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## Two-controlling mechanisms model for hydrogen desorption in the $\text{Li}_4(\text{NH}_2)_3\text{BH}_4$ doped $\text{Mg}(\text{NH}_2)_2-2\text{LiH}$ system

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### ABSTRACT

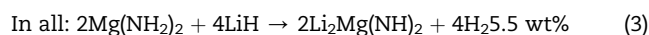
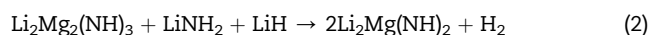
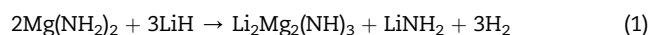
The limiting step of the dehydrogenation process and the desorption kinetic model of the composite  $0.7\text{Mg}(\text{NH}_2)_2-1.4\text{LiH}-0.2\text{Li}_4(\text{NH}_2)_3\text{BH}_4$  under different hydrogen back pressures at low temperature (200 °C) were studied in this work. It was determined that a single mechanism model was not able to explain the behavior of the reaction at low and high reacted fractions simultaneously. A combination of two controlling mechanisms, which reproduce accurately the behavior of the system, was proposed. The rate equation deduced involves the contribution of a second grade Avrami model and a 3D diffusion model as a function of pressure and conversion. At low conversions, the limiting step of the reaction is the formation of the products. Once a thin layer of product is formed on the surface, the diffusion through it becomes the new limiting step. With pressure increase, the mechanism change occurs later during desorption due to the higher difficulty in creating nucleation points on a surface exposed to a higher concentration of hydrogen.

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### Introduction

Solid-state hydrogen storage for mobile applications is a safe and efficient method which provides improved volumetric energy densities at moderate pressures and temperatures. Among the complex metal hydrides storage systems intensively explored in the past years, the  $\text{Mg}(\text{NH}_2)_2-\text{LiH}$  composite has attractive features for onboard utilization owing to its good reversibility, moderate operating temperatures, 5.5 wt% hydrogen content, and suitable  $\Delta H$  ( $\sim 44.1 \text{ kJ mol}^{-1} \text{ H}_2$ ), determining a desorption temperature lower than 100 °C at

atmospheric pressure [1–6]. The hydrogen sorption reaction was presented by Hu et al. [4], according to the following pathway:



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However, in order to achieve reasonable desorption rates, temperatures over 200 °C are required, indicating the presence of a relatively high kinetic barrier for this reaction to be surmounted, inhibiting its application as a commercial hydrogen storage material. One strategy in this direction, with positive effects on its kinetics, is the addition of catalysts, such as alkali metal compounds or metal borohydrides [7–13]. However, in order to improve the hydrogen desorption kinetics and lower the operating temperature, the reaction mechanism has to be understood. As it will be presented, a deep analysis of the kinetics of the Li–Mg–N–H system has not been conducted so far and there is no doubt that such complete studies are necessary in order to provide guidelines for improving the kinetics of this type of systems in the future.

The mechanism of the transformation between lithium amide and lithium imide for the Li–N–H system was proposed by David et al. [14]. They demonstrated that the rate controlling step was the movement of Li<sup>+</sup> in LiNH<sub>2</sub> to create a Frenkel defect pair, a charged interstitial [LiLiNH<sub>2</sub>]<sup>+</sup>, and a lithium vacancy [Li□NH<sub>2</sub>]<sup>−</sup> in a non-stoichiometric manner [14]. Wu et al. [15] found that in addition to the migration of the small mobile ions Li<sup>+</sup> and H<sup>+</sup>, the mobile H<sup>−</sup> in hydrides had a key role in the hydrogen storage of Li<sub>2</sub>Mg(NH)<sub>2</sub>. For the heterogeneous solid-state reaction of Mg(NH<sub>2</sub>)<sub>2</sub> and LiH, Chen et al. [16] indicated that the reaction rate was controlled by the interface reaction between amide and hydride in the preliminary stage and mass transport through the imide layer in the subsequent stage. Then, the kinetics is particle size dependent. Concerned about the high operating temperature and slow kinetics that retarded the practical applications of the Li–Mg–N–H system, Liu et al. [6] investigated the dependence on particle size of the hydrogen storage performance. They synthesized Li<sub>2</sub>Mg(NH)<sub>2</sub> by sintering a mixture of Mg(NH<sub>2</sub>)<sub>2</sub>–2LiNH<sub>2</sub> with a subsequent ball milling of the product for different periods to obtain particles of different sizes, and they observed that the particle size reduction improved sorption kinetic properties. For the dehydrogenation reaction, a three-dimensional diffusion-controlled kinetic mechanism was identified by analyzing isothermal hydrogen desorption curves. In agreement with previous works, it was concluded that the rate-controlling step for dehydrogenation of the Li–Mg–N–H system should be the diffusion of the mobile small ions in both the amide and the imide [6]. Markmaitree et al. studied the isothermal hydrogenating kinetics of the pure Li<sub>2</sub>Mg(NH)<sub>2</sub> phase synthesized via dehydrogenating treatment of a ball milled 2LiNH<sub>2</sub>–MgH<sub>2</sub> mixture [17]. Even though different possible controlling mechanisms were taken into account, they concluded that the hydrogenation process of Li<sub>2</sub>Mg(NH)<sub>2</sub> at 180, 200, and 220 °C could be described as a diffusion-controlled reaction [17]. A dependence of the onset dehydrogenation temperature and the dehydrogenation rates of the Mg(NH<sub>2</sub>)<sub>2</sub>–2LiH system on the gas back pressure was presented by Liang et al. [18]. It was found to be the key factor for the formation of different crystal structures of Li<sub>2</sub>Mg(NH)<sub>2</sub> (cubic or orthorhombic). Considering all the information presented, it can be said that there seems to be a general agreement that there is a diffusion-controlled kinetic mechanism for both the Li–N–H and the Li–Mg–N–H systems [6,17,19,20].

