Hydrogen storage in thin film magnesium–scandium alloys

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Abstract

Thorough electrochemical materials research has been performed on thin films of novel magnesium–scandium hydrogen storage alloys. It was found that palladium-capped thin films of $Mg_xSc_{(1-x)}$ with different compositions (ranging from $x = 0.50$–0.90) show an increase in hydrogen storage capacity of more than 5–20% as compared to their bulk equivalents using even higher discharge rates. The maximum reversible hydrogen storage capacity at the optimal composition ($Mg_{80}Sc_{20}$) amounts to 1795 mAh/g corresponding to a hydrogen content of 2.05 H/M or 6.7 wt.%, which is close to five times that of the commonly used hydride-forming materials in commercial NiMH batteries. Galvanostatic intermittent titration technique (GITT) measurements show that the equilibrium pressure during discharge is lower than that of bulk powders by one order of magnitude (10^{-7} mbar versus 10^{-6} mbar, respectively).
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1. Introduction

In recent years, the use of portable equipment has increased tremendously, resulting in ongoing research towards improved low-power electronics but also high energy density rechargeable batteries. Presently, Li-ion batteries and nickel-metal hydride (NiMH) batteries are the main rechargeable systems being used on a large scale in small electronic equipment like portable telephones, laptops, shavers, etc. [1,2]. To increase the energy density of future NiMH batteries new electrode materials, which are able to store a larger amount of hydrogen, need to be developed.

Commercially used MischMetal-based hydride-forming electrodes developed through the years show hydrogen storage capacities of about 300 mAh/g corresponding roughly to 1.1 wt.% hydrogen stored [3]. Recently, Notten et al. showed that alloys comprising of Mg and Sc showed very promising storage capacities of close to 1500 mAh/g, more than four times that of the MischMetal-based materials [4]. It was demonstrated that a catalyst such as Pd or Rh is crucial in en-

abling hydrogen absorption by the alloys. Furthermore, it was argued that the fluorite structure of the hydride is essential in achieving enhanced hydrogen transport properties.

Although throughout the years electrochemical studies have been performed on thin films comprised of various rare-earth metals (Y, Gd) [5–7] and Mg-based alloys [8] no detailed electrochemical studies on $Mg_xSc_{(1-x)}$ thin films have been reported up to now. In the present study, a thorough account is given on the electrochemical properties of 200 nm thick $Mg_xSc_{(1-x)}$ thin films capped with a 10 nm Pd layer. The ultimate goal of the research on these metal hydride films is to enhance the fundamental understanding of hydrogen absorption using a 2D model system. A selection of electrochemical measurement techniques is used to investigate distinct similarities and differences between the electrochemical properties of thin films and their bulk counterparts.

2. Experimental

Thin films of $Mg_xSc_{(1-x)}$, with a nominal thickness of 200 nm, were deposited on quartz substrates (Ø 20 mm) by means of high-vacuum deposition (base pressure 8×10^{-8} to 4×10^{-7} mbar). Films were manufactured in which

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the Mg content was varied in the range $x = 0.50$–0.90. The quartz substrates were thoroughly cleaned beforehand using an in-house procedure. Cap layers of 10 nm Pd were deposited on top of the thin films. During deposition of the alloys the deposition rates of Mg and Sc were between 0.15 and 0.63 nm s^{-1}. Uniformity of composition throughout the entire film was checked by means of Rutherford backscattering spectroscopy (RBS), which showed that the deposition rates were controlled well. Furthermore X-ray reflectometry (XRR) was used to measure the deposited layer thickness and the standard powder diffraction geometry to identify the crystallographic phases. Finally, the morphology of the films was verified by means of scanning electron microscopy (SEM) and electron probe microanalysis (EPMA). The calculation of hydrogen content in the thin film is solely based on the RBS measurements, of which the accuracy is around 1%.

