

Cite this: *RSC Adv.*, 2018, 8, 15667

# Nanolayer-like-shaped $\text{MgFe}_2\text{O}_4$ synthesised *via* a simple hydrothermal method and its catalytic effect on the hydrogen storage properties of $\text{MgH}_2$

N. A. Ali,<sup>a</sup> Nurul Hayati Idris,<sup>a</sup> M. F. Md Din,<sup>b</sup> N. S. Mustafa,<sup>a</sup> N. A. Sazelee,<sup>a</sup> F. A. Halim Yap,<sup>a</sup> N. N. Sulaiman,<sup>a</sup> M. S. Yahya<sup>a</sup> and M. Ismail<sup>✉\*</sup><sup>a</sup>

In this study, the effect of nanolayer-like-shaped  $\text{MgFe}_2\text{O}_4$  that is synthesised *via* a simple hydrothermal method on the performance of  $\text{MgH}_2$  for hydrogen storage is studied.  $\text{MgH}_2 + 10 \text{ wt\% MgFe}_2\text{O}_4$  is prepared by using the ball milling method. The  $\text{MgFe}_2\text{O}_4$ -doped  $\text{MgH}_2$  sample started to release  $\text{H}_2$  at approximately 250 °C, 90 °C and 170 °C lower than the milled and pure  $\text{MgH}_2$  respectively. At 320 °C, the isothermal desorption kinetic study has shown that the doped sample has desorbed approximately 4.8 wt%  $\text{H}_2$  in 10 min while the milled  $\text{MgH}_2$  desorbed less than 1.0 wt%  $\text{H}_2$ . For isothermal absorption kinetics, the doped sample can absorb approximately 5.5 wt%  $\text{H}_2$  in 10 min at 200 °C. Meanwhile, the undoped sample absorbs only 4.0 wt%  $\text{H}_2$  in the same condition. The activation energy of 10 wt%  $\text{MgFe}_2\text{O}_4$ -doped  $\text{MgH}_2$  composite is 99.9 kJ mol<sup>-1</sup>, which shows a reduction of 33.1 kJ mol<sup>-1</sup> compared to the milled  $\text{MgH}_2$  (133.0 kJ mol<sup>-1</sup>). X-ray diffraction spectra display the formation of new species which are Fe and MgO after dehydrogenation, and these new species are believed to act as the real catalyst that plays a crucial role in improving the sorption performance of the  $\text{MgFe}_2\text{O}_4$ -doped  $\text{MgH}_2$  system by providing a synergetic catalytic effect.

Received 13th March 2018

Accepted 18th April 2018

DOI: 10.1039/c8ra02168f

rsc.li/rsc-advances

## 1. Introduction

To prepare for the future and ensure global environmental viability, energy systems have to be reliable, clean, low cost, environmentally friendly and flexible. Humanity is expected to use 40 TW of power (40 billion of kW) in the future. To satisfy this demand, different sources of renewable energy, such as hydrogen, are needed. Sustainable hydrogen is an ideal clean energy carrier because there is no carbon dioxide or other greenhouse gas emission at the end-user level. Commonly, there are 3 forms of storing hydrogen which is high-pressure gas, cryogenic liquid hydrogen in tanks (stored at 21.2 K) and as solid state hydrogen storage by either reacting with chemical compounds or absorbing. Among these approaches, solid-state hydrogen storage has higher potential for higher hydrogen density and may yield greater utility towards the practical implementation of hydrogen storage. Among the various materials for solid-state hydrogen storage,  $\text{MgH}_2$  considered as one of the most potential material due to its high hydrogen storage capacity (7.6 wt%), excellent reversibility and low cost.<sup>1</sup> However,  $\text{MgH}_2$  is restricted by the decomposition temperature,

which is high with slow sorption kinetics and is excessively stable thermodynamically.<sup>2</sup> Many research have been conducted to overcome these disadvantages by altering the thermodynamics and improve the kinetic properties by producing nanostructures<sup>3,4</sup> and utilizing catalysts such as carbon-based materials,<sup>5,6</sup> metals,<sup>7–10</sup> metal hydrides,<sup>11,12</sup> metal oxides,<sup>13–18</sup> metal halides,<sup>19–21</sup> and nanosized alloys.<sup>22–24</sup>

Previous research has proved that catalyst based on ternary metal oxides greatly improved the hydrogen storage performance of  $\text{MgH}_2$ .<sup>15,25–35</sup> Zhang *et al.*<sup>25</sup> demonstrate that ferrite nanoparticles ( $\text{MnFe}_2\text{O}_4$ ,  $\text{ZnFe}_2\text{O}_4$ ,  $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$  and  $\text{CoFe}_2\text{O}_4$ ) can greatly lower the decomposition temperature of  $\text{MgH}_2$ .  $\text{CoFe}_2\text{O}_4$  provides the best catalytic effect compared with other ferrites. New by-products are found after the dehydrogenation process, and its phase shows a great catalytic effect on the properties of hydrogen storage of  $\text{MgH}_2$ . Furthermore, Li *et al.*<sup>26</sup> shows a significant improvement in the desorption performance of  $\text{MgH}_2$  when catalysed with  $\text{MnFe}_2\text{O}_4$ . X-ray photoelectron spectroscopy and X-ray diffraction (XRD) tests show that  $\text{Fe}_{0.872}\text{O}$  and  $\text{Mg}_2\text{MnO}_4$  phases take part as significant role in enhancing the dehydriding performance of  $\text{MgH}_2$ . Meanwhile, we showed in our previous study that  $\text{MnFe}_2\text{O}_4$  synthesised *via* a simple hydrothermal method provides a remarkable effect in improving the hydrogen storage performance of  $\text{MgH}_2$ .<sup>27</sup> Interestingly, our result showed that Fe metal formed after dehydrogenation instead of  $\text{Fe}_{0.872}\text{O}$  species, as claimed by Li *et al.*<sup>26</sup> This variation paved the way for the debate

<sup>a</sup>School of Ocean Engineering, Universiti Malaysia Terengganu, 21030 Kuala Terengganu, Malaysia. E-mail: mohammadismail@umt.edu.my; Fax: +609-6683991; Tel: +609-6683487

<sup>b</sup>Department of Electrical and Electronic Engineering, Faculty of Engineering, National Defence University of Malaysia, Kem Sungai Besi, Kuala Lumpur, Malaysia

on how ternary metal oxides, particularly ferrites, work as catalysts in improving the hydrogen sorption performance of  $\text{MgH}_2$ . Moreover, the difference in the synthesis method of the catalysts may also provide a different effect in the catalytic role.

