

Electrochemical approaches to prepare magnesium-based hydrogen storage materials

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Electrochemical approaches to prepare magnesium-based hydrogen storage materials

Chaoqi Shen

A thesis in fulfilment of the requirements for the degree of
Doctor of Philosophy



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Magnesium hydride has been extensively investigated as a promising hydrogen storage candidate due to its high gravimetric capacity, but with high operational temperature and slow kinetics. However, a nanosizing approach and catalyst introduction may provide unprecedented opportunities to improve these properties. In this thesis, an electrochemical deposition method was developed to synthesise the magnesium-based nanostructures to enable hydrogen storage at low temperature.

Firstly, the properties of components used in the electrochemical system such as magnesium precursors and stabilisers were investigated. It was found that functional groups in cationic, anionic and non-ionic stabilisers significantly influenced the morphologies of final magnesium deposits. The study was then extended to the hydrogen storage properties of Mg thin film formed on metal electrodes and results indicated that small magnesium particles (68 ± 11 nm) deposited on catalytic Ni substrate achieved low hydrogen desorption activation energy (37.8 ± 0.7 kJ·mol⁻¹ H₂). However, the heavy substrate limited the hydrogen capacity, thus the approach to generate isolated Mg nanoparticles was investigated with stabiliser and deposition current modifications. Mg nanoparticles prepared with a combination of cationic, anionic and non-ionic stabilisers could absorb 4 mass% H₂ after hydrogenation at 100 °C.

Since the electrochemical deposition method showed potential to prepare Mg nanoparticles with improvement of hydrogen storage properties, a catalyst (Ni) was introduced into the electrodeposition system via codeposition strategy. Mg/Ni nanocomposites were *in-situ* synthesised with different conditions, the final product with proper control was fully hydrogenated at 100 °C and exhibited a high content (30.6 %) of metastable γ -MgH₂, which led to a low desorption temperature (< 200 °C). The external addition of catalysts was also studied but only showed minor improvements. Preliminary investigations of magnesium codeposited with carbon materials suspended in electrolyte did not exhibit better hydrogen storage properties compared to bulk magnesium, while a multilayered Mg/polypyrrole sandwich structure could absorb/desorb hydrogen at low temperature. Electrochemical deposition is still a novel method to synthesise magnesium-based hydrogen storage nanostructures, but it provides a highly promising avenue for practical developments in energy in the future.

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LIST OF PUBLICATIONS

Journal papers

1. Shen, C.; Aguey-Zinsou, K.-F. Electrodeposited magnesium nanoparticles linking particle size to activation energy. *Energies* 2016, 9, 1073. (Published)
2. Sun, Y.; Shen, C.; Lai, Q.; Liu, W.; Wang, D.-W.; Aguey-Zinsou, K.-F. Tailoring magnesium based materials for hydrogen storage through synthesis: Current state of the art. *Energy Storage Materials* 2017. (Published)
3. Shen, C.; Aguey-Zinsou, K.-F. Can γ -MgH₂ improve the hydrogen storage properties of magnesium? *Journal of Materials Chemistry A* 2017, 5, 8644-8652. (Published)
4. Shen, C.; Aguey-Zinsou, K.-F. Electrochemical synthesis of Mg decorated carbon nanotubes and the hydrogen storage properties. (In progress)
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1. The 2nd Australian Energy Future Conference, “Hydrogen storage properties of electrochemically deposited magnesium on catalytic substrates” (Oral)

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LIST OF ABBREVIATIONS

Abbreviation	Full name
DSC	Differential Scanning Calorimetry
EDS	Energy Dispersive X-Ray Spectroscopy
FTIR	Fourier Transform Infrared Spectroscopy
HR-TEM	High Resolution-Transmission Electron Microscopy
HSAG	High Surface Area Graphite
ICP-OES	Inductively Coupled Plasma-Optical Emission Spectrophotometry
MS	Mass Spectrometry
NHE	Normal Hydrogen Electrode
PCI	Pressure-Composition-Isotherm
PCT	Pressure-Composition-Temperature
SEM	Scanning Electron Microscopy
TBAB	Tetrabutylammonium Bromide
TEM	Transmission Electron Microscopy
TGA	Thermogravimetric Analysis
THF	Tetrahydrofuran
XRD	X-Ray Diffraction

CHAPTER 1 INTRODUCTION

Energy storage systems of the future will have to be reliable, available, clean, flexible, and cost-efficient to ensure global environmental sustainability and energy security. The widely used fossil fuels are producing too much carbon dioxide and pollutants, while they will power our planet at least for decades in this way because of mature industrial applications. With the purpose of reducing the effect of fossil fuels combustion, hydrogen is regarded as a promising alternative due to its high energy density and clean combustion. In the hydrogen cycle (from water to water), hydrogen storage is the main obstacle compared to its production and utilisation. Storing hydrogen under mild conditions with high capacity has been the focus of significant investigations. Magnesium with a storage capacity of 7.6 mass% could provide a solution toward the safe and compact storage of hydrogen. However, the slow kinetics and relatively high operation temperature are the significant technical barriers. Following initial findings, nanosizing and addition of catalysts appear to be effective routes toward ambient temperature hydrogen storage with Mg. However, these findings are still far from delivering practical materials.

In this thesis, the aim is to electrochemically synthesise nanosized magnesium-based hydrogen storage materials which could absorb and desorb hydrogen at low temperatures. The assumption is that electrochemical methods could allow control over Mg morphology and doping.

Following this idea, the research has been focused along the following objectives:

- Investigate the electrochemical properties of potential Mg precursors and stabilisers as a base to establish reliable electrochemical system

- Synthesise Mg nanostructures from the magnesium precursors with stabilisers on metals, carbons and conductive polymers to facilitate the control of the physical and chemical properties of magnesium
- Synthesise isolated Mg nanoparticles and investigate the effect of electrochemical conditions on hydrogen storage properties
- Develop Mg/Ni codeposition method to improve hydrogen storage properties via *in-situ* electrochemical doping

The thesis is structured as:

Chapter 2 reviews the literature and current state of hydrogen storage research. Introduction of the properties of magnesium and magnesium hydrides, and the synthesis and modification methods to improve hydrogen storage properties of magnesium-based materials are discussed.

Chapter 3 summarises the electrochemical properties of magnesium precursors and evaluates potential combination of magnesium precursors and stabilisers to achieve an “ideal” electrochemical deposition of magnesium.

Chapter 4 investigates the properties of magnesium electrochemically deposited on metallic substrates as well as its hydrogen storage properties and the potential catalytic effect of the substrates.

Chapter 5 explores different options of stabilisers influencing the properties of the deposited magnesium. Effect of anionic, cationic or non-ionic stabilisers and their combinations is discussed.

Chapter 6 aims at developing method to prepare Mg particles catalysed by Ni generated *in-situ* during the electrochemical synthesis. In particular, one of the main findings of

this work is the possibility of Mg/Ni nanocomposite to form metastable γ -MgH₂ phase after hydrogenation.

Chapter 7 states another potential route to improve hydrogen storage properties of Mg by depositing Mg on carbon-based materials such as carbon nanotubes and graphite as well as conductive polymer, and presents preliminary findings into their feasibility.

Chapter 8 concludes the key accomplishments of this research and recommends potential developments for future study.

CHAPTER 2 MAGNESIUM-BASED MATERIALS FOR HYDROGEN STORAGE

2.1 Introduction

Our societies have developed extremely rapidly since the industrial revolution owing to the growth of technical knowledge in utilising more complex primary energy sources of increasing energy density in the form of coal, oil and natural gas (Figure 2-1). Growing consumption of fossil fuels also generates a substantial amount of carbon dioxide (CO_2) and pollutants posing significant long-lasting environmental impacts and health issues.[1,2]

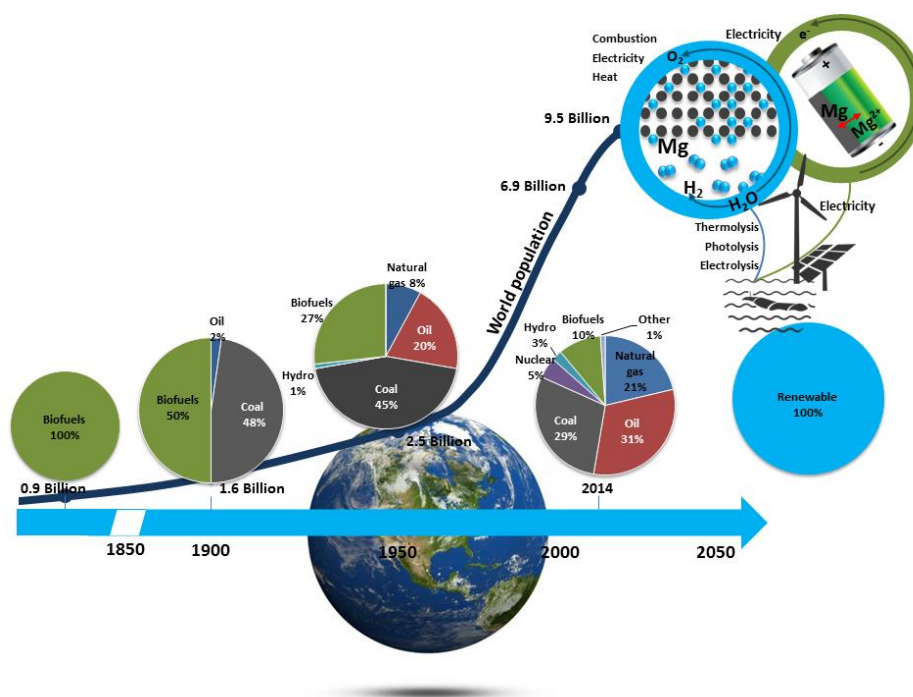


Figure 2-1: Evolution of the world total primary energy supply (data from ref. [1,2]) and the world population supported by the earth ecosystem.

More versatile, high-energy-density, carbon-free energy carriers are considered to be the alternative to fossil fuels.[3] Currently batteries, especially lithium ion batteries, are the

favoured options due to their relatively high energy density and flexibility in terms of use. However, better batteries with improved performance and safety at reduced costs need to be developed to meet more demanding applications such as electrical vehicles requiring high power density.[4] Hydrogen and batteries are often viewed as competitive technologies, while their complementary implementation is needed to overcome the complexity of energy supply/demand at different time and length scales. The beauty of hydrogen as a clean energy carrier remains the simplicity of the idea although there are still some technical and intellectual challenges such as the storage of hydrogen toward the practical targets. This review covers recent advances in the research of magnesium-based hydrogen storage materials, with a special emphasis on the synthetic approaches developed over the past decades and their effectiveness in leading to the improvement in hydrogen kinetics and thermodynamics for the magnesium/hydrogen system.

2.2 Hydrogen storage overview

2.2.1 Hydrogen storage as energy carrier

In an ideal model (Figure 2-1), hydrogen can be produced by splitting water (H_2O) from renewable resources.[3,5] It can then be used as an alternative fuel providing high energy density complementary to the capability of batteries, since the amount of energy per unit mass of hydrogen ($120 \text{ MJ}\cdot\text{kg}^{-1}$) is about three times that of gasoline and almost seven times higher than the energy obtained from coal in an equal mass.[6]

As an energy source, hydrogen can be used for different purposes including portable electronic, transport and stationary applications. However, considering the projected growth of individual vehicles and the fact that current vehicles mostly rely on fossil fuels resources, the electrification and wide application of hydrogen across the transport

sector would provide a significant step toward sustainable clean energy systems.[7] The idea of using hydrogen for transport is not new. Indeed, the first experimental combustion engine developed in 1807 by François Isaac de Rivaz burnt a mixture of hydrogen and oxygen manually ignited by electric spark (Figure 2-2). 55 years later, Étienne Lenoir ran his hippomobile on hydrogen over 9 km in Paris. Currently, Toyota and Hyundai developed their own hydrogen powered Mirai and ix35 respectively. Compared to stationary applications, the requirements for transport are more demanding owing to the need of high energy density and fast recharging rate.[8,9] In this respect, a series of targets regarding capacity, thermodynamics, kinetics and cost-efficiency have been set to guide research and development (Table 2-1) with the aim of achieving hydrogen fuel cell vehicles with performances comparable to existing technologies.

Table 2-1: U.S. Department of Energy technical targets for on board hydrogen storage systems.[10]

Storage parameter	Units	700 bar Type IV compressed tank	Ultimate
Gravimetric capacity	kWh·kg ⁻¹	1.7	2.5
	mass% H ₂	5.2	7.5
Volumetric capacity	kWh·L ⁻¹	0.85	2.3
	g H ₂ ·L ⁻¹	26.3	70
Delivery temperature	°C	-	-40/95-100
Operational cycle life	Cycles	> 5000	1500
Delivery Pressure	bar (min/max)	-	3/12
		-	35/100*
Kinetics (full flow rate)	(g H ₂ ·s ⁻¹) ·kW ⁻¹	-	0.02

*Internal combustion engine



Figure 2-2: Development of hydrogen powered automobiles through history.

2.2.2 Hydrogen storage systems

Conventional hydrogen storage methods include compressed gas (350-700 bar at room temperature) or condensed liquid (-253 °C, 5-10 bar).[11] These technologies are relatively mature and have been implemented in various prototype vehicles.[9,12] The first commercial hydrogen fuel cell vehicle Mirai is equipped with 70 MPa hydrogen composite tanks (Figure 2-2). However, the use of highly pressurised compressed tanks incurs safety risks; and even at pressures as high as 700 bar the density of hydrogen is only 26.3 g·L⁻¹. [11,13] For condensed liquid hydrogen, in spite of a much higher volumetric density of liquid hydrogen (70.8 g·L⁻¹), the unavoidable hydrogen loss resulting from heat transfer and the large amount of energy required to liquefy hydrogen have significantly hindered practical application.[8,11]

The alternative is in the form of solid state hydrogen storage as the distance between the hydrogen atoms significantly decreases once packed into hydride materials.[14] Over the past decades, significant efforts have been made toward the development of practical hydrogen storage materials. In particular, approaches have targeted: i) adsorbents for hydrogen physisorption, ii) metal hydrides, and iii) complex hydrides. Liquid organic hydrogen carriers such as cyclohexane, methylcyclohexane, and decaline

have also been investigated, but the high temperature required for hydrogen release and the need for noble-metal catalysts are significant drawbacks.[15]

Materials investigated for the physisorption of hydrogen are mainly carbon-based materials and more recently Metal Organic-Frameworks (MOFs) owing to their low density, high specific surface area and porosity.[11,16] MOFs consist of metal ions or clusters connected by multidentate organic ligands leading to exceedingly large specific surface areas over $5000 \text{ m}^2\cdot\text{g}^{-1}$ and tuneable properties.[8,17] The adsorption of hydrogen on these adsorbents relies on van der Waals interactions and thus significant hydrogen uptake is only possible at cryogenic temperatures (Figure 2-3a). The hydrogen uptake of these materials at ambient condition is quite low and usually $< 2 \text{ mass}\%$, [2,18] and approximately proportional to the surface area and micropore volume.[14,19,20]

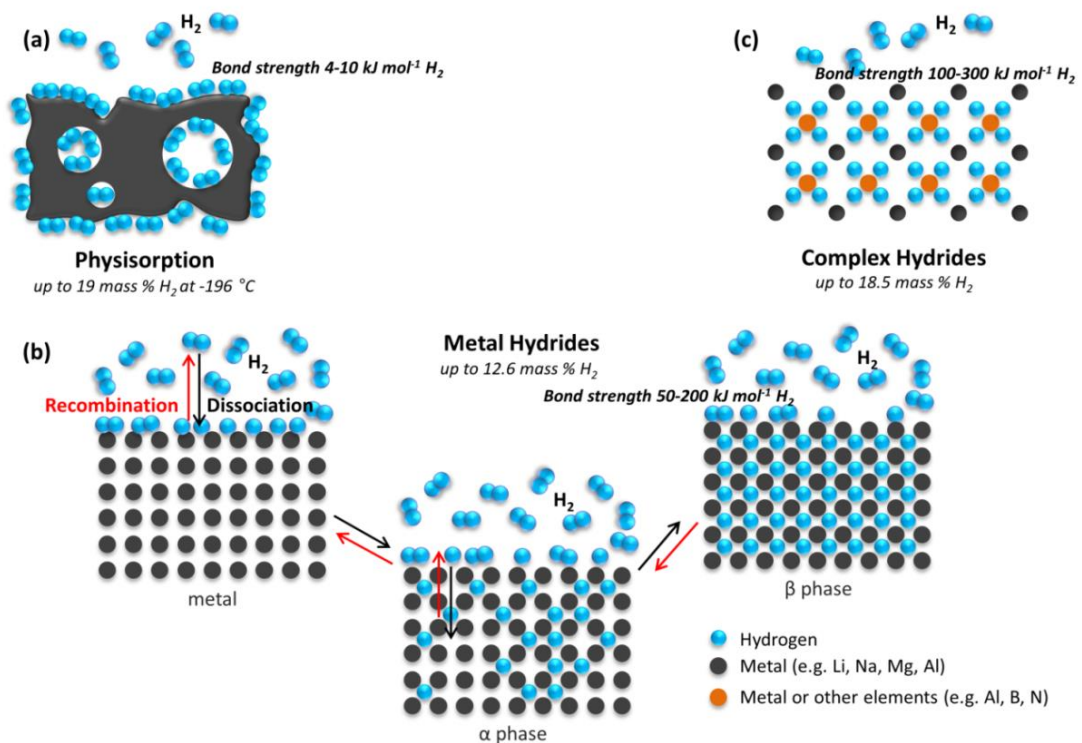


Figure 2-3: Schematic representation of current approaches to store hydrogen with materials.

For metal hydrides (e.g. LaNi_5H_6 , MgH_2) and complex hydrides (e.g. $\text{Mg}(\text{BH}_4)_2$, LiAlH_4), the hydrogen storage process involves the formation of bonds with the host material that can be classified as metallic, ionic or covalent (Figure 2-3b and c). The reversibility of the hydride formation depends on the bond strength, accordingly, metallic > ionic > covalent.[21] Various metals and alloys are capable of reversibly storing hydrogen under moderate conditions.[22] The type of metal-hydrogen bonds in these metal hydrides are diverse, for example, transition metals tend to form interstitial metal hydrides with variable and non-stoichiometric composition and metallic metal-hydrogen bonds with good reversibility including TiFeH_2 and LaNi_5H_6 . [9,21,23] However, the gravimetric density of these hydrides is low due to the large mass percentage of the metals,[9] which restricts practical use to niche applications.

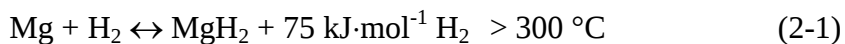
Higher hydrogen storage gravimetric density of metal hydrides can only be achieved by using light elements such as Li, Be, Na, Mg and Al. LiH has a mass density of 12.6 mass% but it has an extremely high hydrogen release temperature (720 °C). This desorption temperature can be reduced to 350 °C through a nanosizing approach but this temperature is still too high for any practical use.[24,25] BeH_2 and AlH_3 also have significant hydrogen storage capacity, 18.2 mass% and 10 mass% respectively. However, BeH_2 is highly toxic and AlH_3 is not reversible even at the nanoscale.[26-28] The storage capacity of NaH (4.2 mass%) is too low. Accordingly, this leaves MgH_2 with a maximum gravimetric capacity of 7.6 mass% and good reversibility as a promising candidate for high capacity hydrogen storage.

The next step towards increasing the storage capacity is to consider complex hydrides of Mg based on alanates $[\text{AlH}_4]^-$, amides $[\text{NH}_2]^-$ or borohydrides $[\text{BH}_4]^-$. Complex hydrides of Mg can reach a higher gravimetric and volumetric storage capacity, e.g. 14.9 mass% and $1.47 \text{ kg}\cdot\text{L}^{-1}$ for $\text{Mg}(\text{BH}_4)_2$, respectively. However, covalent bonding of

the hydrogen atoms to Al, N or B leads to poor reversibility. In fact, complex hydrides were not considered as potential reversible candidates for hydrogen storage until the recent findings of hydrogen reversibility in NaAlH₄. [29,30]

2.2.3 Hydrogen storage in magnesium hydride

Since the discovery of hydrogen absorption in palladium in 1868,[31] and major advances in the 1970s with the discovery of LaNi₅ and FeTi, a range of materials tabulated in the extensive hydrogen storage materials database [32] have shown ability to reversibly store hydrogen with high density. Of particular interest, magnesium (Mg) has remained at the centre of investigations owing to its abundance, benignancy and capacity to absorb hydrogen. The reaction of Mg with hydrogen yields a stable hydride (MgH₂) with a hydrogen gravimetric and volumetric capacity of 7.6 mass% and 110 g·L⁻¹ following reaction (2-1)



However, there are two major impediments in the practical utilisation of such a reaction: the kinetics of hydrogen uptake and release is slow and the thermodynamic dictates the need of high temperatures for hydrogen release.

Upon application of hydrogen pressure, the hydrogen atoms initially occupy the tetrahedral interstitial sites within the Mg lattice to lead a solution of hydrogen in Mg and the α -phase for a hydrogen concentration up to 0.4 mass% (Figure 2-3).[33] At higher hydrogen concentration the interaction between the hydrogen atoms, resulting from the increased hydrogen concentration, makes the nucleation of the β phase energetically favourable,[21,34,35] such tetragonal MgH₂ phase is marked as β -MgH₂. The hydride decomposition (hydrogen release) process is the reverse of the hydriding process. Unlike pure ionic hydride, e.g. LiH and NaH, all MgH₂ phases are accepted to

have a mixture of ionic and covalent bonding and the Mg-H bond shows the following charge distribution $\text{Mg}^{+1.91} \text{H}^{-0.26}$. [36]

Figure 2-4 summarises some of the attempts to destabilise the Mg/MgH₂ system through the alloying and nanosizing approaches and the evolution of the dissociation pressure of MgH₂ as a function of temperature. Nanoconfinement of Mg seems a promising approach; however the resulting hybrid materials suffer severely from low practical hydrogen capacities (usually < 1 mass%).

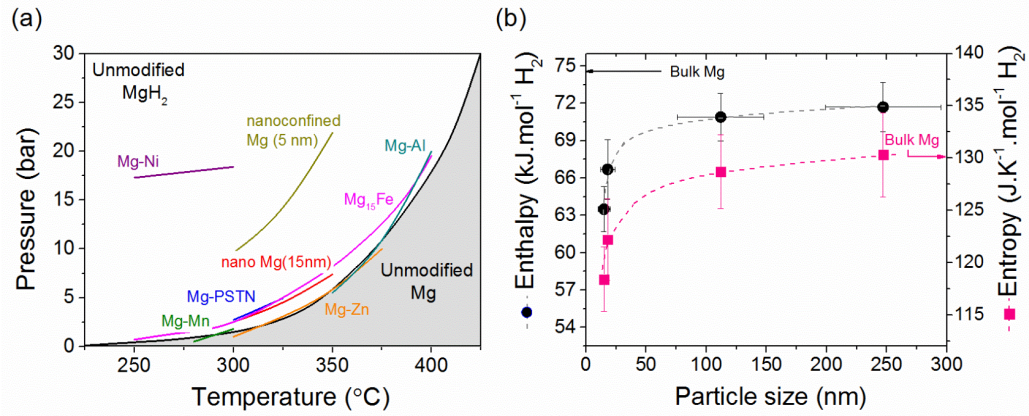


Figure 2-4: (a) Temperature dependence of the dissociation pressure of MgH₂ and associated evolution of such a dissociation pressure for various approaches investigated [37-44], and (b) evolution of ΔH and ΔS as function of the particle size of Mg.[40]

Another approach is through the formation of metastable phases.[45] In particular, it is known that the metastable γ -MgH₂ phase is of lower stability compared to the β -MgH₂ phase (Table 2-2). This lower stability can be understood through the evolution of structural transformations undergone by the hcp Mg phase as it absorbs hydrogen and evolves to different crystalline structures as γ -MgH₂ and β -MgH₂ (Figure 2-5).[46] Hence, the heavily distorted MgH₆ octahedron in the γ -MgH₂ structure as compared to the slightly squeezed MgH₆ octahedron along the axial bonds in β -MgH₂ has been predicted to facilitate hydrogen diffusion.[47]

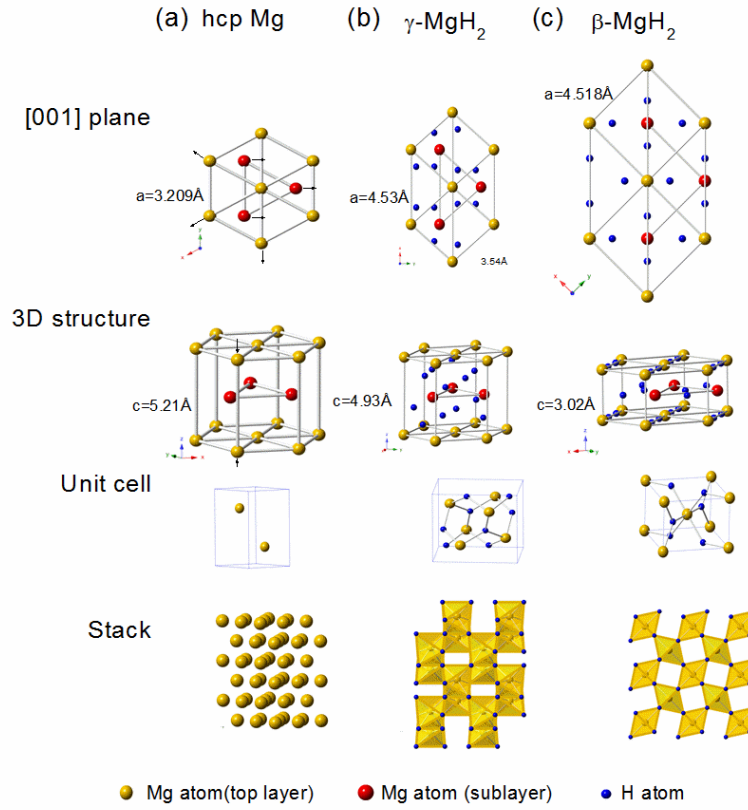


Figure 2-5: Evolution of the crystalline structure of (a) hcp Mg when it is transformed to (b) γ -MgH₂, and (c) β -MgH₂ upon hydrogen absorption. As the hydrogen atoms are introduced the Mg atoms of the A and B stacking slide as indicated by the arrows, and as a result the length of the Mg-Mg bond increases.

Furthermore, the greater distance between Mg and H in the γ -MgH₂ (Table 2-2) could reduce the Coulombic attraction, thus lowering the formation energy and facilitating H motion atom in γ -MgH₂. [47,48] Metastable γ -MgH₂ is usually synthesised by ball milling with low content [49,50] or from magnetron sputtering as a thin film, [51] while after long duration of ball milling, the content of γ -MgH₂ could reach 61 %. [52] Nevertheless, magnesium/nickel composite synthesised from chemical reduction could also form γ -MgH₂ phase after hydrogenation. [53] However to date, this phase has not been successfully stabilised during hydrogen cycling and irreversibly reverts back to β -MgH₂ at 300 °C. [49,54,55]

Table 2-2: Crystal structure data for Mg, γ -MgH₂ and β -MgH₂ and associated enthalpy.

Component phase	Mg	γ -MgH ₂	β -MgH ₂	Ref.
Space group	<i>P6₃/mmc</i>	<i>Pbcn</i>	<i>P4₂/mnm</i>	
Unit cell parameters/Å	a = 3.209	a = 4.53	a = 4.518	
	-	b = 5.44	-	
	c = 5.21	c = 4.93	c = 3.02	
	V = 46.48 Å ³	V = 121.49 Å ³	V = 61.63 Å ³	
Average Mg-H distance (Å)	-	1.9472	1.9418	[47]
		1.920	1.906	[55]
ΔH (kJ·mol ⁻¹ H ₂)/surface energy (J·m ²) of plane [110]	-	44.66/1.23	78.16/0.19	[56]
ΔH (kJ·mol ⁻¹ H ₂)/surface energy (J·m ²) of plane [001]	-	54.41/0.97	50.75/1.09	[56]

2.3 Development in MgH₂-based hydrogen storage materials

2.3.1 Thermodynamics and destabilisation

The reaction of hydrogen with Mg is exothermic with an enthalpy of reaction of 74.5 kJ·mol⁻¹ H₂ and an entropy variation of -135 J·K⁻¹·mol⁻¹ H₂. [57] This means that a temperature of at least 278 °C is required to release hydrogen from β -MgH₂ under a pressure of 1 bar (Van't Hoff plot in Figure 2-6a). Thus unmodified magnesium can only be operated at elevated temperatures, which is inefficient owing to the implication of significant heat management during hydrogen uptake and release.

$$\ln P_{H_2}^{eq}/P^\ominus = \Delta H^\ominus/RT - \Delta S^\ominus/R \quad (2-2)$$

From the associated Van't Hoff plot (2-2) it can be seen that in order to decrease the operating temperature for hydrogen release, $\Delta H^\ominus$ and $\Delta S^\ominus$ must be adjusted accordingly. Hence, taking into consideration that $\Delta S^\ominus$ is very similar for most metal-hydrogen systems (~ -130 J·K⁻¹·mol⁻¹ H₂) one strategy has been to adjust $\Delta H^\ominus$ by alloying Mg

with elements forming less stable hydrides (Figure 2-6b) in order to destabilise the hydrogenated state,[9,34,58] and reach thermodynamically acceptable ranges for application, i.e. a $\Delta H^\ominus$ of 20-50 kJ·mol⁻¹ H₂. [58] An archetypical example is the alloying of Mg and Ni leading to the Mg₂Ni/Mg₂NiH₄ system with a reduced enthalpy of 62 kJ·mol⁻¹ H₂, however this is at the expense of the storage capacity reduced to 3.6 mass%. [41,53]

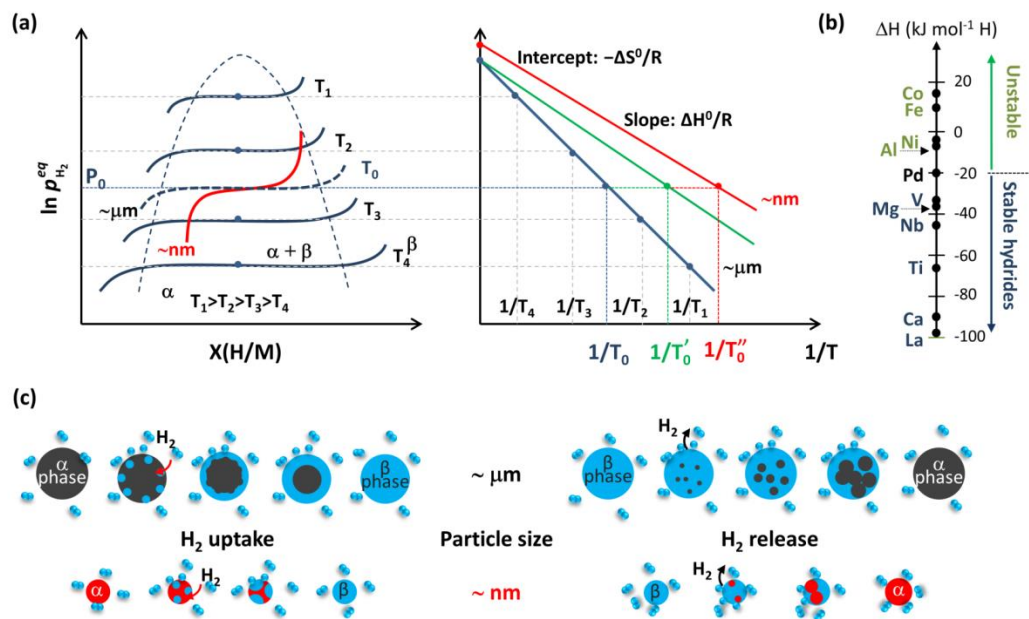


Figure 2-6: (a) PCT plot (left) and the corresponding Van't Hoff plot (right) of metal hydrogen systems, (b) enthalpy of formation of various metal hydrides,[59] and (c) schematic of the hydrogen absorption/desorption process in magnesium as function of particle size. The Van't Hoff plot (in green) illustrates a potential reduction in ΔH when Mg is alloyed with metals forming unstable hydrides such as Ni. The PCT (in red) illustrates the effect of reducing particle size to a few nanometres on the plateau pressure and Van't Hoff plot, i.e. a narrowing of the miscibility gap and a sloppy plateau potentially leading to a reduction of ΔH often compensated by a similar evolution of ΔS .

Another potential avenue is via the extreme reduction of Mg particle size (Figure 2-6c). With the increase in surface area for nanomaterials, more atoms are exposed at the surface, which leads to an increase in surface energy. In the particular case of hydrogen desorption from nanosized MgH_2 , the Van't Hoff equation takes a new form by considering these additional surface factors:[49]

$$\ln \frac{P_{nano}^{eq}}{P^{\ominus}} = \frac{1}{RT} \left(\Delta H^{\ominus} + \left(\frac{3V_{Mg}\gamma_{Mg}}{r_{Mg}} - \frac{3V_{MgH_2}\gamma_{MgH_2}}{r_{MgH_2}} \right) \right) - \frac{\Delta S^{\ominus}}{R} \quad (2-3)$$

Hence, if the surface energy of the hydride is larger than that of the metal, part of the formation heat will be stored as an excess surface energy which will result in a lower enthalpy. This may be achieved through nanosizing approaches involving the stabilisation of magnesium particles through nanoconfinement,[37,60-62] or electrostatic/steric repulsion with surfactants,[49,63,64] and/or the nanostructuring of magnesium with the formation of nanosized grains leading to many grain boundaries and thus an excess of enthalpy at these grain boundaries.[34]

The coupling of nanosizing with additional compressive stress could also provide an additional means for destabilisation of the Mg-H bond strength. Indeed, if the Mg lattice is not free to expand, the elastic constraints imposed by an external shell clapping magnesium nanoparticles would induce a repulsive H-H interaction instead of the usual attractive interaction leading to high desorption temperatures.[65] Such a possibility of elastic destabilisation has been pointed out in 2-D MgH_2 thin films.[66] However, this assumes that no alloying occurs between the capping shell and the MgH_2 core.

2.3.2 Kinetics and catalysis

The desorption temperatures higher than 300 °C are required for unmodified MgH_2 , which is due to the activation energy barrier (E_a) and thus both thermodynamics and

kinetics restrict the operation temperature of the Mg/MgH₂ system. A general approach to measure the reaction rate is by determining the reaction rate coefficient, $k(T)$. According to the Arrhenius equation:

$$k(T) = Ae^{\frac{-E_a}{RT}} \quad (2-4)$$

The absorption/desorption of hydrogen in Mg is a heterogeneous solid/gas reaction involving several factors with different energy barriers.[49] The challenge to enable fast hydrogen kinetics is thus to identify and reduce the key limiting steps and energy barriers. The kinetics of hydrogen in Mg and associated rate limiting steps are highly dependent upon the synthetic approach, the state of the material, e.g. surface reactivity, particle size, nanostructuration, and experimental conditions for hydrogen cycling. Hence, attempts to identify the main rate limiting steps from hydrogen kinetics data by the Johnson-Mehl-Avrani equations are often not convergent.[45,49]

Owing to the low capability of splitting or recombining hydrogen on the Mg surface, the first step to improve the reaction kinetics is through the addition of an effective catalyst to facilitate this process. Through ab-initio density functional calculations, Pozzo and Alfé reported an inverse volcano plot by taking into account the dissociation barrier of hydrogen molecules as well as the associated barriers for its diffusion away from the catalytic site (Figure 2-7b).[67] According to their results, on a Mg(0001) surface, Fe, Ni, and Rh would have both abilities to effectively decrease the energy barrier for the dissociation of hydrogen and subsequent hydrogen diffusion. Pd at the top of activity for the hydrogen evolution reaction (Figure 2-7a and b) would be less active for storage of hydrogen in Mg. However, experimentally Ni, Fe and Rh have not been reported to be the most effective catalysts,[49] and this further highlights the difficulty of drawing accurate models to help with the design of catalysts for the hydrogen/Mg reaction.

