Coupled manometric – calorimetric measurements on Mg-based materials for H_2 storage

INTRODUCTION

In recent years, increased efforts are under way to develop materials with reversible H_2 storage properties meeting the targets for on-board applications fixed by the US Department of Energy. With this respect, it is fundamental to evaluate with accuracy both the thermodynamic and the kinetics sorption properties of the candidate materials.
On the analytical point of view, the coupling between a manometric technique (GASPRO) and a calorimetric technique (CALVET PRO DSC) is very interesting as both the absorbed/desorbed volume of hydrogen together with the corresponding enthalpy is measured on the same sample.

EXPERIMENT

About 30 mg of Mg 80.75 wt% – Ni 14.25 wt % – C 5 wt% composite prepared by mechanical milling were charged in the high-pressure cell of the CALVET PRO DSC under Ar in the glove box.
The cell was introduced in the CALVET PRO DSC furnace and directly connected to the GASPRO using a 1/8" Swagelok tube.
The sample was activated by 10 charging/discharging runs at 350 °C and H_2 pressure equal to 15 bar/0.9 bar (Figure 1).
Subsequently it was re-charged at 15 bar and 350 °C and cooled down to 200 °C at 10 °C/min before a TPD measurement was performed by heating at 2 °C/min up to 350 °C under H_2 pressure equal to 0.9 bar (Figure 2).
The volumetric and calorimetric data that are shown on figures 1 and 2 are obtained simultaneously on the same sample.
Data acquisition and treatment are obtained via the Calisto software.

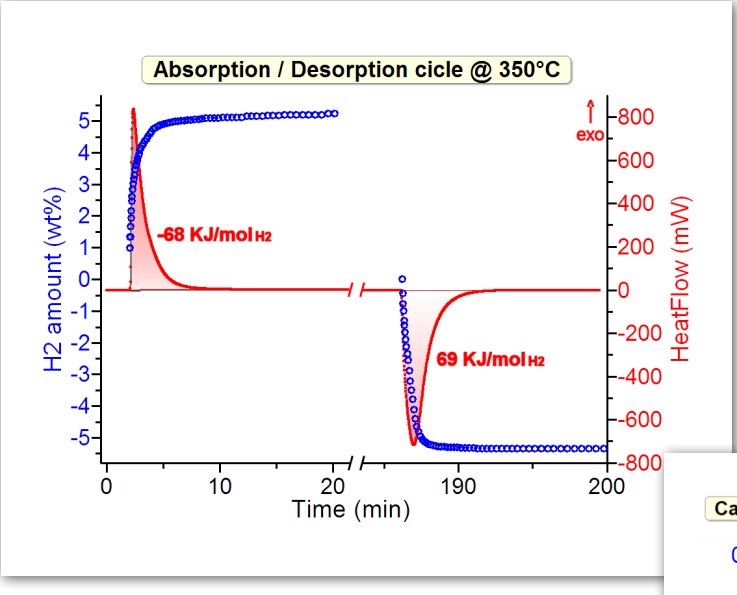

Figure 1

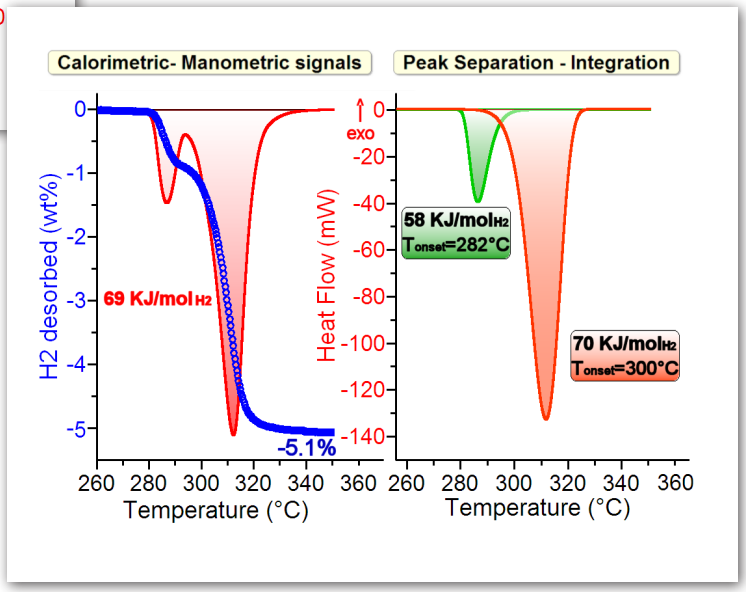

Figure 2

RESULTS AND CONCLUSION

At the end of the activation procedure (Figure 1), the sample reversibly exchanges 5.4 wt % H_2, i.e. a value higher than the DOE target for 2010 (4.5 wt %). Up to 5 wt % H_2 is absorbed/released in 2 min/4min respectively. The hydrogenation/dehydrogenation enthalpy values (-68 kJ/mol H_2 and + 69 kJ/mol H_2 respectively) are very close and lower than the value obtained for pure MgH_2 (74.5 kJ/mol H_2). Two desorption steps can be distinguished in the TPD profile (Figure 2), the low temperature one (282 °C) due to the dehydrogenation of Mg2NiH4, the high temperature one (300 °C) attributable to MgH_2 dissociation. The desorption enthalpy values obtained by the deconvolution of the peaks (58 kJ/mol H_2 and 70 kJ/mol H_2) are once again well lower than the data reported in literature for the pure compounds dehydrogenation (64.5 kJ/mol H_2 and 74.5 kJ/mol H_2 respectively). The integration of the whole signal gives a value equal to that obtained in isothermal conditions (Figure 1). All these data underlines the good destabilizing effect played by C towards the Mg/MgH_2 and the Mg_2Ni/Mg_2NiH_4 systems.

Reference: C. Milanese, A. Girella, A. Marini, H2 Lab, Department of Physical Chemistry, University of Pavia, Viale Taramelli 16, I-27100 Pavia, Italy
E. Wirth, Setaram Instrumentation, 7, Rue de l'Oratoire - 69300 Caluire - France
C. Milanese et al., Int. J Hydrogen Energy, in press. doi: 10.1016/j.ijhydene.2009.11.057.

INSTRUMENT

GASPRO

-260°C to 500°C

VARIETY OF MODES OF OPERATION
ability to combine PCT, kinetics and cycle life modes to 200bar to determine the quantity and rate of sample gas interaction and its aging characteristics all in one instrument and operation

PRECISION MEASUREMENT OF SMALL SAMPLES
using the patented microdoser option to inject small doses of gas on the sample

HIGH ACCURACY VERSION
to reduce cumulative error across multiple measurements points

EXTERNAL CALORIMETER COUPLING CAPABILITY
to increase your research options