DESIGNING ADVANCED LITHIUM-ION BATTERIES WITH NOVEL ARCHITECTURE, AND HIGH-PERFORMANCE CELL ELEMENTS WITH ENHANCED THERMAL SAFETY ASPECTS

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ABSTRACT

To compete with traditional hydrocarbon energy sources and meet the demands of battery applications, the next generation of lithium-ion batteries (LIBs) needs to have high specific energy, high energy density, low cost, and reliable safety characteristics. To improve electrochemical characteristics without sacrificing thermal safety, a deeper understanding of the material synthesis/ fabrication, interfacial behavior, and in situ thermochemical stabilities are vital. Along with these understandings, it is essential to understand the other limitations of LIBs in terms of lifetime, economic aspects, etc. With the boom of electric vehicles, high stress is applied to extract the extra juice out of the batteries to achieve a longer mile range. For electric vehicles, there is a unique requirement of greater than 240 Wh kg^{-1} energy density and a lifetime of more than ten years to ensure economic and longer driving distances. To overcome all these challenges, further developments are required in the (de)-intercalation reactions and the geometric design of LIBs. This thesis aims to provide a thorough understanding of the various challenges of LIBs, through a comprehensive experimental approach combining electrode synthesis, separator design or modifications, battery design, sensors, advanced material characterization, and electrochemical-analytical techniques.

Silicon anodes have over ten times more theoretical capacity (3579 mAh g^{-1}) than graphite anode (372 mAh g^{-1}), however, the alloyed Si, $Li_{3.75}Si$, swells in volume by about 320% during charging, which results in anode cracking, fracturing, loss of electrical contact (delamination), unstable solid electrolyte interface (SEI), and even catastrophic cell failure. Here, a novel composite graphite-carbon-silicon (GCSi) anode material with its formation mechanism established via in situ environmental transmission electron microscopy, and through a combination of ex-situ, and in situ characterizations, and cell performance testing–a complete picture of the silicon anode behavior, advantages, and drawbacks were obtained. During thermal runaway tests, silicon composite anode with lithium cobalt oxide cathode (LCO) demonstrated slightly lower heat generation per cell energy compared to the LCO/graphite chemistry. To further evaluate and predict the thermal stability of LIBs, in situ sensing of thermal signatures using an internal resistance temperature detector (RTD) was devised with an attempt to predict the thermal runaway prior to an external sensor. Sensing the temperature beneath the anode gave direct access to the heat liberated, including SEI decomposition-related heat generation. External short circuit (ESC) and overcharge tests were conducted to trigger the thermal runaway event, and temperatures of 36.4 ℃ and 48.4 ℃ were recorded using internal RTDs, which were 9 ℃ and 20 ℃ higher than with external RTD, respectively. Interestingly, internal RTD has detection ability for 90% temperature rise 14 times faster. Using thermal signatures from RTD, an advanced battery management system can lead to conducive LIBs.

Separators influence the transport of Li^+ ions across the electrodes, safety aspects, energy density, cycle life, and economics of the batteries. Polyolefin membranes have been the mainstay of the industry for the past few decades;

however, they fail at critical high operating temperatures. Through the use of novel aramid nanofibers and modified microporous membrane separators, high-performance LIBs and lithium-sulfur chemistry have been realized at varied critical temperatures of 40 ℃ and 50 ℃. Post diagnostic analysis of aramid nanofiber separator system, following multimode calorimetry, demonstrated mechanical integrity even after 300 ℃. Finally, to address the energy and power density challenges, there is an urgent need for innovation in the design of LIBs. With the development of high-capacity anode materials, there is a requirement to develop high-capacity cathodes. Various high-capacity cathodes viz., sulfur or V_2O_5 are available, however, they do not contain Li^+ ions in their atomic framework, to begin with. Hence, they cannot be combined with the graphitic anode to form a full cell. Also, in conventional LIBs, the solid electrolyte interface (SEI) layer formation consumes Li^+ ions, which renders the system energy exhausted within 4–5 years of service. Various strategies like pre-lithiation, blended cathodes, lithium-additives, and film-forming additives have been proposed, however, either they are not practical or alter the cell voltage behavior. Here, we proposed a novel configuration to LIBs called *reserve lithium-ion batteries* (RLIBs), which utilizes a reservoir electrode to supplement Li^+ ions to lithium-deficient cathodes such as V_2O_5, S, FeS_2, etc. and to recover capacity losses that incur due to SEI formation and long-term cycling. Such tailored systems enable LIBs with high energy density and lifetimes for realizing high energy requirement systems in space, transportation, military applications, and grid-storage.