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Improved hydrogen storage properties of MgH$_2$ by addition of Co$_2$NiO nanoparticles

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Abstract

A sample of MgH$_2$ and 10 wt.% Co$_2$NiO was prepared by the ball milling technique. The hydrogen storage properties and reaction mechanism of the sample were examined. The temperature-programmed desorption result shows that the addition of 10 wt.% Co$_2$NiO to MgH$_2$ exhibited a lower onset desorption temperature of 300 °C, which was decreased to 117 and 70 °C compared to as-received and as-milled MgH$_2$, respectively. The de/rehydrogenation kinetics of MgH$_2$ + 10 wt.% Co$_2$NiO showed improvement compared to un-doped MgH$_2$. The results of the Kissinger plot shows that the activation energy for the hydrogen desorption of MgH$_2$ was reduced to about 65.0 and 15.0 kJ/mol compared to as-received and as-milled MgH$_2$, respectively. Meanwhile, the X-ray diffraction analysis shows the formation of a new phase of Mg-Co alloy and Co$_{1.29}$Ni$_{1.71}$O$_4$ after the dehydrogenation and rehydrogenation process. It is reasonable to conclude that the Co$_2$NiO additive plays a catalytic role through the formation of active species of Mg-Co alloy and Co$_{1.29}$Ni$_{1.71}$O$_4$ during the heating process, thus improving the hydrogen storage properties of MgH$_2$. 

1. Introduction

The U.S Department of Energy has established a minimum target of 5.5 wt.% ab/desorption hydrogen storage capacity for the year 2015.\(^1\) MgH\(_2\) can be seen as a promising material among metal hydrides due to its high gravimetric hydrogen storage (7.6wt.%), good reversibility, and low cost.\(^2\) However, MgH\(_2\) have deficiencies, including high decomposition temperature and slow desorption/absorption kinetics.\(^3\) In order to make MgH\(_2\) feasible as one of the potential materials for solid state hydrogen storage, different approaches have been used including improving the surface and kinetics by ball milling,\(^4\) adding catalyst,\(^5,6\) and using the destabilization concept.\(^7-12\) The addition of catalysts by ball milling into MgH\(_2\) has produced a significant effect on hydrogen sorption properties,\(^5,6\) thus it has caught the interest of many researchers. Various additives have been doped into MgH\(_2\) such as metal,\(^13-15\) alloy,\(^16,17\) metal oxide,\(^18-21\) metal halide,\(^5,22-27\) carbon materials,\(^28-30\) and metal hydrides.\(^31,32\)

The addition of transition metal oxides has shown promising results in the ab/desorption kinetics of MgH\(_2\). This enhancement could be associated with a highly effective catalysis shown by the transition of metal compounds due to the high affinity of metal cation transition towards hydrogen.\(^33-37\) Besides that, transition metal oxides also can act as a good catalyst by facilitating the dissociation of hydrogen molecules and the recombination of hydrogen atom towards the molecular state.\(^38\) It is believed that the additive oxide phase facilitates to overcome the MgO layer formed on the surface of MgH\(_2\) particles, thus improving the reaction kinetics.\(^39,40\)

To the best of the author’s knowledge, no reported study has used Co\(_2\)NiO nanoparticle as an additive for the hydrogen storage properties of MgH\(_2\). The selection of Co\(_2\)NiO as an additive was driven from several studies, which used Ni- and Co-based additives. Ni- and Co-based additive have been given considerable attraction due to their ability to destabilize the
dehydrogenation of MgH\textsubscript{2}.\textsuperscript{41,42} Mao et al. reported that the dehydrogenation temperature and the sorption kinetics of MgH\textsubscript{2} were improved by doping with NiCl\textsubscript{2} or CoCl\textsubscript{2}. Their results suggest that all the dehydrogenation products MgCl\textsubscript{2}, Mg\textsubscript{2}Ni and Mg\textsubscript{2}Co may play an important role in improving the hydrogen sorption kinetic properties of MgH\textsubscript{2}, while MgCl\textsubscript{2} may play a dominant role.\textsuperscript{38} A recent study by Cabo et al. showed that the addition of mesoporous Ni- and Co based oxides reduced the onset dehydrogenation temperature and lowered the activation energy of MgH\textsubscript{2}.\textsuperscript{43} Meanwhile, Mandzhukova et al. reported that the addition of 10 wt.% nickel cobaltite, NiCo\textsubscript{2}O\textsubscript{4} improved the dehydrogenation kinetics of MgH\textsubscript{2}.\textsuperscript{44,45}

In this paper, the additive effect of Co\textsubscript{2}NiO nanoparticle on the hydrogen storage properties of MgH\textsubscript{2} was investigated. The aim of this study is to combine the \textit{in situ} active species factors together thus enhancing the de/hydrogenation properties of MgH\textsubscript{2}. The hydrogen storage properties and reaction mechanism of MgH\textsubscript{2} and Co\textsubscript{2}NiO were investigated using a Sieverts-type pressure-composition-temperature (PCT) apparatus, X-ray diffraction (XRD), differential scanning calorimetry (DSC), and scanning electron microscope (SEM).

