Abstract

The rapid progress toward the commercialization of sodium-ion batteries has intensified the need to bridge fundamental materials design with practical cell-level performance requirements, including high energy density, fast kinetics, and stable operation under practical cell conditions. Among high-voltage polyanionic cathodes, $Na_3V_2(PO_4)_2F_3$ (NVPF) is particularly attractive owing to its robust open framework, high operating voltage, and rapid Na^+ transport. However, its intrinsically limited electronic conductivity and high surface reactivity promote unstable electrode-electrolyte interphases, electrolyte decomposition, and sluggish charge-transfer kinetics, restricting its rate capability and cycling stability. Herein, I develop a surface-regulated NVPF cathode through a boron-doped carbon (BDC) matrix of bimodal spherical NVPF particles. The optimized 10 wt% BDC@NVPF composite delivers a higher initial discharge capacity of ~101 mAh g^{-1} compared with ~ 89 mAh g^{-1} for parent NVPF at C/10, together with an improved initial coulombic efficiency of ~ 82% *vs*. ~ 68% for the electrode containing > 90 wt% active material and < 5 wt% conductive carbon in a half-cell configuration using a diglyme-based electrolyte. When paired with a hard carbon (HC) anode, the BDC@NVPF cathode also enables improved full-cell energy density of ~ 171 Wh kg^{-1} *vs.* ~ 155 Wh kg^{-1} in a diglyme-based electrolyte and ~ 187 Wh kg^{-1} *vs.* ~ 176 Wh kg^{-1} in a carbonate-based electrolyte. Electrochemical impedance spectroscopy (EIS), Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS), and X-ray Photoelectron Spectroscopy (XPS) reveal that the BDC matrix stabilizes the cathode interphase by reducing solvent-derived decomposition products ($C_2H_3O^-$, $C_3H_7O^-$), while enriching inorganic F- and B- containing species that facilitate Na transport. In contrast, parent NVPF undergoes continuous interfacial reconstruction during cycling.

Further, to design greener sodium-ion cells, I employ a water-based, economical electrode processing route instead of toxic and expensive N-methyl-2-pyrrolidone-based slurry

preparation. I compare the electrochemical activity considering a realistic formulation (Active material > 90 wt%, Conductive carbon < 5 wt%; Loading- Cathode: 14-16 mg cm^{-2}, Anode: 6-7.5 mg cm^{-2}) in a half- and full coin cell orientation using NASICON $Na_3V_2(PO_4)_3$ (NVP) and HC in diglyme and carbonate electrolytes. Here, the optimized aqueous-processed carbonate-based NVP|HC exhibits a discharge capacity of ~ 84 mAh g^{-1} with ~ 92% capacity retention after 100 cycles at a C/5 rate. The optimized combination is upscaled to a single-layer pouch cell, revealing an initial discharge capacity and gravimetric energy density of ~ 75 mAh g^{-1} and ~ 143 Wh kg^{-1}, respectively, with a capacity retention of 82.7% after 300 cycles at C/5.

To impart safety attributes to the developed greener cells and mitigate the hazardous impact of the employed carbonate-based electrolyte, I integrate biphenyl (BP) into the electrolyte mixture. Here, the moderate dosage (3 w/v%) of BP demonstrates an anti-overcharge capability by restraining the upper cutoff voltage at ~ 4.3 V-4.45 V, while a low (1 w/v%) seems insufficient, and an excessive composition (5 w/v%) results in rapid capacity attenuation once overcharged. The EIS and XPS measurements provide the rationale behind the single overcharge-cycle inhibition behavior of BP-added cells with the retrieved cycled cathode, revealing an interphase composed of electro-polymerized oligomers, detrimental to further sodium-ion migration with enhanced interfacial resistance, and the anode confirming the efficiency of BP in retarding carbonate electrolyte decomposition.

Additionally, to improve the energy density of fabricated safer, greener cells, I employ a direct-contact presodiation technique for the hard carbon to alleviate the initial irreversible capacity loss during solid electrolyte interphase (SEI) formation and comprehend the underlying mechanism of artificial SEI formation using an array of microscopic, spectroscopic, and electrochemical analyses. The optimized presodiated HC paired with the NVP cathode reveals improved initial discharge capacity, coulombic efficiency, and energy density of ~ 94 mAh g^{-1} (*vs.* ~ 86 mAh g^{-1}), ~ 94% (*vs.* ~ 85%), and ~ 202 Wh kg^{-1} (*vs.* ~ 180 Wh kg^{-1}), respectively,

at C/10 with good cycling stability of ~ 79% at 1C after 200 cycles in a carbonate-based electrolyte.

Overall, the work here focuses on employing surface modification, electrode, and electrolyte engineering to design better interphases and develop energy-efficient SIB cells.