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Hydrogen Storage: Materials, Kinetics and Thermodynamics

Athule Ngqalakwezi and Diakanua Bevon Nkazi

Abstract

The need for cleaner sources of energy has become a serious need now more than ever due to the rising effects of fossil fuels on the environment. Technological advancement in society today has necessitated the need for fast and robust materials that will match the speed at which society is moving forward. Hydrogen as an alternative source, has garnered a lot of attention due to its zero emission characteristic. In this chapter, a background on hydrogen storage and its impact on the 'envisioned green environment' is discussed. Graphene and borohydrides hydrogen storage materials are reviewed extensively and the kinetic models thereof. Furthermore, the reaction mechanism of graphene nanocomposites is also discussed.

Keywords: hydrogen storage, hydrides, kinetics, graphene, nanocomposites

1. Introduction

The generation of the 21st century has had to deal with the effects of centuries of environmental mismanagement due to industrialization and modernization. To put things into perspective, approximately 6587 billion metric tons of carbon dioxide, a main contributor to climate change, were emitted into the atmosphere in 2015 through the use of fossil fuels [1]. In 2017, these numbers increased and they are continually increasing every year (**Figure 1**).

As such, the implementation of green systems and processes has become a priority in order to try and mitigate the damages to the environment. The remedial actions implemented to reduce the effects on the environment include the institution of legislations that fine high carbon emitters, green technologies and green alternatives to support energy and electricity demands. Hydrogen is amongst the green alternative researched as a substitute for fossil fuels. However, it is acknowledged that the transition from fossil fuels or carbon based sources is not going to be an easy one because of the demand and the complexity of introducing a different system. The United States of America has already started introducing the hydrogen fuelled cars and currently, there is about 6558 hydrogen fuelled cars. This number is expected to surge in the coming years, in 2027 it is expected that there demand would increase to 70,000 units [2].

The implementation of the hydrogen economy is driven by the Department of Energy in the United States. The DoE set the standards and requirements for hydrogen storage materials for practical application in hybrid cars (**Figure 2**).

Various hydrogen storage materials have been synthesized and tested for hydrogen storage applications. However most of these materials have not met the

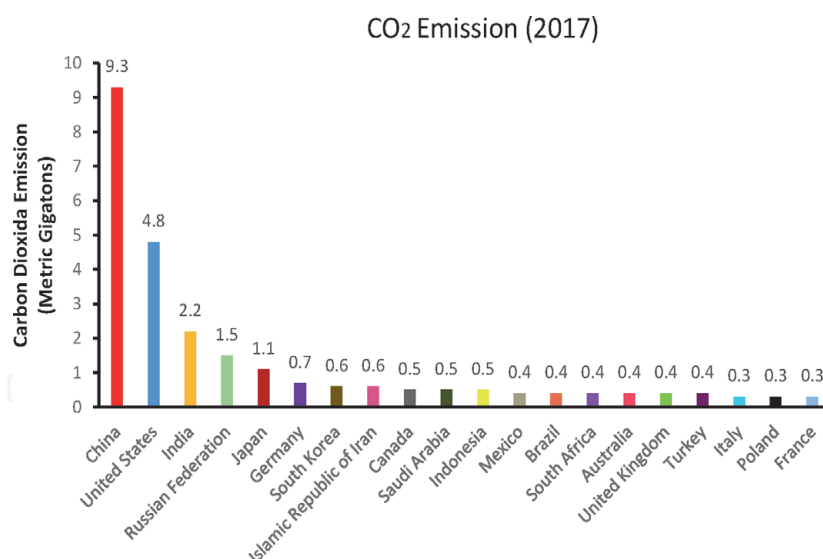


Figure 1.
World's biggest carbon dioxide emitters (Economics help, 2017 [2]).

