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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 A\(_2\)B\(_3\)-type materials. The gravimetric storage capacities of these new materials were determined to be 1790 mAh/g for Mg\(_{80}\)Sc\(_{20}\), 1750 mAh/g for Mg\(_{80}\)Ti\(_{20}\), 1700 mAh/g for Mg\(_{80}\)V\(_{20}\), and 1325 mAh/g for Mg\(_{80}\)Cr\(_{20}\) 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 Mg\(_{80}\)Sc\(_{20}\) 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. As 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 greater than the Sc content. 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 ScH\(_2\) is retained, even when Sc is partially substituted by Mg. It was experimentally determined that the Mg\(_{80}\)Sc\(_{20}\) 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 Mg\(_7\)Ti\(_3\). The same anvil-cell technique was used to create Mg\(_3\)V\(_2\)H\(_9\) by Kyo et al. in 2004. Finally, Mg\(_7\)Cr\(_3\)H\(_9\) was discovered by the same group in 2003 and additionally investigated by Rönnebro et al. Although the complexity of the anvil-cell technique is very high and the conditions applied very extreme, it shows that crystalline Mg\(_x\)X\(_{20}\) 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 Mg\(_{80}\)X\(_{20}\) (X = Sc, Ti, V, or 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 Mg\(_{80}\)X\(_{20}\) 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**

Mg\(_{80}\)X\(_{20}\) thin films were manufactured using electron-beam deposition (base pressure between \(10^{-7}\) and \(2 \times 10^{-7}\) 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 Mg80Si20 layers and was not dissolved into the underlying MgX layer. For the Mg80Ti20 thin film a strong reflection is present of [111] oriented fcc-structured Pd. In the case of Mg80Sc20, the Pd topcoat is still oriented in the [001] direction, but the reflection is much weaker and therefore hard to distinguish in the XRD data. Notably, the Pd topcoat of the Mg80V20 and Mg80Cr20 thin films has a different preferred orientation, namely the [200] direction (Fig. 1c and d). Note that RBS measurements (not shown here) indicated that all Pd was indeed present as a separate layer on top of the Mg80X20 layers and was not dissolved into the underlying MgX layer.

Hydrogenation of the MgX thin films was achieved by electrochemical means. Electrochemical hydriding/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

\[ \text{H}_2 + M + e^{-} \rightarrow \text{MH}_{\text{ads}} + \text{OH}^- \]  \hspace{1cm} [1]

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

\[ \text{MH}_{\text{ads}} + e^{-} \rightarrow \text{MH}_{\text{ads}}^- \]  \hspace{1cm} [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 Mg80X20 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 (~1000 mA/g), and +0.012 mA (~100 mA/g), respectively. Note that in these experiments the layers were first fully hydrogenated.

As no reflections were observed that could be linked to the hexagonal close-packed (hcp) structure of pure Sc or Ti, or the bcc structure of either pure V or Cr, it is concluded that a single-phase solid solution of Sc, Ti, V, or Cr in Mg was formed. Besides the responses of the Mg80X20 layers, reflections were measured that could be linked to the Pd topcoat. It seems that the orientation of the Pd is strongly dependent on the degree of orientation of the underlying Mg80X20 layer. For the Mg80Ti20 thin film a strong reflection is present of [111] oriented fcc-structured Pd. In the case of Mg80Sc20 the Pd topcoat is still oriented in the [111] direction, but the reflection is much weaker and therefore hard to distinguish in the XRD data. Note that RBS measurements (not shown here) indicated that all Pd was indeed present as a separate layer on top of the Mg80X20 layers and was not dissolved into the underlying MgX layer.

