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# Enhanced hydrogen sorption kinetics of co-doped $MgH_2$ hydrides

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ABSTRACT

Double substituted $MgH_2$ sorption kinetic is studied by combining density functional theory (DFT) and Kinetic Monte Carlo (KMC) simulations. The DFT calculations were performed to compute the energy barriers of the relevant elementary processes, which will be used as a database for the KMC simulations. The study provides a discussion of the mechanism behind the hydrogen reaction path on magnesium hydride (adsorption, dissociation, surface migration, penetration, and diffusion) as we took into account the density distribution of hydrogen atoms as well as the filling ratios, the diffusion time and finally the temperature. Based on the obtained results, the double substitution not only improves $MgH_2$ stability and desorption temperature but also its adsorption and desorption kinetics. Among the studied systems $Mg_{14}ZnLiH_{32}$ exhibits the best results with the fastest ab/desorption kinetic, in addition to its ideal heat of formation ΔH = -38.27 kJ/mol and high gravimetric capacity 7.25 wt%.

## 1. Introduction

The need for an alternative, -sustainable and clean- energy, source is becoming more pressing, as the world faces serious challenges such as global warming, depleted energy sources (i.e. fossil fuels) and overpopulation. Hydrogen, as an energy carrier, has attracted researchers' attention for its exceptional characteristics, like its high energy density, abundance and environmental friendliness. Although hydrogen appears as the most versatile and viable alternative; its storage remains the biggest hurdle to its practical applications.

Magnesium hydride ($MgH_2$) is one of the promising candidates for on-board hydrogen storage, due mainly to its high gravimetric capacity 7.65 wt% [1]. However its industrial application is hindered by its high stability, desorption temperature as well as slow hydrogenation/dehydrogenation kinetics [2]. Many experimental and theoretical researches, have been carried out to assess $MgH_2$ hydrogen, storage properties improvement, through different approaches like "Mechanical alloying [3,4]; alloying with transition metals oxides [5,6]; simple substitution [7–11]; double substitution with transition metals [12,13]. In addition to these works, other studies investigated hydrogen sorption kinetic improvement [14,15].

In our previous studies [9–12] we investigated the influence of single and double substitution, with different elements from the periodic table, on $MgH_2$ hydrogen storage properties. The improvement of $MgH_2$ thermodynamic properties was very apparent, in all the studied cases. However, it was shown that the stability is improved at the expense of the gravimetric capacity or vice versa. Yet in the case of double substitution, the stability was reduced and the gravimetric capacity was maintained around that of $MgH_2$. For $Mg_{14}ZnLiH_{32}$ and $Mg_{14}TiAlH_{32}$ their heats of formation were $\Delta H = -38.27$ kJ/mol and $\Delta H = -37.26$ kJ/mol respectively [12], far below $MgH_2$ heat of formation $\Delta H = -62.57$ and close to the heat of formation required for hydrogen storage materials $\Delta H = -40$ kJ/mol (H2) [16], and their gravimetric capacities were 7.25 wt% and 7.21 wt% respectively, indeed below $MgH_2$ gravimetric capacity of 7.65 wt%,as the doping elements are heavier (Transition metals), however above the DOE target for 2017 (5.5 wt%) and around the DOE optimum target (7.5 wt%) [17]. Since the effect of double substitution, on $MgH_2$ thermodynamics, was displayed via the decrease of the stability and desorption temperature, its effect on $MgH_2$ kinetics remains to be identified.

The objective of this paper is assess the effect of double substitution on the sorption kinetics of $MgH_2$.This is through an investigation of the absorption/desorption kinetic of $Mg_{14}ZnLiH_{32}$ and $Mg_{14}TiAlH_{32}$ by combining density functional theory (DFT) and Kinetic Monte Carlo (KMC) simulations. Throughout the DFT calculations, the energy barriers, of the elementary processes, were computed so to be later used as a database for the KMC simulations.

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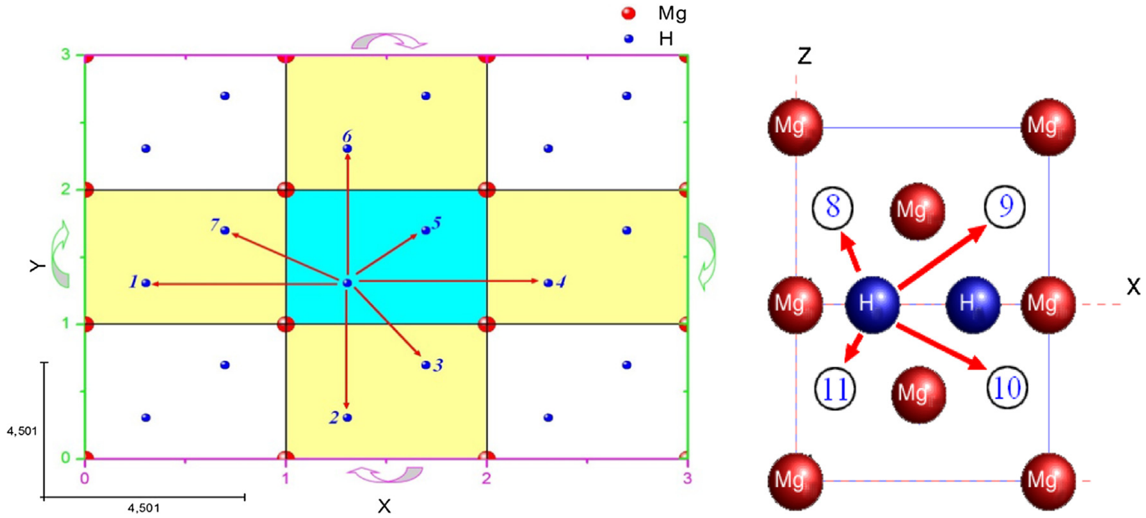

