

Available online at www.sciencedirect.com



Transactions of Nonferrous Metals Society of China

www.tnmsc.cn



Trans. Nonferrous Met. Soc. China 33(2023) 3465-3475

Catalytic effect of two-dimensional Mo₂TiC₂ MXene for tailoring hydrogen storage performance of MgH₂

Hao-yu ZHANG¹, Gui-bin TIAN¹, Fu-ying WU¹, Zhen-dong YAO², Jia-guang ZHENG¹, Liu-ting ZHANG¹

School of Energy and Power, Jiangsu University of Science and Technology, Zhenjiang 212003, China;
 School of Materials and Chemistry, China Jiliang University, Hangzhou 310018, China

Received 26 May 2022; accepted 21 October 2022

Abstract: Two-dimensional Mo₂TiC₂ MXene material was synthesized by etching Mo₂TiAlC₂ and then doped into MgH₂ to tailor its hydrogen storage performance. The initial hydrogen desorption temperature of the Mo₂TiC₂-doped MgH₂ was significantly reduced from 330 °C (pristine MgH₂) to 187 °C. Isothermal dehydrogenation analysis indicated that the MgH₂+9 wt.% Mo₂TiC₂ composite rapidly discharged 6.4 wt.% H₂ at 300 °C within 4 min. For hydrogenation, the dehydrogenated MgH₂+9 wt.% Mo₂TiC₂ uptook 6.5 wt.% H₂ at 175 °C within 5 min. By calculation, the activation energy for MgH₂+9 wt.% Mo₂TiC₂ was calculated to be (135.6±1.9) kJ/mol for the desorption reaction and (46.1±0.2) kJ/mol for the absorption reaction. After 20 cycles, 1.0 wt.% H₂ was lost for the MgH₂+9 wt.% Mo₂TiC₂ composite. Microstructure analysis results showed that the presence of Mo in Mo₂TiC₂ enhanced the thermal stability of MXene and reduced the amount of active Ti during cycling, leading to poorer catalytic effect of the catalyst compared to Ti₃C₂.

Key words: hydrogen storage performance; magnesium hydride; Mo2TiC2 MXene; catalytic mechanism

1 Introduction

As a clean, safe, efficient and renewable energy, hydrogen is regarded as one of the most promising alternatives for achieving a carbon-free society [1]. Served as a bridge connecting hydrogen production and utilization, the technology of hydrogen storage plays an important role in realizing a future hydrogen economy [2–7]. MgH₂, which can store 7.6 wt.% H₂ reversibly, safely and environmentally friendly, meets the harsh requirements of on-board hydrogen storage [8–10]. Nevertheless, challenges such as high operating temperatures and slow reaction kinetics stand in its practical application [11–13]. In order to solve the above problems, attempts including alloying [14,15], nanosizing [16,17], and catalytic doping [18–20] have been exerted to enhance the hydrogen storage performance of MgH_2 .

Two-dimensional MXene, a grapheme-like transition metal carbide and nitride family, was discovered [21-24] and attracted enormous attention in the research areas of energy conversion and storage afterwards [25,26]. For example, the multilayer Ti₂CT_x MXene showed excellent hydrogen storage performance by reversibly storing over 8 wt.% H₂ under 5-6 MPa pressure at room temperature, which was twice that of previously reported materials in identical conditions in Ref. [27]. Recently, materials that can store hydrogen under moderate conditions have been demonstrated to be served as hydrogen pump to accelerate the absorption/desorption kinetics of MgH₂ [28-31]. MXene was also verified as a remarkable catalyst for hydrogen storage materials.

Liu-ting ZHANG, Tel: +86-15262913186, E-mail: zhanglt89@just.edu.cn

DOI: 10.1016/S1003-6326(23)66347-2

Corresponding author: Fu-ying WU, Tel: +86-18344819581, E-mail: wufuying@just.edu.cn;

^{1003-6326/© 2023} The Nonferrous Metals Society of China. Published by Elsevier Ltd & Science Press

3466

LIU et al [32] found that the addition of 5 wt.% Ti_3C_2 enabled the Mg/MgH₂ system to discharge 6.2 wt.% H₂ within 1 min at 300 °C and charge 6.1 wt.% H₂ within 30 s at 150 °C. CHEN et al [33] found that the onset dehydrogenation temperature of LiBH₄ with 40 wt.% Ti_3C_2 MXene was only 120 °C. The LiBH₄+40 wt.% MXene sample released about 5.4 wt.% H₂ within 1 h at 350 °C. LU et al [34] proved that MgH₂+ 10 wt.% V₂C showed excellent cycle stability without any capacity loss in up to 10 cycles.