Results and Discussion

Figure 1 shows the XRD spectra of Mg80X20 thin films freshly prepared by means of high-vacuum deposition [(a) Mg80Sc20, (b) Mg80Ti20, (c) Mg80V20, and (d) Mg80Cr20]. All four thin films show a strong preferred orientation, which is characteristic for thin films. The strongest reflection belongs to the [002] orientation of hcp Mg. For all four compounds, this peak is shifted with respect to pure Mg (34.5° 2θ) due to the fact that Sc, Ti, V, or Cr host atoms are incorporated into the Mg-structure.17 Taking the Mg80Ti20 thin film as an example (Fig. 1b), it can be seen that the main peak has shifted to a higher angle. This shift is brought about by partial substitution of Ti, which has a smaller molar volume than Mg, causing the lattice to shrink and the peak to shift.
A third and final plateau is reached when the electrode is charged to the fully loaded state. The overall discharge behavior of the Mg80Sc20 compound shows a very flat plateau at about −0.67 V which 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 Mg80Sc20 and Mg80Ti20 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 Mg80Sc20 and Mg80Ti20 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 Mg80Sc20 and Mg80Ti20 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 [34, 62]. The results are listed in Table I and are given as gravimetrical storage capacity in both [mAh/g] and [wt % H]. The measured hy-

<table>
<thead>
<tr>
<th>Material</th>
<th>Gravimetrical 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>
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Table I. Gravimetrical storage capacities of MgX compounds (X = Sc, Ti, V, or Cr).
hydrogen storage capacities of the Mg80X20 compounds is close to six times that of commercially used AB5-type materials.\(^4\)\(^5\)\(^6\)\(^7\) 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 ScH\(_2\) and TiH\(_2\) are reported to be very negative, i.e., \(-100\) and \(-70\) kJ/mol H\(_2\), respectively.\(^8\)\(^9\)\(^10\) 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 (\(\eta\)). \(\eta\) can be represented by

\[
\eta = \eta_{\text{IR}} + \eta_{\text{kin}} + \eta_{\text{diff}} \tag{3}
\]

where IR is the Ohmic drop, \(\eta_{\text{kin}}\) is the kinetic overpotential, and \(\eta_{\text{diff}}\) 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 \(\eta\) can be attributed to a decrease in \(\eta_{\text{kin}}\), 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 Pd/KOH interface. Research is currently in progress in which the underlying effects of this reduction in \(\eta\) 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 and subsequent relaxation of the thin film electrodes induces changes at the Pd/KOH interface. Research is currently in progress in which the underlying effects of this reduction in \(\eta\) are investigated. The results will be published in a forthcoming paper.

Figure 6. Electrochemical response of a Mg80Sc20 thin film electrode during a GITT measurement. Besides the equilibrium curve of the material (\(\gamma\)), 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).

The equilibrium discharge curves of all the Mg80X20 compounds are depicted in Fig. 7. As expected from the galvanostatic responses shown before (see Fig. 2-5), the isotherms show a similar behavior for all Mg80X20 compounds. Clearly, the initial solid solution behavior, up to a discharge capacity of about 400 mAh/g, seems to be dependent on X in MgX. This solid solution has the most negative equilibrium potential for the Mg80Sc20 and Mg80V20 compounds, which can be understood when the correlation between equilibrium potential \(E_{\text{eq}}\) and the heat of formation \(\Delta H_f\) is used. \(\Delta H_f\) is directly linked to the partial hydrogen pressure \(P_{\text{H}_2}\) via

\[
\Delta H_f = \frac{RT}{2} \ln \frac{P_{\text{H}_2}}{P_{\text{ref}}} - E_{\text{MH}} - \frac{dQ}{dP} \tag{4}
\]

where \(R\) is the gas constant, \(T\) the temperature, and \(S_{\text{H}_2}\) the standard molar entropy of hydrogen gas (130.8 J/K mol H\(_2\)). Furthermore, \(P_{\text{MH}}\) can be expressed as the \(E_{\text{MH}}\) through

\[
E_{\text{MH}} = -0.931 \ln \frac{F_{\text{ref}}}{P_{\text{ref}}} - \frac{RT}{2F} \ln \frac{P_{\text{H}_2}}{P_{\text{ref}}} \tag{5}
\]

in which \(F\) is the Faraday constant, \(P_{\text{ref}}\) the reference pressure (1 bar), and \(E_{\text{MH}}\) is expressed with respect to the Hg/HgO

Figure 7. Equilibrium discharge curves of (a) Mg80Sc20, (b) Mg80Ti20, (c) Mg80V20, and (d) Mg80Cr20 compounds obtained by means of GITT.
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 mAh/g for Mg$_{80}$Sc$_{20}$, 1750 mAh/g for Mg$_{80}$Ti$_{20}$, 1700 mAh/g for Mg$_{80}$V$_{20}$, and 1270 mAh/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 MgX, without introducing detrimental effects.

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