Inspired by the role of active species that formed during the heating process in the  $\text{MgH}_2$ -ternary metal oxides catalyst system, it is quite interesting to investigate the use of other ferrites (e.g.  $\text{MgFe}_2\text{O}_4$ ) as catalysts to improve the hydrogen sorption performance of  $\text{MgH}_2$ . Therefore, in this work,  $\text{MgFe}_2\text{O}_4$  was synthesised by using a simple hydrothermal method, and its catalytic effects on the hydrogen sorption performance of  $\text{MgH}_2$  were systematically studied. To the best of authors' knowledge, this paper is the first to study the hydrogen sorption performance of  $\text{MgH}_2$  catalysed with  $\text{MgFe}_2\text{O}_4$ . The possible catalysis mechanisms of  $\text{MgFe}_2\text{O}_4$  in the sorption performances of  $\text{MgH}_2$  are also discussed in this paper.

## 2. Experimental details

The nanolayer-like-shaped  $\text{MgFe}_2\text{O}_4$  was synthesised *via* a hydrothermal method. In a typical synthesis, a stoichiometric amount of  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (Sigma-Aldrich) and  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (Sigma-Aldrich) were dissolved in 50 ml distilled water. A total of 10 ml of  $\text{H}_4\text{N}_2 \cdot \text{H}_2\text{O}$  (Sigma-Aldrich) was added dropwise to the above solution to attain the resultant pH of  $>9$ . The mixture

was then transferred into a sealed Teflon lined stainless-steel autoclave (125 ml capacity) and heated for 12 h at  $180^\circ\text{C}$ . The final product was washed several times with deionised water and dried overnight at  $60^\circ\text{C}$  under vacuum. A total of 10 wt% of as-prepared  $\text{MgFe}_2\text{O}_4$  was mixed with 300 mg of  $\text{MgH}_2$  (95% pure; Sigma-Aldrich) and undergo intensive ball milling for 1 h in a planetary ball mill at the rate of 400 rpm. For comparison, pure  $\text{MgH}_2$ , and  $\text{MgH}_2$  added with 10 wt% Fe (Alfa Aesar) and 10 wt%  $\text{MgO}$  (R&M Chemicals), respectively were also prepared under the same conditions. All preparations, including loading and weighing, were conducted in an argon atmosphere glove box (MBraun Unilab).

The onset decomposition temperature and sorption kinetic measurement for doped and undoped samples were characterised by using Sievert-type pressure-composition-temperature apparatus (Advanced Materials Corporation). For onset decomposition temperature measurement, the samples were heated from room temperature to  $450^\circ\text{C}$  at a heating rate of  $5^\circ\text{C min}^{-1}$  in vacuum chamber. Meanwhile, the sorption kinetics was conducted under 1.0 atm at  $320^\circ\text{C}$  for desorption kinetic measurement and under 33.0 atm at  $200^\circ\text{C}$  for absorption kinetic measurement. The thermal properties of the doped and undoped samples were performed using differential scanning calorimeter (DSC)/thermogravimetric analysis from Metler Toledo. With a flow of  $50\text{ ml min}^{-1}$  argon, the samples

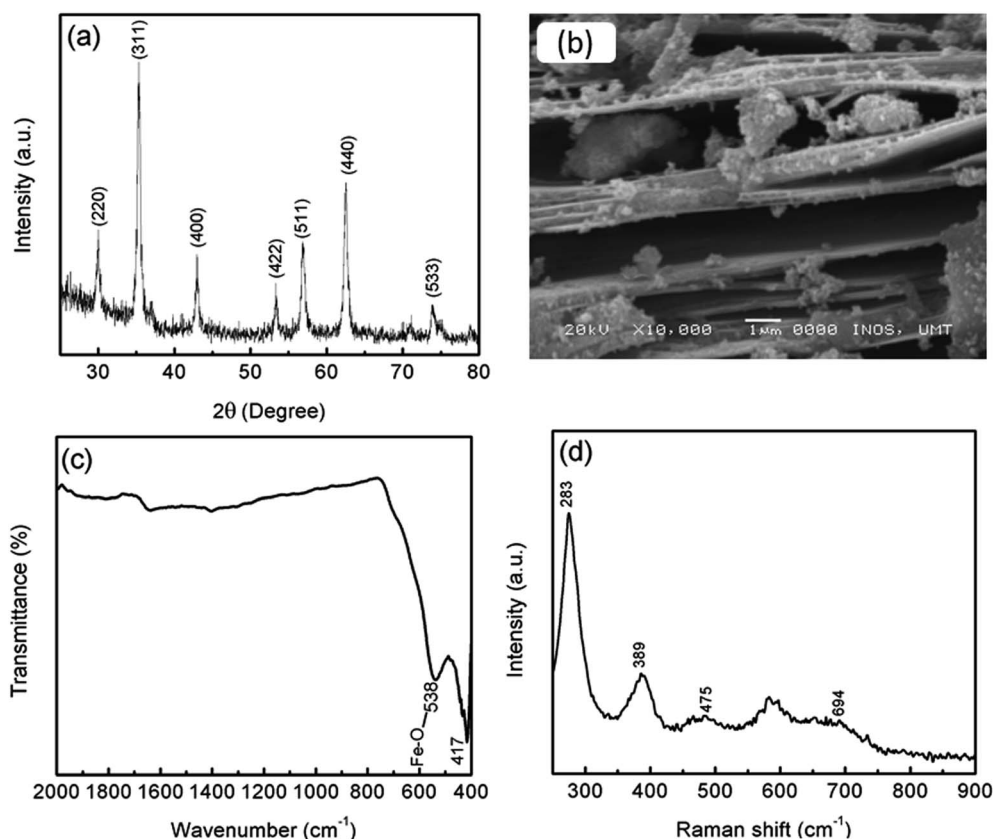


Fig. 1 (a) XRD pattern, (b) SEM image, (c) FTIR spectra and (d) Raman spectra of  $\text{MgFe}_2\text{O}_4$ .



were heated with 15, 20, 25 and 30 °C min<sup>-1</sup> heating rate from 25 °C to 500 °C.

The phase composition of the samples was analysed by XRD via a Rigaku MiniFlex X-ray diffraction apparatus equipped with Cu K $\alpha$  radiation. Data were collected in the 2 $\theta$  range 20° to 80° at 2° min<sup>-1</sup>. The morphologies of the samples were observed by scanning electron microscopy (SEM) (JEOL JSM-6350LA). Fourier transform infrared (FTIR) spectrometry was recorded on an IR Shimadzu Tracer-100 between 400 and 2000 cm<sup>-1</sup>. Raman spectra were recorded on Renishaw Raman spectroscopy (532 nm radiation) extended with 0.1% power laser measurement at room temperature.