To tune the catalytic effect of catalysts, atom substitution is widely adopted as it may present a synergetic effect by forming two or more phases. ZHANG et al [35] found that the 10 wt.% TiVO_{3.5}modified MgH₂ exhibited optimal hydrogen storage performance, as it desorbed 5.0 wt.% H₂ in 10 min at 250 °C and reabsorbed 3.9 wt.% H₂ in 5 s at 100 °C under 5 MPa hydrogen pressure. Besides, a Hamamelis-like structure of K2Ti6O13 showed a remarkable catalytic effect on improving the dehydrogenation of MgH₂ at low temperatures [36]. Inspired by the above results, it is reasonable to conclude that the catalytic effect of MXene can be adjusted by constructing a bimetal MXene. For instance, WANG et al [37] demonstrated that the MgH₂+9 wt.% NbTiC sample had a reduced initial hydrogen desorption temperature of 195 °C. Lately, CHEN et al [38] discovered that Mo was beneficial to the synergy effect between Mo and Ni to promote the break of Mg-H bonds and the dissociation of hydrogen molecules, thus greatly improving the kinetics of Mg/MgH₂ system. Herein, to investigate the effect of Mo on the tuning the catalytic effect of Ti_3C_2 , Mo_2TiC_2 was synthesized by selectively etching the Al layer from the Mo₂TiAlC₂ MAX phase with hydrofluoric acid (HF). The catalytic effect was investigated by measuring the sorption behavior of Mo₂TiC₂-modified MgH₂. Combining hydrogen storage performance with microstructure analysis, the catalytic mechanism was also studied in detail.

2 Experimental

2.1 Sample preparation

All raw materials were used as received without further purification. Mo₂TiAlC₂ powders with a particle size of 38 µm were purchased from Laizhou Kai Kai Ceramic Materials Co., Ltd. HF (40 wt.%) was purchased from Aladdin. Mo₂TiC₂ MXene was synthesized as follows (shown in Fig. 1): 1.5 g Mo₂TiAlC₂ was slowly added to 30 mL of HF and stirred for 2 d at 60 °C. The obtained solution was centrifuged at 8000 r/min 6 times. The obtained precipitates were washed by pure water until the pH value was above 6. The product was finally collected after vacuum drying at 60 °C for 24 h. The MgH₂ powers were prepared by mechanical ball milling and hydrogenation treatment in our laboratory [11]. The as-prepared MgH₂ was mixed with Mo₂TiC₂ MXene by balling mill at 400 r/min for 4 h to form MgH2+6 wt.% Mo2TiC2, MgH2+9 wt.% Mo2TiC2 and MgH2+12 wt.% Mo₂TiC₂ composites, respectively. The mass ratio of ball-to-material for ball milling was 40:1.

2.2 Characterization

An X' Pert Pro X-ray diffraction (PANalytical, the Netherlands, 40 kV, 40 mA) with Cu K_{α} radiation was used to characterize the phase composition of samples at a scanning speed of 5 (°)/min. The microstructure of Mo₂TiC₂ MXene was observed by transmission electron microscope (TEM, Tecnai G2 F30 S-TWIN). The surface chemical information was analyzed by X-ray photoelectron spectroscopy (XPS). The specific surface area and pore diameter of the samples before and after etching were analyzed by nitrogen adsorption–desorption specific surface area test (BET).

The thermal decomposition behavior of the samples was studied by differential scanning calorimetry (DSC). The hydrogen desorption and



Fig. 1 Schematic synthesis process of Mo₂TiC₂

absorption tests were carried out on a Sievert facility. The non-isothermal dehydrogenation was conducted by heating 150 mg of sample from 25 to 450 °C at a rate of 2 °C/min in a self-made reactor, and hydrogenation test was carried out from 25 to 400 °C at a heating rate of 1 °C/min under 3.2 MPa H_2 pressure. In addition, all operations and transfers were carried out in a glove box filled with Ar.

3 Results and discussion

3.1 Characterization of as-prepared Mo₂TiC₂

 Mo_2TiC_2 MXene was synthesized by etching the Mo_2TiAlC_2 matrix. Figure 2(a) presents the XRD patterns of Mo_2TiAlC_2 and Mo_2TiC_2 . The XRD data of the prepared Mo_2TiC_2 are consistent with previously reported one [39]. After etching, the intensity of the (002) diffraction peak increased dramatically, proving the successful formation of the MXene phase. Figure 2(b) shows the TEM image of as-synthesized Mo₂TiC₂. It can be seen clearly that the synthesized Mo₂TiC₂ presents the morphology of transparent graphene-like layers with a thickness of 22.2–28.0 nm. Besides, a typical interlayer spacing of 1.01 nm is shown in HRTEM image of selected area in Fig. 2(c) [40]. EDS mappings in Fig. 2(d) revealed that Mo, Ti, and C were evenly distributed in Mo₂TiC₂. Figures 3(a) and (b) show the nitrogen adsorption-desorption curves (BET) before and after etching. Compared with Mo₂TiAlC₂, the specific surface area of Mo₂TiC₂ was dramatically increased from 6.542 to $26.421 \text{ m}^2/\text{g}.$



Fig. 2 XRD patterns of Mo₂TiAlC₂ and Mo₂TiC₂ (a), TEM images (b, c) and EDS mappings (d) of Mo₂TiC₂



Fig. 3 BET curves of Mo₂TiAlC₂ (a) and Mo₂TiC₂ (b) (*P* is actual gas pressure, P_0 is saturated vapor pressure of gas at measured temperature, and *V* is adsorption capacity)

3468

3.2 Catalytic effect of Mo₂TiC₂ on dehydrogenation property of MgH₂

The catalytic effect of Mo_2TiC_2 on the dehydrogenation performance of MgH_2 was measured by non-isothermal dehydrogenation experiments at a constant heating rate of 2 °C/min. Figure 4(a) shows non-isothermal dehydrogenation curves of MgH_2 with and without Mo_2TiC_2 . MgH_2 and ball-



