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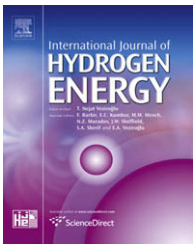

A Round Robin characterisation of the hydrogen sorption properties of a carbon based material

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ABSTRACT

A Round Robin exercise has been carried out in the frame of the European project NESSHY (Novel and Efficient Solid State HYdrogen storage systems) to evaluate the hydrogen physisorption on a commercial microporous carbon material. Fourteen laboratories have measured pressure–composition–isotherms at 77 K and ambient temperature following a test protocol. The dispersion of isotherms increases with pressure. Four similar isotherms measured by different methods from different laboratories are proposed as standard hydrogen sorption behaviour. The hydrogen capacities are 1.40(±0.1) and 0.07(±0.01) wt.% for 1 MPa hydrogen pressure at 77 K and ambient temperature, respectively. A statistical evaluation of the results is applied in order to point out laboratories that might need a corrective action. Tentative recommendations for optimising the acquisition of physisorption isotherm data and a check list for data reporting are proposed. The authors advise this carbon material as being suitable for benchmarking of laboratories in this field.

1. Introduction

The increasing research effort in the hydrogen storage field requires reliable and accurate methods of measurement to determine the hydrogen uptake. Consistent and precise measurements are also needed to verify previous claims in the literature and to facilitate comparison among results especially for porous materials, which are subjected to great controversy [1–10]. Difficulties are encountered in order to find a correlation between hydrogen sorption properties obtained by different laboratories for carbonaceous materials [1–3,8,9].

Accurate measurements rely on high-quality test protocols (method). The accuracy of measurements expresses the precision of a test method and the closeness to the accepted reference value. Two measurements concepts are used to express the precision of a test method: repeatability and reproducibility [11]. Repeatability deals with variability between independent tests obtained within a single laboratory. The effort of improving repeatability remains at the level of individual laboratory. Reproducibility concerns variability between single test results obtained in different laboratories. The reproducibility can be estimated by an interlaboratory study, which can take the form of a Round Robin Test (RRT). Unavoidable random errors may be introduced by factors such as the experimental procedure, the operator, the equipment used, the calibrations of the equipment or the environment. An RRT permits to evaluate the variability between measurement results as obtained by different laboratories on the same sample or on random portions of a homogenous material. The statistical analysis of results gives an overall picture of the dispersion of results as well as pointing out particular laboratories that surpass or approach critical values.

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In the frame of the European Integrated Project NESSHY (Novel and Efficient Solid State HYdrogen storage systems) series of RRT exercises have been organized. The present study reports on the results of the RRT on measurements of hydrogen physisorption on a microporous carbon material. Main objective of the exercise has been the determination of the variability of the hydrogen capacity values delivered by the participant laboratories. A statistical analysis has been applied in order to determine particular laboratories that surpass or approach critical values. By means of a measurement protocol and reporting guideline, the RRT exercise aimed also at the identification of possible weaknesses in some of the experimental measuring steps.

We further propose a test protocol and a reference material for future benchmarking of new laboratories and give tentative of recommendations for optimising the physisorption isotherm measurements and for reporting data in literature. Although these recommendations are based on this RRT exercise, most of them have been already covered by guidelines proposed by the International Union of Pure and Applied Chemistry (IUPAC): ''Recommendations for the characterisation of porous solids'' [12] and ''Reporting physisorption data for gas/solid systems'' [13]. Comprehensive information about different aspects of the hydrogen physisorption on porous materials topic such as accuracy of measurements, detailed description of experimental conditions, set up calibration procedures, experimental protocols, methodologies and development of instrumental design can be found in the following references [6,7,10,14–22]. The report of data in literature must always be accompanied by a thorough presentation of experimental parameters and procedures in order to guarantee potential reproducibility of results by external laboratories. The completeness in the reporting of results is essential to facilitate compilation of data and to promote scientific and interdisciplinary cooperation [23].

2. Participants and confidentiality of results

The invitation to participate to the RRT has been sent to all NESSHY partners and to the members of the Research and Training Network HyTrain, focussing on similar research subjects. Sixteen volunteering laboratories have accepted to participate out of which fourteen have completed and reported experimental data. The names of fourteen laboratories and countries are: Johnson Matthey (UK), University of Birmingham (UK), University of Nottingham (UK), University of Salford (UK), Institut Néel, CNRS (France), Laboratoire de Chimie Métallurgique des Terres Rares, CNRS (France), Leibniz Gemeinschaft (Germany), Max Plank Society (Germany), National Center for Scientific Research Demokritos (Greece), European Commission, JRC-IE (The Netherlands), University of Alicante – 2 laboratories (Spain), General Research Institute for Nonferrous Metals (China) and Southwest Research Institute (USA). In order to assure the confidentiality of the RRT results, anonymous random numbers have been used instead of laboratory names.

3. Material choice and characterisation

3.1. RRT material

A commercial microporous carbon molecular sieve from Takeda Chem. Ind. Japan (CMS 4A) has been selected as RRT material. This material answers at best the selection criteria, briefly explained in the following.

- Carbon material: the choice of a microporous carbon is supported by the significant discrepancies of the hydrogen storage capacity values of carbon based materials reported in the literature. Values ranging from few to several tens of hydrogen wt% have been published [1–10]. This demonstrates the strong need for the accurate determination of hydrogen uptake on low density materials. Previous studies clearly proved the effect of density uncertainty on volumetric measurements of hydrogen uptake [16].
- Relatively low hydrogen capacity: It is assumed that every laboratory performs at installation and/or at periodic intervals a calibration check by means of well known standard material. This RRT wants to map interlaboratory measurement dispersions in rather difficult conditions, i.e. at the limit of the accuracy of the usual equipments (especially for the measurements at room temperature).
- Unknown material to the hydrogen storage scientific community, to avoid bias between the experimentally measured values and the expected capacity values as from already published results.
- Commercial availability in sufficient quantity to distribute several grams to all participants.
- Batch homogeneity and already available procedure for pretreatment of material (outgassing temperature, time and vacuum range).
- Available general material characterisation from literature. Takeda molecular sieves properties have been already presented in various publications [24,25].

The Takeda material (CMS 4A) is the object of other Round Robin Tests on determination of porosity and gas adsorption properties organized within the frame of European Network of Excellence InsidePores[1].

3.2. RRT material characterisation

Before starting the RRT, the organisers have determined the physical and chemical properties of the microporous CMS 4A Takeda material. The carbon material is in the form of extruded pellets of cylindrical shape of approximately 2.2 mm diameter.

Secondary electron microscopy (SEM) and Energy Dispersion Spectroscopy (EDS) measurements have been performed to control the homogeneity of the material. Fig. 1 shows an SEM image of the material. Individual particles dimension

[1] Rodriguez-Reinoso F. *Round Robin experiments for the characterisation of 4 reference adsorbents*, oral communication in COP-VIII, 10–13 June 2008, Edinburg.