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Influence of particle size on electrochemical and gas-phase hydrogen storage in nanocrystalline Mg

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Abstract

Nanocrystalline Mg powders of different particle size were obtained by inert gas evaporation and studied during electrochemical and gas-phase hydrogen cycling processes. The samples were compared to dehydrided samples obtained by mechanical milling of MgH₂ with and without 2 mol% Nb₂O₅ as catalyst. The hydrogen overpotential of the pure Mg, which is a measure of the hydrogen evolution at the electrode surface, was observed to be reduced with smaller particle sizes reaching values comparable to samples with Nb₂O₅ additive. On the other hand gas-phase charging experiments showed the capacity loss with smaller particle sizes due to oxidation effects. These oxidation effects are different depending on the synthesis method used and showed a major influence on the hydrogen sorption kinetics.

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1. Introduction

Magnesium as a light, abundant and cheap metal with high hydrogen capacity of 7.6 wt.% is a very attractive material for hydrogen storage. Hydrogen charging can hereby be performed from the gas-phase [1] or in solution by electrochemical methods [2,3]. The disadvantage of using Mg in the gas-phase however lies in the slow sorption kinetics and the high thermodynamic stability of the MgH₂, which demand high temperatures (>300 °C). In the case of the electrochemical hydrogenation the corrosion behavior of Mg in electrolytes reduces the hydrogen capacity and kinetics as well as the cycle stability. By using nanocrystalline MgH₂ obtained by mechanical milling [4–6] with transition metal oxides as milling additives [7–11] big improvements of the sorption kinetics have been achieved for the sorption kinetics. Nb₂O₅ has been shown to behave as one of the best additives [12,13] for hydrogenation in the gas-phase at the present time, and has been demonstrated to catalyze significantly also the electrochemical charging process as reported in [14]. The mechanism however is not yet understood. One of many possible explanations for the sorption improvement is the particle size reduction and formation of MgH₂ nanoparticles due to the Nb₂O₅ [15,16]. The milling additive helps to break the MgH₂ particles and avoids its agglomeration leading to cold welding during the milling process.

The aim of the present work was to investigate the influence of the Mg particle size on the hydrogen sorption mechanisms by electrochemical and gas-phase methods. Therefore samples of variable size prepared by inert gas evaporation technique (IGE), which consist of ultrafine Mg nanoparticles, were compared to samples synthesized by high energy ball milling (BM) with and

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Sample type	Label	Preparation method	Analysis
Commercial (Mg rod)	Mg bulk	_	PM
	BM-Mg	BM of MgH_2 + dehydrogenation	PM
BM	BM-Mg/Nb ₂ O ₅	BM of MgH_2/Nb_2O_5 + dehydrogenation	PM
BM-Mg	BM-MgH ₂	BM of MgH ₂	XRD
	IGE700-Mg	IGE of Mg at 700 °C	TEM, HS, PM
	IGE900-Mg	IGE of Mg at 900 °C	TEM, HS, PM
$^{\text{iE}}$ IGE700-MgH ₂ IGE of Mg at 700 °C + hydridation	IGE of Mg at 700 $^{\circ}$ C + hydridation	XRD	
	IGE900-MgH ₂	IGE of Mg at 900 °C + hydridation	XRD

 Table 1

 Overview of samples analyzed in the presented work

BM: ball milling; IGE: inert gas evaporation; PM: polarization measurements; HS: hydrogen sorption measurements; XRD: X-ray diffraction; TEM: transmission electron microscopy.

without Nb₂O₅ as milling additive with respect to their electrochemical properties and their gas-phase sorption behavior.

2. Experimental

2.1. Sample preparation

The samples studied in this paper were prepared by two different methods, the inert gas evaporation and the high energy ball milling. An overview of the samples and the corresponding analysis methods is presented in Table 1.

The IGE method was performed by thermal evaporation of Mg (supplied by Aldrich with purity >99.98%) in a He gas atmosphere of 3 Torr and by collecting the powder (IGE-Mg) on a nitrogen-cooled container and subsequent transfer of the sample in He to the glove box as described in [17].

