

# Morphology and Preferred Orientation of Pulse Electrodeposited Magnesium

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A nanocrystalline magnesium material with a high specific surface area is expected to react rapidly and reversibly with hydrogen gas to yield magnesium hydride, a hydrogen storage medium. In this paper, the feasibility of the synthesis of magnesium materials for hydrogen storage applications by pulse electrodeposition of magnesium from ethereal electrolytes containing Grignard reagents was investigated. Deposition onto flat stainless steel electrodes established that, as in dc deposition, the morphology of the deposits varied widely with electrolyte composition and charge density. Irregular, nanocrystalline magnesium films were formed at low current density ( $0.4 \text{ mA cm}^{-2}$ ) and low charge density ( $1 \text{ C cm}^{-2}$ ) using butylmagnesium chloride electrolytes in dibutyl diglyme, while at a higher current density ( $15 \text{ mA cm}^{-2}$ ) in tetrahydrofuran, dense films were favored. © 2010 The Electrochemical Society. [DOI: 10.1149/1.3298883] All rights reserved.

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Magnesium hydride is an attractive material for solid-state hydrogen storage due to its high gravimetric energy density, simplicity, high reversibility, and low cost. However, the speed of hydrogen insertion and extraction from magnesium hydride is slow and the thermodynamics is unfavorable. The kinetic restriction has been largely overcome by the use of fine-grained, high specific surface area powders, typically generated by milling large-grained materials to a fine-grained product, and by the inclusion of suitable catalysts.<sup>1-4</sup> Although milling produces particles with multiple defects and grain boundaries near the surface, which favor nucleation of the hydride,<sup>3</sup> the milling process is time-consuming, requires a high energy input, leads to the incorporation of impurities, and gives an irregular product with a wide distribution of particle sizes.

Much attention has recently been directed to the deposition of magnesium thin films using a variety of techniques including dc magnetron sputtering, electron-beam physical vapor deposition, plasma sputter, pulsed laser deposition, and oblique angle deposition.<sup>5-9</sup> An alternative route for the direct deposition of fine particles and thin films of magnesium is pulse electrodeposition. This technique has been widely applied for the generation of metallic nanoparticles in both aqueous and nonaqueous electrolytes.<sup>10,11</sup> Precise control of grain size within a narrow range has been demonstrated by a variation in the deposition parameters. This technique has the potential for industrial application and the generation of large amounts of material at low cost.

The electrodeposition of magnesium is not possible in aqueous solutions due to the high electronegativity of magnesium, but it is possible in organic solutions and ionic liquids. Several investigators have successfully used dc electrodeposition to deposit magnesium from ethereal solutions, and the size and morphology of electrodeposited magnesium particles varies dramatically, depending on the deposition conditions.<sup>12-15</sup> There have been only two papers to date on the pulse electrodeposition of magnesium in ethereal electrolytes. Hassen et al.<sup>16</sup> compared dc and pulse electrodeposited layers of magnesium on mild steel substrates for corrosion protection using electrolytes of methyl magnesium chloride in tetrahydrofuran (THF) and pulse electrodeposition resulted in a finer grain structure than dc deposition with grains of about 3  $\mu$ m. Haas and Gedanken<sup>1</sup> recently reported the synthesis of magnesium nanopowders with an average grain size of 4-6 nm by a sonoelectrochemical route, which couples the electrochemical deposition on a Ti sonoelectrode surface with a sonic pulse to release the electrodeposit from the surface. The very small grain sizes reported for their products raise the possibility of tailoring fine-grained magnesium deposits to optimize their usefulness as hydrogen storage materials by fine-tuning the deposition conditions. Little work has been reported on the electrodeposition of

magnesium specifically for the purpose of optimizing hydrogen storage properties. Tatiparti and Ebrahimi<sup>18</sup> studied the dc electrodeposition of dendritic aluminum–magnesium deposits from ethereal solutions for hydrogen storage applications using current densities from 60 to 150 mA cm<sup>-2</sup>. Details of the hydrogen storage properties of their deposits have been published recently.<sup>19</sup>

In this study, the direct synthesis of electrodeposited magnesium with particle and grain sizes in the desired range by an appropriate selection of deposition conditions was investigated. The effect of the variation in the current density, electrolyte composition, and electrolyte concentration was studied.