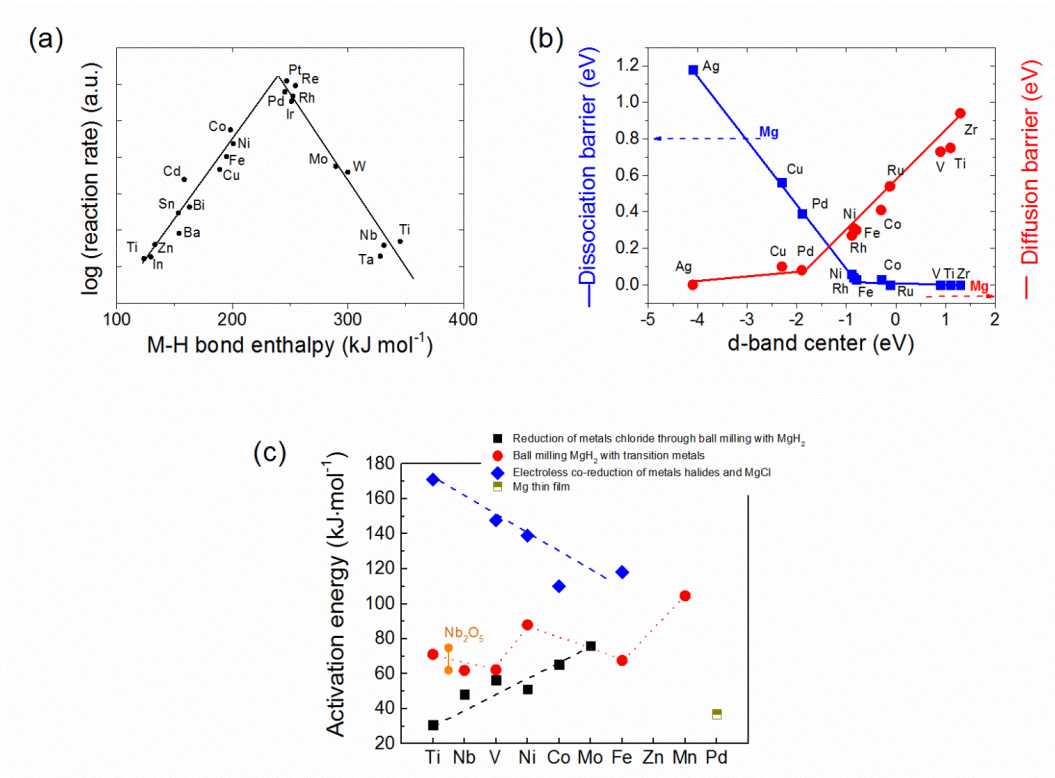


Figure 2-7: (a) Trassati's volcano plot for the hydrogen evolution reaction in acidic as function of the metal hydrogen (M-H) bond enthalpy,[68] (b) calculated activation energy barrier for hydrogen dissociation and diffusion of hydrogen at Mg(0001) surfaces as function of the d band centre positions (adapted from ref. [67]), and (c) experimentally determined activation energies for hydrogen absorption in Mg upon doping with various transition metals. [69-76]

Another approach to enhancing the kinetics is by decreasing the particle size to a few nanometres. Smaller particles possess a larger surface area and thus more dissociation sites for hydrogen. Moreover, decreasing the particle size may also increase the concentration of steps, kinks and corner atoms, which could also facilitate the dissociation of hydrogen.[77,78] The stabilisation of specific surface planes of Mg/MgH₂ through a nanosizing approach may also facilitate the chemisorption of hydrogen and thus reduce the need for a catalyst for this initial barrier. For example, the

MgH₂ (110) plane with a surface energy of 1.3 J·m⁻² is less stable than the plane MgH₂ (001) (0.48 J·m⁻²).[79,80] Finally, through particle size reduction, diffusion processes should become easier owing to the shorter diffusion paths (Figure 2-6c).[60] Hence, at a particle size of a few nanometres it can be expected that the remaining barrier will only be the last step, i.e. nucleation and growth of the hydride phase.[63]

2.3.3 Nanoconfinement of magnesium-based hydrogen storage materials

Significant investigations have been undertaken to improve the properties of Mg toward the requirements for practical application. The different approaches investigated include i) alloying with d-elements (e.g. Ni, Cu, Co, Ti, Fe),[42,81-83] p-elements (e.g. Si, Al, Ge), rare earths;[84-86] ii) destabilisation via the formation of metastable phases and solid solutions,[39,87,88] and iii) nanosizing/nanoconfinement.[37,49,61,62,89,90]

In particular, alloying magnesium with transition metals such as Co,[83] Ni,[41,82] and Fe [42] has led to the discovery of new ternary complex hydrides with a volumetric storage capacity exceeding that of pure β -MgH₂, e.g. 1.5 kg·H₂·L⁻¹ for Mg₂FeH₆. [91] In other cases when alloying is not possible, improvements can still be observed. Hence, Mg is immiscible with Ti but the formation of MgH₂-TiH₂ nanocomposites has been shown to display very fast hydrogen desorption kinetics owing to the diffusion paths created by the TiH₂ phase embedded within the Mg particles.[92,93]

Destabilisation with Si,[94] for example, or formation of metastable phases with Al has also been investigated.[95,96] Hence, alloying Si with MgH₂ was shown to significantly destabilise the Mg-H bond with an enthalpy reduced to 38.9 kJ·mol⁻¹ H₂. [94] However, the rehydrogenation of Mg₂Si was found to be severely limited by the reaction kinetics and the mass transport of Mg and Si into separate phases.[97,98] The binary Mg-Al system showed different intermetallic phases of possible interest for hydrogen storage.

The first hydrogenation of $\gamma\text{-Mg}_{17}\text{Al}_{12}$ is associated with an enthalpy of $72 \text{ kJ}\cdot\text{mol}^{-1} \text{ H}_2$, [99] while the second step involving Mg_2Al_3 has a lower enthalpy of $62 \text{ kJ}\cdot\text{mol}^{-1} \text{ H}_2$. [100] More remarkably, alloying MgH_2 with Ge (58.3 mass%) has been shown to lead to a dramatic decrease of the enthalpy to $14 \text{ kJ}\cdot\text{mol}^{-1} \text{ H}_2$, however reversibility was not achieved. [101] Destabilisation was also reported via the formation Mg-Nb bcc alloys [102] and solid solutions such as Mg-In, for example. [87] But all these attempts including those involving rare earth and multicomponent alloys resulted in a significant loss of storage capacity and temperatures for hydrogen release still $> 300^\circ\text{C}$

More recently, nanosizing Mg particle size down to a few nanometres, has emerged as an alternative approach, and despite potential difficulties in the synthesis of “free standing” Mg nanoparticles, several synthetic methods have been developed. For example, through the decomposition of Mg precursors stabilised Mg nanoparticles with a particle size ranging from 100 to 5 nm have been reported [40,49,103-105] and a decrease in activation energy (from 120-213 to 25-79 $\text{kJ}\cdot\text{mol}^{-1}$) [105] and enthalpy (from 74.5 to 63.5 $\text{kJ}\cdot\text{mol}^{-1} \text{ H}_2$) [40] has been observed as particle size is reduced. Following early theoretical calculations it has been commonly accepted that only very small particles $< 3 \text{ nm}$ would undergo thermodynamic alterations. [106,107]

An easier synthetic route toward nanosizing is via the confinement of Mg particles within the nanoporosity of a host material. Various porous carbons have been used for this purpose owing to their lightness, high surface area, low-cost and inertness toward hydrogen, [60] as well as the high thermal conductivity. [73] In the best cases, monodispersed Mg particles with a size $< 20 \text{ nm}$ have been synthesised, and these nanoparticles showed improved thermodynamics. [37,61,62,90,108-110] More conventional doping in the form of transition metals, e.g. Ni or Cu in the carbon

scaffold, has also been found to improve the desorption kinetics of nanoconfined MgH_2 . [90,108] Ultra-small Mg particles of 1.3 nm confined in ordered microporous carbon also start to release hydrogen below 100 °C with a peak at 200 °C, however the evolution of enthalpy for such small particles was not reported.[111] To maintain the gravimetric storage capacity, graphene has been used to effectively disperse and support 6 nm Mg particles with a total Mg loading of 75 mass % at the graphene surface.[73] Following this strategy, a hydrogen storage capacity of 5.7 mass % was reached but hydrogen desorption still required 300 °C.

Another issue is to improve hydrogen kinetics of the Mg/hydrogen system especially the desorption process with some additives/dopants. The absorption process is exothermic and thus should proceed at room temperature assuming that the magnesium surface is catalytically active and hydrogen diffusion is facilitated. For example, hydrogen absorption at lower than 200 °C [53,73,112,113] and even at room temperature [75,114,115] has been reported for Mg with Al, Ni and Nb_2O_5 as catalysts. Accordingly, when hydrogen absorption is carried out at relatively high temperatures the kinetics is always fast and controlled by the nucleation and growth of the hydride phase.[49,105]

Various compounds including metals, metal oxides, metal halides and some alloys have been claimed to have a catalytic effect on the hydrogen storage properties of Mg. The catalyst is either doped directly to Mg in the form of a highly dispersed metal,[42,112,113,116] generated *in-situ* with Mg through the reaction of precursors with Mg or MgH_2 ,[53] or the catalytic precursors are reduced in solution with the presence of Mg.[117,118] From the various findings, it is obvious that similar catalysts affect the performances of Mg/ MgH_2 differently. In particular the activation energy (E_a) reported upon catalyst doping is often inconsistent across investigations. Such a

discrepancy highlighted in Figure 2-7c may be explained by the fact that the properties of final material are also influenced by many other factors including the composition, particle size, local chemical/physical environment, chemical state and dispersion of the catalyst. [53,69,119]

Compared to the reverse volcano plot determined from theoretical modelling (Figure 2-7b), the generally best accepted catalysts are based on Nb or its oxide Nb₂O₅, although the activation energy reported for this oxide varies greatly (Figure 2-7c). It is notable that with the doping of 1 mol % Nb₂O₅, the material can absorb 4.5 mass% H₂ within 15 s at room temperature and desorb 5.3 mass% under a flow of helium at 163 °C.[75] The exact role of these transition metals on the kinetics of Mg/MgH₂ remains unclear given the number of hypotheses advanced. For example, it has been suggested that Nb or Nb₂O₅ can act as a hydrogen pump splitting/recombining and transporting the hydrogen in or outside the Mg particles.[120-122]

2.4 Controlling the properties through synthesis

The first important step to the effective modification of the properties of Mg is the preparation approach. It will determine the formation of the appropriate crystalline phases, the nanostructuration of Mg and the effective dispersion and location of catalysts and doping elements. Since the first metallurgical methods developed to alloy Mg with various components,[78] alternative ball milling techniques have been thoroughly investigated for the preparation of new Mg alloys and the generation of nanostructured magnesium and defects to promote hydrogen diffusion. Physical/chemical deposition and wet chemical as well as electrochemical approaches are also revisited in order to synthesise nanosized Mg for potentially both enhanced kinetic and thermodynamic properties. These synthetic approaches are reviewed below.

2.4.1 Mechanical milling

Nowadays mechanical milling is the most common method of modifying the properties of Mg. Various types of milling machines exist, including planetary, vibrational, rotational, magnetic and attritor mills.[123] Additional inlet/outlet valves can be used to fill the vials with reactive gases. More recently some milling vials have been equipped with electronic devices to follow the pressure and temperature during the milling process and this has enabled novel processes for performing reactive milling.[124] Additional parameters including the milling speed, time, atmosphere, pressure and temperature can be controlled. In some cases and in particular for ductile materials, a process control agent (PCA) such as hydrocarbons, carbon materials or salts reduces agglomeration of the milled particles and thus the particle refinement of the powder can also be used (Figure 2-8a).[123] In particular, it was shown that MgO and other metal oxides were PCAs enabling an effective reduction of MgH₂ particle size and thus fast hydrogen kinetics.[125,126] The use of various carbons (graphite, activated carbon, carbon nanotubes and fullerenes) ball milled with Mg or MgH₂ could also improve kinetics and prevent MgH₂ particle growth during the de/hydrogenation cycling.[127,128]

As Mg is ductile, ball milling brittle MgH₂ is more common in research. Zaluska and Zaluski were among the first groups to show the effectiveness of ball milling on the hydrogen storage properties of MgH₂. [129-131] Ball milled MgH₂ can result in several effects which are often difficult to discriminate between and this has led to some confusion in the interpretation of the improvements obtained with MgH₂. Effects induced by ball milling include: i) a reduction in particle size (from a few μm to ~ 500 nm), and thus a subsequent increase in surface area (from 1.1 to 9.1 $\text{m}^2\cdot\text{g}^{-1}$), [126] ii) the formation of defects, iii) a significant decrease in crystallite size (from 400 to below 9

nm),[126,129,132] and therefore a nanostructuration leading to an increased number of grain boundaries, and iv) fresh surfaces free from oxide layer and hence facilitated hydrogen chemisorption.[133,134]

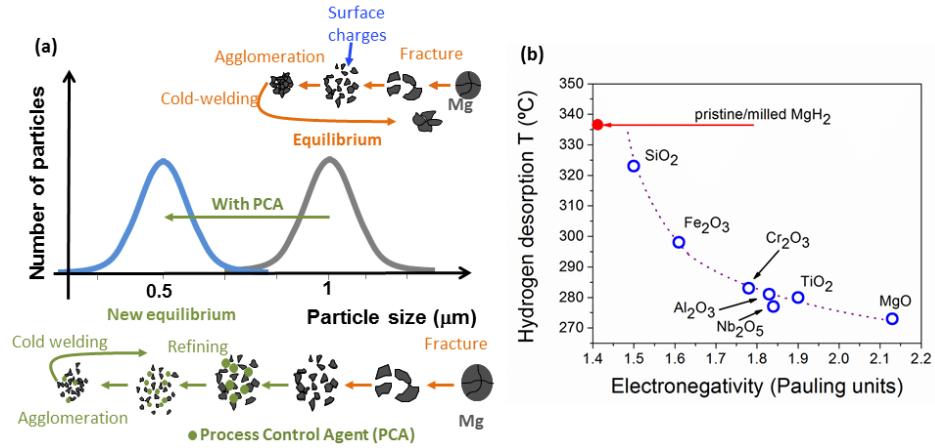


Figure 2-8: (a) Schematic representation of the evolution of particle size and the fracturing/cold welding equilibrium upon ball milling, and (b) correlation between the hydrogen desorption temperature of MgH_2 ball milled with metal oxides and the electronegativity of the metal oxide additives.[125]

The formation of a nanocrystalline structure and associated defects through mechanical milling is often perceived as a means to lead to the enhanced hydrogen kinetics.[129,135] However, nanocrystalline MgH_2 resulting from ball milling undergoes a significant growth in crystallite size (typically from the initial 9 nm to sizes > 100 nm) and a subsequent structural relaxation of any defects upon the very first hydrogen cycles.[136-138] Accordingly, no improvements in thermodynamics have been observed for ball milled MgH_2 despite the small nanocrystals achieved.[34] Thus the improvements obtained after milling may be understood from a combination of particle size effects and fresh Mg surfaces leading to improved hydrogen chemisorption and shortened hydrogen diffusion paths.

The catalytic mechanism associated with the very fast kinetics achieved with the catalysed ball milled Mg/MgH₂ system is still a matter of debate. Hence, the reduced activation energy measured (ranging from 25 to 97 kJ·mol⁻¹) may suggest that the catalyst located at the surface of the Mg particles facilitates the chemisorption of hydrogen molecules and thus significantly decreases the energy barrier existing at the Mg surface.[45] Further catalytic particles embedded within the Mg particles may provide additional paths for the rapid diffusion of hydrogen upon hydrogen cycling.[139,140] However, transition metal oxides also facilitate MgH₂ particle size refinement, and the embedment of metal oxides within MgH₂ particles during ball milling restrains the recrystallisation and growth of the nanostructure.[125,126,137,141] As metal oxides of higher electronegativity hold bonding electrons more tightly and have a lower tendency to chemically bind with their neighbouring oxides, which were proposed to lead to lower shearing at the interface of sliding oxide particles, hence lower friction coefficients, ultimately a reduction of particle size would lead to faster hydrogen kinetics for MgH₂ (Figure 2-8b). Such an effect coupled with some potential catalysis at the magnesium surface and additional restriction in grain growth during hydrogen cycling could explain the significant improvement observed.

2.4.2 Physical and chemical vapour deposition

Physical and chemical vapour deposition generally involve a metal source which is first vaporised by plasma, arc, laser or heating before deposition onto a substrate. In current literature, different types of deposition methods, including hydrogen plasma metal reaction, vapour-transport, pulsed laser deposition, magnetron sputtering, etc., have been used to generate Mg nanostructures.[39,44,115,142-145]

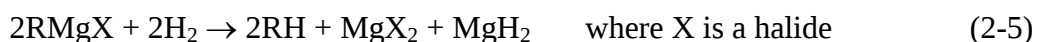
Using a hydrogen plasma deposition method, Shao *et al.* reported the synthesis of hexagonal Mg with a particle size ranging from 50 to 500 nm,[146] as well as Mg-Ti-V, Mg-Zn and Mg-Al nanocomposite alloys.[38,39,147] However, at such large particle sizes all materials required temperatures in excess of 300 °C to effectively desorb hydrogen. Li *et al.* also reported through the evaporation of Mg, the formation of Mg nanowires with improved hydrogen storage properties.[148] Hence at a temperature of 300 °C, the nanowires released about 6.7 mass% of hydrogen in 15 min.[149] However, these nanostructures collapsed after a few hydrogen cycles.

Deposition methods such as pulsed laser deposition and magnetron sputtering are also widely used for the preparation of Mg thin films with Pd capping acting as both a protective and catalytic layer.[143,150,151] Typical multilayered Pd/Mg thin films, e.g. three-layered Pd(50 nm)/Mg(800 nm)/Pd(50 nm) films readily absorb hydrogen (5 mass%) at the ambient while desorption can be achieved at higher temperatures, e.g. at 90 °C or simply exposing the film to air.[150,152]

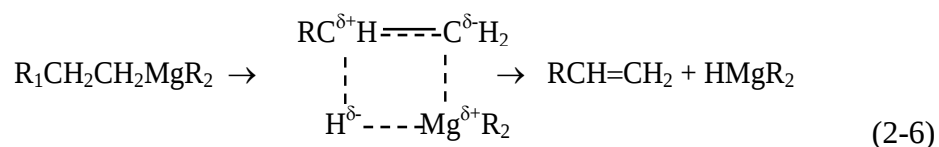
Alloying Mg with other metals is another possible approach towards improving hydrogen storage properties. Some works have been done on Mg alloys thin films synthesised by direct current assisted magnetron sputtering. MgNi(40 nm)/Pd(16 nm) multilayer thin films with total layer thickness of 1.7 µm absorbed up to 4.6 mass% H₂ and desorbed 3.4 mass% H₂ at room temperature.[145] Mg-Al-Ti alloy with film thickness of 1.5 µm showed remarkable kinetics at 200 °C, with absorption in seconds and desorption in minutes with good cycling properties.[153] Mg-Cr-V alloy films were also investigated and achieved 5 mass% H₂ absorption in 1 h at room temperature.[154]

2.4.3 Thermolysis

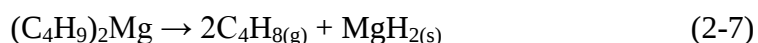
Another approach to generate Mg nanoparticles is through the thermal decomposition of a Mg precursor. In this respect, di-*n*-butylmagnesium (MgBu₂) leading to MgH₂ has been the most used in the recent literature to produce MgH₂ nanoparticles stabilised by nanoconfinement.[32,60,155] The synthesis of MgH₂ by hydrogenolysis of Grignard reagents was first reported by Becker and Ashby in 1964 (2-5).[156]



Reaction (2-5) was found to proceed at relatively mild temperatures (75-230 °C, depending on the Grignard reagent) but harsh conditions of hydrogen pressures in excess of 100 bar were often used.[156-158] However, recent investigations have shown that MgH₂ could directly be generated from the decomposition of Grignard reagents under inert atmosphere and at temperatures as low as 200 °C.[159,160] The mechanism for such a behaviour is uncertain, but the previously suggested intramolecular mechanism involving a concerted four-center intermediate (2-6) would be a tangible hypothesis.[161]



Depending on the Grignard precursor, the decomposition will lead to MgH₂ only or a mixture of MgH₂ and the corresponding halide.[159] Hence, most investigations have only used MgBu₂ as a precursor to generate MgH₂ following reaction:



In particular, the use of MgBu₂ was found to lead to stabilised nanocrystalline MgH₂ structures with an impressive hydrogen storage capacity of 6.8 mass%, and remarkable hydrogen kinetics.[159] Hence, it was possible to achieve hydrogen desorption without

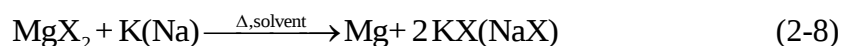
any catalyst at 250 °C in less than 2 h, while at 300 °C hydrogen desorption took only 15 min.

The decomposition of MgBu_2 is also commonly used for the nanoconfinement of Mg. In a typical synthesis, a solution of MgBu_2 is impregnated into a porous scaffold and then decomposed at elevated temperatures (~ 300 °C).[37,61,110,162] Following this principle, Mg/MgH₂ particles with a size ranging from 1.3 to 20 nm have been confined in porous carbons.[61,110,111,163] Incorporating Mg into the porous host structures leads to a significant decrease of the temperature for hydrogen release. For example, MgH₂ nanoparticles of 5-6 nm nanoconfined in mesoporous carbon CMK-3 released hydrogen from 50 °C and desorbed about 20 % of their hydrogen content before reaching 200 °C. Such a low temperature for hydrogen desorption may be attributed to the reduced particle size and additional effects at the confined MgH₂/CMK-3 interface.[163] Alteration of thermodynamics has also been observed for confined MgH₂. In particular, 3 nm MgH₂ particles nanoconfined in activated carbon fibres showed a reduction in reaction enthalpy from 74.5 to 63.8 kJ·mol⁻¹ H₂. [61] This was attributed to a combination of particle size effect and strain due to the particle/support interaction.

2.4.4 Chemical reduction

As a bottom-up approach, chemical reduction is an interesting method for the synthesis of Mg-based material nanoparticles. Chemical reduction in solution provides several advantages including: i) the convenience of stabilisation of nanoparticles with various capping ligands, ii) potential for the control of morphology with appropriate stabilisers, iii) ease of separation of the nanoparticles generated from the by-products of the reaction, iv) facile post synthesis modifications, and v) potential for easy scale up.[164]

Owing to the low redox potential (-2.37V vs NHE) of Mg^{2+}/Mg , this can only be achieved with very strong reducing agents following the method developed by Rieke in 1972.[165-167] In the original work, Rieke reduced Mg salts by melting an alkali metal in an organic solvent.[166] The reaction proceeds at the melting point of the alkali metal but below the boiling point of the solvent following:[168]



The main drawback of this initial approach is the need for high temperatures which leads to some contamination of the Mg particles owing to the decomposition of the organic solvent at the magnesium surface. Additional agglomeration, sintering and recrystallisation of the Mg particles may also occur during the synthesis.[168] In order to avoid high reaction temperatures, electron carriers including biphenyl, anthracene and phenanthrene[103,169] can be used to facilitate the electron transfer process between the alkali metal and the magnesium salt.[165] Organomagnesium compounds, e.g. biscyclopentadienyl magnesium (MgCp_2)[103,105] and di-*n*-butylmagnesium (MgBu_2) [40] with better solubility in organic solvents than magnesium halides also lead to easier synthetic processes. Other reducing agents, e.g. LiAlH_4 , instead of alkali metals can also be used.[168]

Recently, such a method has been adapted for the preparation of magnesium nanoparticles for hydrogen storage purposes. Hence, Norberg *et al.* prepared Mg nanocrystals (25, 32 and 38 nm) with undefined morphologies by reducing MgCp_2 with potassium by using biphenyl, phenanthrene or naphthalene as electron carriers.[103] The magnesium nanoparticles obtained reversibly stored hydrogen but at relatively high temperature 335 °C. Air-stable Mg nanoparticles (~5 nm) have also been synthesised by introducing poly(methylmethacrylate) as a stabiliser into the reaction system.[105] The

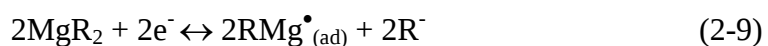
reaction was carried out by reducing MgCp_2 in tetrahydrofuran using lithium naphthalenide and the resulting magnesium nanoparticles were able to cycle hydrogen at 200 °C. Instead of MgCp_2 , MgBu_2 was used as a precursor with lithium as a reducing agent and a catalytic quantity of naphthalene as an electron carrier.[40] Besides, Liu *et al.* reported the possibility of *in-situ* catalytic doping during the Rieke's reaction.[53] Mg-Ni nanocomposites were synthesised by directly reducing a mixture of MgCl_2 and NiCl_2 with lithium and naphthalene. The effect of different transition metals (Co, Fe, Ni, Si, or Ti) deposited at the surface of Mg nanoparticles in a core-shell fashion was also investigated through a similar synthetic approach.[118]

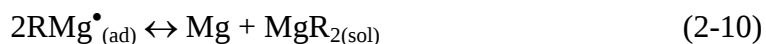
Considering the morphology of the Mg nanoparticles synthesised by wet chemical reduction, isolated and irregularly shaped nanoparticles are usually obtained with particle size ranging from 7 to 60 nm depending on the synthetic conditions.[53,103,170] Near spherical nanoparticles of ~5 nm were synthesised with poly(methylmethacrylate). [105] Switching the Mg precursor from MgBu_2 or MgCp_2 to MgCl_2 , Liu *et al.* reported plate-shaped particles.[53]

2.4.5 Electrochemical deposition

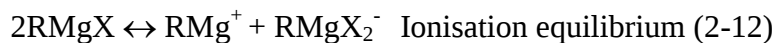
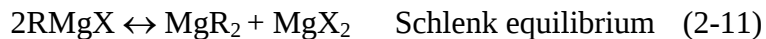
To date only a few groups have reported on the electrochemical synthesis of magnesium-based hydrogen storage materials,[63,171,172] owing to the low reduction potential of the Mg^{2+}/Mg couple and the difficulty of reducing magnesium salts by electrochemical means. Magnesium can be deposited from Grignard reagents (MgR_2 or RMgX where R is an alkyl or aryl groups and X is a halogen) on electrode surface [173-175] following the electrochemical deposition paths [176]:

With MgR_2

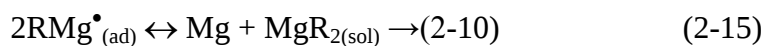




or with RMgX

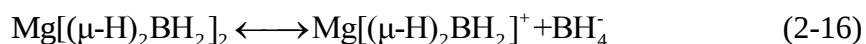


or



where “ad” corresponds to adsorption and “sol” to solution. Addition of Lewis acid such as AlCl_3 or EtAlCl_2 further enhances the ionisation reaction (2-12) and thus facilitates the deposition of Mg.[177,178] However, the use of RMgX may also lead to the precipitation of the halide.[179]

As well as organic Mg salts, the electrochemical reaction of inorganic ones was also investigated. Only a few species of inorganic Mg compounds can dissolve in organic solvent, the most widely used is magnesium borohydride ($\text{Mg}(\text{BH}_4)_2$), which is also a hydrogen storage material. $\text{Mg}(\text{BH}_4)_2$ was proposed as the contact ion pair $\text{Mg}[(\mu\text{-H})_2\text{BH}_2]_2$, which partially dissociates into $\text{Mg}[(\mu\text{-H})_2\text{BH}_2]^+$ and BH_4^- as in (2-16); since the different B-H bands most likely overlap, it is not possible to distinguish all the species.



Where $\text{Mg}[(\mu\text{-H})_2\text{BH}_2]^+$ may further dissociate:



The structures of $\text{Mg}(\text{BH}_4)_2$ in different solvents are investigated and identified by NMR, $\text{Mg}(\text{BH}_4)_2$ will form coordination structures as $\text{Mg}(\text{BH}_4)_2 \cdot \text{DGM}$, $\text{Mg}_2(\text{BH}_4)_4 \cdot (\text{DME})_3$, $\text{Mg}(\text{BH}_4)_2 \cdot (\text{THF})_3$ in diglyme (DGM), dimethoxyethane (DME) and tetrahydrofuran (THF) respectively (Figure 2-9). The electrochemical characterisation showed that LiBH_4 additive acts as the second coordination ligand (BH_4) and chelating solvent and increased (BH_4) concentration can substantially improve the stripping process through synergetic effects.[180]

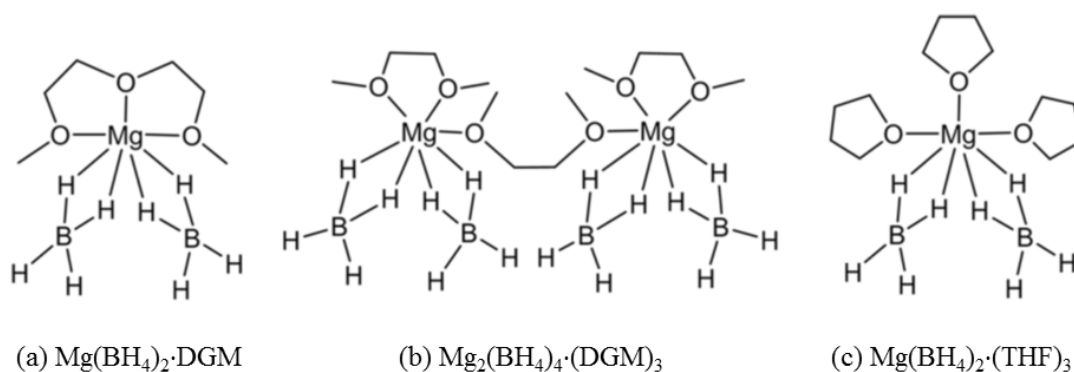


Figure 2-9: Coordination structures of $\text{Mg}(\text{BH}_4)_2$ in DGM, DME and THF.[180,181]

Reversible Mg deposition and stripping from $\text{Mg}(\text{BH}_4)_2$ could be obtained in DME and THF solution, and higher current density and lower overpotential were achieved in DME compared to those in THF. Significant improvement in columbic efficiency and current density was accomplished by the addition of LiBH_4 , as LiBH_4 enhanced $\text{Mg}(\text{BH}_4)_2$ dissociation in DME.[182] However, the presence of Li ions was shown to lead to the codeposition of Mg-Li solid solution in which the composition depended on the potential and mass transfer.[183]

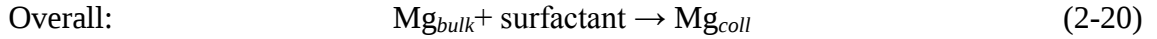
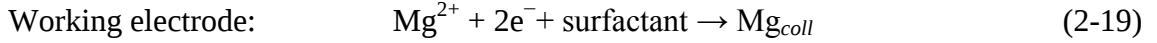
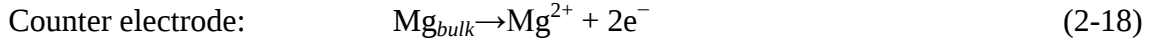
Considering the high reactivity of magnesium the choice of the electrolyte is essential not only to enable deposition within a stable and wide electrochemical window

preventing any degradation of the electrolyte but also to avoid any deposition of side products at the freshly created magnesium surfaces. Similar to Li, Mg particles generated by electrochemical means are most likely covered by a stable organic film composed of Mg organic or inorganic salts formed spontaneously by the reactions between the active metal and the species in solution.[176,184] The influence of such a film and its thermal stability with respect to hydrogen properties of Mg are still unclear, although it can be assumed that the film will be partially degraded upon an initial vacuum treatment and exposure to hydrogen pressure.

Using the electrochemical deposition approach, Haas *et al.* reported the sonoelectrochemical synthesis of 4 nm magnesium nanoparticles deposited at the tip of a sonicating probe with ethylmagnesium chloride (EtMgCl) or butylmagnesium chloride (BuMgCl) as a magnesium precursor and AlCl₃ to facilitate the deposits.[171] Similarly, Mg nanowires were electrodeposited onto a Pt electrode with EtMgCl as precursor. Owing to the lower ionic conductivity of n-butyl or phenyl Grignard's reagents (compared to methyl magnesium chloride and EtMgCl), only heterogeneous Mg thin films have been obtained.[172] Hence, the deposition of Mg at substrates is highly sensitive to the Mg precursors. No hydrogen sorption was reported for these investigations, owing to the difficulty of characterising a few Mg particles deposited at the surface of the electrode.

An alternative, to generate "free standing" Mg nanoparticles by electrochemistry is through the use of surfactants during the electrochemical deposition process.[185,186] Hence, with a cationic surfactant adsorbed at the working electrode where Mg is deposited, direct adsorption onto the electrode surface of the reduced Mg is prevented through steric repulsion, and the subsequent nucleation and growth of Mg nanoparticles

are limited through additional surfactant stabilisation in solution. [186,187] Using Mg as the counter electrode, the electrochemical process then follows the reactions:



where “bulk” refers to the electrode strip, and “coll” to colloidal Mg. The advantage of such an approach is that it also allows the control of the particle size following equation (2-21). Hence, higher current density would lead to smaller clusters, and vice versa lower currents to a slower nucleation and growth process and thus larger particles.

$$r_{\text{crit}} = 2M\gamma/nF\eta\rho \quad (2-21)$$

The radius of the metal nanoparticle r_{crit} is inversely related to overpotential η . The latter is directly proportional to the current density.[188]

Following this idea, surfactant-stabilised magnesium nanoparticles with a diameter of 5 nm were synthesised by electrochemical synthesis in THF using TBAB as stabiliser.[63] The particles exhibited unique hydrogen storage properties, as the reversible storage was ~7.6 mass% hydrogen near room temperature (1.34 mass% by taking into account the surfactant). Furthermore, full hydrogen desorption was obtained with this colloidal MgH_2 at 85 °C, while micro-sized MgH_2 requires at least 350 °C. However, the cyclability of colloidal MgH_2 was found to rapidly degrade owing to the reaction of the surfactant with the Mg surface. It should be noted that achieving an effective synthesis of nanosized Mg through electrochemical means requires careful considerations of the supporting electrolyte, Mg precursor and capping ligand since the low reduction potential required to reduce Mg compounds can lead to significant side reactions

including a degradation of all the electrolyte components ultimately affecting the reactivity of the Mg surface and thus the hydrogen properties.

2.5 Scope of the current work

The main problem of storing hydrogen in magnesium is the high operation temperature and slow kinetics of the sorption process. As discussed above, the alternative routes to optimise the properties are preparing nanosized magnesium structures and adding catalytic materials. Compared to other synthetic methods, electrochemical deposition of magnesium nanostructures still lacks investigation. This approach is worth exploring as it can enable control of particle size and versatility in the synthesis of alloy and composite/hybrid materials.

Aurbach *et al.* investigated the mechanism of deposition and dissolution of magnesium in organic solution intensively.[176,179,184] However, the deposited magnesium only formed a compact layer on working electrode surface. In order to establish a suitable electrolysis system to generate magnesium nanostructures, the mechanism of magnesium deposition must be investigated as a function of the solvents, stabilisers, magnesium precursors and electrolysis parameters.

As most of the current research about magnesium deposition only generates magnesium layer on substrates rather than isolated nanoparticles, it is worth checking the hydrogen storage properties of such deposit as a reference for subsequent study. Furthermore, how to modify the electrochemically formed Mg morphologies should be determined as to improve its hydrogen sorption properties.

Based on the successful synthesis of transition metal nanoparticles by electrochemical deposition with surfactants, generating magnesium nanoparticles should be possible. To this aim, the condition of the electrolysis system must be well designed. Furthermore,

electrochemical synthesis has also the potential to generate alloys and this could provide a means to modify Mg nanostructures. Examples include Ni-W,[189] Zn-Co [190] and Ni-Mo [191] composites. Such an alloying strategy could be implemented by using a sacrificial anode to supply metal ions that can be reduced with Mg. This has been shown to work with PtCl_2 salt and a sacrificial tin electrode, Pt-Sn bimetallic clusters were then yielded in the presence of $(\text{Bu}_4\text{N})\text{Br}$ as supporting electrolyte and stabiliser.[186] Thus the strategy could be translated for the synthesis of Mg-based nanocomposite.

Besides the *in-situ* electrochemical codeposition, external additives such as metal particles, oxides and carbon materials can also be suspended in electrolyte to form composites through electrochemical codeposition. Inorganic materials such as SiC,[76] ZrO_2 [192] and Al_2O_3 [193] were codeposited with metals to produce metal matrix composites to improve mechanical properties (hardness, wear resistance and flow stress). Highly dispersed Pd nanoparticles supported on graphene were successfully prepared by a one-step electrochemical codeposition approach. Cu-graphite [194] and Cu/Ni-multiwalled carbon nanotubes (MWCNs) composites [195] were also prepared with graphite and MWCNs suspension to enhance thermal conductivity and corrosion resistance.[196,197] Thus such strategy could also be used to prepare Mg-based composites.

Another route to improve the properties of electrodeposited metals is using surface modified electrodes, usually with conductive polymers as substrate. The latter can then be removed after Mg deposition to lead to a “free standing” Mg film. Platinum nanoparticles and bimetallic Pt-Ru nanoclusters were successfully electrodeposited *in-situ* on an organic conductive polymer, poly(3,4-ethylenedioxythiophene) (PEDOT) to improve the electrocatalytic behaviour for methanol oxidation.[198,199] Similarly,

uniformly distributed Ni[200] and Ag[201] nanoparticles can be formed on a polypyrrole decorated electrode by electrodeposition. Such an approach thus offers a new means of preparing Mg films.

The scope of this work is therefore to determine the potential of electrochemical synthesis for the preparation of Mg-based hydrogen storage materials with improved hydrogen sorption properties.

2.6 Conclusion

The world is rapidly transiting toward renewable energy systems. In this context, the rise of hydrogen as an alternative energy carrier is rather slow owing to the cost of the technology when associated with fuel cells and the lack of mature solid state hydrogen technology of extremely high energy density. Magnesium has the potential to provide the basis for high energy density storage systems at a relatively low cost considering its abundance. However, Mg as a hydrogen storage material still suffers from the need for high temperatures for practical hydrogen uptake and release.

In the current state of knowledge, it is apparent that modifying the properties of Mg towards the targets above strongly depends upon the choice of a synthetic approach, although it can also be argued that the Mg/hydrogen system is dynamic in nature as reflected by the evolution of the nanostructures. It is thus important to better link synthetic approaches controlling the destabilisation and catalysis of Mg with specific hydrogen features and ultimately engineering targets.

Assuming that the organisation of Mg atoms can be controlled and stabilised, nanosizing could potentially lead to a finer control of the Mg-H bond strength as well as hydrogen kinetics. Experimental evidence for such a control have appeared through the nanoconfinement of Mg, the synthesis of “free standing” Mg nanoparticles, and the

characterisation sandwiched Mg thin films. However, full control of such an approach is still rather challenging owing to large knowledge gaps in the synthesis, control and stabilisation of nanostructures of highly reactive metals such as Mg and the lack of established nanostructure/hydrogen properties relationships (if any).

With respect to the synthetic approaches toward nanosized Mg, various routes including physical and chemical vapour deposition, chemical reduction and electrochemical deposition can be used. However, the capability of such approaches to lead to advanced control over Mg atomic organisation is still in its infancy. More importantly, can an effective nanostructuration/nanosizing of Mg be sufficient to achieve the desired practical targets? From past investigations, the types of elements that can be alloyed or reacted with Mg are known, as well as potential catalyst additives. Assuming that they behave in a similar manner at the nanoscale, new synthetic routes need to be developed to control the location and level of doping of such additives as to maximise their effects while retaining or surpassing the storage capacity of unmodified Mg. Such a level of control is often achieved in other areas such as catalysis.[202] Assuming that theoretical calculations can help the design of improved models and more sophisticated synthetic guides be designed toward the control of reactive nanostructures, new paths toward Mg-based hydrogen storage materials will emerge.

Electrochemical deposition is an effective method of synthesising nanostructure and nanocomposite, while the investigation of Mg is rare because of the low reduction potential. The aim of this work is thus to establish electrochemical synthetic routes to explore the potential of achieving the preparation of Mg nanomaterials with favourable hydrogen storage properties compared to other methods. Currently, magnesium film and nanoparticles as well as nanofibers have been synthesised, and some of them exhibited impressive hydrogen sorption properties.[63,171,172,179] The components and

parameters of the electrolysis system still require intensive investigations, then the mechanism of magnesium nanostructure generation can be understood. With the purpose of optimising the properties of Mg deposits, magnesium nanostructures need to be electrosynthesised with various conditions to form diverse morphologies and compositions. It is proposed that routes for the synthesis of magnesium thin films on metal substrates, isolated magnesium nanoparticles, Mg/Ni and Mg/carbon nanocomposites as well as Mg/conductive polymer multilayered sandwich structure will be established in this work.

