Synthesis and characterization of nanostructured, heteroatom-doped carbon materials for use in sodium-ion capacitors

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Presented in 2025, Instituto de Ciencia y Tecnología del Carbono (CSIC), Oviedo, Spain.

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Objectives and novelty

The increasing demand for sustainable and efficient energy storage devices is one of the major challenges in the global transition towards renewable energy systems that can allow the decarbonization of our society. Lithium-ion batteries currently dominate the market, but the scarcity and uneven geographical distribution of lithium resources raise serious concerns regarding their long-term viability. In this context, sodium-ion based technologies have emerged as a cost-effective and sustainable alternative due to the natural abundance and low cost of sodium. Among them, sodium-ion hybrid capacitors (NICs) are particularly attractive, as they combine the high energy density of batteries with the high power density and long cycle life of supercapacitors, thus representing a promising technology for renewable energy integration.

The main goal of this thesis was the design, synthesis and characterization of new carbon materials to be used as electrode components in NICs. The research focused on overcoming key limitations of current carbon electrodes, namely insufficient reversible capacity, poor rate capability, and low coulombic efficiency. In addition, the work emphasized the employ of sustainable synthesis strategies, including the use of biomass-derived carbon precursors and environmentally benign dopants.

The novelty of this research lies in the combination of two complementary strategies to overcome the main limitation in the development of this technology, that, is, the design of a battery-type negative electrode able to match the fast kinetics of the adsorption-type positive electrode:

1. Nanostructuring of disordered and porous carbons through salt-templating (endo-templating) methods, yielding sponge-like morphologies that minimize Na^+ diffusion resistance.

2. Sulfur-doping using either elemental sulfur or magnesium sulfate ($MgSO_4$), to enhance pseudocapacitive charge storage mechanisms and improve electrochemical performance.

Results

The synthesis of nanostructured carbons via salt-templating produced sponge-like materials characterized by interconnected thin carbon walls, providing short Na^+ diffusional pathways (Figure 1a). As a result, these materials exhibited enhanced rate performance, retaining significant reversible capacity at high current densities (140-179 mAh g^{-1} at 10 A g^{-1}). Systematic optimization revealed that precursor-to-salt ratios above 3:1 were ideal for achieving the desired sponge morphology.

Sulfur-doping experiments demonstrated that the doping temperature plays a decisive role. At 600–650 °C, the incorporation of sulfur enhanced the structural disorder of the carbons (increasing interlayer spacing and defect concentration) and improved their electrochemical behavior. Both elemental sulfur and $MgSO_4$ were evaluated as doping agents. $MgSO_4$ proved particularly attractive due to its dual role as a sulfur source and porogen, generating highly porous structures when combined with inert salts. This strategy led to the development of a versatile synthesis route capable of producing both battery-type (negative electrode) and capacitor-type (positive electrode) carbons (Figure 1b).

The optimized S-doped, sponge-like carbons displayed improved initial coulombic efficiency (ICE >70 compared to 50 for non-doped materials), higher sodium storage capacity (410 and 515 mAh g^{-1} at 0.1 A g^{-1} compared to 150 and 307 mAh g^{-1} for non-doped materials), and excellent stability during prolonged cycling (retention of capacity between 90 and 95% after 200 galvanostatic charge–discharge cycles at 0.2 A g^{-1}). Importantly, sulfur doping not only increases the overall capacity of the carbon materials, but also enhances sodium storage at low potentials (<1.5 V vs. Na^+/Na). This is the capacity effectively exploited in full cell operation, as previously observed in our own work and consistently reported in the literature.

For the positive electrodes, the carbon sponges were further activated, either through conventional activation or by taking advantage of the dual role of $MgSO_4$, which at high temperatures not only serves as a sulfur dopant but also as an effective activating agent. This approach yielded highly porous carbons with surface areas as high as 2600 m² g^{-1}, ideally suited for fast ion adsorption/desorption in sodium-ion capacitors.

Full NIC devices were assembled using the optimized negative and positive electrodes following the strategies described above. These devices delivered competitive energy densities combined with high power densities, as illustrated by Ragone-like plots (100-114 Wh kg-1 at low powers and 41-72 Wh kg^{-1} at ~24 kW kg^{-1})(Figure 1a y b). Moreover, long-term cycling tests confirmed the durability of the devices, which showed capacity retentions higher than 97 % after 10000 cycles at 2 A g^{-1}.