#### **Experimental**

The Grignard reagents, 3 M methylmagnesium chloride (CH<sub>3</sub>MgCl) in THF, 2 M butylmagnesium chloride (BuMgCl) in THF, and 1.45 M BuMgCl in dibutyl diglyme (DBG), and anhydrous aluminum chloride (AlCl<sub>3</sub> > 99%) were obtained from Sigma-Aldrich. All experiments were carried out in a glove box under a protective ultrahigh purity argon atmosphere (BOC gas).

A two-electrode glass cell was used for the electrodeposition experiments. All glassware were dried in a drying oven before use. The cathode consisted of a 316 stainless steel  $(5 \times 15 \times 1 \text{ mm})$ sheet, polished with SiC paper, and cleaned and dried before use. The anode consisted of a magnesium ribbon (>99% purity, Sigma-Aldrich). The anode surface was scraped with a nylon scourer in the glove box to remove any surface oxidation layer before loading into the electrochemical cell. The electrolyte volume was approximately 5 mL. The deposition experiments were performed under constant current conditions using a purpose built constant current power supply coupled to a signal generator to generate the pulse train. Typical deposition parameters used were  $t_{on} = 2$  ms and  $t_{off} = 8$  ms with a current density of 20–150 mA cm<sup>-2</sup>. The deposition time was typically 15-60 min. Additional measurements were performed using a Princeton AG&G Versastat 3 potenstiostat/galvanostat in the fast galvanostatic pulse mode. Deposited samples were washed in anhydrous THF (Aldrich) and vacuum dried before analysis.

Powder X-ray diffraction (XRD) patterns were recorded using a Siemens D5000 diffractometer with copper K $\alpha$  radiation. Samples were sandwiched between two layers of polyimide Kapton tape (ChemTools) in the glove box to prevent exposure of the samples to the atmosphere during XRD analysis. Grain sizes were determined from the XRD peak broadening using the Scherrer equation<sup>20</sup> after peak fitting with the XFIT program (freeware).<sup>21</sup> Pearson VII (PVII) functions were used for the fitting of the XRD line profiles. Correction for instrumental broadening was made using data from a lanthanum hexaboride (LaB<sub>6</sub>) standard (NIST 660a).

The morphology of the sample surfaces was examined with a JEOL JSM-5410LV scanning electron microscope.

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Table I. A summary of the electrodeposition parameters used in this study. $i_{av}$ = average current density and $i_{peak}$ = peak current densit	iy. All
samples were deposited with $t_{on} = 2$ ms, $t_{off} = 8$ ms (duty cycle = 20%), and temperature = 25°C.	

Sample	Electrolyte	[AlCl <sub>3</sub> ] (M)	$(\mathrm{mA}^{i_{\mathrm{av}}}\mathrm{cm}^{-2})$	$(\mathrm{mA}^{i_{\mathrm{peak}}}\mathrm{cm}^{-2})$	Charge density (C cm <sup>-2</sup> )
Mg <sub>1</sub>	3 M CH <sub>3</sub> MgCl in THF	0	15	75	54
Mg <sub>2</sub>	2 M BuMgCl in THF	0	15	75	54
Mg <sub>3</sub>	1.45 M BuMgCl in DBG	0	0.4	2	1
$Mg_4$	1.5 M CH <sub>3</sub> MgCl in THF	0.125	15	75	54
Mg <sub>5</sub>	1 M CH <sub>3</sub> MgCl in THF	0.167	15	75	54
Mg <sub>6</sub>	1 M CH <sub>3</sub> MgCl in THF	0.167	30	150	54
Mg <sub>7</sub>	1 M CH <sub>3</sub> MgCl in THF	0.167	3	15	0.18
Mg <sub>8</sub>	1 M CH <sub>3</sub> MgCl in THF	0.167	3	15	1.8

