Modeling hydrogen storage on Mg–H₂ and LiNH₂ under variable temperature using multiple regression analysis with respect to ANOVA

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Abstract
The world is facing a major problem due to the depletion of conventional energy sources. Hydrogen is considered one of the most promising sources of energy. Recently, one of the problems facing utilization of hydrogen energy is the storage. Therefore, finding materials to store hydrogen based on the adsorption/desorption methodology (i.e. metal hydrides) is considered extremely vital issue. During this work two candidate materials (i.e. Mg–H₂ and LiNH₂) were investigated at different temperatures (25–45 °C). The results revealed that both candidate materials possessed long cycle life and cyclibility which opens the wide door to use these materials in vehicular applications. On the other hand the generated mathematical models based on the multiple regression analysis with respect to ANOVA showed that increasing temperature will increase the weight of hydrogen adsorption for both candidate materials.

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Introduction
Hydrogen fuel is an attractive alternative source of energy since it is clean, non-toxic and renewable especially when it is produced from renewable resources (i.e. Sea Water and Solar Energy) [1], making it as a substitute for petroleum derived fuels in vehicular applications. However, the greatest challenge in making hydrogen available for use in transportation lies in the development of safe, compact, portable and cost effective hydrogen storage systems. Hydrogen can be stored as (i) pressurized gas, (ii) cryogenic liquid, (iii) solid fuel as chemical or physical combination with materials, such as metal hydrides and Metal Organic Frameworks (MOFs). Metal hydrides compose of metal atoms that constitute a host lattice and hydrogen atoms. Hydrogen storage in metal hydrides depends on different parameters and consists of several mechanistic steps. Metals differ in the ability to dissociate hydrogen, this ability being dependent on:
A. Surface structure.
B. Morphology and purity.

An optimum hydrogen-storage material is required to have the following properties [2,3]:

A. High hydrogen capacity per unit mass and unit volume which determines the amount of available energy.
B. Low dissociation temperature.
C. Moderate dissociation pressure.
D. Low heat of formation in order to minimize the energy necessary for hydrogen release.
E. Low heat dissipation during the exothermic hydride formation.
F. Reversibility.
G. Limited energy loss during charge and discharge of hydrogen.
H. Fast kinetics.
I. High stability against O₂ and moisture for long cycle life.
J. Cyclibility.
K. Low cost of recycling and charging infrastructures.
L. High safety.

There is considerable research on magnesium and its alloys due to their high hydrogen storage capacity by weight and low cost. Besides, the Mg-based hydrides possess good-quality functional properties, such as heat-resistance, vibration absorbing, reversibility and recyclability. Several researchers have investigated magnesium and its alloys from various angles. Fry et al. [4] have improved hydrogen cycling kinetics of nano-structured magnesium/transition metal multilayer thin films, while Shahi et al. [5] have conducted studies on de/rehydrogenation characteristics of nanocrystalline Mg–H₂ co-catalysed with Ti, Fe and Ni. James Jr. et al. [6] have studied the fundamental environmental reactivity testing and analysis of the hydrogen storage material 2LiBH₄–MgH₂. Utke et al. [7] have investigated the effect of using 2LiBH₄–MgH₂ for reversible hydrogen storages. Mustafa et al. [8] have studied the influence of adding K₂TiF₆ on the hydrogen sorption properties of MgH₂. Song et al. [9] have investigated the improvement of hydrogen-storage properties of MgH₂ by adding Ni, LiBH₄, and Ti. Gattia et al. [10] have studied the effect of hydrogen cycling on the microstructure and morphological changes in MgH₂. Korablov et al. [11] have investigated activation effects during hydrogen release and uptake from MgH₂. It is worth of mention that Shao et al. [12] have studied the hydrogen storage and thermal conductivity of Mg–based materials while Rusman et al. [13] have conducted a review on the current progress of metal hydrides for solid-state hydrogen storage applications. Tran et al. [14] have investigated the dehydriding mechanism of Mg₃NiH₆ using in-situ ultra-high voltage transmission electron microscopy (TEM) combined with Synchrotron powder X-ray diffraction (XRPD) and differential scanning calorimetry (DSC). They found that the hydrogen release is based on a mechanism of nucleation and growth of Mg₃NiH₆ (x ~ 0–0.3) solid solution grains which is greatly enhanced in the presence of crystal defects occurring as a result of the polymorphic phase transformation. Li et al. [15] investigated the hydrogen storage properties and mechanisms of the Ca (BH₄)₂-added 2LiNH₂–MgH₂ system. The results indicated that the dehydrogenated 2LiNH₂–MgH₂–0.1Ca (BH₄)₂ sample could absorb 4.7 wt% of hydrogen at 160 °C and 100 atm while only 0.8 wt% of hydrogen was recharged into the dehydrogenated pristine sample under the same conditions. Lin et al. [16] have studied the Mg (NH₂)₂–LiNH₂–4LiH composite in order to improve its kinetics, thermodynamics and cycling properties. While Barison et al. [17] studied the influence of different high energy milling times and of the addition of catalysts such as Nb₂O₅, TiCl₃ and graphite on the hydrogen absorption/desorption (A/D) kinetics of a mixture of 2LiNH₂ + 1.1MgH₂ in the temperature range (220–240) °C. Lan et al. [18] investigated the characteristics of hydrogen storage of LiNH₂/MgH₂ (1:1). Albanesi et al. [19] improved the hydrogen sorption kinetics by adding 1 mol% AlCl₃ to LiNH₂-LiH. They showed that Al⁺³ is incorporated into the LiNH₂ structure by partial substitution of Li⁺ forming a new amide in the Li—Al—N—H system, which is reversible under hydriding/dehydriding cycles. They assured that the substituted amide improved hydrogen storage properties with respect to LiNH₂–LiH. As a result a stable hydrogen storage capacity of about 4.5–5.0 wt% under cycling and completely desorbed in 30 min at 275 °C for the Li—Al—N—H system. Burger et al. [20] studied several material properties, like bulk density and thermodynamic data, isothermal absorption and desorption experiments. They have generated two-step model equations to be utilized to capture the experimentally measured reaction rates and can be used for model validation of the design simulations.

