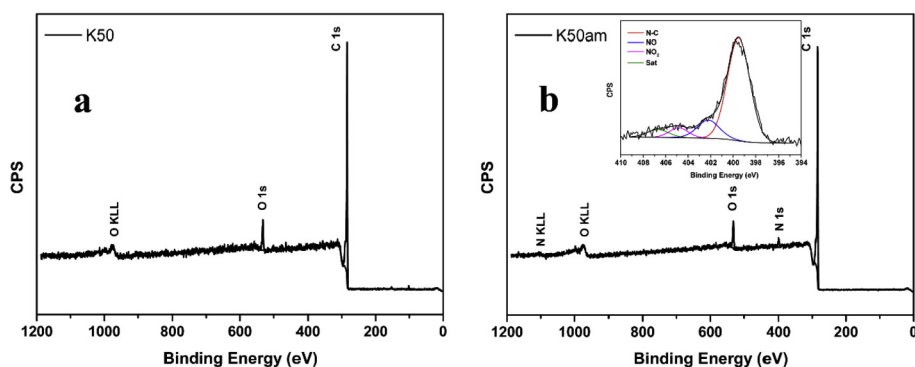


Fig. 5. XPS survey spectra on: a - k50, b - k50am. The inset shows N1s peak for k50am. (A colour version of this figure can be viewed online.)

Table 2

Chemical composition of k50 and k50am samples by XPS analysis.

k50			k50am		
Peak	Position eV	%at	Peak	Position eV	%at
C1s	284.35	94.63	C1s	284.30	91.78
O1s	531.85	5.37	O1s	532.30	5.68
			N1s	399.80	2.54

60 mV with respect to k50ox300. Only E_0 potential is shifted by 90 mV. This might be associated with the removal of CO₂-evolving functionalities at 450 °C (groups less acidic than in the case of k50ox300).

The ammonia treatment significantly impacts the electrode limiting potentials (Fig. 6b). The potentials are shifted towards more negative values and are more cumulated comparing to non-ammoniated samples. The E_0 potentials oscillate between 0 and 100 mV (for comparison, with non-ammoniated samples they are more dispersed in the range of 200 mV). No direct correlation between oxidation state and the potential range is found, due to the fact that ammonia imposes acid-base properties of these carbons disproportionately. However, the calculation of E_0 potential

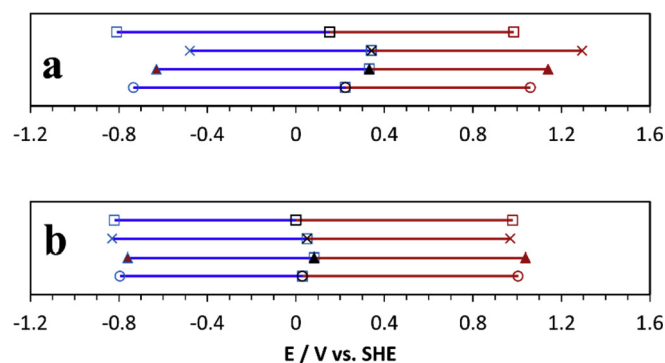


Fig. 6. Limiting electrode potentials for symmetric systems (1.8 V): □ - k50, × - k50ox, ▲ - k50ox300, ○ - k50ox500. The electrodes terminal potentials and E_0 are marked. a - before ammonia treatment, b - after ammonia treatment. (A colour version of this figure can be viewed online.)

differences between non-ammoniated and ammoniated sample of respective carbons increase in the order of its oxidation stage. k50 - 150 mV, k50ox - 290 mV, k50ox300 - 250 mV, k50ox500 - 195 mV. It reflects ammonia adsorption capacity and roughly informs about

