

**Katarzyna Gajewska**

## **Synthesis and characterization of phosphorus- and nitrogen-doped graphene materials as electrode materials for supercapacitors**

### **Abstract**

One of the key directions in supercapacitor development is the design of electrode materials with a higher specific capacitance than activated carbon, which is currently widely used in large-scale supercapacitors. Aqueous electrolytes are particularly important in this context because they provide high ionic conductivity, low cost, and non-toxicity. Their use, however, is intrinsically limited by the operating voltage of the device, constrained by the theoretical potential for water decomposition (1.23 V), which significantly reduces the energy density stored in aqueous supercapacitors. In recent years, graphene-based materials, especially heteroatom-doped reduced graphene oxides (rGO), have attracted considerable interest because their enhanced electrochemical activity in aqueous media can partially compensate for the narrow electrochemical window of aqueous electrolytes.

The aim of this doctoral dissertation was to develop synthesis routes for phosphorus-doped rGO (P-rGO), nitrogen and phosphorus co-doped rGO (N,P-rGO), and nitrogen-doped rGO (N-rGO), and to evaluate their electrochemical properties as active electrode materials in symmetric supercapacitors operating in various aqueous electrolytes (neutral, acidic, and redox).

This work presents several groups of rGO-based materials. The first group comprises phosphorus-doped rGO (P-rGO). P-rGO graphene materials were investigated as electrodes in devices operating in aqueous 2 M NaClO<sub>4</sub> and 1 M Na<sub>2</sub>SO<sub>4</sub> electrolytes. The study was then extended to the preparation of graphene aerogels, including aerogels co-doped with phosphorus and nitrogen (N,P-rGO aero) as well as nitrogen-doped aerogels (N-rGO aero). Both groups of materials were tested in 1 M Na<sub>2</sub>SO<sub>4</sub>, 1 M H<sub>2</sub>SO<sub>4</sub>, and in electrolytes containing an active redox additive (1 M H<sub>2</sub>SO<sub>4</sub> + HQ/PPD).

A wide range of physicochemical methods was used to characterize the materials, including FESEM, XPS, TGA, N<sub>2</sub> adsorption, and XRD. The influence of morphology, porous texture, elemental composition, and the distribution of phosphorus- and nitrogen-containing functional groups on electrochemical performance was determined based on symmetric supercapacitor measurements using cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), and

electrochemical impedance spectroscopy (EIS). The obtained results were used to determine key device performance parameters such as specific capacitance, energy density, power density, and cycling stability.

Applying a hydrothermal process combined with freeze-drying, instead of conventional vacuum drying, enabled substantial development of the rGO porous structure, which significantly improved the electrochemical characteristics of the obtained materials. Particularly beneficial effects were observed for nitrogen-doped aerogels operating in a redox electrolyte. A symmetric, two-electrode supercapacitor based on N-rGO aero and 1 M H<sub>2</sub>SO<sub>4</sub> + 0.2 M HQ electrolyte achieved a specific capacitance of 432 F g<sup>-1</sup> (per single electrode) at a current density of 0.2 A g<sup>-1</sup>, corresponding to an energy density of 29.3 Wh kg<sup>-1</sup> at a power density of 0.076 kW kg<sup>-1</sup>. The device combined the pseudocapacitive contribution arising from nitrogen in the active material with redox processes occurring at the electrode/electrolyte interface. It exhibited exceptional stability, retaining high capacitance after 12 000 cycles in a voltage window exceeding the theoretical limit of water decomposition (0-1.4 V).

The results indicate that N-rGO aerogels are a particularly promising class of materials for supercapacitors with aqueous electrolytes. The three-dimensional, porous structure of these materials prevents aggregation of graphene layers and provides a large active surface area for electrochemical reactions, leading to a significant improvement in device performance. Combining nitrogen doping with freeze-drying represents a highly promising strategy for designing advanced materials for future energy-storage technologies.

Future research should include optimization of N-rGO aerogel synthesis parameters and exploration of other redox additives to further increase the capacitance and operational stability of aqueous supercapacitors.

Katarzyna Gójska