### 3. Results and discussion

Before milling with MgH<sub>2</sub>, the phase structure of MgFe<sub>2</sub>O<sub>4</sub> was confirmed by XRD, as shown in Fig. 1(a). The crystallographic planes of (220), (311), (400), (422), (511), (440) and (533) correspond to the diffraction peaks at 2 $\theta$  of 30.1°, 35.4°, 43.1°, 53.5°, 57.0°, 62.6° and 74.1°, respectively. This result is in good agreement with the standard cubic spinel structure (JCPDS 71-1232). No other peaks were detected in the sample. The average crystallite size of MgFe<sub>2</sub>O<sub>4</sub> was approximately 19 nm, as determined by using Scherrer's formula:

$$L = k\lambda/B \cos \theta, \quad (1)$$

where  $L$  is the average crystallite size (nm),  $\theta$  is the angle of diffraction,  $k$  is Scherrer's constant ( $k = 0.94$ ),  $\lambda$  is the X-ray wavelength (0.15405 nm) and  $B$  is the full width at half maximum of the diffraction peak in radian (FWHM). The SEM image (Fig. 1(b)) reveals that the MgFe<sub>2</sub>O<sub>4</sub> forms a large layer with a nanosized thickness. From the FTIR spectrum (Fig. 1(c)), two typical peaks of MgFe<sub>2</sub>O<sub>4</sub> were observed at the low wave-number, thus indicating the formation of spinel ferrite structure.<sup>36,37</sup> The peak at 417 cm<sup>-1</sup> can be ascribed to the Fe–O vibration in the octahedral site, and the peak at 538 cm<sup>-1</sup> can be assigned to the Fe–O vibration in the tetrahedral and octahedral sites. Furthermore, the Raman peaks (Fig. 1(d)) at 475 and 694 cm<sup>-1</sup> can be assigned to the typical characteristic peaks of MgFe<sub>2</sub>O<sub>4</sub>,<sup>38</sup> whereas the peak at 283 cm<sup>-1</sup> corresponding to the stretching vibration of the Mg–O chemical bond.<sup>39</sup> The XRD, FTIR and Raman spectroscopy results confirm that pure MgFe<sub>2</sub>O<sub>4</sub> was successfully synthesised by the hydrothermal method.

Fig. 2(a) shows the onset decomposition temperature results for the pure MgH<sub>2</sub>, milled MgH<sub>2</sub> and MgH<sub>2</sub> with 10 wt% MgFe<sub>2</sub>O<sub>4</sub>. Before milling, pure MgH<sub>2</sub> started to desorb hydrogen at approximately 420 °C. The total amount of hydrogen desorbed is approximately 7.0 wt%. After milling for 1 h, the onset decomposition temperature of MgH<sub>2</sub> was decreased to approximately 340 °C. This phenomenon demonstrate that the sorption performance of MgH<sub>2</sub> also influenced by the milling

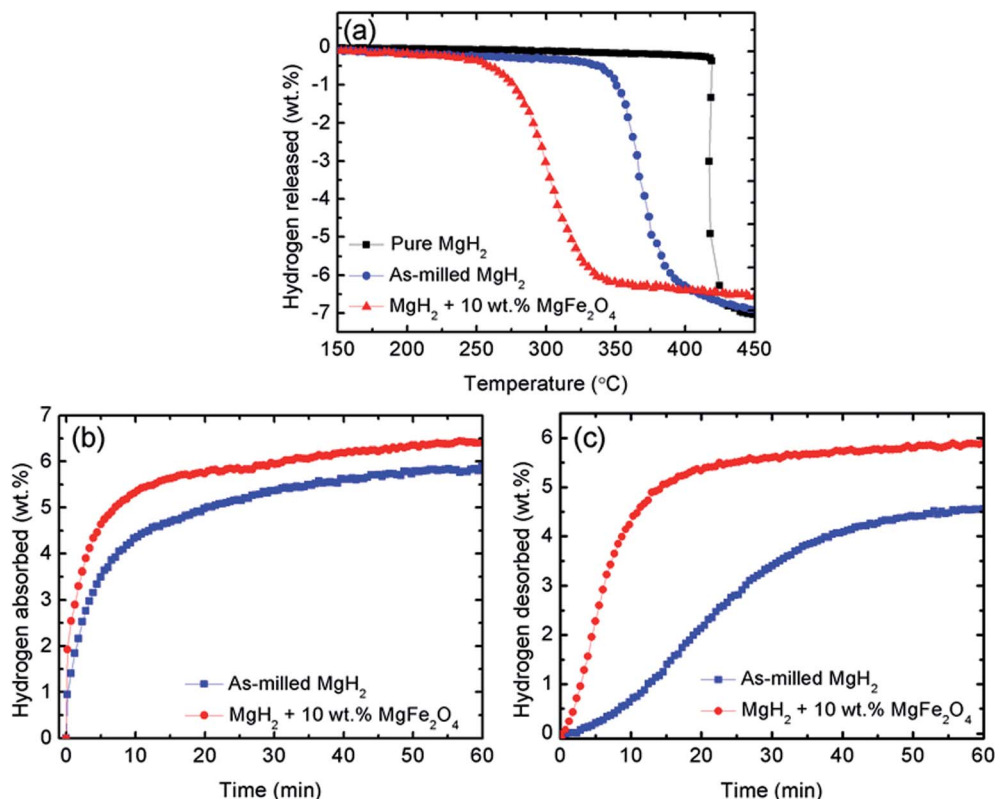


Fig. 2 (a) Decomposition temperature profile of pure and milled MgH<sub>2</sub>, and 10 wt% MgFe<sub>2</sub>O<sub>4</sub>-doped MgH<sub>2</sub> sample, (b) measurement of isothermal absorption kinetics for the milled MgH<sub>2</sub> and 10 wt% MgFe<sub>2</sub>O<sub>4</sub>-doped MgH<sub>2</sub> sample at 200 °C under 33.0 atm H<sub>2</sub> pressures, and (c) measurement of isothermal desorption kinetics for the milled MgH<sub>2</sub> and 10 wt% MgFe<sub>2</sub>O<sub>4</sub>-doped MgH<sub>2</sub> sample at 320 °C under 1.0 atm.



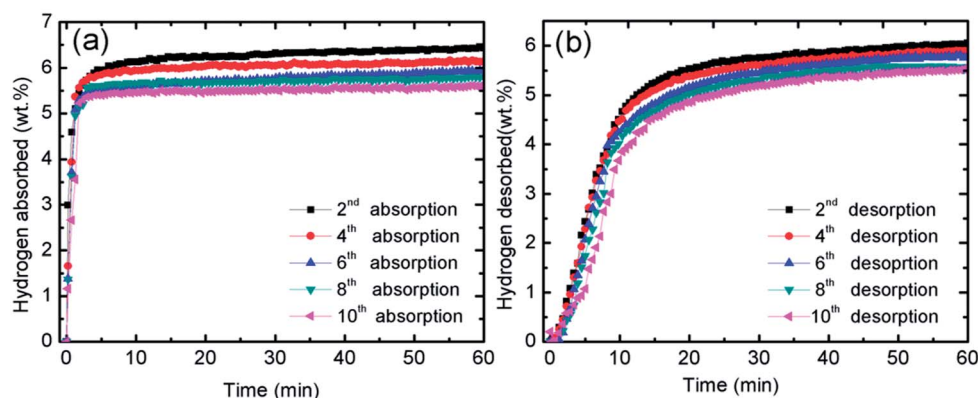


Fig. 3 (a) Measurement of isothermal absorption kinetics for the 10 wt%  $\text{MgFe}_2\text{O}_4$ -doped  $\text{MgH}_2$  sample in the 2<sup>nd</sup>, 4<sup>th</sup>, 6<sup>th</sup>, 8<sup>th</sup> and 10<sup>th</sup> cycle at 320 °C under 33.0 atm  $\text{H}_2$  pressures and (b) measurement of isothermal desorption kinetics for the 10 wt%  $\text{MgFe}_2\text{O}_4$ -doped  $\text{MgH}_2$  sample in the 2<sup>nd</sup>, 4<sup>th</sup>, 6<sup>th</sup>, 8<sup>th</sup> and 10<sup>th</sup> cycle at 320 °C under 1.0 atm.