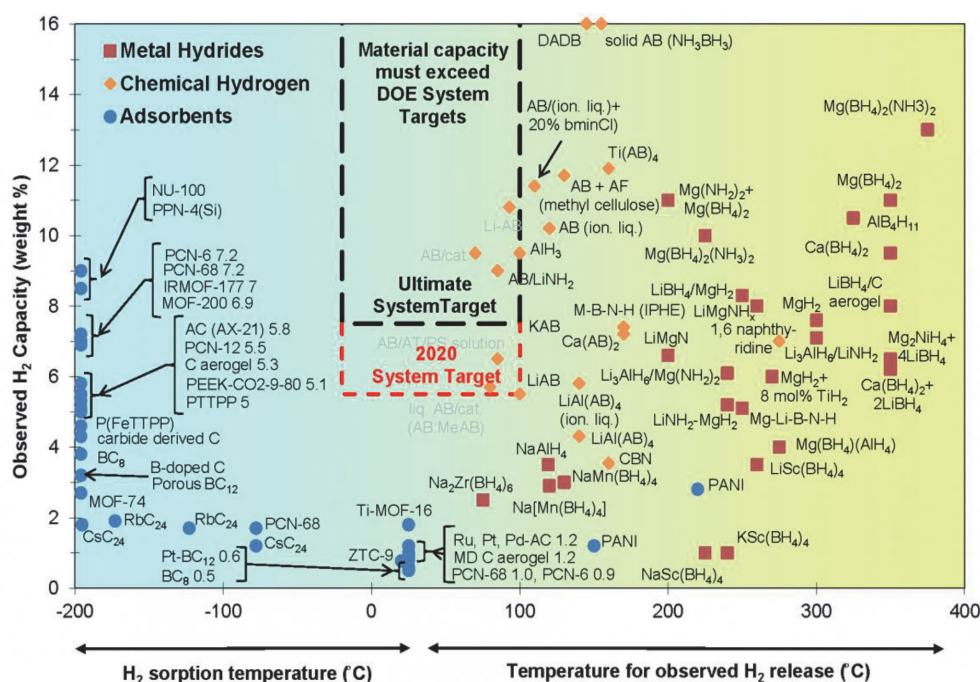


Figure 2.
2020 hydrogen storage requirements for hybrid cars (Department of Energy, United States).

requirements for applicable hydrogen storage. In this book chapter, the synthesis and first principles studies thereof of new classes of materials will be reviewed, their kinetics will also be reviewed in great details.

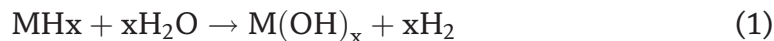
An immense effort has been put towards finding novel material for hydrogen storage that will have optimum conditions as indicated by the D.o.E. A great number of light-weight nanostructures consisting of nitrogen, carbon and boron have received favorable attention due to their large volume-to- surface ratio and light-weight characteristic [3]. These materials have been studied intensely and recent works, depicts an improvement and a ray of light in terms of practical applicable hydrogen storage in them.

The interest in these materials was instigated by their unique characteristics. Boron based nanostructures have similar porous structural characteristics with carbon based materials however, boron based materials are much more lighter [3]

making them an interesting candidate for practical hydrogen storage. Boron based materials are synthesized using various methods such as hydrolysis and pyrolysis of chemical hydrides.

Hydrolysis:

Hydrolysis is the liberation of hydrogen gas through the reaction of water with a hydride. The overall reaction is summed up as follows:



Where x is the valence number of the metal, M is the metal and X is a trivalent group III element.

Pyrolysis:

Pyrolysis is the breakdown of a substance due to heating. The overall pyrolysis reaction is summed up as follows:



Where M is an alloy or a metal.

Boron hydrides are interesting chemical H₂ storage materials that have high hydrogen capacity however the kinetics and thermodynamics of these materials have limited their practical use for hydrogen storage. Different approaches have been employed to decrease the kinetics and thermodynamics of these materials. Popular boron hydrides include LiBH₄ (Lithium borohydride) and NH₃BH₃ (ammonia borane) [1]. The reaction mechanism with boron hydrides can be summed up into four main steps: 1. the decomposition or breakdown of the material through heating to generate hydrogen (Pyrolysis), 2. The interaction of the material with water to release hydrogen (pyrolysis), 3. Improvement of the kinetics through the addition of boron to the electrodes on the metal hydride battery, 4. The storage of hydrogen via the boron nitride nanotubes which can also release the hydrogen when heating [4]. A lot of remedial actions have been employed to improve the kinetics of these materials however the research still continue.

2. Graphene based materials

Graphene, a 2D carbon allotrope that is positioned in a sp²-bonded aromatic structure, has attracted a lot of attention for hydrogen storage application due to its low weight, cost and ability to be synthesized in large quantities [5]. This two dimensional material configuration is formed by covalent bonds that are distributed on the hexagonal honeycomb lattice [6]. Apart from this, graphene has intriguing properties which have made them applicable in these fields: energy storage, sensors, electrodes, field effect devices, nanocomposites and solar cells [6].

The large surface area of graphene (2630 g²m⁻¹) is tremendously beneficial for hydrogen storage. The interaction of graphene systems is based on instantaneous dipole-dipole induced forces because hydrogen is a non-polar molar [7]. A number of theoretical studies have been undertaken to explain the adsorption of hydrogen on the surface of graphene material and give more information on the pathway experimentalist need to take [7]. These studies have shown that the spatial distribution of adsorbed hydrogen on the surface of graphene is delocalized and that molecular hydrogen exhibits unrestricted lateral movement [7].

3. Graphene nanocomposites

Nanocomposites, where nanocatalysis and nanostructure are combined, are the next research advancement of high performance of hydrogen storage materials. These materials have distinct functionalities due to the shortened diffusion distance, increased surface area and the multiplied grain boundaries [6]. Graphene, graphene nanocomposites and its derivatives depict a promising potential for different applications such as automotive industry, aerospace, electronics and green energy. This is because graphene has intriguing thermal, mechanical and electrical properties [6, 8, 9].