## **Results and Discussion**

Pulse electrodeposition of magnesium.— Table I gives a summary of the deposition conditions of the samples prepared for this study. An initial sample, Mg<sub>1</sub>, was electrodeposited using a 3 M solution of CH<sub>3</sub>MgCl as electrolyte and deposition conditions as indicated in Table I. The deposit surface was matte and white. A small section of the electrode was covered with very fine gray dendrites. The XRD pattern of the white deposit in the range 30–80° 20 (Fig. 1a) shows sharp peaks, which can be indexed to the crystallographic reflections of hexagonal magnesium (space group P63/mmc), indicating a coarse-grained polycrystalline deposit. Additional peaks from the stainless steel substrate are indicated in Fig. 1. The ratio of the (002)/(101) peak intensities (Table II) for this sample is 2.1 compared to 0.26 for a standard Mg sample. The enhancement of the intensity of the 002 peak suggests a preferential



**Figure 1.** Powder XRD patterns of electrodeposited magnesium (a)  $Mg_1$  indexed to space group *P*63/*mmc*.  $\blacklozenge$  indicates peaks from the stainless steel substrate and magnified images of 30–40° 2 $\theta$  region for (b)  $Mg_1$ , (c)  $Mg_2$ , and (d)  $Mg_3$ .

orientation of the Mg crystallites parallel to the 002 crystallographic planes, indicating that crystal growth occurs along the *c*-axis. This agrees well with the results of Hassen et al.<sup>16</sup>

The experiment was repeated using two other electrolytes, 2 M BuMgCl in THF (Mg<sub>2</sub>) and 1.45 M BuMgCl in DBG (Mg<sub>3</sub>) for comparison. DBG was selected for evaluation as it has a far lower vapor pressure than THF and is therefore preferred from a safety point of view. Due to the high viscosity and low ionic conductivity of the DBG electrolyte, the maximum possible current density obtained was 0.4 mA cm<sup>-2</sup>. An enlarged plot of the powder XRD patterns for the 30–40°  $2\theta$  region is shown for each electrolyte in Fig. 1b-d. In each case, characteristic magnesium peaks were obtained, but in the latter two electrolytes, there was no evidence of significant preferential orientation, as seen from the ratios of the (002):(101) peak intensities in Table II. The values of the grain sizes of the deposits calculated from the Scherrer formula based on the line peak broadening of the (101) peak at  $36.61^{\circ} 2\theta$ , after the correction for instrumental broadening, are given in Table II for each of the samples. However, the Scherrer formula does not take into account the broadening of the XRD peaks due to microstrain and may therefore only be considered to give approximate values for grain size.

Scanning electron micrographs of the samples are shown in Fig. 2a-c. Mg<sub>1</sub> shows a dense coating consisting of large particles of the order of 10  $\mu$ m across, which appear to be largely oriented parallel to the electrode surface. This confirms the preferential orientation indicated by the XRD pattern (Fig. 1a). The thickness of the film was approximately 70  $\mu$ m, and the efficiency of the deposition was 75%. Mg<sub>2</sub> deposited using BuMgCl in THF electrolyte is typical of the crystalline deposits reported by other investigators for dc deposition of magnesium in ethereal electrolytes.<sup>22</sup> Randomly oriented, pyramidal particles approximately 3–5  $\mu$ m across are visible and the surface is not completely covered by the film. In this case, the film was approximately 60  $\mu$ m thick and the deposition efficiency was 57%. Mg<sub>3</sub> shows a completely different morphology with an irregular surface, with particles of the order of 2  $\mu$ m across. This

Table II. Average crystallite size of electrodeposited magnesium
calculated using the Scherrer formula and the value of the (002)/
(101) peak intensities.