Fig. 4 Non-isothermal dehydrogenation curves of MgH_2 and Mo_2TiC_2 -modified MgH_2 (a), isothermal dehydrogenation curves of MgH_2 (b) and MgH_2+9 wt.% Mo_2TiC_2 (c)

milled MgH₂ (4 h) began to release hydrogen at 350 °C. Clearly, the addition of Mo₂TiC₂ can remarkably enhance the dehydrogenation performance of MgH₂. Specifically, the dehydrogenation process for MgH2+6 wt.% Mo2TiC2 composite began at 216 °C. The onset desorption temperature of 9 wt.% Mo₂TiC₂ and 12 wt.% Mo₂TiC₂ was further reduced to 210 and 187 °C, respectively. With increasing the doping amount of Mo₂TiC₂, the initial desorption temperature was decreased. However, the dehydrogenation capacity was reduced accordingly. By taking the onset desorption temperature and capacity into consideration, the MgH₂+9 wt.% Mo₂TiC₂ composite which started to release hydrogen at 210 °C with a final capacity of 6.9 wt.% was chosen for the following research. Figures 4(b) and (c) show the isothermal dehydrogenation curves of MgH₂ and MgH₂+9 wt.% Mo₂TiC₂ at different temperatures, respectively. It can be found that MgH₂+9 wt.% Mo₂TiC₂ discharged 5.5 wt.% H₂ in 5 min at 275 °C and 6.4 wt.% H₂ in 3.7 min at 300 °C, respectively. In contrast, higher temperatures of 350 and 375 °C were needed for MgH₂ to release 5.6 wt.% and 6.8 wt.% H₂ in 15 min.

DSC measurements of the MgH₂ and MgH₂+ 9 wt.% Mo₂TiC₂ composite at different heating rates (5, 8, 10, and 12 K/min) were carried out, and the results are shown in Figs. 5(a) and (b), respectively. Kissinger's formula $(\ln (C/T_p^2))$ = $-[E_a/(RT_p)]+A_1$) (C is heating rate, T_p is thermodynamic temperature at maximum reaction rate, R is molar gas constant, and A_1 is a constant) was used to calculate the activation energy $(E_{\rm a})$ of dehydrogenation reaction [15]. The dehydrogeneration apparent activation energy of MgH2 and MgH₂+9 wt.% Mo₂TiC₂ samples was calculated to be 151.4 and 135.6 kJ/mol, respectively (Fig. 5(c)). The reduced activation energy was responsible for the improved hydrogen desorption property of Mo₂TiC₂-modified MgH₂. Compared with other MgH₂-catalyst systems (Table 1), though the activation energy of MgH₂+9 wt.% Mo₂TiC₂ was medium, its onset dehydrogenation temperature was the lowest among them.

Figure 6 shows the pressure-compositiontemperature PCT curves of MgH_2 and MgH_2 + 9 wt.% Mo₂TiC₂ at different temperatures. It can be found that the desorption platform pressures of MgH₂ are 0.227, 0.419, 0.87 and 1.511 MPa at 325, 350, 375 and 400 °C, respectively. The platform pressures of MgH₂+9 wt.% Mo₂TiC₂ at 300, 325, 350 and 375 °C are 0.145, 0.281, 0.605 and 0.872 MPa, respectively. As shown in Fig. 6(c), the enthalpy (ΔH) of hydrogen desorption reaction of MgH₂+9 wt.% Mo₂TiC₂ estimated by van't Hoff equation was 76.2 kJ/mol, slightly lower than that of pure MgH₂ (87.3 kJ/mol).



Fig. 5 DSC curves of MgH_2 (a) and MgH_2+9 wt.% Mo_2TiC_2 (b) at various heating rates, and corresponding Kissinger's plot (c)

Table	1	Hydrogen	storage	performance	of	various
MgH2-	bas	sed hydrogen	n storage	materials		

	n storage mate	11410	
Material	Onset- desorption temperature/ °C	Desorption activation energy/ (kJ·mol ⁻¹)	Source
MgH ₂ + 10 wt.% CeCl ₃	300	149	[41]
4MgH ₂ +Cd	255	143	[42]
MgH ₂ + 10 wt.% LaCl ₃	300	143	[43]
MgH ₂ + 10 wt.% (Ti _{0.5} V _{0.5}) ₃ C	210	77.3	[44]
MgH ₂ + 10 wt.% V ₂ C	190	87.6	[34]
MgH ₂ + 9 wt.% Mo ₂ TiC ₂	187	135.6	This work

3.3 Catalytic effect of Mo₂TiC₂ on hydrogen absorption behavior of MgH₂

To explore the effect of Mo₂TiC₂ on hydrogen absorption property of MgH₂, non-isothermal hydrogen absorption tests were conducted and the results are shown in Fig. 7(a). The non-isothermal hydrogenation experiments were carried out at 3.2 MPa hydrogen pressure. MgH₂ began to absorb H₂ at 182.9 °C, 2.9 wt.% and 6.0 wt.% H₂ were charged at 225 and 275 °C, respectively. In contrast, the addition of 9 wt.% Mo₂TiC₂ lowered the initial absorption temperature to about 50 °C and 6.9 wt.% H₂ was absorbed at 156 °C. To further study the hydrogen absorption performance of Mo₂TiC₂modified MgH₂ system, isothermal hydrogen absorption tests were carried out, as shown in Figs. 7(b) and (c).