A lot of studies have been done with graphene and nanocomposites thereof for the practical application in on-board application [7–10]. Graphene nanocomposites can be synthesized using various techniques. These include the self-assembly technique, solution mixing, sol–gel method, hydrothermal or the solvothermal method and other methods [11]. Graphene nanocomposites have been preferred for hydrogen storage application mainly because of their light weight characteristic. Weight of the material is an important factor when considering the practical applications for hybrid cars according to the DoE standards. Graphene alone is a physisorbent material and does not take up a lot of hydrogen however its kinetics are interesting [11–15]. The incorporation of metals on the graphene matrix enhances the functions of the system and improves the hydrogenation of this material to make it more appealing for practical use in hybrid cars [16, 17]. Various metals have been used in this regard to improve the hydrogen uptake of the graphene nanocomposite. Zhou et al., synthesized a Ni/graphene nanocomposite and a Pd/graphene nanocomposite [18]. Ngqalakwezi et al. synthesized a novel Ca/graphene nanocomposite [10]. The graphene nanocomposites can be used and applied in different industries for hydrogen generation in the electrolysis process, in the photo degradation of pollutants, energy storage and other applications.

Furthermore, nanomaterials permit favorable charge, mass and heat transfer, these are added advantages when considering practical application of these materials for on board applications [13, 17, 19]. In addition, nanomaterials assist in dimensional alteration of particular phase transitions and chemical reactions [6]. Nanomaterials not only help and aid in the kinetics of hydrogen storage materials, but they also help to destabilize the thermodynamics of chemisorption materials.

4. Synthesis methods for graphene nanocomposites

4.1 Self-assembly technique

The self-assembly process is one of the primary techniques for synthesizing complex materials from molecules in macro, micro and nano scales [20]. In the bottom up techniques in nanotechnology, this method has been considered as one of the most effective methods [21]. In this technique, molecules are utilized as precursor material for synthesizing graphene nanocomposites under environmentally conducive parameters. As such, graphene sheets prepared using the top down approach (mechanical and chemical exfoliation of graphite), can be utilizing as precursor material for the self-assembly technique [20]. The mechanism of self-assembly of graphene can be quite complex and understanding it necessitates the full understanding of the non-covalent and interlayer covalent interactions between graphene derivatives [22]. These interactions include the dipole–dipole interactions, p–p interactions, van Der Waals forces and electrostatic forces. Non-covalent interactions in the self-assembly technique, aid the graphene in producing composites with novel functions and structures [22, 23].

These non-covalent interactions are active in various organic solvents and they permit homogenous dispersion for the anticipated self-assembly. Furthermore, graphene molecules allow for functionalization which is double sided and thus creates novel structural architecture with double-sized decoration of functional groups on the graphene sheet. These functional groups in principle, permit layer-by-layer coordinated assembly in a supramolecular manner [23].

To take advantage of the characteristics of graphene at nanoscale in macro-sized devices, it is crucial to incorporate the graphene sheets into 3D micro-sized structures with better maneuver of the geometry and dimensionality of the material [24]. Various methods have been reported for the fabrication of 3D porous structures, 2D thin films and 1 dimensional fiber-like molecules [24]. For 3D porous structures these methods have been used; freeze casting self-assembly, breath figure 3D assembly, diffusion driven 3D self-assembly, 3D self-assembly through the hydrothermal process, pickering emulsions for 3D molecules and 3D assembly through chemical reduction [25–28]. For 2D structures these methods have been used; vacuum assisted assembly, Rayleigh and Taylor instability and Marangoni effect self-assembly method, liquid–liquid interfacial 2D assembly method, evaporation induced 2D self-assembly method, electrophoretic method and the Langmuire-Blodgett method [27, 29, 30]. For 1D fibers these methods have employed; 1D self-assembly self-intertwining method, direct drawing self-assembly method, electrophoretic 1D self-assembly and flow directed wet-spinning 1D self-assembly. All of these methods have been successfully employed to synthesize these different structures under various parameters [31–33].

4.2 Solution mixing method

The solution mixing method is one of the easiest method for the synthesis of polymer based graphene nanocomposites. The method comprises of three simple steps which are; the scattering of the filler, the polymer incorporation and the solvent removal through the distillation process or evaporation [34]. This method is also relatively cheap because it does not need the use of expensive equipment or expensive operative protocols, although it has a many steps [35]. Other advantages about this technique are; the method allows for good dispersion of thin particles because of the efficient fragmentation of organoclay agglomerates [35, 36]. This in effect, generates greatly filled key batches that can later be mixed with pristine polymer through the melt compounding process. Furthermore this process allows for the production of highly exfoliated graphene nanocomposites that can be attained through mixing the physical coupling process with chemical reaction.