Sample	Corrected peak width (°)	Average crystallite size (nm)	(002)/(101) peak intensities
Mg <sub>1</sub>	0.03	>200	2.1
Mg <sub>2</sub>	0.05	160	0.2
Mg <sub>3</sub>	0.13	60	0.1
$Mg_4$	0.02	> 200	0.3
Mg <sub>5</sub>	0.08	140	0.2
$Mg_6$	0.05	180	1.4



Figure 2. SEM micrographs of (a)  $Mg_1$ , (b)  $Mg_2$ , and (c)  $Mg_3$  showing the dramatic change in morphology with different deposition conditions.

may be due to the much lower charge density in this case  $(1 \text{ C cm}^{-2})$ . Aurbach et al.<sup>15,22</sup> reported that the dc deposition of magnesium from ethereal solutions results in a porous deposit, at low charge density, with a different morphology from the pyramidal crystals formed at higher charge density, although the morphology of their sample produced using dc deposition is somewhat different from that found in the present study. However, using dc deposition, the porous morphology only persists below 0.5 C cm<sup>-2</sup>, after which the angular crystallites form. It therefore appears that the pulse deposition technique may extend the charge density range in which the porous deposits are formed in DBG solutions. The sono-electrochemical products generated by Haas and Gedanken,<sup>17</sup> with reported grain sizes from XRD line broadening of 25 nm, were produced using 600 s pulses at 0.5 mA cm<sup>-2</sup>, corresponding to a



**Figure 3.** Powder XRD patterns of electrodeposited magnesium samples (a)  $Mg_4$ , (b)  $Mg_5$ , and (c)  $Mg_6$  showing the effect of  $AlCl_3$  addition and current density.

charge density of 0.3 C  $\,\mathrm{cm^{-2}}$  per pulse. Their deposits would therefore have been made in the porous regime found at a low charge density.

These three samples confirm that the choice of electrolyte and deposition conditions has a profound effect on the morphology and crystallite size of pulse electrodeposited magnesium. It is tempting to speculate as to which morphology may be expected to be optimal for hydrogen storage applications and whether the preferred orientation is advantageous in any way. Dense, large-grained films like Mg<sub>1</sub> would not be expected to perform well as hydrogen storage media as the penetration of hydrogen would be limited. The preferential orientation of the deposit actually appears to facilitate dense packing and minimizes the formation of voids, further limiting the hydrogen flow. However, the results reported by Leon et al.<sup>23</sup> for hydrogen storage in 30 µm thick, preferentially orientated magnesium films formed by thermal evaporative deposition appear to indicate that the [002] preferential orientation facilitates hydrogen absorption and desorption, in this case. The evaporatively grown films, however, have a very fine grain structure and columnar growth morphology, which is very different from the samples under consideration here.

 $Mg_2$  has numerous voids between particles, probably due to the less efficient packing of randomly oriented particles and a finer grain structure compared with  $Mg_1$ . It is expected that both these factors would be advantageous for hydrogen absorption. An irregular, finegrained sample with a high specific surface area like  $Mg_3$  may, however, be expected to offer the best morphology, as it would allow the gas to penetrate readily into the bulk of the film.

*Effect of AlCl<sub>3</sub> addition.*— When AlCl<sub>3</sub> is added to alkylmagnesium halide electrolytes, the ionic conductivity increases and complex ionic species form in solution, resulting in improved voltage stability.<sup>22</sup> These enhanced electrolytes offer the possibility of increased deposition efficiency at a high current density while avoiding problems of electrolyte decomposition at high overvoltages.

Two samples,  $Mg_4$  and  $Mg_5$ , were prepared with increasing ratios of AlCl<sub>3</sub> to CH<sub>3</sub>MgCl to assess the effect of AlCl<sub>3</sub> addition on the morphology and grain size of the pulse electrodeposited magnesium. Both samples gave white, matte deposits, with no dendrites. Figure 3a and b shows the XRD patterns in the range  $30-40^{\circ}$  2 $\theta$  for samples with a [CH<sub>3</sub>MgCl]:[AlCl<sub>3</sub>] ratio of 12:1 and 6:1, respectively. The XRD patterns show characteristic magnesium XRD peaks indicating crystalline magnesium and no evidence of preferential orientation, as determined from the ratio of the (002):(101) peak intensities (Table II). No aluminum peaks were present in the XRD pattern, but this alone does not exclude the possibility of some Al codeposition. However, Viestfrid et al.<sup>24</sup> reported that, based on



Figure 4. SEM micrographs of (a) Mg<sub>4</sub> and (b) Mg<sub>5</sub>.