**Fig. 1.** Representative scheme of neighbor's sites. Left denotes the seven neighbors in the same plane; Right denotes the four neighbors in the upper and lower adjacent plane.

## 2. Computational method and model

$MgH_2$ crystallizes in a rutile structure. Its space group is (P42/mnm, N°136), and lattice parameters are: a = b = 4.501 Å and c = 3.01 Å [18]. Mg and H wyckoff positions are 2a (0, 0, 0) and 4f (0.304, 0.304, 0) respectively. In this study, a 2 × 2 × 2 supercell consisting of 16 Mg atoms and 32H atoms has been used. In this atomic representation, two Mg atoms are substituted by Li and Zn in the first system whereas in the second system they are substituted by Al and Ti, which correspond to a concentration of 12.6%. All lattices parameters are relaxed.

### 2.1. Kinetic Monte Carlo simulations

To investigate the hydrogen diffusion in our systems, we apply KMC method [19] to our model described in detail in the reference [14]. We consider a large super cell and periodic boundary conditions along X and Y-directions to simulate an infinite system. Each hydrogen atom has eleven nearest neighbors, seven in the same plane and four in the upper and lower adjacent plane Fig. 1.

Various possible events including processes of dissociation, adsorption, diffusion to the free neighbors and desorption are considered. At each KMC step one of the above processes is randomly selected with a probability:

$$P_i = \frac{R_i}{R} \tag{1}$$

The rate transition $R_i$ associated to the $i^{th}$ process and the total rate transition R are given respectively by:

$$R_i = \upsilon_0 \exp\left(\frac{E_i^a}{K_\beta T}\right) \tag{2}$$

$$R = \sum_{i=1}^{N} R_i \tag{3}$$

where $\upsilon_0$ describes the jump frequency (usually set to $10^{13}$ Hz), $E_i^a$ the activation energy of $i^{th}$ process taken from first principles calculations (see Section 3.1) and $K_\beta$ the Boltzmann constant. The time of hydrogen atoms displacement is incremented by t, which is defined as the inverse of the total rate transition:

$$\Delta t = -\frac{\ln(u)}{R} \tag{4}$$

where u is a uniformly distributed random variable between $0 < u < 1$.

The adsorption of the hydrogen molecule, which is located at the surface (0 0 1) of a super-cell, containing initially only magnesium and (Li, Zn) for the first system and (Al, Ti) for the second, start by its decomposition into two H atoms that diffuse from an interstitial site to another according to the corresponding activation energies. These energies are obtained from the DFT calculations and implemented in the KMC algorithm.

### 2.2. Density functional theory calculations

For each material more than 300 configurations are required to determine the different energy barriers for the hydrogen diffusion. In order to compute such barriers, we have used ab initio calculations based on the all-electron full-potential local-orbital minimum-basis scheme FPLO9.00-34 [20,21] to solve the Kohn-Sham equations using the scalar-relativistic. The parameterization of the exchange–correlation energy has been done within the generalized gradient approximation GGA [22]. To ensure a high accuracy in our calculation, we used self-consistent criteria for both the energy and the density with precision of $10^{-8}$ Ha and $10^{-6}$, respectively. A mesh of (6 × 6 × 6) k-points in the Brillouin zone was used in our calculation. The total energy is calculated using the scalar-relativistic scheme, for all configurations.

## 3. Results and discussion

The DFT calculations are performed to compute the heat of formation as well as the energy barriers of the relevant elementary processes, so to be used as a database for the KMC simulations.

As previously mentioned this study is a follow up study. Based on our previous founding [12], double substituted $MgH_2$ systems exposed excellent thermodynamic improvement, as well as great gravimetric capacities, compared to pure and single substitution $MgH_2$ (Table 1). The aim of this study is to assess the effect of double substitution, as

**Table 1**
Calculated heat of formation (kj/mol $H_2$) and gravimetric capacities (wt%).

| System | Gravimetry (wt%) | Heat of formation (kJ/mol $H_2$) |
|---|---|---|
| $MgH_2$ | 7.65 | −62.57 |
| $Mg_{15}TiH_{32}$ | 7.25 | −51.24 |
| $Mg_{14}TiAlH_{32}$ | 7.21 | −37.26 |
| $Mg_{15}ZnH_{32}$ | 6.97 | −53.04 |
| $Mg_{14}ZnLiH_{32}$ | 7.25 | −38.27 |