The synthesis step of this method typically involves dissolving a polymer in a solvent and suspending the filler in a different compatible solvent. Different solvents such as acetone, tetrahydrofuran (THF), toluene, chloroform, dimethylformamide and cyclohexane are utilized in this method [35]. As mentioned above, the solution blending ensures excellent exfoliation and dispersion of the filler within the elastomeric matrix [37].

Ultrasonication or high speed shear mixing are employed during the solution blending process to ensure the polymer solution and filler suspension are mixed thoroughly [36]. This technique has been efficient in dispersing nanofillers regardless of the polarity of the polymer. As much as this method has a lot of advantages, it does however have disadvantages as well. The main disadvantage of this technique is the thorough and efficient removal of solvents utilized during the process. Another major disadvantage is the scale up; the solvents utilized are very expensive and scaling up this process would pose financial difficulties and strains [35, 36].

Lastly, the entire process involves a lot of steps and this can influence the subsequent outcome of the process.

A couple of researcher have used this method to synthesize graphene nanocomposites. Wang et al. utilized Cu (OH)₂ composite sheets and reduced graphene oxide to synthesize thin micro layered structure of rGo-Cu powder [38]. Tang et al. synthesized graphene nanosheets decorated with Ni nanoparticles utilizing the in situ chemical reduction method [39]. The resulting nanocomposite after wet mixing electrolytic Cu to obtain Ni-graphene nanosheets/Cu nanocomposite, depicted interesting mechanical properties with a yield strength of 268 MPa and a high Young Modulus of 132 GPa [39]. Furthermore, Zeng et al. incorporated Al powder in the GO suspension solution and ultrasonicated the mixture [40]. Al-graphene nanocomposite was obtained with a tensile strength of 255 MPa [40]. Li et. al, on the other hand used precursor organic graphite to synthesize graphene oxide using the Hummers method and decorated the graphene with Ni nanoparticles [41]. Ngqalakwezi et al. also synthesized Ca/graphene using the Improved Tours Method and chemical reduction the Ca ions on the surface of the GO [10].

The solution mixing method has been successfully employed to synthesis graphene nanocomposites.

4.3 Sol-gel method

The sol-gel method is also a simple method that allows the synthesis of a homogenous material that has great compositional controls [42]. This method utilizes metal chlorides or metal alkoxides as the precursor material [11]. The chlorides or alkoxides are treated through a series of condensation and hydrolysis reactions and later the cured composites are dried and calcined [11]. A number of researchers have prepared graphene nanocomposites through the sol-gel method. A SiO₂/graphene nanocomposite was synthesized with good cyclic stability and spectacular specific capacitance of Fg^{-1} with a current density of 1 Ag^{-1} by Rezaei et al. [43]. Patil et al. fabricated functional nanographene sheets using cobalt sulphide which had a good rate of cyclic ability and high reversible capacity ranging at about 466 mAhg^{-1} [44]. Wang et al. fabricated TiC/graphene nanocomposite using the sol gel method [45]. In this work, furfuryl alcohol was utilized as a carbon and this nanocomposite was synthesized for impact or shock absorptions [45]. Furthermore, Sun et al. synthesized various nanoparticles of platinum on sulfonated graphene and used them as anode electrocatalysts in direct ethanol fuel cell using the sol gel method [46]. The particles sized of the nanoparticles on the graphene surface ranged 1.7 nm to 13.9 nm. The sulfonic acid on the graphene improved the adsorption energy of platinum, this was observed through theoretical calculations [46].

The synthesis work done using the sol gel method has proved to be effective in synthesis graphene nanocomposites and thin-film coating materials. This method required decreased reaction temperatures and it is also not complex to follow and conduct although the still challenges in the formation of the sol.

4.4 Hydrothermal method

The hydrothermal technique has been utilized to fabricate graphene nanocomposites using autoclaves under high pressures and temperatures. The first hydrothermal reaction was reported in 1845 by Schafhautl when he noticed the synthesis of quartz microcrystals from silicic acid [47]. Since then, his method has been developed over the years by many other scientists and other novel synthesis methods have also been reported. The hydrothermal technique is not restricted to the fabrication of common and advanced materials but it also covers a wide range of

interdisciplinary subdivisions in the sector of energy storage, simulating biohydrothermal and geothermal process and waste treatment [48]. In principle, the word hydrothermal, was initiated from geological sciences where it refers to a regime of water pressures and high temperatures [49]. Hydrothermal reaction traditionally involves water as catalyst and seldom, as a component of the solid phase during the synthesis at high pressures and temperatures. This technique has many advantages to it such as, excellent dispersion in water, the synthesis using this method is inexpensive due to instrumentation, environmentally friendly, one pot synthesis method, mild operation conditions and the material precursor are also inexpensive [50].

