

### Neutron Scattering Methodology for Absolute Measurement of Room-Temperature Hydrogen Storage Capacity and Evidence for Spillover Effect in a Pt-Doped Activated Carbon

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**ABSTRACT** A neutron scattering methodology is proposed to simultaneously determine the total hydrogen adsorption, the excess hydrogen adsorption, and hydrogen gas confined in the porous sample. This method is capable of an absolute measurement of the hydrogen content without need for any calibration. It involves the least amount of corrections and is not likely to be affected by the instrumental factors compared to the traditional gravimetric and volumetric methods. We used this method to study the physisorption behavior at room-temperature (RT) of a Pt-doped activated carbon sample as a function of hydrogen pressure. This method will become a simple and important tool for solving various problems arising from the traditional measurements of RT hydrogen storage capacities. It can be combined with an in situ small-angle neutron scattering to study the hydrogen spillover effect in the kinetic adsorption process. Storage capacity and spatial distribution of the hydrogen adsorbed due to spillover are concurrently revealed.

SECTION Energy Conversion and Storage

eversible storage of a large amount of hydrogen near room-temperature (RT) is crucial for the future hydrogen economy. The target criteria of the Department of Energy for on-board hydrogen storage have been set around ambient temperature. 1-3 However, the RT hydrogen storage capacities of porous materials with spillover effect measured from different laboratories was disputed because of the difficulties in obtaining reproducible data.<sup>3-8</sup> Except for the factors of material quality and activation procedure,<sup>5,8</sup> the discrepancy is mainly due to many potential sources of measurement errors and their experimental validations.<sup>3,4,6,7</sup> Measurement of the relatively low uptake of hydrogen (<5 wt %) in porous materials at RT and high pressures have resulted in many challenges for traditional volumetric and gravimetric methods.<sup>7</sup> The disadvantages of the volumetric method (Sieverts apparatus) are, for example, (1) the potential leakage at high pressure, (2) the temperature gradients on the measured pressure (1 °C temperature rise can cause an artifact of 2.6 wt % adsorption),<sup>7</sup> and (3) the other uncertainties coming from instrumental calibrations.<sup>4,7</sup> One limitation of the gravimetric method is to correct for the volume buoyancy effect, which is further amplified for low-density materials.<sup>4</sup> The accuracy of both methods is subject to the many instrumental calibrations. The so-called surface excess hydrogen adsorption can be experimentally determined by both traditional



methods. Total or absolute adsorption (the amount of gas adsorbed in the volume occupied by the bulk material) can not be measured experimentally<sup>6,9</sup> but can be evaluated by a given value of pore volume<sup>6,10</sup> (which is also an error source). Improving the technique or designing a new method for hydrogen storage measurement is critically necessary to develop and test the promising materials.<sup>6</sup>

This study proposes a neutron scattering methodology to simultaneously determine the total hydrogen adsorption, the excess hydrogen adsorption, the hydrogen gas confined in the porous sample, and the bulk density of sample (see next paragraph for the details). This methodology is based on the interaction of a neutron with a nuclei inside a sample. Because of the high incoherent scattering cross section (= 80.26 barn) of hydrogen, neutron scattering is a powerful tool to directly probe hydrogen at an atomic scale compared to the X-ray technique. Our method is simple and capable of directly measuring the hydrogen storage capacity accurately with a small amount of sample without the need for laborious calibrations such as empty volume or buoyancy corrections

Received Date: April 7, 2010 Accepted Date: April 26, 2010 Published on Web Date: April 29, 2010

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Figure 1. Schematic drawing of the investigated carbon powder sample.

that are crucial for traditional methods. Our method estimates the hydrogen uptake based on the scattering cross section of hydrogen. It is not likely to be affected by the instrumental factors from the traditional gravimetric and volumetric methods mentioned above. This methodology is applied here to successfully study the physisorption behavior at RT of hydrogen in a Pt-doped activated carbon (Pt/AC) sample as a function of hydrogen pressure. It would be considered to be an important tool to independently validate the other methods. Recently, the use of the spillover technique to enhance RT hydrogen storage capacity has attracted widespread interest.<sup>1-3,11-13</sup> However, the mechanistic details of hydrogen spillover is still poorly understood.<sup>3,8,12</sup> The application of neutron scattering to the study of the spillover effect is rare.<sup>14</sup> This work combined the above-mentioned neutron transmission methodology and an in situ small-angle neutron scattering (SANS)<sup>15</sup> to observe the temporal variation of the storage capacity and the corresponding distribution of excess hydrogen adsorbed due to the spillover.

