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ABSTRACT

Mg-based hydrogen storage alloys are promising candidates for many hydrogen storage applications because of the high gravimetric hydrogen storage capacity and favourable (de)hydrogenation kinetics. In the present study, we have investigated the synthesis and electrochemical hydrogen storage properties of metastable binary Mg_{y}Ti_{1−y} (y = 0.80–0.60) and ternary Mg_{0.63}Ti_{0.27}X_{0.10} (X = Ni and Si) alloys. The preparation of crystalline, single-phase, materials has been accomplished by means of mechanical alloying under controlled atmospheric conditions. Electrodes made of ball-milled Mg_{0.80}Ti_{0.20} powders show a reduced hydrogen storage capacity in comparison to thin films with the same composition. Interestingly, for a Ti content lower than 30 at.% the reversible storage capacity increases with increasing Ti content to reach a maximum at Mg_{0.70}Ti_{0.30}. The charge transfer coefficients (α) and the rate constants (K_1 and K_2) of the electrochemical (de)hydrogenation reaction have been obtained, using a theoretical model relating the equilibrium hydrogen pressure, electrochemically determined by Galvanostatic Intermittent Titration Technique (GITT), and the exchange current. The simulation results reveal improved values for Mg_{0.65}Ti_{0.35} compared to those of Mg_{0.80}Ti_{0.20}. The addition of Ni even more positively affects the hydrogenation kinetics as is evident from the increase in exchange current and, consequently, the significant overpotential decrease.

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Introduction

The rapidly decreasing amount of fossil fuels and altering environment conditions have led to the development of a sustainable fuel economy [1–3]. Hydrogen is considered to be one of the major energy carriers in developing new strategies to fulfill our future energy demands [4–6]. However, the viability of the technologies for hydrogen production, storage and on-board usage are still under debate.

Hydrogen-storage is a crucial step in the hydrogen economy [7,8]. Hydrogen can be stored in three different ways, as a compressed gas in lightweight composite cylinders (up to 800 bars), as a liquid under cryogenic conditions or as a solid in a metal or other chemical hydrides [9]. In near future, new lightweight composite cylinders are anticipated to store hydrogen even higher pressures. However, their lower volumetric capacity and high energy requirement for hydrogen compression limits their practical use. In contrast to storing hydrogen in molecular form, it can also be stored as atomic hydrogen in metals and intermetallic compounds (MH), leading to higher volumetric density. Advantageously, MH provide relatively safe storage at ambient pressure conditions compared to compressed hydrogen gas, and these materials can therefore be handled relatively easily [10].

\( \text{MgH}_2 \) has a high gravimetric hydrogen-storage capacity of about 7.6 wt.\% of hydrogen. Therefore due to its high storage capacity and low cost, \( \text{MgH}_2 \) turned out to be one of the most promising materials for hydrogen storage [11,12]. Despite these advantages, \( \text{MgH}_2 \) has its own limitations, such as slow rate of (de)hydrogenation and high thermodynamic stability, i.e. \( \text{MgH}_2 \) is too stable with a partial hydrogen pressure of 1 bar at 300 °C [11,12]. Magnesium can be modified in different ways, such as making use of nanoparticles and addition of catalysts. Quantum mechanical calculations by Wagemans et al. [13] reports that the desorption enthalpy of nanosized \( \text{MgH}_2 \) clusters (size of ~0.9 nm) is much lower than that bulk \( \text{MgH}_2 \). This decrease in desorption enthalpy would potentially enable the hydrogen desorption reaction to take place at lower temperatures in nanoclusters compared to bulk materials. The formation of Mg nanoparticles is, however, complicated and oxidation of Mg nanoparticles is another serious limitation. Embedding nanoparticles in carbon or polymer-type of materials have proven to be effective in avoiding oxidation of Mg [14,15]. Addition of metal oxide catalysts, such as TiO\(_2\), V\(_2\)O\(_5\), Cr\(_2\)O\(_3\), Mn\(_2\)O\(_3\), Fe\(_3\)O\(_4\), CuO, and Nb\(_2\)O\(_5\) leads to further improvement in the kinetics. Among various oxides, Nb\(_2\)O\(_5\) revealed much more improved (de)hydrogenation kinetics. More specifically, nanocrystalline Nb\(_2\)O\(_5\) has been reported to have superior kinetic properties [12]. Another way to overcome all the these limitations is to alloy Mg with transition metal (TM). It has been theoretically and experimentally shown that Mg alloyed at >20 at.% TM (Sc, Ti, V, Cr, Y, Zr, Nb, Hf) reveals excellent reversible storage capacities [16,17]. The reason for this remarkable increase in reversible storage capacity is the formation of the favourable fluorite crystal structure after hydrogenation [18]. The hydrogen mobility is significantly higher in fluorite-structured MgT\(_m\)H\(_x\) compared to that in rutile-structured Mg\(_2\)H\(_x\). It has been proven that MgSc hydrides show the rutile-to-fluorite phase transformation when Sc content exceeds 20 at.% [18]. However, the rare-earth metal Sc is expensive. It therefore remains inevitable to replace Sc with a more abundant and less expensive alternative.