Lee et al. discovered a novel hydrothermal fabrication route to synthesize graphene nanocomposites to improve the photocatalytic activity of TiO_2 under visible light. In the method, graphene was decorated or wrapped with TiO_2 particles [51]. A high catalytic CeO_2 /graphene was synthesized by Srivastava using the hydrothermal method [52]. A Ag/graphene nanocomposite with exceptional electroconductivity was synthesized by Yang et al. using the hydrothermal method. In this work, Yang et al. used a hydrazine reductant as a reducing agent and had control over the morphology and the size of Ag nanoparticle on the surface of graphene [53]. Zhang et al. prepared a one pot method for the synthesis of $\text{Fe}_2\text{O}_3\text{-Ni(OH)}_2$ /graphene nanocomposite. The nanocomposite had a good rate capability (at 100% retention), impressive cyclic stability (5000 cycles) and elevated specific capacitance at approximately 857 F/g [54]. A ZnO/graphene nanocomposite was synthesized using the hydrothermal at lower temperature 90 and 80°C [55]. The nanocomposites both displayed good catalytic activity during photocatalytic degradation against rhodamine-B dye [55].

5. Graphene nanocomposites reaction mechanism for hydrogen storage

Various authors have synthesized the graphene nanocomposites and discussed the kinetics thereof. Ngqalakwezi et al. synthesized a Ca/graphene nanocomposite using the solution mixing method for hydrogen storage purposes [10]. The calcium clusters in the nanocomposite bind hydrogen molecules without dissociation through the Kubas interaction and through the unidirectional polarization. Furthermore, they realized the Ca atoms on the graphene matrix increased the binding energy and therefore catalyzed the adsorption of the hydrogen molecule because of the polarization of the molecule [10]. The diagram below depicts the kinetic of the hydrogen storage into the graphene matrix (**Figure 3**).

Zhou et al. synthesized Pd/graphene nanocomposite for hydrogen storage [9]. In this work, four hydrogen storage performances were hypothesized for the uptake of hydrogen in the Pd/graphene nanocomposite: hydrogen molecules bind to the Pd atoms on the graphene matrix, hydrogen dissociates and forms a palladium hydride (PdH_x), atomic hydrogen binds at the unsaturated sites of graphene or the hydrogen molecule is trapped within the graphene matrix [9]. The presence of the Pd atoms on the graphene matrix also elevate the binding energy and thus speeding up the adsorption of the hydrogen molecule due to the polarization of the hydrogen molecule orbitals with the Pd orbitals. The sluggish kinetics of Pd result in the dissociation of the hydrogen molecule on the surface of the Pd atom. Some of the dissociated hydrogen atoms are ejected into the gas phase and some diffuse into the Pd lattice and form the palladium hydride (PdH_x) [9]. The diagram below is a conceptual figure of the reaction mechanism for the Pd/graphene nanocomposite. Zhou et al. further synthesized a Ni/Graphene nanocomposite and hypothesized the same reaction mechanism as the Pd/graphene nanocomposite [18] (**Figure 4**).

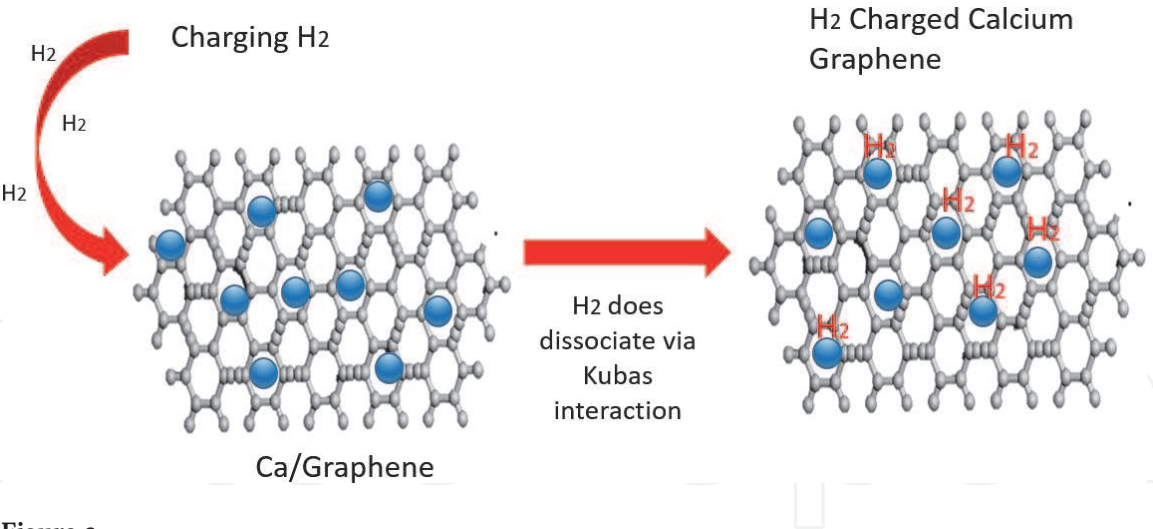


Figure 3.
Reaction mechanism of Ca/Graphene nanocomposite.