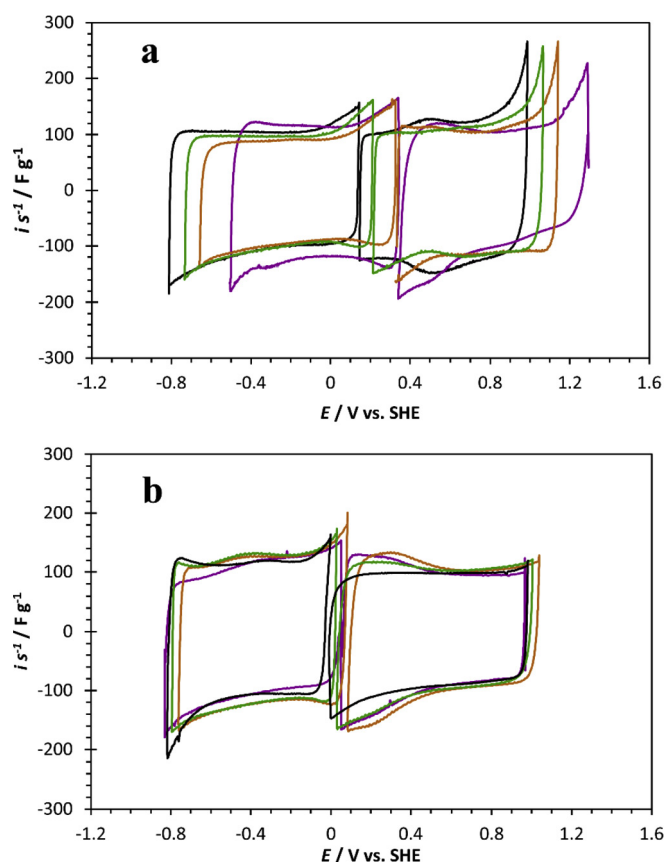


Fig. 7. Contribution of electrodes during voltammetry sweep of two-electrode cell (10 mV s^{-1}), black - k50, purple - k50ox, gold - k50ox300, green - k50ox500. a - before ammonia treatment, b - after ammonia treatment. (A colour version of this figure can be viewed online.)

the modification degree.

The symmetric capacitor prepared using untreated carbon, k50, polarized up to 1.8 V , is characterized by EDL type of response with the onset of sharp current increase on positive electrode responsible for electrolyte solvent decomposition (Fig. 7a) and hardly reversible oxidation of carbon material. Additionally, the reversible peak originating from quinone/hydroquinone redox activity is observed. The negative electrode resembles reversible hydrogen electrosorption evidenced by its respective oxidation current. The nitric acid oxidation of carbon material has a strong impact on electrochemical charge exchange dynamics. Upon oxidation, the three-electrode voltammetry of positive electrode response deviates from rectangularity, meaning that charge exchange dynamics, apart from being of EDL character is enriched in redox processes owing to the response of functionalities developed during the oxidation process. It can be seen that further thermal treatment leads to the withdrawal of changes caused by oxidation. In k50ox300 sample oxidation potential is shifted more to its initial value. It is even more shifted for k50ox500. Interestingly, the samples oxidized and treated at temperatures 300°C and 500°C do not show significant contribution of quinone/hydroquinone redox couple as in the case of the unmodified and oxidized sample. The oxidation of stored hydrogen is hindered as the degree of oxidation increases. It is in common with results presented elsewhere [29], where it is stated that reversible hydrogen storage is most favoured in alkaline medium. Consequently, the reason is that the pH at the electrode surfaces becomes more acidic with a higher oxidation degree.

