ABSTRACT

Warburton, Robert E. Ph.D., Purdue University, December 2019. Interfacial Reactivity Studies of Electrochemical Energy Storage Materials from First Principles. Major Professor: Jeffrey P. Greeley.

Since their commercialization in the early 1990's, rechargeable lithium ion batteries (LIBs) have become ever-present in consumer electronics, and the share of electric vehicles within the transportation sector has become much more significant. *Ab initio* modeling techniques - namely density functional theory (DFT) - have played a significant role in describing the atomic scale nature of Li^+ insertion and removal chemistry in LIB electrode materials, and have been pivotal in accelerating the design of energy dense battery materials based on their bulk properties. Despite these advances, there remains a knowledge gap with respect to understanding the many complex reactions that occur at the surfaces and interfaces of rechargeable battery materials. This work considers several case studies of surface and interfacial reactions in energy storage materials, using DFT modeling techniques to develop strategies that can rationally control the interfacial chemistry for optimal electrochemical performance.

The first portion of this thesis aims to understand the role of interfacial modification strategies toward mitigating Mn dissolution from the spinel $LiMn_2O_4$ (LMO) surface. First, a thermodynamic characterization of LMO surface structures is performed in order to develop models of LMO substrates for subsequent computational surface science studies. A subset of these surface models are then used analyze interfacial degradation processes through delithiation-driven stress buildup and crack formation, as well as reaction mechanisms for ethylene carbonate and hydrofluoric acid to form surface Mn^{2+} ions that are susceptible to dissolution. Surface passivation mechanisms using protective oxide and metallic coatings are then analyzed, which

elucidate an electronic structure-based descriptor for structure-sensitive atomic layer growth mechanisms and describe the changes in lithiation reactions of coated electrodes through electronic band alignment at the solid-solid interface. These studies of protective coatings describe previously overlooked physics at the electrode-coating interface that can aid in further development of coated electrode materials. Using the LMO substrate models, a thermodynamic framework for evaluating the solubility limits and surface segregation tendencies of cationic dopants is described in the context of stabilizing LMO surfaces against Mn loss.

Next, solid-solid interfacial models are developed to evaluate the role of nanostructure in catalyzing the lithiation of NiO to form reduced Ni and Li_2O as concurrent discharge products. Applying a Ni/NiO multilayer morphology, interfacial energies are evaluated using DFT and implemented into a classical nucleation model at a heterogeneous interface. These calculations, alongside *operando* X-ray scattering measurements, are used to explain atomic scale mechanisms that reduce voltage hysteresis in metal oxide LIB conversion chemistry.

The structure between a Li metal anode and the lithium lanthanum titanate solid electrolyte are subsequently analyzed as a model system to understand potential interfacial stabilization mechanisms in solid-state batteries. This analysis combines bulk, surface, and interfacial thermodynamics with *ab initio* molecular dynamics simulations to monitor the evolution of the interfacial structure over short time scales, which provides insights into the onset of degradation mechanisms. It is shown that the reductive instability of Ti^{4+} is the primary driving force for interfacial decomposition reactions, and that a lanthanum oxide interlayer coating is expected to stabilize the interface based on both thermodynamic and electronic band alignment arguments.

In the last part of this thesis, charge transfer kinetics are studied for several applications using constrained DFT (cDFT) to account for electronic coupling and reorganization energies between donor and acceptor states. Charge hopping mechanisms to and from dichalcogenide-based electrocatalysts during O_2 and CO_2 reduction/evolution reactions in Li-O_2 and Li-CO_2 battery systems are first evaluated.

Then, the role of the spatial separation Li^+ vacancies and interstitials on hole and electron polaron hopping in the prototypical Li_xCoO_2 cathode is analzyed. The results demonstrate that Marcus rate theories using cDFT-derived parameters can reproduce experimentally observed anisotropies in electronic conductivity, whereas conventional transition state theory analyses of polaron hopping do not. Overall, this proof-of-concept study provides a framework to understand how charged species are transported in battery electrodes and are dependent on charge compensating defects.

Finally, the key insights from these studies are discussed in the context of future directions related to the understanding and design of materials for electrochemical energy conversion and storage.