Undoped MgH₂ absorbed 3.1 wt.% and 4.6 wt.% H₂ in 30 min at 210 and 230 °C, respectively, showing a rather slow hydrogenation kinetics. In contrast, the MgH₂+9 wt.% Mo₂TiC₂ composite uptook 3.1 wt.% and 6.5 wt.% H₂ at 150 and 175 °C in 5 min, respectively.

The hydrogenation activation energy was calculated based on the data of isothermal hydrogenation and Johnson–Mehl–Avrami–Kolmogorov (JMAK) linear equation [45]. Figures 8(a) and (b) show the JMAK curves with and without additives. According to the experimental data obtained from isothermal hydrogenation examination, the relationship between $\ln[-\ln(1-\alpha)]$ (α is mass



Fig. 6 Pressure-composition-temperature (PCT) curves of MgH_2 (a), MgH_2+9 wt.% Mo_2TiC_2 (b) at different temperatures and corresponding van't Hoff plot (c)

fraction of Mg converted to MgH₂ within time t) and ln t can be obtained. Subsequently, the E_a of the hydrogen absorption reaction was estimated by the Arrhenius equation:

$$k = A \exp[-E_a/(RT)] \tag{1}$$

where k is the effective dynamic parameter, T is the operating temperature and A means the pre-exponential factor. Figure 8(c) shows that the hydrogenation E_a of the MgH₂+9 wt.% Mo₂TiC₂ was calculated to be (46.1±0.2) kJ/mol with R^2 = 0.994, which was significantly lower than that of pure MgH₂ ((73.8±0.5) kJ/mol, R^2 =0.991).



Fig. 7 Non-isothermal hydrogen absorption curves for MgH_2 and MgH_2+9 wt.% Mo_2TiC_2 (a), and isothermal hydrogen absorption curves for MgH_2 (b) and MgH_2+9 wt.% Mo_2TiC_2 (c)



Fig. 8 Hydrogenation JMAK plots for MgH_2 (a) and MgH_2+9 wt.% Mo_2TiC_2 (b), and calculated rehydrogenation activation energy for MgH_2 and MgH_2+9 wt.% Mo_2TiC_2 (c)

3.4 Cycling property of MgH₂+9 wt.% Mo₂TiC₂ composite

Cycle stability is an important parameter for evaluating hydrogen storage performance. The cycle performance of MgH_2+9 wt.% Mo_2TiC_2 composite was measured at 300 °C (3.2 MPa hydrogen pressure for hydrogenation). As shown in Fig. 9, for the first hydrogen absorption and desorption process, the MgH₂+9 wt.% Mo₂TiC₂ composite could quickly release 6.5 wt.% H₂ and absorb 6.4 wt.% H₂. Though a capacity of 6.2 wt.% H₂ was maintained after the 10th cycle, the absorption and desorption capacity gradually decreased with increasing the cycling number. After 20 cycles, it released 5.5 wt.% H₂ and only 85% of the initial capacity was maintained.



Fig. 9 Cyclic isothermal dehydrogenation/hydrogenation curves of MgH₂+9 wt.% Mo₂TiC₂ composite

3.5 Evolution of Mo₂TiC₂ during cycling and catalytic mechanism

To uncover the evolution of Mo_2TiC_2 in the dehydrogenation and hydrogenation process, XRD measurement was conducted. Figure 10 shows that MgH₂ or Mg was the main phase after ball-milling, absorption, and desorption. However, no signal of Mo₂TiC₂ was detected, which may be due to the low doping content. Thus, XPS analysis was conducted to better understand the evolution of Mo₂TiC₂ in the process of hydrogen absorption and desorption. Figure 11 shows XPS profiles of MgH₂+9 wt.% Mo₂TiC₂ in different stages. The binding energy of magnesium (Mg 1s) in ball-milled, dehydrogenated and hydrogenated states is 1302.78, 1303.23 and 1302.88 eV, respectively, meaning that Mg changed from +2 valence to 0 valence and then to +2valence in cycling. The binding energies at 229.93 and 233.2 eV are determined as Mo-C peaks (Fig. 11(d)). The XPS profiles of Mo in Figs. 11(d, e, f) are almost the same in these three states. However, we found that the spectra of Ti in Figs. 11(g, h, i) can be mainly divided into Ti⁰ (453.9/459.9 eV) and Ti^{2+} (456.3/461.5 eV). The occurrence of Ti⁰ suggests the breakage of Ti-C bond and formation of metallic Ti during cycling.