The milling was done under argon atmosphere (<10 ppm water and oxygen) with a Fritsch P5 planetary mill applying 100 g Cr-hardened balls as milling tools within a 300 ml stainless steel vial. MgH₂ (purchased from Goldschmidt AG with purity >95% (rest being Mg)) was milled for 20 h (BM-MgH₂) and additional milled for 100 h with Nb₂O₅ additive (BM-Mg/Nb₂O₅, 2 mol% Nb₂O₅, supplied by Sigma–Aldrich with purity >99.99%). The ball to powder ratio was 10/1.

For the electrochemical experiments the BM-MgH₂ samples were first dehydrogenated at 300 °C. The obtained BM-Mg or the as-produced IGE-Mg is then compacted with 5 wt.% graphite and 5 wt.% PTFE to a pressed pellet electrode suitable for electrochemical hydrogenation (compaction pressure of 6.2 N/mm^2). Thereby the polymer (PTFE) was chosen to increase the void fraction for hydrogen transport and the graphite to enhance conductivity, which results in higher capacity and improved hydrogen kinetics as shown in [18]. The electrode preparation was performed inside the glove box under pure Ar atmosphere. Since the preparation by IGE is very complex and the yield of sample is very low only the electrochemical characterization of the IGE700-Mg sample by potentiodynamic polarization was done up to now. For comparison the obtained results are compared to a bulk Mg rod.

2.2. Sample characterization

The microstructural characterization was carried out by X-ray diffraction (XRD) with a Bruker D8 advance X-ray diffractometer using Cu K α radiation in conventional Bragg–Brentano configuration and by transmission electron microscopy (TEM) and electron diffraction (ED) in a Philips CM200 with 200 kV electron acceleration voltage and a point-to-point resolution of 0.24 nm. For the TEM analysis the nanocrystalline Mg powder was dispersed in toluene as protective agent against oxidation before introduction in the pre-vacuum chamber of the microscope [19].

The potentiodynamic polarization curves were obtained using a FAS1 potentiostat (Gamry Instruments) with a voltage scan rate of 1 mV/s. For all measurements a three-electrode electrochemical cell was used with an Hg/HgO reference electrode and a platinum counter electrode. All the potential values are reported with respect to the Hg/HgO reference electrode. The electrochemical tests using the DC (potentiodynamic polarization) technique were

carried out in a de-aerated, not stirred, 6 M KOH electrolyte at $25 \,^{\circ}\text{C}$. The samples were embedded in a thermoplastic resin to provide electrical isolation. Sample surfaces were ground with a 1200 grid SiC-emery paper and ethanol.

The kinetic sorption measurements from the gas-phase were carried out by a volumetric Sievert apparatus designed by HERA Hydrogen Storage Systems [20]. The measurements consisting of hydrogen absorption and desorption cycles were performed at 300 °C and 1 MPa of hydrogen pressure for absorption and 0.1 kPa of hydrogen pressure for desorption. Therefore the samples of about 100 mg were loaded into a reactor under argon atmosphere and transferred to the Sievert apparatus without air exposure.

3. Results and discussion

3.1. Microstructural characterization of IGE samples by TEM

Compared to samples prepared by high energy milling, with particle sizes ranging from about 0.1 μ m to 1 μ m [19], the magnesium synthesized by IGE displays a different microstructure that consists of isolated particles of variable size and shapes depending on the evaporation temperature. At 700 °C (IGE700-Mg), the particles are almost spherical, single-crystal and well dispersed with an average diameter of about 35 ± 8 nm (see Fig. 1a).

Fig. 1b shows the analysis of Mg powder prepared by inert gas evaporation at a higher synthesis temperature of 900 °C (IGE900-Mg). Here the spherical particles (from the synthesis at 700 °C) are replaced by platelets or particles with isometric shapes of hexagonal symmetry as schematically illustrated in Fig. 1c. The particle size distribution of Fig. 1b shows the variation of hexagonal diameter and width of these particles. The comparison of the particle size histograms for both samples illustrates the increase in particle size and dispersion with the increment in synthesis temperature. In other words, the particle size distribution is less homogeneous and the mean value increases substantially with the increment of evaporation temperature during the gas-phase condensation. A characteristic selected area electron diffraction pattern (SAED) is represented in Fig. 1d. The rings observed in the SAED can be assigned to polycrystalline magnesium metal together with a magnesium oxide phase. This latter phase is constituted by smaller nanocrystalline grains than the pure magnesium metal as can be concluded by the presence of diffuse diffraction rings of MgO appearing in the diffraction pattern.