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CHAPTER 3 ESTABLISHING THE ELECTROCHEMICAL SYNTHETIC ROUTES FOR THE NANOSIZED MAGNESIUM

3.1 Introduction

The first aim of this thesis is to establish viable electrochemical deposition methods to prepare nanostructured magnesium. From previous literature, a conventional method to generate nanoparticles is through the use of steric repulsion and surfactants. Additionally the alteration of a combination of factors including current density, surfactant type and concentration could also lead to the synthesis of nanoparticles with different morphology and size distribution.[1-4] Different from utilising nanoparticles to decorate the electrode surface, producing enough nanomaterials to characterise other properties requires that the deposits are facile to remove from the surface of electrode.

Electrochemical reduction of transition and noble metallic nanoparticles is widely reported, however, electrochemical deposition of light metals is still rare. The difference between transition and light alkaline metals is the reduction potential, which influences the double layer at the electrode surface. The low reduction potential of light metals results in a compact double layer, which leads to stronger interaction between the deposits and electrode surface.[5] Only when dendrites or big clusters are formed, can the deposits depart from the electrode surface because of the flux of the electrolyte under stirring. However, for magnesium deposition, the most common deposits are compact films or aggregated clusters.[6-9]

The use of surfactants, especially quaternary ammonium (R_4N^+), in the proposed work is to stabilise the as-prepared nanostructures via electrostatic effects and hinder deposition at the electrode surface.[10] However, the concentration of surfactant needs to be carefully assessed since they will specifically adsorb on electrode surfaces and

modify the double layer, up to decreasing the reaction rate at high concentrations. This effect attributed to the blocking of the electrode surface is exacerbated by the size of the R group (Butyl > Propyl > Ethyl > Methyl).[11]

In this chapter, the components affecting the electrochemical synthesis of Mg particles are investigated. The properties of solvents, electrodes, surfactants/stabilisers and magnesium precursors are discussed, and then the interaction among these components is also investigated. In particular, the use of magnesium borohydride ($\text{Mg}(\text{BH}_4)_2$) and di-*n*-butylmagnesium (MgBu_2) as suitable magnesium precursors is investigated.

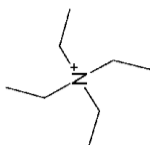
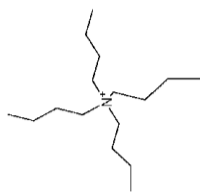
3.2 Experimental section

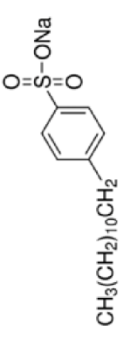
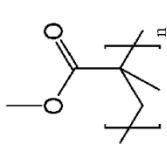
3.2.1 Chemicals

Magnesium ribbon and platinum wire were purchased from Goodfellow. Tetrahydrofuran (THF) was purchased as HPLC grade from Fisher Scientific and dried using a LC Technology SP-1 solvent purification system. The inorganic magnesium precursor magnesium borohydride ($\text{Mg}(\text{BH}_4)_2$) was prepared according to the method of Zanella *et al.*[12] Organic magnesium precursor di-*n*-butylmagnesium (MgBu_2) in heptane (with 1 mass% AlCl_3 additive as stabiliser), pure MgBu_2 in ether (> 99.8 %), *p*-tolylMgBr, isopropylMgBr, allylMgBr, tert-butylMgCl, EtMgCl were purchased from Sigma-Aldrich. AlCl_3 was from Fluka.

The surfactants and stabilisers used were summarised in Table 3-1. The cationic surfactants include a series of quaternary ammonium salts to investigate the influence of different alkyl groups and counterions to the magnesium deposition. Sodium dodecylbenzenesulfonate (SDBS) is an anionic surfactant, and poly(methylmethacrylate) (PMMA) and 1-dodecanthiol (DDT) are non-ionic stabilisers. All the reagents were from Sigma-Aldrich, except tetrabutylammonium bromide (TBAB) from Fluka.

Table 3-1: Surfactants and stabilisers used for the electrochemical reduction of Mg precursors.

Surfactant/stabiliser	Cationic group		Abbreviation	Solubility in THF (mol·L ⁻¹)	Electrochemical window (V)
	Counterions				
Tetraethylammonium tetrafluoroborate (99 %)		BF ₄ ⁻	TEABF	< 0.01 [13]	-3.0-3.6 (vs SCE in PC) [14]**
Tetraethylammonium perchlorate (99 %)		ClO ₄ ⁻	TEAP	< 0.01 [13]	-3.0-3.1 (vs SCE in PC) [14]**
Tetraethylammonium hexafluorophosphate (99 %)		PF ₆ ⁻	TEAPF	< 0.01*	-3.0-3.6 (vs SCE in PC) [14]**
Tetrabutylammonium bromide (98 %)		Br ⁻	TBAB	0.14	-1.2-2.1 (vs Mg) *
Tetrabutylammonium borohydride (98 %)		BH ₄ ⁻	TBABH	0.35	0.1-1.0 (vs Mg) *
Tetrabutylammonium acetate (99 %)		CH ₃ COO ⁻	TBAA	0.22	-
Tetrabutylammonium trifluoromethane sulfonate (99 %)		CF ₃ SO ₃ ⁻	TBATFMS	2.35 [13]	-1.8-2.0 (vs Mg)*
Tetrabutylammonium tetrafluoroborate (99 %)		BF ₄ ⁻	TBABF	2.02 [13]	-3.2-1.6 (vs SCE) [15]
Tetrabutylammonium perchlorate (99 %)		ClO ₄ ⁻	TBAP	1.48 [13]	-3.4-2.0 (vs SCE) [15]
Tetrabutylammonium hexafluorophosphate (99 %)		PF ₆ ⁻	TBAPF	1.58	-
Tetrabutylammonium fluoride (95%)		F ⁻	TBAF	> 1	-

	Tetraoctylammonium bromide (98 %)		Br ⁻	TOAB	2.06	-1.44-1.75 (vs Mg) *
	Tetraoctylammonium tetrafluoroborate (97 %)		BF ₄ ⁻	TOABF	2.24	-
Anionic	Sodium dodecylbenzenesulfonate (technical grade)			SDBS	1.82	-
Non-ionic	Poly(methyl methacrylate) (analytical standard)			PMMA	3 mg·mL ⁻¹	-
	1-Dodecanthiol (98 %)			DDT	-	-

*The electrochemical window is from the current investigation.

**The solubility of tetraethylammonium salts in THF is too low, thus the electrochemical stability is referred to the solution in Petane (PC).

3.2.2 Conditions for the electrochemical test of surfactants/stabilisers and magnesium precursors

The surfactants/stabilisers were dissolved in 18 ml THF to form the electrolyte, Pt wire and magnesium ribbon were used as working and counter electrode, respectively. Another Mg ribbon was used as a reference electrode. To investigate the stability of these electrolytes, the cyclic voltammograms were recorded with a Biologic VMP3 potentiostat. For magnesium precursors, they were mixed with different surfactants/stabilisers and cyclic voltammograms were recorded in the same three electrodes cell. In some cases, AlCl_3 was added to study the ability to improve the conductivity.

3.2.3 Electrochemical deposition of magnesium

In order to investigate the deposition capability of the electrolytes and the morphology of magnesium deposits, a -1 mA deposition current was used to reduce Mg from the electrolytes. The deposition duration was 10 h and the final products were collected and washed with THF, then centrifuged when possible.

3.3 Options of solvents and electrodes

Solvents and electrodes are at the base of the electrolysis system. All electrochemical reactions and phenomena occur in the electrolyte containing dissolved ions which are mobile and able to support current flow. Electrochemical reactions are heterogeneous in nature with the reaction kinetics being controlled by the properties of the electrode-electrolyte interface and the concentration of reactants available at this interface.[16] The electron transfer process at the electrode can occur via the following steps: i) electron transfer with interfacial charge; ii) coupling of electron transfer and ion dynamics; or iii) intermolecular electron transfer at structured interfaces.[17] As a result,

the stability and composition of the interface will dominate the electrochemical reaction. Hence, the choice of the electrode/electrolyte combination is important.

From the viewpoint of electrochemical deposition of magnesium, a suitable solvent should have several important properties. These include i) the ability to dissolve and dissociate salts to achieve a reasonably high ionic conductivity; ii) the inertness toward the Mg precursors, surfactants or Mg nanoparticles; iii) the ability for an appropriate electrochemical window. Figure 3-1 presents a summary of selected potential limits for some common combinations of solvent and electrolyte with a Pt electrode.[15,18]

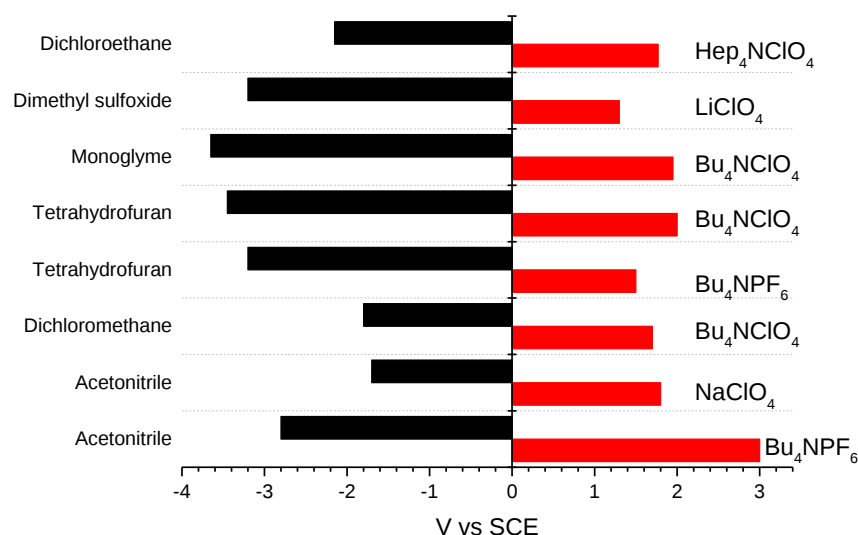


Figure 3-1: Potential limits for some common combinations of solvents and electrolytes with a Pt electrode. (Black and red colours correspond to the negative and positive potentials regions)

Herein, we focus on solvents suitable for magnesium. As an active metal, magnesium is naturally covered by surface films that comprise Mg oxide, Mg hydroxide, and/or Mg carbonate layers. Mg reacts readily with protic solvents, and may also react with most of the polar aprotic solvents (e.g. esters, alkyl carbonates, amines, acetonitrile). Dimethylformamid, dimethylacetamide, diethylacetamide, γ -butyrolactone or binary

mixtures of these solvents are too reactive and undergo reaction with the magnesium, instead of forming a metal deposit.[19-21] Suitable solvents for magnesium deposition are ethers, such as THF and cyclohexane with a ring structure which leads to a more stable solvent.[18]

In the literature, THF is widely used for electrochemical investigation of Mg and has been found to lead to relatively stable electrochemical processes involving Mg deposition/oxidation.[22-24] Hence, our investigation was limited to THF.

For a solid material to function as an electrode, it must possess several characteristics: i) electrical conductivity, ii) chemical and electrochemical stability over a wide range of conditions, iii) rapid electron transfer for a wide variety of redox systems, and iv) reproducible electrical, microstructural, and chemical properties. With the purpose of supplying enough Mg^{2+} during electrolysis, magnesium can be employed as a sacrificial anode. The working electrode can then be chosen from many materials, including Pt,[25] Cu,[26] and Ag.[7] In this chapter, Pt was chosen as the working electrode as it is inert. The surface of Pt is “stable” and this will facilitate the reproducible and comparable results.

In summary, the combination of THF, Mg, Pt was chosen as a base of system for the investigations throughout this chapter.

3.4 Options of surfactants/stabilisers

In the current investigation, surfactants are used to act as supporting electrolytes and stabilisers.[27,28] Basically, surfactants can be divided into cationic, anionic and non-ionic types. The instinctive properties such as solubility in solvents and stability under potential will influence the choice of surfactant as well as their possible reactions with the magnesium precursors.

The solubility of surfactants depends on their structures and functional groups. For example, tetraalkylammonium salts with ethyl groups are harder to dissolve than butyl group with longer carbon chains.[13] A saturated concentration of TEAB is lower than 10 mM in THF, TBAB is at 50 mM, but when a Mg precursor (e.g. MgBu_2) is added, more TBAB can be dissolved and this is ascribed to the transfer of Br^- enhancing the dissociation of MgBu_2 . TOAB with octyl chains possesses a much higher solubility, which is about 0.2 M in THF (Table 3-1).

The stability of surfactants under voltage was checked by cyclic voltammetry, as shown in Figure 3-2, 50 mM TBAB in THF was stable from -1.22 V to 2.21 V vs Mg, while TBABH started to be reduced at 0.1 V vs Mg. For TBATFMS, the stability under negative potential was better than TBAB (-1.76 V vs Mg), however, there were a pair of peaks around 1 V vs Mg, which should be ascribed to the interaction between the TFMS group and the Pt electrode surface. TOAB with a bromide counterion and a longer carbon chain exhibited stronger stability when negatively scanned (-1.44 V vs Mg) compared to TBAB, but the oxidation potential was lower (1.75 V vs Mg). It can then be concluded that the counterions determine the electrochemical stability to some extent. TOAB did not show superior stability compared with TBAB and TBATFMS, but the long surfactant chain (e.g. octyl) would block the electrode surface and thus should be avoided.

Apart from cationic surfactants, anionic surfactants such as sodium dodecyl sulfate (SDS) and SDBS are usually employed as templates to synthesise nanoparticles.[29-32] Herein, only SDBS with phenyl group can be dissolved in THF. The cyclic voltammogram of SDBS is shown in Figure 3-2, the current is quite low compared to the cationic surfactants, which indicated that SDBS has a higher stability in THF. However, one important issue for anionic surfactants is counterions. For example, Na^+

may also be reduced during electrolysis and contaminate the final deposit. In addition, if Na^+ reacts with other species such as Cl^- and Br^- in solution, precipitation may occur.

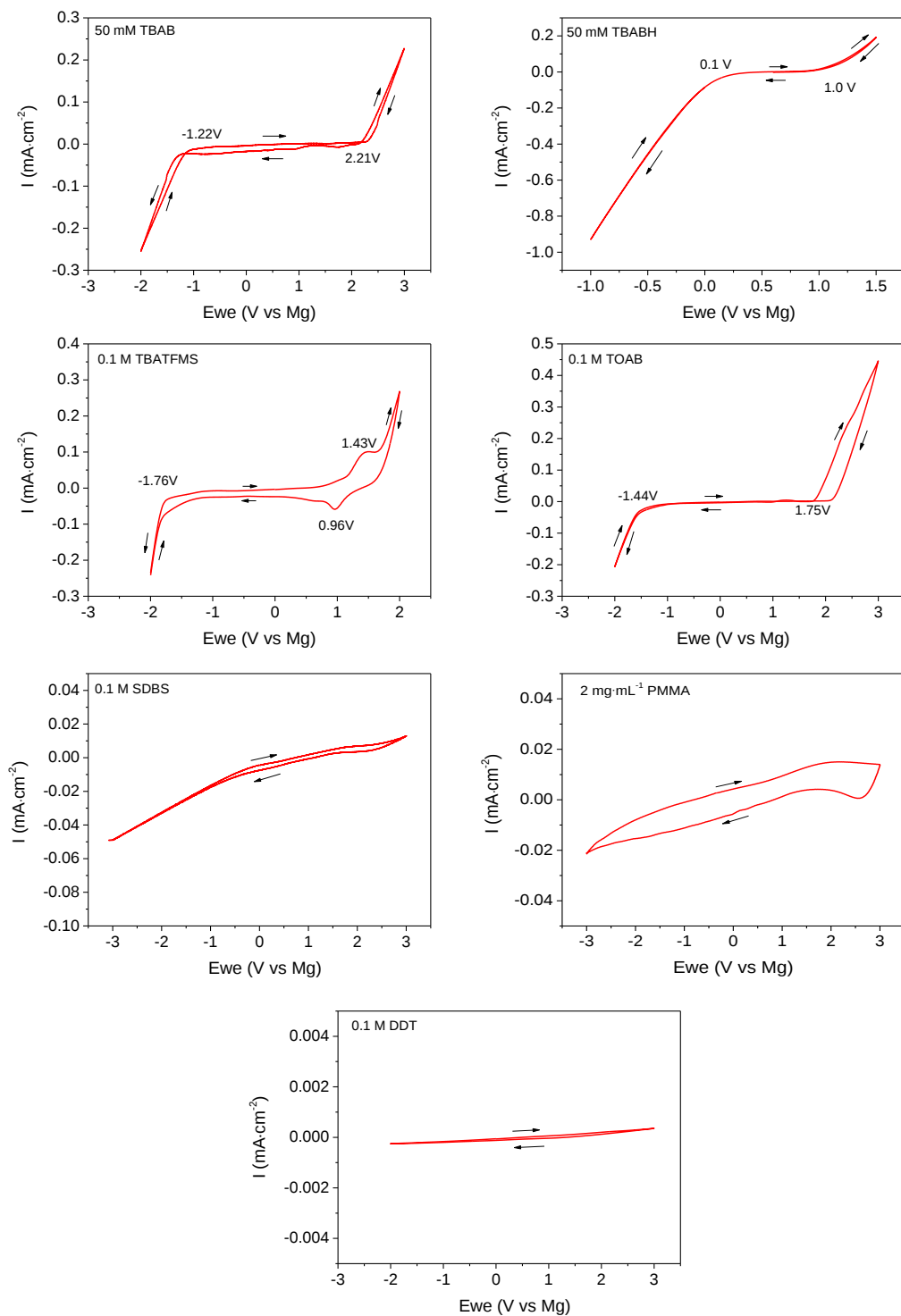


Figure 3-2: Cyclic voltammogram profiles of surfactants in THF. E_{we} refers to the potential of working electrode.

Non-ionic stabilisers such as oleyamine, dodecanethiol and polymers will not release any ions into solution; and these are usually utilised to stabilise nanoparticles. [29,33-36] Here, we chose PMMA and DDT as candidates, because they show a much lower current by cyclic voltammetry as compared to the other cationic or anionic surfactants investigated (Figure 3-2).

In summary, the solubility and electrochemical stability of typical cationic surfactants tetraalkylammonium salts depends on the length of alkyl groups and counterions. Anionic surfactant SDBS and non-ionic stabilisers PMMA and DDT, are quite stable under potential and show low electrochemical activity. The choice of surfactant also depends upon the conductivity of magnesium precursors introduced in the electrochemical system. Magnesium borohydride with low conductivity will need the use of cationic surfactants such as TBAB and TBATFMS to supply adequate conductivity, while for Grignard reagents, all of the three types can be chosen.

3.5 Electrochemical investigation of magnesium borohydride as a Mg precursor

For optimum electrochemistry, the magnesium precursors should possess sufficient solubility in the solvent (i.e. THF) and appropriate electrochemical activity, i.e. dissociation rate and electron transfer rate. Furthermore, there should not be any reaction once mixed with the surfactants. Although there are many Mg compounds, not all of them are active for electrochemical reduction. For example, inorganic magnesium halides including MgCl_2 are relatively chemically inert and they have very low conductivity in aprotic organic solvents.[37] As a result, AlCl_3 is needed to form a magnesium-aluminium-chloride complex to supply adequate “active Mg cations” in the forms of MgCl^+ and Mg_2Cl_3^+ .[38] $\text{Mg}(\text{ClO}_4)_2$ and $\text{Mg}(\text{BF}_4)_2$ were also found

incompatible with the Mg anode as an ion-blocking layer was formed at the electrode surface during electrochemical reduction.[39] However, as an inorganic magnesium compound, $\text{Mg}(\text{BH}_4)_2$ achieved reversible Mg deposition and stripping in THF solution.[24]

Once dissolved in THF, magnesium borohydride will coordinately combine with THF to form $\text{Mg}(\text{BH}_4)_2 \cdot (\text{THF})_3$. [40] Accordingly, the initial conductivity is quite low and a relatively high concentration of LiBH_4 ($\text{LiBH}_4 : \text{Mg}(\text{BH}_4)_2 > 3$) should be added to compensate for this.[24,41] To investigate the electrochemical properties of $\text{Mg}(\text{BH}_4)_2$, this compound was first investigated alone, and then tested with LiBH_4 . TBAB and TBATFMS were employed as supporting electrolytes in this section.

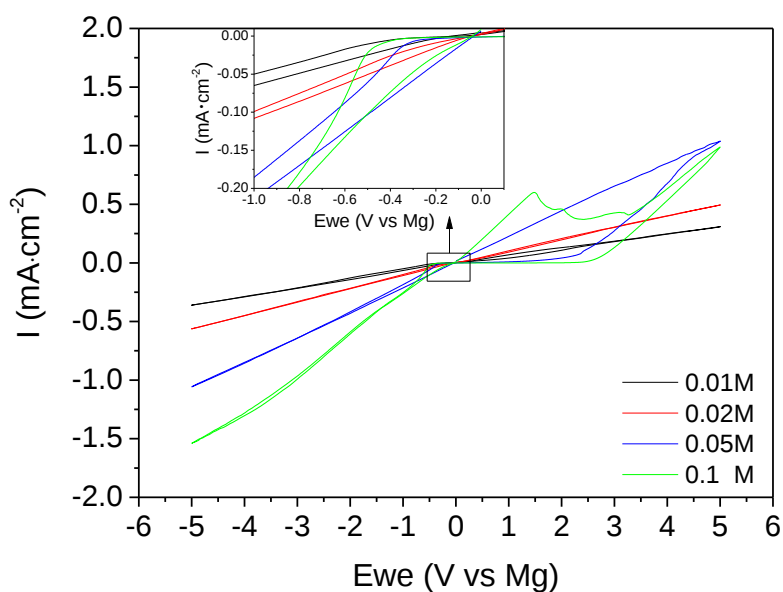


Figure 3-3: Cyclic voltammogram profiles of 0.1 M $\text{Mg}(\text{BH}_4)_2$ with various concentrations of TBAB on a Pt wire electrode. Ewe refers to the potential of working electrode.

From Figure 3-3, it can be observed that with a low concentration of TBAB (0.01 and 0.02 M), the cyclic voltammogram curves are almost flat between -5 and 5 V vs Mg,

without clear oxidation/reduction peaks of magnesium means that the resistance of the electrolyte is high. It is only when TBAB is added at a concentration of 0.1 M, that a magnesium oxidation peak appeared. The initial reduction of Mg was around -0.4 V vs Mg (inset), and this was not significantly affected by the concentrations of TBAB. Such phenomenon demonstrated that TBAB improved the conductivity of the electrolyte while coordinating with $\text{Mg}(\text{BH}_4)_2$ as $[\text{Bu}_4\text{N}]_2[\text{Mg}(\text{BH}_4)_4]$ formed to facilitate the dissociation of $\text{Mg}(\text{BH}_4)_2$. [42]

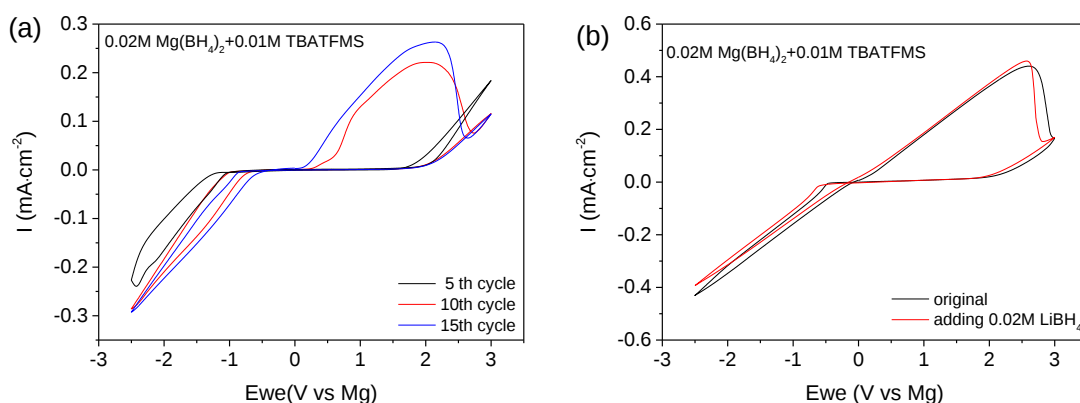


Figure 3-4: Cyclic voltammogram profiles of (a) $\text{Mg}(\text{BH}_4)_2$ with TBATFMS in THF after several cycles and (b) the effect of LiBH_4 . Ewe refers to the potential of working electrode.

The surfactant TBATFMS was also used as a substitution for TBAB to investigate the influence of the counterion on the electrochemical properties of $\text{Mg}(\text{BH}_4)_2$. From the cyclic voltammogram profiles of the surfactants (Figure 3-2), TBATFMS is more stable than TBAB and has higher solubility in THF. Figure 3-4a shows that an initial preconditioning of the electrode exists before a Mg oxidation peak can be observed. Hence, after the 5th cycle, oxidation/reduction is observed. This result differs from that reported by Mohtadi,[24] who observed a stable cyclic voltammogram from the first cycle. So the presence of the surfactant delays the process of magnesium reduction, and

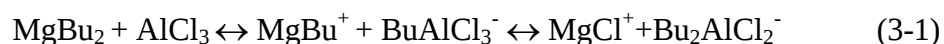
this is most likely due to the surfactant strongly covering the surface of the working electrode. The addition of LiBH_4 did not seem to change this behaviour (Figure 3-4b). It is noteworthy that compared with TBAB, TBATFMS is able to realise magnesium reduction/oxidation with lower concentrations of $\text{Mg}(\text{BH}_4)_2$ and surfactant. This suggests that the counterion of cationic surfactant influences the deposition process of $\text{Mg}(\text{BH}_4)_2$ as the existence of TFMS^- ions can reduce the interaction between the cationic ions and electrode surface, thus Mg is more easily reduced.[43]

3.6 Electrochemical investigation of Grignard reagents

Different from inorganic magnesium precursors, most of the organic ones in the form of Grignard compounds have been shown to be electroactive and reducible.[44-46] Herein, the electroactivity of MgBu_2 and other Grignard reagents was investigated.

3.6.1 Cyclic voltammetry test of Grignard reagents with TBAB

Compared to other Grignard reagents, MgBu_2 has no halide ions and thus the codeposition of the halide can be avoided. MgBu_2 is commonly used in Mg batteries as the electrolyte to transfer Mg^{2+} between the cathode and the anode. In fact, MgBu_2 itself is not capable of acting as electrochemical active species; the radicals generated during electrolysis or produced with additives (e.g. AlCl_3 or EtAlCl_2) can enhance the type/amount of electroactive species in the form of MgBu^+ , MgCl^+ , etc. [47]



Aurbach investigated the types of radicals generated from MgBu_2 during electrolysis.[48] From the cyclic voltammogram profiles of pure MgBu_2 and the one corresponding to MgBu_2 with additional AlCl_3 , it can be clearly observed that AlCl_3 significantly enhanced the deposition/dissolution of magnesium (Figure 3-5). MgBu_2

alone showed a very low reaction current, and when 0.1 M TBAB was added, such a current was further reduced. In contrast, 0.01 M AlCl_3 improved conductivity and reactivity dramatically, the overpotential of Mg reduction was close to pure MgBu_2 (inset).

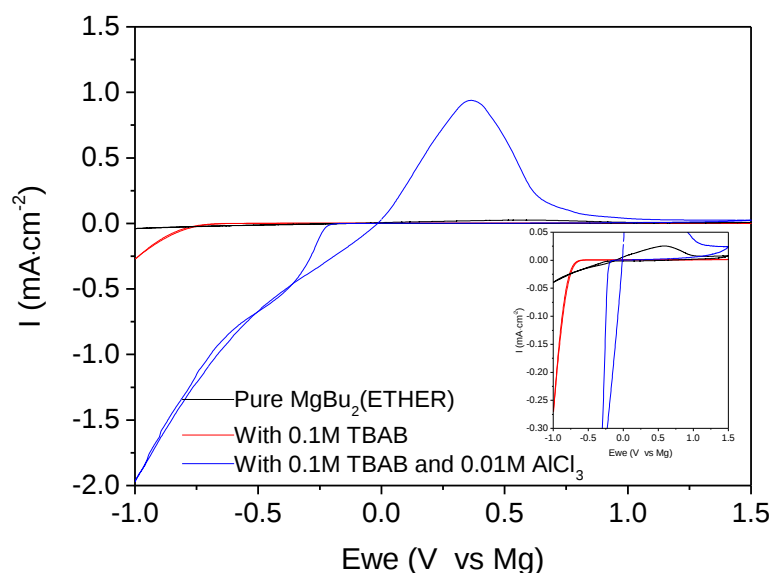


Figure 3-5: Cyclic voltammogram profiles of 0.1 M pure MgBu_2 with and without TBAB in electrolyte (0.01 M AlCl_3 was added to increase electroactivity later). E_{we} refers to the potential of working electrode.

Commercially MgBu_2 can be supplied pure (> 99.8 %) or stabilised with 1 mass% AlCl_3 , the electrochemical properties of these two kinds of MgBu_2 were compared to analyse the influence of AlCl_3 additive (Figure 3-6). Although the conductivity of pure MgBu_2 was enhanced by TBAB, the reaction of magnesium was not just straightforwardly related to the concentration of TBAB. On the other hand, MgBu_2 with AlCl_3 exhibited impressive oxidation/reduction capability (Figure 3-6). The conductivity was also improved with TBAB concentration increasing, while the inset demonstrated that higher TBAB concentration made the reduction of magnesium much more difficult as the overpotential of reduction increased and the area of oxidation peaks was smaller. Such a

phenomenon demonstrates that the addition of TBAB interacts with the interface on the electrode surface because more TBA^+ ions are adsorbed, which inhibit the reduction process and deposit less Mg. However, such behaviour is useful to generate deposition with controlled morphology away from the formation of large Mg deposits stuck on the electrode surface.

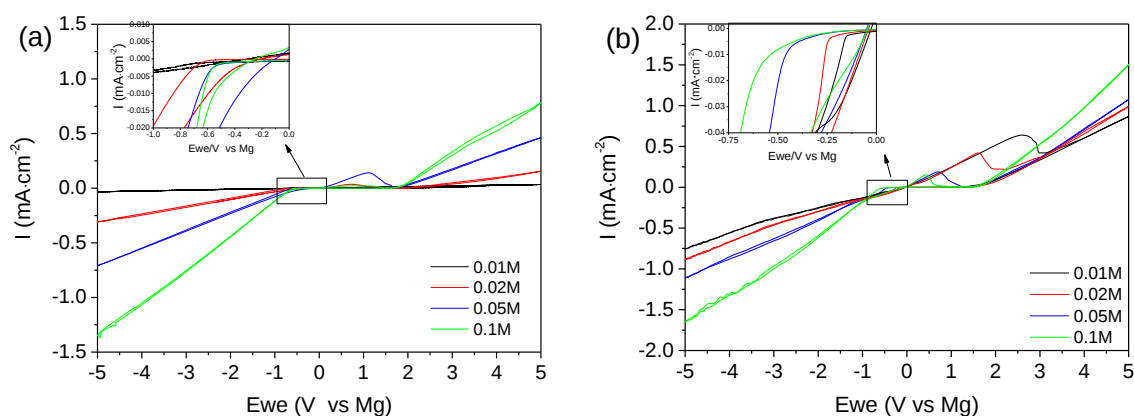


Figure 3-6: Cyclic voltammogram curves of 0.1 M MgBu_2 (a) without and (b) with 1 mass% AlCl_3 additive mixed with various concentrations of TBAB.

In addition to MgBu_2 , several other Grignard reagents were tested by cyclic voltammetry in a 0.1 M TBAB/THF solution (Figure 3-7). Compared with MgBu_2 , they showed much higher conductivity and reactivity because of their strong dissociation as discussed in Chapter 2. The inset indicates the potential of the initial deposition of magnesium was different with various organic groups, p-tolylMgBr required -0.6 V vs Mg to start Mg reduction, while other Grignard reagents needed lower overpotential of -0.4 V. This should be assigned to the steric hindrance of p-tolyl group that made the Mg harder to be reduced. Thus the magnesium oxidation peak of p-tolylMgBr was much smaller than other Grignard reagents as less magnesium was reduced on the electrode. The results indicate that the functional groups in Grignard reagents dominate their electrochemical properties.[49]

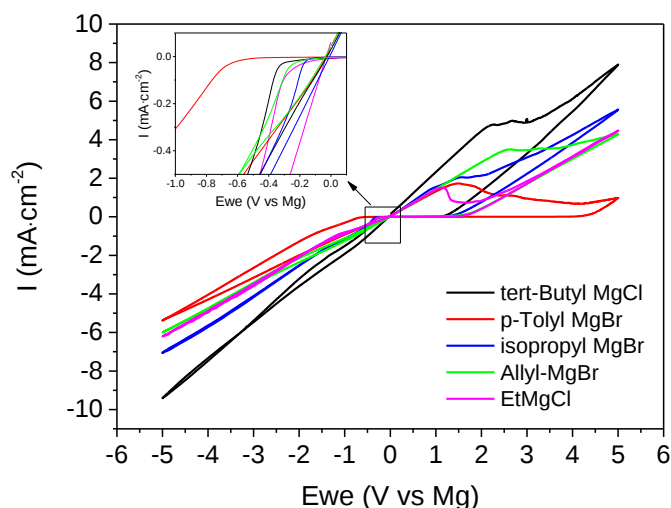


Figure 3-7: Cyclic voltammograms of Pt electrode in THF solutions with 0.1 M TBAB as surfactant of 0.1 M tert-butylMgCl, p-tolylMgBr, isopropylMgBr, allylMgBr, and EtMgCl as indicated.

The effect of AlCl_3 was also investigated for these Grignard reagents. As an example, the addition of AlCl_3 to EtMgCl promoted the deposition of magnesium, which can be seen from the increasing current (Figure 3-8). However, the position of the oxidation peak did not shift upon addition of AlCl_3 , which implied that the mechanism for magnesium deposition from EtMgCl was different compared to MgBu_2 deposition. This can be attributed to the great number of species such as MgCl^+ that were inherent to EtMgCl dissociation and thus the addition of AlCl_3 did not influence this process significantly.

As a summary, comparing MgBu_2 and other Grignard reagents, the electrolyte consisting of MgBu_2 and TBAB is more stable under oxidative conditions and the reduction potential of MgBu_2 can be improved by AlCl_3 additive. Using MgBu_2 can suppress the passivation of Mg by high concentration of halide ions, when considering the need for high hydrogen storage capacity. Hence, MgBu_2 was chosen as the “ideal” precursor for Mg nanoparticles generation.

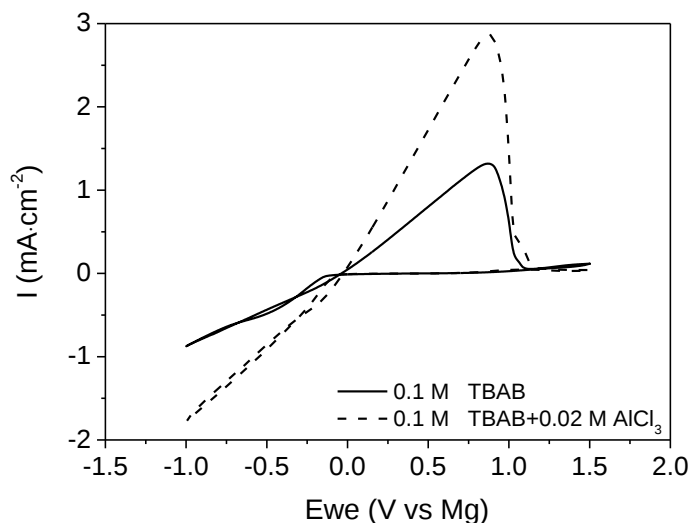


Figure 3-8: Cyclic voltammograms of AlCl_3 and surfactant mixed with 0.1M EtMgCl.

3.6.2 Electrochemical test of MgBu_2 with different stabilisers

With the purpose of investigating the influence of different stabilisers to facilitate the formation of dispersed nanosized Mg from the reduction of MgBu_2 , cationic surfactants (tetraalkylammonium salts), anionic surfactant (SDBS) and non-ionic stabilisers (PMMA and DDT) were investigated. Here MgBu_2 solution in heptane with 1 mass% AlCl_3 additive was used to ensure conductivity.

As tetraethyl ammonium salt surfactants could only be dissolved into THF with a low solubility ($< 0.01 \text{ mol} \cdot \text{L}^{-1}$), the interaction between MgBu_2 and electrolyte/electrode interface was weak. Consequently, MgBu_2 was easily reduced and oxidized at the electrode surface without significant interference of the surfactant (Figure 3-9). The corresponding magnesium oxidation peak was quite obvious for the electrolyte even with saturated tetraethylammonium salts. However, tetrabutylammonium with longer alkyl chain and higher solubility in THF exhibited a different electrochemical property. Even with the same counterions as tetraethyl, there was not a magnesium oxidation peak for TBABF and TBAP. For TBAPF, however, the Mg oxidation was possible.

This difference indicated that the nature of counterions significantly influenced the reduction and oxidation of magnesium. This can be explained in that the tetrabutylammonium ions tend to adsorb on a working electrode surface to block it, while the existence of counterions will modify this tendency.

