Enhanced capacitive behavior of activated carbon through activation and/or introduction of redox activity by ammonia treatment

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The specific performance of carbon electrode based supercapacitors can be enhanced by optimizing the porous structure of electrode material [1-3] or by modifying the surface chemical composition to introduce reversible redox processes in addition to the double layer formation [4-6]. Therefore, electrode materials as well as electrolytes of the high-power energy storage devices, supercapacitors, are under continuous development.

Gas-phase surface modification of commercial mainly microporous activated carbon powder Dacarb (S_{BET} = 1056 $m^2 g^{-1}$, further indicated as Da) and oxidized form of this powder (Da-OX, oxidized in HNO_3 at 80 °C) by ammonia or ammonia/nitrogen mixture was done at elevated temperatures with different treatment duration. For some samples, an additional treatment at the same elevated temperature was done under H_2 and N_2 mixture. The changes taking place with carbon powder surface during modification were studied by N_2 adsorption and XPS analysis. Electrochemical characteristics of the treated carbon powder based electrodes were studied in 1 M H_2SO_4 electrolyte by cyclic voltammetry, constant current charge/discharge and impedance spectroscopy measurements. Wettability of electrode with electrolyte was analyzed by contact angle measurements.

The carbon mass change during modification and remarkable increase in surface area (up to ~1720 $m^2 g^{-1}$) at 800 °C treatment conditions showed that intensive carbon surface activation process takes place. At the same time, the highest amount of nitrogen functional groups (up to 4.5 at%) was incorporated into carbon powders during gas-phase modification at lower temperature (400 °C). After modification of Da and Da-OX under same conditions more N-containing surface groups were found for Da-OX. The nature and proportion of oxygen and nitrogen functionalities was studied by deconvolution of XPS spectra and analyzed in accordance with the carbon treatment conditions. It was also found that the wettability of Da was somewhat improved by different surface treatments, including oxidation.

The different carbon powders were studied as supercapacitor electrode materials in 1 M H_2SO_4 aqueous solution. An increase in the gravimetric capacitance up to 35% was observed after surface modification. In Fig. 1, there are wide capacitive maxima on the cyclic voltammograms for the modified carbon materials, indicating redox processes taking place with some active surface functional groups.

During 10000 constant current charge/discharge cycles the capacitance of the studied supercapacitor test cells decreased by 2.5 to 10%, depending on the modified material used (Fig. 2).

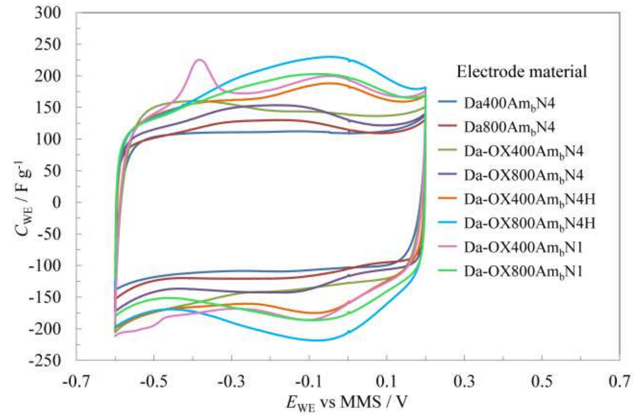

Figure 1. Comparison of gravimetric capacitance vs. WE potential curves for three-electrode test cells with Da and Da-OX electrode materials modified at 400 or 800 °C under NH_3:N_2 mixture for 1 or 4 h, with or without additional H_2 treatment (ν = 1 mV s^{-1}).

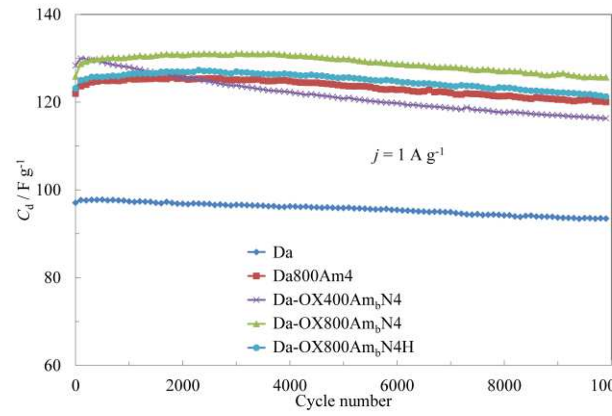

Figure 2. Discharge capacitance for 10000 charging/ discharging cycles (with current density 1 A g^{-1} ≈ 10 mA cm^{-2}) for different electrode materials.

Acknowledgements
This work has been partially supported by Estonian Science Foundation Grant No. 8172, Estonian Ministry of Education and Research (project SF0180002s08), graduate school ‘Functional materials and processes’ receiving funding from the European Social Fund under project 1.2.0401.09-0079 in Estonia, European Social Fund and Archimedes Foundation, and Estonian Centre of Excellence in Research (project TK117 3.2.0101-0030). Authors of the paper would like to thank Roland Benoît from CRMD for assisting in the XPS measurements and Dacarb® for providing activated carbon.

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