The ammoniation process significantly influences the voltammetry response of supercapacitor electrodes (Fig. 7b). First of all, no solvent oxidation peak at the positive electrode is observed, no matter what oxidation degree of the electrode. Instead, the reversible peak at low positive potentials is visible. Although during the ammoniation process, the ammonia gas is adsorbed into porosity, it does not influence the reversible hydrogen storage. It may mean that once the electrodes are immersed in an electrolyte, ammonia escapes from carbon leaving active sites available for nascent hydrogen formation or rather both processes occur in pores of different diameter. For the sample treated by ammonia an irreversible peak at -0.4 V vs. SHE during discharge appears on the negative electrode. As in the case of the reversible peak at the positive electrode, it may originate from the interaction between ammonia and carbon material leading to shifting of equilibrium potentials or overpotentials for water decomposition reactions, which may explain superior performances of ammoniated carbons with respect to non-ammoniated ones. As it may be noticed from the voltammetry curves in Fig. 7, neither the oxidation, further thermal treatment nor ammoniation does not decrease the gravimetric capacitance of carbon. It confirms that the presence of ammonia adsorbed on the surface does not block the electrochemically active area responsible for charge storage. It is not in agreement with the results from active surface area presented in Fig. 2, where the capacitance would be anticipated to be lower in oxidized samples than for non-treated. It shows that the nitrogen adsorption measurements can be used as an indication of the surface area of porous material, but the gravimetric capacitance of the carbon cannot be concluded based on the measurement. It is probably interfered by the surface functionalities which block the accessibility of nitrogen but do not influence the flux of electric field negatively.

The electrochemical results are complemented by the determination of pH values of the carbons. It has been found that

Table 3
Surface functionalities character of carbon electrodes.

	Before ammonia treatment		After ammonia treatment	
	acidic groups mmol g^{-1}	basic groups mmol g^{-1}	acidic groups mmol g^{-1}	basic groups mmol g^{-1}
k50	0.16	0.17	0.71	0.2
k50ox	0.42	0.25	0.58	0.38
k50ox300	0.33	0.38	0.45	0.43
k50ox500	0.3	0.43	0.41	0.46

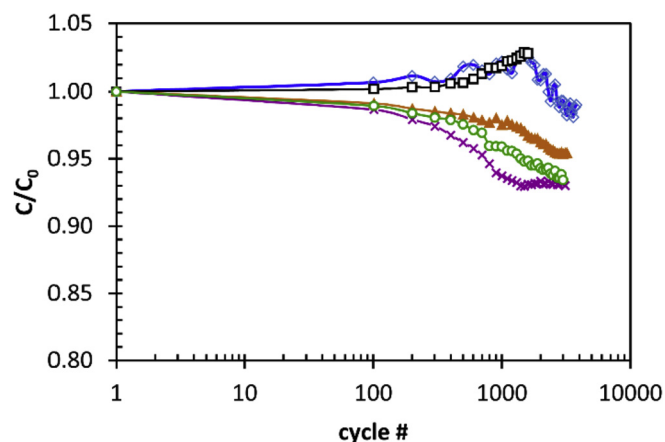


Fig. 8. Galvanostatic cycling $0\text{--}1.8 \text{ V}$ at 0.8 A g^{-1} . The markers represent the system: \square - k50am, \times - k50oxam, \blacktriangle - k50ox300am, \circ - k50ox500am and \diamond - k50. (A colour version of this figure can be viewed online.)

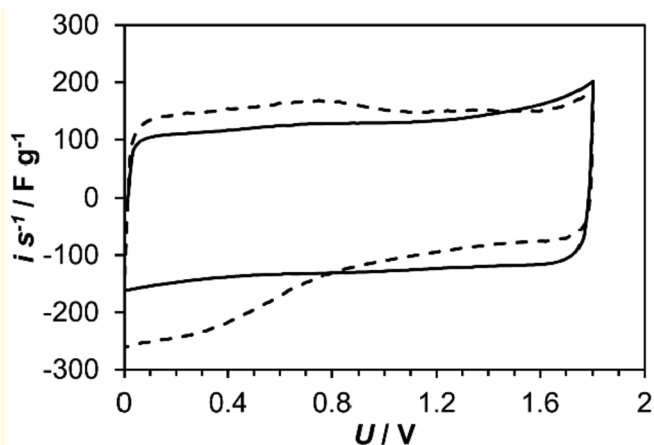


Fig. 9. Voltammetry curve (10 mV s^{-1}) of two-electrode cell (k50, non-modified) recorded before (solid lines) and after (dashed lines) the cycling test.

unmodified carbon k50 presents comparable amounts of acidic and basic sites (Table 3). Oxidation of carbon results in more than two-fold increase in the amount of acidic groups. Further thermal treatment progressively decreases the acidity level. The slightly more complex situation is found for basic groups amount - oxidation, as well as thermal treatment, cause the continuous increase of their amount. Finally, considering both polar groups, the most acidic properties are attributed to k50ox, while the most basic properties to k50ox500. The number of basic groups in case of

ammoniated carbons is slightly increased with respect to non-ammoniated carbons.

