Sustainable materials and processes for energy storage and CO_2 capture exploiting green supercapacitors

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Abstract

Global warming, driven by anthropogenic CO_2 emissions, represents one of the most critical challenges facing modern society. In this context, the development of technologies capable not only of capturing CO_2 but also of extracting value from it is of increasing interest. This thesis explores an innovative electrochemical approach in which carbon dioxide is exploited as an active species for energy harvesting in electric doublelayer supercapacitors. The proposed device consists of two carbon-based electrodes separated by a polymeric separator impregnated with an imidazole-based ionic liquid that acts simultaneously as electrolyte and CO_2 capture medium. When CO_2 interacts with the ionic liquid, carbamate species are formed, inducing a modification of the electrode-electrolyte interfacial structure. Selective exposure of one electrode to CO_2 creates an asymmetry between the two interfaces, leading to the spontaneous development of a voltage difference across the cell that can be exploited to extract electrical energy. This mechanism, which couples CO_2 capture chemistry with interfacial electrostatics, represents a novel operating principle for electrochemical energy harvesting. To maximize device performance, both electrolyte and electrode materials were systematically engineered. The intrinsically high viscosity of ionic liquids, which limits ion transport and power output, was mitigated by mixing them with selected solvents. Some of these act as hydrogen bond donors, forming deep eutectic solvents with the ionic liquid and leading to electrolytes with much lower viscosity than the bare [HDBU][Im]. These electrolytes exhibit enhanced ionic mobility while preserving, and in some cases modifying, the CO_2 capture mechanism through the simultaneous formation of carbonate and carbamate species. On the electrode side, hierarchical porous carbons were synthesized using a ZnO nanoparticle templating strategy to achieve high surface area and tailored pore architecture. Nitrogen-doped carbons and carbon/carbon-nitride nanohybrids were prepared using cyanamide as nitrogen precursor, allowing control over nitrogen content, bonding configuration, and porosity. These features were found to play a key role in both capacitive behavior and CO_2 induced voltage response. The combined optimization of electrolyte chemistry and electrode structure resulted in a performance enhancement exceeding two orders of magnitude with respect to the initial device configuration, reaching energy densities up to 0.5 $J\ m^{-2}$. Overall, this work establishes a new paradigm in which CO_2 capture and electrochemical energy storage are intrinsically coupled by using a capacitive device.