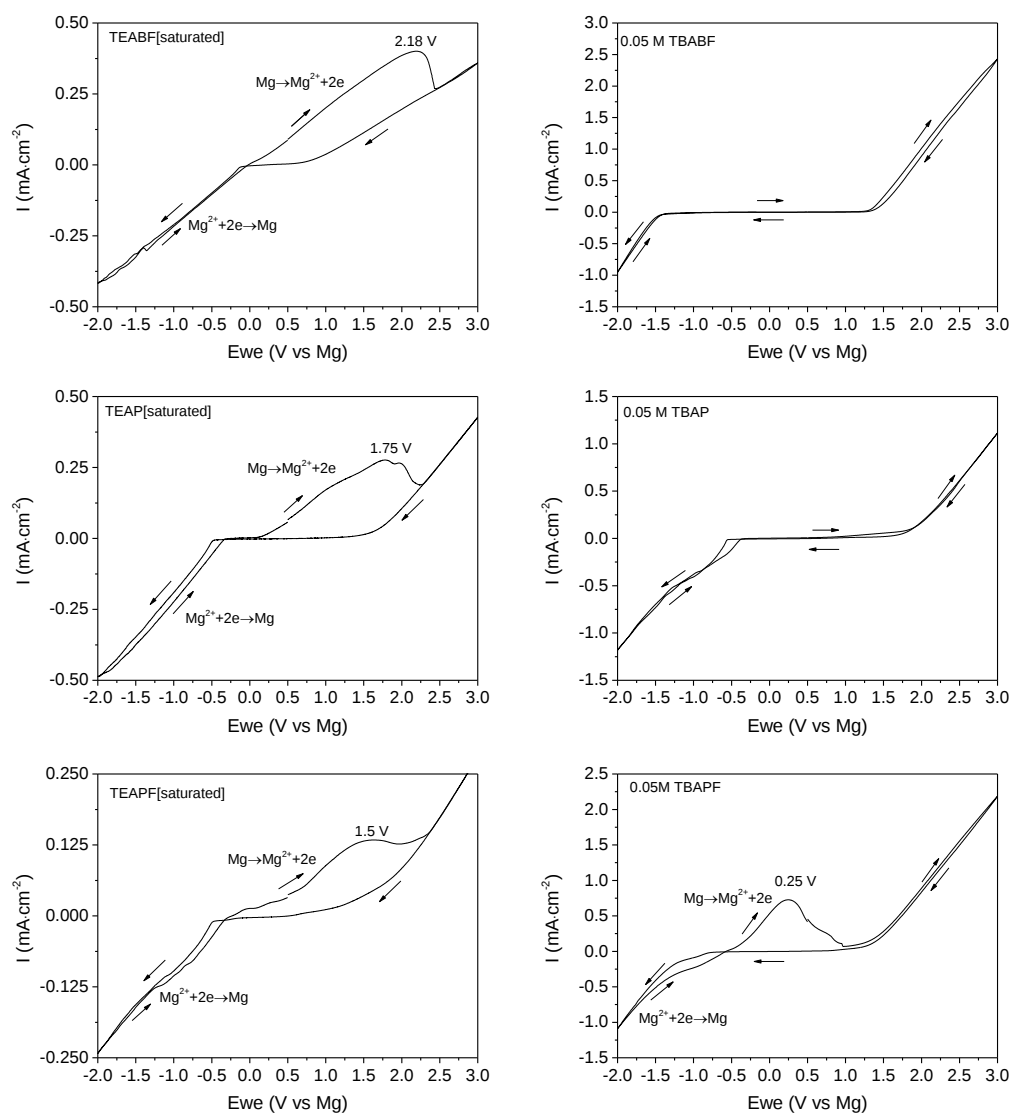


Figure 3-9: Cyclic voltammograms of saturated tetraethylammonium (TEAX) and 50 mM tetrabutylammonium (TBAX) salt surfactants with same counterions, and the concentration of MgBu_2 was 20 mM. $\text{X}=\text{F}^-$, ClO_4^- and PF_6^- .

For the other surfactants with tetrabutyl groups, the effect from the counterions was more obvious (Figure 3-10). TBABH and TBATFMS displayed Mg oxidation peaks

which meant that Mg was easily reduced with these two surfactants. The other surfactants i.e. TBAB, TBAA and TBAF did not show any electrochemical activity of magnesium. It is noteworthy that with TBAB, 20 mM MgBu_2 cannot be reduced even at -2 V. However, at a higher concentration of 0.1 M MgBu_2 , a small oxidation peak was observed at the electrode surface (Figure 3-6b). Such phenomenon demonstrates that the existence of TBAB suppresses the reduction of magnesium.

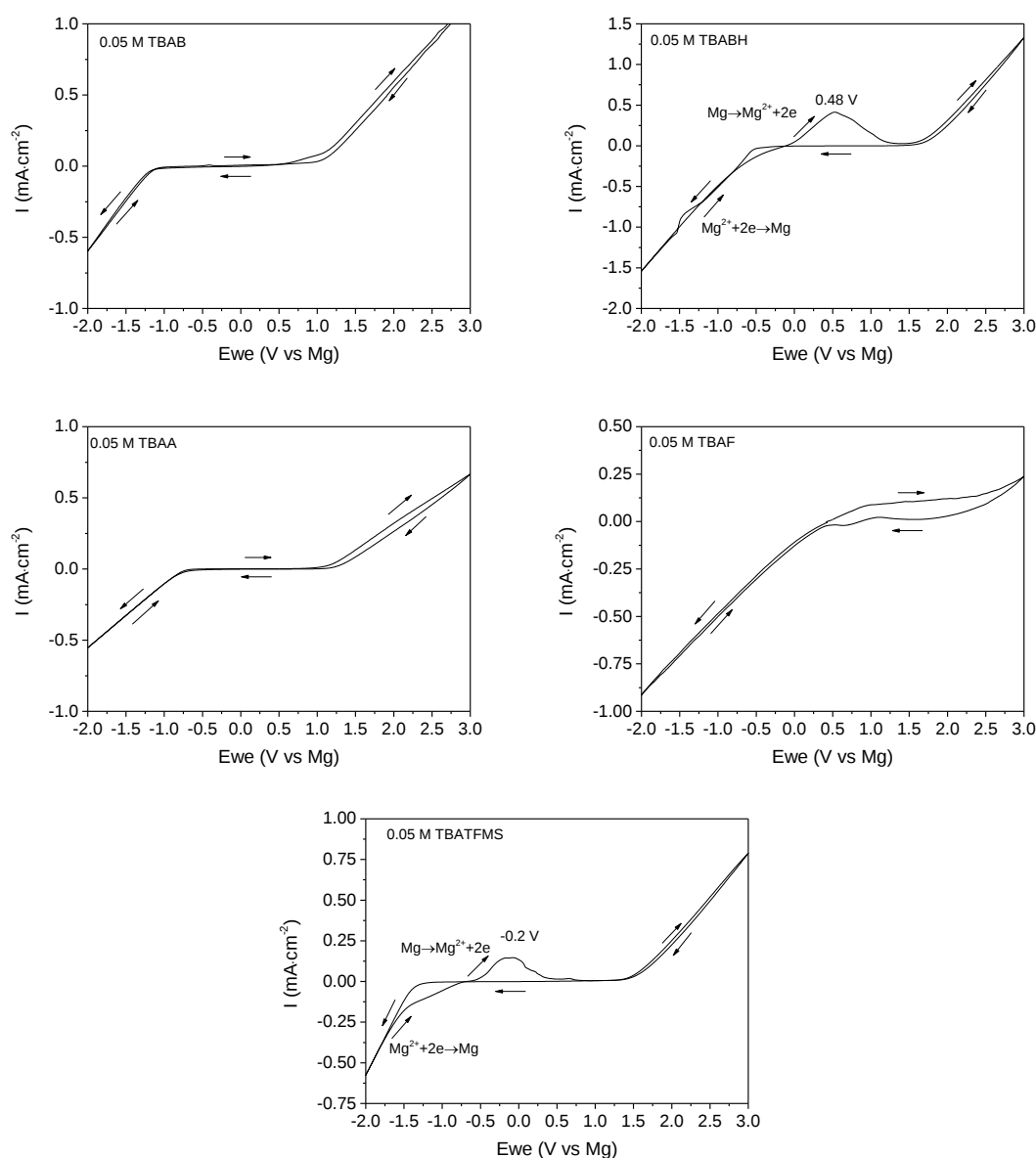


Figure 3-10: Cyclic voltammograms of 50 mM tetrabutylammonium salts with 20 mM MgBu_2 at Pt electrode.

For the surfactants with a tetraoctyl group only flat cyclic voltammogram curves were observed. The difference of reduction onset was assigned to the effect of the counterions.

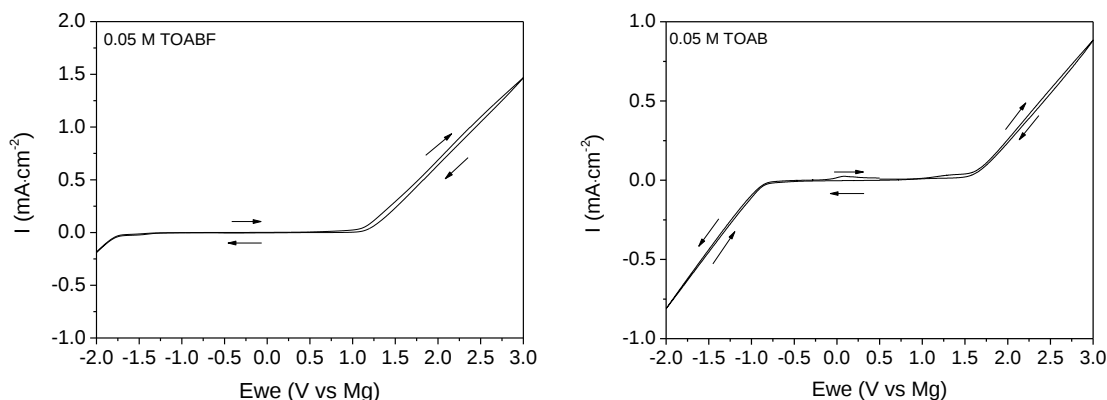


Figure 3-11: Cyclic voltammograms of 50 mM tetraoctylammonium salt surfactants with 20 mM MgBu₂ at Pt electrode.

The behaviour of MgBu₂ mixed with the anionic surfactant SDBS was similar to the observation above. As shown in Figure 3-12, even at varied concentrations of SDBS or MgBu₂, there was no oxidation of Mg. This means that SDBS inhibited the reduction/oxidation of magnesium significantly. Such phenomenon was assigned to a strong interaction between Mg²⁺ and DBS⁻ ions.[32]

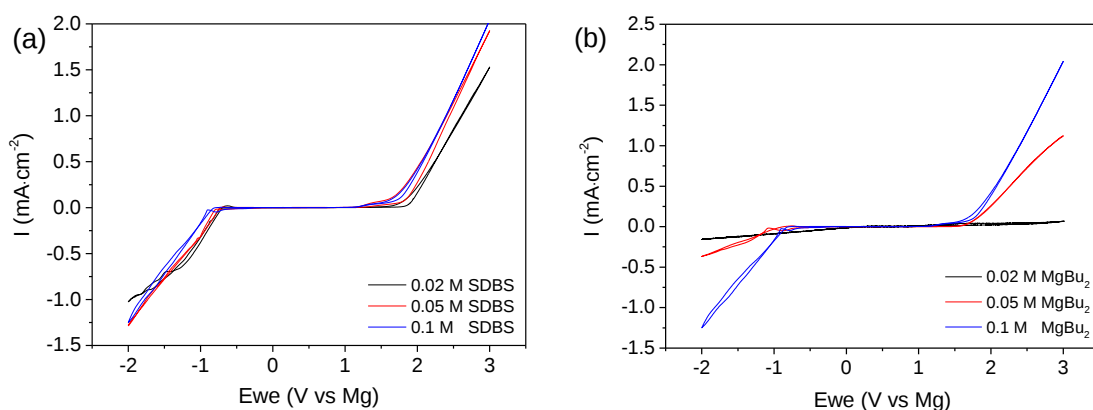


Figure 3-12: Cyclic voltammograms of (a) various concentrations of SDBS with 0.1 M MgBu₂ and (b) various concentrations of MgBu₂ with 0.1 M SDBS.

The addition of non-ionic stabiliser PMMA showed a unique electrochemical property. The cyclic voltammogram of pure MgBu_2 with PMMA led to a strong Mg oxidation peak (Figure 3-13). This suggests that the low interaction of PMMA at the electrode/electrolyte interface would not inhibit the magnesium reduction although the dissociation of pure MgBu_2 was weak. When PMMA was mixed with MgBu_2 (with 1 mass% AlCl_3 additive), the initial reduction of magnesium was -0.12V vs Mg. This low overpotential suggested that the Mg deposition process was not significantly influenced by PMMA compared to cationic and anionic surfactants.

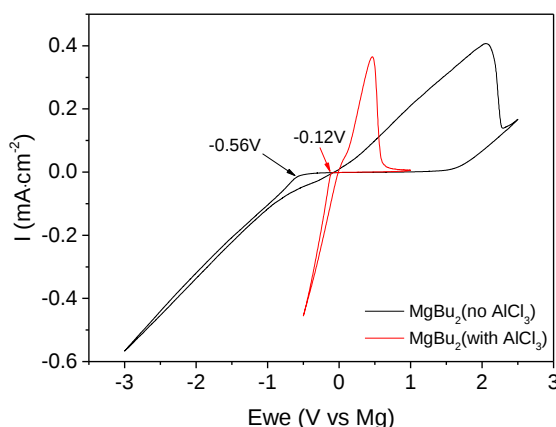


Figure 3-13: Cyclic voltammograms of $1\text{mg}\cdot\text{mL}^{-1}$ PMMA mixed with 20 mM MgBu_2 with and without 1 mass% AlCl_3 .

For the other non-ionic stabiliser DDT, the interaction with MgBu_2 can be observed upon decreasing the concentration of DDT. With 20 mM, the magnesium oxidation peak is obvious, while with 50 mM DDT, the peak disappeared and meanwhile the reduction current decreased significantly. Such phenomenon may be explained by the bond formed between the thiol end group and Mg^{2+} . [34] This is similar to SDBS, but the effect is weaker because DDT could not dissociate anions to combine with Mg^{2+} firmly. It is also possible that the DDT adsorbed at the electrode surface and blocked the reduction and oxidation of Mg. [50]

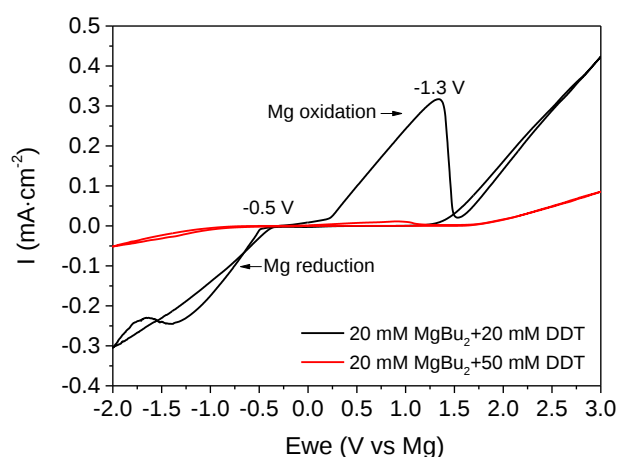


Figure 3-14: Cyclic voltammograms of different concentrations of DDT with 20 mM MgBu₂.

3.6.3 Morphologies of typical deposits

The results obtained above were used to direct investigation toward the deposition of magnesium with sufficient amount to enable investigation into H₂ storage properties. The magnesium deposits produced with different surfactants/stabilisers and MgBu₂ showed distinct morphologies (Figure 3-15).

The solubility of tetraethylammonium surfactants was too low to exhibit the effect to stabilise the magnesium deposits, long magnesium dendrites with silver colour were formed during deposition process and connected working and counter electrodes to stop further reaction. As a result, they are not suitable for electrochemical deposition of Mg.

Among the cationic surfactants (TBAPF, TBABH and TBATFMS) showing Mg oxidation, TBAPF produced a white suspension, may be MgF₂, [51] TBABH did not lead to any deposit even after 10 h electrolysis. Only TBATFMS generated Mg magnesium particles successfully in solution although the morphology was irregular. For the cationic surfactants (TBAB for example) are not able to show Mg oxidation, there is a white layer on the working electrode surface after deposition, which is

compact and hard to remove. The different results should be ascribed to the effect of counterions in these surfactants,[43] the existence of TFMS^- ions can reduce the interaction between the cationic ions and electrode surface, which leads to a weak adsorption of Mg adatoms at the electrode (Pt) surface thus avoiding the formation of a compact magnesium layer.

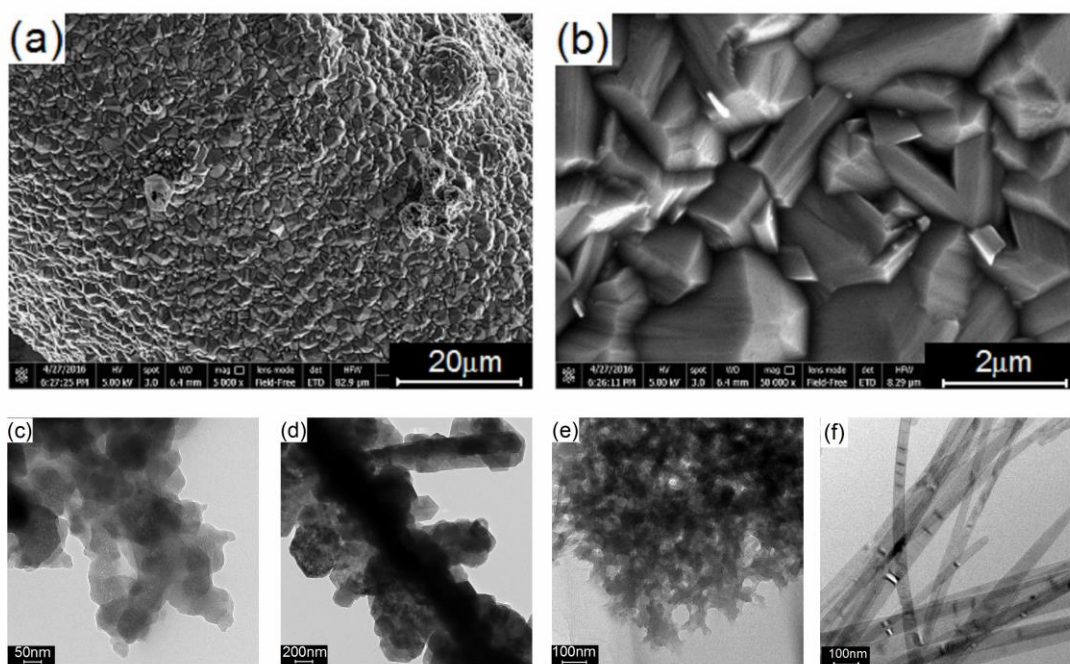


Figure 3-15: (a, b) SEM images of compact magnesium film deposited on Pt wire with TBAB; (c) the magnesium nanoparticles prepared with TBATFMS, (d) dendrite grew on Pt wire with SDBS, (e) magnesium matrix generated with PMMA, (f) magnesium belts generated with DDT.

The anionic surfactant SDBS seems unable to generate Mg deposits as a magnesium oxidation signal was hard to detect in cyclic voltammograms. However, after a long deposition time, some magnesium was reduced from the electrolyte and the morphology of magnesium deposits was branch-like dendrite (Figure 3-15d). This can be explained by the fact that an anionic surfactant should have a limited effect on double layer on a working electrode in preventing direct deposition at the electrode surface. Consequently,

the magnesium deposition grew freely at the Pt electrode surface and formed a dendrite structure.

Non-ionic stabiliser PMMA contributed to form “dispersed” magnesium particles as shown in Figure 3-15e. This should be ascribed to the steric hindrance effect induced by stabiliser adsorbing on particle surface. [52] In the electrolyte with DDT, the shape long “belt” with a width of 100 nm was obtained, which should be attributed to the thiolated electrode surface that controls the growth direction of Mg.[50]

In summary, the functional groups and counterions of cationic surfactants not only influenced their solubility but also the magnesium reduction process and the morphologies of final deposits. Evolution of morphologies as a function of the surfactants/stabilisers can be explained by the interaction between magnesium active species and functional groups, and the effect of the surfactants/stabilisers in modifying on the electrode surface double layer.

3.7 Discussion

Solvents, surfactants and magnesium precursors were investigated in this chapter and MgBu_2 and $\text{Mg}(\text{BH}_4)_2$ were found to be suitable sources to prepare magnesium nanoparticles via electrochemical deposition method in THF solution. TBATFMS and PMMA were also found to be the most appropriate surfactant/stabiliser.

The functional groups of surfactants not only affect the solubility and electrochemical stability under potential, but also influence the magnesium deposition process because of the interaction occurring at the electrode/electrolyte interface. In order to minimise the impurities generated during electrolysis and maintain the compositions in electrolyte, the electrolysis is better proceeded within the electrochemical window of the electrolytes. This has thus guided the choice toward TBATFMS which has a relatively

low reduction potential. On the other hand, MgBu_2 must contain AlCl_3 to enhance the instinctive conductivity; otherwise it is very hard to approach practical current density to reduce magnesium and produce enough Mg particles for H_2 characterisation.

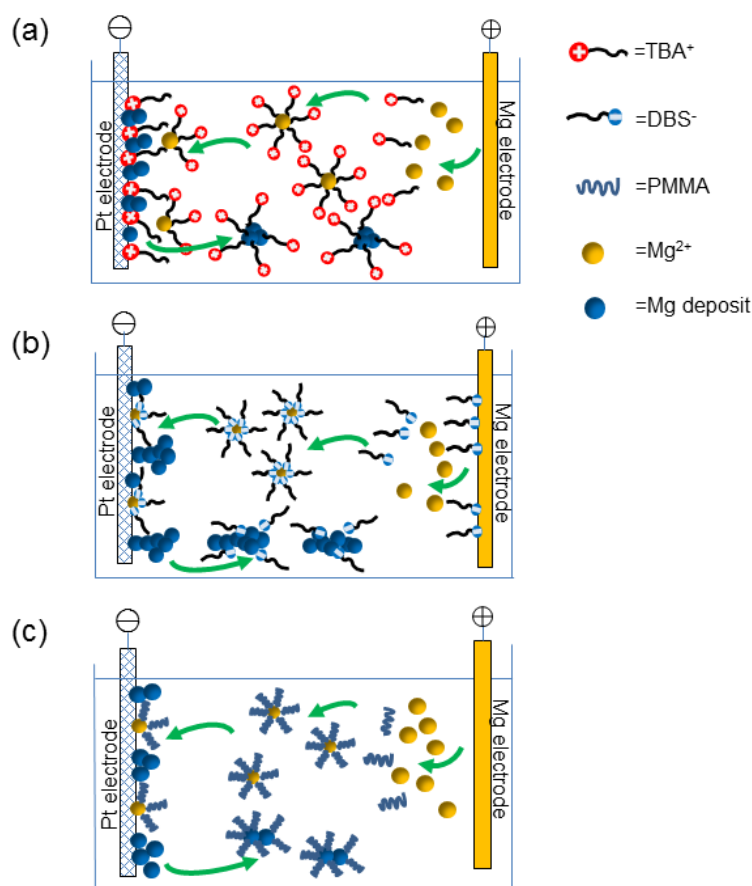


Figure 3-16: Schematic representation of magnesium deposition with different types of stabilisers.

Morphology evolutions of electrochemical deposition influenced by surfactants/stabilisers are widely reported [53,54] and the observations reported in the literature are in agreement with what was observed for MgBu_2 . The inhibition effect of cationic surfactants was especially obvious. As quaternary ammonium ions were adsorbed on electrode surface, this increased the overpotential of the reduction process (Figure 3-16a). Besides, the adsorbed cationic ions changed the net charge on the Mg^{2+} and increased the migration force to the cathode. As a result, the dendrite growth was

suppressed and only compact films with large crystal size were formed. [52,55,56] TBATFMS showed very different morphology, and this can be attributed to the counterion effect. TFMS^- must weaken the adsorption of TBA^+ on electrode surface[43] and make the deposition more loose and easy to strip.

Combining this with the results obtained from SDBS and PMMA (Figure 3-16b and c), conclusions can be drawn that the surfactant should not have too strong an interaction with the electrode surface. In contrast a weak interaction will lead to Mg freely growing as dendrites.[32,52]

3.8 Conclusion

In this chapter, we tried to choose solvents, electrodes, surfactants and magnesium precursors to establish a suitable system to deposit magnesium nanostructures. Properties of components were discussed and the electrochemical performance of electrolytes was investigated. THF was an adequate solvent with sufficient stability and ability to dissolve the chosen surfactants/stabilisers and magnesium precursors. $\text{Mg}(\text{BH}_4)_2$ was studied as representative of inorganic precursors. For organic ones, MgBu_2 was tested in detail, and preferred to other Grignard reagents with halide groups. The integration of magnesium precursors and surfactants/stabilisers significantly influenced the electrochemical properties. Most compositions of electrolytes generated compact magnesium deposits on the working electrode, which was not suitable to prepare magnesium nanostructures to store hydrogen. However, the hydrogen storage properties of thin films can be studied to compare with other methods. MgBu_2 with TBATFMS or PMMA led to preparing magnesium nanoparticles suspended in the electrolyte. The products from these two routes are thus potential candidates for further hydrogen investigation.

As discussed above, magnesium film is easy to form on metal electrode, so the capability of hydrogen storage of such a structure is worthy to check and compare with film structure produced by other methods. Furthermore, magnesium nanoparticles preparation based on MgBu₂ with TBATFMS and PMMA should be investigated in detail to find out the best conditions of electrolyte and the corresponding hydrogen storage properties.

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CHAPTER 4 ELECTRODEPOSITED MAGNESIUM NANOPARTICLES ON TI AND NI SUBSTRATES

4.1 Introduction

As mentioned in Chapter 3, isolated magnesium nanoparticles were hard to generate through the electrochemical conditions investigated. Compact magnesium films were mainly formed on the working electrodes. This result inspired us to explore whether it was possible to prepare magnesium films with improved hydrogen sorption properties. Usually, magnesium thin films are generated through plasma, vapour deposition, pulsed laser deposition and magnetron sputtering, with Pd, Nb or Ti acting as substrates or catalytic layers. The structuration of Mg as thin films has been found to improve the diffusion of hydrogen and the catalytic effect induced from the additional transition metal layers accelerated the kinetic properties of hydrogen absorption and desorption.[1-5]

In this chapter, the deposition of Mg nanoparticles on catalytic Ni foam and non-catalytic Ti foil has been investigated as a function of the electrolyte compositions and electrochemical parameters. The two magnesium precursors, di-*n*-butylmagnesium (MgBu_2) and magnesium borohydride ($\text{Mg}(\text{BH}_4)_2$), were chosen to minimise the contamination from halide ions. These two precursors behaved differently during electrochemical deposition and followed different electrochemical mechanisms. The MgBu_2 deposited on the Ni substrate with -1 mA for 1 h could form a thin magnesium film consisting of nanoparticles, which exhibited low activation energy of hydrogen desorption ($37.8 \pm 0.7 \text{ kJ} \cdot \text{mol}^{-1} \text{ H}_2$), while on Ti, the hydrogen sorption properties were poor because of the non-catalytic substrate and the bigger particle size. Furthermore, the mass from the substrates could not be excluded in this investigation, which made the

hydrogen capacity quite low compared with the magnesium thin film structure prepared by other methods.[2,6]

4.2 Experimental section

Magnesium deposited on the metallic substrates by using $\text{Mg}(\text{BH}_4)_2$ or MgBu_2 as precursors and tetrabutylammonium bromide (TBAB) as surfactant. The electrodes consisted of Mg as a sacrificial anode and Ni foam or Ti foil as a working electrode on which Mg was deposited.

4.2.1 Chemicals

MgBu_2 in heptane purchased from Sigma-Aldrich was used as received. TBAB from Fluka was dried under vacuum at 50 °C prior to use to remove moisture. $\text{Mg}(\text{BH}_4)_2$ was synthesised from MgBu_2 and $\text{BH}_3 \cdot \text{S}(\text{CH}_3)_2$ (Sigma-Aldrich) following the method of Zanella *et al.*[7] THF was purchased as HPLC grade from Fisher Scientific and dried using a LC Technology SP-1 solvent purification system. Magnesium ribbon, titanium foil, platinum wire and nickel foam were purchased from Goodfellow. Ni foam was used instead of a foil to increase the surface area. The surface of the Ni foam was cleaned by treating the foam for 1 h under a hydrogen flow of $20 \text{ ml} \cdot \text{min}^{-1}$ at 300 °C. The surface of the Mg and Ti was polished with abrasive paper and washed with THF to remove the oxide layer. The apparent surface area of working and counter electrodes is about 2 cm^2 .

4.2.2 Synthesis of supported magnesium nanoparticles at Ni and Ti substrates

The magnesium nanoparticles were electrochemically deposited on Ti and Ni substrates. To this aim, a three-electrode cell was used with the Mg ribbon acting as the counter electrode, the Ni foam or Ti foil as the working electrode and a Pt wire as the reference

electrode. The electrolyte consisted of 18 ml THF solution of 20 mM magnesium precursor and 20 mM TBAB. TBAB was used to facilitate the deposition of the Mg nanoparticles and also acted as a supporting electrolyte. Electrochemical deposition was performed by applying a current of -1 mA between the working and counter electrodes using a Biologic VMP3 potentiostat. At the end of the deposition process, the Ni foam and Ti foil were washed with THF and dried under vacuum on a Schlenk line. Finally, the supported Mg nanoparticles were hydrogenated under a hydrogen pressure of 3 MPa at 200 °C on a home-made Sievert apparatus to form MgH_2 . Different electrolysis durations (1, 5 and 10 h) with -1 mA current were investigated to verify the influence of the deposition time on the growth of magnesium layer and its morphology. The products were nominated such as Ni/1h depending on the substrate and deposition time.

4.3 The electrochemical conditions for depositing Mg at Ni and Ti substrates

Before deposition, the colour of the Ni foam was silver and from SEM analysis, its surface was clean and smooth. For the Ti foil, after polishing with abrasive paper, stripes could be observed by SEM (Figure 4-1).

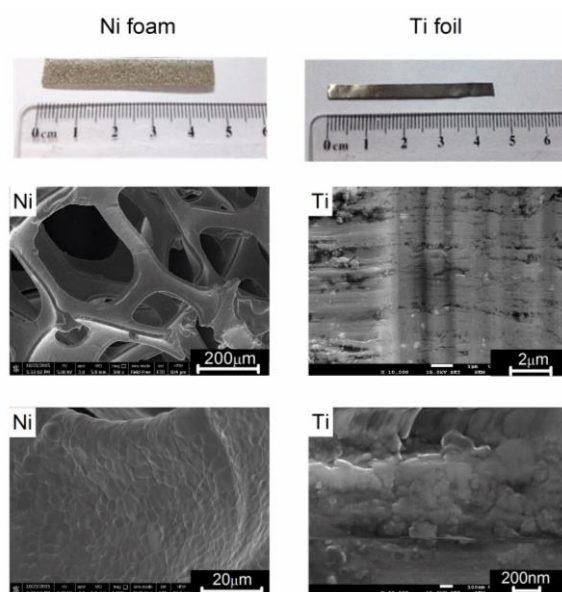


Figure 4-1: The photos and SEM images of pristine Ni foam and Ti foil.

Cyclic voltammetry was first acquired to confirm the deposition conditions at the different substrates. Figure 4-2 shows the cyclic voltammograms of MgBu_2 with and without TBAB on Ni and Ti substrates. Mg was effectively deposited and re-oxidised within a broad electrochemical window as per previous reports.[8] The cyclic voltammograms of the TBAB background only showed a low current indicating no reaction at the electrode. Upon addition of MgBu_2 , the cyclic voltammograms displayed strong Mg oxidation peaks indicating that Mg readily deposited from MgBu_2 without surfactant. On both Ni and Ti the addition of TBAB as a supporting electrolyte reduced the intensity of the re-oxidation peak indicating a better ability to form more strongly bonded Mg deposits in agreement with previous reports.[9]

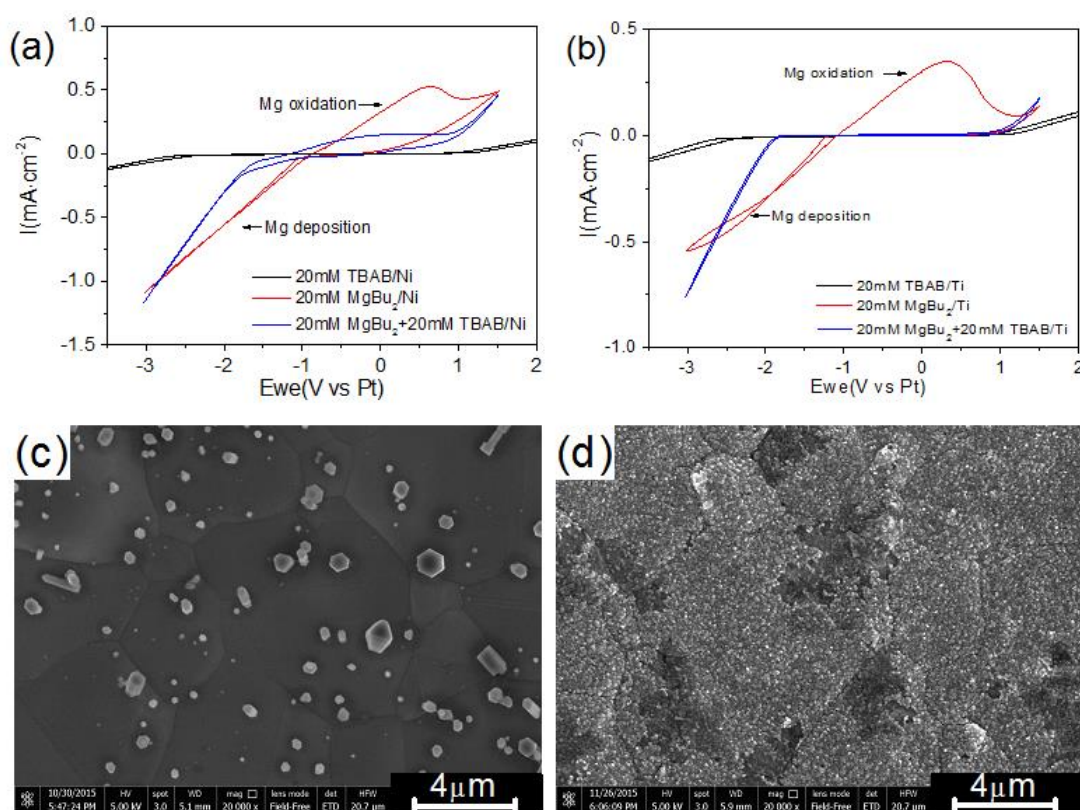


Figure 4-2: Cyclic voltammograms of MgBu_2 with and without TBAB on (a) the Ni foam electrode and (b) the Ti foil electrode. The SEM images correspond to the deposits (c) without and (d) with TBAB surfactant.

It is noteworthy that the reduction current at the Ni foam was higher when compared to the Ti foil, and this was attributed to the higher surface area of the foam. Following the cyclic voltammogram and to ensure a rapid nucleation and growth of the magnesium phase at the surface of the substrate a current of -1 mA was used. Furthermore, the SEM images showed that the existence of TBAB could assist in forming a thin film structure consisting of magnesium nanoparticles (Figure 4-2c and d), so in subsequent investigation, the deposition from MgBu_2 with TBAB would be focused.

Magnesium borohydride ($\text{Mg}(\text{BH}_4)_2$) was also used to deposit Mg on Ni foam and Ti foil. Owing to the low conductivity of $\text{Mg}(\text{BH}_4)_2$, it was necessary to mix it with TBAB to improve the electrochemical deposition. The composition of electrolyte was then 20 mM $\text{Mg}(\text{BH}_4)_2$ and 20 mM TBAB. The onset of reduction and the potential of magnesium oxidation peak illustrated that $\text{Mg}(\text{BH}_4)_2$ was more easily deposited on Ti foil while the oxidation of Mg was harder, which means the state of deposits was quite different (Figure 4-3). The morphology and deposition mechanism of $\text{Mg}(\text{BH}_4)_2$ reduction on Ni foam and Ti foil need further investigation.

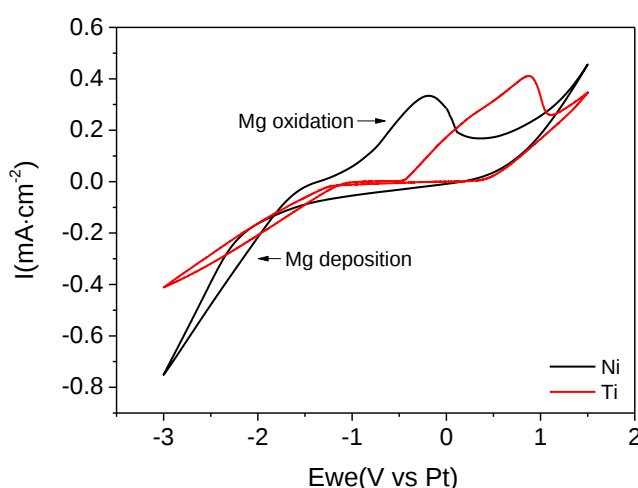


Figure 4-3: Cyclic voltammogram of 20 mM $\text{Mg}(\text{BH}_4)_2$ with 20 mM TBAB on the Ni foam and the Ti foil electrodes.