2. \textbf{Experimental details}

MgH\textsubscript{2} (hydrogen storage grade, 98 % purity) and Co\textsubscript{2}NiO (<150 nm size particle, 99 % trace material basis) were purchased from Alfa Aesar and Sigma Aldrich, respectively and were used as received without further purification. Sample handling was performed in an MBraun Unilab glove box filled with high-purity Ar atmosphere. Approximately 200 mg MgH\textsubscript{2} was added with 10 wt.% Co\textsubscript{2}NiO. This mixture was loaded into a sealed stainless steel vial together with four hardened stainless balls. As-milled MgH\textsubscript{2} sample under the same condition was prepared for comparison. Ball milling was performed in a planetary ball mill (NQM-0.4) for 1h.
by milling for 1/4 h, resting for 2 min, and then milling for another 1/4 h in a different direction for 3 cycles at the rate of 400 rpm. The ratio of the weight of the balls to the weight of the powder was 80:1.

The temperature-programmed desorption (TPD) and re/dehydrogenation kinetics experiments were performed in a Sieverts-type pressure-composition-temperature (PCT) apparatus (Advanced Materials Corporation). The sample was loaded into a sample vessel in the glove box. For the TPD experiment, the samples were heated in a vacuum chamber from room temperature to 450 °C with a heating rate of 5 °C/min and the lowest decomposition temperature determined by the amount of desorbed hydrogen. The re/dehydrogenation kinetics experiments were performed at temperature of 320 °C with hydrogen pressure of 30 atm and 1 atm, respectively.

The phase structure of as-milled samples, before and after desorption and after rehydrogenation were measured using Rigaku MiniFlex II Diffractometer with Cu Kα radiation. Before the measurement, a small amount of sample was spread uniformly in the sample holder and wrapped with a plastic wrap to prevent oxidation. θ - 2θ scans were carried out over the diffraction angles from 20° to 80° at a speed of 2.00°/min. Meanwhile, the microstructure of the samples were characterized using a scanning electron microscope (SEM; JEOL JSM-6360LA) by preparing the samples on the surface of carbon tape and then coating it with gold spray under vacuumed condition. All samples were also prepared in the glove box in order to minimize oxidation. A DSC analysis was carried out using a Mettler Toledo TGA/DSC 1. About 5-6 mg weight of the sample was loaded in an alumina crucible in the glove box. The crucible was then placed in a sealed glass bottle in order to prevent oxidation during transportation from the glove
box to the DSC apparatus. The samples were heated from room temperature to 480-550 °C under Ar atmosphere with different heating rates. An empty alumina crucible was used for reference.

3. Results and discussion

The dehydrogenation behavior of as-received MgH₂, as-milled MgH₂, and the MgH₂ + 10 wt.% Co₂NiO composite was investigated using a Sieverts-type PCT apparatus. Fig.1 presents the temperature-programmed-desorption (TPD) performances of as-received MgH₂, as-milled MgH₂, and the MgH₂ doped with 10 wt.% Co₂NiO. From the TPD curves, it can be seen clearly that the addition of 10 wt.% of Co₂NiO decreased the onset decomposition temperature compared to as-milled and as-received MgH₂. The onset decomposition of as-received and as-milled MgH₂ was about 417 and 370 °C with a total dehydrogenation capacity of 6.2 and 5.4 wt.% H₂ at 450 °C, respectively. These results show that the ball milling process also has an influence in reducing the onset desorption temperature of MgH₂ due to the larger surface area in magnesium surfaces. Therefore, a higher diffusion hydrogen absorption can be achieved.⁴,¹⁹ However, the as-milled MgH₂ showed slightly lower hydrogen desorption capacity compared to as-received MgH₂, and this could happen due to the released hydrogen during ball milling process. MgH₂ + 10 wt.% Co₂NiO had a positive effect on the onset desorption temperature of MgH₂ since the desorption started at around 300 °C with a total dehydrogenation capacity of 5.3 wt.% hydrogen at 450 °C, which was lowered by 117 °C and 70 °C compared to the as-received and as-milled MgH₂. These results suggest that the Co₂NiO component in the doped MgH₂ could play a catalytic role and thus, improving the onset temperature of MgH₂.