It confirms again that the sorption of ammonia is the highest in oxidized samples, owing to its preferential dissociation to produce NH_4^+ and OH^- . This conclusion is adequate to the E_0 potential values determined in Fig. 6. However, it does not explain the high overpotential of oxidation at the positive electrode, where the acidic environment would be preferred. One of the explanation could be that ammonia also exists as NH_2^- , producing H_3O^+ evidenced by the increase in acidic groups amount, especially for non-oxidized carbon. However, this form of ammonia is less favoured in aqueous solution than NH_4^+ .

The improved performance of the cells with electrodes modified by ammonia is verified by long term cycling ($0-1.8 \text{ V}$) at 0.8 A g^{-1} and compared with non-oxidized, non-ammoniated carbon (k50). According to Fig. 8, the cells are characterized by high capacitance retention during 3000 cycles. The capacitance slightly increases for non-oxidized samples, and slightly fades in the case of oxidized + ammoniated carbons. From this Figure it might be deduced that ammoniated, non-oxidized carbon (k50am) retains the best performance since its capacitance increases. Similar conclusion could be made by observing capacitance retention for non-ammoniated, non-oxidized carbon (k50). Other non-ammoniated carbons (k50ox, k50ox300 and k50ox500) have comparable performance to k50, therefore, they are not shown. However, in order to correctly interpret the graph and avoid misleading information, the qualitative cyclic voltammetry is implemented before and after long term cycling test. Although the capacitance retention after cycling test is close to 1 for k50 sample, the charge exchange dynamics is strongly deteriorated proved by

