Research Article

Electrochemical Properties of $\text{La}_2\text{Mg}_{17}/\text{Ni}$ Electrodes Prepared via TiF_3 -Catalysed Mechanical Milling

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In order to improve the hydrogen storage capacity of conventional $\text{La}_2\text{Mg}_{17}$ electrode alloys, a nanocrystalline/amorphous-structured $\text{La}_2\text{Mg}_{17}$ -Ni composite material was produced by high energy ball milling in the presence of TiF_3 . Subsequent analysis of the discharge/charge cycle performances of this electrode material revealed that its cycle stability and electrochemical capacity were greatly improved, with the latter reaching a maximum value of 787.07 mAh/g with optimisation of the TiF_3 addition. Moreover, a remarkable enhancement in the reversibility of electrochemical reactions on the material's surface was also observed. Hydrogen diffusion coefficients for the material were calculated by means of a potential step method, confirming that TiF_3 markedly improves the long-range diffusion of hydrogen within the material.

1. Introduction

Of the various energy conversion and storage materials that have been developed over recent years, amorphous composites based on a La-Mg system alloy that is combined with Ni powder by mechanical milling are considered amongst the most promising, by virtue of their high electrochemical discharge capacity [1–3]. Indeed, Y. Wang and X. Wang [4] have already demonstrated that the ball milling of $\text{Pr}_5\text{Mg}_{41}$ with 200 wt.% Ni can achieve an excellent electrochemical hydrogen storage capacity, reaching as high as 1016.2 mAh/g. Rousselot et al. [5] have also obtained an improved discharge capacity of 475 mAh/g through the high energy ball milling of an Mg-Ti alloy and noted a microscale structural transformation of the Mg-Ti phase during charge/discharge cycles.

There has, however, been little consideration given to the use of TiF_3 as a catalyst in electrochemical applications; its use instead has been largely confined to the adsorption and release of gaseous hydrogen. Notable exceptions include the work of Liu et al. [6, 7], in which TiF_3 doping of LiAlH_4 during ball milling was used to achieve rapid hydride decomposition. Ma et al. [7, 8] have also demonstrated that using 4 mol.% TiF_3 as a catalyst significantly improves the hydrogen

absorption/desorption performance of Mg alloys. This is made possible by the inherently high corrosion resistance of Ti, and the resulting relative instability of its fluoride. The use of TiF_3 as a catalyst for electrochemical hydrogen storage therefore certainly warrants further research. To this end, this paper explores the effect of TiF_3 addition on the formation of a $\text{La}_2\text{Mg}_{17}$ alloy-Ni powder composite by mechanical grinding and how this influences its room-temperature electrochemical properties.

2. Experimental Materials and Methods

2.1. Alloy Preparation and Mechanical Ball Milling. Ingots of $\text{La}_2\text{Mg}_{17}$ alloy were prepared under a 0.04 MPa helium atmosphere using a vacuum induction furnace and once cooled they were mechanically pulverized to a +200 mesh powder. Composite material samples, each with a weight of 10 g, were obtained through further mechanical grinding of the $\text{La}_2\text{Mg}_{17}$ alloy powder in conjunction with 150 wt.% Ni and y wt.% TiF_3 (where $y = 0, 3, 5$, hereafter denoted as TiF_3 -0, TiF_3 -3, and TiF_3 -5). The purity of both the Ni powder and TiF_3 was greater than 99.7%, and Cr-Ni stainless steel balls were charged at a weight ratio of 40:1. All milling

FIGURE 1: The granular morphologies and XRD patterns of the composites.

was performed under an argon atmosphere in a laboratory planetary mill at a speed of 350 rpm for 60 hours. The resulting composite samples were handled in an argon-filled glove box and sealed in vessels under an argon atmosphere until required for testing.

2.2. Microstructural Analysis. The phase of structure of the composite samples was analysed by X-ray diffraction (XRD, X'Pert Pro MPD), with Jade6.0 software that is used to determine the material composition. The morphology of the as-cast alloy and ball-milled composite powders was examined scanning electron microscopy (SEM, JSM 6400, and FEI Quanta 400) and optical microscopy (Neophot 21).

2.3. Measurement of Electrochemical Properties. Round electrode pellets measuring 15 mm in diameter were prepared by cold pressing a 1:4 mixture (by weight) of the composite powder and a carbonyl nickel powder with 35 MPa of pressure. After being allowed to dry for 4 hours, the electrode pellets were then immersed for 24 hours in a 6 mol/L KOH electrolyte solution to fully wet the electrodes prior to electrochemical measurement. These electrochemical measurements were performed at 30°C using a trielectrode open cell, consisting of a working electrode and a sintered Ni(OH)₂/NiOOH counter electrode. The charge/discharge current density used was 40 mAh/g.

