Electrochemical Hydrogen Storage Characteristics of Thin Film MgX (X = Sc, Ti, V, Cr) Compounds

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The hydrogen storage characteristics of thin film MgX (X = Sc, Ti, V, Cr) compounds were investigated electrochemically. The successful preparation of these metastable, crystalline single-phase, MgX compounds was achieved by means of electron-beam deposition at room temperature. The reversible hydrogen storage capacity of these compounds is excellent and up to six times higher than commercial AB2-type materials. The gravimetric storage capacities of these new materials were determined to be 1790 mAh/g for Mg80Sc20, 1750 mAh/g for Mg80Ti20, 1700 mAh/g for Mg80V20, and 1325 mAh/g for Mg80Cr20, corresponding to 6.7, 6.5, 6.4, and 4.9 wt % H, respectively. The hydrogen absorption and desorption kinetics are profoundly influenced by the element X incorporated in the MgX compound. Galvanostatic measurements show that the rate capability of the Sc- and Ti-containing compounds is significantly better than that of the V- and Cr-containing compounds. Isotherms of these systems are obtained using galvanostatic intermittent titration technique, revealing that the equilibrium potential of the main charge/dischARGE plateau, apart from the Mg80Sc20 compound, only slightly depends on X in MgX. The electrochemical measurements show that low-cost Ti is an excellent substitute for the expensive Sc in MgSc, without introducing detrimental effects.

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As it is expected that a hydrogen-driven economy might be a viable solution to the shortage of fossil fuels in the future, technologies need to be developed to effectively store large amounts of hydrogen. However, the best way of storing the hydrogen is still a topic of serious debate. Until now, hydrogen can be stored in different ways: As compressed gas, in its liquid form, physisorbed onto highly porous materials, and interstitially or chemically as a metal hydride (MH). An important advantage of using MH compounds, as compared to the low-temperature storage techniques like liquid hydrogen and physisorption, is that the hydrogen can be stored and released at moderate temperatures. MHs also provide a safe way of storage as they can be handled without extensive safety precautions, unlike compressed hydrogen gas. With this in mind, MHs might be a serious storage alternative for compressed or liquid hydrogen, especially when considering mobile applications like hybrid electric vehicles (HEV).

Of course, hydride-forming materials can also be used in many other applications, for instance, as negative electrode material in rechargeable batteries. The use of portable electronic equipment has increased tremendously over the last decade, research towards improved high energy density rechargeable batteries is becoming a necessity. Small electronic equipment like portable telephones, laptops, shavers, power tools, etc. are nowadays powered by either Li-ion or Nickel-Metal Hydride (NiMH) batteries. Because the energy consumption of present portable equipment is growing steadily, future NiMH batteries are required which are able to store a larger amount of energy without leading to an increase in weight. This can be achieved by replacing the existing electrode materials by new MH compounds that have a higher energy density, i.e., higher hydrogen storage capacity.

Commercially used MH electrodes developed through the years show hydrogen storage capacities of about 300 mAh/g, corresponding to −1.1 wt % hydrogen stored. Recently, Notten et al. showed that MgSc compounds exhibit very high storage capacities of up to six times higher than ScH2. It is therefore desirable that Sc is (partly) replaced by a less expensive material without introducing detrimental effects. It was argued that, depending on the Sc content, the MgSc hydride is either rutile-structured or face-centered cubic (fcc)-structured of which the latter structure shows superior hydrogen transport properties. The favorable fcc structure of the MgSc hydride most likely originates from the fact that the fcc structure of ScH2 is retained, even when Sc is partially substituted by Mg. It was experimentally determined that the Mg80Sc20 composition yielded an optimum in hydrogen storage capacity, while exhibiting excellent rate capability (i.e., fcc-structured hydride).

Therefore, a logical substitute for Sc would be a material that forms an fcc-structured hydride when alloyed with Mg. Additionally, the material should be similar in weight as compared to Sc. Promising candidates, based on these criteria, are Ti, V, and Cr. Unfortunately, these materials do not form intermetallics with Mg under standard alloying conditions. During the last few years, several researchers have investigated both the preparation and the hydrogen sorption characteristics of the MgTi, MgV, and MgCr systems. Kyo et al. used 8 GPa and 873 K to synthesize metastable Mg7TiH6. The same anvil-cell technique was used to create Mg7VH6 by Kyo et al. in 2004. Finally, Mg7CrH6 was discovered by the same group in 2003 and additionally investigated by Könnebro et al. Although the complexity of the anvil-cell technique is very high and the conditions applied very extreme, it shows that crystalline MgX hydrides (X = Ti, V, Cr) can exist in bulk form. Until now, only a few researchers have tried to synthesize and characterize the same compounds via a thin film approach. Richardson et al. used magnetron sputtering to prepare MgTi thin films and subsequently examined the properties of this system during hydrogenation. However, as these films were amorphous in their as-deposited state, no indication could be given whether or not a single-phase compound was formed. Additionally, no information was given on the stoichiometry of the hydride.

