Abstract: Gel polymer electrolytes for Li metal protection

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Over the past thirty years, lithium-ion batteries (LIBs) have solidified their status as the definitive benchmark for reliable, high-efficiency energy storage by enabling the miniaturization and widespread accessibility of smartphones, tablets, and laptops. Due to the internationally mandated necessity for decarbonization, efficient energy storage systems are now more than ever fundamental in the energy transition from fossil fuels to renewable sources. Although, LIBs have been thoroughly studied and optimized, the technology is currently approaching its fundamental electrochemical limits. To overcome these theoretical limits, research has pivoted toward next-generation lithium metal batteries (LMBs), which employ metallic lithium as the anodic material due to its high theoretical capacity and low redox potential.

However, the commercial viability of LMBs is hindered by the inherent reactivity of lithium, which triggers catastrophic dendrite growth, interfacial degradation, and the accumulation of "dead" lithium. Consequently, traditional liquid electrolytes are no longer viable choices, necessitating a shift toward next-generation electrolyte architectures, such as solid or semi-solid polymeric electrolyte systems. In this optic, gel polymer electrolytes (GPEs) represent an ideal compromise between mechanical stability and electrochemical performance. Despite their potential, however, GPEs implementation is typically hindered by the sensitivity towards oxygen and water during the polymerization reaction.

In the first part of this dissertation, a GPE composed of PEGDA and a thiol-containing crosslinker was developed through the oxygen-insensitive thiol-ene reaction mechanism. A comparative analysis between two different thiol-containing crosslinkers was performed to evaluate the impact of the crosslinker functionality and the reaction environment on the GPE physico-chemical and electrochemical properties. The T4 crosslinker and the dry room environment demonstrated superior ionic conductivity and Li^+ transport properties. An *in-situ* deposition and UV curing of the precursor solution was additionally demonstrated, resulting in a faster and simpler GPE production process with superior cell performance. In this context, the effect of the cathode calendering on the deposition process was investigated, demonstrating a decrease in cathode porosity and internal cell resistance, resulting in superior cycling stability.

The subsequent section presents a speculative feasibility study on the scalability of the GPE production process to a 100 MWh $year^{-1}$ pilot line. COMAU benchmarks and state-of-the-art LIB production data have been employed to validate the technical and economic viability of the deposition process in the context of LMBs production. The transition to integrated cathode/GPE single-sheet stacking is deemed industrially viable, utilizing slot-die coating and laser triangulation profilometry for in-line quality control. Although UV-mediated curing and Li metal anode production increase the total cell production energy consumption, the roll-to-roll compatibility of *in-situ* GPE deposition offers a scalable pathway toward efficient manufacturing.

Lastly, a novel GPE was developed employing a deep eutectic solvent (DES) as the liquid electrolyte. The PEGDA/T4 polymeric matrix previously developed was *in-situ* UV cured in a LiTFSI and TFA-based DES, with and without the addition of an EC/DEC solution. The carbonate solution addition results in a weaker Li^+ coordination associated with improved Li^+ transport properties and superior interfacial stability. Moreover, the developed DES-based GPE retains the favourable non-flammability feature and the low volatility even after the carbonate addition. The superior physico-chemical and electrochemical properties demonstrated by the GPE after the carbonate solution addition result in superior cycling performance, cell lifetime and lower cell polarization.

These investigations demonstrate the applicability and versatility of the *in-situ* GPE production process and the thiol-ene reaction mechanism over a potentially wide range of electrolyte formulations, paving the way for their application in next-generation LMBs production.