process. From the curve, it can be seen that after milling, the amount of hydrogen desorb of  $\text{MgH}_2$  slightly decreases. This might be ascribed to the hydrogen released from  $\text{MgH}_2$  during the milling process. After doping with 10 wt% of  $\text{MgFe}_2\text{O}_4$ , it is clear that the onset decomposition temperature of the  $\text{MgH}_2$  was dramatically reduced to 250 °C, 90 °C and 170 °C lower than that for the milled and pure  $\text{MgH}_2$ , respectively. However, the hydrogen desorption capacity decrease slightly to approximately 6.5 wt% because the dopant used in this study, namely,  $\text{MgFe}_2\text{O}_4$ , does not contain hydrogen.<sup>40</sup> From Fig. 2(a), it can be concluded that  $\text{MgFe}_2\text{O}_4$  additive plays a positive role in decreasing the decomposition temperature of  $\text{MgH}_2$ .

To further examine the sorption properties of the  $\text{MgFe}_2\text{O}_4$ -doped  $\text{MgH}_2$  sample, the isothermal absorption kinetic was studied. The amount of hydrogen absorbed from the milled  $\text{MgH}_2$  and the  $\text{MgFe}_2\text{O}_4$ -doped  $\text{MgH}_2$  sample was measured under 33.0 atm  $\text{H}_2$  and at constant temperature of 200 °C, as shown in Fig. 2(b). The  $\text{MgFe}_2\text{O}_4$ -doped  $\text{MgH}_2$  sample shows better absorption kinetics than undoped  $\text{MgH}_2$ . For the  $\text{MgFe}_2\text{O}_4$ -doped  $\text{MgH}_2$  sample, the amount of 5.5 wt%  $\text{H}_2$  was absorbed in 10 min, whereas the milled  $\text{MgH}_2$  only absorbed approximately 4.0 wt%  $\text{H}_2$  within the same time. From the result, it clearly shows that the addition of  $\text{MgFe}_2\text{O}_4$  enhanced the rehydrogenation kinetics of  $\text{MgH}_2$ .

For further studies on the catalytic effect of  $\text{MgFe}_2\text{O}_4$  on the sorption kinetic of  $\text{MgH}_2$ , isothermal desorption kinetic was performed under 1.0 atm at 320 °C. As shown in Fig. 2(c), the  $\text{MgFe}_2\text{O}_4$ -doped  $\text{MgH}_2$  sample shows significant enhancement compared with the milled  $\text{MgH}_2$ . The results shows that the undoped  $\text{MgH}_2$  released less than 1.0 wt%  $\text{H}_2$  after 10 min, whereas the doped sample can released approximately 4.8 wt%  $\text{H}_2$  under the same condition. In contrast, it can be seen that  $\text{MgFe}_2\text{O}_4$  also plays a significant role in enhancing the dehydrogenation kinetic of  $\text{MgH}_2$ .

The catalytic effect of  $\text{MgFe}_2\text{O}_4$  was further studied with the cycling performances of  $\text{MgFe}_2\text{O}_4$ -doped  $\text{MgH}_2$  system. Fig. 3(a) presents the isothermal absorption kinetics of the 10 wt%  $\text{MgFe}_2\text{O}_4$  doped with  $\text{MgH}_2$  at 320 °C under a hydrogen pressure of 33.0 atm over 10 cycles. From the result, it can be seen that

after the ten cycles, the absorption kinetics show a small reduction in the hydrogen capacity. After completing the 10<sup>th</sup> cycle, the system is able to absorb 5.6 wt% of hydrogen in 60 minutes. The result shows that the doped system displays good absorption properties even after 10 cycles. As for the desorption kinetics, Fig. 3(b) shows the isothermal desorption kinetics for 10 cycles that was carried out at 320 °C and under 1.0 atm of pressure. Like the absorption kinetics, a small hydrogen capacity degradation is shown after completing the 10<sup>th</sup> cycle. The doped system possesses a good performance after completing the 10<sup>th</sup> cycle as it is able to desorb about 5.5 wt% of hydrogen within 60 minutes. These results demonstrated that  $\text{MgFe}_2\text{O}_4$  plays a vital catalytic role for the cycle life of  $\text{MgH}_2$ .

The thermal properties of the 10 wt%  $\text{MgFe}_2\text{O}_4$ -doped  $\text{MgH}_2$  and undoped  $\text{MgH}_2$  sample were further studied by DSC at heating rate of 30 °C min<sup>-1</sup> and under a flow of 50 ml min<sup>-1</sup> argon (Fig. 4). Obviously, the DSC trace for the pure  $\text{MgH}_2$  showed one endothermic peak at approximately 482.9 °C. This strong endothermic peak related to the released of hydrogen

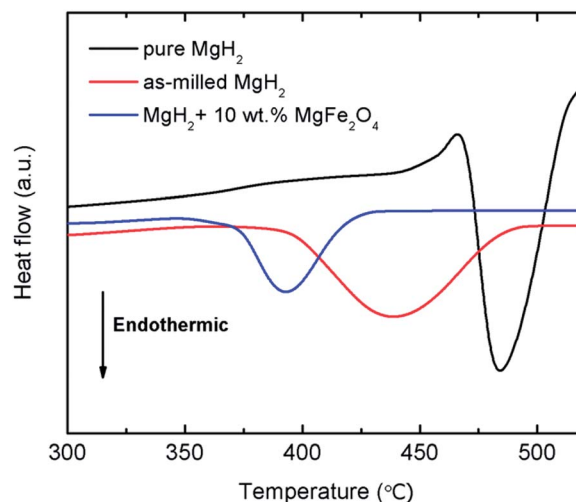


Fig. 4 DSC curves of pure  $\text{MgH}_2$ , milled  $\text{MgH}_2$ , and 10 wt%  $\text{MgFe}_2\text{O}_4$ -doped  $\text{MgH}_2$ .





from the  $\text{MgH}_2$ . Similar to the pure  $\text{MgH}_2$ , DSC traces of the milled  $\text{MgH}_2$  and  $\text{MgFe}_2\text{O}_4$ -doped  $\text{MgH}_2$  showed only one strong endothermic peak at  $438.8^\circ\text{C}$  and  $393.3^\circ\text{C}$  respectively. The peaks correlated to the decomposition of  $\text{MgH}_2$  but at lower temperatures.

