Electrochemical behaviour of a pristine and partially oxidized CDC materials in pH-neutral aqueous electrolytes

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Among many carbon materials, carbide-derived carbon (CDC) with well-tuned pore size distribution (PSD)[1] is gaining attention as a high-performance electrode material for ultracapacitors[2]. The electric double-layer capacitor (EDLC) with a liquid electrolyte is the most attractive storage type for nanoporous carbon electrodes, mainly because of the similar sized electrolyte ions and nanopores. In the case of EDLCs, the principle applies that the greater the carbon surface available to the electrolyte, the greater the capacitance of the device[2].

This study investigates the TiC-derived carbon electrode materials in the pristine form (CDC) and as the partially oxidized derivative (ox-red-CDC) oxidized by a modified Hummers method.[3,4] To evaluate the electrochemical properties of the carbon materials, cyclic voltammetry, galvanostatic cycling, and electrochemical impedance spectroscopy measurements were performed at 1 M Li_2SO_4 and Na_2SO_4 concentrations using 2- and 3-electrode test-cells.

The results indicate that Hummers' oxidation method, followed by back-reduction with hydrogen, largely preserves the specific surface area of the nanoporous material. However, a slight decrease in S_{BET} of ox-red-CDC from 1500 to 1300 $m^2\ g^{-1}$ was observed compared to the pristine CDC due to a decrease in porosity in the submicron pore diameter range, as evidenced by N_2 and CO_2 physisorption analysis. The highest capacitance values were obtained for the pristine CDC, which was also in good agreement with a slightly larger volume of subnanometer-sized pores of CDC compared to ox-red-CDC. On the other hand, the ox-red-CDC showed better resistance to oxidation at positive potentials, indicating that Hummers oxidation successfully passivates the active centers on the surface of the nanoporous CDC.

An asymmetric 2-electrode ultracapacitor, with ox-red-CDC as an anode and pristine CDC as a cathode, demonstrated excellent cycle life exceeding 10,000 charge-discharge cycles at an operating voltage of 1.5 V in case of 1M Li_2SO_4. Temporary repolarization of the ultracapacitor after 5000 charge-discharge cycles notably increased the capacitance (from 116 to 137 F g^{-1} in the case of Na_2SO_4 and from 119 to 142 F g^{-1} in the case of Li_2SO_4, measured at 2 mV s^{-1}). Repolarization also improved the cycling characteristics, likely due to cleaning and regeneration of the electrode surface.

This study demonstrates that partially oxidized CDC is an excellent anode material for ultracapacitors using pH-neutral electrolytes while exhibiting stable cycling properties.

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References

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