Fig. 10 XRD patterns of hydrogenated MgH_2+9 wt.% Mo_2TiC_2 (a), dehydrogenated MgH_2+9 wt.% Mo_2TiC_2 (b), and ball-milled MgH_2+9 wt.% Mo_2TiC_2 (c)

Figure 12 presents the TEM images of the MgH₂+9 wt.% Mo₂TiC₂ composite in the ballmilled state. Figure 12(a) shows that the average particle size of MgH₂+9 wt.% Mo₂TiC₂ composite is about 700 nm. Figures 12(b) and (c) present the HRTEM images of MgH₂+9 wt.% Mo₂TiC₂. The d-spacing of 0.260 and 0.258 nm is related to the MgH₂ (101) plane, which is larger than 0.251 nm of MgH₂ (101) from PDF No. 12-0697, indicating that the addition of Mo₂TiC₂ slightly expanded the MgH₂ lattice and resulted in a decreased ΔH in Fig. 6. In addition, Mo₂TiC₂ MXene was clearly imbedded in the matrix of MgH₂, creating Mo₂TiC₂/ MgH₂ interfaces to enhance the catalytic effect of Mo₂TiC₂. As a good catalyst, Ti can improve the kinetic performance of dehydrogenation and reduce



Fig. 11 XPS profiles of MgH₂+9 wt.% Mo₂TiC₂ in ball-milled (a, d, g), dehydrogenated (b, e, h) and hydrogenated states (c, f, i)



Fig. 12 TEM images of MgH₂+9 wt.% Mo₂TiC₂ composite in ball-milled state

the activation energy of the dehydrogenation reaction. In the system of Ti_3C_2/MgH_2 , the in situ formed metallic Ti facilitated the dissociation and recombination of molecular hydrogen on its surface, improving the dehydrogenation/hydrogenation kinetics of MgH_2[32]. In this work, two thirds of Ti was substituted by Mo and the Mo—C bonds remained stable in cycling. Though TEM evidenced that Mo₂TiC₂ MXene had close contact with MgH₂, the amount of in-suit formed Ti was reduced in Mo₂TiC₂-modified MgH₂, resulting in a poorer catalytic effect of Mo₂TiC₂ than that of Ti₃C₂.

4 Conclusions

(1) Two-dimensional Mo_2TiC_2 MXene was successfully prepared and doped into MgH_2 to enhance the hydrogen storage performance. The addition of Mo_2TiC_2 not only accelerated the hydrogen desorption kinetics of MgH_2 , but also slightly reduced its thermal stability.

(2) The MgH₂+9 wt.% Mo₂TiC₂ began to desorb hydrogen at 210 °C, and 5.5 wt.% H₂ could be released within 5 min at 275 °C. By adding Mo₂TiC₂, the dehydrogenation activation energy of MgH₂ was decreased from (151.4 \pm 1.4) to (135.6 \pm 1.9) kJ/mol. Importantly, the fully dehydrogenated MgH₂+9 wt.% Mo₂TiC₂ could absorb hydrogen at 50 °C, and 6.5 wt.% H₂ was charged in 5 min at 175 °C.

(3) Microstructure analysis showed that the Ti-C bond in Mo_2TiC_2 was broken during ball milling, while the Mo-C bond maintained stable. The existence of Mo enhanced the stability of the MXene, resulting in the reduced amount of in suit formed Ti and moderate catalytic action of Mo_2TiC_2 MXene on MgH₂.

Acknowledgments

The authors would like to acknowledge financial support from the National Natural Science Foundation of China (No. 51801078), and the Natural Science Foundation of Jiangsu Province, China (No. BK20210884).

References

- MORADI R, GROTH K M. Hydrogen storage and delivery: Review of the state of the art technologies and risk and reliability analysis [J]. International Journal of Hydrogen Energy, 2019, 44(23): 12254–12269.
- [2] ZHONG Hai-chang, LIN Chen-long, DU Zi-yu, CAO Chun-yan, LIANG Chu, ZHENG Qing-rong, DAI Le-yang. Hydrogen storage properties of Mg(Al) solid solution alloy doped with LaF₃ by ball milling [J]. Transactions of Nonferrous Metals Society of China, 2022, 32(6): 1969–1980.
- [3] ZHANG Jian, HE Liu, YAO Yuan, ZHOU Xiao-jie, JIANG Li-kun, PENG Ping. Hydrogen storage properties of magnesium hydride catalyzed by Ni-based solid solutions [J]. Transactions of Nonferrous Metals Society of China, 2022, 32(2): 604–617.
- [4] LI Qian, LU Yang-fan, LUO Qun, YANG Xiao-hua, TAN Jun, DONG Zhi-hua, DANG Jie, LI Jian-bo, CHEN Yuan, JIANG Bin, SUN Shu-hui, PAN Fu-sheng. Thermodynamics and kinetics of hydriding and dehydriding reactions in Mg-based hydrogen storage materials [J]. Journal of Magnesium and Alloys, 2021, 9: 1922–1941.
- [5] LI Qian, LIN Xi, LUO Qun, CHEN Yuan, WANG Jing-feng, JIANG Bin, PAN Fu-sheng. Kinetics of the hydrogen absorption and desorption processes of hydrogen storage alloys: A review [J]. International Journal of Minerals, Metallurgy and Materials, 2022, 29: 32–48.
- [6] LIN Huai-jun, LU Yan-shan, ZHANG Liu-ting, LIU Hai-zhen, EDALATI K, RÉVÉSZ A. Recent advances in metastable alloys for hydrogen storage: A review [J]. Rare Metals, 2022, 41: 1797–1817.
- [7] ZHANG Xin, LIU Yong-feng, REN Zhuang-he, ZHANG Xue-lian, HU Jian-jiang, HUANG Zhen-guo, LU Yun-hao, GAO Ming-xia, PAN Hong-ge. Realizing 6.7 wt.%

3474

reversible storage of hydrogen at ambient temperature with non-confined ultrafine magnesium hydrides [J]. Energy & Environmental Science, 2021, 14: 2302–2313.