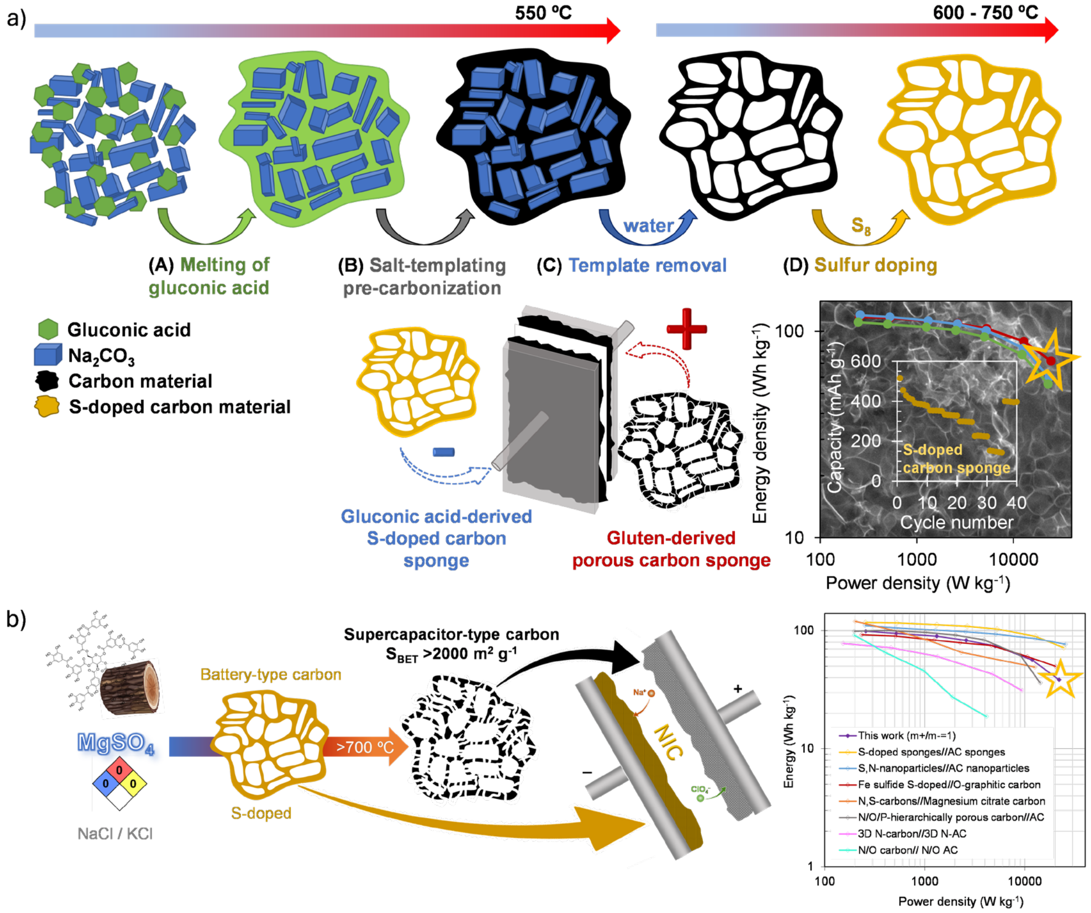

Figure 1. a) Experimental strategy used for the synthesis of the S-doped carbon sponges and Ragone-like plot showing the energy/power performance of the NICs. b) Synthesis scheme followed for the preparation of foam-like and highly porous, foam-like carbons from tannic acid using magnesium sulfate and Ragone-like plot showing the energy/power performance of the NICs compared to the state-of-the-art.

Conclusions

This thesis demonstrates that nanostructuring and sulfur-doping are effective strategies for tailoring the properties of carbon materials towards their application as negative electrodes in sodium-ion capacitors. Nanostructured, sponge-like carbons shortened the diffusional pathways, improving thereby the high-rate performance. Sulfur-doping enhanced the pseudocapacitive contributions and improved the initial coulombic efficiency. $MgSO_4$ has been proven to be an effective dual-function reagent, acting as both sulfur source and porogen depending on the synthesis temperature, constituting a versatile method for production of negative and positive electrode carbons. The developed NIC devices exhibited an optimized trade-off energy and power densities together with remarkable cycle life.

Overall, this doctoral research contributes to the sustainable development of sodium-based energy-grade materials and provides useful guidelines for the design of next-generation hybrid capacitors.

Related publications

[1] S. Payá, M. Sevilla, N. Díez. Biomass-derived carbon sponges for use as sodium-ion capacitor electrodes. Sustainable Energy & Fuels, 2023; 7 (10), 2378-2389.

[2] S. Payá, M. Sevilla, N. Díez. $MgSO_4$ as an effective, low-temperature sulfur dopant for carbon materials enabling fast sodium storage. ACS Applied Energy Materials, 2024; 7 (21), 10061-10072.

[3] S. Payá, M. Sevilla, N. Díez. A single route for the production of battery-type and capacitor-type electrode materials. Carbon, 2025; 235, 120056.

[4] MD. Casal, N. Díez, S. Payá, M. Sevilla. Cork-derived carbon sheets for high-performance Na-ion capacitors. ACS Applied Energy Materials, 2023; 6 (15), 8120-8131.

Full Thesis can be downloaded from:
https://digibuo.uniovi.es/dspace/handle/10651/79887