In the present study it will be shown that Mg80X20 (X = Sc, Ti, V, Cr) thin films, manufactured by means of electron-beam deposition, are highly crystalline and single-phase. This shows that it is possible to synthesize these metastable compounds without using extremes in pressure and temperature. The hydrogen storage properties of these promising Mg80X20 compounds are investigated electrochemically in an alkaline environment. To protect the films from corrosion and to catalyze hydrogen sorption, the films were capped with a 10 nm Pd topcoat. Thin films were used in this study because they can serve as a 2D model system, enabling accurate determination of material kinetics, thermodynamics, and hydrogen transport phenomena.

Experimental

Mg80X20 thin films were manufactured using electron-beam deposition (base pressure between 10−7 and 2 × 10−7 mbar). During deposition the substrates were kept at room temperature. The thin
films, having a nominal thickness of 200 nm, were deposited on quartz substrates (20 mm). An in-house procedure was used to clean the substrates prior to deposition. A Pd topcoat, 10 nm thick, was deposited on top of the Mg80X20 thin films. Rutherford backscattering spectroscopy (RBS) was used to check the film composition. Based on these measurements it was concluded that the Mg80X20 composition was uniform throughout the film. Additionally, RBS measurements were used to calculate the exact mass of the Mg80X20 compounds, resulting in 120, 123, 120, and 127 μg for the Mg80Sc20, Mg80Ti20, Mg80V20, and Mg80Cr20 films, respectively. Calculations regarding the hydrogen storage capacity are solely based on the RBS measurements. As a maximum deviation in the hydrogen storage capacity of the Mg80X20 compounds can occur of no more than 3%, no correction is made for the Pd cap layer. X-ray diffraction (XRD), using Cu Kα radiation, was employed to identify the crystallographic phases of the freshly prepared samples.

A three-electrode setup, of which the details are described elsewhere, was used to electrochemically characterize the thin films. The electrochemical cell was thermostated at 25°C and filled with 6 M KOH electrolyte. The potential of the thin film electrode was measured with respect to a Hg/HgO reference electrode 6 M KOH electrolyte. The potential of the thin film electrode was taken to prevent surface poisoning of the thin film electrodes. Galvanostatic dehydriding of the thin film can be described by a two-step mechanism. The first step is the charge transfer reaction at the Pd/KOH interface, which can be represented by

$$H_2O + M + e \rightarrow MH_{abs} + OH^-$$  \[1\]

Once adsorbed hydrogen atoms (H_{ads}) are formed at the electrode surface, they are absorbed (H_{abs}) by the Pd topcoat and subsequently by the underlying MH according to

$$MH_{abs} \rightarrow MH_{ads}$$  \[2\]

According to Reaction 1, one electron is transferred for each hydrogen atom inserted into or extracted from the hydride-forming compound, therefore Coulomb counting can be used to determine the hydrogen content. Advantageously, electrochemical hydrogen loading can thus be used to accurately control the hydrogen content in the MgX thin film electrodes.

The electrochemical response of the Mg80Sc20 thin films was compared during galvanostatic hydrogen insertion (charging) and hydrogen extraction (discharging). Figure 2-5 show the charge, discharge, and deep-discharge curves of each of the four compounds. Currents were used of -0.6 mA (~5000 mA/g), +0.12 mA (~10000 mA/g), and +0.012 mA (~100 mA/g), respectively. Note that in these experiments the layers were first fully hydrogenated...
A third and final plateau is reached when the electrode was allowed to equilibrate for 1 h. Subsequently, deep-discharging was performed [curves (c)]. Finally, the electrodes were again charged to the fully loaded state [curves (d)].