The improvement in desorption behaviour is correlated with the kinetic barrier of the hydrogen desorbed from the  $\text{MgH}_2$ . By doping  $\text{MgH}_2$  with  $\text{MgFe}_2\text{O}_4$ , low value of activation energy for released hydrogen is obtained. Kissinger analysis<sup>41</sup> (eqn (2)) was conducted to determine the activation energy of doped and undoped  $\text{MgH}_2$  samples.

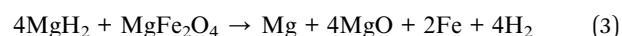
$$\ln[\beta/T_p^2] = -E_A/RT_p + A, \quad (2)$$

where  $\beta$  is the heating rate,  $E_A$  is the activation energy,  $R$  is the gas constant,  $T_p$  is the peak temperature of DSC curves and  $A$  is the linear constant. Fig. 5 illustrates the curves of DSC for the milled  $\text{MgH}_2$  and  $\text{MgH}_2$  doping with 10 wt%  $\text{MgFe}_2\text{O}_4$  samples at heating rates of 15, 20, 25, and  $30^\circ\text{C min}^{-1}$ . From the Kissinger plot of the DSC data (Fig. 5(c)), it can be perceived that the activation energy,  $E_A$ , for the  $\text{MgFe}_2\text{O}_4$ -doped  $\text{MgH}_2$  composite is  $99.9 \text{ kJ mol}^{-1}$ , which is decrease  $33.1 \text{ kJ mol}^{-1}$  compared with the milled  $\text{MgH}_2$  ( $133.0 \text{ kJ mol}^{-1}$ ). The result indicates that addition of  $\text{MgFe}_2\text{O}_4$  reduces the decomposition activation energy and boost the desorption performances of  $\text{MgH}_2$ .

Fig. 6 presents the microstructures of the pure and milled  $\text{MgH}_2$ , and  $\text{MgFe}_2\text{O}_4$ -doped  $\text{MgH}_2$ . From the images, it can be

seen clearly that the particle size of the pure  $\text{MgH}_2$  is around  $50\text{--}100 \mu\text{m}$  (Fig. 6(a)). Fig. 6(b) shows the image of the  $\text{MgH}_2$  after 1 h ball milling. The size of the milled  $\text{MgH}_2$  was decreased dramatically compared to the pure  $\text{MgH}_2$ . However, the image shows agglomeration and inconsistent particle sizes. Fig. 6(c) shows that the particle size of 10 wt%  $\text{MgFe}_2\text{O}_4$ -doped  $\text{MgH}_2$  was the smallest and had less agglomeration than the pure and milled  $\text{MgH}_2$ . Smallest particle size gives a larger region of contact to the  $\text{MgH}_2$ , thus resulting in the higher rate of reaction of  $\text{MgH}_2$ .

To investigate the phase structure, XRD measurement was performed on the 10 wt%  $\text{MgFe}_2\text{O}_4$ -doped  $\text{MgH}_2$  sample, as shown in Fig. 7. From Fig. 7(a), it can be observed that the  $\text{MgH}_2$  and  $\text{MgFe}_2\text{O}_4$  phases are present in the as-milled  $\text{MgFe}_2\text{O}_4$ -doped  $\text{MgH}_2$  sample. No additional peaks were found from the spectra. After dehydrogenation at  $450^\circ\text{C}$  (Fig. 7(b)), the XRD pattern showed that the  $\text{MgH}_2$  was completely dehydrogenated to Mg. This result demonstrates that the decomposition of  $\text{MgH}_2$  was completed after heating for up to  $450^\circ\text{C}$ . Furthermore, a small peak of MgO and Fe formed after the desorption process, thus demonstrate that the partial reaction of  $\text{MgH}_2$  with  $\text{MgFe}_2\text{O}_4$  may occur during the heating process as follows:



The standard Gibbs Free energy,  $\Delta G_f^\circ$ , of  $\text{MgH}_2$ ,  $\text{MgFe}_2\text{O}_4$  and MgO are  $-35.9824$ ,  $-1317.1232$  and  $-569.024 \text{ kJ mol}^{-1}$ ,

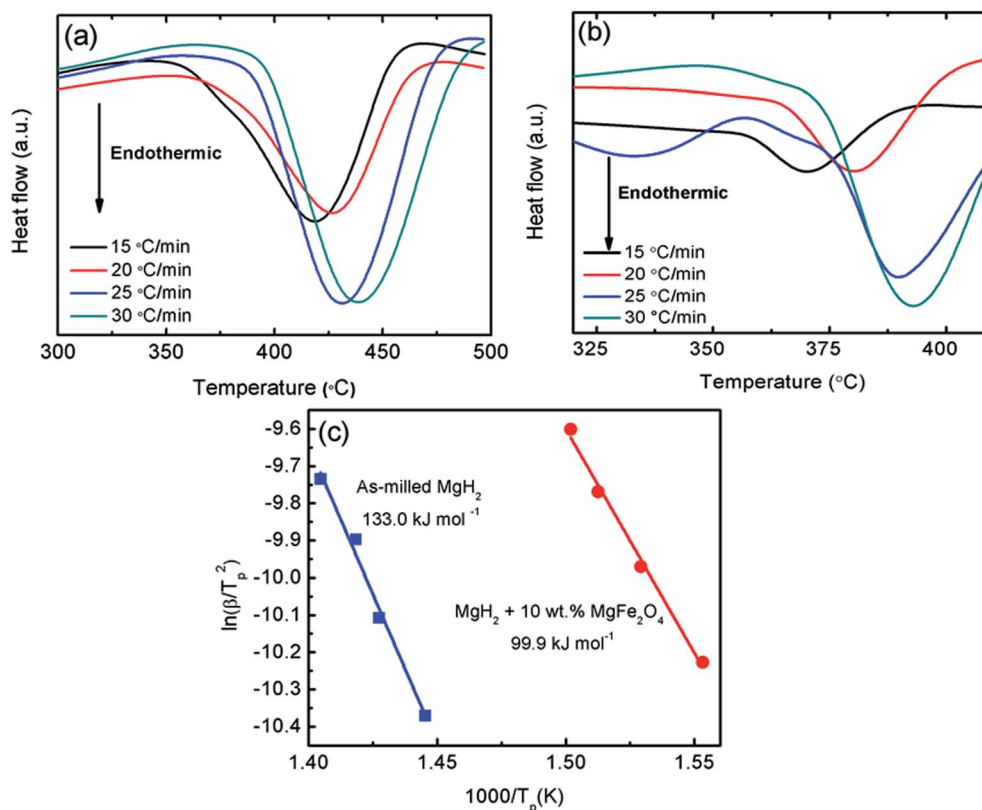


Fig. 5 DSC curves at heating rates of 15, 20, 25, and  $30^\circ\text{C min}^{-1}$  for (a) milled  $\text{MgH}_2$ , (b)  $\text{MgH}_2 + 10 \text{ wt}\% \text{ MgFe}_2\text{O}_4$  and (c) the Kissinger plot of decomposition for 10 wt%  $\text{MgFe}_2\text{O}_4$ -doped  $\text{MgH}_2$  composite and milled  $\text{MgH}_2$ .



