

As the future of energy looks increasingly electrified, the development of safe and sustainable battery technologies has never been more relevant. This is particularly critical for applications in stationary energy storage and transportation, where batteries must be produced and stored at large scale. Sustainability is necessary to meet the volume of demand at reasonable cost without straining resources. Safety is also paramount since fires can easily spread from one cell to the next and result in catastrophe when batteries are stored in proximity for large power banks or EVs. The focus of this thesis is thus to design and engineer materials for rechargeable batteries, which improve safety and sustainability while still enhancing the electrochemical performance. Towards this end, polymers play a central role throughout this thesis work due to their tunable chemical and physical properties.

Potassium-ion batteries (KIBs) are investigated as a sustainable alternative to lithium-ion batteries (LIBs) for applications where cost and scalability takes priority over energy density, such as stationary energy storage. KIB precursors are much cheaper than LIB precursors due to the higher abundance of K over Li in the earth's crust (2.0 vs. 0.002%). However, the graphite anode swells much more upon intercalation of potassium (63%) versus lithium (10%) ions due to the larger ionic radius (1.38 vs. 0.76 Å). The consequences are exacerbated pulverization, loss of electrical contact with the current collector, and fracturing of the solid-electrolyte interphase (SEI) passivation layer. KIBs with worsened capacity fading and shorter cycle lifetimes are therefore not currently commercially viable. Herein, electrically conductive poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) binder is thoroughly investigated for graphite KIB anodes. Thorough elucidation of the physical, electrochemical, and thermal safety aspects reveals that PEDOT:PSS facilitates greater capacity retention by enabling continuous electrical contact between graphite particles and the current collector, inhibiting the continuous growth of the SEI, and even improves thermal safety.

The relation between physical properties of the PEDOT:PSS and thermal safety aspects are further explored in LIBs. Compared to those with standard PVDF binder, anodes with PEDOT:PSS show a lower surface area and reduced wettability with the organic electrolyte as investigated using gas-sorption and contact angle measurements. PEDOT:PSS therefore provides a protective layer which inhibits thermally-unstable SEI formation and reactions between the reductive lithiated graphite and organic electrolyte, as shown with calorimetry. This protective effect can prevent the initiation of an unstoppable thermal runaway event.

Lithium sulfur batteries (LSBs) are considered for applications in EVs due to their much higher theoretical energy density over LIBs (2600 vs. 570 Wh kg⁻¹). Further, resources used for the cathodes are much more sustainable and cost effective. Whereas sulfur costs \$150 ton⁻¹ and comprises 0.042% of the earth's crust, cobalt costs \$75,000 ton⁻¹ and comprises only 0.003%.

Unfortunately, sulfur cathodes similarly suffer from severe capacity fading due to large volumetric expansion (80%) as well as the shuttling of soluble lithium polysulfide (LiPS) species. Herein, an environmentally benign water-soluble carboxymethyl cellulose (CMC) binder is modified with dopamine (DOP) to improve adhesion of cathode materials to the current collector as well as improve binder affinity towards LiPS species. LSBs with CMC-DOP binder effectively retain sulfur at the cathode and mitigate capacity loss.

An alternative method to mitigate LiPS shuttling is using a modified separator which can block LiPSs in addition to performing its usual function of preventing an internal short circuit. Dilithium terephthalate (Li₂TP) and dipotassium terephthalate (K₂TP) salts are synthesized from plastic soda bottle waste and coated onto glass fiber paper (GFP). K₂TP shows the highest calculated binding energy for LiPSs in computational studies and subsequently greatest improvement in capacity retention when coated onto GFP separator during testing of LSBs.

Although coated separators are a common strategy in the literature to improve LSB performance, they will invariably add additional mass and volume to the overall cell. A novel approach towards mitigating LiPS shuttling is investigated, where a nanoporous atomically thin graphene membrane (NATM) with negligible thickness or weight is transferred onto traditional polypropylene (PP) separator. The tailored pore size of 0.7-1.0 nm provides a sieving effect that selectively allows passage of Li⁺ while blocking bulky LiPS anions. Impedimetric studies show the atomic thinness introduces negligible resistance, and elemental analysis of the anode shows greatly reduced sulfur content, confirming the LiPS confinement at the cathode.