Fig.2 shows the isothermal desorption kinetics curve for as-milled MgH₂ and MgH₂ + 10 wt.% Co₂NiO composite measured at 320 °C under 1.0 atm pressure. The result shows that the
sample doped with 10 wt.% Co$_2$NiO released about 2.5 wt.% hydrogen in 6 min. In contrast, almost no hydrogen was released in the same period by as-milled MgH$_2$. Therefore, it can be assumed that Co$_2$NiO also had significant effect on improving the dehydrogenation kinetics of MgH$_2$. Fig.3 shows the isothermal rehydrogenation kinetics for as-milled MgH$_2$ and MgH$_2$ + 10 wt.% Co$_2$NiO samples. The samples were soaked at a constant temperature of 320 °C and under 30.0 atm hydrogen pressure. The hydrogen absorbed by MgH$_2$ doped with 10 wt.% Co$_2$NiO samples reached about 2.5 wt.% hydrogen within 1.7 min, with a total hydrogen absorption of 3.75 wt.%.

Meanwhile, as-milled MgH$_2$ took about 3.4 min to absorb the same amount of hydrogen with a total hydrogen absorption of 3.78 wt.%.

It can be seen that the doped sample showed better rehydrogenation kinetics than as-milled MgH$_2$. Taken together, these results suggest that the rehydrogenation kinetics of MgH$_2$ can also be improved by doping it with Co$_2$NiO.

Fig. 4 represents the cyclic performance of MgH$_2$ + 10 wt.% Co$_2$NiO sample at temperature of 320 °C and under 30 atm hydrogen pressure. The hydrogen absorption kinetics of the sample shows some degradation after prolonged cyclic. However, the degradation was involving small values. After the 10$^{th}$ cycle, the absorption continued to be good with hydrogen capacity of 3.44 wt.%. Meanwhile, the cycle performances for the desorption kinetics of MgH$_2$ + 10 wt.% Co$_2$NiO sample also shows good performances even after 10$^{th}$ cycle as shown in Fig. 5 with the desorption kinetics of the sample in 60 minutes for 10$^{th}$ cycle was 3.75 wt.%. The hydrogen desorption also degrades after prolonged time with involving small amount hydrogen. This result shows that the good cyclic performances of MgH$_2$ can be achieved by doping with Co$_2$NiO.
Fig. 6 shows the recyclability capacity of the MgH$_2$ + 10 wt.% Co$_2$NiO sample after 60 min absorb/desorb for the ten cycles. From the graph, it can be seen that for all cycles, the hydrogen desorption have slightly higher capacity compared to hydrogen absorption. It can be seen that the amount of hydrogen absorbed and desorbed degrades after prolonged cyclic. For hydrogen desorption, shows only slight degradation observed in hydrogen capacity of the 5$^{th}$ to 10$^{th}$ cycles compared to amount degrades for the first four cycles.

Fig. 7 presents the DSC curves of the MgH$_2$ + 10 wt.% Co$_2$NiO sample at a heating rate of 15 °C/min. As-received MgH$_2$ and as-milled MgH$_2$ were included for comparison purposes. The DSC curve of as-received MgH$_2$ showed only one strong endothermic peak at approximately 454.06 °C, which corresponds to the decomposition of MgH$_2$. Meanwhile, the DSC curves for as-milled MgH$_2$ and MgH$_2$ + 10 wt.% Co$_2$NiO had strong endothermic peaks at 418.72 °C and 412.66 °C, respectively. The noticeable reduction in the peak temperatures of the samples based on the DSC results revealed that dehydrogenation was improved by adding Co$_2$NiO. However, it could be seen that the onset decomposition temperature of the samples in DSC were slightly higher than those in TPD (Fig. 1), which could be due to the differences in heating rates and atmospheres between DSC and PCT measurements, as discussed in our previous papers.$^{46-49}$ TPD measurement was conducted from 1.0 atm vacuum with a 5 °C/min heating rate, while DSC measurement was run under 1.0 atm argon flow with heating rate of 15 °C/min.