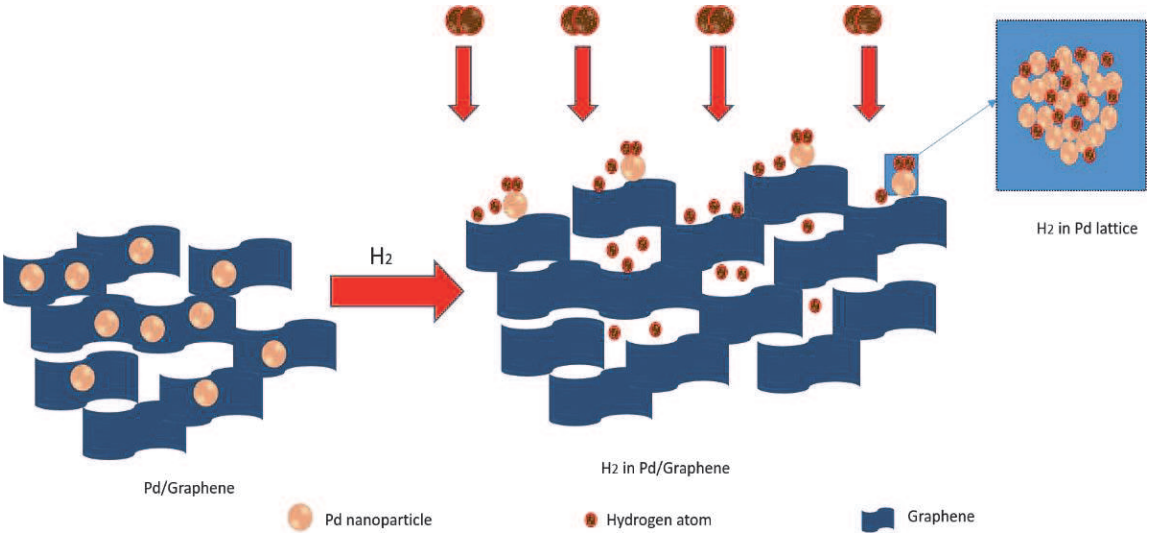


Figure 4.
Reaction mechanism of Pd/Graphene nanocomposite (adapted from [18]).

6. Kinetics of energy storage materials

The issues of kinetics in energy storage has been tackled through many scientific interventions including ball milling, alloying, thin films and catalysis. However, to date, no material has satisfied the requirement for practical energy storage. The development of hybrid material such as graphene nanocomposites has been researched to fill in the gap. In energy storage, kinetics of the materials considered for practical energy storage are complex and not easily understand and thus in this section, hydrogen storage kinetic models are reviewed.

6.1 Kinetic models

The uptake of hydrogen and release of hydrogen in hydrogen storage systems is made of adsorption, penetration through the surface, internal diffusion and chemical reaction [56]. **Figure 5** below show the detailed steps of these processes:

The two possible reaction modes for hydrogenation and dehydrogenation reactions are geometrical contraction and nucleation growth. These reaction routes are supported by theoretical and experimental research [57]. Hydrogen storage