Ti was found to exhibit a similar phase transformation [18]. Mg\(_x\)Ti\(_y\)H\(_z\) thin films show a maximum reversible capacity when \( y = 0.20 \). For compositions with \( y > 0.20 \), the crystal structure is fluorite and for \( y < 0.20 \) the unfavourable rutile structure has been reported. Even though addition of Ti increases the rate of (de)hydrogenation, the thermodynamics properties, such as the equilibrium pressure of Mg\(_2\)H\(_2\) are not altered [19]. It has been shown that addition of a ternary alloying element can induce thermodynamic destabilisation and improve the (de)hydrogenation kinetics further [20]. In the present study two ternary metals, Ni and Si, have been selected to add as ternary element to MgTi alloys. Addition of Ni is expected to show a destabilizing effect according to rule of reversed stability, which states that more stable alloys or intermetallic compounds form less stable hydrides [21]. Ni is reported to have a negative enthalpy of mixing with both Mg and Ti, which stably bind with both Mg and Ti and increase the stability of ternary alloys [22]. Si has also been selected, according to the Miedema model [21,23] as a suitable ternary alloying element to induce thermodynamic destabilization. It has been experimentally proven in the case of thin films that the addition of Si increases the stability of the MgTi alloy and, consequently, increases the partial hydrogen pressure during dehydrogenation [20].

Inspired by the above interesting facts and developments, we aim to better understand the alloy formation and electrochemical hydrogen storage properties of binary MgTi and ternary MgT\(_m\)X (X = Ni, Si) alloys. Considering the positive enthalpy of mixing of Mg and Ti [24], these alloying elements are expected to form a metastable alloy which tends to phase segregate at higher temperatures and pressures. Several attempts has been made to synthesize Mg-Ti thin film alloys, bulk alloy powders and nanoparticle/composites via sputtering [25], ball-milling [26–31] and spark discharge generation [32]. Electrochemical (de)hydrogenation/(de)deuteration offers a solution to prevent phase segregation as the reaction takes place at room temperature. It has been shown that MgTiD single phase fluoro-structured compounds are formed with no large-scale phase segregation [33]. Moreover, unlike gas-phase hydrogenation, electrochemical hydrogenation can be successfully applied to accurately monitor and control the hydrogen content. Furthermore, the thermodynamically controlled equilibrium pressure can be directly related to the equilibrium electrode potential measured during Galvanostatic Intermittent Titration Technique (GITT) experiments [34]. MgTi binary and ternary alloys of various composition were synthesized via mechanochemical syntheses and investigated, using XRD and electrochemical characterisation methods.

Experimental

The alloys were prepared by mechanical alloying pure magnesium (Alfa Aesar with particle size of ~50 μm and 98.5% purity), titanium (Sigma Aldrich: ~50 μm, 99.5%), nickel (Alfa...
Aesar: ~50 μm, 99%) and silicon (Alfa Aesar: ~50 μm, 99%). Ball-milling was carried out in a SPEX mill installed inside an Argon glove box to avoid oxygen and water contamination. A 55 ml tungsten carbide milling vial and 10 mm diameter tungsten carbide balls as milling media were used in the milling process. In order to avoid other contaminations and undesired reaction products no process control agents were used. The milling process was stopped every 60 min and checked for cold-welding. The as-milled alloys were finally milled with 5 at.% Pd (Sigma Aldrich: ~50 μm, 99.5%), acting as electro-catalyst, for 120 min. The as-prepared active materials were mixed with silver powder (Sigma Aldrich: ~50 μm, 99.5%) in a 4:1 ratio and pressed into 8 mm pellets which were used as MH-electrodes.

Standard double-walled three-electrode electrochemical cells were used for the electrochemical investigations. The electrochemical cells were filled with 6 M KOH electrolyte and purged with argon to remove oxygen. The counter electrode was a partly hydrogenated palladium rod. The potential of the powder electrode was measured with respect to a Hg/HgO reference electrode filled with 6 M KOH. All experiments were performed under thermostatic control at 25 °C. Galvanostatic (dis)charging was performed using automated cycling equipment (Maccor). The cut-off potential for the dehydrogenation (discharging) process was −0.1 V vs Hg/HgO in all cases.

GITT and Electrochemical Impedance Spectroscopic (EIS) measurements were carried out with a potentiostat equipped with a frequency response analyser (Autolab). GITT was performed during charging with a constant current of 50 mA g⁻¹ active (MH) electrode material. A charging pulse consisted of one hour followed by a resting period of 3 h. GITT during discharging was performed with 10 mA g⁻¹ for 3 h followed by a resting period of 3 h. EIS measurements were performed under potentiostatic control at the end of each resting period, using an alternating current with amplitude of 5 mV in the frequency range of 50 kHz to 1 mHz.