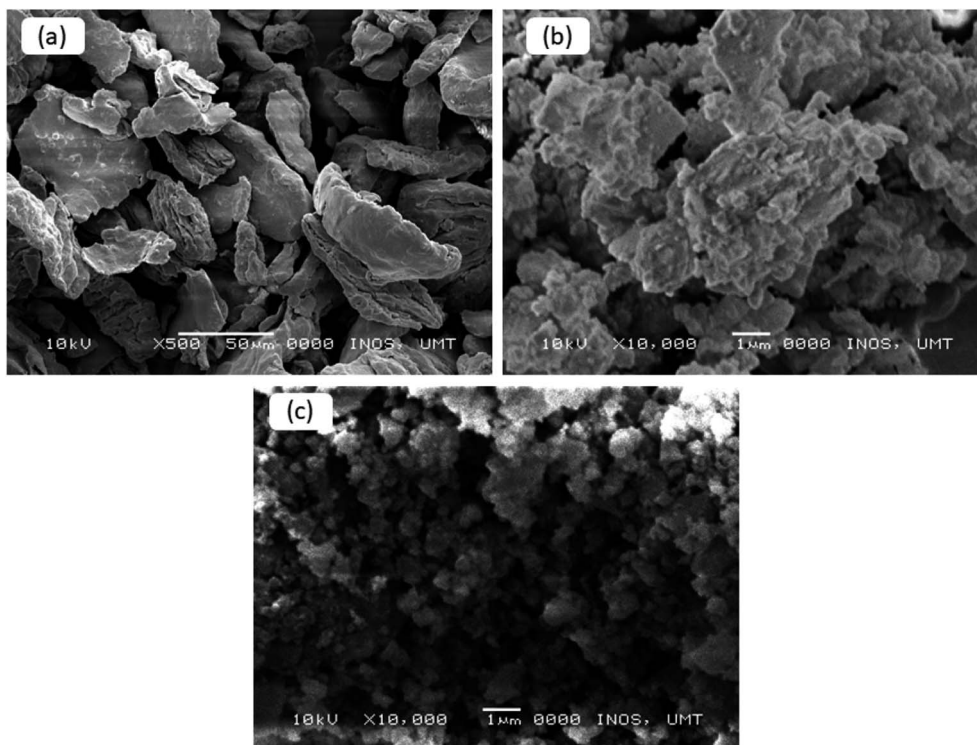


Fig. 6 SEM images for the pure  $\text{MgH}_2$  (a), milled  $\text{MgH}_2$  (b) and  $\text{MgH}_2 + 10 \text{ wt\% MgFe}_2\text{O}_4$  (c).

respectively.<sup>42</sup> The total change  $\Delta G$  correlated with the reaction in eqn (3) is  $-815.0168 \text{ kJ mol}^{-1}$ . These values can confirm the possibility of the reaction in eqn (3) from thermodynamic potentials. Fig. 7(c) shows the XRD patterns for the rehydrogenated sample under 33.0 atm  $\text{H}_2$  at 320 °C. The result illustrates that the phase of Mg was fully converted into  $\text{MgH}_2$ . Furthermore, the peak of Fe and MgO still remained after undergo rehydrogenation.

From the above analyses, the improvements in the sorption properties of  $\text{MgH}_2$  doped with 10 wt%  $\text{MgFe}_2\text{O}_4$  may be resulted from the formations of Fe and MgO. Fe and MgO may act as the real catalysts that play a vital role in the improvements of  $\text{MgH}_2$  sorptions. Therefore, to verify the effect of Fe and MgO on  $\text{MgH}_2$ , samples of 10 wt% MgO-doped  $\text{MgH}_2$  and 10 wt% Fe-doped  $\text{MgH}_2$  were prepared and the TPD profiles for the dehydrogenations were shown as in Fig. 8. It is clearly seen that the decomposition temperature of  $\text{MgH}_2$  are reduced with the addition of MgO or Fe as compared to the pure and milled  $\text{MgH}_2$ . However, the performance of these MgO and Fe are not significant as the sample of 10 wt% of  $\text{MgFe}_2\text{O}_4$  doped with  $\text{MgH}_2$ . This demonstrated that the *in situ* generated MgO and Fe from the reaction of  $\text{MgH}_2 + 10 \text{ wt\% of MgFe}_2\text{O}_4$  may play a significant role that introduce a synergetic catalytic effect that cause a significant improvement on the dehydrogenation performances of  $\text{MgH}_2$  doped with 10 wt% of  $\text{MgFe}_2\text{O}_4$ . In addition, the *in situ* formed Fe and MgO in the  $\text{MgH}_2 + 10 \text{ wt\% of MgFe}_2\text{O}_4$  sample are speculated to have a higher degree of dispersion and more compact phase segregation as compared to the milled  $\text{MgH}_2 + 10 \text{ wt\% Fe}$  and milled  $\text{MgH}_2 + 10 \text{ wt\%}$

MgO. This would be likely to lead the improvement of the sorption kinetics.

From the result obtained, we postulate that formation of fresh and fine MgO and Fe species which resulted from the reaction between  $\text{MgH}_2$  and  $\text{MgFe}_2\text{O}_4$  during the dehydrogenation process may play significant role in improving the sorption performances of  $\text{MgH}_2$ . Numerous studies have claimed that the newly active species formed during the de/absorption process may play as a real catalyst in the enhancement of  $\text{MgH}_2$  sorption.<sup>43,44</sup> Many works have proven that Fe is

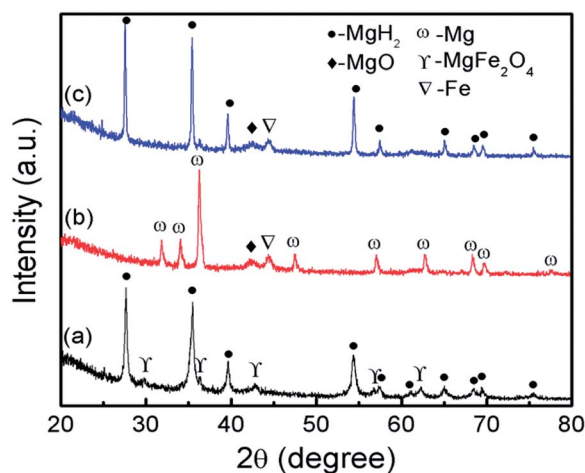


Fig. 7 XRD spectra of the  $\text{MgH}_2 + 10 \text{ wt\% MgFe}_2\text{O}_4$  (a) after ball milling for 1 h, (b) after desorption under 1.0 atm at 450 °C and (c) after absorption under 33.0 atm at 320 °C.



