ELUCIDATING MOLECULAR-LEVEL INSIGHTS OF BATTERY CHEMISTRIES USING FIRST-PRINCIPLES CALCULATIONS

The climate crisis from anthropogenic activity necessitates the adoption of renewable, non-carbon emitting energy sources to maintain the current levels of human progress while reducing greenhouse gas emissions. However, these alternative energy sources, such as wind and solar, do not offer the same conveniences as traditional energy sources, such as coal and natural gas, that can be generated consistently at centralized locations. Thus, the development of effective, cost-efficient energy storage solutions will be crucial to the widespread utilization of clean energy. In this regard, the most prominent energy storage solution of the 21st century has become electrochemical storage, particularly Li-ion batteries. While Li-ion technology has revolutionized what was once possible with battery storage, Li-ion chemistry remains challenged by fundamental chemistry limitations, particularly low gravimetric energy densities with respect to fossil fuels and the sustainable sourcing of key elements for their construction. Consequently, the continued development of alternative battery chemistries will be of paramount importance in the coming decades, and this thesis details our current research efforts for two such alternative chemistries.

The bulk of the work herein details our research on the Na-O_2 battery chemistry, a chemistry that relies on a redox reaction with an ambient O_2 environment, rather than ion intercalation, as is the case for Li-ion batteries, which consequently gives rise to a higher gravimetric energy density potential. Compared to other metal-O_2 battery chemistries, notably Li-O_2, Na-O_2 battery cells have demonstrated low overpotential losses, which along with the greater elemental abundance of sodium, make them promising candidates for future research. However, despite over a decade of efforts, Na-O_2 cells remained hampered by instabilities that prevent long-term operation and, in-turn, commercial viability. Thus far, traditional research approaches have failed to elucidate key physical insights into these instabilities and new, novel research approaches are needed to identify practical solutions to enable long-term operation. Herein, we utilize atomistic-scale modeling techniques, namely density functional theory (DFT) and *ab initio* molecular dynamics (AIMD) calculations, coupled with experimental observations to probe the molecular level interactions giving rise to the observed instabilities in Na-O_2 cells.

In Na-O_2 battery cells, one primary instability arises at the interface between the liquid cell electrolyte and the desired solid-oxide discharge product, sodium superoxide (NaO_2), that becomes deposited on the cathode during the discharge cycle. To model these undesirable interactions, a

detailed description of the NaO_2 discharge product surface chemistry is needed, and firstly, an exhaustive surface phase analysis is performed to identify chemically relevant surface terminations of the NaO_2 discharge product. From the developed surface model of the discharge product, the energetics of the observed degradation processes are examined. Using atomistic-scale modeling, including potential of mean (PMF) calculations with an explicit liquid solvent, we find that the surface chemistry of the NaO_2 discharge product plays a significant role in driving the observed degradation, with undercoordinated surface features, such as the NaO_2 cube edges, being highly susceptible to undesirable interactions with the cell electrolyte. The research approaches developed herein lay the groundwork for future studies which can directly compare electrolyte degradation trends with experiments and allow for the intelligent design of a more stable electrolyte-discharge product system.

To demonstrate the broadly applicable materials discovery potential of the methods used in the current study of Na-O_2 battery cell instability, an alternative anode material for Li-ion batteries is also explored. While traditional Li-ion batteries have utilized graphite anodes, significant improvement in the low temperature performance of the Li-ion chemistry has been observed when the graphite anode is replaced with novel MXene materials, such as Ti_3C_2. However, while improvement in the low temperature performance with these anode materials has been observed, the exact mechanism giving rise to these performance gains is unknown, which prevents intelligent optimization of the MXene composition and interface. To investigate this phenomenon, we generate Ti_3C_2 structures with experimentally relevant terminating groups and explore the Li diffusion energetics across the surface. In comparing the diffusion kinetics at the MXene surfaces with commonly used graphite, we find that more facile Li diffusion at MXene surfaces is not responsible for the increased electrochemical performance at low temperatures, but rather, different materials properties, such as the greater intercalation spacing between the MXene layers, must give rise to the observed performance.

The overarching goal of this work is to demonstrate the broad applicability of atomistic-scale materials modeling, closely coupled with experiments, to accelerate materials discovery. While these methods have been largely utilized in the computational catalysis space, we blueprint their potential to study relevant interfaces of a variety of battery chemistries. Computational modeling efforts, such as this work, could enable rapid research and development of new battery chemistries, ready to meet the renewable energy storage needs for a more sustainable future.