- [8] SI Ting-zhi, ZHANG Xue-yang, FENG Jing-jing, DING Xiao-li, LI Yong-tao. Enhancing hydrogen sorption in MgH₂ by controlling particle size and contact of Ni catalysts [J]. Rare Metals, 2021, 40: 995–1002.
- [9] LUO Qun, LI Jian-ding, LI Bo, LIU Bin, SHAO Huai-yu, LI Qian. Kinetics in Mg-based hydrogen storage materials: Enhancement and mechanism [J]. Journal of Magnesium and Alloys, 2019, 7: 58–71.
- [10] LIU Xiao-sheng, LIU Hai-zhen, QIU Ning, ZHANG Yanbing, ZHAO Guang-yao, XU Li, LAN Zhi-qiang, GUO Jin. Cycling hydrogen desorption properties and microstructures of MgH₂-AlH₃-NbF₅ hydrogen storage materials [J]. Rare Metals, 2021, 40: 1003–1007.
- [11] ZHANG Liu-ting, JI Liang, YAO Zhen-dong, YAN Nian-hua, SUN Ze, YANG Xing-lin, ZHU Xin-qiao, HU Shuang-lin, CHEN Li-xin. Facile synthesized Fe nanosheets as superior active catalyst for hydrogen storage in MgH₂ [J]. International Journal of Hydrogen Energy, 2019, 44(39): 21955–21964.
- [12] JAIN I P, LAL C, JAIN A. Hydrogen storage in Mg: A most promising material [J]. International Journal of Hydrogen Energy, 2010, 35(10): 5133–5144.
- [13] CHEN Yan, ZHANG Hao-yu, WU Fu-ying, SUN Ze, ZHENG Jia-guang, ZHANG Liu-ting, CHEN Li-xin. Mn nanoparticles enhanced dehydrogenation and hydrogenation kinetics of MgH₂ for hydrogen storage [J]. Transactions of Nonferrous Metals Society of China, 2021, 31: 3469–3477.
- [14] FENG Dian-chen, SUN Hao, WANG Xi-tao, ZHANG Yang-huan. Effect of milling duration on hydrogen storage thermodynamics and kinetics of ball-milled Ce-Mg-Nibased alloy powders [J]. Journal of Iron and Steel Research International, 2018, 25: 746-754.
- [15] YONG Hui, GUO Shi-hai, YUAN Ze-ming, QI Yan, ZHAO Dong-liang, ZHANG Yang-huan. Phase transformation, thermodynamics and kinetics property of Mg₉₀Ce₅RE₅ (RE= La, Ce, Nd) hydrogen storage alloys [J]. Journal of Materials Science & Technology, 2020, 51: 84–93.
- [16] DUAN Cong-wen, TIAN Ya-ting, WANG Xin-ya, WU Meng-meng, FU Dong, ZHANG Yu-ling, LV Wei, SU Zhao-hua, XUE Zhi-yong, WU Ying. Ni-CNTs as an efficient confining framework and catalyst for improving dehydriding/rehydriding properties of MgH₂ [J]. Renewable Energy, 2022, 187: 417–427.
- [17] LU Yan-shan, KIM H, SAKAKI K, HAYASHI S, JIMURA K, ASANO K. Destabilizing the dehydrogenation thermodynamics of magnesium hydride by utilizing the immiscibility of Mn with Mg [J]. Inorganic Chemistry, 2019, 58: 14600–14607.
- [18] HU Chao-dong, ZHENG Zhi-wen, SI Ting-zhi, ZHANG Qing-an. Enhanced hydrogen desorption kinetics and cycle durability of amorphous TiMgVNi₃-doped MgH₂ [J]. International Journal of Hydrogen Energy, 2022, 47(6): 3918–3926.
- [19] REN Shu-qin, FU Yao-kun, ZHANG Lu, CONG Lian, XIE Yi-chao, YU Han, WANG Wen-feng, LI Yuan, JIAN Lu, WANG Yu, HAN Shu-min. An improved hydrogen storage

performance of MgH₂ enabled by core-shell structure Ni/Fe₃O₄@MIL [J]. Journal of Alloys and Compounds, 2022, 892: 162048.

