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# Hydrogen storage properties of in-situ stabilised magnesium nanoparticles generated by electroless reduction with alkali metals

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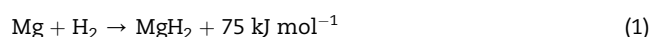
## ABSTRACT

As strong reducing agents, alkali metals including Li, Na and K enable the electroless synthesis of magnesium nanoparticles. In this investigation, we determined the effects of such alkali metals on the properties of magnesium at the nanoscale. The magnesium nanoparticles were successfully synthesised by directly reducing di-*n*-butylmagnesium with an excess amount of alkali-metal naphthalenide in order to coat individual magnesium nanoparticles within an alkali matrix. Upon heat treatment under hydrogen pressure a perovskite structure  $\text{MMgH}_3$  was formed on Na- and K-coated magnesium nanoparticles under mild conditions but was absent on the Li-coated materials leading to  $\text{LiH}$  only. These perovskite structures were found to have no significant influence on the thermodynamics of magnesium. Compared to ball-milled  $\text{MgH}_2$ , these materials showed lower hydrogen absorption plateau pressure ( $\sim 0.05$  MPa). However, the magnesium particles generated with potassium had fast hydrogen kinetics and low reaction enthalpy due to their small size. More remarkably these coated magnesium nanoparticles remained stable upon cycling which provides a new route to stabilise magnesium nanoparticles.

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## Introduction

Magnesium (Mg) is an attractive candidate for solid-state hydrogen storage due to its abundance, nontoxicity and high reversible storage capacity (7.6 mass %  $\text{H}_2$ ). Furthermore, magnesium readily reacts with hydrogen in a single step process (1) leading to the formation of magnesium hydride ( $\text{MgH}_2$ ), which in principle should be easier to control than the multistep paths involved with complex hydrides.



However, the remaining challenges for on-board application of magnesium are the high thermodynamic stability of  $\text{MgH}_2$  and slow kinetics for hydrogen uptake and release.

To overcome these barriers, nanosizing has been proposed as an alternative approach to nanostructuring by mechanical milling and conventional alloying/destabilisation methods [1–4]. With magnesium particle sizes decreasing below 3 nm,

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theoretical calculations using density functional theory predicted a significant drop in enthalpy for the Mg/MgH<sub>2</sub> reaction [5,6]; and these theoretical predictions have been verified experimentally to some extent. Hence, a decrease in enthalpy of 11.9 kJ mol<sup>-1</sup> as compared to the bulk was observed for 3 nm magnesium nanoparticles confined within porous carbon scaffolds [7]. While 7 nm MgH<sub>2</sub> nanoparticles embedded in a LiCl matrix showed an enthalpy decrease of 2.84 kJ mol<sup>-1</sup>H<sub>2</sub>, only [8]. However, we recently found that larger magnesium nanoparticles could also undergo significant thermodynamic alterations. Hence, magnesium nanoparticles (~16 nm) synthesised from di-*n*-butylmagnesium were found to undergo a 15% reduction in enthalpy [9]. Oumellal also observed that MgH<sub>2</sub> of 10–40 nm by electrochemical conversion reaction of MgH<sub>2</sub> with Li ion decreased the enthalpy from -74 kJ mol<sup>-1</sup>H<sub>2</sub> to -56 kJ mol<sup>-1</sup>H<sub>2</sub> [10]. It is noteworthy that such a reduction of enthalpy was also accompanied by a decrease in entropy due to the weaker Mg–H bond, i.e. 118.4 ± 3.1 J K<sup>-1</sup> mol<sup>-1</sup> H<sub>2</sub> instead of the 139.0 ± 3.1 J K<sup>-1</sup> mol<sup>-1</sup> H<sub>2</sub> observed for ball milled magnesium [9]. Hence, the use of particle size effects to tune the thermodynamics properties of magnesium may be limited by the enthalpy/entropy compensation effects.