4.4 Physical properties of Mg films deposited on Ni foam and Ti foil substrates

4.4.1 Magnesium film deposited from MgBu_2

The type of deposits varied depending on the deposition conditions, with MgBu_2 alone (without a surfactant), only generating isolated Mg particles with $\sim 1\ \mu\text{m}$ size (Figure 4-4). The perfect hexagonal shape of crystals indicating preferable orientation of growth was [002] plane. Homogeneous magnesium nanowires could be formed with Grignard reagents without other additives, and both of the highly orientated nanowire and agglomerated plate structures were obtained at Pt, Ni and carbon steel substrates when changing deposition current density and potential. [10,11]

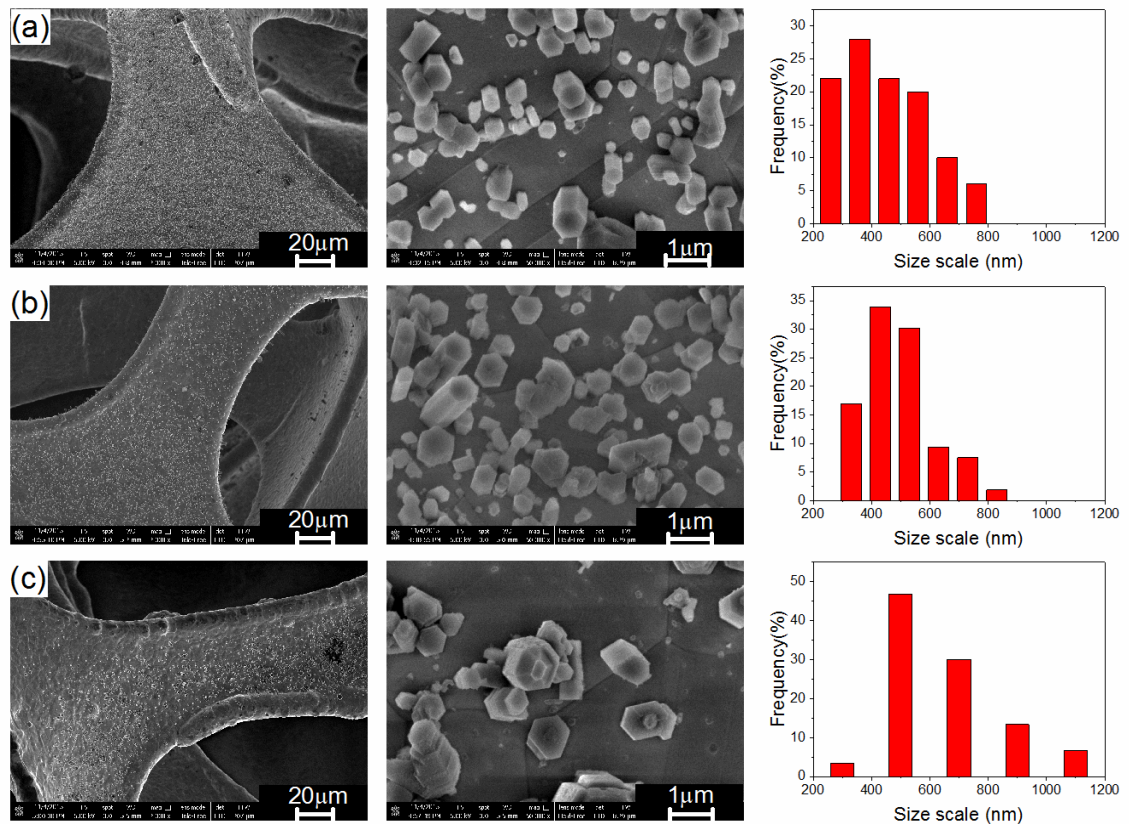


Figure 4-4: SEM images of the magnesium nanoparticles obtained at different deposition times (a) 1 h, (b) 5 h, and (c) 10 h of MgBu_2 alone at the Ni surface.

In comparison, the addition of TBAB to the electrolyte led to a more homogeneous growth at the Ni substrate. For MgBu₂ with TBAB, the analysis of the Ni substrate by SEM confirmed the uniform deposit of small magnesium particles with an average size of 68 ± 11 nm after 1 h of deposition. The film is quite thin and follows the morphology of the Ni foam. Longer deposition times led to the growth of these nanoparticles up to an average size of 421 ± 70 nm after 10 h of deposition (Figure 4-5 and Table 4-1). The Ni surface was entirely covered by a magnesium layer no matter how long the deposition time was.

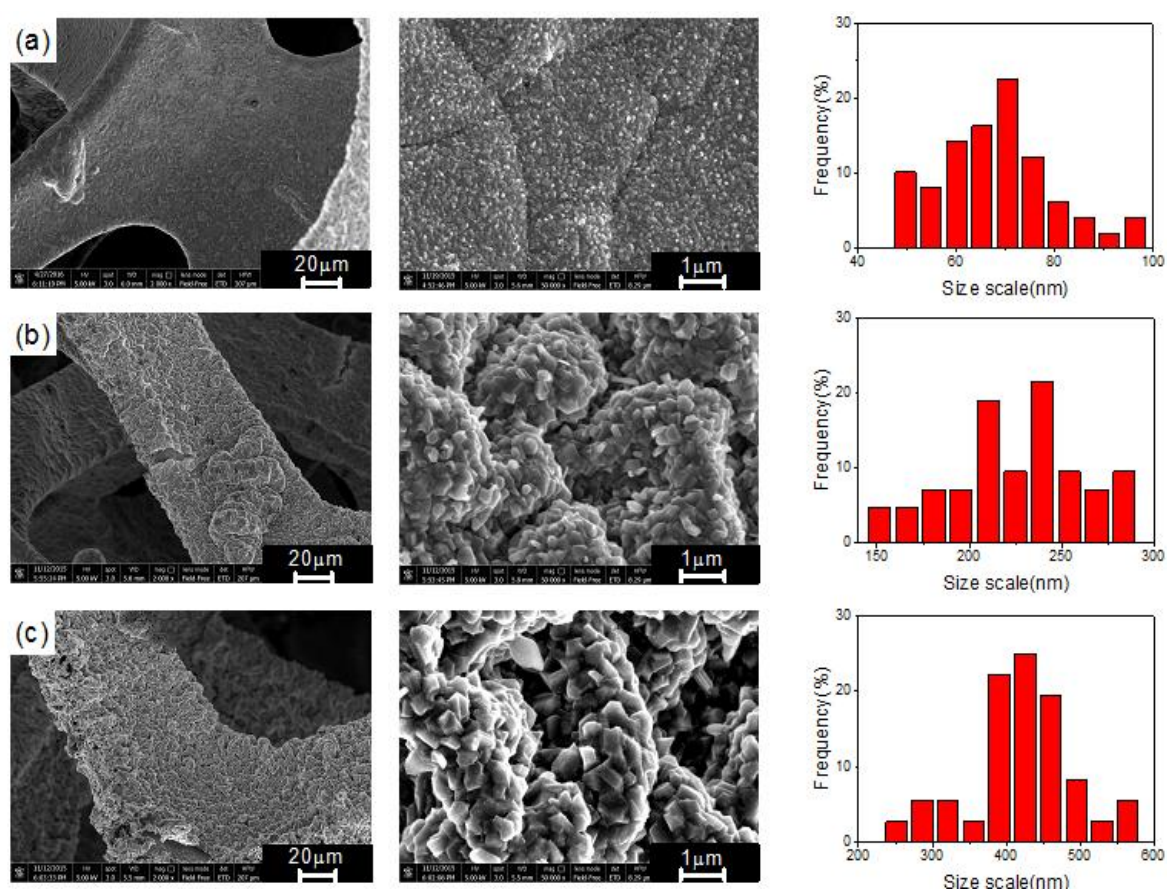


Figure 4-5: SEM images and particle size distribution of the magnesium nanoparticles obtained at different deposition times (a) 1 h, (b) 5 h, and (c) 10 h of MgBu₂ with TBAB at the Ni surface.

Table 4-1: Summary of the physical and hydrogen desorption properties of the magnesium nanoparticles deposited on Ni and Ti. Particle size was determined by SEM and activation energy (E_a) by using the Kissinger method.

Substrate	Deposition time (h)	Particle size (nm)	H ₂ desorption temperature(°C)	$E_a(\text{kJ}\cdot\text{mol}^{-1} \text{H}_2)$
Ni	1	68 ± 11	270	37.8 ± 0.7
	5	225 ± 35	315	49.4 ± 2.1
	10	421 ± 70	380	56.1 ± 4.2
Ti	1	341 ± 60	380	125.4 ± 2.6
	15	-	385	240.1 ± 12.7

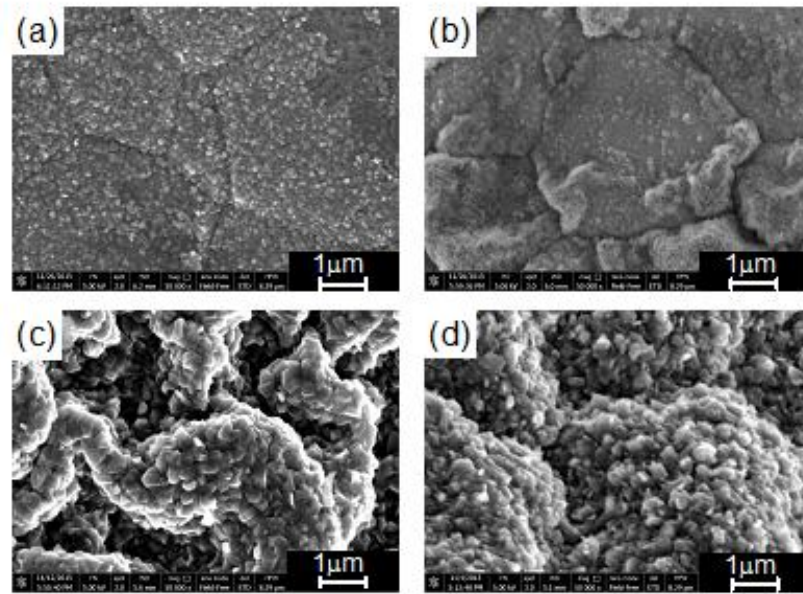


Figure 4-6: SEM images of the magnesium nanoparticles obtained with 1 h deposition time after (a) 200 and (b) 300 °C hydrogenation, as well as the Mg films with 5 h deposition time after (c) 200 and (d) 300 °C hydrogenation.

In order to assess the hydrogen properties of the magnesium nanoparticles deposited on the Ni substrate, the materials were first hydrogenated at 200 °C under a hydrogen pressure of a 3 MPa. At this temperature, the magnesium deposits with the smallest

particle size were found to be stable (Figure 4-6a). However, at a higher temperature of 300 °C the film of the agglomerated magnesium nanoparticles started to degrade and generated a wrinkle-like structure (Figure 4-6b). However, the morphology did not change significantly for the samples with bigger particle size even at 300 °C. For example, MgBu₂ with TBAB deposited on Ni foam for 5 h did not show any significant evolution of morphology (Figure 4-6c and d).

The crystal structure of the deposited Mg was analysed by XRD. As shown in Figure 4-7, the results demonstrate that the electrodeposited material corresponded to hexagonal magnesium with very broad diffraction peaks. The low intensity and breadth of these diffraction peaks suggested the formation of nanocrystalline magnesium at short deposition durations. With longer deposition time, the growth of the Mg particles resulted in larger size and thus slightly more pronounced different peaks. However, after subjecting the 10 h deposition to H₂ pressure at 200 °C it was difficult to observe MgH₂ phase by XRD. This means that the MgH₂ may have a lower crystallinity as compared to the as-prepared Mg.

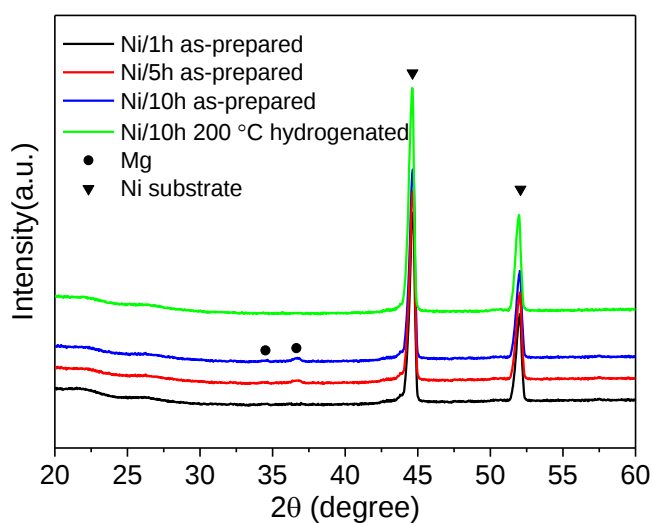


Figure 4-7: XRD patterns of Mg deposited at Ni foam with MgBu₂ and TBAB at different electrolysis times and H₂ absorption at 200 °C for the 10 h deposit.

The same deposition condition of MgBu_2 with TBAB at the Ti substrate led to a more rapid deposition of magnesium due to the smaller surface area. After 1 h, a relatively thick film of agglomerated magnesium particles with an average size of 341 ± 60 nm was already observed (Figure 4-8).

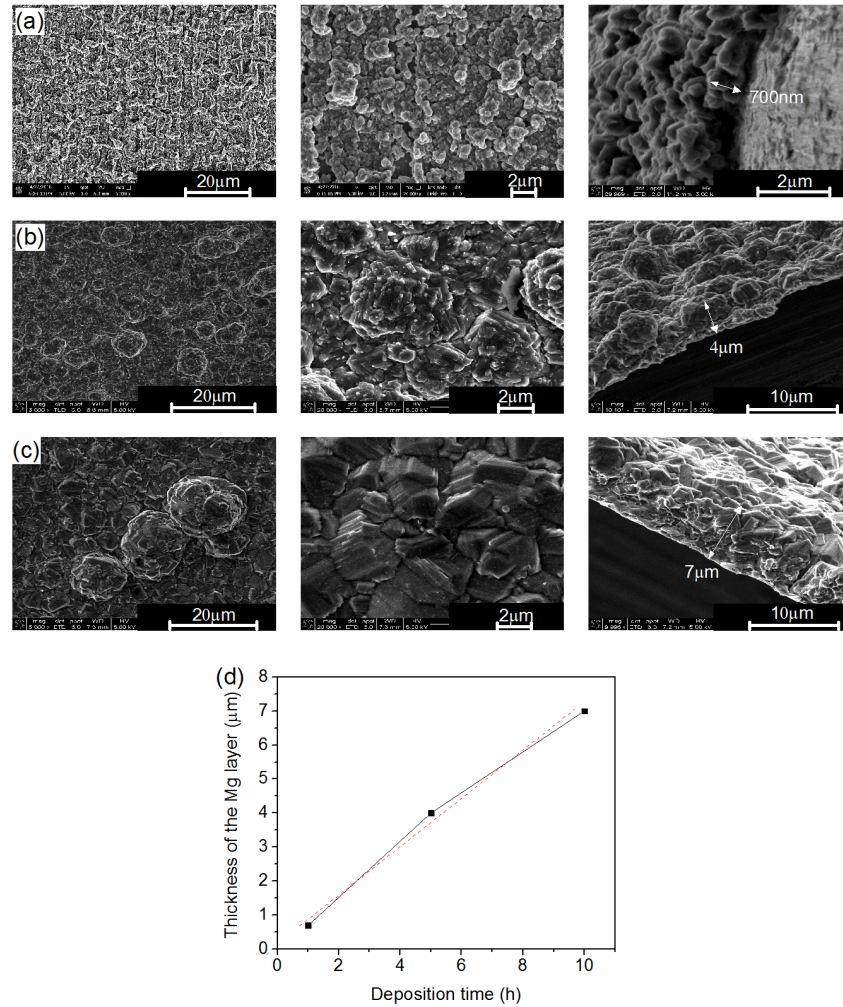


Figure 4-8: SEM images of the magnesium nanoparticles obtained at different deposition times (a) 1 h, (b) 5 h, and (c) 10 h of MgBu_2 with TBAB at the Ti surface. (d) Plot of Mg layer thickness as function of the deposition time.

The thickness of the magnesium layer observed from a vertical view was about 700 nm. With longer deposition time, mushroom-like structures with a size of several microns were formed. The corresponding thickness of 5 and 10 h deposition was 4 μm and 7 μm.

The evaluation of thickness was also found to be linear as a function of the deposition time, which means the depositing rate was constant during reduction process and followed the equation below:

$$L=0.71 \times I \times t \quad (4-1)$$

where L is the thickness of magnesium layer, I and t are deposition current and time respectively.

In order to refine the XRD analysis and minimise the signal of the substrates, a Thin-Film XRD was used (Figure 4-9). The deposition was prolonged to 15 h to obtain a thick enough Mg layer on the Ti foil. However, the peaks corresponding to Ti were still obvious. After hydrogen absorption, XRD analysis confirmed that the deposited Mg could absorb hydrogen at 200 °C, and the small Mg peak remaining may indicate that the absorption of hydrogen is kinetically controlled by the growth of the hydride phase and the diffusion of H₂ through this hydride phase observed with “conventional” Mg thin films.[12,13]

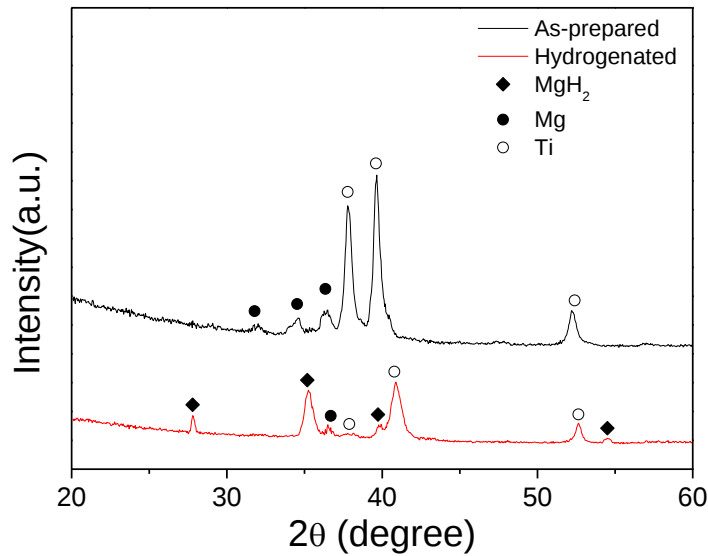


Figure 4-9: Thin film XRD of MgBu₂ deposited on Ti for 15 h before and after 200 °C hydrogenation.

4.4.2 Magnesium particles deposited from $\text{Mg}(\text{BH}_4)_2$ on Ni foam and Ti foil substrates

Different from MgBu_2 deposition, isolated magnesium particles were generated initially on the Ni surface with $\text{Mg}(\text{BH}_4)_2$ (Figure 4-10). The size distribution of the particles for 1, 5 and 10 h deposition times is $1.4 \pm 0.3 \mu\text{m}$, $3.8 \pm 0.3 \mu\text{m}$ and $6.2 \pm 0.8 \mu\text{m}$, respectively. This means that with longer deposition time, the magnesium particles grew up. The coverage of Mg particles on Ni surface was not very high, and this occurred even after 10 h electrolysis. Such phenomenon demonstrates that the deposition mechanism of $\text{Mg}(\text{BH}_4)_2$ is different from MgBu_2 . Mg tended to form isolated particles rather than continuous film with $\text{Mg}(\text{BH}_4)_2$, then growth rate of the semi-spherical convex of the small particles was larger than other place, thus no more tiny particles were formed to cover Ni surface. [14]

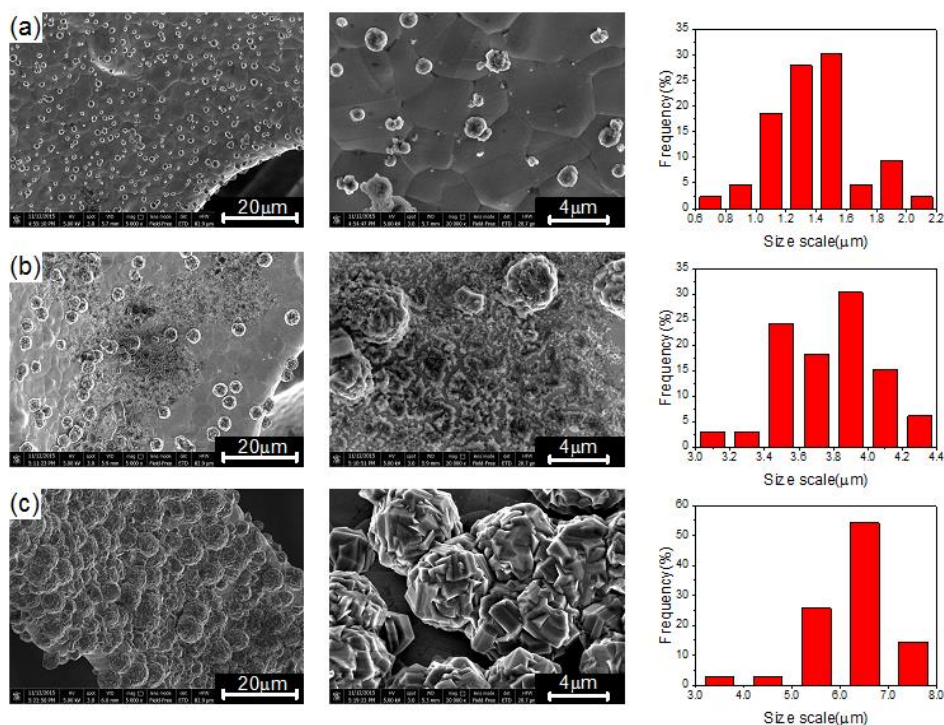


Figure 4-10: SEM images of the magnesium particles obtained at different deposition times (a) 1 h, (b) 5 h, and (c) 10 h of $\text{Mg}(\text{BH}_4)_2$ with TBAB at the Ni surface.

$\text{Mg}(\text{BH}_4)_2$ with TBAB deposited on Ti was more interesting (Figure 4-11). After the same electrolysis duration, much bigger (15-20 μm) magnesium “balls” were produced, and some smaller deposits distributed randomly. In contrast to the clusters generated on the Ni foam, the “balls” on Ti would not grow continuously and the size was limited to around 20 μm . Such phenomenon illustrated that the mechanism of magnesium particles growth on Ni foam and Ti foil was different. The smaller surface area of Ti foil compared to Ni foam resulted in larger overpotential to make the nucleation and growth of deposits fast, when the size of islands was stabilised as the concentration of electrochemical active species on the big island surface was close to the bulk, the progress led to the overlap of deposited islands. [15-17]

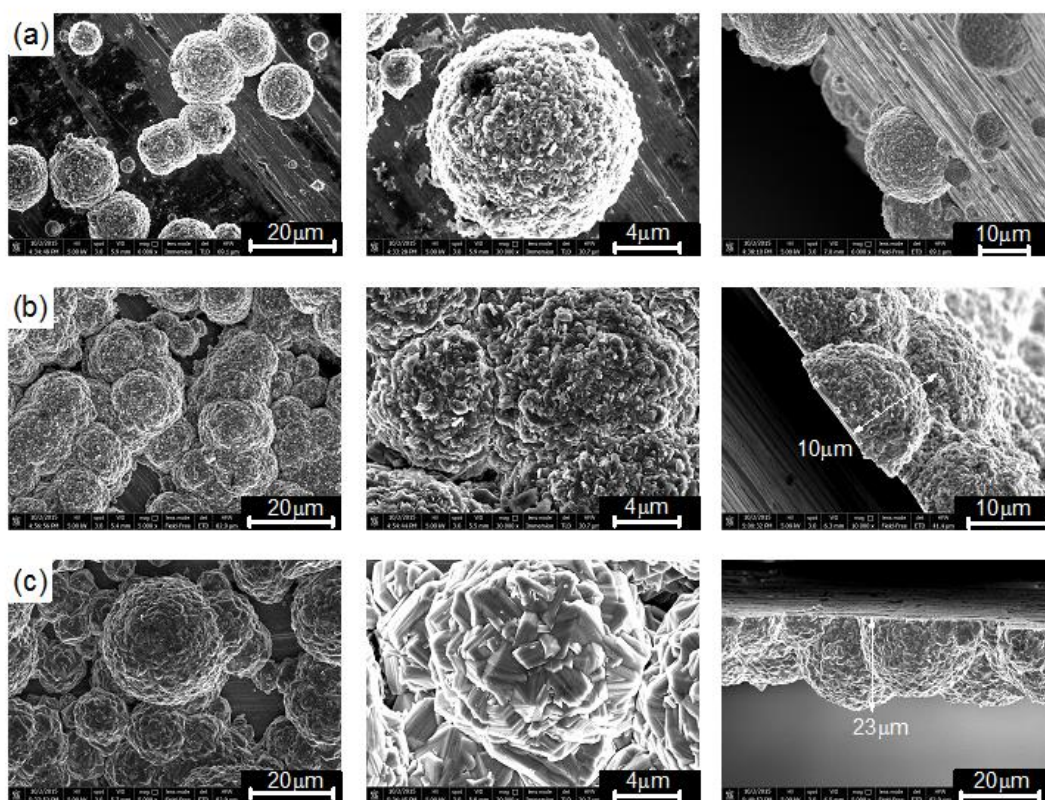


Figure 4-11: SEM images of the magnesium nanoparticles obtained at different deposition times (a) 1 h, (b) 5 h, and (c) 10 h of 20 mM $\text{Mg}(\text{BH}_4)_2$ with 20 mM TBAB at the Ti surface.

4.5 Hydrogen storage properties of magnesium deposited from MgBu_2 and TBAB at Ni and Ti substrates

4.5.1 Hydrogen desorption properties of Mg films

The hydrogenated materials were then analysed by TGA-MS to determine their hydrogen desorption profiles. As shown in Figure 4-12a, deposition of 1 h on the Ni substrate led to the lowest hydrogen desorption temperature, the desorption started at 210 °C with a peak at 270 °C. Longer deposition times led to an increase in the temperature at which hydrogen was released (Figure 4-12a), but remarkably the onset for hydrogen release remained at 210 °C. This may be regarded as the initial point to trigger hydrogen desorption and thus was assigned to the catalytic effect of the Ni substrate in facilitating the recombination of hydrogen atoms at the magnesium surface.[18,19] The initial desorption of hydrogen at 210 °C on the Ni substrate is also consistent with reported thermal desorption spectra of molecular hydrogen adsorbed at Ni surfaces. [20-22] It could thus be concluded that the shift in desorption temperature observed on the Ni catalytic substrate from 270 to 380 °C as particle size increased from 68 ± 11 to 421 ± 70 nm was related to other rate limiting steps than hydrogen recombination at the magnesium surface.

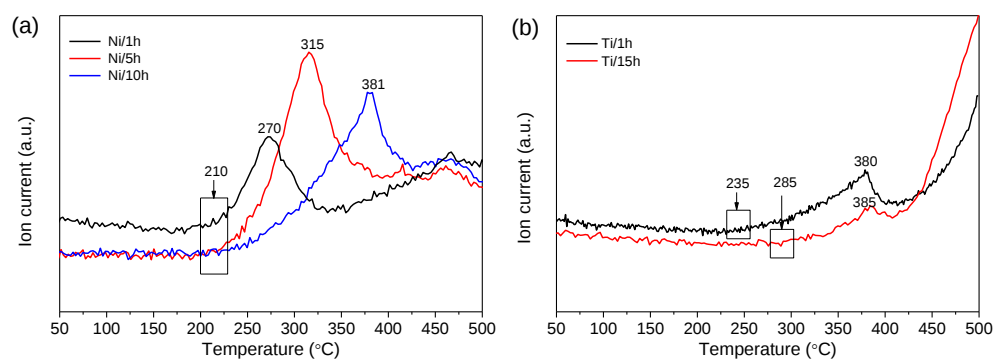


Figure 4-12: Hydrogen desorption profiles of the magnesium nanoparticles deposited with MgBu_2 on (a) Ni, and (b) Ti after being hydrogenated at 200 °C.

Indeed, on the non-catalytic Ti substrate the onset temperatures for hydrogen desorption significantly differed (by 50 °C) as particle size increased and the surface area decreased accordingly (Figure 4-12b) in agreement with previous reports.[23] Compared to the Ni substrate after 1 h deposition on Ti, the hydrogen desorption temperature was higher (> 381 °C) owing to the larger Mg particles formed, thus the kinetics was slow.

4.5.2 Kinetic properties of magnesium deposition on Ni foam with MgBu₂ and TBAB

In order to determine the evolution of the overall activation energy (E_a) of the hydrogen desorption process, hydrogen desorption profiles were measured with different heating rates and the E_a evaluated from the Kissinger's equation (Figure 4-13a).[24] The results are summarised in Table 4-1 and Figure 4-13b.

Remarkably, E_a was found to be significantly lower on the catalytic Ni substrates than Ti. For example, the 341 ± 60 nm magnesium particles on the Ti substrate had E_a of $125.4 \text{ kJ}\cdot\text{mol}^{-1} \text{ H}_2$, which is more than twice the activation energy of the 421 ± 70 nm magnesium particles at the Ni substrate. This is in agreement with previous reports showing a significant reduction of the activation energy when Ni is incorporated in the Mg/MgH₂ system to minimise the first initial energy barrier of hydrogen dissociation/recombination at the magnesium surface.[25,26] For example, Hanada *et al.* reported the significant decrease in E_a from 323 ± 40 to $94 \text{ kJ}\cdot\text{mol}^{-1} \text{ H}_2$ upon incorporation of nanosized Ni to ball milled MgH₂. [19] It is noteworthy that for the smallest particle size of 68 ± 11 nm, E_a decreased to $37.8 \text{ kJ}\cdot\text{mol}^{-1} \text{ H}_2$, and to the best of knowledge this is almost the lowest activation energy observed for the release of hydrogen from MgH₂.

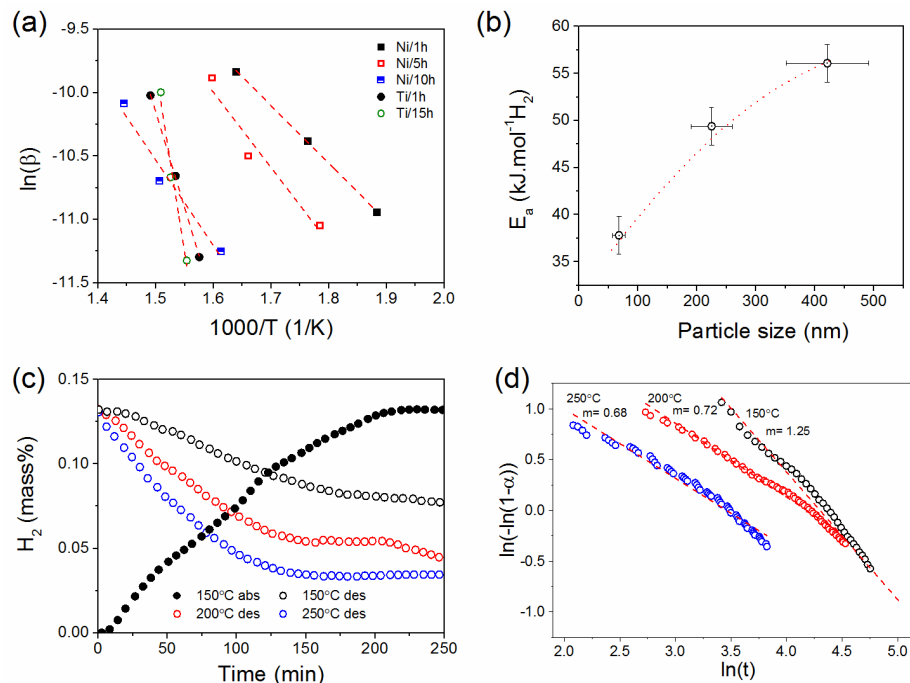


Figure 4-13: (a) Kissinger plot related to the hydrogen desorption from the magnesium nanoparticles deposited on Ni and Ti, (b) associated E_a as function of magnesium average particle size obtained on the Ni substrates at 1, 5 and 10 h deposition times; (c) hydrogen kinetics for the material obtained after 5 h of electrochemical deposition, and (d) associated fit of the hydrogen kinetic desorption curves obtained at 150, 200 and 250 °C. Full hydrogen desorption was not achieved at low temperatures because the material required at least 270 °C as indicated by the hydrogen desorption profile in Figure 4-12a.

Similarly on the Ti substrate, E_a was found to decrease with particle size (Table 4-1) similar to other systems including palladium,[27] sodium alanate,[28] and lithium amide.[29] It is thus apparent that E_a depends upon particle size of magnesium with the initial step of hydrogen dissociation/recombination as the main rate limiting step. However, once this barrier is minimised through the use of a catalyst, additional rate limiting steps will remain in the form of the hydrogen penetration, diffusion, and nucleation and growth of the hydride phase.

Table 4-2: Summary of main model functions describing solid-gas kinetics.

Mechanism	Functional Time Dependence $G(\alpha)$	m
Surface control		
S_1	α	1.24
Random nucleation and growth (Avrami equations)		
A_1	$[-\ln(1 - \alpha)]^{1/4}$	4.00
A_2	$[-\ln(1 - \alpha)]^{1/3}$	3.00
A_3	$[-\ln(1 - \alpha)]^{2/5}$	2.50
A_4	$[-\ln(1 - \alpha)]^{1/2}$	2.00
A_5	$[-\ln(1 - \alpha)]^{2/3}$	1.50
Shrinking core with constant velocity: controlled by interface reaction		
IP_2 —contracting surface	$1 - (1 - \alpha)^{1/2}$	1.11
IP_3 —contracting volume	$1 - (1 - \alpha)^{1/3}$	1.07
Shrinking core with decelerating velocity: controlled by diffusion		
D_1 —1-D diffusion	α^2	0.62
D_2 —2-D diffusion	$(1 - \alpha)\ln(1 - \alpha) + \alpha$	0.57
D_3 —Jander, 3-D diffusion	$(1 - (1 - \alpha)^{1/3})^2$	0.54

In order to determine the initial rate-limiting step of the hydrogen desorption process from the magnesium nanoparticles and assess the potential catalytic effect of the Ni substrate, the material after 5 h deposition was cycled and the kinetics curves obtained were fitted using the general equation of a solid-state reaction (4-2): [30]

$$G(\alpha) = k \times t \quad (4-2)$$

where α is the amount of hydrogen released in time t , $k = k(T, P, r)$ is the reaction rate, and $G(\alpha)$ is a function depending on the mechanism controlling the reaction. The main theoretical functions $G(\alpha)$ are summarised in Table 4-2. In order to facilitate the fitting of the hydrogen curves measured and ease the distinction of reaction mechanisms, the method of Hancock and Sharp was used.[31] Since nucleation and growth processes in

condensed systems follow the almost universal equation (4-3), the method consists of plotting $\ln(-\ln(1 - \alpha))$ versus $\ln(t)$.

$$\alpha = 1 - \exp(-Bt^m) \quad (4-3)$$

where B is a constant that depends on the nucleation frequency and linear rate of the grain growth, and m is a constant that varies according to the geometry of the system. Hence, determining the value of m would indicate the main rate-limiting step of the hydrogen desorption process.

Such an analysis was only possible for the material after 5 h electrochemical deposition, owing to the minimum amount of magnesium required to obtain meaningful kinetic curves and the need for relatively low hydrogen desorption temperatures to avoid any significant degradation of the magnesium film. The amount of magnesium deposited on the Ni foam after 5 h was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES), according to ICP analysis, the Ni-foam substrate, after 5 h of deposition, contained 1.7 ± 0.1 mass% of Mg, which corresponds to an overall storage capacity of 0.13 ± 0.01 mass% H_2 for the material based on Mg.

Figure 4-13c,d show the hydrogen kinetics of the magnesium nanoparticles at different temperatures after initial hydrogen absorption at 150 °C, and the associated fits following the method of Hancock and Sharp [31] for α values comprised between 0.1 and 0.5 to minimise uncertainties related to the initial conditions of desorption, as well as any variations related to particle size distribution and other geometrical effects. At the low temperature of 150 °C, the hydrogen desorption kinetics were slow and the slope of the fit was found to be close to $m = 1.25$ (Figure 4-13d), which indicates that the desorption process is surface-controlled. This is in agreement with the hydrogen

desorption profiles observed at the Ni substrate (Figure 4-12a) and the significant hydrogen evolution happening for temperatures above 210 °C.

At higher temperatures, the hydrogen desorption kinetics were faster, and the slope of the fits shifted to values of $m = 0.72$ at 200 °C and $m = 0.68$ at 250 °C (Figure 4-13d). The rate-limiting step was thus assigned to a shrinking core model controlled by diffusion (i.e., the desorption is controlled by the reaction at the Mg/MgH₂ shrinking core interface with the interface reaction proceeding at constant velocity and not the surface anymore). Hence, for the magnesium particle size of 225 ± 35 nm, at low temperatures (< 210 °C) the hydrogen desorption kinetics would be controlled by the ability of the surface to recombine hydrogen, while at higher temperatures (where this is facilitated by Ni), the main rate-limiting step would be the diffusion of hydrogen at the Mg/MgH₂ interface. As particle size is reduced, such a rate-limiting step should be facilitated in agreement with the reduction in E_a observed (Table 4-1).

4.6 Discussion

Utilising electrochemical deposition to generate magnesium film on substrate is not a novel idea; however, the results reported usually only formed coarse deposition with large particle size [32-34] and the hydrogen sorption properties of electrochemically deposited magnesium films are usually not investigated. Investigations in this chapter showed that different magnesium precursors generated magnesium deposits with distinct morphologies. The morphologies of these magnesium deposits depend not only on the composition of electrolytes, but also the state of electrodes. The results demonstrate that the deposition mechanism of different magnesium precursors is diverse, which can be explained in terms of a strong interaction of adsorbed metal ions between the substrate and deposited metal.

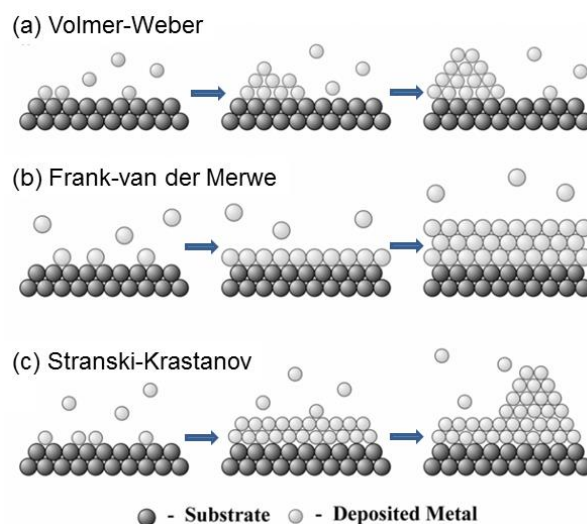


Figure 4-14: Schematic representation of the metal epitaxial growth on foreign substrate: (a) Volmer-Weber (3D), (b) Frank-van der Merwe (2D) and (c) Stranski-Krastanov (2D+3D). [35]

Generally, three modes of electrochemical metal growth have been reported: “Volmer-Weber” (VW), “Frank-van der Merwe” (FM) and “Stranski-Krastanov” (SK) modes as shown in Figure 4-14.[35] The two main factors to determine the modes of metal deposition are i) the binding energy required to deposit on substrate and on native metal, and ii) the misfit of lattice structure between metal and substrate. Once the binding energy of metal depositing on substrate is lower than that on native metal, the metal follows VW mode which prefers to be reduced on itself to form island growth independent of the misfit. In contrast, if the binding energy on substrate is higher than that on native metal, the effect of misfit between metal and substrate will exhibit. When the misfit is neglectable, the metal deposits grow layer-by-layer epitaxially (FM mode). Otherwise the initial layers between metal deposit and substrate contain considerable internal strain, and the growth of subsequent unstrained metal islands follows SK mode.

