ABSTRACT

Mitigating global climate change and pollution caused by various anthropogenic activities and excess use of fossil fuels is one of the greatest challenges of the 21st century. Electro-chemical devices, as a result of their coupling to renewable sources and their portable nature, are central to solving many of these challenges. One of the biggest challenges in successful utilization of electro-chemical devices is identifying optimal materials, which will increase the overall economic and energy efficiency of these devices to ultimately replace traditional modes of energy storage and conversion. Electro-catalytic devices form an important subset of electro-chemical devices, making use of a catalytic material to drive the underlying electro-chemical processes, and include devices such as fuel cells, electrolyzers and metal-air batteries. However, compared to their thermal counterparts, these devices are still in their infancy and have been commercialized for only chemical feedstocks containing small molecules such as Cl_2, H_2, O_2 and H_2O. One of the major bottlenecks is the complex nature of the electrified interface, present at the catalyst – electrolyte boundary, which makes it difficult to identify optimal catalytic candidates for such devices. Therefore, to overcome these challenges, there is a pressing need to understand the fundamental, governing interactions, and this work is dedicated to utilizing first-principles based atomistic simulations to understand the underlying chemistry of such interfaces.

First principles-based methods have been key in understanding the underlying atomistic interactions and reaction mechanism for a range of heterogeneous catalytic reactions. Though successful, the utilization of these methods to understand electrified interfaces incorporating complex feedstocks, such as ethanol, nitrate, and biofuels, amongst others, has been limited. Such studies have been bottlenecked by complexities arising at these interfaces, including solvent effects, co-adsorption effects, solvent dissociation effects and charge transfer from the double layer, amongst others. From a first-principles simulation standpoint, these underlying challenges can be broadly assigned to two factors: (i) resulting from large phase space of possible atomic configurations, (ii) resulting from the complexities associated with accurately describing the underlying chemo-physical phenomenon at such interfaces. This work aims to address these challenges by development of powerful new algorithmic frameworks and workflows. A graph-theory based in-house algorithm is introduced to tackle problems related to the first challenge and sophisticated workflows utilizing ab-initio based molecular dynamics, datamining, and charge

transfer barrier estimation schemes are utilized to mitigate the latter problems. These algorithms and workflows are then utilized to successfully understand complex electrocatalytic reactions including NO, CH_3CH_2OH and O_2 reacting at Pt and its alloys catalysts. Through our results we show that such algorithmic and workflow driven approaches now form the basis to understand even more complex electro-catalytic morphologies and chemistries including, three phase boundaries, aprotic electrolytes, and larger reactant molecules such as those relevant to biomass chemistries.