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SANS characterization of porous magnesium for hydrogen storage

Jorge Omar Gil Posada*, Peter J. Hall

Chemical and Biological Engineering, University of Sheffield, Sir Robert Hadfield Building, Mappin Street, Sheffield S1 1XJ, England, UK

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ABSTRACT

Porous magnesium was produced through the thermal decomposition of various additives in an effort to increase hydrogen storage capacity. Samples were characterized using SANS and different theoretical models were applied to the results and discussed. The poly-disperse self-assembled (PSA) model was found to best represent the scattering from these materials as this model incorporates the polydispersity of the pores and allows for variations in structure factor. Pure magnesium produced using the same thermal method absorbed a negligible amount of hydrogen, and hydrogen uptake was found to increase with increasing porosity as determined using the PSA model. Maximum hydrogen uptake (1.3%) was found when 0.3% Cs_2CO_3 and 0.5% Ni were combined as an additive during thermal treatment. In addition, the development of porosity was found to promote hydrogen desorption at lower temperatures. SANS represents an indispensable method by which to characterize materials and the PSA model described in this work has the potential to be extremely useful in the characterisation of porous metallic systems.

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Introduction

Hydrogen has been identified as one of the best candidates to replace fossil fuels due to its high energy density, ease of production from renewable sources and lack of undesirable combustion products. Whilst significant improvements have been made in order to utilize hydrogen as a clean fuel through the use of fuel cells, the storage of hydrogen in a safe and efficient manner remains a challenge.

Magnesium is one of the most abundant elements in the earth's crust, and is well known not only for its large

theoretical hydrogen storage capacity (ca. 7.6 wt.%) but also for its poor hydrogenation characteristics. In particular, the process of hydrogen absorption/desorption in pure magnesium is incredibly slow and requires temperatures in excess of 350 °C [1–3]. Many efforts have been made in order to enhance these kinetics through such methods as reducing particle size, controlling surface oxidation or through the inclusion of different elements [3–9].

It is thought that a reduction in the hydrogen desorption temperature can be achieved by distorting the metallic matrix of magnesium through the inclusion of small voids. Originating from liquid-metal routes, metallic foams have restricted

* Corresponding author.

E-mail addresses: jogp1234@yahoo.com, j.o.gil-posada@sheffield.ac.uk (J.O. Gil Posada).

morphologies (pores are closed and separated from each other by thin films) and exhibit interesting physical and mechanical properties such as low density and good energy absorption.

Unfortunately, the literature does not contain a great deal of information regarding the production of pure magnesium-based foams for hydrogen storage. However some research regarding the production of foams from magnesium based alloys has been reported [10–14]. Production of foams via the molten metal gas injection method is reported to yield a product with a poorly defined pore size distribution [15].

Porous materials can also be produced by blending magnesium powder with a blowing agent (a substance that decomposes near the melting temperature of magnesium), melting and rapidly cooling the mixture. To the best of our knowledge this strategy has not yet been implemented with magnesium based systems for hydrogen storage.

Due to the nature of this process the majority of generated pores are occluded, and therefore traditional pore characterization techniques such as gas adsorption or mercury porosimetry are of limited use. Small angle neutron scattering (SANS), on the other hand, is a valuable tool when characterizing samples that contain closed porosity. SANS has provided a useful method by which to characterize porosity in many different materials such as carbons [16–18], porous polymers [19–24], biomaterials [25], metallic systems [26–34] and minerals [29]. However, due to the complexity of porous metals, basic SANS models (such as the Guinier approximation or Porod's law) are of limited use when trying to understand the intrinsic nature of such systems.

As little research in the area of porous magnesium for hydrogen storage has been reported, the characterization of such systems has also received limited attention. Although, different forms of magnesium (such as nanocrystalline and intermetallic alloys) for hydrogen absorption have been investigated using SANS [36,37], the models used to interpret scattering from such systems are not suitable for the characterization of porosity in highly porous samples.