Focusing on the response of the Mg80Ti20 compound, corresponding to the first time the electrode is hydrogenated, it is clear that the curve reveals three sloping plateaus (see Fig. 3a). Based on the total amount of material present in this thin film electrode, the first plateau roughly corresponds to the hydrogenation of Ti to TiH2. Analogously, the second plateau could explain hydrogenation of Mg to MgH2. A third and final plateau is reached when the electrode attains its fully hydrogenated state and is due to hydrogen gas formation. The Mg80Sc20 compound shows, compared to the Mg80Ti20, a similar behavior during its initial hydrogenation (see Fig. 2a). However, the transition from the first (Sc to ScH2) to the second plateau (Mg to MgH2) is much less pronounced. First-time charging of the Mg80V20 and Mg80Cr20 compounds shows a more complex response, especially during the early stage of charging (see Fig. 4a and 5a). Most notably, the main plateau, linked to hydrogen absorption, is more flat and manifests itself at more negative potentials (−1.00 to −1.15 V) as compared to the MgSc and MgTi compounds (−0.8 to −1.1 V). Like before, the final plateau can be attributed to hydrogen gas formation.

The discharge curves of all Mg80X20 compounds, [depicted in Fig. 2-5, curves (b)], reveal a sloping response when the film is in the hydrogen-rich state. This response can be linked to a solid solution behavior, which clearly depends on the metal X. Furthermore, a very flat plateau at about −0.67 V can be seen for the Mg80Sc20 and Mg80Ti20 compounds, indicative of a two-phase coexistence region (see Fig. 2b and 3b). The Mg80V20 and Mg80Cr20 compounds, however, cannot be discharged this effectively using the same current and no plateau is observed (see Fig. 4b and 5b). Subsequent deep-discharging results in all four compounds being completely discharged. In the case of the MgSc and MgTi compounds, the largest part of the hydrogen was already extracted at high current, effectively only showing a second solid solution behavior in the hydrogen-depleted state (see Fig. 2c and 3c). The lower current used during deep-discharging enabled the release of the remaining hydrogen from the Mg80V20 and Mg80Cr20 compounds (Fig. 4c and 5c). The potential response now also shows a two-phase coexistence region for these materials, similar to that of the MgSc and MgTi compounds. Comparing the extracted charge at both high and low currents, it is clear that the rate capability of the Mg80V20 and Mg80Cr20 materials is significantly lower than that of the MgSc and MgTi compounds. To illustrate this fact, about 1300 mAh/g of charge can be extracted from the Mg80Sc20 and Mg80Ti20 thin films within 1.3 h, whereas it takes over 11 h to extract the same amount from the Mg80V20 or Mg80Cr20 films.

The hydrogen storage capacity of the four compounds was determined by adding the measured discharge capacity of the first discharge and the first deep-discharge [see Fig. 2-5, curves (b) and (c)]. The results are listed in Table I and are given as gravimetric storage capacity in both [mAh/g] and [wt % H]. The measured hy-

Table I. Gravimetric storage capacities of MgX compounds (X = Sc, Ti, V, or Cr).

<table>
<thead>
<tr>
<th>Material</th>
<th>Gravimetric storage capacity [mAh/g]</th>
<th>[wt % H]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg80Sc20</td>
<td>1790</td>
<td>6.67</td>
</tr>
<tr>
<td>Mg80Ti20</td>
<td>1750</td>
<td>6.53</td>
</tr>
<tr>
<td>Mg80V20</td>
<td>1700</td>
<td>6.38</td>
</tr>
<tr>
<td>Mg80Cr20</td>
<td>1325</td>
<td>4.90</td>
</tr>
</tbody>
</table>
drogen storage capacities of the Mg80X20 compounds is close to six
times that of commercially used AB5-type materials.4,18

If the charging curves are compared, measured when hydrogenating the thin films for the first and second time, other interesting facts come to light [see Fig. 2-5, curves (a) and (d)]. It is evident that the amount of charge (or hydrogen) that can be stored in the materials when charged for the second time, is less than during their first hydrogenation. This shows that part of the hydrogen stored during the first charging step is irreversibly incorporated and cannot be released under the experimental conditions applied. The curves corresponding to the second time the Mg80Sc20 and Mg80Ti20 compounds are charged, only show a single large plateau. This indicates that hydrogen must have been irreversibly bound to Sc and Ti initially [see Fig. 2 and 3, curves (a) and (d)]. This is plausible, as it is known from literature that the heats of formation of ScH2 and TiH2 are reported to be very negative, i.e., −100 and −70 kJ/mol H2, respectively.19 The curves corresponding to the second time that the Mg80V20 and Mg80Cr20 film are charged reveal a similar trend and less hydrogen could be absorbed [Fig. 4 and 5, curves (a) and (d)]. The most notable difference between the first and the second time the compounds are hydrogenated is, however, the significant reduction of the overpotential (η). η can be represented by

\[ \eta = \eta_{\text{IR}} + \eta_{\text{kin}} + \eta_{\text{dif}} \]  