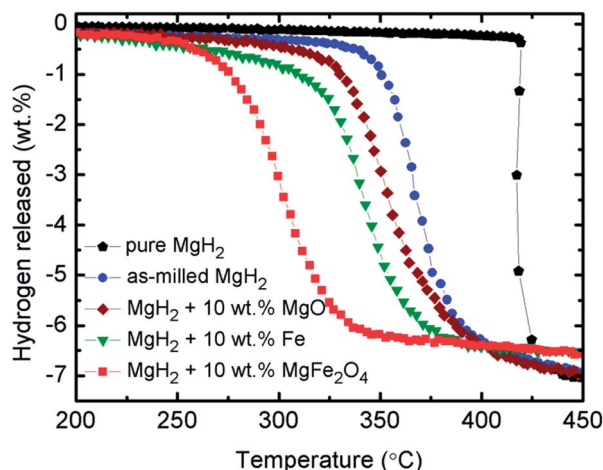


Fig. 8 Decomposition temperature profile of pure and milled  $\text{MgH}_2$ , 10 wt%  $\text{MgO}$ -doped  $\text{MgH}_2$ , 10 wt%  $\text{Fe}$ -doped  $\text{MgH}_2$  and 10 wt%  $\text{MgFe}_2\text{O}_4$ -doped  $\text{MgH}_2$  sample.

an excellent catalyst for sorption performance in  $\text{MgH}_2$ .<sup>7–9</sup> It is believed that the presence of fresh and fine  $\text{Fe}$  could interact with  $\text{H}_2$  molecules, thus possibly leading to the dissociation of  $\text{H}_2$  molecules and the improvement of the de/rehydrogenation kinetic. Furthermore, previous studies have shown that the sorption performance in  $\text{MgH}_2$  can be enhanced with the addition of  $\text{MgO}$ . Ares-Fernández and Aguey-Zinsou<sup>45</sup> claimed that the addition of  $\text{MgO}$  to  $\text{MgH}_2$  during the milling process led to an enhancement of sorption kinetics because of the high electronegativity  $\text{MgO}$ . In another study, the same group also claimed that during the milling process,  $\text{MgO}$  may act as a process control agent that can lead to the reduction of the particle agglomeration of  $\text{MgH}_2$  by an optimal breakage rate, thus aiding the high stability of these particles and evading the use of cold welding.<sup>46</sup> Shan *et al.*<sup>15</sup> also revealed that  $\text{MgO}$  has a great catalytic effect on the  $\text{MgH}_2$  sorption performance. Their study showed that during the heating process in  $\text{CoFe}_2\text{O}_4$ -doped  $\text{MgH}_2$  composite system,  $\text{MgO}$  is formed. The catalytic effect of  $\text{MgO}$  could work together with the catalytic role of the  $\text{Fe}$  metal to create a synergetic effect. Therefore, the *in situ* active species of  $\text{Fe}$  and  $\text{MgO}$  may actually act as real catalysts and further enhance the hydrogen sorption performance of  $\text{MgH}_2$ . However, further studies are needed to elucidate more details on the exact role of  $\text{MgFe}_2\text{O}_4$  addition in  $\text{MgH}_2$ .

## 4. Conclusion

In this study, nanolayer-like-shaped  $\text{MgFe}_2\text{O}_4$  was successfully synthesised through a rapid, simple hydrothermal method. The addition of 10 wt% as-synthesised  $\text{MgFe}_2\text{O}_4$  to  $\text{MgH}_2$  reduces the onset decomposition temperature and enhances sorption kinetics. The  $\text{MgFe}_2\text{O}_4$ -doped  $\text{MgH}_2$  sample has started to release  $\text{H}_2$  at approximately 250 °C, 90 °C and 170 °C lower than milled and pure  $\text{MgH}_2$  respectively. In a duration of 10 min, the isothermal desorption kinetic study showed that the doped sample can release

approximately 4.8 wt%  $\text{H}_2$  at 320 °C while the milled  $\text{MgH}_2$  only desorbed less than 1.0 wt%  $\text{H}_2$  under the same condition. For isothermal absorption kinetics, the doped sample can absorb approximately 5.5 wt%  $\text{H}_2$  in 10 min at 200 °C. By contrast, the milled  $\text{MgH}_2$  sample absorbed only 4.0 wt%  $\text{H}_2$  in the same condition. From the Kissinger analysis, the apparent activation energies,  $E_A$ , for the  $\text{MgFe}_2\text{O}_4$ -doped  $\text{MgH}_2$  sample were calculated to be 99.9  $\text{kJ mol}^{-1}$ , which is decreased by 33.1  $\text{kJ mol}^{-1}$  compared with the milled  $\text{MgH}_2$  (133.0  $\text{kJ mol}^{-1}$ ). The XRD exploration displays the formation of new species of  $\text{Fe}$  and  $\text{MgO}$  after the dehydrogenation process, and these species remained unchanged after rehydrogenation. It is believed that the new species of  $\text{Fe}$  and  $\text{MgO}$  play a synergistic role in enhancing the hydrogen storage performances of  $\text{MgH}_2$ .

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

The authors thank the Ministry of Higher Education of Malaysia for financial support through the Fundamental Research Grant Scheme (FRGS 59362). The authors also would like to give appreciation to Universiti Malaysia Terengganu for the good facilities to accomplish this project.