The sample irradiated by neutron beam is comprised of carbon grains, pores in the grain, voids between carbon grains, the excess hydrogen adsorption, and pressure-dependent hydrogen gas confined in the sample (voids and pores). Figure 1 shows a schematic drawing of the above-mentioned sample system: void volume =  $V_{\text{void}}$ , carbon volume =  $V_{c}$ , pore volume =  $V_{\text{pore}}$ , total volume irradiated by neutron beam =  $V_{\text{tot}}$  $(V_{\text{tot}} = V_{\text{void}} + V_{\text{c}} + V_{\text{pore}})$ , carbon mass =  $W_{\text{c}}$ , mass of total hydrogen adsorption =  $W_{\rm H}$ , mass of excess hydrogen adsorption =  $W_{H1}$ , weight of hydrogen gas confined in the sample (voids and pores) =  $W_{H2}$ , bulk density of carbon sample (considering the grain packing and internal pores) =  $d_{\text{bulk}}$  $(d_{\text{bulk}} = W_{\text{c}}/V_{\text{tot}})$ , skeletal (solid state) density of carbon =  $d_{\text{s}}$  $(d_s = W_c/V_c)$ , hydrogen gas density as a function of pressure =  $ho_{gas}$ . For determining the various adsorption capacities, the neutron transmission measurement of the bulk sample was performed in combination with in situ SANS measurement on the NG-7 instrument of the National Institute of Standard and

Technology (NIST). The neutron transmission factor is defined as the ratio of transmitted beam intensity and incident beam intensity. According to the basic theory,<sup>16</sup> the neutron transmission factor can be expressed as  $\exp(-\Sigma \cdot t)$  and can be accessibly and accurately measured by the direct beam of neutron scattering instrument. Here,  $\Sigma$  is macroscopic cross section of material, which is equal to the sum of the macroscopic coherent scattering cross section,  $\Sigma_{\rm coh}$ , the macroscopic incoherent scattering cross section,  $\Sigma_{\rm inc}$ , and the macroscopic absorption cross section  $\Sigma_{\rm abs}$ . Parameter *t* is the known sample thickness parallel to the incident neutron beam.

A two-step measurement is conducted for measuring the adsorption capacity at a given hydrogen pressure  $P_0$ : (1) measure the neutron transmission factor (i.e., the  $\Sigma_C$  value) of the carbon sample at P = 0 (vacuum), and (2) measure the transmission factor (i.e., the  $\Sigma_{C+H}$  value) of the carbon sample with the adsorbed hydrogen at  $P_0$ . The following equation system can be established from the first principle:

$$\Sigma_{\rm C} = \sigma_{\rm C} N_{\rm C} = \sigma_{\rm C} \frac{W_{\rm C}}{M_{\rm C} V_{\rm tot}} N_0 \quad (\text{at } P = 0) \tag{1}$$

$$= \sigma_{\rm C} N_{\rm C} + \sigma_{\rm H} N_{\rm H}$$
$$= \sigma_{\rm C} \frac{W_{\rm C}}{M_{\rm C} V_{\rm tot}} N_0 + \sigma_{\rm H} \frac{W_{\rm H}}{M_{\rm H} V_{\rm tot}} N_0 \quad (\text{at } P = P_0) \quad (2)$$

 $\Sigma_{\rm C}$  .

where  $\sigma_i$ ,  $N_i$ , and  $M_i$  are the microscopic cross section, the atomic number density, and the atomic weight of the element *i*, respectively.  $N_0$  is the Avogadro number. On the basis of eq 1 and the measured  $\Sigma_c$  value, the value of  $d_{\text{bulk}}$  can be determined as

$$d_{\text{bulk}} = \frac{W_{\text{C}}}{V_{\text{tot}}} = \Sigma_{\text{C}} \times \frac{M_{\text{C}}}{\sigma_{\text{C}} N_0}$$
(3)

Subtracting eq 1 from eq 2, we directly obtain the total adsorption capacity  $W_{\rm H}/V_{\rm tot}$  (volumetric form) as given by

$$\frac{W_{\rm H}}{V_{\rm tot}} = (\Sigma_{\rm C+H} - \Sigma_{\rm C}) \times \frac{M_{\rm H}}{\sigma_{\rm H} N_0} \tag{4}$$

