Evaluation of Self-Supporting and Ink-Based Hard Carbon Electrodes: Impact on Sodium-Ion Storage

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Self-supporting, binder- and additive-free hard carbon nanofibers (HCNF) present significant advantages for sodium-ion battery (SIB) electrodes, particularly in simplifying the manufacturing process and enhancing electrochemical performance. In this study, high-quality HCNF were fabricated through the supersonic solution blowing (SSB) technique, employing polyacrylonitrile (PAN) as a precursor. The influence of carbonization temperature, ranging from 1000 °C to 1600 °C, on structural parameters and sodium storage performance were comprehensively evaluated. Among the investigated temperatures, the sample carbonized at 1400 °C demonstrated an optimal balance of microstructural features, including pore size distribution, specific surface area, interlayer spacing, and defect concentration, crucially affecting Na^+ storage capabilities. Through advanced analytical methods such as operando Raman spectroscopy, galvanostatic intermittent titration technique (GITT), and ex-situ high-resolution transmission electron microscopy (HRTEM), a multi-step Na^+ storage mechanism was revealed, involving initial adsorption onto defect sites, intercalation within pseudo-graphitic domains, and the formation of quasi-metallic Na nanoclusters within micropores. The optimized nanofiber structure at 1400 °C achieved a high reversible capacity of 363 mAh g^{-1} and excellent initial Coulombic efficiency (78%), outperforming conventionally prepared ink-based electrodes (98 mAh g^{-1} with only 36% efficiency). Furthermore, the pristine nanofibrous electrode demonstrated superior rate capability and stable long-term cycling, maintaining structural integrity after extensive electrochemical cycling, whereas the ink-based electrodes suffered significant morphological degradation. We found that the negative impact observed in the HC14-ink-based electrode is primarily due to the reduction in plateau capacity caused by binder infiltration into the micropores. This comparative study underscores the detrimental impact of conventional processing techniques, highlighting how binder infiltration and additive incorporation obstruct micropores and compromise electrochemical performance. The insights obtained here are valuable for advancing the structural optimization of carbon-based electrodes, emphasizing the potential of self-supporting nanofibrous structures to significantly enhance energy density, rate capability, and durability in SIB applications. These findings contribute substantially to the ongoing development of efficient sodium-based energy storage solutions.

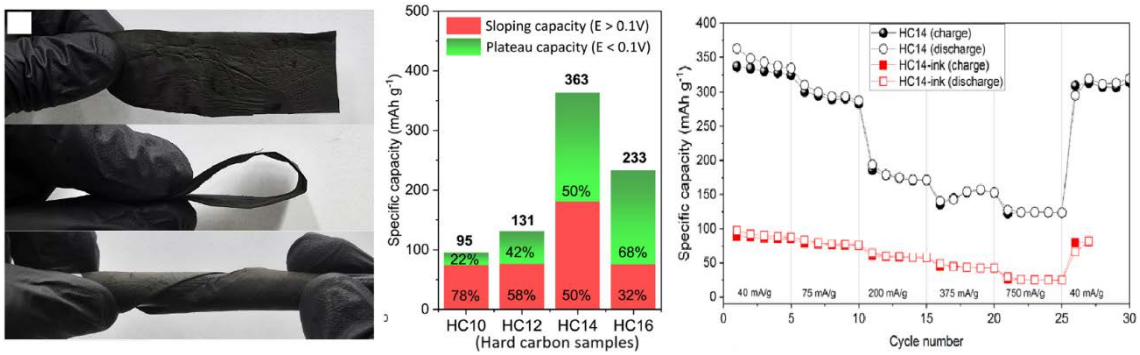

Figure 1. Flexible HCNF produced by SSB, corresponding slope and plateau capacity contributions, and rate capability of the HCN, and ink-based electrodes.

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