## References

- 1 I. P. Jain, C. Lal and A. Jain, *Int. J. Hydrogen Energy*, 2010, **35**, 5133–5144.
- 2 L. Ouyang, J. Tang, Y. Zhao, H. Wang, X. Yao, J. Liu, J. Zou and M. Zhu, *Sci. Rep.*, 2015, **5**, 10776.
- 3 M. Polanski, J. Bystrzycki and T. Plocinski, *Int. J. Hydrogen Energy*, 2008, **33**, 1859–1867.
- 4 J. Huot, G. Liang, S. Boily, A. Van Neste and R. Schulz, *J. Alloys Compd.*, 1999, **293–295**, 495–500.
- 5 N. N. Sulaiman and M. Ismail, *Dalton Trans.*, 2016, **45**, 19380–19388.
- 6 M. A. Lillo-Ródenas, Z. X. Guo, K. F. Aguey-Zinsou, D. Cazorla-Amorós and A. Linares-Solano, *Carbon*, 2008, **46**, 126–137.
- 7 N. Hanada, T. Ichikawa and H. Fujii, *J. Phys. Chem. B*, 2005, **109**, 7188–7194.
- 8 H. Chen, H. Yu, Q. Zhang, B. Liu, P. Liu, X. Zhou, Z. Han and S. Zhou, *J. Power Sources*, 2016, **322**, 179–186.
- 9 G. Liang, J. Huot, S. Boily, A. Van Neste and R. Schulz, *J. Alloys Compd.*, 1999, **292**, 247–252.
- 10 S. A. Shevlin and Z. X. Guo, *J. Phys. Chem. C*, 2013, **117**, 10883–10891.
- 11 J. Lu, Y. J. Choi, Z. Z. Fang, H. Y. Sohn and E. Ronnebro, *J. Am. Chem. Soc.*, 2009, **131**, 15843–15852.
- 12 N. Patelli, M. Calizzi, A. Migliori, V. Morandi and L. Pasquini, *J. Phys. Chem. C*, 2017, **121**, 11166–11177.
- 13 N. S. Mustafa and M. Ismail, *J. Alloys Compd.*, 2017, **695**, 2532–2538.



- 14 D. Pukazhselvan, N. Nasani, P. Correia, E. Carbó-Argibay, G. Otero-Irurueta, D. G. Stroppa and D. P. Fagg, *J. Power Sources*, 2017, **362**, 174–183.
- 15 J. Shan, P. Li, Q. Wan, F. Zhai, J. Zhang, Z. Li, Z. Liu, A. A. Volinsky and X. Qu, *J. Power Sources*, 2014, **268**, 778–786.
- 16 Z. Jalil, A. Rahwanto, F. Mulana and M. Mustanir, *Int. J. Technol.*, 2016, **7**, 1301–1306.
- 17 T. Ma, S. Isobe, Y. Wang, N. Hashimoto and S. Ohnuki, *J. Phys. Chem. C*, 2013, **117**, 10302–10307.
- 18 M. S. Yahya and M. Ismail, *Int. J. Hydrogen Energy*, 2018, **43**, 6244–6255.
- 19 N. N. Sulaiman, N. S. Mustafa and M. Ismail, *Dalton Trans.*, 2016, **45**, 7085–7093.
- 20 L. P. Ma, X. D. Kang, H. B. Dai, Y. Liang, Z. Z. Fang, P. J. Wang, P. Wang and H. M. Cheng, *Acta Mater.*, 2009, **57**, 2250–2258.
- 21 N. N. Sulaiman, N. Juahir, N. S. Mustafa, F. A. Halim Yap and M. Ismail, *J. Energy Chem.*, 2016, **25**, 832–839.
- 22 D. Wu, L. Ouyang, C. Wu, H. Wang, J. Liu, L. Sun and M. Zhu, *J. Alloys Compd.*, 2015, **642**, 180–184.
- 23 X. B. Yu, Y. H. Guo, H. Yang, Z. Wu, D. M. Grant and G. S. Walker, *J. Phys. Chem. C*, 2009, **113**, 5324–5328.
- 24 X. B. Yu, Z. X. Yang, H. K. Liu, D. M. Grant and G. S. Walker, *Int. J. Hydrogen Energy*, 2010, **35**, 6338–6344.
- 25 J. Zhang, J. Shan, P. Li, F. Zhai, Q. Wan, Z. Liu and X. Qu, *J. Alloys Compd.*, 2015, **643**, 174–180.
- 26 P. Li, Q. Wan, Z. Li, F. Zhai, Y. Li, L. Cui, X. Qu and A. A. Volinsky, *J. Power Sources*, 2013, **239**, 201–206.
- 27 N. H. Idris, N. S. Mustafa and M. Ismail, *Int. J. Hydrogen Energy*, 2017, **42**, 21114–21120.
- 28 N. Juahir, N. S. Mustafa, A. Sinin and M. Ismail, *RSC Adv.*, 2015, **5**, 60983–60989.
- 29 Q. Wan, P. Li, J. Shan, F. Zhai, Z. Li and X. Qu, *J. Phys. Chem. C*, 2015, **119**, 2925–2934.
- 30 T. Zhang, S. Isobe, A. Jain, Y. Wang, S. Yamaguchi, H. Miyaoka, T. Ichikawa, Y. Kojima and N. Hashimoto, *J. Alloys Compd.*, 2017, **711**, 400–405.
- 31 T. Zhang, S. Isobe, Y. Wang, H. Oka, N. Hashimoto and S. Ohnuki, *J. Mater. Chem. A*, 2014, **2**, 4361–4365.
- 32 G. Xu, N. Shen, L. Chen, Y. Chen and W. Zhang, *Mater. Res. Bull.*, 2017, **89**, 197–203.
- 33 N. S. Mustafa, N. N. Sulaiman and M. Ismail, *RSC Adv.*, 2016, **6**, 110004–110010.
- 34 M. Baricco, M. W. Rahman, S. Livraghi, A. Castellero, S. Enzo and E. Giamello, *J. Alloys Compd.*, 2012, **536**(supplement 1), S216–S221.
- 35 M. S. Yahya and M. Ismail, *J. Energy Chem.*, 2018, DOI: org/10.1016/j.jechem.2017.10.020.
- 36 A. Pradeep, P. Priyadharsini and G. Chandrasekaran, *J. Magn. Magn. Mater.*, 2008, **320**, 2774–2779.
- 37 K. B. Modi, M. C. Chhantbar and H. H. Joshi, *Ceram. Int.*, 2006, **32**, 111–114.
- 38 Y. Yin, W. Liu, N. Huo and S. Yang, *ACS Sustainable Chem. Eng.*, 2017, **5**, 563–570.
- 39 Z. Yan, J. Gao, Y. Li, M. Zhang and M. Guo, *RSC Adv.*, 2015, **5**, 92778–92787.
- 40 Y. Liu, C. Liang, H. Zhou, M. Gao, H. Pan and Q. Wang, *Chem. Commun.*, 2011, **47**, 1740–1742.
- 41 H. E. Kissinger, *Anal. Chem.*, 1957, **29**, 1702–1706.
- 42 <http://www.chemistry-reference.com/StandardThermodynamicValues.pdf>.
- 43 Y. Cheng, W. Zhang, J. Liu, K. Cheng and Z. Zhao, *Int. J. Hydrogen Energy*, 2017, **42**, 356–365.
- 44 M. Ismail, N. S. Mustafa, N. Juahir and F. A. H. Yap, *Mater. Chem. Phys.*, 2016, **170**, 77–82.
- 45 J.-R. Ares-Fernández and K.-F. Aguey-Zinsou, *Catalysts*, 2012, **2**, 330.
- 46 K. F. Aguey-Zinsou, J. R. Ares Fernandez, T. Klassen and R. Bormann, *Mater. Res. Bull.*, 2006, **41**, 1118–1126.