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Fig. 1. TEM micrographs with particle size distributions of Mg nanoparticles produced by gas-phase condensation in He atmosphere (3 Torr) at evaporation temperatures of (a) 700 $^{\circ}$ C and (b) 900 $^{\circ}$ C. A schematic picture of the hexagonal Mg particles is depicted in (c) and a representative ED for the samples is presented in (d).

A representative HRTEM image of the microstructure for these IGE-Mg samples is presented in Fig. 2. It is important to note that the particles exhibit a core-shell structure showing a crystalline core of metallic magnesium and an oxide passivation layer, which shows some degree of crystallinity and also some amorphous regions (insets A and B in Fig. 2). Thereby the thickness of this oxide layer is in the range of 3-4 nm, which is of similar thickness to that determined for a milled and dehydrided MgH₂ sample [19]. The inset in the top left side of the image corresponds to the digital diffraction pattern (DDP) obtained from the bulk of the particle. The measurement of 2.8 Å at 60° on this DDP allows us the identification of the [001] orientation of the Mg h c p crystal structure. The same geometry is repeated when the DDP is calculated over different areas in the image, pointing out the single-crystalline nature of the particle. This single-crystalline character is a general feature of this type of sample.

3.2. Characterization of the electrochemical hydrogen charging behavior

The main reactions occurring during electrochemical charging and discharging of metal hydride electrodes in, e.g. alkaline solutions, can be described as

 $M + H_2O + e^- \leftrightarrow MH_{ads} + OH^-$ (Volmer reaction)

followed by solid state transfer of hydrogen:

$$MH_{ads} \leftrightarrow MH_{\alpha}$$

$$MH_{\alpha} \leftrightarrow MH_{\beta}$$

The hydrogen atoms adsorb at the electrode surface by the reduction of water (MH_{ads}), diffuse into the electrode material and form a solid solution in the host lattice (MH_{α}). The formation of a metal hydride (MH_{β}) proceeds after exceeding solubility limit of hydrogen. If the hydrogen diffusion into the material proceeds slower than the charge transfer step additional competing reactions can be observed. The adsorbed hydrogen participates in chemical and/or electrochemical recombination steps resulting in the release of molecular hydrogen

 $2MH_{ads} \leftrightarrow H_2 + 2M$ (Tafel reaction)

 $MH_{ads} + H_2O + e^- \leftrightarrow H_2 + OH^- + M$ (Heyrowsky reaction)

The evolution of molecular hydrogen reduces the efficiency of the hydriding/dehydriding cycles of the metal hydride elec-



Fig. 2. HRTEM micrographs of the nanocrystalline Mg sample obtained by IGE showing the core-shell microstructure. The selected zones A and B show zooms on the oxide surface layer whereas in the upper left corner of the graph the digital diffraction pattern (DDP) of the bulk of this particle is presented.

trode. Therefore it is necessary to develop electrodes which allow a preferred Volmer reaction with low hydrogen overpotential, which is a measure of the hydrogen evolution at the electrode surface, relative to the Tafel as well as Heyrowsky reaction and an increased diffusion into the metal.

Potentiodynamic polarization experiments (see Fig. 3) give information regarding the surface reactions at the electrodes, especially regarding the hydrogen overvoltage and the corrosion and passivation behavior of the investigated IGE-Mg electrodes in comparison to the ball milled with and without Nb₂O₅ additives (BM-Mg and BM-Mg/Nb₂O₅). In general it was observed that Nb₂O₅ decreases the hydrogen overvoltage (η_{20} , current density of 20 mA/g), but reduces the corrosion resistance of the milled and dehydrided MgH₂ (Table 2). As reported earlier [21] no significant influence of the addition of graphite as well as PTFE on the hydrogen overvoltage was observed. The reduced hydrogen overvoltage due to the catalyst is assumed to accelerate the hydrogen adsorption at the electrode surface. At lower current densities it is assumed that the Volmer reaction will become the speed limiting reaction and the competing hydrogen recombination reactions will be irrelevant for the BM-Mg/Nb2O5 electrodes. It is also assumed that at very low current densities the electrochemical equilibrium is moved to the anodic reaction, which are influenced by the corrosion current density and the passive current density and leads to a lower storage capac-



