

# NEW NANONICKEL CATALYST FOR HYDROGEN STORAGE IN SOLID HYDRIDES

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## Introduction

Recently, fine nickel powders came into view as a catalyst for hydrogen storage in solid hydrides for PEM fuel cells. Nickel metal powders can be produced by the Mond process, which involves chemical vapour deposition from Ni carbonyl, Ni(CO)<sub>5</sub> (carbonyl Ni CVD). In a commercial variant of this process specialized micrometric nickel powders are manufactured by ValeInco nickel refineries in Clydech, Wales, and Copper Cliff, Canada by decomposing nickel carbonyl in thermal reactors. Fine Ni powders produced by the Ni CVD have been produced for metal powder markets for almost 60 years, and more recently, successfully utilized in rechargeable batteries, incl. NiMH batteries [1]. The same process has been used to make experimental batches of nanometric Ni powders [2]. A small particle size in nanonickel powders (n-Ni) gives a very large surface area/mass ratio (specific surface area-SSA) that is beneficial for catalytic applications involving splitting and recombination of hydrogen molecule. The finest grades of these n-Ni powders showed a potential as efficient catalysts in the development of reversible hydrogen storage in both metal hydrides and some solid chemical hydrides [3].

The morphology and the surface microstructure of n-Ni powders which is peculiar to the Ni CVD process were reported to have deciding effect on their properties [1]. Analytical transmission electron microscopy (TEM) in combination with in-situ energy dispersive spectroscopy (EDS) and electron energy loss spectroscopy (EELS) proves particularly useful for revealing nanometric scale carbon or oxides coating their surfaces to varying degrees. Here, we report results of microstructural characterization study of these powders and relate their microstructure to improvement in H<sub>2</sub> storage properties for ball-milled and nanostructured Mg and MgH<sub>2</sub> powders. Extension to this study that focuses on complex hydrides will be presented in another report (Varin et. al. 2009 this conference).

## Results and discussion

Fig. 1 shows bright-field TEM image of typical particles of the high SSA nanonickel catalyst (SSA = 30.3 m<sup>2</sup>/g; cryst.size < 20 nm), exhibiting a branched, filamentary structure. The catalyst particles are composed essentially of dislocation-free Ni nanocrystals that often took the form of a coral colony-like structure. Only rarely the crystals are twinned. Intriguingly, the Ni crystals are encapsulated in an amorphous coating phase, up to 15 nm thick, which seems to grow from the crystal surface and extends into the space between crystals (see inset). This coating contains C, and O but no Ni, as is indicated by EDX mapping in STEM. In consequence, the highest SSA nanonickel powders are heavily contaminated with 5.4 wt% O and 0.59 wt% C. Nano-Ni powders having SSA = 7 to 14 m<sup>2</sup>/g were distinctly "cleaner" as a result of the lower C (0.41 wt%) and much lower O concentration (O = 0.56 wt%). Thus, only a thin amorphous surface film, less than ~10 nm in thickness, could be observed at the edges of some of the Ni particles. Such powders exhibit a more complex microstructure with very extensive, fine-scale twinning, with some crystallites composed of 5 twins. Occasionally, nanoporous films of crystalline graphite were observed around the Ni crystallites, as reported previously [4]. This peculiar microstructure should determine properties of Ni nanopowders in a hydrogen storage bed.

Simple admixing of a few percent of n-Ni to as-received or pre-milled commercial-grade Mg dihydride did not affect hydrogen storage properties. However, even short milling of MgH<sub>2</sub> with 2 to 5 wt% nanonickel causes drastic decrease in the H<sub>2</sub> desorption temperature. The Differential Scanning Calorimetry (DSC) traces show outstanding drop in the onset of hydrogen release at ca.175° C (fig. 2a). The release of H<sub>2</sub> at 275° C into 1 bar H<sub>2</sub> reservoir was non-existent for the non-catalyzed hydride while it achieved ~6 wt % in ~ 2000 s, and ~4.5 wt% in ~6 min for the n-Ni

catalyzed  $\text{MgH}_2$  (fig. 2b). Both, charging Mg and recharging  $\text{MgH}_2$  hydride powders are greatly facilitated. The most interesting is “mechanical” charging of the nanonickel-catalyzed Mg powder in the ball-mill reactor which results in a full synthesis of Mg in 15 h milling under supply of low-pressure  $\text{H}_2$  and at ambient temperatures; this can be compared to 50 h when using non-catalyzed Mg.