Results and discussion

X-ray diffraction

Fig. 1a shows the X-ray diffraction pattern of Mg₈₀₅₀Ti₀₂₀ at various stages of the milling process. The lattice constants of pure Mg are a = 3.20 and c = 5.20 Å. As a result of the alloying process the Mg reflections clearly shift towards higher angles and the intensity of Ti reflections decreases with increasing milling time. This shift and decrease in Ti-reflections are caused by partial substitution of Mg by Ti [27]. Shifts in the reflections of Mg towards higher angles are an indication that the Mg unit cell decreases. Such a lattice contraction is indeed to be expected when Mg is alloyed with Ti, which has lower molar volume (Mₛ₅ = 10.64 cm³/mol) in comparison to that of Mg (Mₘ = 14.00 cm³/mol). The milling process attains saturation after 28 h as there is no change in lattice parameters thereafter. Furthermore, the Ti reflections are hardly visible anymore after 28 h. A hcp-type solid solution is formed with lattice constants a = 3.15 and b = 5.07 Å. A similar alloying trend was also found with the other binary compositions. However, this was accompanied with clear peak broadening at increasing Ti content (Fig. 1b), indicating that the material starts to become amorphous at higher Ti content. The formation of a hcp-structured solid solution in Mg₆₇Ti₃₃₋ₓ (y = 0.80–0.60) powder alloys is in agreement with the Mg₆₇Ti₃₃₋ₓ (55 < x < 95) thin film results [35]. The formation of various crystallographic phases has been reported in powder alloys. The formation of bcc, hcp and fcc crystal structures were reported while changing the composition and milling media [36]. Kalisvaart et al. reported the formation of hcp solid solution in Mg₆₅Ti₃₅ when milled without process control agent (PCA) and the formation of two fcc phases when milling with PCA [37].

A ternary element (10 at.% of either Ni or Si) has been added after the formation of Mg₇₀₃₀Ti₃₀ was completed. Consequently, the MgTi reflections shift towards lower angles and the intensity of the Ni reflections are decreasing with increasing milling time (Fig. 1c). After 12 h of additional milling the Ni reflections are no longer visible in the XRD patterns. A similar trend was observed for the Mg₆₅₃₅Ti₇₅₂₇Si₉₀ alloy (Fig. 1d). All as-milled powders were finally milled with 5 at.% Pd, which was added to obtain good electrochemical (de)hydrogenation properties and also to protect the underlying Mg alloy from oxidation.

Electrochemical properties

Galvanostatic (dis)charging

Electrochemical (de)hydrogenation of binary Mg₉₀₅₀Ti₀₂₀ (y = 0.80–0.60) and ternary Mg₆₅₃₅Ti₀₂₇X₀₁₀ (X = Ni and Si) electrodes was carried out by applying a constant (dis) charging current. Application of a constant charging current results in reduction of H₂O at the metal (M)/electrolyte interface, according to [38]

\[
\text{H}_2\text{O} + e^{-} \xrightarrow{\text{discharging}(K_d)} \text{MH}_{\text{ad}} + \text{OH}^{-} \tag{1}
\]

where K_c and K_d are the rate constants for the reduction and oxidation reaction, respectively. After the formation of adsorbed hydrogen atoms (H_{ad}) at the electrode surface, H_{ad} is absorbed by Pd and, subsequently, by the underlying MH materials resulting in absorbed hydrogen (MH_{abs})

\[
\text{MH}_{\text{ad}} \rightleftharpoons \text{MH}_{\text{abs}} \tag{2}
\]

Once the Mg alloy reaches it maximum storage capacity any further supply of H_{ad} will result in recombination of adsorbed hydrogen atoms at the surface, leading to hydrogen gas evolution [38]

\[
2\text{MH}_{\text{ad}} \rightleftharpoons 2\text{M} + \text{H}_{\text{g}} \uparrow \tag{3}
\]

According to Eq. (1) each hydrogen atom requires a single electron transfer. Therefore, coulomb counting can conveniently be used to determine the exact hydrogen content in the electrode, simply by integrating the current over time. The electrochemical storage capacity Q (mAh g⁻¹) can easily be converted into a hydrogen weight fraction \(V_{H} \) (%), according to

\[
V_{H} = \frac{360Q}{FM_{\text{H}}} \tag{4}
\]
where $M_H$ is the molar mass of hydrogen (1.008 g mol$^{-1}$) and $F$ is the Faraday constant ($9.65 \times 10^4$ C mol$^{-1}$).

Fig. 2 shows the electrochemical charging (a) and discharging (b) voltage curves of the various binary Mg$_y$Ti$_{1-y}$ ($y = 0.80-0.60$) alloys. The current density used for charging, (high-current) discharging and (low-current) deep discharging are 50 mA g$^{-1}$, 50 mA g$^{-1}$ and 10 mA g$^{-1}$, respectively. The reversible storage capacity obtained from these results is defined as the summation of the high- and low-current discharge capacity. The charging curves (Fig. 2a) generally consist of three voltage regions. The sloping voltage regions generally found during the initial stages of charging can be attributed to hydrogen absorbed in the solid solution of the $\alpha$-phase. As the reaction proceeds a hydrogen-rich $\beta$-phase starts to nucleate and grow and, consequently, a flat voltage plateau is formed in this two-phase coexistence region. Once the $\beta$-phase is fully formed the alloy reaches its maximum storage capacity and H$_4$ atoms start to recombine to H$_2$ gas at more negative potentials, according to Eq. (3).

