Modelling Hydrogen Storage in Novel Nanomaterials

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Abstract

Gas storage using nanomaterials has been researched as possible enhancement of gas tanks in fuel cell vehicles. The structures of nanomaterials and its interaction with gases are often explored using computer simulations and experiments which are both time consuming and expensive. In this thesis, we overcome these problems by performing these investigations through a simplified mathematical modelling approach.

In this approach, we first develop simple solutions to calculate the interaction energies between hydrogen gas and the materials using symmetric building blocks to represent the cavity of the structure. The gas uptake in the nanomaterial can then be calculated using these solutions to identify the quantity of gas stored in the adsorbed and bulk states. We also introduce a novel method, the thermodynamic energy optimisation (TEO) model, to calculate the energy produced by a hydrogen fuel cell coupled with a materials storage device.

In this thesis these models are used to explore beryllium linked with benzene tribenzoate (Be-BTB) and porous aromatic frameworks (PAF). The models are able to identify reasons why these materials have demonstrated potential for gas storage and suggest ways to improve and optimise the struc-

tures.

Our investigation into Be-BTB reveals that the beryllium rings contribute strongly to the hydrogen interaction with the framework. We propose that beryllium rings of 10 Å at 298 K and 15 Å at 77 K will optimise the fractional free volume for adsorption within the material. Investigations using the TEO method demonstrate that current high performing MOFs are unable to outperform gas tanks for fuel cell vehicles. To improve uptake capacity further improvements are required to decrease specific heat capacity and heat of adsorption while also ensuring that the material possesses optimal cavity sizes to maximise the fractional free volume.

Another application of the mathematical model is undertaken on PAFs, in particular PAF-302 and PAF-303. Using analytical methods, three possible modifications on PAFs are adopted to investigate their effects on gas uptake; (i) fullerene impregnation, (ii) lithium doping, and (iii) a combination of methods (i) and (ii). Results show that lithiation strengthens the interaction energy whilst fullerene impregnation doubles the number of attractive surfaces. The final results indicate that 8%Li-PAF-303 provides the highest gravimetric uptake at 77 K and 298 K, and 8%Li-PAF-302 provides the highest volumetric uptake at 77 K and 298 K.

Signed Statement

I certify that this work contains no material which has been accepted for the award of any other degree or diploma in my name in any university or other tertiary institution and, to the best of my knowledge and belief, contains no material previously published or written by another person, except where due reference has been made in the text.

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List of Publications

1. K. Konstas, J. W. Taylor, A. W. Thornton, C. M. Doherty, W. X. Lim, T. J. Bastow, D. F. Kennedy, C. D. Wood, B. J. Cox, J. M. Hill, A. J. Hill, and M. R. Hill, "Lithiated porous aromatic frameworks with exceptional gas storage capacity", *Angewandte Chemie (International ed. in English)*, vol. 51, pp. 6639–6642, 2012.

2. W.-X. Lim, A. W. Thornton, A. J. Hill, B. J. Cox, J. M. Hill, and M. R. Hill, "High performance hydrogen storage from Be-BTB metal-organic framework at room temperature", *Langmuir*, vol. 29, pp. 8524–8533, 2013.

3. W.-X. Lim and A. W. Thornton, "Analytical representations of regular-shaped nanostructures for gas storage applications", *ANZIAM Journal*, vol. 57, pp. 43–61.