the atomic absorption spectroscopy results, no codeposition of Al occurs for Grignard reagent/Al salt ratios greater than 1/3. The calculated values of the crystallite size are given in Table II. For Mg<sub>4</sub> with a 12:1 ratio of  $[CH_3MgCl]$ : [AlCl<sub>3</sub>], there is no reduction in the crystallite size, but as the proportion of AlCl<sub>3</sub> in the solution increases to 6:1, there is an increase in the XRD peak width and a decrease in the crystallite size of the magnesium deposits to 140 nm. Scanning electron microscope (SEM) images of Mg<sub>4</sub> and Mg<sub>5</sub> shown in Fig. 4a and b, respectively, revealed a very similar morphology to Mg<sub>2</sub> (Fig. 2b).

Effect of current density.- In pulse electrodeposition experiments using aqueous electrolytes, an increase in current density leads to an increase in overvoltage, which results in increased nucleation rate and a reduction in grain size.<sup>11</sup> A sample (Mg<sub>6</sub>) was electrodeposited under the same deposition conditions as sample Mg5, but with double the peak current density (150 mA  $\text{cm}^{-2}$ ). Figure 5a shows a scanning electron micrograph of sample Mg<sub>6</sub>. It shows a crystalline deposit with large, well-defined, pyramidal crystallites approximately 5 µm across. In particular, the facets of the crystal are clearly visible. The XRD pattern of this sample is shown in Fig. 3c and indicates a large-grained material with some 002 preferential orientation, although the preferred orientation is less marked than in Mg<sub>1</sub> (see Table II). This is confirmed by SEM, which shows some of the crystallites orientated with the apex of the pyramids perpendicular to the surface. The crystallite size calculated from the XRD line broadening is given in Table II. The increase in the current density in this pulse regime results in grain sizes that are comparable, within the accuracy of the technique, to those found at a lower current density.

*Effect of charge density.*— Figure 5b shows an SEM image of a magnesium sample  $(Mg_7)$  deposited under the same conditions as



Figure 5. SEM micrographs of (a) Mg<sub>6</sub>, (b) Mg<sub>7</sub>, and (c) Mg<sub>8</sub>.

sample Mg<sub>5</sub> but with a peak current density of 15 mA  $cm^{-2}$  and a deposition time of 1 min to give a total charge density of 0.18 C cm<sup>-2</sup>. Sparsely distributed submicrometer crystallites with the same geometry as those deposited at a high charge density are visible, and it can be seen how the small crystallites agglomerate to form larger particles. It therefore appears that, under pulse deposition conditions in the THF-based solutions with a current density of 15 mA  $cm^{-2}$ , the deposit maintains the same morphology even at a low deposition charge density. This is in contrast to the findings of Aurbach et al.,<sup>15</sup> where they consistently reported a different morphology for dc deposits at a low charge density ( $<0.5 \text{ mA cm}^{-2}$ ). It is speculated that an evenly dispersed coating of these small particles may react rapidly with hydrogen gas as they would be easily accessible to the gas, and the small particle size would reduce the diffusion distance of hydrogen into the bulk of the particles. It was not possible to determine the grain size of these particles as the sample size was too small to allow for powder XRD analysis. Figure 5c shows Mg<sub>8</sub> prepared under the same conditions as Mg<sub>7</sub>, but deposited for 10 min to give a charge density of 1.8 C cm<sup>-2</sup>. The same angular particles are visible, but they are much larger than in Mg<sub>7</sub> and are agglomerated to form a layer which still includes fairly large voids.

### Conclusions

In this work, it was demonstrated that, by varying the pulse deposition conditions, the morphology, preferential orientation, and grain size of the electrodeposited magnesium particles can be varied from dense films with strong preferential 002 orientation to irregular, nanocrystalline films with a random crystallite orientation. The irregular films deposited at a low current density and a low charge density in DBG electrolytes are promising materials for hydrogen storage applications as they have particle sizes in the 2–3  $\mu$ m range and grain sizes less than 100 nm. The process is also rapid, with deposition times of 1 h compared to milling times of 20-100 h to achieve a similar morphology.

Further studies are underway to assess the hydrogen storage properties of the pulse electrodeposited magnesium.

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