Development of Cellulose-Based Composite Separator Membranes for Energy Storage Devices

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Abstract

This thesis presents a comprehensive study on the design, fabrication, characterization and application of cellulose paper-based composite separators as sustainable, safe and scalable alternatives to conventional polyolefin separators for lithium-ion batteries and related energy storage systems. Motivated by the limited thermal stability, poor electrolyte affinity and environmental concerns associated with commercial PP/PE membranes, an industry-friendly wet-coating process for paper separator fabrication in an in-house double-decker roll-to-roll fabricator equipment, was developed to functionalize commercially available cellulose paper with polymer binders, passive and active ceramic fillers, chelated metal-oxide precursors and montmorillonite clay. The work proceeds in a systematic progression: (i) conversion of raw paper to sized, polymer and ceramic-treated paper separators (Paperator), (ii) incorporation of passive ceramics (Al_2O_3, SiO_2, $BaTiO_3$, ZrO_2) and chelated zirconia domains to tune surface chemistry and salt dissociation, (iii) development of montmorillonite (MMT) paper-clay composites as low-cost flame-retardant separators, (iv) Li-ion conducting garnet ($Li_7La_3Zr_2O_{12}$) to produce ion-active ceramic-loaded separators, and (v) fabrication of paper-supported composite solid polymer electrolytes for flexible solid-state cells. A broad experimental matrix links processing → structure → properties → performance: structural and compositional analyses (XRD, FTIR, FESEM/EDX), porosity, wettability and surface area (Gurley, BET, electrolyte uptake), mechanical testing (tensile, flexibility), thermal stability and safety (TGA/DTA, SET, shrinkage), and electrochemical evaluation (EIS/DRT, LSV, DC polarization, galvanostatic cycling in symmetric and full-cell configurations). Key findings show that polymer sizing and controlled ceramic or clay impregnation produce hierarchical paper matrices with tunable pore architecture, enhanced electrolyte wettability and improved mechanical integrity. Moderate loadings of functional fillers yield the best balance between ionic transport and structural integrity, extend electrochemical stability windows beyond 5.0 V versus Li/Li^+, reduce interfacial resistance, and deliver superior full-cell cycling stability and coulombic efficiency compared with commercial PP separators. Montmorillonite-loaded papers demonstrate marked flame retardancy and self-extinguishing behavior, retaining electrochemical functionality after flame exposure. Chelated ZrO_2 domains promote Li-salt dissociation via Lewis acid-base interactions of $LiPF_6$ with undersaturated Zr^{4+} and Zr-OH moieties. LLZO impregnation induces active ion-conducting pathways in paper matrix. In case of polymer electrolytes, the dual polymer approach helps to enhance ionic conductivity and reduce crystallinity of the base polymer matrix, while paper reinforcement enables better flexibility and cycling performance. Collectively, the results establish cellulose-based composite membranes as viable and scalable components for eco-friendly, high performance and high-safety next generation battery systems.

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