

Mesoporous Titanium Oxide Composites in Hydrogen Storage

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In 1999 Vettrano and Antonelli showed that mesoporous Ti oxide could be reduced by one equivalent of alkali metal to give the world's first fully reducible molecular sieve. While this process is currently being explored in Li battery anode materials where the 700-1000 m²/g surface areas and controlled nanoporosity are an advantage over standard layered lithium titanates and graphite intercalates, the reduction of surface Ti is of crucial importance to hydrogen storage. Previous work showed that dense phase Ti-based materials begin to absorb hydrogen only in the reduced form. More recent work showed that low valent Ti can be deposited on the surface of the mesostructure by bis(toluene) titanium to give a metallic oxide coat on the inside of the pores. These materials possess metallic conductivity and are so reactive that they cleave dinitrogen, a notoriously inert molecule. While the nitrogen cleavage is important for other reasons and has led to a US Patent application, the surface Ti species, determined to be Ti(II) by XPS is in an even lower oxidation state than the alkali metal reduced materials, which are Ti(III) as measured by XPS. The ability to modify the oxidation state of the surface and control the pore size make these ideal candidates for hydrogen storage studies. Indeed, unpublished results from work at General Motors show that the bis(toluene) titanium-reduced materials absorb up to 6% hydrogen at 200 °C and 1400 PSI (Figure 1), relatively mild conditions which have not yet been optimized. Li-reduced mesoporous Ti oxide doped with C₆₀ showed reversible absorption of almost 9% hydrogen above 200 °C and 1400 PSI (Figure 2). Samples of unreduced mesoporous Ti (IV) oxide only absorbed 1% hydrogen and this process was not reversible (Figure 3). These results indicate that the framework must be in a reduced form to absorb hydrogen, suggesting that a mechanism other than capillary action is indeed involved. The reason that temperatures of over 200 °C are required is not yet clear, although detailed examination of the materials after cycling with hydrogen at this temperature will be presented with a view of determining the mechanism of adsorption and possible methods of optimizing the materials for even better hydrogen storage properties.

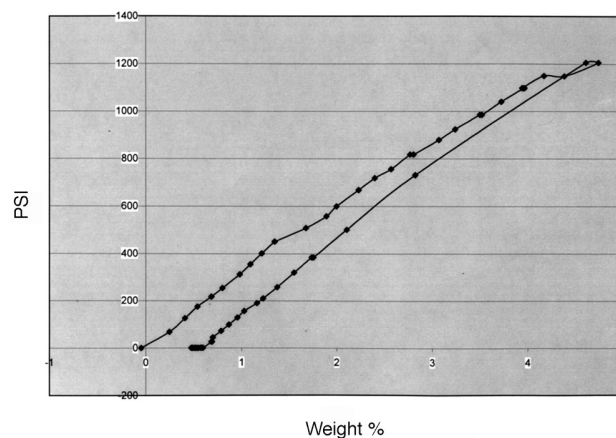


Figure 1: Hydrogen adsorption-desorption isotherm at 200 °C of mesoporous titanium oxide treated with bis(toluene) titanium.

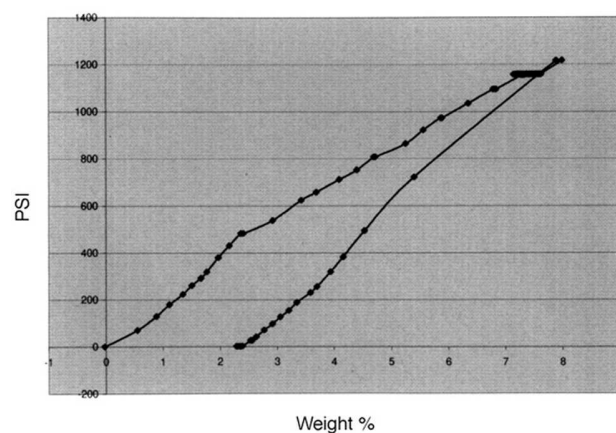


Figure 2: Hydrogen adsorption-desorption isotherm at 200 °C of mesoporous titanium oxide reduced with Li-naphthalene and treated with Buckminsterfullerene.

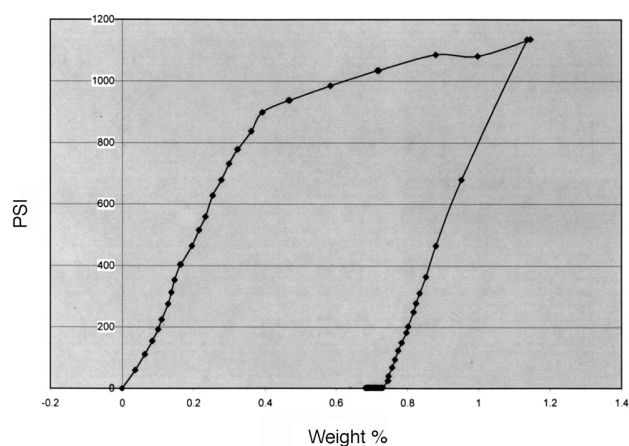


Figure 3: Hydrogen adsorption-desorption isotherm of mesoporous titanium oxide at 200 °C.