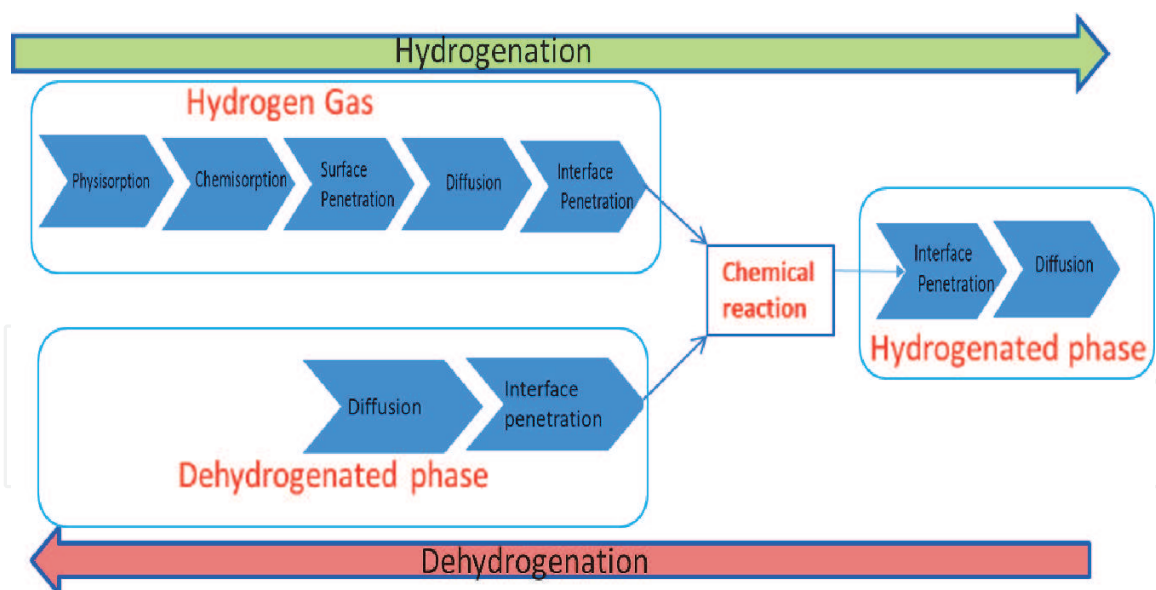


Figure 5.
 Hydrogenation and dehydrogenation steps (Adapted from [58]).

kinetic models are thereby segregated according to these reaction routes. These models are founded on isothermal fitting and non-isothermal calculation analysis methods [58]. These methods help determine kinetic parameters and reaction modes this subsequently leads to a better understanding of the kinetic mechanism.

6.2 Geometrical contraction models

The basis of this model is that hydrogenation and dehydrogenation reactions transpire uniformly from the surface into the bulk of particle and the particles are uniform in size and shape [58]. The reaction fraction relationship between distances in particles of various shapes (sphere, plate and cylinder) is given by:

$$\epsilon = 1 - \left(\frac{r}{r_0}\right)^d \tag{4}$$

Where d = dimensionality, r = lengths of the unreacted part, r_0 = length of the whole particles, ϵ = reaction fraction.

The geometrical contraction models are derived from this relationship equation and assumptions of isothermal conditions ([59–62]; N [63]; Nobuyoshi [64]). These are the geometrical contraction models:

6.3 Contracting volume model

$$\frac{d_r}{d_t} = -k_{int} \tag{5}$$

$$1 - (1 - \epsilon)^{\frac{1}{d}} = \frac{k_{int}}{r_0} t = kt \tag{6}$$

Where k_{int} = rate constant (interface controlled reaction), k = generalized rate constant.

6.4 Jander model

$$\frac{\rho dr}{dt} = \frac{D\Delta C}{r_0 - r} \quad (7)$$

$$\left[1 - (1 - \varepsilon)^{\frac{1}{d}}\right]^2 = \frac{2D\Delta C}{r_0^2 \rho} t = kt \quad (8)$$

Where ΔC = concentration difference, D = diffusion constant, ρ = density.

6.5 Ginstling-Brounshtein model

$$\frac{\rho dr}{dt} = \frac{D\Delta C}{r \ln\left(\frac{r_0}{r}\right)} \quad (9)$$

$$(1 - \varepsilon) \ln(1 - \varepsilon) + \varepsilon = \frac{4D\Delta C}{r_0^2 \rho} t = kt \quad (10)$$

For two dimensional cylinder:

$$\frac{\rho dr}{dt} = \frac{D\Delta C r_0}{(r_0 - r)r} \quad (11)$$

$$1 - \frac{2}{3}\varepsilon - (1 - \varepsilon)^{\frac{2}{3}} = \frac{2D\Delta C}{r_0^2 \rho} t = kt \quad (12)$$

For three dimensional cylinder:

6.6 Valensi-Carter model

$$\frac{\rho dr}{dt} = \frac{D\Delta C}{r - \frac{r^2}{(Zr_0^3 + r^3(1-z))^{\frac{1}{3}}}} \quad (13)$$

$$\frac{z - (1 + (z - 1)\varepsilon)^{\frac{2}{3}} - (z - 1)(1 - \varepsilon)^{\frac{2}{3}}}{z - 1} = \frac{2D\Delta C}{r_0^2 \rho} t = kt \quad (14)$$

Where z = volume ratio of product to reactant.

The *contracting volume model* assumes that rate of hydrogenation is regulated by the interface process. This model is deemed as the simplest method in geometrical contraction volume models because no other assumptions are made. Through this method the dimensionality and a generalized constant can be obtained through fitting a simplified isothermal curve [58, 60]. Bösenberg et al. proved that LiH-MgB₂ with transition metal deposits such as Titanium and Vanadium follow the CV model very well because it is interface control [65].

The *Jander Model* however is readily used for diffusion regulated reactions. The two important assumptions made in this model are: 1. the volume of hydrogen storage materials remains constant before and after absorption and desorption reactions 2. Two and three dimensional diffusion are deemed as one meaning the interface area remains constant for diffusion [59, 66]. However these assumptions are not always applicable for hydrogen storage materials because the volume of some materials increases during the uptake of hydrogen and decrease with the

release of it. In contrast Shao et al. found that nanocrystalline Mg doped with Ti under 1Mpa of H₂ follow this model very well [67].