Tafel polarization curves were obtained for each sample within a potential range of -1.2 to +1.0 V (versus Hg/HgO) using an electrochemical workstation (PARSTAT 2273) and a scan rate of 5 mV/s at 50% DOD. To determine the potentiostatic discharge, fully charged electrodes were discharged at 500 mV potential steps for 5000 s, and the results were interpreted using CorrWare electrochemistry corrosion software.

3. Results and Discussion

3.1. Microstructure of the Composite. The morphologies of the composite samples shown in Figure 1 indicate that ball

milling results in homogeneous spherical particles (with radius being about 10 μm), with some localised fusion. Moreover, the broad and diffuse peaks evident in the accompanying XRD spectra indicate the formation of an amorphous/nanocrystalline structure, though there is also evidence of a residual Ni phase. In the case of TiF₃-5, this Ni peak is greatly reduced and the remaining peaks become broader and shifted to the right. However, this suggests that the use of a TiF₃ catalyst may be conducive to the formation of more amorphous phases. This effect is only slight and therefore it warrants further investigation to confirm such a connection.

3.2. Discharge Capacity and Cycle Stability. The evolution of the discharge capacity of the composite over 20 cycles that is shown in Figure 2 was used to characterise its activation performance. That is, given that all samples were clearly fully activated after the first cycle, they reached their maximum discharge capacity and activation performance at room temperature. This can be attributed to the modification effect of the Ni powder, a material which itself has a high electrocatalytic activity. However, it was also found that the composite electrode material is more readily oxidised in the electrolyte, leading to a greater attenuation of its capacity; the decline in capacity was primarily ascribed to corrosion of the Mg. Nevertheless, the maximum discharge capacity of TiF₃-3 is clearly and greatly improved, reaching a maximum of 787.07 mAh/g. Furthermore, TiF₃-5 exhibits a reduced attenuation at the fourth cycle that would greatly improve the capacity of the material and it is considered to be most likely due to a recombination of Ni and Mg in response to the corrosive environment.

3.3. Charge and Discharge Voltage Characteristics. From the first circulation charge/discharge curves shown in Figure 3, we can see that the use of TiF₃ as a catalyst increases the material's charge resistance, which directly affects the activation charge of the material. This is explained by the fact that Ti helps to increase the transfer of charge between

TABLE 1: HRD values of milled composites as electrode materials.

Composite materials	C_{60}/C_{40} (%)	C_{80}/C_{40} (%)	C_{120}/C_{40} (%)	C_{160}/C_{40} (%)
TiF ₃ -0	83	70	59	52
TiF ₃ -3	85	71	62	54
TiF ₃ -5	87	74	65	57

FIGURE 2: Evolution of the discharge capacity of milled La₂Mg₁₇ + 150 wt% Ni + y wt% TiF₃ ($y = 0, 3, 5$) composites with the cycle number.

occupied active sites, with the overall rate of charge transfer determining the charging resistance [9]. Figure 3 shows the diffusion of hydrogen atoms, and ions are strong in TiF₃-3 under these same conditions and, as mentioned above, are attributable to the amorphous/nanocrystalline structure generated by ball milling. It is claimed by Zhu et al. [10] that the hydrogenated reaction mechanism of a hydrogen storage nanocomposite alloy is self-catalysing due to the presence of different nanoscale phases, whereas a single-phase alloy is regulated by nucleation and growth. This would mean that a nanocomposite alloy has an inherently superior hydrogen storage performance.

3.4. High Rate Discharge Ability (HRD). The electrochemical hydrogen storage kinetics of the composite samples can be defined by their high rate discharge ability, as calculated by [11]

$$\text{HRD} = \frac{C_i}{C_{40}} \times 100\%, \quad (1)$$

where C_i and C_{40} are the discharge capacities of an electrode charged-discharged at current densities of i and 40 mA/g, respectively. The HRD data obtained is listed in Table 1, which demonstrates that a certain improvement is seen with the addition of the catalyst. This can be explained by the TiF₃-assisted reunion of Ni that creates the amorphous

FIGURE 3: The charge/discharge voltage curves of the La₂Mg₁₇ + 150 wt% Ni + y wt% TiF₃ ($y = 0, 3, 5$) composites.

structure observed, which is more conducive to the transfer of hydrogen atoms and ions [9].