Fig. 3. Influence of the particle size on potentiodynamic polarization of Mg (bulk, IGE-Mg700 and BM-Mg) and of a BM-Mg/Nb₂O₅-electrode compacted with a pressure of 6.2 N/mm^2 . Particle size is indicated in the figure.

ity of the BM-Mg/Nb₂O₅ electrodes because of an increased oxidation in the 6 M KOH electrolyte.

In addition the potentiodynamic measurements revealed a significant influence of the particle size on the hydrogen overpotential as well as on the active dissolution and passivation

Table 2

Potentiodynamic polarization parameters of bulk Mg, IGE700-Mg, BM-Mg and Mg/Nb₂O₅-electrodes with different particle sizes compacted with a pressure of 6.2 N/mm^2

Material	Corrosion current density (A/cm ²)	Passive current density (A/cm ²)	Hydrogen overpotential η_{20} at 20 mA/g (mV)
Mg bulk (polycrystalline Mg rod)	1×10^{-5}	4×10^{-5}	226
BM-Mg (µm particle size)	8×10^{-5}	2×10^{-4}	130
IGE-Mg700 (35 nm particle size)	1×10^{-3}	4×10^{-3}	58
BM-Mg/Nb ₂ O ₅ (µm particle size)	4×10^{-3}	4×10^{-4}	61

behavior of nanocrystalline Mg (Table 2). Decreasing the particle size down to 35 nm (IGE700-Mg sample) leads to an improved cathodic reaction with a low hydrogen overpotential but also to strong anodic reactions with high corrosion rates and passive current densities. Further, Mg particles of 35 nm revealed similar hydrogen overpotentials in comparison to nanocrystalline Mg electrodes with Nb₂O₅ and a particle size up to 1 μ m but still the highest affinity for oxidation processes. Thus indicates that smaller Mg particle sizes might improve as well as catalysts the electrochemical hydrogen desorption behavior whereas the electrochemical hydrogen desorption will be strongly influenced by the anodic reaction.

3.3. Hydrogen desorption behavior in gas-phase

Despite the promising electrochemical behavior of the magnesium particles synthesized by the inert gas evaporation method, which resulted in small and little agglomerated particles as shown in Fig. 1, a relatively slow hydrogen sorption behavior at only high sorption temperatures was obtained during H₂ sorption experiments from the gas-phase. Hydrogen desorption at 300 °C, as it is possible for milled MgH₂, could not be achieved for the material from IGE method, so that a temperature of 350 °C was used during the experiments.

Fig. 4 shows the desorption kinetics at 350 °C for the MgH₂ powder synthesized by hydridation of Mg particles prepared by IGE at 700 °C and 900 °C in comparison to the nanocrystalline MgH₂ powder obtained by high energy ball milling. The desorption kinetics of the IGE powder is at 350 °C more or less comparable to the one for milled MgH₂. This is however not very fast considering that the kinetics of the milled MgH₂ is about 10 times slower than for MgH₂ milled with Nb₂O₅ additive, where the sample can de- and absorb within a few minutes [12,13].

The characteristic parameters of desorption are the hydrogen capacity and desorption rate, which are shown quantitatively in Fig. 5. With respect to the hydrogen capacity it can be seen a general decrease for the smaller IGE particles in comparison



Fig. 4. Desorption kinetics of BM-MgH₂ and MgH₂-IGE produced by hydridation of IGE-Mg powder prepared at 700 $^{\circ}$ C and 900 $^{\circ}$ C.