Electrochemical measurements were performed using a three-electrode set-up in which the thin film acted as working electrode (active surface area of 3 cm^2). The potential of the film was measured versus a Hg/HgO reference electrode filled with 6 M KOH solution. The cell was thermostated at 298 K by means of a water jacket and filled with 6 M KOH electrolyte. Argon gas, which was first led through an oxygen scrubber, was used during the measurements to de-aerate the setup. The counter electrode, a Pd rod (99.999%, Ø 5 mm, Drijfhout), was placed in a separate compartment in the cell and care was taken that the total area in contact with the electrolyte was sufficiently large. In a separate setup, this counter electrode was pre-charged with hydrogen (PdH$_x$) to prevent oxygen gas formation at this electrode during the measurements. The thin films were contacted with a wire, which was attached using a conductive adhesive (E-solder No. 3021 from IMI). A chemically inert isolating lacquer (W40, Apiezon) was applied to the contacts and the edges of the substrate shielding them from the electrolyte. Galvanostatic measurements and galvanostatic intermittent titration technique (GITT) were performed using a Maccor M2300 battery tester (Maccor, Tulsa, USA). A cut-off potential of 0 V versus Hg/HgO was used in all experiments.

3. Results and discussion

Fig. 1 schematically shows a cross-section of the Mg$_x$Sc$_{(1-x)}$ thin film electrode. The main (electro)chemical reactions occurring during charging (ch) and discharging (d) are also indicated. Upon charging water is reduced at the Pd/electrolyte interface, generating adsorbed hydrogen (H$_{ad}$). Subsequently, the adsorbed hydrogen atoms are absorbed (H$_{abs}$) by the Pd and finally diffuse into the Mg$_x$Sc$_{(1-x)}$ layer. During discharging the reactions are reversed. SEM analysis indicates that the 10 nm Pd cap layer is a closed film and does not undergo island formation [6]. This means that no Mg alloy is exposed at the interface and thus oxidized. This is also confirmed by RBS measurements
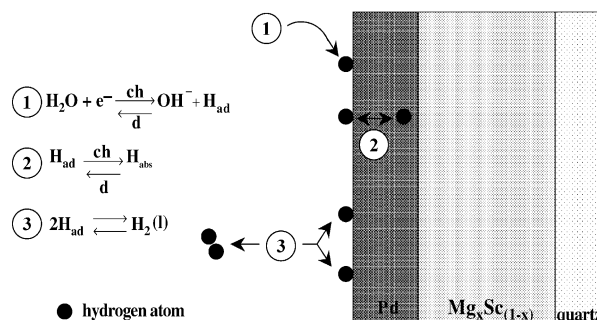

Fig. 1. Schematic representation of a thin film electrode showing the overall geometry. The main electrochemical reactions related to hydrogenation are depicted at the appropriate locations.

on fresh samples, which do not show any oxidation response (not shown here).

A galvanostatic charge/discharge cycle of a fresh, 208 nm thick Mg$_{70}$Sc$_{30}$ layer capped with 10 nm Pd is shown in Fig. 2. The thin film was charged (curve a) and discharged (curve b) using a high current density of 40 μA/cm^2 (or 967 mA/g). Both the charging and discharging curve consist of distinct regions similar to its bulk powder counterpart [4]. The total amount of reversibly extracted charge (Q_d) is 1470 mAh/g, corresponding to a H/M ratio of 1.68 (5.32 wt.%) for this composition. This shows that thin films can be discharged at a much higher rate ($\sim$ 1000 mA/g) as compared to bulk materials (nominally 50 or 10 mA/g) without any apparent capacity loss. Notably, the time needed to completely discharge the electrode at this rate is only 1.5 h.

