

UNDERSTANDING ION TRANSPORT AND ELECTROCHEMICAL STABILITY OF SULFIDE-BASED SOLID SODIUM ELECTROLYTES

Varun Shreyas¹, Sabina Chertmanova¹, Yang Li^{1,2}, Selim Halacoglu¹, William Arnold¹, Jacek B. Jainski²,
, Hui Wang^{1,2}, Badri Narayanan¹

¹Department of Mechanical Engineering Department, University of Louisville

²Conn Center for Renewable Energy Research, University of Louisville

Abstract

Solid-state sodium (Na) batteries (SSSBs) using sulfide-based solid electrolytes (SEs) has been attracting a lot of attention due to their high theoretical specific capacity, enhanced safety, and abundant resources. Especially, Na₃SbS₄ shows tremendous potential as a SE owing to its good Na⁺ ion conductivity of ~1 – 3 mS cm⁻¹. Despite its promise, electrochemical performance of SSSBs based on Na₃SbS₄ SE remain far from commercialization. The major roadblock thwarting progress in SSSBs is the lack of fundamental understanding of atomic-scale mechanisms underlying (a) interfacial reactions with Na anode, and (b) Na⁺ ion conduction (especially in the presence of dopants). Here, we employ ab initio molecular dynamics (AIMD) simulations to identify key reactions occurring at the Na|Na₃SbS₄ interface. Our AIMD simulations indicate that addition of an ionic liquid interlayer results in a stable solid-electrolyte-interphase (SEI) composed mainly of NaF, in excellent agreement with our synthesis and characterization experiments. Similarly, our DFT studies show that Se doping increases the electrochemical stability window of Na₃SbS₄. In terms of Na⁺ conduction, we employ AIMD simulations, and nudged elastic band calculations to understand the effect of (a) valence, and (b) size of cation dopants that partially replace Na in Na₃SbS₄. These cations introduce charge compensating Na-vacancies in the SSE, which in turn, enhance Na⁺ ion conduction. However, size of the cation dopant has a profound impact on the extent of increase in Na⁺ ion conductivity. For instance, Ca-doped Na₃SbS₄ (Na_{2.75}Ca_{0.125}SbS₄) showed Na⁺ conductivity of ~10 times that of pristine Na₃SbS₄ ($r_{Ca^{2+}} / r_{Na^{+}} = 0.98$). On the other hand, larger Ba²⁺ as dopant ($r_{Ba^{2+}} / r_{Na^{+}} = 1.35$) in Na_{2.75}Ba_{0.125}SbS₄ hinders Na-ion hops owing to local strain, thereby, yielding a Na⁺ conductivity ~5 times that of Na₃SbS₄. We will discuss these findings in the context of developing solid-state electrolytes for emerging SSSBs.

Biography of Presenter

Varun Shreyas joined the University of Louisville as a Ph.D. student in August 2019, where he is working with the Predictive Materials Modeling Laboratory (PMML). Prior to joining UofL, Varun received his B.Tech. from the National Institute of Technology Karnataka – Surathkal, India, in 2019. He is passionate in working towards the development of energy storage technologies. Throughout his academic journey, he has acquired a deep understanding of condensed matter physics, which has enabled him to undertake density functional theory calculations and classical and ab initio molecular dynamics simulations. Additionally, he has honed his skills in Python programming and machine learning, which have proven to be valuable tools in his research endeavors. He firmly believes in the power of collaboration and enjoy working with individuals from diverse backgrounds to achieve common goals.