$\text{Mg}(\text{BH}_4)_2$ should follow VW mode to form isolated particles on Ni and Ti substrates as it is easier to deposit on Mg islands. MgBu_2 deposited on Ni foam with TBAB seems to

follow FM mode. The mushroom structure formed with MgBu_2 on Ti after a long time can be explained by SK mode, as with 1 h deposition time, relatively flat magnesium film was produced, then the magnesium islands generated on the top of initial film. From lattice parameter comparison, misfit of lattice between Mg [001] and Ni [001] is $\sim 8.8\%$, which is similar to the value between Mg [001] and Ti [001]. However, the coarse surface of Ti substrate has more defects than smooth Ni foam, thus the effect of misfit is significant.

The existence of surfactant assisted MgBu_2 to produce continuous film consisting of small particles might be explained by the illustration in Figure 4-15 following the theory of ion penetration.[36] After the adsorption of TBA^+ ions at the electrode surface, the inhibitor layer will affect the ionic distribution within the double layer and thus any ion needs to cross this layer to be oxidized or reduced.[37] Accordingly, such an effect can lead to the growth of dendrites (field-oriented growth) to a random growth at the electrode surface.[38] The hypothesis may explain why the vertical growth of hexagonal Mg crystals was suppressed when TBAB was added to solution of MgBu_2 (Figure 4-2). The density of the initial isolated nuclei is determined by concentration of electrolyte and deposition potential,[17] then the film structure can be formed by a large amount of tiny particles or the growth of nuclei during deposition.

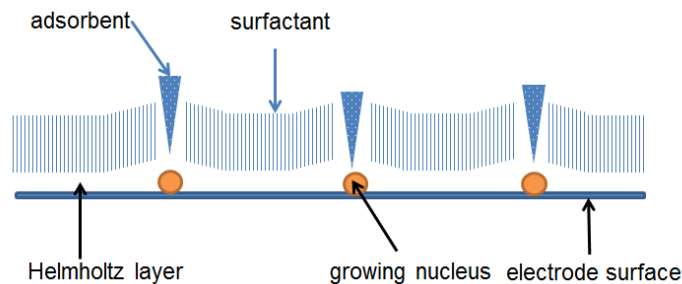


Figure 4-15: The model of surfactant effect of metal electrodeposition.[36]

Additional factors that may affect this growth are parameters including overpotential and reaction time (Figure 4-16).[39,40] With low overpotential, the reaction of metal deposition is under kinetic control with adequate ion diffusion, and the particles then grow up uniformly. However, higher overpotential leads the process to diffusion control as the induced high current requires enough ions to be reduced. Under conditions of diffusion control, a metal particle with its neighbours is mediated by the depleted solution layer surrounding each particle. The number and distance of particles on the substrate lead to a dispersion in the growth rates of individual particles and then results in nonuniform particle size distribution.

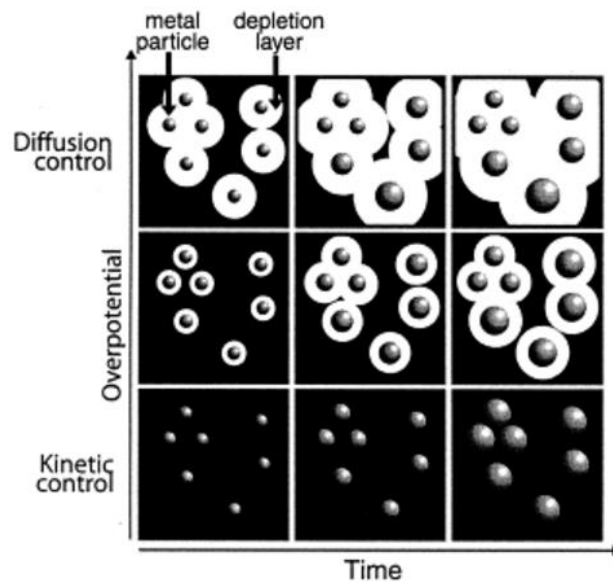


Figure 4-16: Effect of overpotential on the size dispersions of metal particles as a function of the deposition time. [39]

On the Ni foam, the big surface area results in low current density and corresponding low overpotential, which induces that the deposition process is under kinetic control and thus the particles grow uniformly as a function of the deposition time. However, on a Ti foil, higher overpotential could lead to a process controlled by diffusion. Hence magnesium particles with a different size would be generated. MgBu_2 has a higher

electroactivity than $\text{Mg}(\text{BH}_4)_2$ as discussed in Chapter 3, and there are adequate active species suspended in electrolyte with a fast diffusion rate. The deposition reaction thus possesses a broader range of kinetic control than $\text{Mg}(\text{BH}_4)_2$, and as a result, the particle size distribution is improved. The approaches to modify the kinetic control include optimising the deposition current or potential, concentration of electrolyte and temperature.[41]

The investigation of hydrogen storage properties of magnesium deposits showed that small particle size and effective interaction with the Ni catalytic substrate could improve the kinetics of Mg significantly. As has been reported many times in the literature, reducing the particle size enhances the kinetics properties as with shorter diffusion paths, similarly, the catalytic effect of Ni is well known.[42,43] However, as the particles grew beyond 400 nm, the hydrogen desorption degraded toward that of normal bulk magnesium. It is also reported that magnesium deposited on Ti with big grain size was very difficult to hydrogenate even at high temperature.[44]

Previous investigations have shown that for bigger magnesium particles of a few micrometres prepared by ball-milling, the rate-limiting step is mainly controlled by the growth of several nuclei and thus the associated nucleation and growth process. [45] For much smaller magnesium particles of a few hundred nanometres it can be assumed that single nuclei will be formed and thus the reaction will be controlled by diffusion, as currently found.[44] The current results indicated that improving the hydrogen kinetics will require finding effective additives or synthesising novel magnesium nanocrystalline structures to enhance the diffusion of hydrogen. At much smaller particle sizes of a few nanometres, the process has been reported to be controlled by nucleation and growth, owing to the extremely short diffusion distances and the large surface area.[46] Hence, additional improvement will require an adequate catalyst to facilitate this process.

A drawback of the current approach is that the substrates are heavy, therefore a better idea to prepare Mg/Ni nanocomposite on Ni with a higher surface area needs to be found. One alternative is the codeposition of Mg and Ni to form adequate Mg/Ni composites.

4.7 Conclusion

The electrochemical deposition of magnesium from the reduction of different magnesium precursors on Ni and Ti substrates was used to generate magnesium nanostructures with various morphologies. The deposition mechanism of magnesium precursors differed from each other, and the impact of surfactant and electrode would also influence the state of the final products. Large Mg deposits showed similar hydrogen storage properties compared to bulk magnesium, and low hydrogen desorption temperature was not possible.

Mg deposited on the Ni foam from MgBu_2 and TBAB formed relatively small particles and the evolution of E_a for the decomposition of MgH_2 was found to depend upon the particle size. On the Ni substrate magnesium particles with various sizes ranging from 68 ± 11 nm to 421 ± 70 nm were synthesised and these particles showed a significant decrease in E_a as particle size decreased. Hence, E_a was reduced from 56.1 to 37.8 $\text{kJ}\cdot\text{mol}^{-1} \text{H}_2$ as magnesium particle size was reduced from 421 ± 70 to 68 ± 11 nm. E_a on the Ni substrate (56.1 $\text{kJ}\cdot\text{mol}^{-1} \text{H}_2$) was found to be much lower than on the Ti substrate (125.4 $\text{kJ}\cdot\text{mol}^{-1} \text{H}_2$) at similar particle sizes.

More remarkably, E_a was found to depend upon particle size of magnesium with the initial step of hydrogen dissociation/recombination as the main rate limiting step. However, once this barrier was minimised through Ni catalysis, the main rate limiting step was found to be related to the hydrogen diffusion toward the desorbing MgH_2/Mg

interface. It is thus apparent that upon appropriate catalysis of the hydrogen dissociation/recombination, fast hydrogen kinetics should be feasible with very small magnesium particles. Assuming that similar improvements can be achieved with respect to the thermodynamic of the magnesium/hydrogen reaction, the approach of nanosizing may lead to an effective route toward room temperature magnesium-based materials for hydrogen storage.

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CHAPTER 5 ATTEMPT TO SYNTHESISE “ISOLATED” MG NANOPARTICLES BY ELECTROCHEMICAL MEANS

5.1 Introduction

In Chapter 4, magnesium film consisting of particles was electrochemically deposited on metal substrates (Ni and Ti), while the hydrogen storage capacity was poor because of the heavy substrates. Ideally, isolated nanoparticles should be prepared as to remove the need of the substrate. To this aim, the use of organic stabilisers was investigated along the Reetz method (Chapter 2). Reetz *et al.* prepared a series of metal nanoparticles from a sacrificial anode, leading to the formation of small particles (< 5 nm), with an alkylammonium salt as a surfactant acting as the supporting electrolyte and stabilising the nanoparticles.[1-3] Hence for the approach to work, the deposits must be able to leave the surface of the working electrode. If not, the particles will quickly grow into a film strongly adhering at the electrode surface shown in Chapter 4.[4] The electrochemical properties of several organic magnesium precursors and stabilisers have been investigated in Chapter 3, and di-*n*-butylmagnesium (MgBu_2) was identified as the best candidate to generate magnesium deposits. The use of stabilisers to generate “isolated” magnesium particles is investigated in this chapter.

Generally, the electrosynthesis of “isolated” magnesium nanostructures is not widely reported. Most of the literature focuses on the use of organic magnesium precursors as electrolytes for magnesium batteries. Viyannalage *et al.* prepared magnesium nanofibers and particles from EtMgCl , [5] and Haas *et al.* utilised sonoelectrochemical reduction to synthesise isolated magnesium nanoparticles.[6] However, in both reports the hydrogen storage properties were not investigated. In the electrochemical deposition system, the influence of a stabiliser is critical to the morphologies and properties of the final

products. Nambiar *et al.* reported that gold nanoparticles formed only in the presence of cationic surfactant solutions and not with anionic and non-ionic surfactants.[7] The surfactant also influences the crystallisation process, for instance, in a Ni electrochemical deposition study, it was found that [220] plane was the preferred orientation without surfactant, while with sodium dodecylsulphate (SDS) or hexadecyltrimethyl ammonium bromide (CTAB), [200] and [111] planes were formed, respectively.[8]

In chemical synthetic methods, aiming at the synthesis of nanoparticles, a low concentration of surfactant (at the critical micelle concentration) is usually used. However, here a higher concentration is needed to ensure adequate conductivity in the electrochemical deposition system.[9] In this chapter, we thus reported the effect of stabilisers on electrochemical synthesis of magnesium nanoparticles. Cationic, anionic and non-ionic surfactants/stabilisers as well as their combinations were investigated. The various hydrogen storage properties of magnesium products with these diverse surfactants/stabilisers were also investigated in order to determine potential trends and the best combination.

5.2 Experimental section

5.2.1 Chemicals

The magnesium plate and ribbon as well as platinum mesh were purchased from Goodfellow. MgBu_2 in heptane (1.0 M), tetrabutylammonium trifluoromethane sulfonate (TBATFMS), sodium dodecylbenzenesulfonate (SDBS), 1-dodecanethiol (DDT) and poly(methylmethacrylate (PMMA) were purchased from Sigma-Aldrich and tetrabutylammonium bromide (TBAB) from Fluka (Figure 5-1). The solid surfactants/stabilisers were dried on Schlenk line before using to remove the moisture.

Tetrahydrofuran (THF) was purchased as HPLC grade from Fisher Scientific and dried using a LC Technology SP-1 solvent purification system.

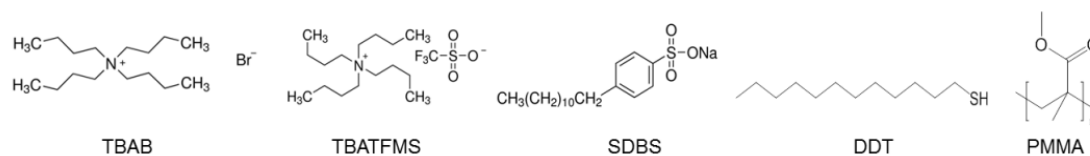


Figure 5-1: The surfactants/stabilisers used in electrochemical deposition process.

5.2.2 Synthetic methodology

Following the concept of Reetz,[1] a cationic surfactant would adsorb at the surface of a cathode to form a protective layer preventing the direct deposition of the metal at the working electrode (Figure 5-2). Accordingly, the nature of the surfactant should influence the deposition process of the magnesium precursor and allow the formation of “free standing” Mg particles. [10,11]

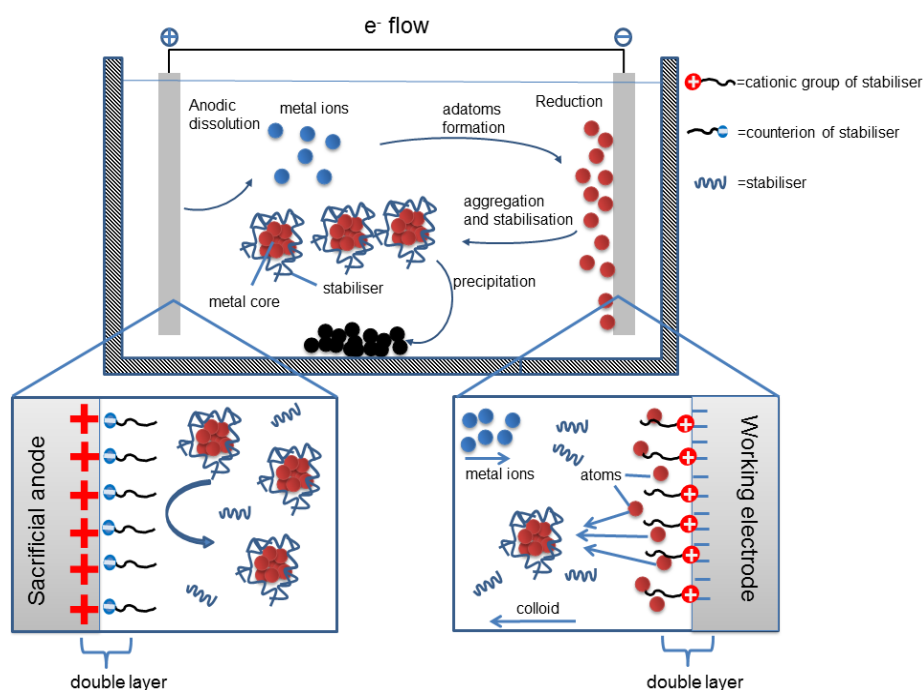


Figure 5-2: Schematic representation of surfactants/stabilisers functionalisation in an electrochemical system.[12]

On the other hand, the counterions of the surfactants would adsorb on the counter electrode to suppress the reoxidation of stabilised metal clusters suspended in electrolyte. In contrast, non-ionic stabilisers would tend to suspend in solution, and thus have little interaction with the electrodes.

Magnesium nanoparticles were prepared in an electrochemical cell with the Mg plate acting as a sacrificial anode, Pt mesh as a working electrode and a Mg ribbon as the reference electrode. The dimension of working and counter electrodes was 3 cm × 5 cm, with an area of 15 cm². The typical electrolyte consisted of 100 mL THF with 20 mM stabiliser and 20 mM MgBu₂, while for PMMA, a concentration of polymer of 1 mg·mL⁻¹ was used due to the limited solubility. Electrochemical deposition was performed by applying a current of -5 mA between the working and counter electrodes using a Biologic VMP3 potentiostat with vigorous stirring. Other compositions of electrolyte and electrolysis currents were also investigated to determine the influence on the morphology and hydrogen storage properties of the synthesised Mg. The conditions of magnesium deposition are summarised in Table 5-1.

Cationic, anionic and non-ionic stabilisers have been used to investigate the effect of the charge of headgroups on the electrodeposition process.[11] As discussed in Chapter 3, TBATFMS, SDBS and PMMA have shown their capability to form loose magnesium deposits with different morphologies. Since the counterions of the surfactants will influence the flux of particles toward the counter electrode, [13] TBAB and TBATFMS with different counterions were also investigated. As an anionic surfactant, SDBS was reported to generate metal deposits with distinct morphology compared to cationic surfactants as a strong interaction exists between metal ions and DBS⁻ ions due to their reverse charges.[14] For DDT, it is reported that the non-ionic stabiliser could cap and stabilise nanoparticles effectively,[15,16] but the properties of stabilisation in an

electrochemical deposition system has not been investigated. PMMA was also used to investigate the effect of non-ionic stabiliser. [17-19]

Table 5-1: Electrochemical deposition conditions of magnesium nanoparticles.

	Stabiliser (mM)					Current (mA)
	TBAB	TBATFMS	SDBS	DDT	PMMA (mg·ml ⁻¹)	
Single stabiliser	20	-	-	-	-	-5
	-	20	-	-	-	-5
	-	-	20	-	-	-5
	-	-	-	20	-	-5
	-	-	-	-	1	-5
Combination of stabilisers	10	-	10	-	-	-5
	-	10	10	-	-	-5
	-	10	10	-	1	-5
	-	10	10	-	1	-10
	-	10	10	-	1	-20

After electrolysis, the products were collected by centrifugation and sonicated, and then washed with THF three times. The samples were centrifuged and dried under vacuum on a Schlenk line at 80 °C overnight to remove any residual THF.

5.3 The thermal stability of stabilisers

The electrochemical stability of stabilisers has been discussed in Chapter 3. The thermal stability of each stabiliser is illustrated by the TGA-DSC-MS profiles (Figure 5-3). The

first two endothermic peaks in the DSC trace of TBAB correspond to its melting, and it is decomposed at 250 °C. TBATFMS is more stable and decomposes completely at 350 °C. The mass loss of SDBS started at 400 °C, the residual mass after decomposition is 70 %, which means that some Na₂SO₄ residue remains. DDT decomposed at 228 °C, with an associated endothermic peak in the DSC trace corresponding to the transition from liquid to gaseous decomposition products. PMMA has a broad endothermic area around 200 °C corresponding to melting, and the decomposition occurs at 375 °C.

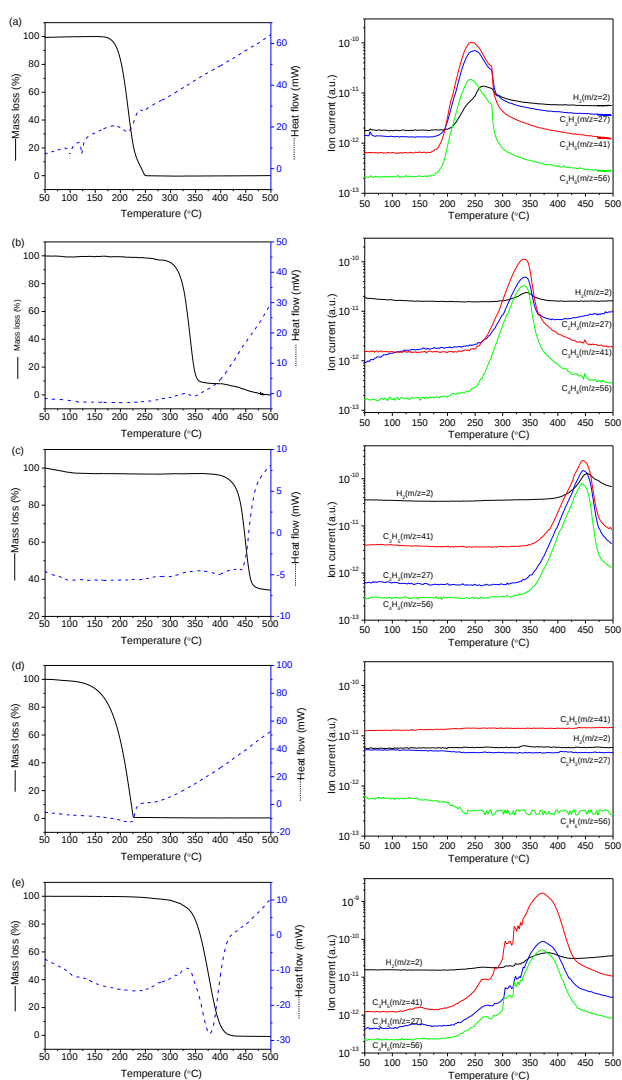


Figure 5-3: Thermal decomposition of (a) TBAB, (b) TBATFMS, (c) SDBS, (d) DDT and (e) PMMA measured by TGA-DSC-MS at a heating rate of 10 °C·min⁻¹ under a 20 mL·min⁻¹ flow of Ar.

The mass spectra of the thermal decomposition process of stabilisers exhibit that most of them release C_2H_3 , C_3H_5 and C_4H_8 fragments from the carbon chain, and the intensity overlaps the hydrogen peak. Table 5-2 summarised the temperature of the decomposition point of stabilisers and the possible bonds formed between these stabilisers and the magnesium surface.

Table 5-2: The temperature of decomposition of selected stabilisers and the possible bonds formed with Mg.

Stabiliser	Decomposition temperature (°C)	Bonds potentially formed with Mg
TBAB	250	Mg-Br
TBATFMS	325	Mg-F
SDBS	400	Mg-SO ₃
DDT	228	Mg-S
PMMA	375	Mg-O

5.4 Magnesium deposited with single stabiliser

5.4.1 Morphology

The morphologies of final products with a single stabiliser as determined by TEM are shown in Figure 5-4. The Mg nanoparticles obtained had irregular morphologies. In particular, both TBAB and TBATFMS are cationic surfactants, while leading to different morphologies of electrodeposited Mg. The sample deposited with TBAB showed relatively isolated particles with a particle size of ~20 nm, while with TBATFMS, only a large “flake” like structure was observed with hexagonal shape. This

indicated that the counterions Br^- and TFMS^- significantly influenced the electrolysis process.

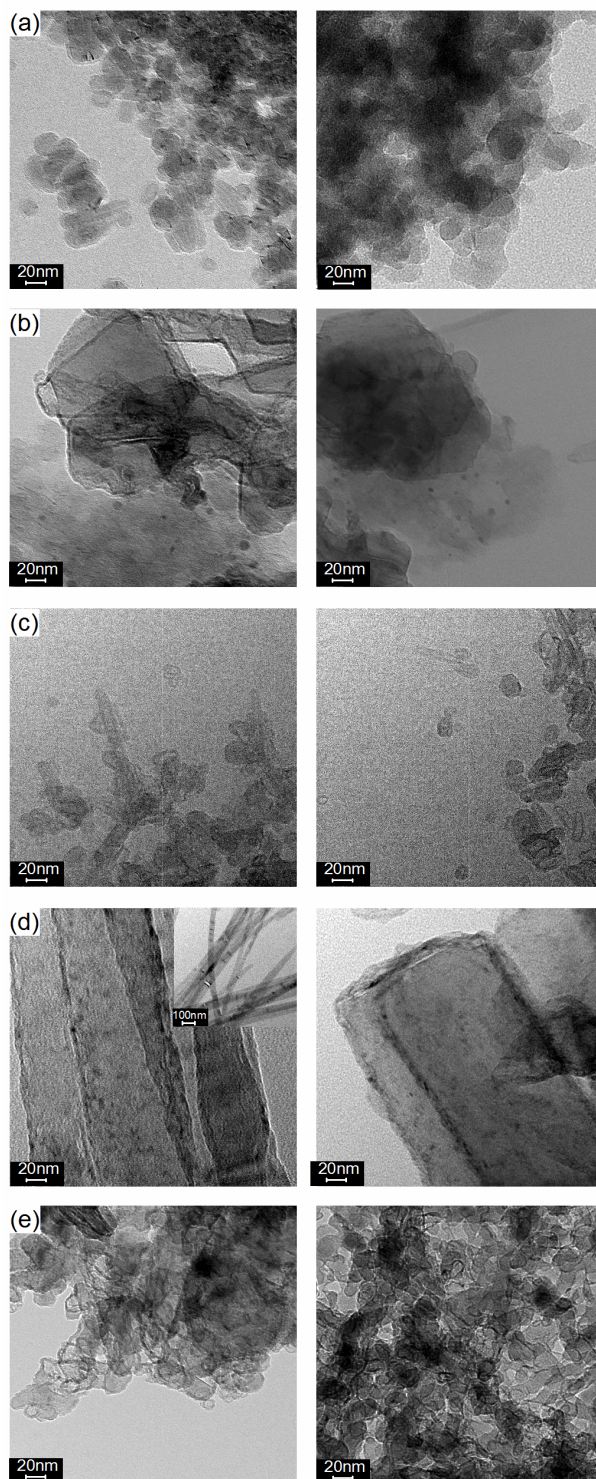


Figure 5-4: TEM images of as-prepared (left) and hydrogenated (right) magnesium deposits with (a) TBAB, (b) TBATFMS, (c) SDBS, (d) DDT and (e) PMMA.

With anionic SDBS, the morphology of the electrosynthesised Mg was aggregated particles with irregular appearance. In the electrolyte with DDT, the long “belt” shape with a width of 100 nm was obtained, and with PMMA, heavily aggregated Mg particles were formed with size ranging 20~30 nm. The results are far from the magnesium nanoparticles generated from chemical reduction routes, which usually have regular shape and uniformly distributed size.[19-21] Such difference should be ascribed to the heterogeneous nucleation process involved in electrodeposition, which is significantly influenced by the deposition conditions.

Furthermore, it can be expected that the counterions of the surfactants interact with Mg^{2+} to influence the magnesium deposition process as previously observed.[14] According to the cyclic voltammograms of TBAB, TBATFMS and SDBS with MgBu_2 (Chapter 3), it is obvious that TBATFMS leads to an easier deposition of magnesium which means that TFMS^- binds less to Mg^{2+} , and thus Mg grows freely along the preferable orientation [002] to generate a hexagonal flake-like morphology.[22,23] The belt shape of the Mg deposits produced with DDT should also be attributed to the thiol group controlling the growth direction of Mg at the electrode surface.[24] PMMA should not have any strong interaction with Mg^{2+} . Hence, the long chain of polymer and carbonyl groups should stabilise Mg deposits at relatively small particle size. The morphology of the magnesium nanostructures does not change significantly after being hydrogenated at 100 °C, as such low temperature for hydrogen absorption does not lead to severely recrystallisation (Figure 5-4).

5.4.2 Structural identification

XRD was carried out to characterise the magnesium materials treated at 80 °C under vacuum before hydrogenation. The diffraction patterns are shown in Figure 5-5a. All of

the as-prepared samples showed diffraction peaks mainly from the hexagonal magnesium phase, which indicated the successful deposition from MgBu_2 during the electrodeposition process.

After being hydrogenated at 100 °C, most of these materials did not convert to MgH_2 except with PMMA (Figure 5-5b), where 70.2 % $\beta\text{-MgH}_2$ was formed according to the Rietveld refinement of XRD pattern. Small diffraction peaks corresponding to Na_2SO_4 in Mg synthesised with SDBS were also observed, and this was derived from Na^+ and the $-\text{SO}_3$ group from SDBS. The poor hydrogen absorption property at low temperature can be attributed to passivated Mg surfaces covered by organic entities generated during electrolysis. As for PMMA, remaining in solution may lead to better stabilisation of Mg nanoparticles and hydrogen properties, which is similar to polymers modified Mg nanoparticles reported before.[19,25]

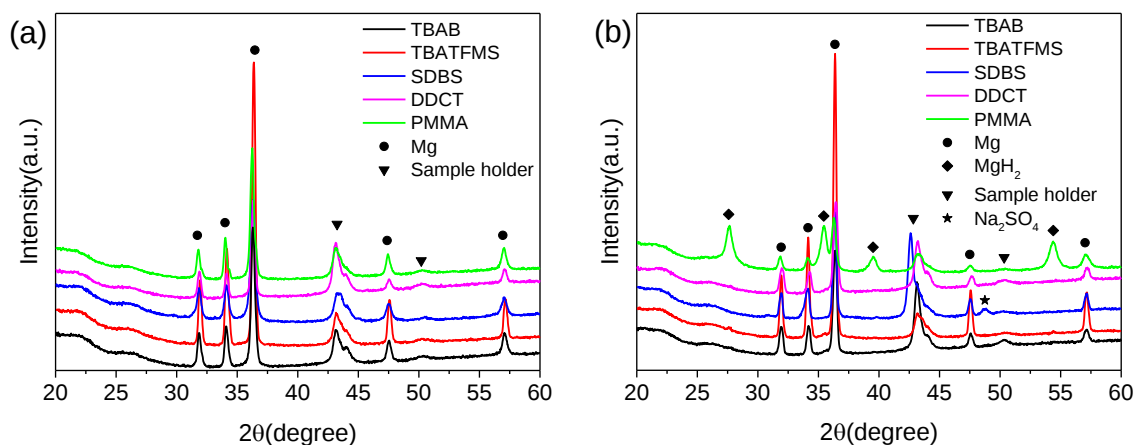


Figure 5-5: XRD patterns of products (a) as-prepared and (b) after being hydrogenated at 100 °C with single stabiliser.

The crystallite size of magnesium nanostructures before and after hydrogenation was calculated according to the XRD patterns following the Scherrer equation (Table 5-3). The results demonstrate that the deposits with various stabilisers possessed similar crystallite size ranging from 20 to 30 nm. After being hydrogenated at 100 °C, the

crystallite size grew a little which might be ascribed to the weak recrystallisation of nanoparticles.

Table 5-3: Crystallite size of magnesium nanostructures with single stabiliser before and after hydrogenation, as well as the conversion rates from Mg to MgH₂.

Stabilisers	Crystallite size of Mg nanostructures (nm)		Conversion rate from Mg to MgH ₂ (%)
	as-prepared	hydrogenated	
TBAB	25.2 ± 1.7	26.3 ± 2.3	0
TBATFMS	27.2 ± 2.0	30.5 ± 2.5	0
SDBS	21.7 ± 2.6	26.4 ± 3.2	0
DDT	22.6 ± 3.4	24.7 ± 2.2	0
PMMA	21.8 ± 3.1	23.4 ± 1.6	70.2

5.4.3 Hydrogen desorption properties of Mg deposits with PMMA

As only Mg nanoparticles prepared with PMMA showed MgH₂ phase after hydrogenation, the TGA-MS profiles were just taken for this sample. In Figure 5-6a and b, the mass loss and mass spectra demonstrate that in the as-prepared sample, there were impurities adsorbed on surface of Mg nanoparticles even after drying. The first mass loss observed at 200 °C corresponded to the decomposition of the butyl group from MgBu₂ as the peaks of fragments $m/z = 27, 41$ and 56 showed in mass spectra.[26] The subsequent mass loss around 400 °C should be ascribed to the decomposition of adsorbed PMMA, the temperature range fitted well to the thermal decomposition of PMMA characterised in Figure 5-3e.

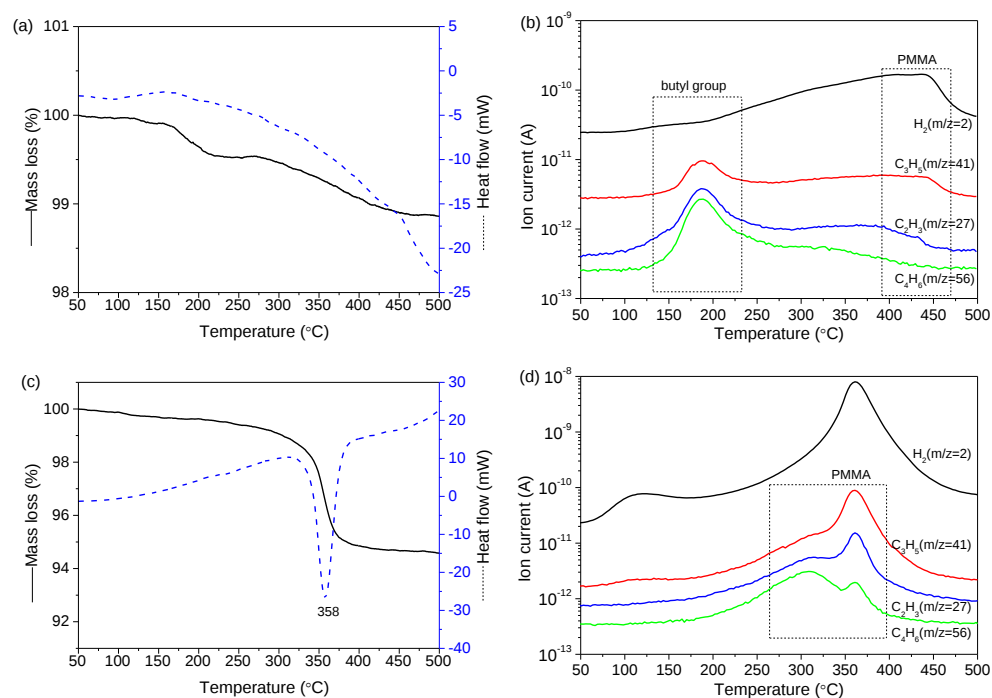


Figure 5-6: TGA-MS profiles of products with PMMA (a, b) as-prepared and (c, d) after being hydrogenated at 100 °C respectively.

The hydrogen desorption temperature after hydrogenation showed a hydrogen peak at 358 °C, similar to that observed for ball milled MgH_2 . The mass loss around 200 °C disappeared which implied that the butyl group from $MgBu_2$ was eliminated during the vacuum cycling and after the hydrogenation process. The impurities ascribed to adsorbed PMMA were released with the hydrogen flux, while the intensity of the strongest C_3H_5 was still two orders of magnitude lower than H_2 , this result indicated that at least 99 % of hydrogen was attributed to the decomposition of MgH_2 . The hydrogen capacity of magnesium nanoparticles produced with PMMA is about 4.5 mass% after 100 °C hydrogenation according to the mass loss before and after hydrogenation, which fits very well to the phase analysis from the XRD diffraction pattern. Compared with magnesium-based hydrogen storage materials reported before, which required catalysts such as Mn/Zr[27], Ni[28] to achieve low absorption temperature, electrochemically

deposited Mg with PMMA behaved in a similar manner. High hydrogen desorption temperature was also observed in polymer modified magnesium nanoparticles due to the larger magnesium particles formed and/or the polystyrene coating.[25,29]

In conclusion, PMMA is the best single stabiliser to prepare Mg nanoparticles with MgBu_2 , and the type of stabiliser drastically affects the morphologies and hydrogen storage properties of the final products.

5.5 Improvement through a combination of stabilisers

In several studies of chemical reduction to produce metal nanoparticles with different morphologies,[8,30] a combination of cationic and anionic stabilisers was used in this section to modify and control reactions at both working and counter electrodes. Hence, in an electrochemical system, anionic stabilisers can adsorb on the anode to form a layer preventing re-oxidation of as-synthesised metal nanoparticles, and also inhibiting the degradation of solvent and counterions. As TBAB would react with SDBS to form the white precipitate NaBr, both stabilisers were first mixed and NaBr was removed by centrifugation, then MgBu_2 was added to form an electrolyte. An alternative was to use a mixture of TBATFMS and SDBS since they did not react together. The addition of PMMA to form a TBATFMS/SDBS/PMMA compositions electrolyte was also investigated to have PMMA further stabilising any Mg particles in solution.

5.5.1 Morphology

TEM images shown in Figure 5-7 indicate that the morphologies of the Mg deposits with TBAB/SDBS was not leading to isolated particles as a single TBAB, but to the formation of “rod-like” structures. Hexagonal shape magnesium crystals (Figure 5-7b) were formed when TBATFMA/SDBS mixture was used. This means that magnesium grew on the electrode surface with a preferable orientation, such performance would

result in poor hydrogen storage properties as hydrogen was hard to diffuse through the [002] plane (marked with red dash in Figure 5-7b).[31] The shape of deposits with TBATFMS/SDBS was similar to that with TBATFMS alone (Figure 5-5b), which implied that the TFMS⁻ dominated the morphology of Mg. For triple compositions of TBATFMS/SDBS/PMMA, the magnesium product possessed less aggregation compared to single PMMA (Figure 5-5e). Hence the synergistic effect of three compositions inhibited the formation of large Mg agglomerates.

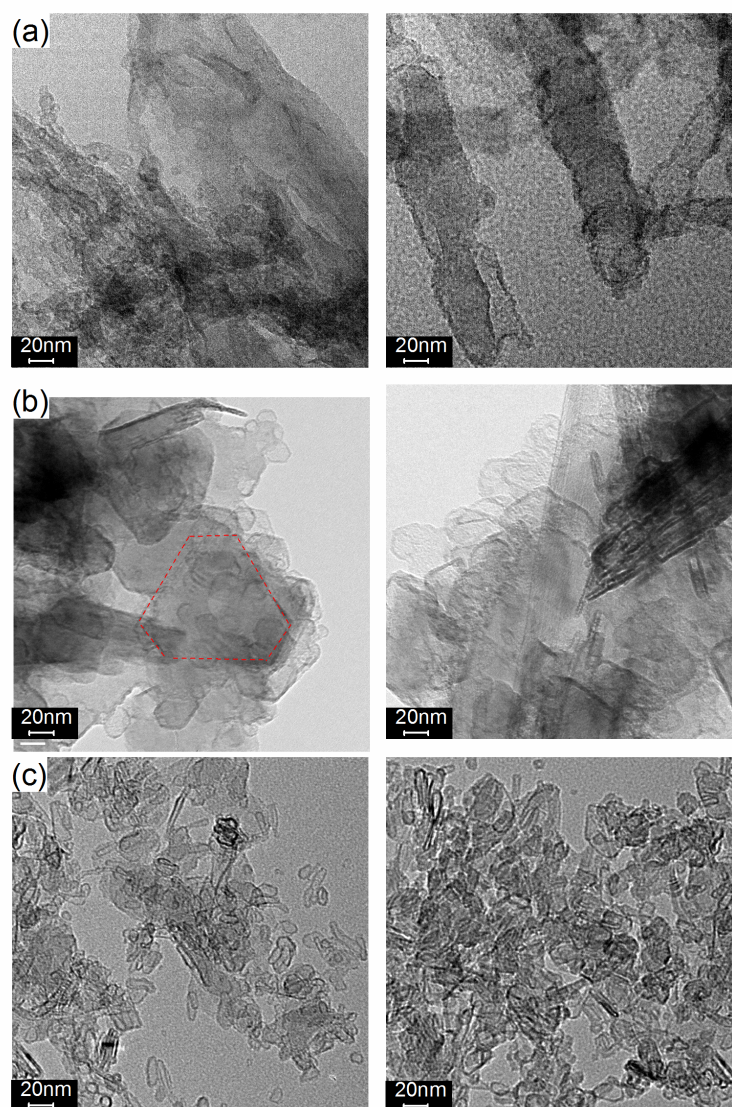


Figure 5-7: TEM images of as-prepared (left) and hydrogenated (right) magnesium deposits with (a) TBAB/SDBS, (b) TBATFMS/SDBS, (c) TBATFMS/SDBS/PMMA.