The excellent rate capability of thin films can also be concluded from Fig. 3 where the influence of the alloy composition on the discharge capacity Q_d is shown for both thin films and bulk powders. Over the entire composition range, in which x in Mg$_x$Sc$_{(1-x)}$ is varied between 0.50 and 0.90,
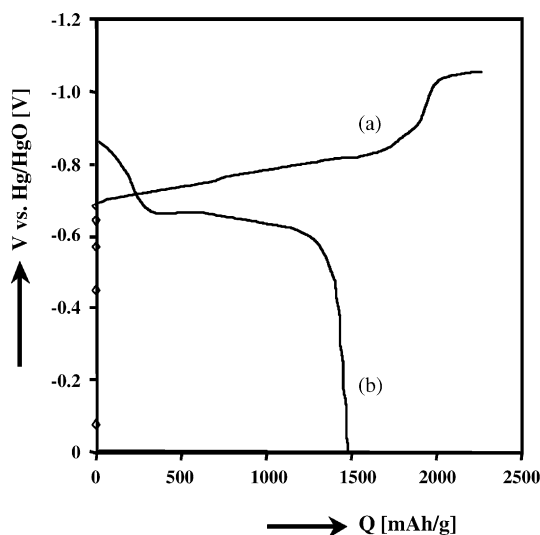

Fig. 2. Typical galvanostatic charge/discharge curve of a 208 nm thick Mg$_{70}$Sc$_{30}$ thin film electrode capped with 10 nm of Pd. Curve (a) shows charging at 40 μA/cm^2 and curve (b) shows discharging at 40 μA/cm^2.
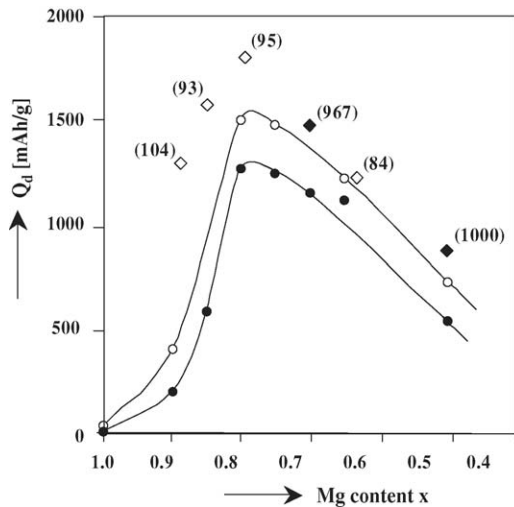
Fig. 3. Comparison of the discharge capacities (Q_d) for thin film electrodes and bulk powders. Measured Q_d at high (♦, 40 μA/cm²) and relatively low current density (◊, 4 μA/cm²) of thin films (200 nm nominal thickness, capped with 10 nm of Pd) with varying composition $Mg_xSc_{(1-x)}$ with x ranging from 0.50 to 0.90. Between brackets the current density in mA/g is given for the thin film samples. Q_d of bulk powders discharged at high 50 mA/g (○) and 10 mA/g (●) current density. The composition of the bulk samples ($Mg_xSc_{(1-x)}Pd_{0.024}$) varied in Mg content ranging from 0.50 to 1 [4].

Q_d is about 5–20% higher for thin films discharged at currents of 4 or 40 μA/cm² (in Fig. 3 these current densities are also converted to mA/g for direct comparison). Similar to bulk powders Q_d increases with increasing Mg content leading to an optimum around the $Mg_{80}Sc_{20}$ composition of 1795 mAh/g. This corresponds to 2.05 hydrogen atoms per metal or 6.7 wt.%. Lower discharge capacities of alloys with $x > 0.8$ is in line with the formation of a rutile-structured hydride with less desirable electrochemical properties [9].