Catalysing the hydrogen uptake and release at the nanosize is also a remaining issue since it appears that the hydrogen kinetics of nanosized magnesium are rather slow. Hence, many of magnesium nanoparticles synthesised so far require more than 2 h to fully release hydrogen at 300 °C [7,11,12], while this can be achieved in a few min with catalysed ball milled magnesium [13–15]. Taking into account the rather large activation energy of 432 kJ mol<sup>-1</sup> H<sub>2</sub> required to split hydrogen at the surface of magnesium this is not surprising [1]. Accordingly, unless the right magnesium surface planes are generated at the nanosize, transition metal catalysts would be required to effectively activate hydrogen at the magnesium surface. Our first attempt to equip the surface of 8 nm magnesium particles with transition metals indeed showed a significant improvement of hydrogen kinetics upon Ni coating as expected. However, this coating strategy was also found to drastically modify the thermodynamics. Hence, upon Ni coating the thermodynamic properties of nanosized magnesium shifted back to that of bulk magnesium [16]. The hydrogen sorption properties of magnesium nanoparticles are thus relatively sensitive to their chemical/physical environment.

The most common method for the synthesis of magnesium nanoparticles is through the electroless reduction of magnesium compounds following the method developed by Rieke [17]. Through this method, Rieke originally synthesised “active magnesium” from magnesium halides for the preparation Grignard reagents. However, by using organomagnesium precursors such a di-*n*-butylmagnesium (Mg(Bu)<sub>2</sub>) of higher solubility in tetrahydrofuran higher reaction yields can be achieved.

In this synthesis process (reactions 1a and 1b), naphthalene acts as the electron carrier enabling the reduction of the magnesium compound by lithium metallic (Li). Hence, depending upon the reductant it should be possible to modulate the nucleation and growth process of the magnesium nanoparticles. Herein, we thus investigated the effect of alternative alkali reductants, i.e. sodium (Na) and potassium

(K), of standard redox potential lower than Li (Table 1). Since Rieke's route will also lead to some remaining alkali metal mixed with magnesium [9]; Li, Na and K were used in excess in order to determine any modification of magnesium properties as compared to previous reports where the synthesis was done under stoichiometric conditions [18,19]. Doping Mg with Li has been predicted to potentially lead to improved hydrogen properties [20], but this has not been observed experimentally [9]. Similarly, Na or K could lead to improved hydrogen properties assuming that perovskite structures, i.e. MMgH<sub>3</sub> (M = Na, K), with enhanced hydrogen diffusion are formed [21,22]. We thus report on a single-step method for the synthesis of alkali metal (M = Li, Na, K) coated magnesium nanoparticles and the formation of their respective hydride/perovskite phase. The hydrogen storage properties of these materials are reported as well as the effect of the alkali metals.

## Material and methods

All operations were carried out under an inert atmosphere in an Argon-filled LC-Technology glove box with oxygen and moisture level less than 1 ppm.

### Materials

Lithium, naphthalene, and 1.0 M di-*n*-butylmagnesium in heptane were purchased from Aldrich. Tetrahydrofuran (THF) was purchased as HPLC grade from Fisher Scientific and dried using a LC Technology SP-1 Solvent Purification System. Naphthalene was dried by recrystallization under vacuum at 60 °C. Sodium from Merck and potassium from Aldrich were washed several times with fresh THF to remove mineral oils on their surface before use. All other chemicals were used as received.

### Synthesis approach

The magnesium nanoparticles were synthesized by reducing di-*n*-butylmagnesium in THF using excess alkali metal as reducing agent to ensure a full reduction of di-*n*-butylmagnesium into magnesium as well as the coating of the magnesium nanoparticles with the respective alkali metals (Scheme 1). Naphthalene was added as an electron carrier in the synthesis medium as indicated in Scheme 1 and since naphthalene can be recycled during the synthesis process, the concentration of naphthalene was 10 mol % that of the alkali metal.

In a typical synthesis, naphthalene (0.436 g, 3.4 mmol) and di-*n*-butylmagnesium solution in heptane (7 mL, 7 mmol) were dissolved in 20 mL THF. This solution was then

**Table 1 – Redox potentials (E) of the reagents used for the synthesis of the alkali coated magnesium nanoparticles [29]. The value for di-*n*-butylmagnesium (Mg(Bu)<sub>2</sub>) is estimated from cyclic voltammetry measurements [45].**

	Mg(Bu) <sub>2</sub>	Naphthalene	Li <sup>+</sup> /Li	Na <sup>+</sup> /Na	K <sup>+</sup> /K
E (V vs NHE)	-1.39	-2.15	-3.04	-2.71	-2.93

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