- [20] LAN Zhi-qiang, FU Hong, ZHAO Ruo-lin, LIU Hai-zhen, ZHOU Wen-zheng, NING Hua, GUO Jin. Roles of in situ-formed NbN and Nb₂O₅ from N-doped Nb₂C MXene in regulating the re/hydrogenation and cycling performance of magnesium hydride [J]. Chemical Engineering Journal, 2022, 431: 133985.
- [21] LV Ze-peng, MA Wan-sen, WANG Meng, DANG Jie, JIAN Kai-liang, LIU Dong, HUANG De-jun. Co-constructing interfaces of multiheterostructure on MXene (Ti₃C₂T_x)modified 3D self-supporting electrode for ultraefficient electrocatalytic HER in alkaline media [J]. Advanced Functional Materials, 2021, 31(29): 2102576.
- [22] LV Ze-peng, MA Wan-sen, WANG Meng, DANG Jie, JIAN Kai-liang, LIU Dong, HUANG De-jun. Induction of Co₂P growth on a MXene (Ti₃C₂T_x)-modified self-supporting electrode for efficient overall water splitting [J]. The Journal of Physical Chemistry Letters, 2021, 12(20): 4841–4848.
- [23] WEI Yi, SOOMRO R A, XIE Xiu-qiang, XU Bin. Design of efficient electrocatalysts for hydrogen evolution reaction based on 2D MXenes [J]. Journal of Energy Chemistry, 2021, 55: 244–255.
- [24] SUN Shui-jing, LIAO Chan, HAFEZ A M, ZHU Hong-li, WU Song-ping. Two-dimensional MXenes for energy storage [J]. Chemical Engineering Journal, 2018, 338: 27–45.
- [25] ZHAN Xiao-xue, SI Chen, ZHOU Jian, SUN Zhi-mei. MXene and MXene-based composites: Synthesis, properties and environment-related applications [J]. Nanoscale Horizons, 2020, 5: 235–258.
- [26] NAN Jian-xiao, GUO Xin, XIAO Jun, LI Xiao, CHEN Wei-hua, LIU Hao, WANG Yong, WU Ming-hong, WANG Guo-xiu. Nanoengineering of 2D MXene-based materials for energy storage applications [J]. Small, 2021, 17: 1902085.
- [27] LIU Shi-yuan, LIU Jie-yuan, LIU Xiao-fang, SHANG Jia-xiang, XU Li, YU Rong-hai, SHUI Jiang-lan. Hydrogen storage in incompletely etched multilayer Ti_2CT_x at room temperature [J]. Nature Nanotechnology, 2021, 16: 331–336.
- [28] ZHANG Liu-ting, CAI Ze-liang, YAO Zhen-dong, JI Liang, SUN Ze, YAN Nian-hua, ZHANG Bei-yu, XIAO Bei-bei, DU Jun, ZHU Xin-qiao, CHEN Li-xin. A striking catalytic effect of facile synthesized ZrMn₂ nanoparticles on the de/rehydrogenation properties of MgH₂ [J]. Journal of Materials Chemistry A, 2019, 7: 5626–5634.
- [29] LU Xiong, ZHANG Liu-ting, YU Hai-jie, LU Zhi-yu, HE Jia-huan, ZHENG Jia-guang, WU Fu-ying, CHEN Li-xin. Achieving superior hydrogen storage properties of MgH₂ by the effect of TiFe and carbon nanotubes [J]. Chemical Engineering Journal, 2021, 422: 130101.
- [30] HUANG Yi-hui, LI Ping, WAN Qi, LIU Zhi-wei, ZHAO Wan, ZHANG Jun, PAN Zhi-li, XU Li, QU Xuan-hui. Catalytic effect of MnFe₂O₄ on dehydrogenation kinetics of NaAlH₄-MgH₂ [J]. RSC Advances, 2017, 7: 34522–34529.
- [31] FU Yao-kun, DING Zhen-min, REN Shu-qin, LI Xin-jun, ZHOU Shu-hua, ZHANG Lu, WANG Wen-feng, WU Lai-lei, LI Yuan, HAN Shu-min. Effect of in-situ formed Mg2Ni/ Mg2NiH₄ compounds on hydrogen storage performance of

MgH₂ [J]. International Journal of Hydrogen Energy, 2020, 45(52): 28154–28162.

- [32] LIU Yong-feng, DU Hu-fei, ZHANG Xin, YANG Ya-xiong, GAO Ming-xia, PAN Hong-ge. Superior catalytic activity derived from a two-dimensional Ti₃C₂ precursor towards the hydrogen storage reaction of magnesium hydride [J]. Chemical Communications, 2016, 52: 705–708.
- [33] CHEN Dan-dan, FAN Yan-ping, CHEN Qiang, LIU Bao-zhong, MA Ming-jie. Hydrogen storage properties of PMMA–LiBH₄ improved by Ti₃C₂ composites [J]. Journal of Synthetic Crystals, 2018, 47(7): 1424–1430. (in Chinese)
- [34] LU Cheng-lin, LIU Hai-zhen, LUO Hui, HE Shi-xuan, DUAN Xing-qing, HUANG Xian-tun, WANG Xin-hua, LAN Zhi-qiang, GUO Jin. Two-dimensional vanadium carbide for simultaneously tailoring the hydrogen sorption thermodynamics and kinetics of magnesium hydride [J]. Journal of Magnesium and Alloys, 2022, 10(4): 1051–1065.
- [35] ZHANG Xin, SHEN Zheng-yang, JIAN Ni, HU Jian-jiang, DU Fang, YAO Jian-hua, GAO Ming-xia, LIU Yong-feng, PAN Hong-ge. A novel complex oxide TiVO_{3.5} as a highly active catalytic precursor for improving the hydrogen storage properties of MgH₂ [J]. International Journal of Hydrogen Energy, 2018, 43(52): 23327–23335.
- [36] KONG Qian-qian, ZHANG Huan-huan, YUAN Zhen-luo, LIU Jia-meng, LI Li-xin, FAN Yan-ping, LIU Bao-zhong. Hamamelis-like K₂Ti₆O₁₃ synthesized by alkali treatment of Ti₃C₂ MXene: Catalysis for hydrogen storage in MgH₂ [J]. ACS Sustainable Chemistry & Engineering, 2020, 8: 4755–4763.
- [37] WANG Ze-yi, ZHANG Xue-lian, REN Zhuang-he, LIU Yong, HU Jian-jiang, LI Hai-wen, GAO Ming-xia, PAN Hong-ge, LIU Yong-feng. In situ formed ultrafine NbTi nanocrystals from a NbTiC solid-solution MXene for hydrogen storage in MgH₂ [J]. Journal of Materials Chemistry A, 2019, 7: 14244–14252.

