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# Enhanced hydrogen desorption property of $MgH_2$ with the addition of cerium fluorides

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ABSTRACT

Hydrogen desorption property of $MgH_2$ doped with cerium fluorides with different valences prepared using ball milling has been studied. $CeF_4$ is catalytically active for hydrogen desorption of $MgH_2$. Hydrogen desorption temperature and apparent activation energy of $MgH_2$ are significantly reduced with dopant of 2 mol% of $CeF_4$, which might be attributed to the formation of a new Ce–F–Mg specie at the $CeF_4/MgH_2$ interface and the easy electron transfer induced from the high valence Ce-cation. The apparent activation energy of hydrogen desorption of $MgH_2$ is reduced from ~160 kJ/mol to ~110 kJ/mol with the dopant of $CeF_4$.



## 1. Introduction

$MgH_2$ is widely considered as a promising candidate for hydrogen and energy storage mainly owing to the hydrogen density of 7.6 wt.% and energy density of 9 MJ/kg Mg [1,2]. However, the desorption temperature as high as 300–400 °C and sluggish kinetics hurdle its practical application. Doping catalytic additives is one of the most efficient and common used strategies to enhance the hydrogen desorption property of $MgH_2$ [3–7].

Cerium compounds have been abundantly applied in catalysis owing to the unique 4*f*-electron of Ce, which is very sensitive for electron transfer and can be easily involved in the hydrogen absorption/desorption of $MgH_2$ [8–12]. Shang et al. found that the formation of $CeO_2$ in the $MgH_2 + Ce$ mixture benefited the desorption kinetics, likely due to the formation of surface defects on $MgH_2$ and surface catalysis induced by the oxide [8]. Gulicovski et al. studied the hydrogen desorption property of the $CeO_2$ doped $MgH_2$, and found that the activation energy for desorption was remarkably decreased by the catalytic effect of vacant $CeO_2$ structure [9]. In previous study, cerium hydrides have been introduced into the $MgH_2$ matrix by direct hydrogen absorption treatment upon the Mg-based alloys. The cerium hydrides enhance the hydrogen absorption/desorption kinetics of $MgH_2$ with apparent activation energy of desorption being remarkably reduced [10,11]. Moreover, symbiotic $CeH_{2.73}/CeO_2$ nanoparticles have been prepared in the Mg-based hydrides, and we found that the high-valence Ce-compounds further reduce the hydrogen desorption temperature of $MgH_2$ [12].

Besides hydrides and oxides, halides are another group of additives that show many benefits for the hydrogen desorption property of $MgH_2$ [13–15]. However, the effect of cerium fluorides, especially $CeF_4$, on hydrogen desorption property of $MgH_2$ has rarely been reported. In the present study, cerium fluorides with different oxidation states (+3 and +4) were doped into $MgH_2$ using ball milling. The effect of cerium fluorides on hydrogen desorption property of $MgH_2$ was studied.

## 2. Experimental

The starting materials $MgH_2$ (98%), $CeF_3$ (99.99%) and $CeF_4$ (99%) were purchased from Alfa Aesar, Aldrich and Sigma–Aldrich, respectively. Mixed powders of $MgH_2 + 0.02CeF_x$ of 500 mg and 20 milling balls with a diameter of ~7 mm were loaded in the milling container with volume of ~30 ml, the weight ratio of ball to powder was ~60:1. The fabrication of $CeF_x$ doped $MgH_2$ was conducted using a Fritsch P7 planetary ball mill at a rotation speed of 400 rpm for 4 h. For comparison, commercial $MgH_2$ was also ball-milled under the same milling parameters.

X-ray diffraction (XRD) to analyze the phase information was performed using a Rigaku Ultima IV diffractometer with Cu Kα radiation. Transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) study were performed using a JEM-2100F microscopy. X-ray Photoelectron Spectra (XPS) were performed using a PHI 5000 Versal Probe II XPS microprobe with Al Kα

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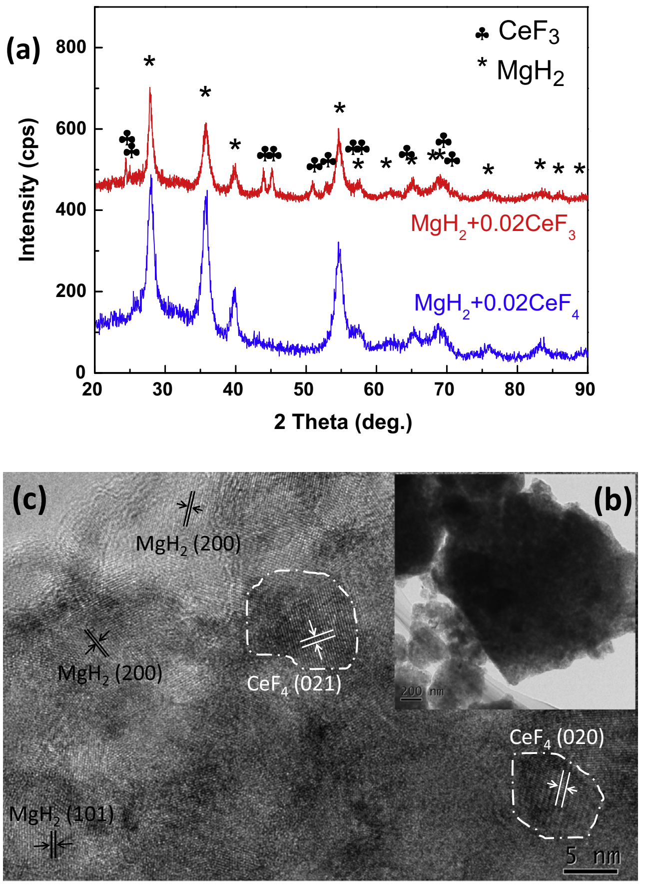