Varin et al. [21] studied the dehydrogenation rate of synthesized hydride nanocomposites of (LiNH₂ + nMgH₂). Zhang et al. [22] studied the effect of adding LiH on the hydrogen absorption/desorption capacities of the Li₃N–MgH₂. Albanesi et al. [23] investigated the hydrogen sorption kinetics and the reactions between LiNH₂–LiH and AlCl₃ additive with a multitechnique approach involving differential scanning calorimetry (DSC), hydrogen volumetric measurements, X-ray powder diffraction (XRPD), Fourier transform infrared analysis (FTIR) and solid-state nuclear magnetic resonance (NMR).

During the current work a special reactor connected to a fully computerized system was designed and fabricated in order to fulfill the needs to study the effect of varying the temperature on the adsorption of hydrogen using Mg–H₂ and LiNH₂ at low temperatures (i.e. 25, 30, 35, 40 and 45 °C) based on the gravimetric method. Two mathematical models were generated based on the multiple regression analysis with respect to ANOVA to show the effect of low temperature on hydrogen adsorption for the given candidate materials.

**Experimental work**

The adsorption of hydrogen using commercial magnesium hydride (i.e. Mg–H₂) supplied by Sigma Aldrich and lithium amide (i.e. LiNH₂) supplied by ChemCruz at low temperatures as mentioned previously was investigated using a special hydrogen storage unit which was designed and fabricated in situ. This unit consisted of three major parts, the first part is a
reactor made from stainless steel 316 L as shown in Fig. 1, connected to the second part which consisted of piping network made also of stainless steel 316 L, kept inside a glove box as shown in Fig. 2. While the third part is a fully computerized system consisted of measurement and control devices in addition to analogue to digital converters were utilized to build the hydrogen adsorption cycle as shown in Fig. 3.

Before each run, 1 g of Mg$_2$H$_2$ or LiNH$_2$ weighed using a sensitive balance and kept inside the reactor shown in Fig. 1 before conducting the run, then the reactor was connected to the hydrogen storage unit shown in Fig. 2 followed by flushing the reactor and piping network using inert gas (i.e. He) for three times in order to get rid of oxygen traces. Then hydrogen was introduced to the reactor followed by increasing the reactor temperature to the desired adsorption temperature (i.e. 25, 30, 35, 40 and 45 °C) using certain procedure which included entering the number of hydrogen doses and the time between the doses in order to measure the weight of hydrogen adsorbed within the storage material using the fully computerized system based on the gravimetric method as shown in Fig. 3.
Fig. 2 – Process flow diagram of the hydrogen storage unit.

Fig. 3 – Control panel of the software package which was utilized to measure and control the hydrogen adsorption desorption cycles.
Results and discussion

Hydrogen storage behaviour of Mg–H₂ and LiNH₂

Twenty cycles were implemented to measure the adsorption of hydrogen using Mg–H₂ at 25, 30, 35, 40 and 45 °C. These cycles were divided into two parts. The first part contained fifteen cycles using the first sample of Mg–H₂ (i.e. three cycles per each temperature). Followed by another five cycles using the second sample of Mg–H₂ (i.e. one cycle per each temperature) in order to investigate the performance and efficiency of the mentioned material. The results reflected good performance and efficiency which indicates that the candidate material (i.e. Mg–H₂) possess long cycle life and cyclibility.

Taking into consideration that the obtained results were in agreement with [13,24–29].

