Round Robin Hydrogen Sorption Performance Characterisation of Carbon Adsorbants, Complex and Metal Hydrides

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P. Moretto, **C. Zlotea**, **E. Weidner**, Institute for Energy, Joint Research Centre of the European Commission

1   Introduction

In the frame of the European funded project NESSHY (Novel Efficient Solid State Storage for Hydrogen), three inter-laboratory comparative measurement campaigns have been undertaken for assessing the hydrogen physi- and chemi-sorption behaviour of storage materials. These Round Robin Testing (RRT) exercises aimed, in the absence of specific measuring standards, to guarantee that the performance parameters of novel hydrogen storage materials as measured in different laboratories are comparable and to identify possible weaknesses in the measurement steps. The overarching objective is to contribute with this work to the data harmonisation and the development of testing protocols for accurately and independently assessing the performance, safety and life cycle stability of hydrogen solid-state materials. This could ultimately serve future codes drafting and standardisation needs in the field.

Very few examples of RRT exercises in the hydrogen sorption field have been reported in the literature. Some RRT's have involved too few partners and had a limited scope, for example the interlaboratory comparison reported by C. Ahn et al. at the 2005 Annual Merit Review Proceedings of the DoE [1]. To our knowledge the RRT exercise has never been published. Some RRT exercises have been organised in Japan to validate the Japanese sorption standards issued by the Japanese Standard Association [2]. Also the results of these RRT's have not been published. A record of this can be found however in an article specifically on the accuracy of gas phase sorption measurements by Wang and Suda [3]. The RRT exercises focussed on classic metal hydrides such as $LaNi_5$ and the compared experiments used mild experimental conditions in term of temperatures and pressures.

The RRT exercises reported here have been organised in a formal way (see next section) and the material choices has taken into account the recent developments in the hydrogen solid-state storage field. We have not been able to identify any previous RRT specifically dedicated to the assessment of hydrogen sorption performances of the three materials chosen for this study, what brings to conclude that these RRT exercises are the first ever formally organised in the world.

2   The NESSHY Round Robin Test Exercises: Materials, Protocol and Organisation

One round robin testing exercise focused on adsorption capacity measurements on a carbon based material. The other two testing campaigns were dedicated to thermodynamic and kinetic properties measurements on alanate- and magnesium-based absorbents.   A

significant number of laboratories, beyond the NESSHY European partners, participated in these exercises, including key, reputable international experimental facilities.

Table 1 gives an overview of the RRT's exercises, with materials, participants and experimental campaigns.

Table 1:   Overview of the three Round Robin Tests.

Material	Microporous carbon molecular sieve TAKEDA 4A	NaAlH$_4$ with 4% CeCl$_3$ additive	MgH$_2$ with 5% transition metals additives
Participants	China: GRINM, France: Institut Néel, CNRS (2 laboratories) Germany: IFW Dresden, MPI für Metallforschung. Greece: Demokritos. Eur. Commission: JRC-IE Spain: University of Alicante (2 laboratories). UK: Johnson Matthey, University of Birmingham, University of Nottingham, University of Salford. USA: SwRI	China: GRINM. Germany: KIT-INR, IFW Dresden, GKSS European Commission: JRC-IE Norway: IFE. Swiss: EMPA. UK: Johnson Matthey. USA: SwRI.	China: GRINM, France: CNRS(3 laboratories) Germany: IFW Dresden, GKSS. Japan: AIST Eur. Commission: JRC-IE. Norway: IFE. Swiss: EMPA. Turkey: METU. UK: Johnson Matthey, University of Salford. USA: University of Nevada, JPL.
Experimental campaign	pcT isotherm absorption and desorption curves at 77 K (-193ºC) and room temperature ~ 288 K (15-20ºC).	pcT isotherm absorption and desorption curves at 298 K (125ºC) and 313 K (140ºC) temperatures.	pcT isotherm absorption and desorption curves at 553 K (280ºC) and 593 K (320ºC) temperatures.
		Absorption isotherm kinetic curves at 298 K (125ºC) and 323 K (150ºC).	Ab- and de-sorption isotherm kinetic curves at 523 (250ºC) and 573 (300ºC).
	Isostherical heat of absorption (optional)	Enthalpy of formation of NaAlH$_4$ and Na$_3$AlH$_6$	Enthalpy of formation of MgH$_2$

For each of the three RRT exercises a specific protocol has been prepared by a group of experts, defining the experiments to be performed, the material preparation required (outgassing, activation, etc.) and the data to be reported. The RRT materials have been carefully characterised to avoid sample-to-sample differences, to minimise handling and transport deterioration, and stability during hydrogenation. When the number of reporting participants was allowing it, the data has been analysed according to the ASTM standard setting a methodology for interlaboratory study evaluation [4]. The original length of 9 months for the performance of each RRTexercise had to be extended to more than one year, to accommodate delays of some participants.

