First-Principles Density Functional Theory Studies on Electrochemical Reactions

By

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Abstract

First-principles density functional theory (DFT) simulation has become a powerful tool to explore the material properties and reaction mechanisms in electrochemical energy conversion and storage devices. In this study, DFT simulations were applied in understanding the electrolyte decomposition mechanisms in lithium-ion batteries (LiBs) on both LiCoO₂ (LCO) and LiNi₁/₃Co₁/₃Mn₁/₃O₂ (NCM) layered cathode materials. It was found that the decomposition of ethylene carbonate (EC) was initiated by ring-opening reaction and followed by H-abstraction reaction on metal oxide surfaces. In another study, Li plating mechanism in Li metal-based batteries was elucidated by DFT simulations for the first time. The extreme reactivity of the Li metal surface induced a strongly inhomogeneous electron distribution upon deposition of a cation on the surface. This strong charge inhomogeneity favored further attraction of cations and their reduction, thus promoting uneven Li growth, which eventually might result in needle or dendritic type of behavior.

DFT calculations were also used to explore electrocatalytic reactions including hydrogen evolution reaction (HER) and CO₂ reduction reaction (CO₂RR) on various advanced electrocatalysts. Pd₃Ru alloy consisting of Ru clusters on catalyst surfaces showed excellent activity toward HER in alkaline solutions. Theoretical simulation results demonstrated that the existence of Ru clusters could weaken the H binding energy, enhance the OH adsorption, and more importantly reduce the reaction barrier of the rate-determining step (RDS). Fe, N co-doped carbon materials (Fe-N-C) showed excellent selectivity on CO during the CO₂RR. DFT simulations revealed that the Fe sites were poisoned by strongly adsorbed *CO, which was consistent with the in situ infrared absorption spectroscopic results. The excellent CO₂RR performance originated from the Fe-N₄ moieties embedded in defective nanoporous graphitic layers with balanced binding energies of adsorbed *COOH and *CO intermediates.