According to Ginstling and Crank the Ginstling-Brounshtein model develops the Jander Model using Fick's Law for radial diffusion for 2D and 3D spheres [61, 68]. Although intricate; this method is regarded as a more accurate model due to its consideration of the variance in interface area due to diffusion. Chaudhary et al. reported that MgH₂-Si synthesized by ball milling, cryomilling and ultrasonication produces desorption curves which follow this model well [69]. The Valensi-Carter model is an extension of the G-B model which regards the change in volume in hydrogen storage materials during adsorption and desorption. This model is reportedly the most accurate in geometrical contraction model however it has not yet been applied to hydrogen storage materials [70–72].

6.7 Nucleation-growth impingement models

The Nucleation growth impingement models are generally described as the Johnson-Mehl-Avrami-Kolomogorov (JMAK) models. The JMAK models define hydrogenation and dehydrogenation reactions as three synchronized processes: nucleation, growth and impingement ([73]; Melvin [72, 74–78]). **Figure 6** is a diagram showing the three processes:

This model is founded on the basis of; 1. Enhancing nucleation, growth and impingement 2. Solving analytical problems [78]. This model is given as:

$$\varepsilon = F \left[\int_0^t I(r) V(r) dr \right] \tag{15}$$

Where I = nucleation module, r = nucleation rate, F = impingement module defining the relationship between real reaction fraction and extended reaction fraction, V = Growth module [79].

A variation of this equation, classical JMAK (C-JMAK), which takes into consideration interface controlled growth and diffusion controlled is given by:

$$V(r) = \left[G_0 \int_r^t \exp \left(\frac{-\Delta E_g}{RT} \right) d\eta \right]^{\frac{d}{m}} \tag{16}$$

Where ΔE_g = activation energy for growth, G_0 = intrinsic growth rate, m = growth mode parameter, $\frac{d}{m}$ = growth inde.

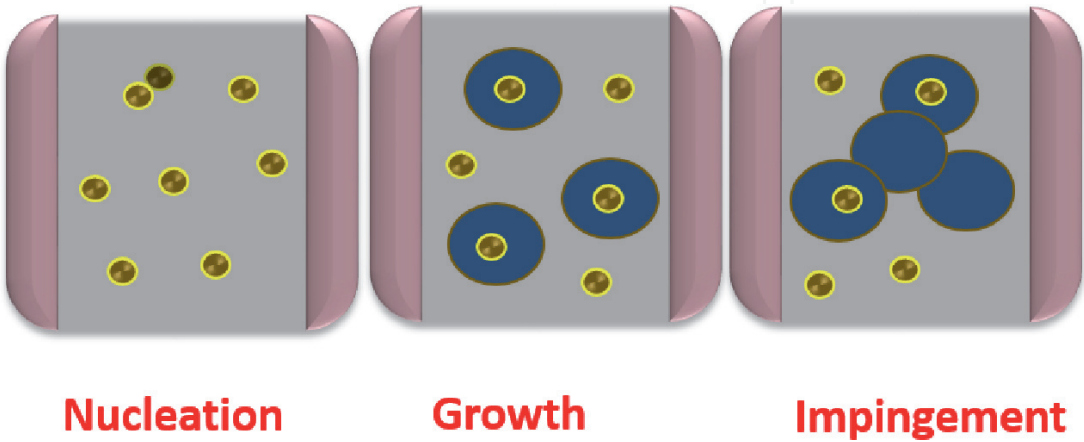


Figure 6.
Nucleation, growth and impingement (Adapted from [58]).

The C-JMAK model defines absorption and desorption of nucleation, growth and impingement very well. Nucleation in this regard refers to site saturation, growth mode to interface and diffusion controlled sites and impingement to randomly scattered nuclei isotropic growth [80]. The Avrami exponent of the desorption reaction of NaAlH_4 doped with Titanium was determined using this model and was found to be 3. This proved that the three dimensional interface process is the rate controlling step. Pang et al. however discovered that the actual nucleation modes propagate continuous nucleation and are not restricted to linear continuous nucleation and site saturation an assumption which this model is founded on [78, 81]. This inhibits the practical application of this model for progressive hydrogen storage applications.

Analysis methods are used to obtain kinetic mechanism by determining and comparing the best fit models and kinetic parameters that go along with it. The two most used analysis methods is isothermal fitting and non-isothermal fitting [82]. However based on literature reviewed understanding the kinetic mechanisms for hydrogen storage materials can be difficult because the analysis have downfalls which may result in misunderstanding of the kinetic mechanisms entirely [58].

7. Conclusion

Nanocomposites have proven to be materials of the 21st century with their flexibility and wide range application. These materials bridge the gap between heterogenous and homogenous catalysis through the combination of different nanomaterials. In this chapter, graphene based nanocomposites were reviewed and discussed intensely for hydrogen storage applications. The kinetic models of hydrogen storage materials was also reviewed. More work needs to be done in terms of the practical application of these material for energy storage, because to date, no material meets the standards for practical application in energy storage.

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