3   Results and Preliminary Conclusions

It is not possible to give a complete report of all the achieved results. In the following only some selected results for each of the three RRT's are given, focussing on thermodynamic properties. The kinetics aspects will be published later.

### 3.1   RRT on physi-sorption (microporous carbon molecular sieve)

The results of this RRT exercise has been published in [5]. We limit here to present its final conclusions. From the detailed analysis of the experimental parameters of each participants, different types of error could be identified: 1) procedural errors such as gas leakage, measurement conditions not allowing for thermodynamic equilibrium and choice of the real equation of gases, 2) operator errors, such as low purity of hydrogen gas and incorrect measured or assumed dry mass, 3) calibration errors such as buoyancy evaluation for gravimetry, reactor and incorrect sample volume determination for volumetry, 4) poor equipment design which causes low accuracy of measurements.

Based on this, the following measurement recommendations can be proposed:

- Methodology: the choice of instrument should be a function of type, amount and geometry of the sample.
- Calibration of the volumes and determination of the gas leakage rate in order to assess the accuracy of the measurement (for example in term of uncertainty based on a value of moles of hydrogen).
- Outgassing of the sample under controlled conditions. Sometime an ultra high vacuum system is required for very small pores.
- Thorough characterisation of the sample before starting experiments.
- Controlling of the experiment in terms of equilibration time, temperature stability and gas state equation.
- Checking the repeatability of isotherms by performing more than one acquisition and always acquiring ad- and de-sorption curves.
- Analysis of the data by critical assessment of the type of isotherm, reason for hysteresis (if present) and nature of adsorption.

3.2   RRT on chemi-sorption: $NaAlH_4$ + $CeCl_3$

Only 9 laboratories have participated to this exercise, and very few have performed all the experiments mentioned in the measuring protocol. Therefore, it is not possible to perform a statistical analysis according to [4]. As an example of results, Figure 1 shows the absorption curves at 125°C. The pcT measurement results can be summarised as follows: the $NaAlH_4$ absorption plateau has been found between 5.0 and 6.0 MPa at 125ºC and between 6.0 and 7.5 MPa at 140ºC. For $NaAl_3H_6$ the plateau ranges between 2.5 and 4.0 MPa at 125ºC and between 4.5 and 6.0 MPa at 140ºC. The full H_2 capacity is evaluated by participants from 3.0 to 4.5 wt% (125°C).
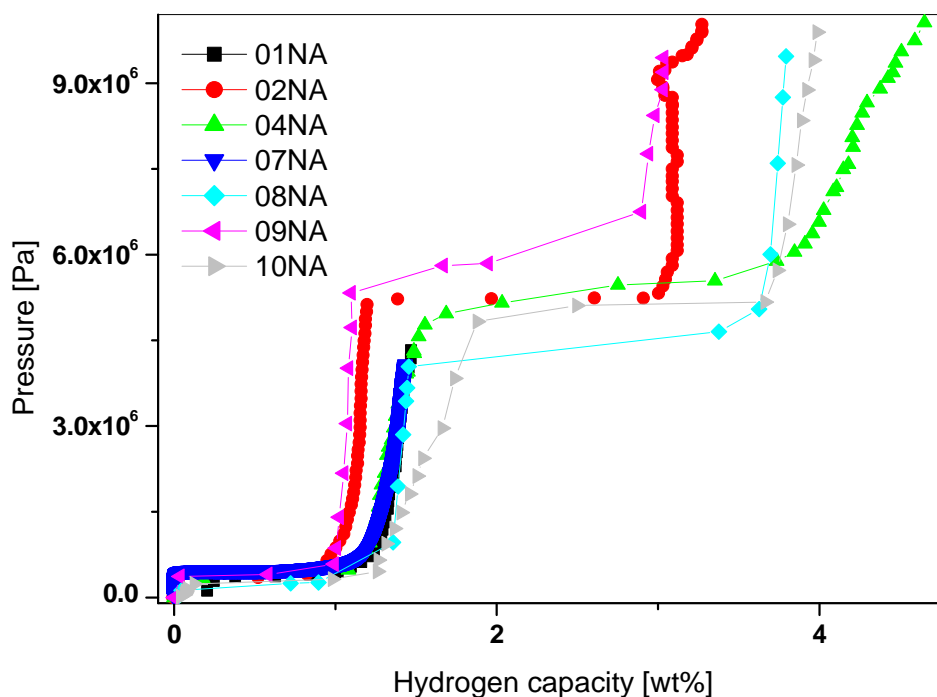
**Figure 1:** **Absorption curves at 125°C for NaAlH₄ with CeCl₃ addictives.**