Fig. 5. Hydrogen capacity and desorption rate for the milled MgH₂ and the hydrided Mg powder obtained by IGE at 700 $^{\circ}$ C and 900 $^{\circ}$ C.

to the ball milled ones, which seems to be correlated to the synthesis temperature, i.e. the particle size, of the IGE powders. Also it can be observed for all samples a decrease of the capacity for successive cycles, which occurs for the IGE samples together with a decrease of desorption rate and for the milled sample with an increase of desorption rate. In the following a detailed analysis of these effects with consequences on the kinetic behavior are presented.

3.3.1. Particle size effect

The general decrease of capacity for the IGE samples with decreasing synthesis temperature can be explained considering the amount of oxide phase by means of some simple geometrical models for spherical (IGE700-Mg) and hexagonal plate particles (IGE900-Mg) as they have been observed by TEM analysis (see Fig. 1). These geometrical models are used to calculate a theoretical chargeable metallic Mg content in the sample based on the following assumption and calculations.

For the IGE700-Mg sample spherical magnesium particles with a surface oxide layer of 3.6 nm (as determined by XPS analysis in [19] and TEM observation) were assumed. Based on this assumption volume ratios between the metallic magnesium and the oxide phase could be calculated with respect to variations in the particle size ("spherical model"). For the IGE900-Mg sample this model had to be modified due to the different morphology of the particles. Here the particles are assumed to be formed of boxes with hexagonal base as illustrated in Fig. 1c "hexagonal model" and they are also surrounded by a magnesium oxide surface layer as observed for the spherical model. Assuming the same oxide layer thickness as for the spherical model (3.6 nm) and a fixed ratio of 0.3 between the width and the hexagonal diameter of the particles as determined by TEM analysis, the volume ratios between the metallic magnesium and the oxide phase was calculated again with respect to the variations in the particle size. For both models we assumed that the particles consist of metallic Mg and MgO with densities of 1.738 g/cm³ and 3.58 g/cm^3 , respectively. By these densities the chargeable Mg content as mass ratio was calculated.

Both models together with selected points for the different IGE-Mg samples (IGE700-Mg and IGE900-Mg), where the particle size values were determined from TEM observations (see Fig. 1) are presented in Fig. 6. Fig. 6 shows the calculated mass ratio of chargeable metallic magnesium with respect to particle size in the comparison to the mass ratio obtained experimentally by the hydrogen weight capacity (see Fig. 5) of the IGE-Mg samples as measured during the first and second hydrogen cycle.

Here it can be seen clearly the effect of particle size on the hydrogen capacity. With smaller particles the surface to bulk ratio increases drastically and leads to a high capacity loss in the sample (i.e. decrease of chargeable Mg), although the oxide layer thickness is identical to that of bigger particles. The hydrogen capacity, obtained by titration measurements, follows the trend of lower metallic Mg content with smaller particle size, but is in general higher than the calculated chargeable Mg content based on the TEM analysis. This may be explained by the uncertainty in the density of the magnesium oxide layer that has been used for the calculations of the gravimetric hydrogen content in the spherical and hexagonal model. Surely the oxide layer on the IGE-Mg particles is not as crystalline and stoichiometric as the crystalline MgO phase, which has been assumed for the conversion. In the real samples we most probably deal with oxide layers of lower densities, which may explain the underestimation of the chargeable Mg content measured by capacity measurements during cycling.

3.3.2. Capacity decrease with cycling (oxide layer barrier effect)

The decrease of capacity with cycling (seen in Figs. 4 and 5) occurs for all samples and is mainly due to an incomplete hydridation of the Mg in the samples. In Fig. 7 the XRD for the BM-MgH₂ and the IGE-MgH₂ samples after two cycles are presented. By comparison of the XRD patterns of the three samples it is seen that a certain amount of Mg remains unhydrided as



Fig. 6. Influence of particle size on chargeable metallic Mg content: the curves present semi-theoretical calculations (based on TEM and XPS) assuming hexagonal and spherical particles consisting of Mg and MgO with densities of 1.738 g/cm^3 and 3.58 g/cm^3 , respectively. The expected and experimental hydrogen capacities are shown for IGE-Mg samples prepared at 700 °C (spherical) and 900 °C (hexagonal).