In this article, we apply different SANS models to characterize the voids in porous magnesium in order to investigate the effects of sample morphology on the hydrogen uptake process. To the best of our understanding, the models discussed herein have the ability to provide a substantially greater degree of structural information than can be attained using traditional methods of analysis [26–37]. In particular, the polydisperse self assembled model has the necessary flexibility to describe complex porous materials and we feel that this could be an extremely useful method in the characterization of porous materials.

Theory

Differential scattering cross-section

The differential scattering cross-section $(\partial\Sigma/\partial\Omega)(Q)$ is the dependent variable measured in a SANS experiment. In fact, the detector actually measures the number of neutrons of a given wavelength scattered thorough a particular angle, arriving at a small area of the detector in a particular unit of time. This flux of neutrons may be expressed as [38]:

$$I(Q) = I_0(\lambda)\Delta\Omega\eta(\lambda)T(\lambda)V_s\frac{\partial\Sigma}{\partial\Omega}(\vec{Q}) \quad (1)$$

where I_0 is the incident flux, (λ) is the wavelength of the scattered neutrons, $\Delta\Omega$ is the solid angle element defined by the size of a detector pixel, η is the detector efficiency, T is the neutron transmission of the sample, and V_s is the volume of the sample illuminated by the neutron beam. The significance of the vector Q is that its modulus, is the independent variable in a SANS experiment. Broadly speaking, the differential scattering cross-section contains information relevant to the size, shape, and interactions between the particles that produce scattering within the sample.

Scattering at low and high values of Q

The Guinier approximation is a traditional method used in the analysis of light and X-ray scattering data [38–41], and establishes proportionality between the logarithm of the differential scattering cross-section and the square of the vector modulus at low values of Q as described in Eq (2) [20].

$$\frac{\partial\Sigma}{\partial\Omega}(\vec{Q}) = \alpha_0 \exp\left[-\frac{(QR_g)^2}{3}\right] \quad (2)$$

where R_g is the radius of gyration and is related to the dimensions of the particle (or void) that produces scattering and α_0 is a constant that depends on the concentration number of scattering centres that produces scattering N , the volume of one scattering centre V , and the scattering length density $\Delta\rho$ [39]. Therefore, a plot of $\text{Ln}[\partial\Sigma/\partial\Omega]$ versus Q^2 should be linear at small values of Q and from its slope is possible to determine the radius of gyration.

For large values of Q , the Guinier approximation is no longer valid; instead a decrease in intensity proportional to the fourth power of Q is found. This behaviour, known as Porod's law, is usually expressed in the following manner.

$$\text{Lim}_{Q \rightarrow \infty} \left[\frac{\partial\Sigma}{\partial\Omega}(\vec{Q}) \right] = \frac{K_p}{Q^4} \quad (3)$$

where K_p is known as the Porod's law constant. Thus a plot of $Q^4 \partial\Sigma(Q)/\partial\Omega$ versus Q^ψ , where ψ is a natural number, should be linear (at high Q values) and independent of Q^ψ with an intercept equal to K_p . The determination of the value of K_p is of importance in that it is related to certain structural parameters of the system, as shown in Eq (4) [8].

$$K_p = \frac{S}{V} \frac{q}{8\pi^3\phi_1\phi_2} \quad (4)$$

where (S/V) is the area of interface per unit volume, ϕ_1 and ϕ_2 are volume fractions of the phases present and

$$q = 4\pi \int_0^\infty Q^2 \frac{\partial\Sigma}{\partial\Omega}(\vec{Q}) dQ = V\phi_1\phi_2(\Delta\rho)^2 \quad (5)$$

and finally

$$\int_0^\infty Q^2 \frac{\partial\Sigma}{\partial\Omega}(\vec{Q}) dQ = 2\pi b_v \phi_s (1 - \phi_s) \quad (6)$$

where the integral defined on the left side of Eq (6) is known as Porod's invariant, $(\Delta\rho)^2$ is the contrast factor between the solid

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