ABSTRACT

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Potassium-ion batteries (PIBs) recently emerged as a next-generation energy storage technology, utilizing abundant and inexpensive potassium as the charge carrier cation. PIBs operate by an analogous mechanism to lithium-ion batteries (LIBs), with reversible potassium intercalation in anode and cathode through an inorganic salt - organic solvent electrolyte medium. Despite its larger size, potassium exhibits several electrochemical advantages over sodium, including a higher affinity for intercalation into graphitic (carbonaceous) anodes, forming a stage-one KC_8 structure in graphite for a specific capacity of 279 mAh g^{-1}. This thesis aims to provide a thorough foundation for PIB carbon anodes, through a comprehensive experimental approach combining electrode synthesis, advanced material characterization and electrochemical-analytical techniques.

Safety concerns have consistently plagued LIBs despite almost three decades of widespread commercialization. Thermal runaway of LIBs can initiate as early as 80°C from exothermic breakdown of the solid electrolyte interphase (SEI) layer that covers the carbon anode surface. The subsequent reaction of lithiated carbon with electrolyte solvent leads to cathode decomposition and oxygen release for cell gassing and combustion. This thesis investigates the thermal runaway behavior of graphite anode for PIBs via differential scanning calorimetry analysis, determining the effect of electrode material, state-of-charge, and cycling history on heat generation. Notably, the PIB system emits significantly less heat overall than for LIBs, albeit an earlier and more intense onset reaction at 100°C raises safety concerns. Strategies to mitigate this exothermic reaction are presented, including electrode binder manipulation to improve graphite particle coverage and enhance SEI layer stability.

To further evaluate the practicality of PIBs, the electrochemical behavior of graphite anode was investigated from 0 - 40°C operating temperature, in comparison to standard LIBs. The poor rate capability of potassium is attributed to sluggish solid-state diffusion and augmented cell impedance, where 3-electrode studies revealed dramatic polarization of the potassium metal

counter electrode at low temperatures. Accelerated cell aging at elevated temperatures is attributed to SEI layer growth induced by the 61% volumetric expansion of graphite during potassiation, as well as the extreme reactivity of potassium metal. A full-cell system with a Prussian blue nanoparticle cathode and graphite anode showed enhanced rate performance at low temperatures by removing potassium metal counter electrode. These results provide valuable mechanistic insight for potassium intercalation in graphite and offer a practical evaluation of temperature dependent electrochemical performance for PIBs.

Supplementary research includes the exploration of carbon nanofibers electrospun from polyacrylonitrile precursor with subsequent pyrolysis as PIB anode. The design of an amorphous, low density carbon with a nanoscale one-dimensional morphology enables mitigation of the 61% volumetric expansion of graphite during potassiation. Remarkable stability (2000 charge-discharge cycles) is thus achieved by preventing electrode pulverization, SEI layer growth, and impedance rise during cycling. Electrochemical analysis revealed a pseudo-capacitance mechanism, enabling rapid charging through surface storage of potassium that could be enhanced by surface functionalization via plasma oxidation treatment. Moreover, two dimensional MXene transition carbonitride sheets were explored as PIB anode with X-ray diffraction and X-ray photoelectron spectroscopy used to study structural changes during potassium insertion.

Finally, the effect of particle morphology was investigated for LIB carbon anodes, wherein commercial graphite is compared with synthesized spherical and spiky carbons. Intercalation dynamics, side reaction rates (e.g. SEI growth), self-heating, and thermal runaway behavior were studied through a combination of electrochemical analysis and modeling by a finite volume method. Spherical particles outperform irregular commercial graphite by eliminating unstructured inhomogeneities that lead to non-uniform current distributions. Interestingly, spiky particles offer a non-trivial response, where the ordered irregularities enhance intercalation dynamics to prevent degradation at extreme operating conditions. These findings emphasize the importance of tailoring particle morphology and structure in promoting desired LIB behavior and suppressing unwanted problems.