Graphite Oxides for preparation of graphene related materials: structure, chemical modification and hydrogen storage properties.

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Akademisk avhandling

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Avhandlingen kommer att försvaras på engelska.

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Abstract

Carbon materials have been studied for hydrogen storage for decades, but they showed too low capacity at ambient temperature compared to target values for practical applications. This thesis includes two parts. First one is fundamental study of graphite oxides (GO) structure and properties. Second part is focused on hydrogen storage properties of graphene related materials prepared using GO as a precursor.

We studied the effects of synthesis methods and oxidation degree on solvation/intercalation properties of GOs. New effect of temperature induced reversible delamination was observed for Hummers GO (HGO) immersed in liquid acetonitrile. Experiments with swelling of Brodie GO (BGO) in 1-octanol revealed parallel orientation of the intercalated solvent molecules relative to graphene oxide (GnO) layers. Chemical functionalization of GO in swelled state allowed us to synthesize the materials with subnanometer slit pores supported by molecular pillars. Structure and properties of pillared GO were characterized by variety of methods. Swelling properties of multilayered GnO membranes were compared to properties of precursor GO. GnO membranes were found to swell similarly to GO powders in some solvents and rather differently in other. Our experiments revealed important limitations in application of GO membranes for nanofiltration. Several parameters were found to affect the size of permeation “channels” provided by interlayers of GnO membrane structure: e.g. nature of solvent, pH of solutions and concentration of solutes.

Hydrogen storage parameters were studied for a set of graphene related materials with broad range of surface areas (SSA) (200 - 3300 m²/g). Hydrogen sorption weight percent (wt%) is found to correlate with SSA for all studied graphene materials following the trend standard for other nanostructured carbon materials. The highest hydrogen uptakes of ~1.2 wt% at 296 K and ~7.5 wt% at 77 K were measured for graphene material with SSA of over 3000 m²/g. Addition of Pd and Pt nanoparticles to graphene materials did not resulted in improvement of hydrogen storage compared to nanoparticles-free samples. No deviation from the standard wt% vs. SSA trends was also observed for pillared GO materials. Therefore, hydrogen storage properties of graphene related materials at room temperatures are not confirmed to be exceptional. However, high surface area graphene materials are found to be among the best materials for physisorption of hydrogen at liquid nitrogen temperature. Moreover, hydrogen storage capacity of 4 wt%, comparable to target values, was observed at temperature of solid CO₂ (193 K) which can be maintained using common refrigeration methods.

Keywords
Graphite oxide, graphene oxide. hydrogen storage, nanomaterials, adsorption, surface area, pore volume