## Abstract

Sodium-ion batteries (SIBs) and potassium-ion batteries (PIBs) are emerging as a sustainable and economical alternative to lithium-ion batteries (LIBs) in battery storage systems due to the elemental abundance of sodium and potassium in the earth's crust and the similar physiochemical and electrochemical properties to lithium. The research community is challenged to develop and design novel anode and cathode materials for faster commercialization of SIBs and PIBs. Hard carbon (HC) - disordered and non-graphitizable carbon, with larger interlayer spacing, ease of synthesis from diverse precursors, and exclusively tunable electronic and structural properties, shows excellent electrochemical performance as anode material in SIBs and PIBs. A holistic understanding of the storage mechanism during charge-discharge cycles and the effect of porosity in improving the battery metrics of the HC anode is vital for the rational design of HC anodes from diverse precursors for SIBs and PIBs. This thesis reports the use of diverse precursors to synthesize cheap and sustainable hard carbon anode with larger interlayer spacing, ultra-micropores, and mesopores with different pore morphologies and their role in improving the battery metrics - reversible capacity, initial Coloumbic efficiency, rate performance, and long-term cycling, and elucidating their charge-storage mechanism for SIBs and PIBs.

At first, an ultramicroporous HC microsphere derived from sucrose precursor via a microwaveassisted solvothermal method shows an excellent reversible capacity of 385 mAh g<sup>-1</sup> at a current density of 30 mA g<sup>-1</sup> in a half-cell. It delivers an energy density of 231 Wh kg<sup>-1</sup> in a full cell with  $[Na_3V_2(PO_4)_3]$  cathode. The sloping and plateau capacity dependence on the current rate and capacity retention on cycling is gauged to understand the storage mechanism further. The subsequent chapter investigates the effect of pre-treatment and subsequent carbonization of jute-based HC to correlate micro/mesoporosity on the electrochemical performance of SIBs and PIBs. Jute-based HC carbonized at a milder temperature of 800 °C delivers the high reversible capacity of 328 mAh g<sup>-1</sup> (HC/Na<sup>+</sup>) and 245 mAh g<sup>-1</sup> (HC/K<sup>+</sup>) at the current density of 30 mA g<sup>-1</sup> with excellent long cyclibility. The Na-ion storage in HC supports a three-stage charge-storage mechanism that significantly contributes to low potential capacity from porefilling.

In contrast, K-ion storage in HC exhibits a two-stage storage mechanism, with adsorption and intercalation dominating the pore-filling mechanism. The thesis further reports that the trash-to-treasure approach for upcycling plastic waste into value-added products helps to generate

sustainable, cost-effective, eco-friendly HC materials. Polyethylene terephthalate (PET)-based HC with abundant mesoporosity of 84% and slit-shaped pore morphology significantly improves the lower potential plateau capacity, accounting for 68% and 32% of the total capacity for SIBs and PIBs, respectively. To investigate the role of electrolytes and interfacial chemistry in improving hard carbons' cycling stability and rate capability, sucrose-derived HC is optimized for ester-based electrolytes, and cyclopentyl methyl ether (CPME) is used as a co-solvent to substitute ethylene carbonate (EC) in PET-derived HC, respectively. 1M NaClO<sub>4</sub> in EC: PC (1:1, v/v%) is optimal, delivering a high reversible capacity of 265 mAh g<sup>-1</sup> at a current density of 300 mA g<sup>-1</sup> (1C). Further, the CPME co-solvent promotes the reduction of more inorganic-based SEI components for a stable and thin SEI layer and shows excellent low-temperature performance with ~30% added capacity and initial Coulombic efficiency (ICE) value compared to EC-PC-based electrolytes at 0 °C.

The plastic waste to a valuable material concept is further extended by synthesizing polyvinyl chloride (PVC)-derived HC with a partially closed ink-bottle-shaped mesopore. PVC/K<sup>+</sup> exhibits a high reversible capacity of 477 mAhg<sup>-1</sup> at the current density of 27.9 mA g<sup>-1</sup>. A distinct K<sup>+</sup> storage mechanism is revealed through differential capacity plots, GITT, and CV analysis to confirm a three-stage storage via surface adsorption, intercalation, and pore-filling mechanism. Using Prussian white (K<sub>2</sub>Mn[Fe(CN)<sub>6</sub>]) as the cathode, the full cell delivers 284 Wh kg<sup>-1</sup> with 93% retention over 1000 cycles at a 1C rate. The final chapter reports a single precursor-derived HC as an anode for LIBs, SIBs, and PIBs. The HC anode delivered the maximum reversible capacity of 422 mAh g<sup>-1</sup> at 0.1 C rate with a plateau contribution of 57%, the best reported reversible capacity for the unmodified/undoped HCs for SIBs. Finally, additional electrochemical characterization techniques (XRD, EPR, Raman, and XPS) of the cycled electrodes are carried out to gain insights into the distinct storage mechanism during alkali-ion insertion/de-insertion.

*Keywords:* Sodium-ion battery; Potassium-ion battery; Hard carbon anode; Diverse Precursor; Storage mechanism.