The thermodynamic properties of the $Mg_xSc_{(1-x)}$ thin films have been investigated using GITT. Fig. 4 shows the equilibrium voltage curve obtained for the same $Mg_{70}Sc_{30}$ film discussed earlier. During the discharge pulse a current of 40 μA/cm² is applied to the electrode, which is subsequently allowed to equilibrate under open-circuit conditions for 60 min. The insets in Fig. 4 show the relaxation behavior after a current pulse at different parts along the equilibrium curve. From left to right behaviors are depicted at 350, 1150 and 1450 mAh/g, respectively. From these it can be concluded that in the initial stages of the discharge and well along the main plateau a stable potential value is reached after about 10 min of equilibration, but that in the final stage it takes the potential more than 30 min to reach a stable value. Using Eq. (1), which describes the relationship between equilibrium voltage (E^{eq}) and partial hydrogen pressure (P_{H_2}), a plateau pressure can be calculated of

$$E^{eq} = -0.931 - \frac{RT}{nF} \ln \frac{P_{H_2}}{P_{ref}} \tag{1}$$

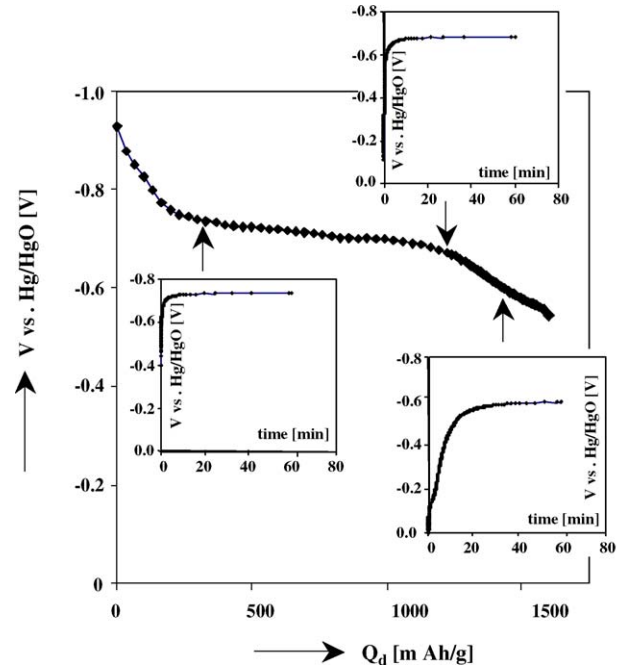the order 10^{-7} mbar (using $P_{ref} = 1$ bar) [2]. This value about one order of magnitude lower as compared to the bulk ma-

Fig. 4. Equilibrium voltage curve of a 208 nm thick $Mg_{70}Sc_{30}$ thin film electrode capped with 10 nm of Pd obtained during a GITT measurement. The insets show, from left to right, the relaxation behavior after the current pulse at Q_d values of 350, 1150 and 1450 mAh/g, respectively.

terials. This shift in plateau pressure might be attributed to hysteresis effects in the thin film. Using the calculated plateau pressure, the enthalpy of formation ΔH_f (J/mol) of the phase transition can be estimated with Eq. (2).

$$\Delta H_f = \frac{RT}{2} \left[\ln P_{H_2} - \frac{S_{H_2}^0}{R} \right] \tag{2}$$

Here, $S_{H_2}^0$ is the standard molar entropy of hydrogen gas (130.8 J/K mol H₂). The determined value of ΔH_f is around −40 kJ/mol H.

4. Conclusions

Electrochemical measurements of thin films of the novel $Mg_xSc_{(1-x)}$ hydrogen storage alloy are presented. Using electrode materials in which x was varied between 0.50 and 0.90, it was shown that the discharge capacity of thin film electrodes is 5–20% higher than that of previously reported bulk powders. The maximum reversible hydrogen storage capacity is obtained with the $Mg_{80}Sc_{20}$ composition and is 1795 mAh/g, corresponding to 2.05 H/M or 6.7 wt.% H, making these materials a promising candidate for usage as battery electrode material or hydrogen carrier. Thermodynamic data was experimentally obtained by GITT and showed that the hydrogen plateau pressure corresponding to the main discharge plateau are of the order of 10^{-7} mbar, which is one order of magnitude lower than their bulk counterparts.

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