3.5. Dynamic Properties of Electrode Materials. Figure 4(a) shows the exchange current density (I_0) of the electrode materials, as derived from the Tafel anodic and cathodic polarization curves by slope extrapolation. This I_0 value is a key parameter in determining the hydrogen desorption reaction kinetics, as it defines the reversibility of the electrochemical reaction and surface electrochemical activity for the hydride electrode [12, 13]. From the values given in Table 2, we can see that there is a clear increase in I_0 with increasing TiF₃ addition. This indicates that the specific surface area of reaction is increased, thereby increasing the electrocatalytic activity of the electrode. In the Tafel polarization curves of all the samples (Figure 4(a)), there is a clear increase in the anodic current density to a limiting current density, I_L , beyond which the current decreases. This is indicative of the oxidation of the electrode surface, with the resulting oxidation product inhibiting the penetration of hydrogen atoms [14, 15]. The decrease in anodic charge current density with repeated cycling also suggests that charging becomes more difficult, and, hence, I_L may be regarded as the critical passivation current density, which is determined by the diffusion of hydrogen in the bulk electrode during anodic polarization [16]. The numerical values of I_L (Table 2) also show that an increase in TiF₃ creates a similar trend to that

TABLE 2: Milled $\text{La}_2\text{Mg}_{17}$ + 150 wt.% Ni + y wt.% TiF_3 ($y = 0, 3, 5$) composite materials polarization fitting results.

Composite materials	I_L (mA/g)	I_0 (mA/g)	$d \log i/dt$	$D \times 10^{-11}$ (cm^2/s)
TiF_3 -0	540.50	53.63	$-4.09668e-5$	1.72
TiF_3 -3	768.13	66.82	$-9.19969e-5$	3.85
TiF_3 -5	1057.07	90.28	$-9.94984e-5$	4.17

FIGURE 4: Dynamics testing of milled $\text{La}_2\text{Mg}_{17}$ + 150 wt% Ni + y wt% TiF_3 ($y = 0, 3, 5$) composite materials: (a) Tafel polarization curves 50% DOD; (b) semilogarithmic curves of anodic current versus time responses.

identified in the aforementioned electrochemical test results, confirming that TiF_3 induces excellent electrochemical performance.

The hydrogen diffusion coefficient of each sample was measured using the potential step method, with the semilogarithmic curves of anodic current versus working duration depicted in Figure 4(b). If it is assumed that the composite particles are perfectly spherical, then the hydrogen diffusion coefficient can be calculated by [17]

$$\log i = \log \left(\pm \frac{6FD}{da^2} (C_0 - C_s) \right) - \frac{\pi^2}{2.303} \frac{D}{a^2} t, \quad (2)$$

$$D = - \frac{2.303a^2}{\pi^2} \frac{d \log i}{dt}, \quad (3)$$

where i is the diffusion current density (A/g), D is the bulk hydrogen diffusion coefficient (cm^2/s), C_0 is the initial hydrogen concentration in the composite (mol/cm^3), C_s is the hydrogen concentration on the surface of the composite (mol/cm^3), a is the alloy particle radius (cm), d is the density of the hydrogen storage composite (g/cm^3), and t is the discharge time (s). It is assumed here that $a = 15 \mu\text{m}$, as this is the aperture size of the sieve over which it was screened. The $d \log i/dt$ in (3) refers to the slope of the linear portion of the semilogarithmic curve of anode current versus working time (Table 2). The D values calculated in this way, assuming

a slope of 55, are shown in Figure 4(b). This demonstrates that TiF_3 greatly improves the hydrogen diffusion coefficient, varying from $1.72 \times 10^{-11} \text{ cm}^2/\text{s}$ for TiF_3 -0 to $3.85 \times 10^{-11} \text{ cm}^2/\text{s}$ and $4.17 \times 10^{-11} \text{ cm}^2/\text{s}$ for TiF_3 -3 and TiF_3 -5, respectively. It is therefore easy to see that a more uniform distribution of TiF_3 in the composite provides more favourable electrochemical reaction activation, thereby facilitating long-range diffusion of hydrogen atoms and improving the electrochemical performance of the composite material.

4. Conclusion

Ball-milled composites of $\text{La}_2\text{Mg}_{17}$, Ni, and TiF_3 were found to have a uniform amorphous/nanocrystalline structure, albeit a small amount of residual Ni phase. The addition of TiF_3 was shown to improve both the corrosion resistance and maximum discharge capacity of the composite, with the latter reaching a maximum of 787.07 mAh/g. Furthermore, the TiF_3 catalyst improved the high rate discharge capacity and charge/discharge reversibility, especially that TiF_3 extended discharge platform of material by a wide margin. The electrochemical kinetics revealed that both Ni and TiF_3 improve the exchange current density and limiting current density, with subsequent measurement of the hydrogen diffusion coefficient, verifying that TiF_3 improves the electrochemical dynamics of the composite.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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