The Kissinger equation$^{50}$ was used to calculate the activation energy (E$_A$) of MgH$_2$ + 10 wt.% Co$_2$NiO at different heating rates. The activation energy of as-received and as-milled MgH$_2$ was included for comparison purposes. Fig. 8 (a) – (c) shows the DSC curves at different heating rates for as-received MgH$_2$, as-milled MgH$_2$, and MgH$_2$ + 10 wt.% Co$_2$NiO, respectively. From the Kissinger equation:

\[
E_A = \frac{R \ln(\beta)}{\ln\left(\frac{T_d}{T_i}\right)}
\]
\[ \ln \left( \frac{\beta}{T_p^2} \right) = \frac{-E_A}{RT_p} + A \]  

(1)

where \( \beta \) is the heating rate, \( T_p \) is the peak temperature in the DSC curve, \( R \) is the gas constant, and \( A \) is a linear constant. Thus, the activation energy, \( E_A \), can be obtained from the slope of the plot, \( \ln \left( \frac{\beta}{T_p^2} \right) \) versus \( 1000/T_p \). Fig. 8 (d) shows the Kissinger plot for the dehydrogenation of \( \text{MgH}_2 + 10 \text{ wt.}\% \text{Co}_2\text{NiO} \) composite compared to as-received and as-milled \( \text{MgH}_2 \). The apparent activation energy for \( \text{MgH}_2 + 10 \text{ wt.}\% \text{Co}_2\text{NiO} \) composite estimated from the Kissinger analysis was found to be 118.0 kJ/mol, which was lower than that of as-received and as-milled \( \text{MgH}_2 \) (183.0 and 133.0 kJ/mol, respectively). These values show that improved dehydrogenation behavior and reduced activation energy can be achieved by doping \( \text{Co}_2\text{NiO} \) with \( \text{MgH}_2 \).

Fig. 9 (a)-(c) show the SEM images of as-received \( \text{MgH}_2 \), as-milled \( \text{MgH}_2 \), and \( \text{MgH}_2 + 10 \text{ wt.}\% \text{Co}_2\text{NiO} \), respectively. In Fig. 9 (a), it can be seen that as-received particles of \( \text{MgH}_2 \) were angular shaped with sizes larger than 100 µm. Fig. 9 (b) shows a sample subjected to 1 h ball milling process, which caused a drastic reduction in \( \text{MgH}_2 \) particles with non-homogenous particles size. Besides that, some agglomeration was detected in the sample. After introducing \( \text{Co}_2\text{NiO} \) through the ball milling process, the size of the particles became smaller compared to as-milled \( \text{MgH}_2 \) sample (Fig. 9 (c)). The hardness of the \( \text{Co}_2\text{NiO} \) helped in breaking \( \text{MgH}_2 \) particles into smaller sizes, increasing the specific surface area and reducing the diffusion length of the hydrogen, thus achieving the minimum onset desorption temperature.\textsuperscript{24,51}

To have a better understanding on the reaction process and mechanism of this sample, XRD measurements were performed on \( \text{MgH}_2 + 10 \text{ wt.}\% \text{Co}_2\text{NiO} \) samples after 1 h of milling, after dehydrogenation at 250 °C, after dehydrogenation at 450 °C, and after rehydrogenation at 320 °C under 30.0 atm hydrogen pressure, as shown in Fig. 10. After 1 h of milling, the \( \text{MgH}_2 \) and \( \text{Co}_2\text{NiO} \) peaks were seen to dominate the XRD pattern with few Mg peaks. Mg peaks
appeared at this stage confirmed there was hydrogen released during ball milling. After heating to 250 °C, it was seen that the same peaks appeared, such as those in ball milling. Further heating to 450 °C caused MgH$_2$ and Co$_2$NiO to disappear. The dehydrogenation of MgH$_2$ can be confirmed with distinct Mg peaks, and the transformation of MgH$_2$ into Mg can be represented as follows:

$$\text{MgH}_2 \rightarrow \text{Mg} + \text{H}_2$$ (2)

MgO peak was also detected in the dehydrogenation spectra due to slight oxygen contamination when transferring the samples to the XRD instrument. In addition, new Mg-Co alloy and Co$_{1.29}$Ni$_{1.71}$O$_4$ peaks could also be seen. The presence of Mg-Co alloy and Co$_{1.29}$Ni$_{1.71}$O$_4$ might have appeared during the dehydrogenation process. XRD examination of the dehydrogenated MgH$_2$ doped with Co$_2$NiO sample verified the formation of Mg-Co alloy and Co$_{1.29}$Ni$_{1.71}$O$_4$ peaks and these peaks remained unchanged after rehydrogenation at 320 °C. Hence, we speculate that the Mg-Co alloy and Co$_{1.29}$Ni$_{1.71}$O$_4$ species could have acted as the real catalysts. In addition, it was seen that Mg was largely transformed into MgH$_2$ after the rehydrogenation process.