In order to quantify the absorption capacity of each individual phase, voltage derivative plots are very useful, as indicated in the upper curves of Fig. 2a. The transition between the $\alpha$- to $\beta$ two phase region, solid solution and $\beta$-H$_2$ transition regions can be discerned with two maxima. The second $\beta$-H$_2$ maxima can be related to the materials absorption capacity. The as-determined electrochemical hydrogen-storage capacities are 720 mAh g$^{-1}$ (2.71 wt.%) for Mg$_{0.80}$Ti$_{0.20}$, 1020 mAh g$^{-1}$ (3.85 wt.%) for Mg$_{0.70}$Ti$_{0.30}$, 920 mAh g$^{-1}$ (3.47 wt.%) for Mg$_{0.65}$Ti$_{0.35}$ and 915 (3.45 wt.%) mAh g$^{-1}$ for Mg$_{0.60}$Ti$_{0.40}$. The absorption capacities show an increasing trend with increasing Ti content up to Mg$_{0.70}$Ti$_{0.30}$ and decreases thereafter. Furthermore it is clear that higher Ti contents generally induce the voltage curves to “lower” (less negative) potentials. The position of these voltage curves can be attributed to a change in the thermodynamic properties and/or absorption kinetics of the MH material by the addition of Ti.

The reversible dehydrogenation capacities (summation of high- and low-current charge) can be obtained from the voltage discharge curves shown in Fig. 2b. 470 mAh g$^{-1}$ (1.77 wt.%) is found for Mg$_{0.80}$Ti$_{0.20}$, 1020 mAh g$^{-1}$ (3.85 wt.%) for Mg$_{0.70}$Ti$_{0.30}$, 920 mAh g$^{-1}$ (3.47 wt.%) for Mg$_{0.65}$Ti$_{0.35}$ and 915 (3.45 wt.%) mAh g$^{-1}$ for Mg$_{0.60}$Ti$_{0.40}$. The absorption capacities show an increasing trend with increasing Ti content up to Mg$_{0.70}$Ti$_{0.30}$ and decreases thereafter. Furthermore it is clear that higher Ti contents generally induce the voltage curves to “lower” (less negative) potentials. The position of these voltage curves can be attributed to a change in the thermodynamic properties and/or absorption kinetics of the MH material by the addition of Ti.

Fig. 1 – X-ray diffractograms of (a) Mg$_{0.80}$Ti$_{0.20}$ at various stages of the milling process (dashed line is marked along the high intense Mg(101) and Ti(101) reflections). (b) Binary MgTi alloys of various composition after completion of the alloying process (28 h). (c) Ternary Mg$_{0.63}$Ti$_{0.27}$Ni$_{0.10}$ (dashed line is marked along the high intense Mg$_{0.70}$Ti$_{0.30}$(101) and Ni(100) reflections). (d) Mg$_{0.63}$Ti$_{0.27}$Si$_{0.10}$ (dashed line is marked along the high intense Mg$_{0.70}$Ti$_{0.30}$(101) and Si(111) reflections) at various stages of the milling process.

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Comparing the charge and discharge capacities it is clear that for all materials quite some hydrogen remains irreversibly bound to the host material, which cannot be removed from the electrodes under the given electrochemical conditions. This has been related to the strongly bound hydrogen atoms at the Ti-sites [33]. Mg0.80Ti0.20 reveals a significantly lower reversible hydrogen storage capacity compared to its thin film equivalent [39]. This might be due to the incomplete conversion of the hcp-to-fluorite structure in the present Mg0.80Ti0.20 powder electrodes. Similar to the absorption capacity, the reversible desorption capacity is also increased with increasing Ti content and attains a maximum for Mg0.70Ti0.30 at 800 mAh g⁻¹. Interestingly, the dehydrogenation kinetics increases remarkably for Mg0.65Ti0.35, which is evident from the high-current discharge capacity (see curve c2 in Fig. 2b) of 550 mAh g⁻¹, about 75% of the total reversible capacity of 730 mAh g⁻¹. This is significantly higher compared to the other compositions.

