



ELSEVIER

Available online at [www.sciencedirect.com](http://www.sciencedirect.com)

ScienceDirect

journal homepage: [www.elsevier.com/locate/ijhydene](http://www.elsevier.com/locate/ijhydene)

## Review Article

# Hydrogen storage in carbon nanostructures via spillover

Darryl S. Pyle\*, E. MacA. Gray, C.J. Webb

Queensland Micro- and Nanotechnology Centre, Griffith University, Nathan, 4111 Brisbane, Australia

## ARTICLE INFO

## Article history:

Received 11 June 2016

Received in revised form

19 July 2016

Accepted 9 August 2016

Available online xxx

## Keywords:

Hydrogen storage

Carbon nanostructures

Spillover

Surface functionalization

## ABSTRACT

The addition of transition metal nanoparticles to carbon nanostructures has been shown to increase the hydrogen storage capacity of carbon nanostructures by dissociating molecular hydrogen and allowing adsorption via chemical means, a process known as hydrogen spillover. This paper is an overview of experimental and theoretical studies on hydrogen storage on transition metal doped carbon nanostructures via the spillover mechanism and the prospects for achieving practical hydrogen storage targets. The most promising materials are found to be high surface area hexagonal system carbons for which the  $\pi$ -conjugation is broken by well dispersed oxygen functional groups or lattice dopants.

Crown Copyright © 2016 Published by Elsevier Ltd on behalf of Hydrogen Energy Publications LLC. All rights reserved.

## Contents

Introduction .....	00
Hydrogen spillover to carbon nanostructures .....	00
Atomic hydrogen interaction with carbon substrate .....	00
Hydrogen surface diffusion .....	00
Hydrogen clustering .....	00
The role of transition-metals in hydrogen spillover .....	00
Nanoparticle size and total mass doped dependencies .....	00
Migration of atomic H to carbon substrate .....	00
Carbon surface functionalization, dopants and defects .....	00
Surface oxygen functionalization .....	00
Lattice dopants and defects .....	00
Conclusion .....	00
References .....	00

\* Corresponding author.

E-mail address: [darryl.pyle@griffithuni.edu.au](mailto:darryl.pyle@griffithuni.edu.au) (D.S. Pyle).<http://dx.doi.org/10.1016/j.ijhydene.2016.08.061>

0360-3199/Crown Copyright © 2016 Published by Elsevier Ltd on behalf of Hydrogen Energy Publications LLC. All rights reserved.

## Introduction

One of the key roadblocks to the spread of hydrogen energy technology is the safe, efficient and reliable storage of hydrogen. Current storage methods require either high pressures for pressurized hydrogen tanks or expensive cryogenic processes for liquefied hydrogen and are not considered viable options for vehicular applications in the long term. The US Department of Energy has specified a gravimetric goal of 5.5 wt.% hydrogen storage for an on board system by 2020 and an ultimate target of 7.5 wt.% [1]. While recent years have seen a number of major motor vehicle manufacturers releasing hydrogen vehicles, all but one model fall below the 5.5 wt.% storage target, with the exception being the Toyota Mirai, claimed to be 5.7 wt.% using 700 bar storage tanks [2], but this is still well below the ultimate target of 7.5 wt.%. It is in this context that solid-state materials, which are able to store large quantities of hydrogen via chemical and physical mechanisms, are considered a potential storage solution. As the US DOE hydrogen storage target of 5.5 wt.% applies to the total system, when the mass of additional components are considered, the reversible hydrogen storage capacity of a solid-state material will need to be significantly greater than 5.5 wt.% for use in an on-board system [3]. In order to minimise the required hydrogen storage capacity much research has focused on light weight solid-state materials.

Of particular research interest over the past 10 years has been carbon with its low weight, low cost and its numerous graphite-derived polymorphs and nanostructures such as graphite [4], activated carbon [5–7], fullerenes [8], nanofibers [9], nanotubes [10,11] and more recently, graphene [12–16]. Hydrogen adsorption to carbon nanostructures is predominantly a surface-area dependent process [17] in which molecular hydrogen is physically bound to the surface via van der Waals forces. Secondary effects from adsorption in pores in activated carbons, carbon nanotubes (CNTs) [18] and other microporous carbons are also evident due to increased physisorption binding energies that arise from the overlap of attractive van der Waals forces from multiple surfaces.