In order to investigate the Co$_2$NiO containing phase after dehydrogenation in detail, we prepared a MgH$_2$ + 50 wt.% Co$_2$NiO sample, as it was difficult to analyse the phase composition with 10 wt.% Co$_2$NiO by XRD. Fig. 11 shows the XRD patterns of MgH$_2$ doped with 50 wt.% Co$_2$NiO sample (a) after 1 h ball milling, (b) after dehydrogenation at 250 °C and (c) after dehydrogenation at 450 °C. After increasing the amount of Co$_2$NiO to 50 wt.%, the Co$_2$NiO peaks increased compared to as-milled MgH$_2$ + 10 wt.% Co$_2$NiO sample as shown in Fig 10 (a). Mg peaks were detected in the XRD spectra indicating that hydrogen was released during ball milling. After heating to temperature 250 °C, the same Mg, MgH$_2$ and Co$_2$NiO peaks were seen with few Mg-Co alloy and Co$_{1.29}$Ni$_{1.71}$O$_4$ peaks. The formation of Mg-Co alloy and
Co$_{1.29}$Ni$_{1.71}$O$_4$ at 250 °C indicates that these active species were formed during the heating process. Further temperature increment to 450 °C saw the disappearance of MgH$_2$ and Co$_2$NiO peaks with more frequent appearance of Mg-Co alloy and Co$_{1.29}$Ni$_{1.71}$O$_4$ peaks. As compared to the XRD pattern of MgH$_2$ + 10 wt.% Co$_2$NiO sample (Fig. 10), the formation of Mg-Co alloy and Co$_{1.29}$Ni$_{1.71}$O$_4$ were more discernible after 50 wt.% Co$_2$NiO was added.

From the results, we speculate that the formation of Mg-Co alloy and Co$_{1.29}$Ni$_{1.71}$O$_4$, which resulted from the reaction of MgH$_2$ and Co$_2$NiO during de/hydrogenation process, could play an important role in the enhancement of hydrogen sorption. The formation of Mg-Co alloy in this study is mutual with the findings by Mao et al. They suggested that Mg-Co alloy formed in the MgH$_2$-CoCl$_2$ system could act as a catalyst besides MgCl$_2$ alloy, thus improving the de/hydrogenation of MgH$_2$ through the additive. It can be speculated that, this additive reduces the barrier of nucleation, and thus hydrogen desorption takes place at a lower driving force and the transition metal helps in facilitating the dissociation of hydrogen molecules and the recombination of hydrogen atom towards the molecular state. In addition, it is believed that the newly formed ball-milled or dehydrogenation product in the complex hydride catalyst system could act as a real catalyst to facilitate the de/rehydrogenation steps. In this study, Co-Ni oxide species with an altered valance state, Co$_{1.29}$Ni$_{1.71}$O$_4$, could have acted as a real catalyst because they could create surface activation and form a large amount of nucleation sites at the surface of the MgH$_2$ matrix. It is also speculated that these finely dispersed ball-milled products could serve as the active sites for nucleation by shortening the diffusion distance of the reaction ions.
4. Conclusion

In summary, the hydrogen sorption properties of MgH$_2$ improved after doping it with 10 wt.% Co$_2$NiO. MgH$_2$ + 10 wt.% Co$_2$NiO composite has a lower onset dehydrogenation temperature of 300 °C, which was decreased to about 117 °C and 70 °C compared to as-received and as-milled MgH$_2$, respectively. In terms of dehydrogenation kinetics, MgH$_2$ + 10 wt.% Co$_2$NiO sample released about 2.5 wt.% hydrogen in 6 min at 320 °C, while as-milled MgH$_2$ sample showed no hydrogen release under the same condition. Meanwhile, for absorption kinetics, MgH$_2$ + 10 wt.% Co$_2$NiO sample absorbed about 2.5 wt.% hydrogen within 1.7 min at 320 °C, but as-milled MgH$_2$ sample took about 3.4 min to absorb the same amount of hydrogen. The results from the Kissinger plot showed that the activation energy for hydrogen desorption of MgH$_2$ was reduced compared to those of as-received and as-milled MgH$_2$ from 183.0 and 133.0 kJ/mol to 118.0 kJ/mol, respectively, after the addition of 10 wt.% Co$_2$NiO. It is reasonable to conclude that, in this study, the Co$_2$NiO additive doped with MgH$_2$ played a catalytic role through the formation of active species of Mg-Co alloy and Co$_{1.29}$Ni$_{1.71}$O$_4$ during the heating process. This newly developed product acted as a real catalyst in improving the hydrogen storage properties of MgH$_2$.