The absorption voltage (derivative) curves of the ternary Mg0.63Ti0.27Si0.10 (curves e1) and Mg0.63Ti0.27Ni0.10 (curves f1) are compared with those of Mg0.65Ti0.35 (curves c1) in Fig. 2c. Based on the derivative curves the storage capacities of the ternary compounds are determined to be 910 mAh g⁻¹ (3.41 wt.%) and 713 mAh g⁻¹ (2.69 wt.%), respectively. The charging voltage curve of Mg0.63Ti0.27Ni0.10 (curve e1) reveals a well-defined plateau at significantly lower potentials than Mg0.65Ti0.35, which must be attributed to the catalytic effect of Ni. In contrast the charging curve of Mg0.63Ti0.27Si0.10 (curve f1) shows a substantially higher (more negative) charging voltage curve compared to those of Mg0.65Ti0.35 (curve c1) and Mg0.63Ti0.27Ni0.10 (curve e1). The measured (reversible) discharge capacities (Fig. 2d) of Mg0.63Ti0.27Ni0.10 and Mg0.63Ti0.27Si0.10 are 760 mAh g⁻¹ (2.86 wt.%) and 500 mAh g⁻¹ (1.88 wt.%), respectively.

**GITT measurements**

Voltage relaxation model. Determination of the equilibrium potential of MH electrodes as function of hydrogen content is
highly relevant to get information of both the thermodynamic ($V_{eq}$) and kinetic (overpotentials, $\eta$) electrode properties. In both cases the determination of $V_{eq}$ as a function of hydrogen content is essential. It has been shown that GITT is effective in experimentally determining the equilibrium voltage after current interruption. However, long relaxation times are often required to reach equilibrium, especially when solid-state diffusion processes are involved. To avoid long voltage-relaxation times it is proposed to mathematically predict $V_{eq}$ by making use of limited relaxation times [40,41]. The experimental current interruption period can mathematically be drastically reduced as will be shown below.

Consider the moments of time ($t_1, ..., t_N$) at which the MH-electrode voltage ($V_{t_i}, ..., V_{t_{N-1}}$) are measured during the relaxation process. An asymptotic equilibrium potential can be predicted on the basis of $N$ subsequent voltage measurements by assuming an exponential model with multiplicative error structure, according to

$$V_t = V_{eq} - \frac{G}{\log^2(t)}$$

where $V_{eq}$ is the final asymptotic relaxation voltage, $\lambda, \gamma, \delta$ are the positive rate-determining decaying constants, $\epsilon$ is the random error term and $G$ is equal to $-1$ for increasing voltages after current interruption during the discharge process and $-1$ for decreasing voltages after current interruption during charging. Parameters $V_{eq}, \lambda, \delta, \gamma$ can be estimated by applying the concentrated Ordinary Least Squares (OLS) scheme. At least $4$ observations are required ($N \geq 4$) to predict the asymptotic equilibrium potentials. Obviously, the benefit is that much shorter relaxation times are required to obtain reliable values for $V_{eq}$.

Fig. 3 shows, as an example, a comparison between the experimentally observed and mathematically predicted value for $V_{eq}$. In the experiment the electrode was charged for one hour and allowed to equilibrate for 12 h after current interruption, which is four times longer than the resting period used in our GITT experiments. The relaxation potential after 3 h is $-826 \text{ mV}$ and after 12 h $-817.2 \text{ mV}$. The predicted voltage curve is based on the experimental 3 h relaxation time and the predicted $V_{eq}$ value of $-818.7 \text{ mV}$ after 12 h relaxation matches well with the experimentally obtained value with a difference of only $\pm 1.5 \text{ mV}$. It can therefore be concluded that the voltage prediction model is very helpful in accurately predicting $V_{eq}$.

**Thermodynamic characteristics**

Fig. 4 shows the as-determined $V_{eq}$ values (symbols) as a function of hydrogen content during charging and discharging together with the corresponding equilibrium voltage curves (black lines) and the dynamic potential responses during current flowing conditions (grey lines) for $\text{Mg}_0.80\text{Ti}_{0.20}$ (a), $\text{Mg}_0.60\text{Ti}_{0.35}$ (b), $\text{Mg}_0.67\text{Ti}_{0.27}\text{Ni}_{0.10}$ (c) and $\text{Mg}_0.67\text{Ti}_{0.27}\text{Si}_{0.10}$ (d) during charging ($50 \text{ mA g}^{-1}$) and discharging ($10 \text{ mA g}^{-1}$). The solid solution regions at the beginning of charging are clearly dependent on the Ti content in the binary compounds (Fig. 4a and b). The equilibrium potential in the two-phase coexistence region, on the other hand, is found to be independent of the Mg-to-Ti ratio for the binary compounds. The equilibrium voltages at the two-phase plateau for charging and discharging are $-820 \text{ mV}$ and $-740 \text{ mV}$, respectively, indicating that a significant hysteresis is apparent, which is often found in phase transition regions [42].

The electrode equilibrium potential can be converted to an equilibrium pressure, according to [43]

$$V_{eq} = -\frac{RT}{nF} \ln \frac{P_{eq}}{P_{ref}} - 0.931,$$

where $R$ is the gas constant, $T$ is the absolute temperature, $F$ is the Faraday constant, $n$ is the number of electrons per molecule (i.e. $n = 1$), $P_{eq}$ is the equilibrium pressure of hydrogen and $P_{ref}$ is the reference pressure, equals to 10 atm. The equilibrium plateau for pressure during discharging is of the order of $10^{-6}$ bar for all alloys and this is similar to that of pure MgH$_2$, suggesting that the thermodynamics of Mg-hydride is dominating. Similar observations were made for the MgTiX ($X = \text{Ni, Si}$) alloys. Therefore no thermodynamic destabilization occurs in ball-milled MgTiX ($X = \text{Ni, Si}$) in contrast to MgTiX ($X = \text{Al, Si}$) thin films which revealed an increase in the partial pressure during discharging [20,44].