## Conclusions

New nanonickel catalyst for hydrogen storage, which is manufactured by Ni CVD carbonyl process, exhibits good performance in both charging and release of hydrogen in/from Mg/Mg dihydride providing the 2-5 wt% n-Ni mixture is slightly milled in ball mills. The onset temperature ( $T_{\text{on}}$ ) for the hydrogen release at low partial pressures of  $\text{H}_2$  (typical of DSC experiment) is as low as  $275^\circ\text{C}$ , and the fastest rate of desorption ( $T_{\text{peak}}$ ) occurs at the range  $270\text{--}280^\circ\text{C}$  after activation of the powder mixture for 15 min in ball mills. Peculiar microstructure, inherent to the high-SSA powder, with coral colony-like crystals lined inside an oxide/carbon thin sleeve, seems to have no direct effect on catalytic properties, although the encapsulated nanocrystals should be less susceptible to alloying with Mg. Yet, the intimate contact of Ni with Mg is still required, but easily provided by slight powder milling. The effect of n-Ni on catalyzed complex hydrides is reported in a separate paper.

## References

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## Acknowledgements

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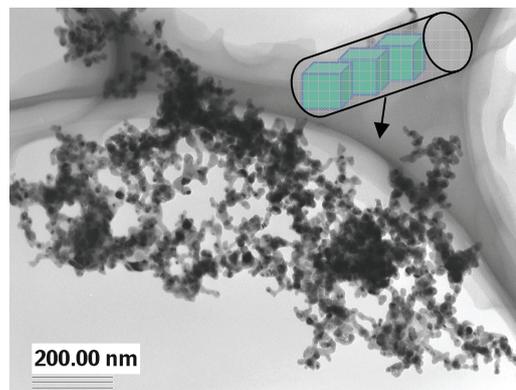


Fig.1. Bright-field TEM of filamentary nano-Ni ( $\text{SSA}=30.3\text{ m}^2/\text{g}$ ); inset showing Ni nanocrystals inside oxide/carbon sleeve.

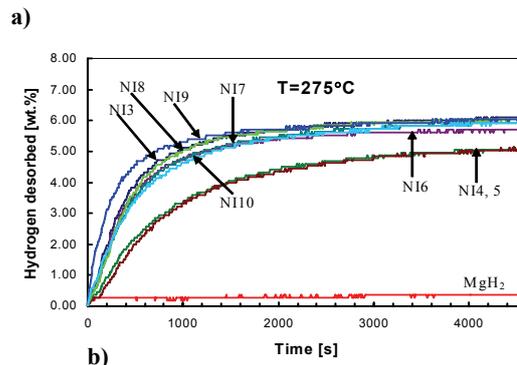
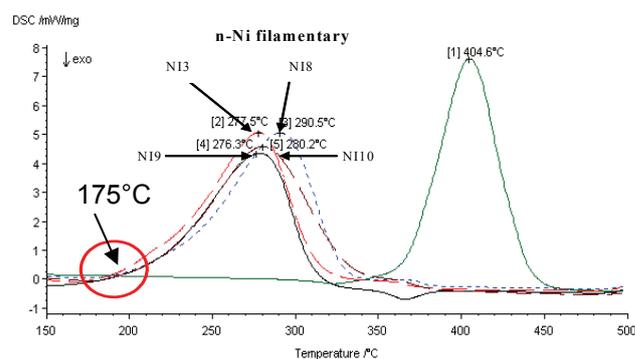


Fig.2. DSC trace (a) and desorption under  $0.1\text{ MPa H}_2$  pressure (b) of ABCR  $\text{MgH}_2+5\text{wt}\%$  n-Ni.

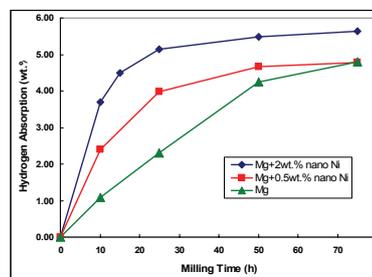


Fig.3.  $\text{H}_2$  absorption during milling Mg with n-Ni.