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Figure captions

Fig. 1 TPD curves for dehydrogenation of the as-received, as-milled and MgH$_2$ + 10 wt.% Co$_2$NiO composite.

Fig. 2 Isothermal dehydrogenation kinetics of the as-milled and MgH$_2$ + 10 wt.% Co$_2$NiO composite at 320 °C.

Fig. 3 Isothermal rehydrogenation kinetics of the as-milled and doped MgH$_2$ + 10 wt.% Co$_2$NiO composite at 320 °C and under 30.0 atm hydrogen pressure.

Fig. 4 Isothermal rehydrogenation kinetics of the as-milled and doped MgH$_2$ + 10 wt.% Co$_2$NiO composite for the ten cycles.

Fig. 5 Isothermal dehydrogenation kinetics of the as-milled and MgH$_2$ + 10 wt.% Co$_2$NiO composite for the ten cycles.

Fig. 6 Recyclability capacity of the MgH$_2$ + 10 wt.% Co$_2$NiO sample after 60 min absorb/desorb for the ten cycles.

Fig. 7 DSC traces of as-received, as-milled and MgH$_2$ + 10 wt.% Co$_2$NiO at heating rate of 15 °C/min.

Fig. 8 DSC traces of (a) as-received, (b) as-milled MgH$_2$, (c) MgH$_2$ + 10 wt.% Co$_2$NiO at different heating rates of 15 – 30 °C/min and (d) the Kissinger’s analysis for (a) as-received MgH$_2$, (b) as-milled MgH$_2$, and (c) MgH$_2$ doped 10 wt.% Co$_2$NiO composites.

Fig. 9 The SEM images of the (a) as-received MgH$_2$, (b) as-milled MgH$_2$ and (c) MgH$_2$ + 10 wt.% Co$_2$NiO.

Fig. 10 XRD patterns of MgH$_2$ doped 10 wt.% Co$_2$NiO (a) after 1 h ball milling, (b) after dehydrogenation at 250 °C, (c) after dehydrogenation at 450 °C and (d) after rehydrogenation at 320 °C.

Fig. 11 XRD patterns of MgH$_2$ doped 50 wt.% Co$_2$NiO (a) after 1 h ball milling, (b) after dehydrogenation at 250 °C and (c) after dehydrogenation at 450 °C.
References


Figures

Figure 1

![Figure 1]

Figure 2

![Figure 2]
Figure 3

![Graph showing hydrogen absorbed vs. rehydriding time for As-milled MgH₂ and MgH₂ with 10 wt.% Co₂NiO.]

Figure 4

![Graph showing hydrogen absorbed vs. rehydriding time for multiple rehydriding cycles.]

This graph illustrates the hydrogen absorbed (wt.%) over the rehydriding time (min) for different rehydriding cycles.
Figure 5

![Graph showing hydrogen released over dehydrogenation cycles](image)

Figure 6

![Bar chart showing capacity over cycles](image)
Figure 7

Heat flow (a.u.)

As-received MgH$_2$
As-milled MgH$_2$
MgH$_2$ doped 10wt.% Co$_2$NiO

Endothermic

Temperature (°C)

300 350 400 450 500

Figure 8

(a) Heat flow (a.u.)

15 °C·min$^{-1}$
20 °C·min$^{-1}$
25 °C·min$^{-1}$
30 °C·min$^{-1}$

Endothermic

Temperature (°C)

350 400 450 500 550

(b) Heat flow (a.u.)

15 °C·min$^{-1}$
20 °C·min$^{-1}$
25 °C·min$^{-1}$
30 °C·min$^{-1}$

Endothermic

Temperature (°C)

300 350 400 450 500

(c) Heat flow (a.u.)

15 °C·min$^{-1}$
20 °C·min$^{-1}$
25 °C·min$^{-1}$
30 °C·min$^{-1}$

Endothermic

Temperature (°C)

360 380 400 420 440 460 480

(d) $\ln(\mu T_p)$ vs. $1000/\Gamma_p (K^*)$

(a) (b) (c)
Figure 11