**Kinetic materials properties**

Information about the electrode kinetics can also be obtained from Fig. 4 by considering the difference between the electrode potential under current flowing conditions (grey lines) and $V_{eq}$ (black lines). Fig. 5 summarises the development of the overpotential during charging for the alloys shown in Fig. 4. In all cases the overpotentials are significantly higher (more negative) in the initial stages of the hydrogenation process, i.e. in the solid solution regions, and decrease with increasing hydrogen content to become more or less constant in the two-phase coexistence (plateau) region. In the case of $\text{Mg}_0.80\text{Ti}_{0.20}$...
The overpotentials are significantly higher in the plateau region than for Mg$_{0.65}$Ti$_{0.35}$, indicating that the formation of the fluorite structure is kinetically more favourable than the rutile structure. Similarly, the overpotentials increase quickly during dehydrogenation (not shown) in the case of Mg$_{0.80}$Ti$_{0.20}$ as a result of the poor hydrogen diffusion in this binary alloy. The overpotential is again much smaller (~30 mV) in the case of Mg$_{0.65}$Ti$_{0.35}$ and remains more or less constant throughout the desorption process, only at the end of the dehydrogenation process where hydrogen becomes depleted it becomes more dominant.

The addition of Ni and Si in the ternary compound (Fig. 5) even reduces the overpotentials to very low values, for Ni even smaller than 8 mV, compared to all other compositions, indicating that Ni and Si are very favourable in improving the electrode kinetics during charging.

Impedance spectroscopy
Electrochemical impedance spectroscopy is used to identify the various processes occurring in the electrolyte, at the electrolyte/electrode interface and in the bulk of the electrode. The EIS spectra are measured at the end of each resting period of

\[
\text{(a)} \quad \text{Voltage (V) vs Hg/HgO} \\
\text{(b)} \quad \text{Voltage (V) vs Hg/HgO} \\
\text{(c)} \quad \text{Voltage (V) vs Hg/HgO} \\
\text{(d)} \quad \text{Voltage (V) vs Hg/HgO}
\]
the GITT measurements. Fig. 6 shows the EIS spectra at various stages of the electrochemical (de)hydrogenation process. Suppressed semi-circles are found in all cases and it is clear that the radii of these semi-circles are significantly reduced at higher hydrogen content, which is in line with the overpotential development reported in Fig. 4. During hydrogenation the radii of the semicircle decrease with increasing hydrogen content, whereas during dehydrogenation, shown in Fig. 7, the radii increase with decreasing hydrogen content. Interestingly, an additional semicircle becomes visible at low frequencies during dehydrogenation and the radius of this second semi-circle also increases with decreasing hydrogen content (see second semicircles indicated by an arrow in Fig. 7).

Fig. 8a schematically shows the various processes taking place at/inside an MH electrode particle. An equivalent circuit (EQC) is often used to quantify the various reaction steps. MacDonald, Montella and Gabrielli et al. identified several steps in the (de)hydrogenation process of MH electrodes [45–47]. The equivalent circuit of such a complex process is schematically shown in Fig. 8b. Apart from the electrical double layer (Cdl), established at the MH electrode/electrolyte interface, the following detailed steps can be distinguished during (de)hydrogenation:

1. Reduction of H2O at the Pd/electrolyte interface
2. Diffusion of adsorbed hydrogen atoms (Had) into the Pd sub-surface to form PdHss
3. Transfer of hydrogen across the Pd/MgTi interface
4. Solid-state diffusion of hydrogen into MgTi to form MgTiHx.

Fig. 7 – Nyquist plot of a Mg0.65Ti0.35 electrode measured by GITT at various stages of dehydrogenation. The development of second semicircle is marked with an arrow.

In the EQC of Fig. 8b, Rs represents the series electrolyte resistance between the working electrode and reference electrode, Rct is the charge transfer resistance (step 1), resulting in the formation of adsorbed hydrogen (Had) at the Pd surface. Herewith it is assumed that charge transfer hardly

Fig. 6 – Electrochemical impedance spectra measured with a Mg0.65Ti0.35 electrode after voltage relaxation at different indicated (open symbols) stages of charging and discharging. The electrode particle morphology is schematically indicated for each measurement.
takes place at the uncovered MgTi as Pd is considered to be much more electrocatalytically active than MgTi. \( H_{\text{ad}} \) is subsequently absorbed by the subsurface of Pd denoted as \( H_{ss} \) (step 2). The resistance corresponding to hydrogen absorption in Pd below the subsurface is negligible and therefore omitted in this scheme. Moreover, hydrogen diffusion in the Pd top surface is neglected as this is very fast in this 10 nm thin film compared to other reaction steps. \( R_{tt} \) and \( C_{tt} \) correspond to the resistance and capacitance associated to transfer of hydrogen from Pd top surface to MgTi bulk, respectively (step 3). \( W_{\text{MgTi}} \) is the Warburg element representing the semi-infinite diffusion of hydrogen (step 4) in the bulk of the MgTi powder.