On the other hand, ten cycles were implemented to measure the adsorption of hydrogen using LiNH₂ at 25, 30, 35, 40 and 45 °C. These cycles were divided into two parts. The first part contained five cycles (i.e. one cycle for each temperature) were implemented using the first sample of LiNH₂. Followed by another five cycles (i.e. one cycle for each temperature) using the second sample of LiNH₂ in order to investigate the performance and efficiency of the mentioned material in terms of hydrogen storage as shown in Fig. 5. The results were very close to Mg–H₂ material which indicates that the candidate material (i.e. LiNH₂) possess also long cycle life and cyclibility. All results were in agreement with [13,24–29].

Modelling of storage data using Mg–H₂ and LiNH₂

The models given in Eqs. (1) and (2) were generated after several trials using multiple regression analysis based on the theory of least square error where an optimization was performed by minimizing the error between the predicted values of the response and the actual ones withdrawn from the experimental run. The resulting ANOVA Tables 1–4 for the Eqs. (1) and (2) outline the analysis of variance for the given response (i.e. hydrogen adsorption weight in (mg)) using Mg–H₂ in Eq. (1) and LiNH₂ in Eq. (2) and the operating condition (i.e. Temperature) as a regressor. Tables 2 and 4 shows also other adequacy measures such as R² and Adjusted R². The two models assured that the temperature played a vital role in increasing the weight of hydrogen adsorption in both candidate materials (i.e. Mg–H₂ and LiNH₂) which are in agreement with the results obtained in Figs. 4 and 5. The resulting ANOVA table for both models showed that the adequacy measures R² and Adjusted R² are close to 1 which are in reasonable agreement and therefore indicate adequate models. An adequate model means that the reduced model has successfully passed all the required statistical tests and can be used to predict the responses [30]. It is worth of mention that the entire adequacy measures are in agreement with the general outlines provided by Eltawahni et al. [31] and Eltawahni et al. [32].

For Mg–H₂:

\[ Wt. \text{(mg)} = -2.06 + 0.133T - 0.00142T^2 \] (1)

where:

- Wt.: hydrogen adsorption weight in (mg).
- T: Temperature in (°C).

For LiNH₂:

\[ Wt. \text{(mg)} = -6.316 + 0.3605T - 0.0043T^2 \] (2)

where:

- Wt.: hydrogen adsorption weight in (mg).
- T: Temperature in (°C).

**Table 1 – Analysis of the regressor coefficients given in Eq. (1).**

<table>
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<tr>
<th>Coe.</th>
<th>SE</th>
<th>t Stat</th>
<th>P-value</th>
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<tr>
<td>Inter</td>
<td>-2.06</td>
<td>1.09</td>
<td>-1.89</td>
</tr>
<tr>
<td>T</td>
<td>0.133</td>
<td>0.064</td>
<td>2.08</td>
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<tr>
<td>T²</td>
<td>0.0014</td>
<td>0.0009</td>
<td>-1.56</td>
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Analysis of variance in addition to $R^2$ and $R^2_{adj}$

<table>
<thead>
<tr>
<th></th>
<th>df</th>
<th>SS</th>
<th>MS</th>
<th>F</th>
<th>$F_{critical}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reg.</td>
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<td>0.602</td>
<td>0.3013</td>
<td>20.66</td>
<td>0.001</td>
</tr>
<tr>
<td>Res.</td>
<td>7</td>
<td>0.102</td>
<td>0.0146</td>
<td></td>
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<tr>
<td>Total</td>
<td>9</td>
<td>0.704</td>
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<tr>
<td>$R^2$</td>
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<td>85.5167</td>
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<td>$R^2_{adj}$</td>
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<td>81.3786</td>
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</table>

Conclusion

Investigating the hydrogen adsorption at the proposed range of temperatures (25–45 °C) using Mg–H$_2$ and LiNH$_2$ showed that both candidate materials possessed long cycle life and cyclibility which opens the wide door to store hydrogen at ambient conditions which is considered very crucial in hydrogen vehicles powered by PEM fuel cells. On the other hand the generated mathematical models based on the multiple regression analysis with respect to ANOVA revealed that increasing temperature will increase the weight of hydrogen adsorption using Mg–H$_2$ and LiNH$_2$ respectively.

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Nomenclature

ANOVA: analysis of variance  
MOFs: metal organic frameworks  
TEM: transmission electron microscopy  
XRPD: X-ray powder diffraction  
DSC: differential scanning calorimetry  
PI: pressure indicator  
GBTS: glove box temperature sensor for hydrogen  
LC: load cell to measure the change in weight of the sample  
TC: temperature controller  
DES: desorption tank  
ADS: adsorption tank  
PC: pressure controller  
TCNT: temperature controller  
NV: needle valve  
SV: solenoid valve  
PT: pressure transmitter  
VT: vacuum transmitter  
PRT: proportional pressure transmitter  
FM: flow meter  
FTIR: Fourier transform infrared  
NMR: nuclear magnetic resonance  
Wt.: weight  
T: temperature  
R²: regression factor  
Coe: coefficient  
SE: standard deviation  
t Stat: t-test  
P: P-value  
df: degrees of freedom  
SS: sum of squares  
MS: mean square  
F: F-value