LiMn$_2$O$_4$ cathode and graphite anode based batteries are being sought after for high power applications like electric vehicles and renewable energy storage due to their high capacity, low cost and low toxicity. However, there are well documented problems with capacity fade and cycle life of this battery chemistry caused by dissolution of manganese from the cathode surface and deposition of dissolved manganese onto the anode. The dissolution of manganese from the surface of the LiMn$_2$O$_4$ cathode into the electrolyte leads to a progressive decrease in the cathode material available for lithium intercalation. A key to improving the retention of manganese is to understand the reactions that occur at the cathode surface. TEM imaging has shown the presence of a layer of electrolyte decomposition products at the cathode surface, but no experimental composition analysis has been possible due to the thinness and delicate structure of this layer. Moreover, fate of the dissolved manganese atoms on the surface of the anode is still highly debated.

In order to bridge this knowledge gap, this work develops and applies reactive force field based molecular dynamics to investigate the reactions occurring at the LiMn$_2$O$_4$ based battery electrode-electrolyte interfaces and the mechanisms of manganese dissolution. The ReaxFF reactive force field is optimized to reproduce the DFT derived energetics of elements comprising the LiMn$_2$O$_4$ based battery system. The developed force field is used to study the anode and cathode half cells of the battery.

The ReaxFF MD simulations reveal that manganese in the anode-electrolyte interface catalyzes polymerization of ethylene carbonate, forming polymers extending from the anode surface into the electrolyte. The cathode-electrolyte interface layer is found to be comprised of oxidation products of electrolyte solvent molecules such as aldehydes, esters, alcohols, polycarbonates and organic radicals, in agreement with the experimentally identified compounds. The oxidation reaction pathways for all the electrolyte solvent molecules reveal the formation of surface hydroxyl species which further react with exposed manganese atoms. An overall cathode-electrolyte interface reaction scheme is proposed in the presence of HF.

The molecular simulation studies reported in this dissertation will inform improvements in the durability and performance of lithium ion batteries for electric vehicles and for other energy storage applications, addressing a technology priority of profound national and global interest. The reactive force fields and DFT property compilations developed in this dissertation will also serve as valuable additions to the body of knowledge on interatomic potentials used by researchers in multiple disciplines of science and engineering.