For moderate storage conditions, i.e. temperature of ~300 K and pressures no greater than 100 bar, carbon nanostructures are yet to be found that can reproducibly store in excess of 2 wt.% [19–22]. This is due to the low binding energies associated with physisorbed molecular hydrogen for which thermal excitations lead to desorption. To improve hydrogen storage capacities, small amounts of transition metals (TM) have been added to carbon nanostructures, either physically mixed with the carbon or directly doped via wet chemistry synthesis. For such cases, hydrogen storage enhancements have been reported to be anywhere between 0% [23,24] and 900% [25], but typically of the order of 100–300% [26–29] above that of the un-doped carbon nanostructure.

The proposed mechanism by which metal-doped carbons achieve an enhanced hydrogen storage capacity is spillover, defined as ‘the transport of an active species sorbed or formed on a first surface onto another surface that does not, under the conditions, adsorb or form the active species’ [30]. In this context the active species is atomic hydrogen, the first surface is a TM nanoparticle and the second surface is the carbon nanostructure,

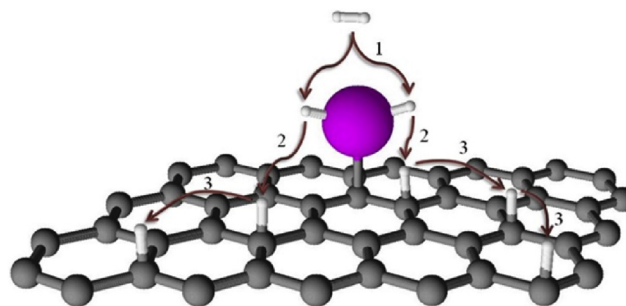
however the spillover mechanism has been long known in the catalysis field [30–33] and has been demonstrated in hydrogen storage of metal-organic frameworks [34–36].

Hydrogen spillover comprises three steps as shown in Fig. 1: 1) molecular hydrogen is dissociated and atomic hydrogen is bound to the surface of TM nanoparticles; 2) atomic hydrogen migrates from TM nanoparticles to the carbon surface and 3) atomic hydrogen diffuses along on the carbon surface eventually forming a stable C–H bond after some distance. Understanding these three key interactions is necessary for a full understanding of the hydrogen spillover process and whether it can be manipulated as a route to achieving a fully reversible hydrogen storage capacity in excess of 5.5 wt.% on carbon nanostructures.

This review provides an overview of the theoretical and experimental studies of hydrogen storage on carbon nanostructures doped with transition metal nanoparticles in order to increase the hydrogen storage capacity by utilising the spillover mechanism. We begin with the nature of the interaction of atomic hydrogen with carbon nanostructures, followed by the role played by transition metal nanoparticles and finish with how carbon nanostructure surface functionalization, lattice dopants and defects affect the hydrogen storage capacity.

## Hydrogen spillover to carbon nanostructures

The nature of the carbon nanostructure is of primary concern for hydrogen spillover, as the majority of stored hydrogen is bound to the carbon substrate while a small percentage is bound to the metal nanoparticle. Experimental studies on hydrogen spillover to carbon materials have been performed on activated carbons [34,37–39], carbon nanotubes [40–48], carbon nanofibers [49–52], templated carbon [53–56], carbon nanospheres [57], fullerenes [58] and graphene-like materials [26,59–62]. The low-density and low hydrogen uptake of carbon substrates present particular difficulties [63,64] in accurately determining hydrogen storage capacity that is reproducible between laboratories [65] and may go some way to explaining the large discrepancies reported for H<sub>2</sub> uptake in TM-doped carbon nanostructures. The capacity of a carbon



**Fig. 1 – Hydrogen spillover mechanism: Step 1) dissociation of molecular hydrogen and formation of TM – H bonds; step 2) migration of atomic hydrogen to the carbon surface; step 3) diffusion of atomic hydrogen along the carbon surface.**

Download English Version:

<https://daneshyari.com/en/article/5147160>

Download Persian Version:

<https://daneshyari.com/article/5147160>

[Daneshyari.com](https://daneshyari.com)