Hydrogen Adsorption by Alkali Metal Graphite Intercalation Compounds

Thesis by

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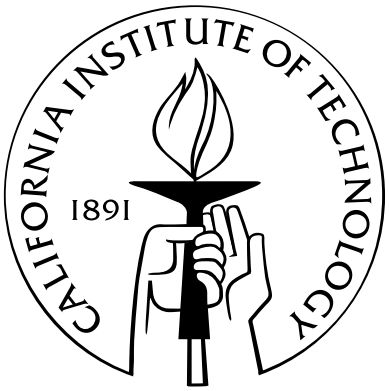

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Abstract

Adsorption occurs whenever a solid surface is exposed to a gas or liquid, and is characterized by an increase in fluid density near the interface. Adsorbents have attracted attention in the ongoing effort to engineer materials that store hydrogen at high densities within moderate temperature and pressure regimes. Carbon adsorbents are a logical choice as a storage material due to their low costs and large surface areas. Unfortunately, carbon adsorbents suffer from a low binding enthalpy for H_2 (about $5\,\mathrm{kJ\,mol^{-1}}$), well below the 15 to $18\,\mathrm{kJ\,mol^{-1}}$ that is considered optimal for hydrogen storage systems. Binding interactions can be increased by the following methods: (1) adjusting the graphite interplanar separation with a pillared structure, and (2) introducing dopant species that interact with H_2 molecules by strong electrostatic forces. Graphite intercalation compounds are a class of materials that contain both pillared structures and chemical dopants, making them an excellent model system for studying the fundamentals of hydrogen adsorption in nanostructured carbons.

Pressure-composition-temperature diagrams of the $MC_{24}(H_2)_x$ graphite intercalation compounds were measured for M = (K, Rb, Cs). Adsorption enthalpies were measured as a function of H_2 concentration. Notably, CsC_{24} had an average adsorption enthalpy of $14.9\,\mathrm{kJ\,mol^{-1}}$, nearly three times larger than that of pristine graphite. The adsorption enthalpies were found to be positively correlated with the interlayer spacing. Adsorption capacities were negatively correlated with the size of the alkali metal. The rate of adsorption

is reduced at large H_2 compositions, due to the effects of site-blocking and correlation on the H_2 diffusion.

The strong binding interaction and pronounced molecular-sieving behavior of KC_{24} is likely to obstruct the translational diffusion of adsorbed H_2 molecules. In this work, the diffusivity of H_2 adsorbed in KC_{24} was studied by quasielastic neutron scattering measurements and molecular dynamics simulations. As predicted, the rate of diffusion in KC_{24} is over an order of magnitude slower than in other carbon sorbents (e.g. carbon nanotubes, nanohorns and carbon blacks). It is similar in magnitude to the rate of H_2 diffusion in zeolites with molecular-sized cavities. This suggests that H_2 diffusion in adsorbents is influenced very strongly by the pore geometry, and less strongly by the chemical nature of the pore surface. Furthermore, the H_2 diffusion mechanism in KC_{24} is complex, with the presence of at least two distinct jump frequencies.

Bound states of adsorbed H_2 in KC_{24} were investigated by inelastic neutron scattering measurements and first-principles DFT calculations. Spectral peaks in the neutron energy loss range of 5 meV to 45 meV were observed for the first time. These peaks were interpreted as single- and multi-excitation transitions of the H_2 phonon and rotational modes. The rotational barrier for H_2 molecules is many times larger in KC_{24} than in other carbon adsorbents, apparently due to the confinement of the molecules between closely-spaced graphitic layers. Evidence was found for the existence of at least three H_2 sorption sites in KC_{24}, each with a distinctive rotational barrier.

Contents

List of Figures

List of Tables