Fig. 7. XRD diffraction patterns of nanocrystalline MgH₂ prepared by IGE at (a) 700 °C and (b) 900 °C or synthesized by (c) high energy ball milling asobtained for the samples after two cycles of H₂ sorption. Symbols correspond to the following indexed phases: MgH₂ (\bigcirc), MgO (∇) and Mg (+).

pure metal. The fraction of this metallic Mg is the lowest for the BM-sample and the highest for the IGE700-MgH₂.

This may be explained by assuming the formation of a MgH₂ layer on the surface of the Mg particles during the hydrogen absorption. The superficial hydride layer grows into the Mg crystals transforming the Mg into MgH₂ (contracting volume model [22]). Since the MgH₂ presents a barrier for hydrogen diffusion, the hydrogen diffusion to the Mg core is more and more hindered with growing MgH₂ phase, so that finally part of the Mg remains inaccessible for the hydrogen. The BM-MgH2 contains bigger particles but very small crystalline domains in the range of 10 nm [19] that are suitable for an almost full charging by hydrogen diffusion. Taking into account the contracting volume model the opposite effect for the two IGE samples would be expected. On the smaller particles as it is the case for the IGE700-Mg sample less hydrogen barrier would be produced by a full charging. However, this sample shows experimentally the highest remaining metallic Mg fraction after cycling of all three samples. To explain these results the microstructural properties of the oxide layer should be considered. Since the thickness of the oxide layer is more or less constant for all samples, the composition and crystallinity can play a major role in hindering the hydrogen diffusion into the material. A more ordered and dense oxide layer can hinder the hydrogen diffusion into the particle [23]. This fact may explain why the hydrided Mg produced by IGE shows slower hydrogen sorption kinetics than the BM-MgH2 produced by milling despite of its smaller particle size. While during the gas-phase condensation the oxide layer can grow unaffected from any mechanical influences, the oxide layer on the BM-MgH₂ is influenced by mechanical deformation and high compressive stresses [24,25], induced by the milling process, which may generate a less dense, crystalline and easier to penetrate oxidation layer. This results also in a different behavior with repeated cycling for the milled sample. In contrast to the IGE samples here the hydrogen sorption kinetics improves with repeated cycling. It can be assumed that micro/nano-cracks in the oxide layer are formed during the cycling [26] which facilitates the hydrogen uptake through the surface.

Apart from this, the crystal growth during hydridation has also to be taken into account. In contrast to the electrochemical experiment, in a gas-phase experiment the Mg sample is heated during cycling, which can lead to a considerable crystal and particle growth. This effect does not occur in electrochemical charging, where pure particle size effects can be observed.

4. Conclusions

The studies of nanocrystalline Mg powder, which was obtained by inert gas evaporation technique, in comparison to that obtained by dehydridation of nanocrystalline MgH₂ prepared by mechanical milling with and without 2 mol% Nb₂O₅ revealed an influence of the Mg particle size on the electrochemical and gas-phase hydrogen sorption. In the case of electrochemical charging, a reduced particle size (35 nm) yielded a performance similar to that obtained using Nb₂O₅ as additive. The hydrogen overpotential of nanocrystalline Mg with a particle size up to 1 μ m is much higher than for a smaller particle size of 35 nm as well as for Mg with Nb₂O₅ catalyst. However, the electrochemical oxidation behavior became more favorable with the decrease in particle size which might influence the hydrogenation negatively at very low current densities. The promising electrochemical behavior of the Mg samples produced by inert gas evaporation could however not be observed for the gas-phase sorption. The gas-phase sorption experiments have shown that the sorption properties of the IGE-Mg samples do not only depend on the particle size, but are influenced very much by the composition and crystallinity of a thin magnesium oxide layer (3-4 nm) covering the magnesium metal underneath. The use of smaller particles leads inevitably to a higher contribution of the oxide component in the sample and consequently to a loss of capacity. The formation in the case of a more ordered and dense oxide layer hinders the hydrogen diffusion into the particle. These factors explained that IGE-Mg particles did not demonstrate better kinetics in spite of their small size and were not suitable to prove any particle size influence on the gas-phase sorption kinetics.

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