The impedance spectra measured during charging consists of a single semicircle and a Warburg component at low frequencies. The semicircle corresponds to the charge transfer resistance at the Pd/electrolyte interface. The double layer capacitance is also a surface property and is expected to remain constant throughout the (dis)charging process. The radius of the semicircle, however, strongly depends on the hydrogen content. As hydrogenation (charging) proceeds the radius of the semicircle increases and is strongly dependent on the hydrogen content. Interestingly, the radius of the second semicircle at low frequencies, which corresponds to \( R_{tt} \), also increases with increasing depth of discharge.

At the initial stages of the hydrogenation the \( \alpha \)-phase is formed at the particle surface and the hydrogen content grows as the charging proceeds (see Fig. 6). The increase in hydrogen content at the peripheral layers leads to nucleation and growth of the hydrogen rich \( \beta \)-phase. The \( \alpha \)-to-\( \beta \) boundary moves inwards at higher hydrogen content. At the end of the hydrogenation process the conversion into the \( \beta \)-phase is completed. At the initial stages of dehydrogenation the hydrogen at the peripheral layers of the hydride starts to oxidize first and, consecutively, the \( \alpha \)-phase is formed at the outer layers of the hydride, as is schematically shown in Fig. 6. As the dehydrogenation proceeds, the \( \beta \to \alpha \) boundary moves towards the outer surface. The transfer resistance \( R_{tt} \) at the Pd/MgTi interface is more pronounced when the \( \alpha \)-phase is formed at peripheral layers of MgTi during dehydrogenation. Although during the initial stages of hydrogenation the \( \alpha \)-phase is formed at the peripheral layer of MgTi, \( R_{tt} \) is less pronounced or even absent.

Relationship between exchange current and partial hydrogen pressure

The exchange current density \( I_0 \) is an important parameter describing the kinetics of the electrochemical (de)hydrogenation reaction. It characterizes the ability of the hydrogen storage material to deliver current at high rates. \( I_0 \) has been related to the charge transfer resistance \( R_{ct} \), according to [48]

\[
I_0 = \frac{RT}{R_{ct} F}
\]  

(7)

The equilibrium pressure is another important MH material characteristic (see Eq. (6)). To achieve a high energy density coupled with high power density, it is necessary that the hydrogen storage material combines an appropriate plateau pressure with excellent electrocatalytic activity for the (de) hydrogenation reaction. Notten et al. has proposed and validated a model to define the relationship between the equilibrium hydrogen pressure and the exchange current [49,50]. According to that model, the exchange current density can be described by

\[
I_0 = \frac{FA_a K_2}{(\sqrt{P_{\text{H}_2}})^{x(1-x)} K_1^{x} (1-x)}^{z(1-x)} \left( \frac{A_{\text{eff}}}{a_{\text{H}_2O}} \right)^{1/z}
\]  

(8)

where \( A_a \) is the electrode surface area, \( a_{\text{H}_2O} \) and \( a_{\text{OH}^-} \) are the activities of OH\(^{-}\) and H\(_2\)O species, respectively, \( x, y, \) and \( z \) are
reaction orders, $\alpha$ the charge-transfer coefficient, and F the Faraday constant. $K_1$ is a constant which value depends on the chemical potential of the adsorbed hydrogen atom ($\mu_{H_2}^{\text{ad}}$) and the standard chemical potential of hydrogen ($\mu_{H_2}^{\text{sat}}$), according to

$$K_1 = \sqrt{\frac{P_{H_2}^{\text{eq}}}{RT}} \exp\left(\frac{2\mu_{H_2}^{\text{eq}} - \mu_{H_2}^{\text{sat}}}{2RT}\right)$$

(9)

in which $P_{H_2}^{\text{eq}}$ is the equilibrium pressure in the reference state (1 bar $\approx 10^5$ Pa). $K_2$ is another constant, which value depends on the rate constants of reduction ($K_c$) and oxidation ($K_a$), according to

$$K_2 = \frac{K_c}{K_a} \left(\frac{1}{C_0}\right) a K_a c$$

(10)

The activities of $\text{OH}^-$ and $\text{H}_2\text{O}$ species are considered constant. The values of the known parameters are listed in Table 1.