The total adsorption capacity is the sum of excess hydrogen adsorption and hydrogen gas confined in the sample as given by  $^{6.9}$ 

$$\frac{W_{\rm H}}{V_{\rm tot}} = \frac{W_{\rm H1}}{V_{\rm tot}} + \frac{W_{\rm H2}}{V_{\rm tot}} \tag{5}$$

The amount of pressure-dependent hydrogen gas confined in the sample can be expressed as

$$\frac{W_{H2}}{V_{tot}} = \frac{V_{pore}\rho_{gas} + V_{void}\rho_{gas}}{V_{tot}} = \rho_{gas} \times \left(\frac{V_{pore} + V_{void}}{V_{tot}}\right)$$
$$= \rho_{gas} \times \left(\frac{V_{tot} - V_{C}}{V_{tot}}\right)$$
(6)

Combining with  $V_{\text{tot}}$ :  $V_{\text{C}} = d_{\text{bulk}}^{-1}$ :  $d_{\text{s}}^{-1}$  and the skeletal density  $d_{\text{s}}$  determined from the helium density method, the amount of hydrogen gas confined in the sample (volumetric form)  $W_{\text{H2}}/V_{\text{tot}}$  can be obtained. Finally, according to eq 5 and the deduced amounts, the excess hydrogen adsorption  $W_{\text{H1}}/V_{\text{tot}}$  can be determined in turn. By dividing by the determined

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**Figure 2.** Measurement of RT hydrogen storage capacity as a function of hydrogen pressure (in terms of total adsorption, excess adsorption and hydrogen gas confined in the sample) for a Pt/AC sample determined by the neutron transmission method, in comparison with the excess adsorption obtained by the Sieverts (volumetric) method.

value of  $d_{\text{bulk}}$  (=  $W_c/V_{\text{tot}}$ ), all calculated values for (1) total hydrogen adsorption, (2) excess hydrogen adsorption, and (3) hydrogen gas confined in the sample could be transformed into the gravimetric form (in units of wt %) from the volumetric form. The above-mentioned transmission factor measurements are a well-established standard procedure for any modern-day SANS experiment. So, there is no need for a separate calibration.

The physisorption behavior at RT of hydrogen in a Pt-doped activated carbon sample studied by this neutron methodology is shown in Figure 2 as a function of hydrogen pressure from 300 to 1500 psi. The measured quantities are the total adsorption (blue triangles), the excess adsorption (red circles) and the hydrogen gas confined in the sample (black dashed line). With the additional information of pore volume  $(V_{\text{pore}}/$  $W_{\rm c} = 0.746 \, {\rm cm}^3/{\rm g}$ ) determined by a nitrogen gas adsorption method, the hydrogen gas confined in the pores in the grains  $(\rho_{\text{gas}} \cdot V_{\text{pore}} / W_{\text{c}})$  can be calculated as shown in the green dashed line of Figure 2. Figure 2 clearly shows the linear pressure-dependence for all four quantities. The result of excess hydrogen adsorption is consistent with that obtained by the volumetric method.<sup>17</sup> In the case of RT physisorption, the hydrogen gas confined in the sample container (voids between the carbon grains and pores in the grains) becomes increasingly higher than the excess adsorption on the adsorbate surface with the increasing hydrogen pressure. From the mutual relationship of the above two curves, we can use this neutron methodology to directly evaluate the capacities of hydrogen gas confined and excess adsorption in a metal storage container. This information is difficult to access by the other methods. It can potentially be a new nondestructive neutron approach to directly examine and in situ monitor the status and capacities in a commercial high-pressure hydrogen-storage container with porous materials. (The experimental procedure, the characteristics of the sample, the effect of Pt and impurity on this method, the used parameters, and a calculation example are described in the Supporting Information.) In this case, it is found that 85% of hydrogen gas



Figure 3. RT hydrogen isotherms measured by the neutron method for a Pt/AC sample under the first and second cycles, together with the excess adsorption obtained by the Sieverts method.

in the sample is confined in the pores of grains. It shows the advantage of using a sample with large micropore volume fraction for the storage of hydrogen.

The second adsorption-desorption cycle (hydrogen isotherm) measured by the neutron transmission method down to low-pressure is shown in Figure 3, in comparison with those of the first cycle measurement shown in Figure 2 and a separate measurement by the Sieverts method. It is shown that the reversible adsorption data is reproducible and in agreement with that by the Sieverts method. The error sources of this methodology consists of (1) counting statistics, (2) the uncertainties of skeletal density, (3) the error of correcting the neutron cross section for the other metal composition, and (4) the error of neutron cross section values (para and ortho hydrogen states, neutron spectrum-averaged cross section, etc.; see the Supporting Information). Items 3 and 4 can be incorporated as a systematic error. After comparison with one of the other experimental measurement (for example, by the Sieverts method as shown in Figures 2 and 3), it can be safely neglected. Therefore, the main error source is the counting statistics. Its deviation of 1 % leads to an error of 10% on the adsorption capacity. The requirement of this method is that counting statistics must be less than 0.1 %.