[3]

where IR is the Ohmic drop, ηkin is the kinetic overpotential, and ηdif the diffusion overpotential. Preliminary electrochemical impedance spectroscopy (EIS) measurements (not shown here) indicate that the Ohmic drop can be ignored, as it is negligible when applying currents equal to those used in this contribution. More importantly, it can be concluded from the EIS data that the reduction in η can be attributed to a decrease in ηkin, which is brought about by improved surface kinetics. As these kinetics are directly linked to the nature of the interface at which the charge transfer takes place (Reaction 1), it must be concluded that hydriding/dehydriding the thin film electrodes induces changes at the Pt/d/KOH interface. Research is currently in progress in which the underlying effects of this reduction in η are investigated. The results will be published in a forthcoming paper.

The isotherms of the Mg80X20 compounds were determined electrochemically by means of GITT measurements. The thin films were first galvanostatically charged to their fully hydrogenated state, using a current of −0.6 mA. Subsequently, the electrodes were allowed to equilibrate for 1 h. Hereafter, the Mg80Sc20 and Mg80Ti20 electrodes were discharged by means of GITT using a current of +0.12 mA during the first fifteen and +0.012 mA during the last few pulses. The Mg80V20 and Mg80Cr20 thin films were, however, discharged using a current of only +0.012 mA. After each current pulse all the electrodes were allowed to equilibrate for 1 h. Figure 6 shows the obtained equilibrium curve (open symbols) as well as the potential response of the Mg80Sc20 compound during each current pulse. The insets show the potential response and subsequent relaxation of a typical GITT pulse at the start (left-hand side) and at the end of the main discharge plateau (right-hand side).

Figure 6. Electrochemical response of a Mg80Sc20 thin film electrode during a GITT measurement. Besides the equilibrium curve of the material (○), the potential response during each GITT pulse is shown. Current used during the GITT pulses: +0.12 mA (bold line), +0.012 mA (gray line). The insets show the potential response and subsequent relaxation of a particular GITT pulse at the start (left side) and at the end of the main discharge plateau (right side).

which can be understood when the correlation between equilibrium potential (\(E_{\text{eq}}^\text{MH}^\text{H2}^\text{0} \)) and the heat of formation (\(\Delta H_f^\text{H2}^\text{0} \)) is used. \(\Delta H_f^\text{H2}^\text{0} \) is directly linked to the partial hydrogen pressure (\(P_{H_2}^\text{H2}^\text{0} \)) via

\[ \Delta H_f^\text{H2}^\text{0} \mathbf{Hf} = \mathbf{RT} \ln \frac{P_{H_2}^\text{H2}^\text{0}}{P_{\text{ref}}} \]  

[4]

where R is the gas constant, T the temperature, and \(S^0_{H_2} \) the standard molar entropy of hydrogen gas (130.8 J/K mol H2). Furthermore, \(P_{H_2}^\text{H2}^\text{0} \) can be expressed as the \(E_{\text{eq}}^\text{MH}^\text{H2}^\text{0} \) through

\[ E_{\text{eq}}^\text{MH}^\text{H2}^\text{0} = -0.931 \frac{F}{F_{\text{ref}}} \ln \frac{P_{H_2}^\text{H2}^\text{0}}{P_{\text{ref}}} \]  

[5]

in which F is the Faraday constant, \(P_{\text{ref}} \) the reference pressure (1 bar), and \(E_{\text{eq}}^\text{MH}^\text{H2}^\text{0} \) is expressed with respect to the Hg/HgO
(6 M KOH) reference electrode. Combining Eqs. 4 and 5 shows that a more negative value of $E_{\text{eq}}^a$ corresponds to a less negative value of $\Delta H_f$. This is indeed in line with the expected values of $\Delta H_f$, based on experimental data obtained by Notten et al. for the reversible transition of ScH$_2$ to ScH$_2$. $^5$ Here it was shown that systematically increasing the amount of Sc in MgSc extends the initial solid solution region.