Fig. 9 shows the measured (symbols) and simulated (lines) exchange current as a function of equilibrium hydrogen pressure for $\text{Mg}_{0.80}\text{Ti}_{0.20}$ (a), $\text{Mg}_{0.65}\text{Ti}_{0.35}$ (b) and $\text{Mg}_{0.63}\text{Ti}_{0.27}\text{Ni}_{0.10}$ (c) during discharging. Good agreement between the experiments and the simulations are found in all cases. The optimized parameters are summarized in Table 2. From this table, it can be concluded that $\alpha$ reveals a reasonable value for all available materials, which is similar to those reported for $\text{MmNi}_{3.9-x}\text{Mn}_{0.4}\text{Al}_x\text{Co}_{0.7}$ ($0 \leq x \leq 0.8$) electrodes [50]. These values indicate that the contribution of the overpotential in the powder electrodes is dependent on the materials composition. Interestingly, $\alpha$ differ significantly for the fluorite-structured $\text{Mg}_{0.80}\text{Ti}_{0.35}$ and $\text{Mg}_{0.63}\text{Ti}_{0.27}\text{Ni}_{0.10}$ compared to $\text{Mg}_{0.80}\text{Ti}_{0.20}$ where complete fluoride conversion is still questionable. $K_1$ shows values below unity, indicating the hydrogen is more easily transferred from the adsorbed state into the adsorbed state. $K_1$ is much lower for $\text{Mg}_{0.80}\text{Ti}_{0.20}$, indicating that the hydrogen transfer is more inhibited. As $K_2$ is directly proportional to $I_o$, the higher $K_2$ values found for $\text{Mg}_{0.63}\text{Ti}_{0.27}\text{Ni}_{0.10}$ and $\text{Mg}_{0.65}\text{Ti}_{0.35}$ indicate an improved electrochemical activity for these two alloys.

Diffusion coefficient

In Ref. [51] the relation between the diffusion coefficient and the Warburg factor had been investigated. The apparent hydrogen diffusion coefficient $D_H$ can be estimated using expression

$$D_H = \frac{1}{\tau_L^2}$$

Fig. 10 shows the dependence of $Z_{im}$ on the reciprocal square root of the frequency in the low-frequency region for the various electrode materials.
D_H = \frac{(RT)^2}{2(A n F C_0 \sigma)^2}, \quad (11)

where C_H is the hydrogen concentration, A is the surface area of the electrode, n is a number of electrons per molecules during oxidation and \( \sigma \) is the Warburg factor which, in turn, can be identified from impedance measurements, according to

\[ Z_{im} = \sigma \omega^{-1/2}, \quad (12) \]

To compare the diffusion processes in all four alloys, the Warburg factors in the Nyquist plots are calculated. Fig. 10 shows the relationship between the experimentally measured imaginary part of the impedance (\( Z_{im} \)) and \( \omega^{-1/2} \) in the low frequency region, and the corresponding theoretical lines given by Eq. (12). Table 3 gives an overview of the estimated Warburg factors. The diffusion coefficient is inversely proportional to the square root of the Warburg factor as expected. \( \sigma \) is higher for \( \text{Mg}_0.80 \text{Ti}_{0.20} \) compared to \( \text{Mg}_0.65 \text{Ti}_{0.35} \), indicating a stronger diffusion limitation in the former material. \( \sigma \) decreases further by the addition of Ni to Mg-Ti. It can therefore be concluded that Ni addition enhances the hydrogen diffusion in the material. In contrast, addition of Si limits the hydrogen diffusion to a certain extent as becomes evident from the slight increase in \( \sigma \).

### Conclusions

The hydrogen storage properties of MgTi and MgTiX have been electrochemically investigated. Binary \( \text{Mg}_y \text{Ti}_{1-y} \) and ternary MgTiX (X = Ni and Si) compounds have been prepared by mechanical alloying. Based on XRD results it was concluded that single phase alloys were obtained. The reversible storage capacity of binary \( \text{Mg}_y \text{Ti}_{1-y} \) increases with increasing Ti content to reach a maximum capacity at \( \text{Mg}_0.70 \text{Ti}_{0.30} \). The equilibrium hydrogen pressure and exchange current were determined by GITT and Impedance spectroscopy, respectively. Rate constants and charge transfer coefficients for the charge transfer reaction were obtained by simulating a theoretical model relating the hydrogen equilibrium pressure and exchange current. The kinetics of the (de)hydrogenation reaction of \( \text{Mg}_0.65 \text{Ti}_{0.35} \) is better compared to \( \text{Mg}_0.80 \text{Ti}_{0.20} \), as became evident from the higher exchange current. Addition of Ni reduces increases the exchange current considerably and, consequently, the overpotentials. However, addition of Si, reduces the overpotentials only marginally during hydrogenation. The dehydrogenation behavior is not favourable, causing the reversible storage capacity to decrease significantly. The hydrogen diffusivities have been investigated by impedance spectroscopy and reveal that the hydrogen diffusion is improved in the Ni-containing \( \text{Mg}_0.65 \text{Ti}_{0.27} \text{Ni}_{0.10} \) alloy. Even though the reversibility of the reported Mg-based binary and ternary alloys still low, it is scientifically interesting to investigate the (de)hydrogenation characteristics of these materials further. This eventually would improve the performance of these interesting hydrogen storage alloys in future applications.

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