Figure 4a shows the kinetic adsorption result of a Pt/AC sample at 1100 and then 1500 psi using the neutron transmission method. The excess adsorption capacity at 1100 psi linearly increases with the adsorption time (at a rate of 15% in 8 h). The temporal behavior of adsorption at 1100 psi is evidence of the spillover effect observed by the neutron method. The kinetics of physisorption is very fast (a few minutes in this Pt/AC sample).<sup>7</sup> The previous works studied by the traditional measurement methods<sup>1,11–13,18,19</sup> and simulation analysis<sup>20</sup> showed that the characteristic of the spillover effect is slow kinetics (on the order of several hours). However, the subsequent excess adsorption capacity at 1500 psi remains unchanged in the kinetic adsorption process, indicating the disappearance of the spillover effect. There are two reasons to explain why it is unstable in this step: (1) the size of catalyst Pt ( $\sim$ 4 nm) is too large due to the scale-up production to serve as a good spillover source.<sup>18</sup> and (2) the activation pretreatment for the Pt particle before the experiment

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**Figure 4.** (a) Kinetic (excess) adsorption measurement of a Pt/AC sample at 1100 and 1500 psi, respectively, using the neutron transmission method. The single point at 1300 psi is taken between 1100 and 1500 psi. (b) Difference of SANS intensity profiles between the initial and final states in the kinetic adsorptions corresponding to panel a.

is not effective. The combined SANS profile can reveal the locally nanoscale structure.<sup>15</sup> The difference of the SANS intensity profiles between the initial and final states in the kinetic adsorption process at 1100 psi (Figure 4b) represents a significant amount of excess adsorption due to the spillover effect and the corresponding spatial distribution of the spiltover hydrogen in the pores. The difference of SANS intensity profiles at 1500 psi shows no net increase in the magnitude of intensity, indicating no kinetic adsorption behavior. In the kinetic adsorption study, the storage capacity and locally spatial distribution of adsorbed hydrogen are consistently revealed in the combined neutron transmission and in situ SANS methods. The local high-density structure formed by the adsorbed hydrogen ranges from 1 to 6 nm based on the corresponding length scale  $(L \sim 2\pi/Q)$ . On the other hand, we can evaluate the adsorption capacity due to the physisorption using the data in the literature<sup>21</sup> and the common relationship between RT hydrogen uptake and surface area for porous carbons. The adsorption capacity of undoped AC at RT and 1500 psi by physisorption can be determined to be 0.4 wt %. Compared to our data (0.46 wt % at 1500 psi shown in Figure 4a), it can be conjectured that there might be a little spillover effect due to the adsorption of Pt metal (fast kinetics as physisorption). The time resolution of this methodology for kinetic study mainly depends on the counting statistics of the measured total counts. In this case, 3 min per step is for the neutron transmission measurement, 1 h per step is for the SANS measurement.

In conclusion, the proposed neutron methodology is a new approach that can independently and complementarily validate the traditional methods of hydrogen uptake measurement in porous materials at RT. It can simultaneously solve various hydrogen adsorption capacities that are difficult to access by the other methods. It would be a potentially nondestructive tool for direct examination and in situ monitoring of the hydrogen storage properties in a commercial hydrogen-storage container. The combined neutron transmission and SANS methods can concurrently reveal the various adsorption capacities (averaged in the bulk scale) and the local distribution of hydrogen. This neutron scattering methodology also provides a method for the study of the hydrogen spillover effect. **SUPPORTING INFORMATION AVAILABLE** The experimental procedure, the characteristics of sample, the effect of Pt and impurity on this method, the used parameters, a calculation example, and a detailed discussion on the neutron cross section values (para and ortho hydrogen states, etc.). This material is available free of charge via the Internet at http://pubs.acs.org.

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**ACKNOWLEDGMENT** The research at MIT is supported by DOE Grant No. DE-FG02-90ER45429. We thank the NIST Center for Neutron Research for allocation of beamtime in NG-7 SANS. C.-S.T. acknowledges the hospitality of the Department of Nuclear Science and Engineering of MIT during his stay as a Visiting Scientist.

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