5.5.2 Structural identification

With the combinations of these stabilisers, a small amount of MgH_2 phase could be formed in hydrogenated Mg nanoparticles prepared with TBAB/SDBS and TBATFMS/SDBS (Figure 5-8). However, when adding PMMA to form the triple compositions electrolyte, a much higher conversion from Mg to MgH_2 was achieved (85.8 %) after hydrogenation at 100 °C. This result demonstrates that the existence of PMMA in electrolyte helps stabilise the surface of magnesium prior to the adsorption of cationic and anionic surfactants.

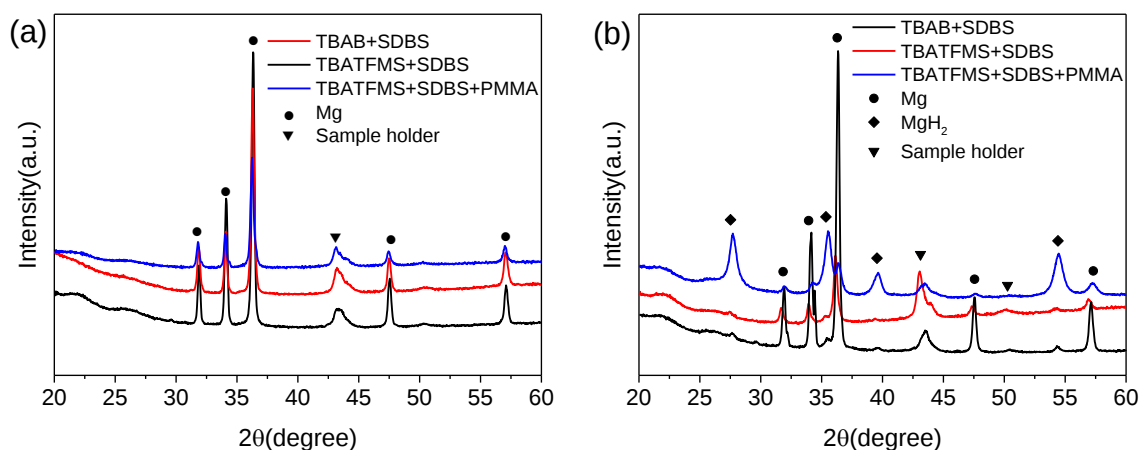


Figure 5-8: XRD patterns of products (a) as-prepared and (b) after hydrogenation at 100 °C with stabilisers combination.

The crystallite size of magnesium nanostructures before and after hydrogenation calculated in Table 5-4 showed that the deposits from the triple stabilizer compositions led to much smaller Mg crystals after hydrogenation, which could be explained by the easier hydrogenation observed. The hydrogen diffused into as-synthesised magnesium crystallite, then the magnesium phase was substituted for the formation of the magnesium hydride phase to decrease the size of Mg. The crystallite size growth for the other two samples might be ascribed to the recrystallisation of nanoparticles.

Table 5-4: Crystallite size of magnesium nanostructures with stabilisers combination before and after hydrogenation, as well as the conversion rates from Mg to MgH₂.

Stabilisers	Crystallite size of Mg nanostructures (nm)		Conversion rate from Mg to MgH ₂ (%)
	as-prepared	hydrogenated	
TBAB/SDBS	34.2 ± 2.1	35.1 ± 3.3	5.3
TBATFMS/SDBS	31.3 ± 3.7	32.5 ± 2.4	6.1
TBATFMS/DSBS/PMMA	28.3 ± 1.2	18.7 ± 1.7	85.8

5.5.3 Hydrogen desorption properties of Mg deposits with stabilisers combinations

After hydrogenation, the clear hydrogen desorption peaks in TGA-MS profiles demonstrated the hydrogen desorbing from MgH₂ and the different desorption temperatures among stabilisers combinations (Figure 5-9).

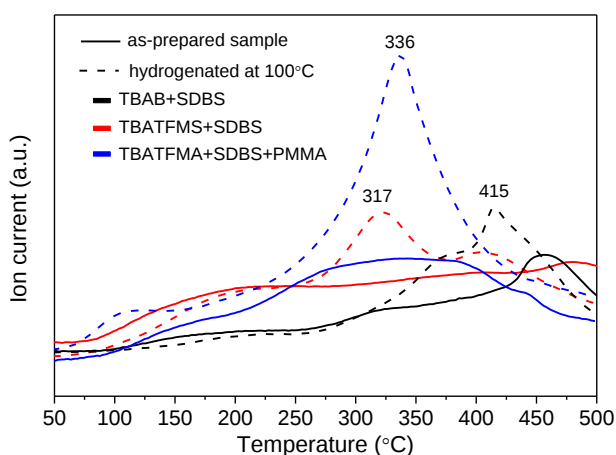


Figure 5-9: Hydrogen desorption profiles of as-prepared and hydrogenated products with stabilisers combinations.

With TBAB/SDBS, the temperature of the main H₂ peak was 415 °C, even higher than bulk Mg, which suggested that the combination of TBA⁺ and DBS⁻ was negative for Mg

deposited with MgBu_2 as a precursor. The product from the TBATFMS and SDBS combination displayed a relatively low hydrogen desorption peak at 317 °C, almost 100 °C lower than that with TBAB/SDBS. Such a decrease of temperature suggested the importance of the stabiliser type, and the TFMS⁻ ions in helping with the stabilisation of Mg nanoparticles. In contrast, TBATBMS/SDBS/PMMA combined the advantage of a low desorption temperature from TBATFMS/SDBS and a high conversion rate from PMMA. The 336 °C desorption temperature was 20 °C lower than using PMMA alone.

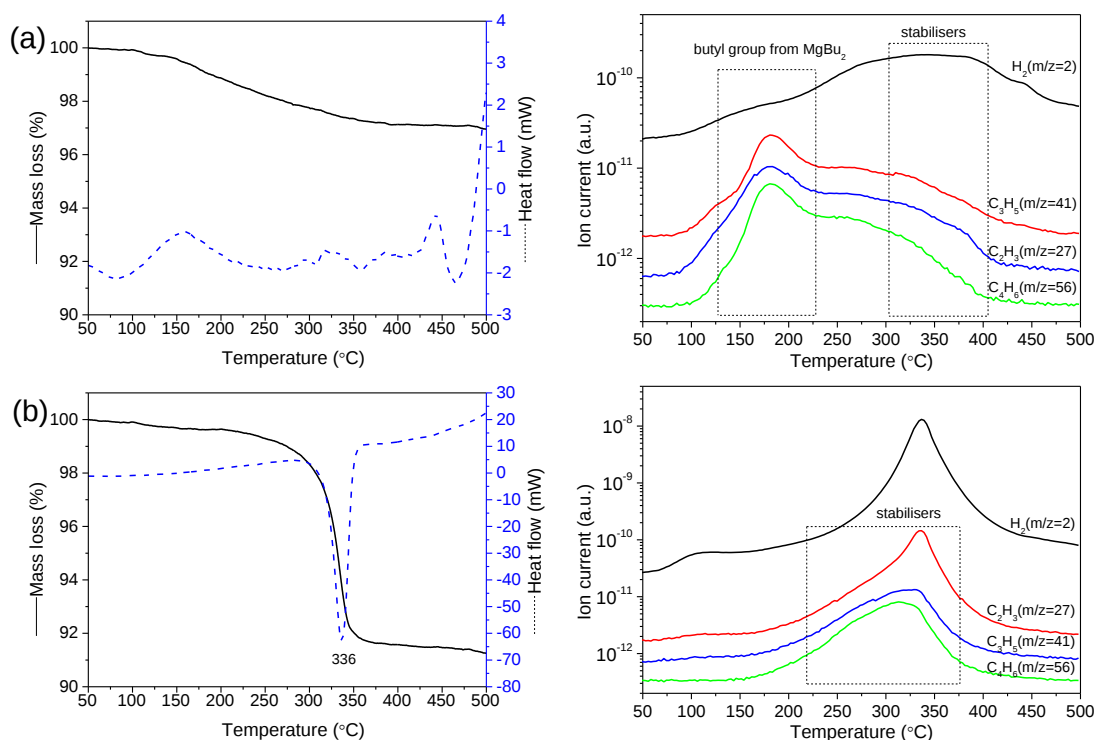


Figure 5-10: TGA-DSC-MS of (a) as-prepared and (b) after hydrogenation at 100 °C magnesium particles with TBATFMS/SDBS/PMMA at 5 mA.

The mass loss of the as-prepared sample with TBATFMS/SDBS/PMMA (Figure 5-10a) demonstrated that there were more impurities ~4 mass% adsorbed on the Mg particles in addition to PMMA. This confirmed that although the electrolyte containing TBATFMS and SDBS generated more adsorbents on the Mg surface, PMMA could

eliminate the influence to hydrogen absorption significantly. It can be concluded that the interaction between PMMA and Mg was stronger than TBATFMS and SDBS which might be attributed to its carboxyl groups.[19] The hydrogen capacity of magnesium nanoparticles is about 5.6 mass% after 100 °C hydrogenation according to the mass loss before and after hydrogenation.

In conclusion, the combination of cationic and anionic surfactants could only improve the hydrogen storage properties of electrochemically deposited Mg nanoparticles in a limited way. The counterion type influenced hydrogen desorption temperature effectively, and the existence of PMMA led to a specific morphology of Mg deposits. TBATFMS/SDBS/PMMA triple compositions electrolyte achieved the highest conversion rate from Mg to MgH₂ after being hydrogenated at 100 °C and the desorption temperature was improved compared to single PMMA.

5.6 Optimisation of the triple stabilisers TBATFMS/SDBS/PMMA

The results analysed above illustrated that a TBATFMS/SDBS/PMMA combination is a suitable electrochemical system to produce Mg nanoparticles. In this section, current density was modified to investigate the influence on morphology and hydrogen storage properties. The currents used to deposit Mg were set at 5, 10 and 20 mA.

5.6.1 Effect of current densities

The morphology evolution is shown in Figure 5-11. TEM images indicate that the isolated magnesium particles could be generated with different currents, although they were aggregated and the shape of deposits was more regular with high current, while the particle size remained at ~20 nm. This suggested that the triple compositions electrolyte was able to stabilise the deposits effectively under different current densities.

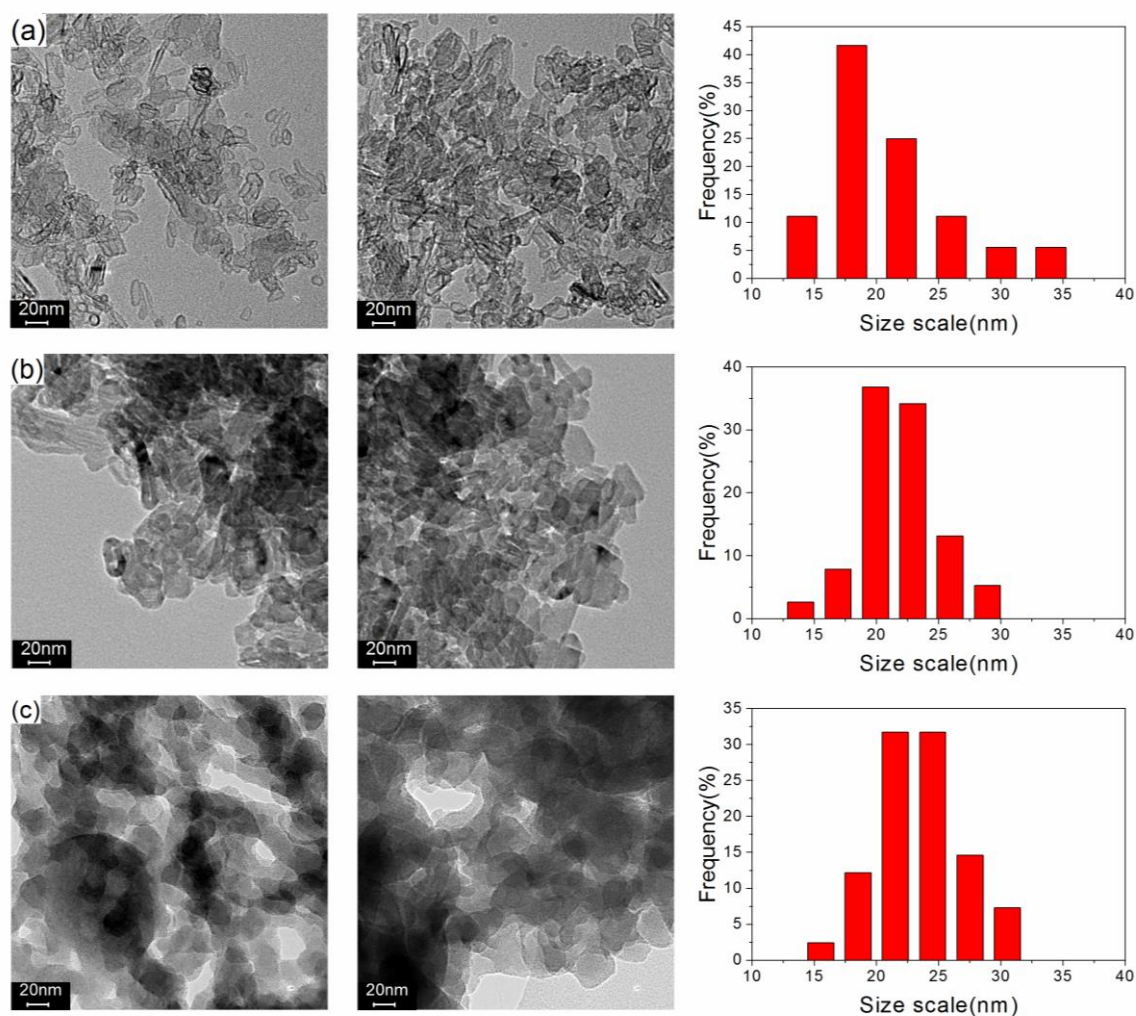


Figure 5-11: TEM images of as-prepared (left) and hydrogenated (right) magnesium particles with (a) 5 mA, (b) 10 mA, (c) 20 mA current in TBATFMS/SDBS/PMMA electrolyte.

5.6.2 Structural identification

XRD patterns of hydrogenated magnesium particles with TBATFMS/SDBS/PMMA at different currents demonstrated that the conversion rate of Mg to MgH_2 is lower when the current increased (Figure 5-12 and Table 5-5). This phenomenon could be explained in that more impurities were generated during electrolysis with higher current density. A contamination and passivation of the Mg surface would lead to a more difficult absorption process at the Mg surface.[32,33]

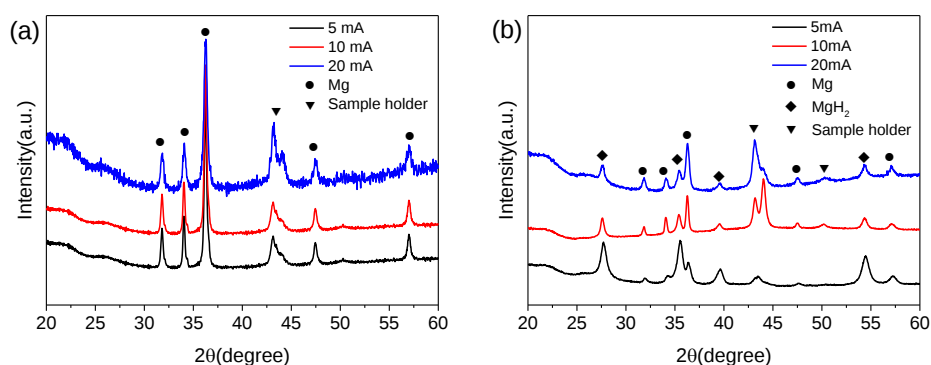


Figure 5-12: XRD patterns of magnesium particles with TBATFMS/SDBS/PMMA at different currents (a) as prepared and (b) after hydrogenation at 100 °C.

The crystallite size of the as-prepared Mg nanoparticles was smaller when using 20 mA deposition current (Table 5-5). This is in agreement with previous reports on electrochemical synthesised noble and transition metal nanoparticles.[12]

Table 5-5: Crystallite size of magnesium nanostructures with different currents before and after hydrogenation, as well as the conversion rates from Mg to MgH₂.

Currents	Crystallite size of Mg nanostructures (nm)		Conversion rate from Mg to MgH ₂ (%)	Crystallite size of MgH ₂ (nm)
	as-prepared	hydrogenated		
5 mA	28.3 ± 3.1	18.7 ± 2.7	85.8	12.5 ± 1.5
10 mA	25.1 ± 2.3	22.4 ± 2.4	65.3	15.6 ± 1.3
20 mA	21.9 ± 3.2	24.2 ± 2.3	47.4	17.4 ± 1.8

5.6.3 Effect of current densities to hydrogen sorption properties

The mass loss of the as-prepared nanoparticles produced with 10 mA and 20 mA was 6.5 and 11 mass%, respectively (Figure 5-13a and c), which increased significantly compared to 5 mA which was only 4 mass%.

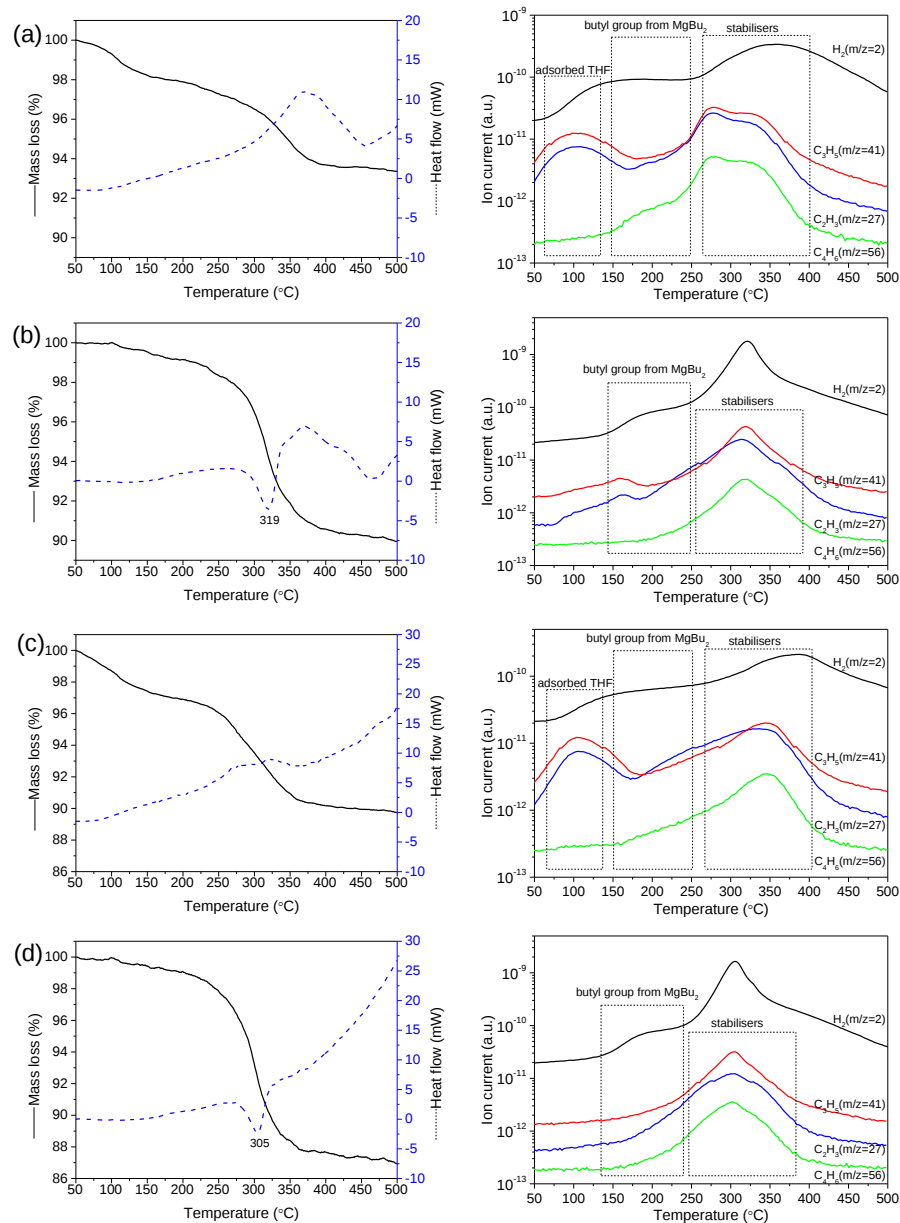


Figure 5-13: TGA-DSC-MS of (a) as-prepared and (b) hydrogenated at 100 °C magnesium particles with TBATFMS/SDBS/PMMA at 10 mA. The same material synthesised at 20 mA (c) as-prepared and (d) hydrogenated at 100 °C.

There are two main mass loss steps observed in as-prepared samples by TGA (Figure 5-13 a and c). The initial mass loss at 100 °C should be attributed to the release of adsorbed THF. This was different from product prepared with 5 mA which did not show any THF peak. Such phenomenon indicated that the high current tends to generate more

impurities on Mg surface; as a result, THF would bind in the final product. The later mass loss step consisted of decompositions of the butyl group from MgBu_2 around 200 °C and the impurities from stabilisers around 350 °C.

Magnesium particles deposited with higher currents displayed a lower desorption temperature after being hydrogenated at 100 °C (Figure 5-13 b, d). With 10 mA, 3.5 mass% hydrogen capacity desorbed at 319 °C, and for 20 mA, the hydrogen desorbed at 305 °C with 3.3 mass%. It is impressive that the desorption temperature with 20 mA current was 30 °C lower than that from 5 mA, the improvement should be ascribed to the smaller crystallite size achieved at higher current density (28.3 ± 3.1 nm at 5 mA versus 21.9 ± 3.2 nm at 20 mA). These results also implied that impurities on the magnesium surface did not influence the hydrogen desorption process significantly, while mainly inhibiting the hydrogen absorption step. This is far from having the magnesium surface passivated by an oxide layer, where higher desorption temperature (~ 20 °C) is required to release hydrogen than pristine MgH_2 . [29]

5.6.4 The hydrogen sorption properties at low temperature for Mg deposited with 5 mA

TBTFMS/SDBS/PMMA stabilisers combination also exhibited favourable hydrogen sorption properties at low temperatures as Figure 5-14 showed. Even at room temperature, hydrogen could be absorbed and then released at 256 °C. When the absorption temperature increased, the desorption temperature rose as well. This was understood by the fact that the hydrogenation process starts at the surface of Mg. At high temperature more hydrogen would be absorbed in the magnesium core. [34] When hydrogen is released, the curves of the hydrogen desorption profile almost overlapped with each other at the initial stage, which demonstrate a similar desorption process. A

higher temperature is then needed to release H₂ from the Mg core. This may be an indicator of binding energies of H₂ in nanosized Mg, the same result has been observed in Pd.[35,36]

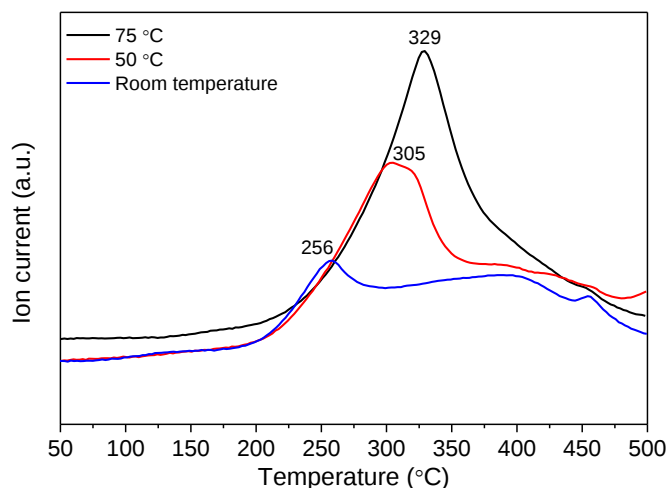


Figure 5-14: Hydrogen desorption profiles of magnesium particles produced with 5 mA in TBATFMS/SDBS/PMMA electrolyte after being hydrogenated at different temperatures.

In conclusion, the triple compositions electrolyte consisting of TBATFMS, SDBS and PMMA could effectively stabilise the magnesium nanoparticles generated via electrochemical deposition, while at higher current, more impurities adsorbing on the magnesium surface degraded the hydrogen absorption properties. However, hydrogen desorption was improved as smaller magnesium crystallites were prepared. Hence the effect of current density requires comprehensive evaluation based on which kind property is to be enhanced.

5.7 Discussion

The electrochemical reduction method proved to be an effective pathway for producing magnesium nanoparticles. Investigation in this chapter showed that with different stabilisers or their combinations, metallic Mg nanoparticles with distinct morphologies

could be generated using MgBu_2 as a precursor. Although the electrolytes contained the same TBA^+ as cationic ion when using TBAB, TBATFMS, TBAB/SDBS, TBATFMS/SDBS and TBATFMS/SDBS/PMMA as stabilisers, the different counterions influenced the morphologies of final products. Such effect can be explained by the adsorption of stabilisers on the electrode surface, which modifies the deposition and aggregation process of metal nanostructures.[13,37] For DDT, the explanation of the long belt shape is that the long chain of DDT adsorbed on the working electrode surface limited the growth direction of Mg as a template.[38] The existence of PMMA remaining in solution resulted in the deposited magnesium maintaining similar morphologies even mixed with TBATFMS and SDBS in electrolyte. Such phenomenon suggests that PMMA has stronger interaction with Mg nanoparticles than those two surfactants although the concentration of PMMA was relatively low ($1 \text{ mg}\cdot\text{mL}^{-1}$).

Metal nanoparticles produced via the chemical reduction method can obtain isolate particles with distinct morphologies while the size distribution was almost uniform.[10,39-41] However, the magnesium particles produced with electrodeposition are aggregated rather than isolated no matter with which kind of supporting electrolyte. As previously reported, the stabiliser type, as well as the ratio between precursor and stabiliser will influence the morphology of final products from electrodeposition. [41,42] Furthermore, mixed surfactants were also used to control the nucleation process of deposition and obtain products with various shape and size. [30,43]

The aggregation of electrodeposited magnesium nanoparticles seems hard to avoid compared to transition metals such as Ni, Pt and Pd,[2,3] even with sonicate during electrolysis as done by Haas *et al.*[6] Generally, the aggregation of nanoparticles is ascribed to the high surface energy, as a result, the surface must be passivated by capping agents (e.g. stabiliser) during synthesis and the growth of the particles is

suppressed.[44] However, the real mechanism is more complicated,[45] Ni and Pd with higher surface energy than Mg are still stabilised by capping agents effectively.[46] The main factor of magnesium nanoparticles aggregation should be that the low reduction potential of Mg leads to a large amount of stabiliser molecules adsorbing on the working electrode surface. The inhibiting layer reduces Mg^{2+} ion access to the electrode and causes high overpotential to deposit Mg, thus the as-reduced Mg particles adhere to the electrode surface firmly becoming hard to remove, then agglomerate during subsequent deposition.[47] For transition metals, the high reduction potential does not have such a significant effect for the stabiliser, the interaction between particles and working electrode surface is much weaker as well.

The hydrogen absorption of deposited magnesium at 100 °C was only achieved by PMMA among five single stabilisers. The poor absorption property of the other four should be ascribed to the magnesium passivated by the function groups in stabilisers. The bromine, fluorine as well as sulphur in sulphonate and thiol groups will form hydrogen-inactive compounds with magnesium.[48,49] Non-ionic polymer PMMA significantly improved hydrogen storage properties of deposited Mg due to its structure and functional group. On the other hand, improvement of PMMA might be ascribed to the electrochemical stability of polymer which generated less impurity to contaminate the Mg surface. The residual Mg in 100 °C hydrogenated sample and the corresponding high desorption temperature indicated that the kinetics is still slow; one possible explanation is that the aggregation of nanoparticles decreased the diffusion rate of hydrogen. Such result is similar to hexadecylamine (HDA) stabilised Mg nanoparticles, which were fully hydrogenated at 118 °C, while the major desorption was observed around 350 °C because of sintering of Mg nanoparticles.[25]

The combination of TBSTFMS and SDBS was capable of decreasing the hydrogen desorption temperature of deposited Mg nanoparticles to 317 °C on TGA after hydrogenation at 100 °C. This was quite low compared to magnesium without catalyst,[27,50] while still higher than that of well controlled ultra-small magnesium nanoparticles.[19] The contamination from electrolyte derived from long deposition duration that limited the kinetics of the hydrogen sorption process, which made the transformation from Mg to MgH₂ very hard at low temperature. The existence of PMMA in triple TBSTFMS/SDBS/PMMA electrolyte improved the hydrogen sorption properties significantly, which demonstrated that the strong interaction between PMMA and Mg reduced the effect from ionic surfactants. Compared with single PMMA, the protective layers formed on working and counter electrodes by TBATFMS and SDBS also help to prevent further oxidation or growth of as-prepared magnesium particles with electrostatic repulsion, which led to more stable nanostructure during electrolysis.[45,51]

The hydrogen absorption at temperatures lower than 100 °C demonstrated that the magnesium nanoparticles generated from TBATFMS/SDBS/PMMA system could achieve excellent hydrogen storage properties. The route to realise such performance with high hydrogen capacity is synthesising uniformly distributed nanoparticles without firm aggregation. However, if without protective layer or stable additives such as transition metals or metal oxides, once subjected to heat and the first hydrogen absorption/desorption cycle, nanostructured magnesium undergoes a major recrystallisation and consequently thermodynamic improvements have never been observed. [52,53] As a result, introducing stable additives to inhibit the aggregation and recrystallisation is necessary. An electrochemical codeposition method should be able to achieve this aim.

5.8 Conclusion

Magnesium nanoparticles were electrochemically deposited in electrolyte consisting of MgBu_2 as precursor and various compositions of stabilisers, while none of the samples presented isolated uniformly distributed nanoparticles. The morphology of magnesium deepened significantly on the type of stabiliser. The hydrogen sorption properties were poor for most of the products with a single stabiliser, even PMMA which showed high hydrogen absorption capacity at 100 °C still exhibited a high desorption temperature. The combination of stabilisers could improve hydrogen sorption properties to some extent, and when mixed with PMMA, the triple compositions TBATFMS/SDBS/PMMA combined advantages from each other and realised low hydrogen desorption temperature and high content of MgH_2 simultaneously after hydrogenation at 100 °C.

Furthermore, with the purpose of preparing magnesium nanostructures with better hydrogen storage properties, the morphology of deposits must be controlled to prevent aggregation. Catalysts can be introduced into the electrochemical deposition system to achieve this aim, meanwhile, the kinetics of hydrogen sorption must be improved.

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CHAPTER 6 ACHIEVING CATALYTIC MG/NI NANOCOMPOSITE BY ELECTROCHEMICAL SYNTHESIS

6.1 Introduction

The investigation of magnesium nanostructures deposited on the catalytic substrate Ni in Chapter 4 showed the synergistic effect of size reduction and catalysis for hydrogen storage. In this chapter, the aim is to optimise the amount of catalyst and modify the distribution of Mg and Ni nanostructures by electrochemical codeposition to improve the hydrogen storage properties of Mg.

The literature review about hybrid metals deposition in Chapter 2 indicated that electrochemical codeposition required close reduction potentials of metals, and this could be realised by the addition of surfactants.[1] There are several routes to forming nanocomposites depending on how the deposition sources are introduced in the electrochemical system. The simplest approach is by mixing soluble precursors to form an electrolyte and then apply a potential to obtain the final composite product.[2-6] Another approach is to add one of the precursors with nanoparticles seeds suspended in the electrolyte. When the electrolysis starts, the precursor dissolved in solution will be deposited on the suspended nanoparticles to form a composite material.[7-9] A sacrificial anode can also be used as a source of codeposition.[10] Magnesium codeposited with other metals has been achieved in molten salts but is still rare in organic solvent.[5,6,11]

In this chapter, we aim to develop a novel electrochemical approach to prepare Mg/Ni nanocomposite via a codeposition strategy. The magnesium precursor used to form electrolyte is magnesium borohydride ($\text{Mg}(\text{BH}_4)_2$), as other precursors such as di-*n*-butylmagnesium (MgBu_2) are not able to produce ideal Mg/Ni nanocomposites which

might be ascribed to the MgBu_2 requiring a lower reduction potential to be deposited in electrolyte with TBAB as discussed in Chapter 4. The composition of electrolyte and current density were modified to optimise the *in-situ* codeposition process. Furthermore, catalytic Ni and Nb_2O_5 (well-known catalysts for Mg) seeds were suspended into electrolyte to investigate the effect of external additives. The morphologies and hydrogen storage properties were characterised and compared for the composites. The Mg/Ni composites synthesised from the electrochemical codeposition route achieved low hydrogen sorption temperature and excellent hydrogen storage properties. The γ - MgH_2 formed during hydrogenation was also investigated to understand the mechanism of formation and decomposition, as well as the effect on hydrogen storage properties of the Mg/ MgH_2 system.

6.2 Experimental section

All operations were carried out under an inert atmosphere in an argon-filled LC-Technology glove box (< 1 ppm O_2 and H_2O).

6.2.1 Chemicals

$\text{Mg}(\text{BH}_4)_2$ was synthesised from MgBu_2 and $\text{BH}_3 \cdot \text{S}(\text{CH}_3)_2$ purchased from Sigma-Aldrich and tetrabutylammonium bromide (TBAB) from Fluka. Tetrahydrofuran (THF) was purchased as HPLC grade from Fisher Scientific and dried using a LC Technology SP-1 solvent purification system. Magnesium (Mg) plate, titanium (Ti) foil, and nickel (Ni) plate were purchased from Goodfellow. The surface of the Mg, Ni and Ti was polished with abrasive paper and washed with THF to remove the oxide layer. Nb_2O_5 was purchased from Merck and Ni nano particles were reduced from NiCl_2 by NaBH_4 as previously reported.[12]

6.2.2 Codeposition of magnesium and nickel to form Mg/Ni nanocomposite

The magnesium-nickel nanocomposite was electrochemically produced at a Ti foil (15 cm²). To this aim, a three electrodes cell was used with a Ni plate acting as sacrificial anode to produce Ni²⁺ ions. The Ti foil acted as the working electrode and a Mg ribbon as the reference electrode. The typical electrolyte consisted of 100 mL THF with 20 mM Mg(BH₄)₂ and 20 mM TBAB. TBAB was used to facilitate the deposition of the Mg nanoparticles and acted as a supporting electrolyte. Electrodeposition was performed by applying a current of 5 mA between the working and the counter electrodes using a Biologic VMP3 potentiostat. Other compositions of electrolyte and electrodeposition currents were also used to investigate the evolution of morphologies and hydrogen storage properties. The various experimental conditions are summarised in Table 6-1.

Table 6-1: Electrochemical deposition conditions for the synthesis of nanocomposites.

Routes	TBAB (mM)	Counter electrode	Working electrode	Seeded electrolyte	Current (mA)
<i>In-situ</i> codeposition of Mg and Ni	20	Ni	Ti	-	2
	20	Ni	Ti	-	5
	20	Ni	Ti	-	10
	10	Ni	Ti	-	5
	50	Ni	Ti	-	5
	100	Ni	Ti	-	5
Additional catalyst	20	Mg	Ti	Ni (3-5 nm)	5
	20	Mg	Ti	Nb ₂ O ₅ (100-200 nm)	5

With the purpose of comparing the difference between *in-situ* and “external” pre-seeding of catalysts, commercial Nb₂O₅ and Ni nanoparticles were introduced into the electrolyte. It has been shown that metals could be electrodeposited on suspended seeds,

hence, a similar strategy was employed here. Ni and Nb₂O₅ have been proven to be effective catalysts for the Mg/MgH₂ reaction.[13,14] In these cases, the anode was changed from Ni to Mg to avoid any catalytic source from the anode. This also served as a reference to compare “*in-situ*” and “*ex-situ*” catalysis.

After electrolysis, the products were collected by centrifugation, then sonicated and washed with THF three times. The samples were centrifuged and dried under vacuum on a Schlenk line at 80 °C to remove residual THF. These materials should be handled with care, as they are sensitive to oxygen and moisture.

6.3 Effect of current density on the Mg/Ni nanocomposites

Magnesium deposited from 20 mM Mg(BH₄)₂ and 20 mM TBAB electrolyte with Mg as the anode forms big magnesium clusters on the Ti foil (Chapter 4), and thus it is difficult to collect any Mg nanoparticles under such experimental conditions. Such a deposit absorbed hydrogen at high temperature (> 300 °C) without full conversion to MgH₂, due to the thickness of the Mg layer and the slow diffusion of hydrogen in the hydride phase. When the Mg anode was changed to a Ni plate, which could supply Ni²⁺ during electrolysis, a loose Mg/Ni nanocomposite was formed. The effect of current density was thus firstly investigated with deposition currents of 2, 5 and 10 mA.

6.3.1 Structural identification

The as-synthesised Mg/Ni nanocomposites were analysed by XRD (Figure 6-1). There was no Ni signal detected in the as-synthesised Mg/Ni composites, which meant that the Ni nanoparticles were ultra-small or in an amorphous form, and the diffraction peaks observed mainly corresponded to that of the hexagonal magnesium phase. Mg/Ni composite synthesised of 5 mA could then be completely hydrogenated to form γ-MgH₂ and β-MgH₂ at 100 °C only. However, under the other two deposition currents, there

was a small amount of Mg left after hydrogenation at 100 °C. The amount of γ -MgH₂ and β -MgH₂ phases were calculated via the Rietveld method with X'pert Highscore Plus and shown in Table 6-2. The highest content of γ -MgH₂ was obtained with 5 mA current, the value was 29.6%; Mg/Ni composites with 2 mA and 10 mA achieved 22.5 % and 18.0 % of γ -MgH₂ respectively. The mechanism of γ -MgH₂ formation is not clear. Conventionally, this is induced from high pressure, while defects also lead to the formation of γ -MgH₂. [15,16]

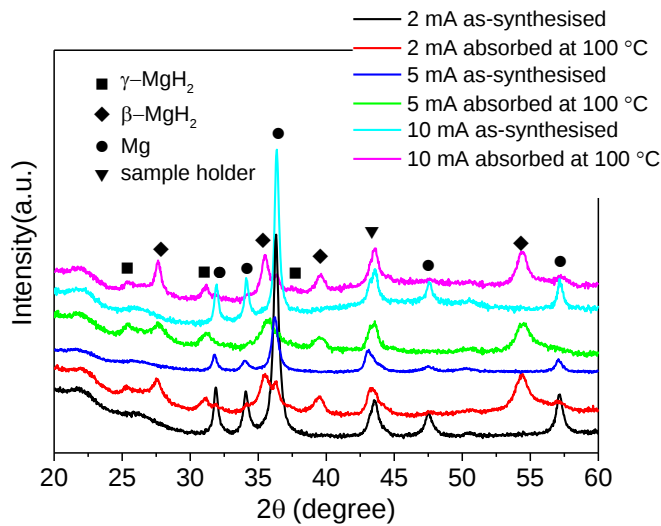


Figure 6-1: XRD patterns of Mg/Ni composites obtained under different deposition currents, as-synthesised and after hydrogenated at 100 °C.