**Fig. 1.** (a) XRD patterns of the ball-milled $0.02CeF_x + MgH_2$ ($x$ = 3 and 4) mixtures. (b) TEM and (c) HRTEM images of the $CeF_4$ doped $MgH_2$.

radiation. Hydrogen desorption properties were studied using a Differential Thermal Analysis (DTA) technique (Rigaku TG/DTA-8120/s) under a He flow of 200 ml/min at various heating rates. Cycling properties were studied using high-pressure differential scanning calorimetry (HP-DSC) in hydrogen atmosphere. The HP-DSC measurements were conducted using a Rigaku TP-8230HP apparatus under a constant pressure of 2 MPa under a $H_2$ flow of 200 ml/min. The temperature range is from 100 to 500 °C at both heating and cooling rates of 20 K/min. All the samples were always handled in a glove box filled with purified Ar gas ($H_2O$ and $O_2$ concentration <1 ppm) in order to avoid oxidation.

## 3. Results and discussion

The $CeF_x + MgH_2$ mixtures have been prepared using planetary ball milling for 4 h. Fig. 1(a) shows the XRD patterns of the as-milled $CeF_x$ doped $MgH_2$. The $CeF_3$ doped $MgH_2$ consists of both $MgH_2$ (ICSD #026624) and $CeF_3$ (ICSD #16965) phases, while the $CeF_4$ doped $MgH_2$ shows only $MgH_2$ diffraction peaks. The absence of $CeF_4$ diffraction peaks should be attributed to the significantly fine grains formed by ball milling. Since the same ball milling process has been applied to both materials, the differences in the as-milled materials should be further studied. The $CeF_4$ content is increased to double, leading to weak and broad CeF4 diffraction peaks for the $MgH_2 + 0.04CeF_4$ composite (XRD results not shown), suggesting the difference between the as-milled $MgH_2 + CeF_4$ and $MgH_2 + CeF_3$ is due to the easier pulverization of $CeF_4$. Fig. 1(b and c) shows the TEM and HRTEM image of the $CeF_4$ doped $MgH_2$, respectively. Obviously, very fine $CeF_4$ (ICSD #089621) in crystallite size of less than 10 nm are homogeneously embedded in the $MgH_2$ matrix. The significantly fine cerium fluorides present abundant interfaces with $MgH_2$, which is beneficial for the catalysis and hydrogen desorption property of $MgH_2$.

Hydrogen desorption behaviors of the $CeF_x$ doped $MgH_2$ are studied using DTA at various heating rates. Fig. 2 displays the DTA traces of the $CeF_x$ doped $MgH_2$, and the commercial $MgH_2$ before/after ball milling are shown as references. As shown in

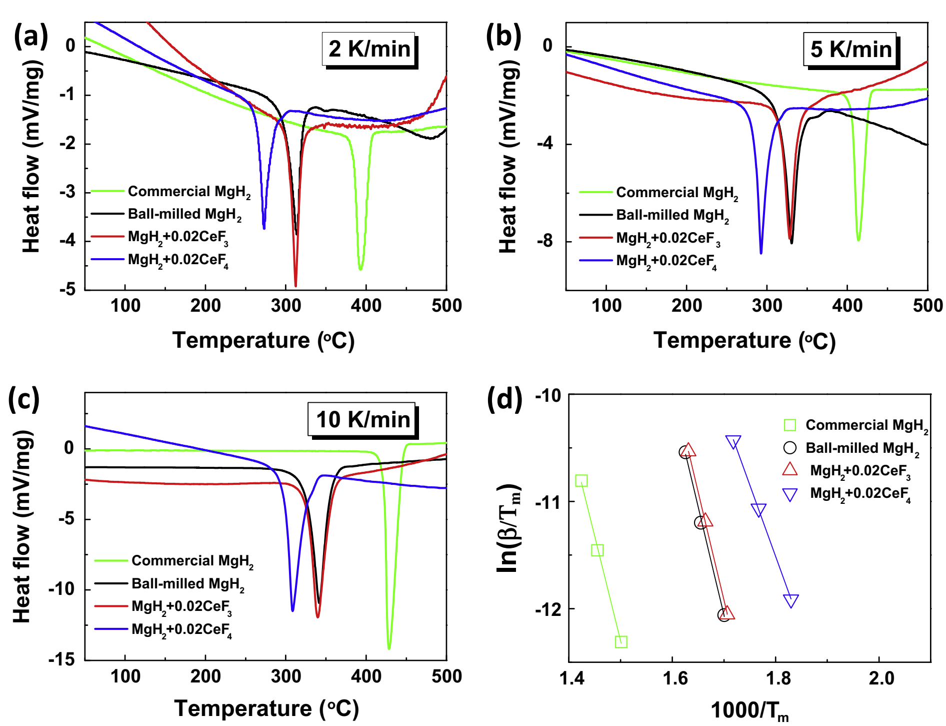


**Fig. 2.** DTA traces of the commercial and ball-milled $MgH_2$, $0.02CeF_x + MgH_2$ ($x$ = 3 and 4) mixtures under different heating rates: (a) 2 K/min, (b) 5 K/min and (c) 10 K/min. (d) Kissinger's plots for the samples.