Recent works have demonstrated that lithium fast-ion conductors have positive effects on the hydrogen storage

properties of the Li–Mg–N–H system [12,13,21,22]. In our previous work, Li<sub>4</sub>(NH<sub>2</sub>)<sub>3</sub>BH<sub>4</sub> doped Mg(NH<sub>2</sub>)<sub>2</sub>–2LiH was formed by mechanical milling of the 2LiNH<sub>2</sub>–MgH<sub>2</sub>–0.2LiBH<sub>4</sub> mixture and posterior annealing under hydrogen pressure [23]. The ionic liquid Li<sub>4</sub>(NH<sub>2</sub>)<sub>3</sub>BH<sub>4</sub> with low melting temperature showed a beneficial effect on the dehydrogenation behavior after successive cycles in comparison to the pristine material (Mg(NH<sub>2</sub>)<sub>2</sub>–2LiH). The dehydrogenation rate was doubled, while hydrogenation could be performed 20 times faster. Although the dehydrogenation rate decreased with the cycle number, the presence of Li<sub>4</sub>(NH<sub>2</sub>)<sub>3</sub>BH<sub>4</sub> stabilized the hydrogen storage capacity with cycling. The catalytic role of Li<sub>4</sub>(NH<sub>2</sub>)<sub>3</sub>BH<sub>4</sub> in improving the dehydrogenation kinetics was associated with the weakening of the N–H bond and the mobile small ion mass transfer enhancing.

The aim of this work is to determine, in the first instance, the limiting step during the dehydrogenation process of the composite 0.7Mg(NH<sub>2</sub>)<sub>2</sub>–1.4LiH–0.2Li<sub>4</sub>(NH<sub>2</sub>)<sub>3</sub>BH<sub>4</sub> under different hydrogen back pressures at low temperature (200 °C). Furthermore, it was attempted to model the desorption kinetics of the system taking into account the different models and equations proposed in the literature to predict the kinetics of metal-hydrogen systems. A single model was insufficient to describe adequately the kinetic performance of the doped composite in the complete range of the reaction at different hydrogen back pressures. The rate equation deduced involves the contribution of two models with different weights during the dehydrogenation process.

## Experimental

### Synthesis of the composites

The starting materials were commercial LiNH<sub>2</sub> (Aldrich, 95%), MgH<sub>2</sub> (Aldrich, 98%), and LiBH<sub>4</sub> (Aldrich, 90%). Due to the high reactivity of the samples, they were handled in an MBraunUnilab argon-filled glove box, with oxygen and moisture levels lower than 1 ppm. For all studies, high purity hydrogen (Linde, 99.999%) and argon (Linde, 99.999%) were used. The sample preparation was carried out by mechanical milling of the 2LiNH<sub>2</sub>–MgH<sub>2</sub>–0.2LiBH<sub>4</sub> mixture, using a sequence of 15 min milling and 10 min pause in a planetary ball mill (Fritsch Pulverisette 6) at 500 rpm with a ball to powder mass ratio of 53:1. The sample was milled for 20 h and to eliminate possible dead zones, the material was manually mixed after 1 h, 3 h, 5 h, 10 h and 15 h. Then, the composite 0.7Mg(NH<sub>2</sub>)<sub>2</sub>–1.4LiH–0.2Li<sub>4</sub>(NH<sub>2</sub>)<sub>3</sub>BH<sub>4</sub> was obtained by this synthesis, followed by thermal treatment for 30 min at 200 °C under 6000 kPa of hydrogen [23]. It is worth pointing out the formation of the new phase Li<sub>4</sub>(NH<sub>2</sub>)<sub>3</sub>BH<sub>4</sub> during mechanical milling and that no excess of any reactive was detected.

### Characterization of the composites

Hydrogen storage properties of the sample were studied using modified Sieverts-type equipment, coupled with a mass flow controller. The sample was transferred in the glove box into a stainless steel reactor which was connected to the Sieverts device. Before the first dehydrogenation, the sample was

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