The discrepancy remarked among the pcT curves of the individual participants could be cause by (a combination of) various causes such as material deterioration during distribution and/or handling, dishomogeneity of the as-produced material, not attainment of the full equilibrium during pcT acquisition, leakage. Since the material has been carefully prepared and sampled and characterised before shipping and the experiments performed, the most plausible, although not demonstrated, cause for the discrepancies is the different handling of the samples at the laboratory of each participant. In other words, partial oxidation of the material could have occurred in laboratories which show reduced capacity and higher plateau pressure.

3.3   RRT on chemi-sorption: MgH₂ + transition metals

Up to 15 laboratories have participated to this RRT exercise. The statistical analysis has not yet been completed because some participants reported very late in 2010. Figure 2 shows the absorption curves at 320°C. The MgH₂ absorption plateau has been found between 0.26 and 0.41 MPa at 320ºC. The full H₂ capacity measured at 1 MPa extend between 5.5 and 6.4 wt% and between 5.4 and 6.6 wt% respectively at 280°C and 320°C. The enthalpy of formation has been evaluated by participants in a range from -60.4 to -80.0 kJ/moleH₂ for absorption and between 60.7 and -80.3 kJ/moleH₂ in desorption.
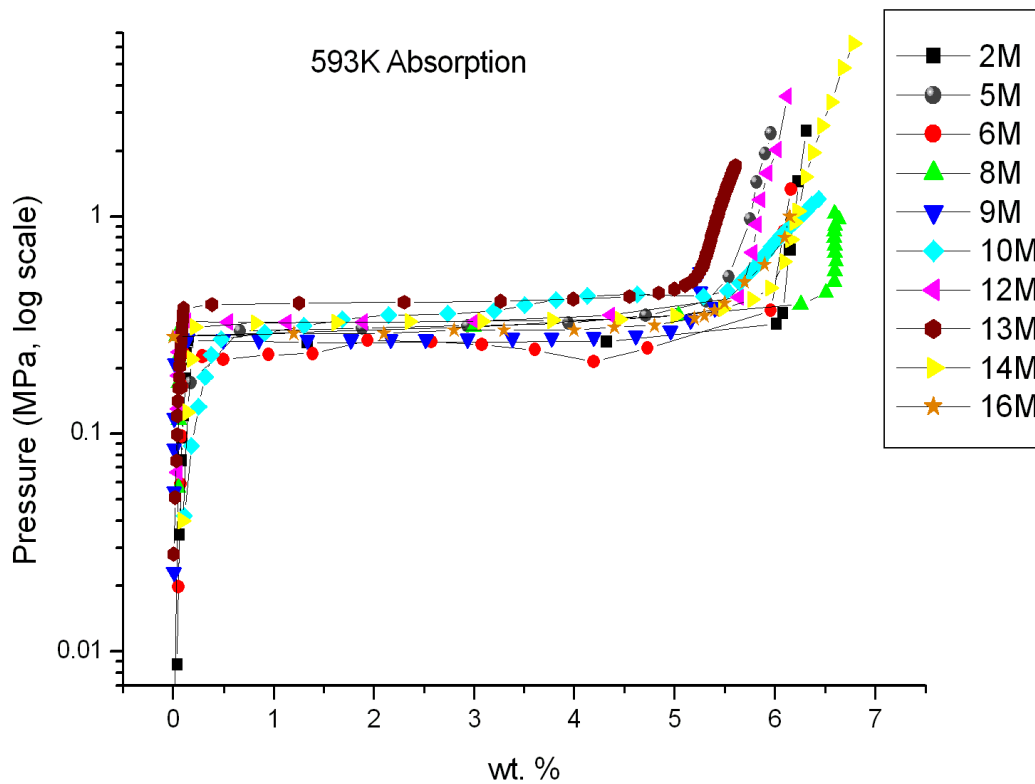
Figure 2:   pcT curve of MgH2 at 593 K as measured by all participants.

The highest data dispersion occurs at higher pressure, and from the shape of many pcT curves, which do not appear vertical in the b-phase, it could be concluded that small leaks at high pressure (> 0.5 MPa) is the most frequently occurring cause of errors.

Acknowledgement

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