For VH, the situation is somewhat more complex. Reilly et al. showed that VH$_2$ ($\gamma$-phase) is unstable at room temperature, but that low-pressure hydrides exist with compositions up to VH ($\alpha$- and $\beta$-phases). $^2$ These have $\Delta H_f$ values of around $\pm 20$ kJ/mol H and lower, which correspond to the experimentally observed equilibrium pressures of the initial solid solution of the Mg$_{80}$V$_{20}$ compound (see Fig. 7c).

The main plateau in the isotherms is situated at $\sim 0.75$ V for all the compounds, except for Mg$_{80}$Sc$_{20}$, which has a somewhat more positive potential at around $\sim 0.74$ to $\sim 0.72$ V. The calculated $\Delta H_f$ corresponding to these plateaus are $\sim 37$ kJ/mol H and $\sim 40$ kJ/mol H for Mg$_{80}$X$_{20}$ ($X = Ti, V, Cr$) and Mg$_{80}$Sc$_{20}$, respectively (using Eqs. 4 and 5). It is rather remarkable that, with the exception of Mg$_{80}$Sc$_{20}$, $\Delta H_f$ seems to be unaffected by $X$ in MgX. Moreover, $\Delta H_f$ seems to be identical to that reported for the transition from Mg to MgH$_2$. $^19$

Figure 8 shows the equilibrium curves of the Mg$_{80}$X$_{20}$ compounds during charging. Similar to its discharge isotherm (see Fig. 7a), the charging isotherm of Mg$_{80}$Sc$_{20}$ has the most positive equilibrium potential (Fig. 8a). The gradually sloping plateau is situated at potential values of $\sim 0.76$ to $\sim 0.79$ V, corresponding to $\sim 36$ to $\sim 33$ kJ/mol H, respectively. This difference in measured equilibrium potential during discharge and charging points to hysteresis, which is frequently observed for both thin film and bulk hydrogen storage materials. The origin of this hysteresis might be attributed to various stress states, induced by (uniaxial) expansion of the lattice, during charging and discharging. $^21$ Unlike the practically superimposing equilibrium plateaus during discharging (see Fig. 7b-d), the plateau value during charging of the Mg$_{80}$X$_{20}$ ($X = Ti, V,$ or Cr) compounds appear to be slightly dissimilar (Fig. 8b-d). The Mg$_{80}$V$_{20}$ thin film exhibits the most negative plateau at around $\sim 0.805$ V, corresponding to $\sim 31$ kJ/mol H. Comparing Fig. 7 and 8, it is interesting to note that all Mg$_{80}$X$_{20}$ compounds show a similar hysteresis effect between charging and discharging. In all cases the difference in plateau value is $\sim 50$ mV or, according to Eq. 5, a factor 50 in plateau pressure.

Conclusions

The hydrogen storage properties of thin film Mg$_{80}$X$_{20}$ ($X = Sc, Ti, V, Cr$) compounds have been investigated. The preparation of these crystalline, metastable MgX compounds was achieved by means of electron-beam deposition at room temperature. Based on XRD measurements it was concluded that single-phase compounds were obtained. The reversible hydrogen storage capacity of these compounds was determined to be up to six times higher than commercial AB$_5$-type materials, reaching 1790 mA h/g for Mg$_{80}$Sc$_{20}$, 1750 mA h/g for Mg$_{80}$Ti$_{20}$, 1700 mA h/g for Mg$_{80}$V$_{20}$, and 1270 mA h/g for Mg$_{80}$Cr$_{20}$, corresponding to 6.7, 6.5, 6.4, and 4.9 wt % H, respectively. The rate capability of the Mg$_{80}$X$_{20}$ compounds is profoundly influenced by the element X incorporated in MgX. Galvanostatic measurements indicated that the rate capability of the Sc- and Ti-containing compounds is far superior to that of the V- and Cr-containing compounds. It was shown that the same amount of hydrogen could be released close to ten times faster from the Sc- and Ti-containing compounds, as compared to the V- and Cr-containing compounds. Isotherms of the MgX systems were obtained using GITT and showed that the equilibrium potential of the main charge/discharge plateau, apart from the Mg$_{80}$Sc$_{20}$ compound, only slightly depended on X in MgX. Finally, electrochemical measurements convincingly showed that low-cost Ti is an excellent substitute for the expensive Sc in MgSc, without introducing detrimental effects.

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