

Hydrogen storage in nano-metal hydrides performed by cold plasma process

SOUTENUE PAR MARIE-CHARLOTTE DRAGASSI

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CAMPUS DES GRANDS MOULINS - UNIVERSITÉ PARIS CITÉ

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Abstract: In this work, we address the development of an innovative path to obtain nanomaterial designed for solid hydrogen storage combining nanomaterial chemistry and physical cold plasma treatment. Nickel hydroxide derivatives had been chosen as a case study for its gradual reduction and hydrogen absorption under cold hydrogen plasma. Those systems had already shown hydrogen storage capability such as *Ni* films and ultrafine *Ni* powders which were successfully transformed into nanohydrides by cold plasma process.

Conventional hydrogen storage usually happens on metallic compounds highly sensitive to oxidation due to atmospheric exposure. Thus we decided to rather try to reduce under cold plasma metal hydroxide, less sensitive to oxidation, more affordable as starting material and able to generate in situ nickel hydride phases. Ellingham calculation confirmed the ability of H^+ plasma species to reduce $Ni(OH)_2$ into Ni_2H or NiH below 400 K, the temperature reached at the surface of the plasma treated sample in our single source microwave plasma reactor.

First, nickel layered hydroxyacetate salts were synthesised by the polyol process and intensely characterised before and after cold plasma treatment varying parameters such as the layered hydroxyacetate salts washing solvent, the cold plasma composition or the exposure time. Due to the high carbon content of the intercalated anions inserted in the lamellar structure, we evidenced the formation under cold plasma exposure of an intermediary Ni_3C phase leading to the ultimate formation of $NiC_x@C_{gr}$ ($x < 0.25$) which was not intended in the theoretical Ellingham calculation.

On a second part, the same study was led on nickel hydroxide obtained by aqueous precipitation process. It was shown that cold Ar/H_2 (10/90) plasma exposure induces the reduction of nickel hydroxide through the following mechanism: $Ni(OH)_2 \rightarrow NiO \rightarrow Ni$. The final *Ni* nanopowders display poor crystalline features hindering the hydrogen storage capacity of the overall material. Those defects, such as grain boundaries or twinning faults, act as hydrogen trapping sites. The trapped hydrogen may also cluster in its atomic or molecular state. Trapped hydrogen accounts for about 1,000 ppm.

Finally, to determine the influence of the defects creation on the hydrogen sorption mechanism, nano-structuring was induced by planetary ball-milling on metallic nickel micro-particles. The as-obtained powders were, as previously, exposed to Ar/H_2 (10/90) cold plasma and intensely characterised to determine the influence of cold plasma treatment on its final microstructure and hydrogen intake. As expected, the presence of crystalline defects in the metallic matrix, inherent to the milling process, hampered the hydrogen storage properties of the material. Similarly to the previous systems, a trapped hydrogen content of the same order was measured, highlighting the limit of such an experimental approach to achieve our goal.

Last but not least, $Ni(OH)_2$ nanocages were prepared in water and exposed to the same cold plasma atmosphere to check the ability of such porous nanopowders to be reduced into nickel metal and to be loaded by hydrogen bubbles inside their cavities, through hydrogen defect trapping and clustering, the idea being that those bubbles might be recovered by a simple mechanical strain. Unfortunately due to some operating limitations due to the use of silver paste to attach the produced hydroxide pellet onto the sampling holders in the plasma reactors the first experiments were not conclusive.

This work opened the path on the use of metal hydroxide derivatives as precursor for solid hydrogen storage and warns us about the complexity of the involved plasma interaction mechanisms and their direct dependency on the chemical and structural nature of the precursor. Further investigations have to go on.