

S-003

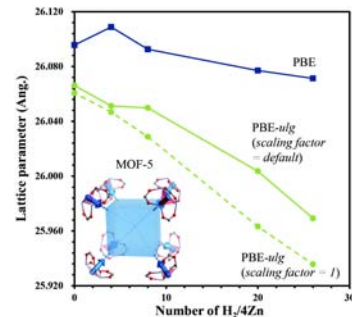
Guest Changes Host: Adsorption Site and Binding Nature of Hydrogen in MOF-5

주재용¹, 김형준², 한상수¹

¹한국과학기술연구원, ²KAIST

Using a density functional theory calculation including van der Waals (vdW) corrections, we report that H₂ adsorption in a cubic-crystalline microporous metal-organic framework (MOF-5) leads to volume shrinkage, which is in contrast to the intuition that gas adsorption in a confined system (e.g., pores in a material) increases the internal pressure and then leads to volumetric expansion. This extraordinary phenomenon is closely related to the vdW interactions between MOF and H₂ along with the H₂-H₂ interaction, rather than the Madelung-type electrostatic interaction. At low temperatures, H₂ molecules adsorbed in the MOF-5 form highly symmetrical interlinked nanocages that change from a cube-like shape to a sphere-like shape with H₂ loading, helping to exert centrosymmetric forces and hydrostatic (volumetric) stresses from the collection of dispersive interactions. The generated internal negative stress is sufficient to overcome the stiffness of the MOF-5 which is a soft material with a low bulk modulus (15.54 GPa).

Keywords: Metal-organic framework, MOF, volume shrinkage, hydrogen adsorption



S-004

Atomistic Investigation of Lithiation Behaviors in Silicon Nanowires: Reactive Molecular Dynamics Simulation

정 현^{1,2}, 주재용¹, 조준형², 이광렬¹, 한상수¹

¹한국과학기술연구원(KIST) 계산과학연구단, ²한양대학교 물리학과

Recently silicon has attracted intense interest as a promising anode material of lithium-ion batteries due to its extremely high capacity of 4200 mA/g (for Li_{4.2}Si) that is much higher than 372 mA/g (for LiC₆) of graphite. However, it seriously suffers from large volume change (even up to 300%) of the electrode upon lithiation, leading to its pulverization or mechanical failure during lithiation/delithiation processes and the rapid capacity fading. To overcome this problem, Si nanowires have been considered. Use of such Si nanowires provides their facile relaxation during lithiation/delithiation without mechanical breaking. To design better Si electrodes, a study to unveil atomic-scale mechanisms involving the volume expansion and the phase transformation upon lithiation is critical. In order to investigate the lithiation mechanism in Si nanowires, we have developed a reactive force field (ReaxFF) for Si-Li systems based on density functional theory calculations. The ReaxFF method provides a highly transferable simulation method for atomistic scale simulation on chemical reactions at the nanosecond and nanometer scale. Molecular dynamics (MD) simulations with the ReaxFF reproduces well experimental anisotropic volume expansion of Si nanowires during lithiation and diffusion behaviors of lithium atoms, indicating that it would be definitely helpful to investigate lithiation mechanism of Si electrodes and then design new Si electrodes.

Keywords: Reactive force field, molecular dynamics simulation, Si nanowire, lithiation