- [38] CHEN Meng, PU Yan-hui, LI Zhen-yang, HUANG gang, LIU Xiao-fang, LU Yao, TANG Wu-kui, XU Li, LIU Shuang-yu, YU Rong-hai, SHUI Jiang-lan. Synergy between metallic components of MoNi alloy for catalyzing highly efficient hydrogen storage of MgH₂ [J]. Nano Research, 2020, 13: 2063–2071.
- [39] MAUGHAN P A, BOUSCARRAT L, SEYMOUR V R, SHAO S Q, HAIGH S J, DAWSON R, TAPIA-RUIZ N, BIMBO N. Pillared Mo₂TiC₂ MXene for high-power and long life lithium and sodium-ion batteries [J]. Nanoscale Advances, 2021, 3: 3145–3158.
- [40] ANASORI B, XIE Yu, BEIDAGHI M, LU Jun, HOSLER B
 C, HULTMAN L, KENT P R C, GOGOTSI Y, BARSOUM
 M W. Two-dimensional, ordered, double transition metals
 carbides (MXenes) [J]. ACS Nano, 2015, 9: 9507–9516.
- [41] ISMAIL M, MUSTAFA N S, JUAHIR N, HALIM YAP F A. Catalytic effect of CeCl₃ on the hydrogen storage properties of MgH₂ [J]. Materials Chemistry and Physics, 2016, 170: 77–82.
- [42] SULAIMAN N N, ISMAIL M. Effects of TiF₃ addition on the hydrogen storage properties of 4MgH₂+Cd composite [J]. International Journal of Hydrogen Energy, 2019, 44(58): 30574–30582.
- [43] ISMAIL M. Effect of LaCl₃ addition on the hydrogen storage properties of MgH₂ [J]. Energy, 2015, 79: 177–182.
- [44] SHEN Zheng-yang, WANG Ze-yi, ZHANG Ming, GAO Ming-xia, HU Jian-jiang, DU Fang, LIU Yong-feng, PAN Hong-ge. A novel solid-solution MXene (Ti_{0.5}V_{0.5})₃C₂ with high catalytic activity for hydrogen storage in MgH₂ [J]. Materialia, 2018, 1: 114–120.
- [45] ZHANG Liu-ting, LU Xiong, SUN Ze, YAN Nian-hua, YU Hai-jie, LU Zhi-yu, ZHU Xin-qiao. Superior catalytic effect of facile synthesized LaNi_{4.5}Mn_{0.5} submicro-particles on the hydrogen storage properties of MgH₂ [J]. Journal of Alloys and Compounds, 2020, 844: 156069.

二维 Mo₂TiC₂ MXene 材料对调节 MgH₂ 储氢性能的催化作用

章浩宇1,田贵宾1,吴富英1,姚振东2,郑家广1,张刘挺1

江苏科技大学 能源与动力学院,镇江 212003;
 中国计量大学 材料与化学学院,杭州 310018

摘 要:通过刻蚀 Mo₂TiAlC₂ 合成二维 Mo₂TiC₂ MXene 材料,并将其与 MgH₂ 复合以调节 MgH₂ 的储氢性能。Mo₂TiC₂ 的掺杂使 MgH₂ 的初始放氢温度从 330 ℃显著降低至 187 ℃。等温放氢性能测试表明,MgH₂+9% Mo₂TiC₂(质量分数)复合材料在 300 ℃时 4 min 内可快速释放 6.4%(质量分数)的氢气。对于吸氢反应,完全脱氢的 MgH₂+9% Mo₂TiC₂ 在 175 ℃时 5 min 内吸收了 6.5%(质量分数)的氢气。经过计算,MgH₂+9% Mo₂TiC₂ 的放氢反应活化能为(135.6±1.9) kJ/mol,吸氢反应活化能为(46.1±0.2) kJ/mol。20 次循环后,MgH₂+9% Mo₂TiC₂ 复合材料的储氢容量损失 1.0%(质量分数)。显微组织分析表明,Mo₂TiC₂ 中的 Mo 使 MXene 的稳定性增强、循环过程中活性 Ti 的生成量减少,从而导致催化剂的催化效果不如 Ti₃C₂。

关键词:储氢性能;氢化镁;Mo2TiC2 MXene;催化机理