

Carbon material synthesis and development of electrical double-layer capacitors in the University of Tartu over two decades

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In recent years, environmentally friendly energy storage devices have gained increasing attention due to the growing requirement for energy storage for sustainable energy applications. Among the various existing energy storage devices, supercapacitors (electrical double-layer capacitors (EDLC) and hybrid capacitors) are considered the most promising short-term energy storage devices due to their high specific power, short characteristic time constant, excellent coulombic reversibility (98% or higher), high energetic efficiency (92–94%), long cycle life (over 10^6 cycles) and wide operation temperature range¹.

Porous carbon materials are considered to be the most promising electrode materials for portable supercapacitors due to their high surface area, good electrical conductivity, good chemical stability, low gravimetric density, and low cost². The classical porous carbon synthesis route uses pyrolysis of organic compounds followed by activation. However, control over pore size distribution is limited. Thus, the development of novel methods for the synthesis of porous carbons with controlled pore size distribution is important for the further development of supercapacitor technology. Therefore, we have studied different classes of carbons, i.e., carbide-derived carbons (CDC), and hydrothermal carbons, enabling better control over the material final porosities³. CDC can be synthesized by halogenation of various carbides like TiC, VC, SiC, Mo₂C, WC, etc. resulting in a wide range of porosities, i.e., pore size distribution, specific surface area, pore volume, the ratio of micro- and mesopore volume. Hydrothermal carbonization of carbohydrates like sucrose, and glucose and subsequent activation by ZnCl₂ and/or KOH enables similar control of the overall porosity of the material³. Additional activation of CDC and hydrothermal carbons by carbon dioxide and/or steam allows control of these carbon materials' porosities even further.

CDC and hydrothermal carbon-based symmetrical EDLCs electrochemical characteristics, i.e., specific series capacitance (C_s), specific energy (E), and power (P) were studied by cyclic voltammetry, electrochemical impedance spectroscopy, constant current charge/discharge, and constant power discharge methods in two non-aqueous electrolytes 1 M 3-ethyl-methylammonium tetrafluoroborate (Et₃MeNBF₄) solution in acetonitrile (AN) (viscosity 0.41 mPa s, electrical conductivity 50.2 mS cm⁻¹) and 1-ethyl-3-methylimidazolium tetrafluoroborate (EtMeImBF₄) (conductivity 13.6 mS cm⁻¹, viscosity 38.2 mPa s)⁴. A noticeable increase in series capacitances from 50 to 138 F g⁻¹ in 1 M Et₃MeNBF₄ in AN and up to 155 F g⁻¹ in EtMeImBF₄ dependent on carbon material porosity characteristics used for symmetrical EDLC has been demonstrated. Stored specific energy of symmetrical EDLC at short charging times of 0.36 sec can be increased from 5 W h kg⁻¹ for the microporous carbon to 20 W h kg⁻¹ for the micro-mesoporous carbon-based systems⁴.

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