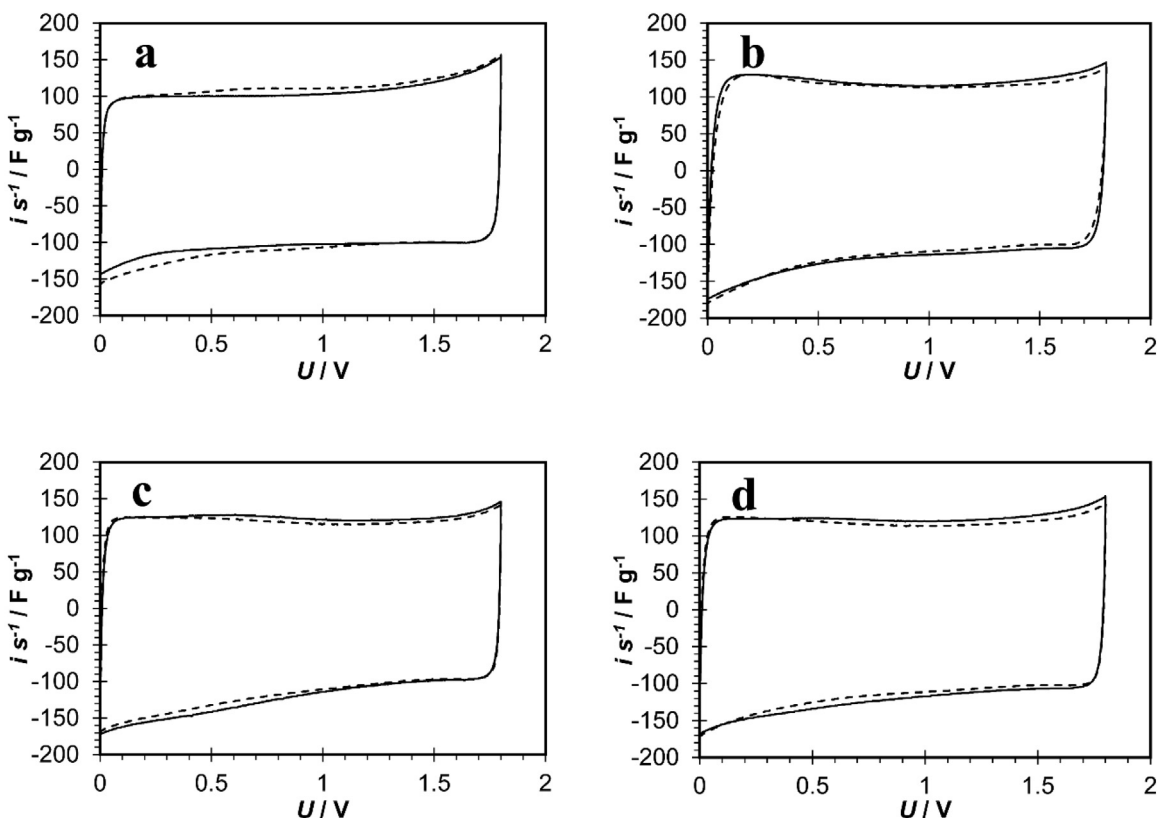


Fig. 10. Voltammetry curves (10 mV s^{-1}) of two-electrode cells recorded before (solid lines) and after (dashed lines) the cycling test, a - k50am, b - k50oxam, c - k50ox300am, d - k50ox500am.

cyclic voltammetry (Fig. 9). The increase of capacitance of ammoniated, non-oxidized carbon (k50am) occurs due to an additional redox process visible as increased current response during potentiodynamic discharge at low voltage values (Fig. 10a). In the literature it has been associated to quinone/hydroquinone redox process, often studied in acidic electrolyte [30]. Its appearance suggests electrooxidation of positive electrode. It might also come from reversible hydrogen storage [31]. The remaining three oxidized, ammoniated carbons (k50oxam, k50ox300am, k50ox500am) are devoid of this behaviour (Fig. 10b, c, d).

In these cases the voltammetry curves recorded after the test are devoid of reversible peaks which were present before cycling. It is the reason why the capacitance starts to slightly decline from 2000th cycle, when the contribution to pseudocapacitance drops. Apart of pH gradient formation on both interfaces, a hypothesis of reversible redox reaction of ammonia and their ionized form can be considered. Such reactions seem to be competitive to irreversible electrolyte decomposition reactions or electrode material oxidation owing to formation of a protective layer. In order to specify the detailed mechanism, an additional research focused on the interactions between ammonia and activated carbon specifically during current polarization should be conducted.

4. Conclusions

The paper aims to present a novel strategy to extend the voltage limit of supercapacitor with excellent cyclability retention. The proposed scenario consists of the introduction of electron-donating and electron-accepting properties, induced by adsorption of amphoteric ammonia. It is validated by high stability during long term cycling, with projected cycle life approaching 1 000 000 cycles. The favourable effects are achieved according to the original hypothesis in which ammonia is intended to increase the local pH. Moreover, the ammonia acts as a protector against carbon oxidation and electrolyte decomposition through formation of functional groups. Furthermore, the presence of ammoniated groups does not reduce the gravimetric capacitance. The cycling test shows that oxidation prior to ammonia adsorption is necessary to ensure excellent long-term operation at high voltage of 1.8 V. The approach presented here should be continued in order to achieve even higher voltage of supercapacitors operating in aqueous medium (preferably above 2 V) making the device more competitive with the capacitors operating using organic solvent. However, one should remember that, according to Pourbaix diagram of water, the modification would allow obtaining not more than 2.2 V. For further energy density increase, the redox contribution, for example, iodides [32] must be included.

This work also puts the stress on cycling results showing capacitance retention in time. They should be interpreted with care and must always be accompanied by showing the performance monitoring (as cyclic voltammogram or galvanostatic cycle) recorded before and after the test in order to be able to attribute the ageing mechanism properly.

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