The crystallite size of the as-prepared and hydrogenated materials was determined by the Scherrer equation. A 5 mA deposition current led to the smallest magnesium crystallite size (16.1 ± 1.2 nm), while current of 2 and 10 mA was bigger, which demonstrated the effect of current on deposits (Table 6-2). The crystallite sizes of γ -MgH₂, β -MgH₂ and residual Mg after hydrogenation were much smaller than as-prepared Mg. This phenomenon can be attributed to the nucleation of the new hydride phase along with hydrogen diffusion through the metal matrix to substitute for the magnesium phase.[17] The different MgH₂ phase conversion rates can be explained in

that the 5 mA realised the smallest crystallite size thus the kinetics was improved by the shortest hydrogen diffusion path. [18,19]

Table 6-2: Crystallite size (nm) and composition content (%) of the materials prepared with various currents as determined by Rietveld analysis of the XRD patterns.

	As-synthesised Crystallite size (nm)	After H ₂ absorption at 100 °C Crystallite size (nm) (Amount of individual phases in %)		
	Mg	γ -MgH ₂	β -MgH ₂	Mg
2 mA	18.8 ± 1.8	12.8 ± 0.5 (22.5)	8.5 ± 0.3 (71.0)	14.6 ± 1.9 (6.5)
5 mA	16.1 ± 1.2	10.9 ± 0.7 (29.6)	8.5 ± 0.2 (70.4)	-
10 mA	24.7 ± 1.7	15.1 ± 0.4 (18.0)	13.2 ± 0.8 (68.9)	10.0 ± 1.7 (13.1)

6.3.2 Morphology

The morphologies of the Mg/Ni nanocomposites are shown in Figure 6-2 and the elemental mapping results indicate that the tiny dark points observed in TEM images corresponded to Ni particles with a size of ~3 nm. In contrast, the lighter particles were assigned to Mg with a particle size ranging from 20 to 50 nm. The shape of the magnesium particles was irregular, which differed from most of the chemical reduction method.[20,21] Assuming a homonucleation mechanism in solution, the morphology of magnesium nanoparticles is monodispersed and with a spherical shape.[16,21,22] In contrast, if magnesium particles grow step by step during the electrolysis process following a heteronucleation mechanism, magnesium particles will aggregate into clusters. [23,24] The TEM and elemental mapping images suggested that with 2 mA

current, fewer Ni particles covered Mg (Figure 6-2a), while a higher current of 5 and 10 mA showed a similar level of Ni coverage.

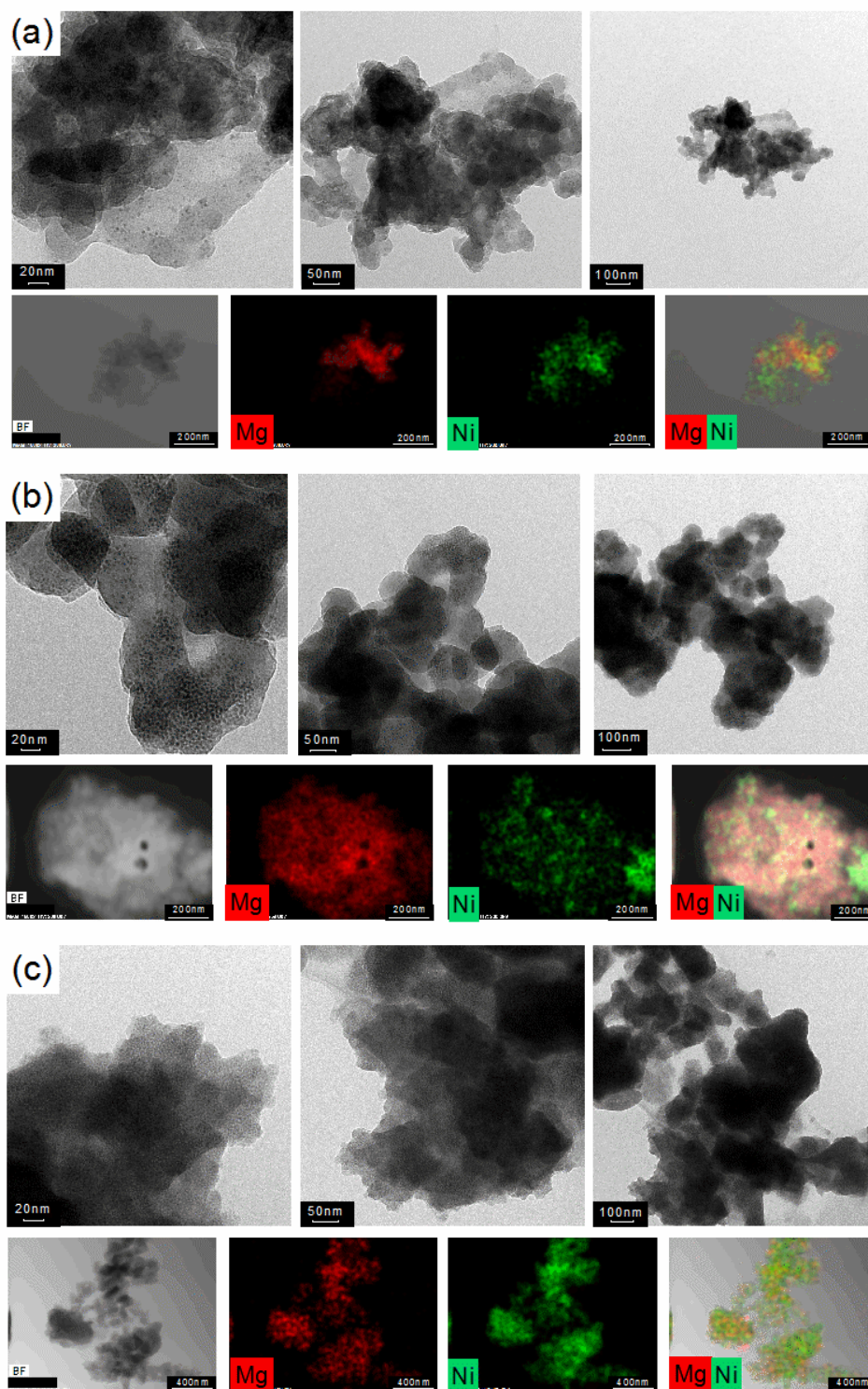


Figure 6-2: TEM images and elemental mapping of as-synthesised Mg/Ni nanocomposites with (a) 2 mA, (b) 5 mA and (c) 10 mA.

HR-TEM of the as-synthesised particles demonstrated the existence of MgO on the surface, which should correspond to the transfer of the material in air to the TEM instrument. Fringes assigned to Mg and Ni were also observed (Figure 6-3a). After being hydrogenated at 100 °C, γ - and β -MgH₂ phases could also be observed when measuring the lattice fringes, as well as fringes related to Ni nanoparticles and the MgO phase formed at the edge of magnesium particles. This means that γ - and β -MgH₂ are closely located and most likely within the same particle rather than separate in different Mg particles.

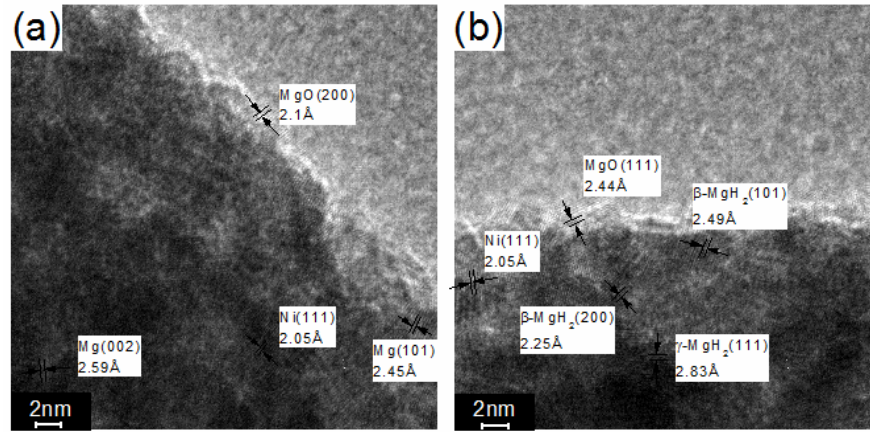


Figure 6-3: HR-TEM images of Mg/Ni composite (a) as-synthesised and (b) after being hydrogenated at 100 °C.

6.3.3 Hydrogen desorption properties

The hydrogen desorption properties were characterised by DSC-MS (Figure 6-4). The hydrogen signal from 50 to 100 °C on MS profiles should be assigned to the decomposition of ultra-small metastable γ -MgH₂ particles. However, the main γ -MgH₂ phase would decompose at higher temperature as demonstrated in further investigation of γ -MgH₂ (Figure 6-17). Two separated desorption peaks (290 °C and 321 °C) were presented in the sample prepared with a current of 2 mA, while with a current of 5 mA

and 10 mA, only one desorption peak showed. As reported, the low temperature peak was assumed to correspond to the desorption from the γ -MgH₂ phase due to its lower stability while the high temperature peak should correspond to the desorption from β -MgH₂. [25,26] However, the coexistence of γ -MgH₂ and β -MgH₂ leading to one single desorption peak in the Mg/Ni nanocomposites generated with higher currents rejects such hypothesis. Hence, γ -MgH₂ and β -MgH₂ should decompose simultaneously.

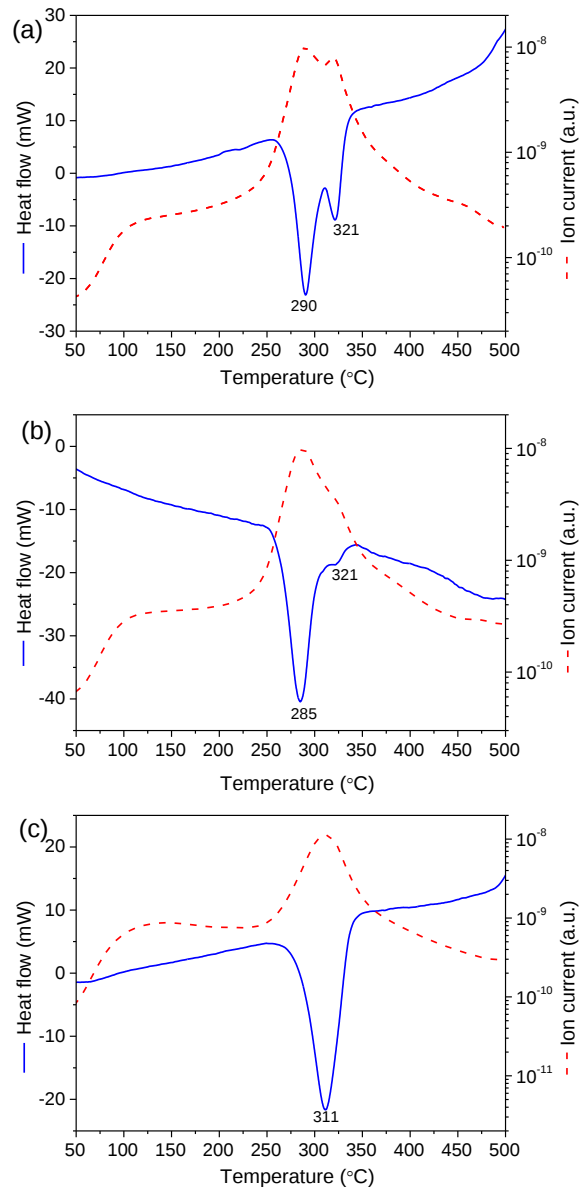


Figure 6-4: DSC and hydrogen release profiles of as-prepared Mg/Ni composites with current modifications after 100 °C hydrogenation, (a) 2 mA, (b) 5 mA and (c) 10 mA.

The two peaks of hydrogen release (Figure 6-4a) were thus attributed to the nonuniform distribution of γ -MgH₂ and β -MgH₂, the later peak was assigned to desorption of β -MgH₂ alone. 5 mA had the lowest desorption temperature (285 °C) as well as the smallest crystallite size (16.1 ± 1.2 nm), while for 10 mA, the single 311 °C peak demonstrated hydrogen release was harder because of bigger crystallite size.

6.4 Effect of concentration to TBAB on the Mg/Ni nanocomposites

As studied in Chapter 5, the surfactant should influence the electrode/electrolyte interface thus modifying the electrodeposition process and therefore affecting the hydrogen storage properties of the final products. Here the Mg(BH₄)₂ concentration was kept at 20 mM and the TBAB concentration changed to 10, 50 and 100 mM at a constant deposition current of 5 mA.

6.4.1 Structural identification

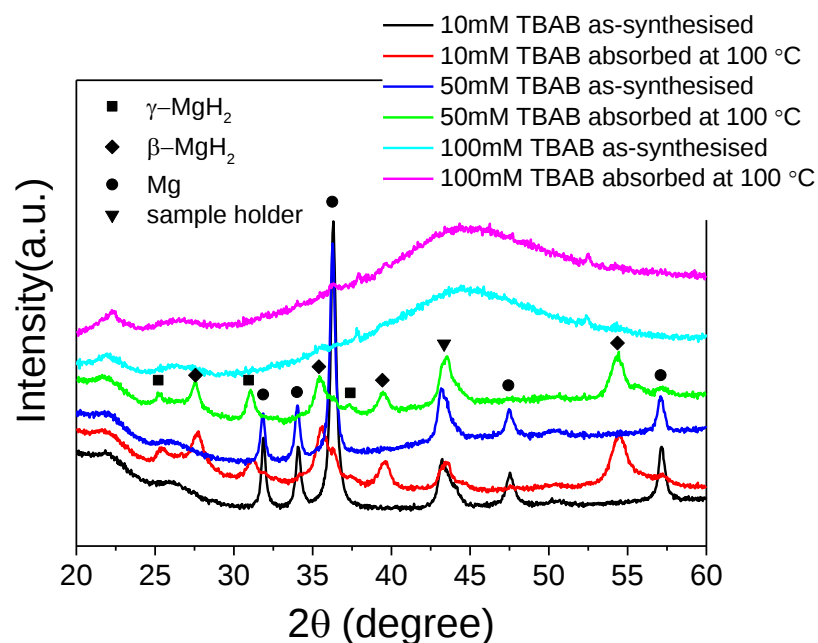


Figure 6-5: XRD patterns of Mg/Ni composites at various TBAB concentrations, as-synthesised and after being hydrogenated at 100°C.

The Mg/Ni nanocomposites synthesised were analysed by XRD and only a hexagonal magnesium phase was detected in the as-synthesised samples. γ -MgH₂, β -MgH₂ and residual Mg coexisted after 100 °C hydrogenation for samples with 10 and 50 mM TBAB respectively which are shown in Figure 6-5. While for 100 mM TBAB, almost nothing could be detected.

The crystallite size and content of these three compositions are summarised in Table 6-3. It is observed that either with 10 mM or 50 mM TBAB, the crystallite size would grow up to over 20 nm. Hence, there is a critical concentration of TBAB controlling crystallite size to some extent. However, if the TBAB concentration was too high (100 mM), there was no visible Mg diffraction peak indicating the lack of Mg nanoparticles or their amorphous nature.

Table 6-3: Crystallite size (nm) and composition content (%) of the materials prepared with various TBAB concentrations as determined by Rietveld analysis of the XRD patterns.

	As-synthesised Crystallite size (nm)	After H ₂ absorption at 100 °C Crystallite size (nm) (Amount of individual phases in %)		
	Mg	γ -MgH ₂	β -MgH ₂	Mg
10 mM	23.9 ± 2.0	12.3 ± 0.5 (26.8)	10.4 ± 0.6 (69.1)	15.2 ± 2.1 (4.1)
20 mM	16.1 ± 1.2	10.9 ± 0.7 (29.6)	8.5 ± 0.2 (70.4)	-
50 mM	22.6 ± 1.5	14.8 ± 0.8 (30.8)	12.7 ± 0.5 (62.7)	10.1 ± 1.4 (6.5)
100 mM	-	-	-	-

ICP analysis confirmed the elemental composition of the samples. The results demonstrated that there was 5 times more Ni than Mg in the composite prepared with 100 mM TBAB (Table 6-4). This explained the lack of a Mg diffraction peak owing to the low Mg content of the material produced of 100 mM TBAB concentration. This behaviour should be ascribed to easier generation of Ni under a high concentration of surfactant, because the surface of the electrode covered with surfactant induced a higher reduction potential and thus results in a faster deposition process of Ni against Mg.

Table 6-4: ICP-OES analysis of Mg/Ni composites electrodeposited with different concentrations of TBAB and -5mA.

TBAB concentration (mM)	Elements content (%)	
	Mg	Ni
10	58	6
20	48	11
50	56	12
100	8	45

6.4.2 Morphology

TEM images and elemental mapping of the products generated at various TBAB concentrations are shown in Figure 6-6. It is quite obvious that the material prepared with 10 mM TBAB possessed a low coverage of Ni, and with Ni nanoparticles located on the top of the Mg particles. This inhomogeneous distribution of Mg and Ni did not influence the formation of γ -MgH₂ significantly (26.8 %). When the concentration of TBAB was increased, a more uniform distribution of Mg and Ni was obtained. Thus

there is Mg in the 100 mM sample, which means that the invisible MgH_2 phase after hydrogenation was attributed to the small amount of magnesium deposits.

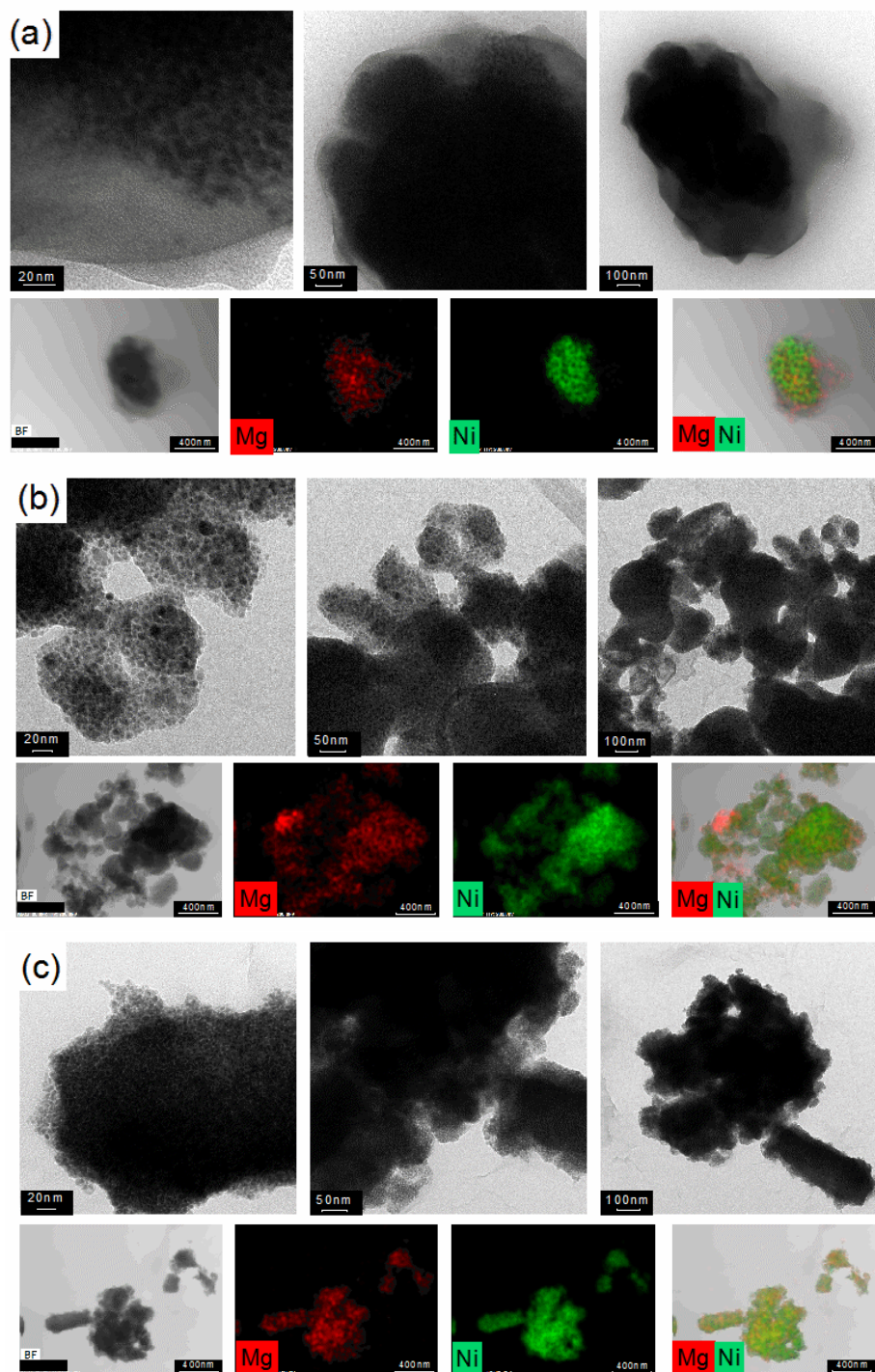


Figure 6-6: TEM images and elemental mapping of as-synthesised Mg/Ni nanocomposites with various concentrations of TBAB, (a) 10 mM, (b) 50 mM and (c) 100 mM.

6.4.3 Hydrogen desorption properties

The hydrogen desorption properties of these materials after hydrogenation at 100 °C were characterised by DSC-MS (Figure 6-7). Two separated desorption peaks (288 °C and 319 °C) were observed in the sample with 10 mM TBAB/5 mA, while the Mg/Ni nanocomposite prepared with 50 mM TBAB/5mA achieved a single peak at 312 °C. However, the Mg/Ni nanocomposite with 100 mM TBAB did not reveal any clear DSC or MS peaks related to hydrogen desorption because of the large amount of Ni as compared to Mg.

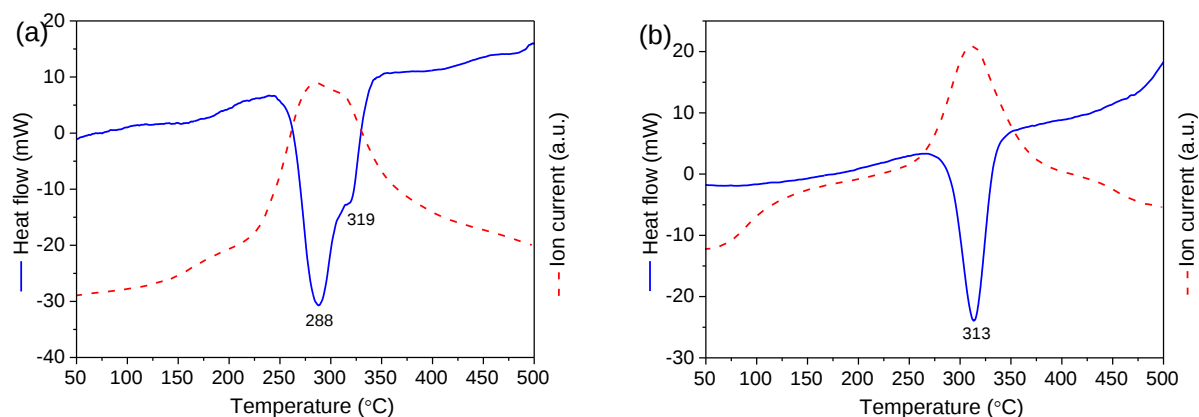


Figure 6-7: DSC and hydrogen release profiles of as-prepared Mg/Ni composite with various concentrations of TBAB after hydrogenation at 100 °C, (a) 10 mM, (b) 50mM. For 100 mM, the amount of hydrogen absorption is too small to be detected.

The separated desorption peaks for low current (20 mM TBAB/2 mA) and low concentration of TBAB (10 mM TBAB/5 mA) should be ascribed to the inhomogeneous distribution of Mg and Ni (Figure 6-2a and Figure 6-6a). As a result, the part Mg effectively coated with Ni obtains a higher activity and thus releases hydrogen prior to the rest. On the other hand, at a high current (20 mM TBAB/10 mA), only a small amount (18.0 %) γ -MgH₂ was generated, which is much less than the high

content of 30.8 % γ -MgH₂ achieved with 50 mM TBAB/5 mA. However, the single hydrogen desorption peak of around 310 °C of these two samples (Figure 6-4c and Figure 6-7b) demonstrated that the amount of γ -MgH₂ is not the key factor influencing the hydrogen desorption process. Comparing the crystallite size of γ - and β -MgH₂ formed after hydrogenation (Table 6-2 and Table 6-3), the crystallite size of Mg seems to be the main factor determining desorption properties.

6.5 Effect of external addition of catalysts

The previous results and interpretations demonstrated the importance of *in-situ* introduction of Ni to improve hydrogen storage properties of Mg, so the external addition of catalysts into this electrolysis system was also investigated as a comparison. Ni nanoparticles and commercial Nb₂O₅ powder were used as sources and introduced at a level of 10 mass% into the electrolyte. These two catalysts are usually mixed with Mg by ball milling.[27,28] In this case Ni, the sacrificial anode, was changed to Mg to avoid an introduction of additional Ni.

6.5.1 Structure identification

As displayed in Figure 6-8, the XRD patterns of the as-prepared materials presented clear diffraction peaks assigned to Mg. This was also the case for Nb₂O₅ owing to the large particle size. For Ni nanoparticles, the signal was too weak to be detected. After hydrogenation at 100 °C, both products showed a little amount of β -MgH₂, and there was no γ -MgH₂ detected. The crystallite size of Mg calculated from the XRD patterns was 39 ± 1.4 and 37 ± 2.2 nm with the Nb₂O₅ and Ni additives respectively. This is much bigger than that from “*in-situ*” generated Mg/Ni composites. The similar crystallite size obtained with Ni and Nb₂O₅ as seeds, demonstrates that no matter what kind of external additives were introduced, the growth of Mg was not influenced.

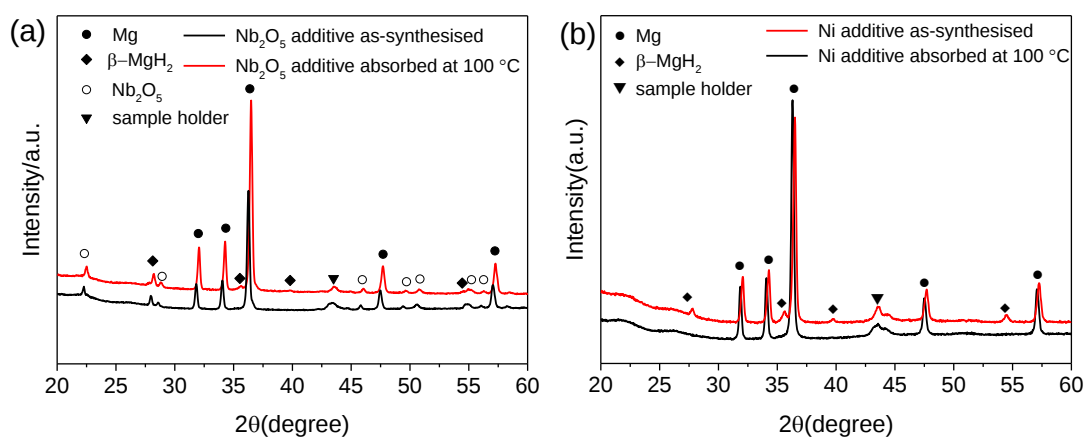


Figure 6-8: XRD patterns of (a) Mg/Nb₂O₅ and (b) Mg/Ni composites with external catalysts addition before and after hydrogenation at 100 °C.

6.5.2 Morphology

From TEM analysis, the distribution of catalyst particles and magnesium was very clear. Neither Nb₂O₅ nor Ni particle seeds were coated with Mg (Figure 6-9 and Figure 6-10). Therefore most of the magnesium was deposited as separated particles with high crystallinity as shown in TEM images and elemental mapping.

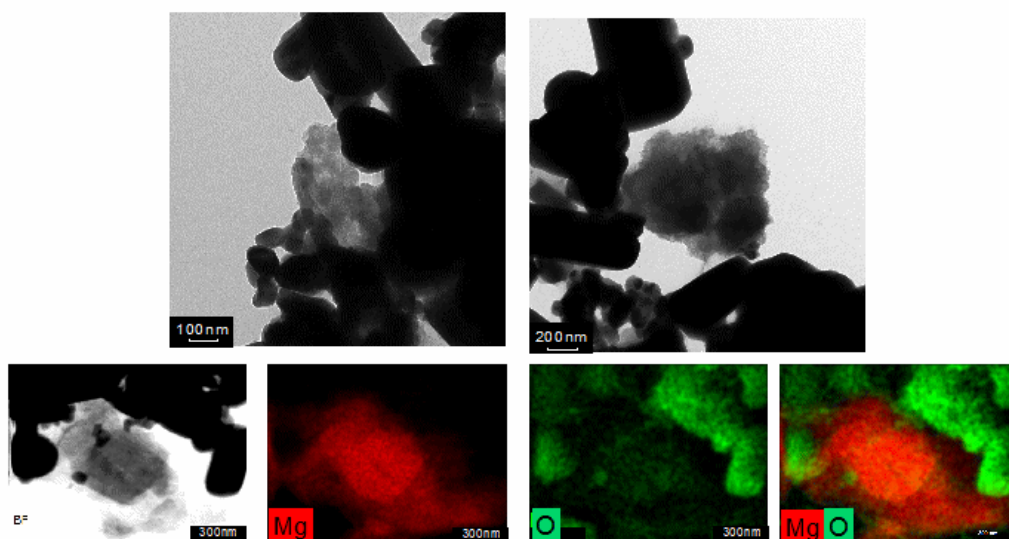


Figure 6-9: TEM images and elemental mapping of as-synthesised Mg/Nb₂O₅ composite with external Nb₂O₅ addition.

During the electrochemical synthesis, Nb_2O_5 maintained its original morphology. Furthermore, as Nb_2O_5 is an insulating material, magnesium was not successfully deposited onto its surface. As Nb cannot be detected in mapping measurement, oxygen was chosen to identify the distribution of Nb_2O_5 .

For Ni nanoparticles, the electrodeposition can lead to both Mg deposits on Ni seeds and directly at the electrode surface. Therefore the distribution of Mg and Ni was heterogeneous. Figure 6-10 shows the composite material obtained at the end of the synthesis. The morphology of the final product is quite different from the “*in-situ*” synthesised composites as shown in Figure 6-10a and b.

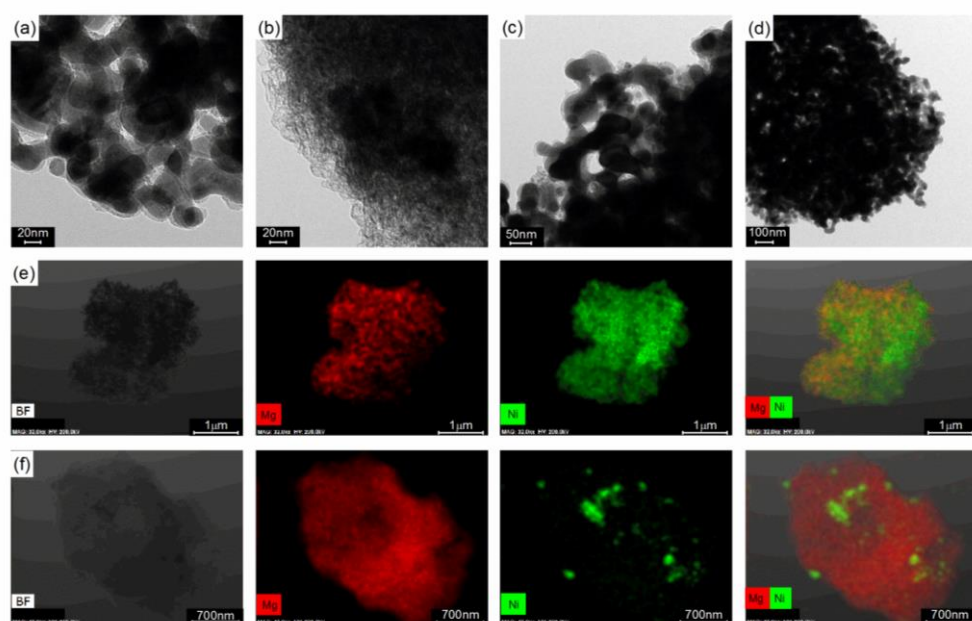


Figure 6-10: TEM images and elemental mapping of as-synthesised Mg/Ni composite with external Ni nanoparticles addition.

Further elemental mapping also suggests that Mg and Ni nanoparticles distributed uniformly at some spots (Figure 6-10e). However, the magnesium deposits were aggregated to some extent (Figure 6-10f), and with a much lower Ni distribution at Mg surface than that achieved via *in-situ* codeposition of Mg and Ni.

6.5.3 Hydrogen desorption properties

The hydrogen desorption properties were characterised by DSC-MS for materials with external additives after being hydrogenated at 100 °C as shown in Figure 6-11.

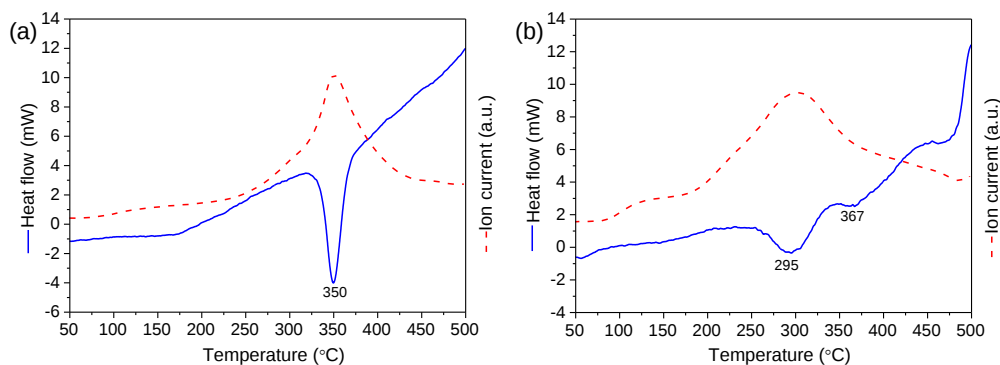


Figure 6-11: DSC and hydrogen release profiles of (a) Mg/Nb₂O₅ and (b) Mg/Ni composites with external catalysts addition after hydrogenation at 100 °C.

The sample with Nb₂O₅ only presented a 350 °C desorption peak similar to bulk magnesium. This indicates a poor catalytic effect of big Nb₂O₅ particles. The sample with Ni nanoparticles presented two weak endothermic peaks at 295 °C and 367 °C. As only a small amount of MgH₂ was formed as characterised by XRD, it is believed that the low hydrogen desorption temperature corresponds to the catalytic effect of Ni. The high desorption temperature peak should be assigned to the decomposition of β -MgH₂. Nevertheless, the low conversion rate of MgH₂ suggests that the external addition of Ni catalytic seeds was not as efficient as *in-situ* codeposited Mg/Ni nanocomposite.

6.6 Kinetic and thermodynamic properties of Mg/Ni nanocomposite

From the results above, the conclusion could be drawn that 20 mM TBAB with 5 mA generates Mg/Ni nanocomposite with the best hydrogen storage properties. Additional characterisations were thus carried out to identify the activation energy, plateau pressure, hydrogen sorption kinetics, ΔH and ΔS .

6.6.1 Kinetics

It is expected that the formation of γ -MgH₂ should lead to both improvements in thermodynamics and kinetics owing to its lower stability as compared to β -MgH₂ and its distorted structure potentially leading to easier hydrogen diffusion.[29,30] In order to assess possible improvements of hydrogen kinetics, the activation energy (E_a) of desorption was determined after hydrogenation at 100 °C, where the γ phase still coexists with β -MgH₂ and after hydrogen cycling at 250 °C with complete conversion of γ -MgH₂ into β -MgH₂ (Figure 6-12).

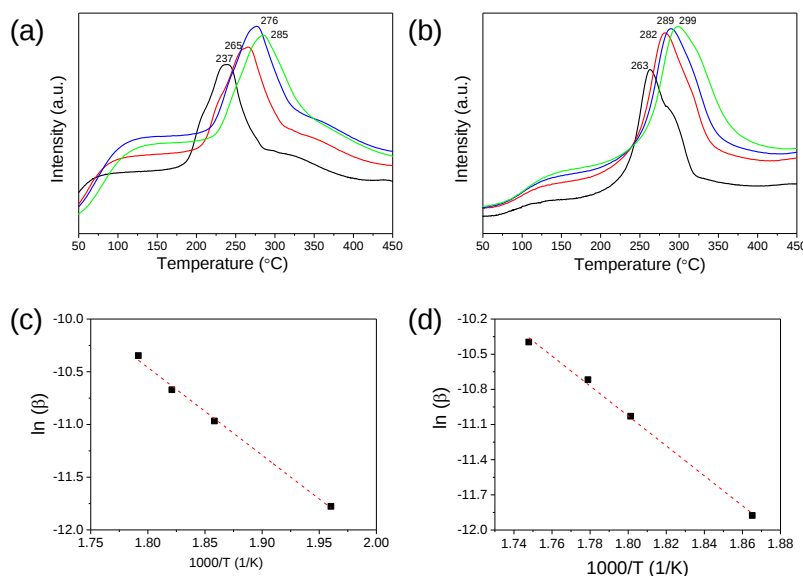


Figure 6-12: TGA-MS profiles of sample with 20 mM TBAB under 5 mA (a) after hydrogenation at 100 °C and (b) after 6 hydrogen cycles at 250 °C with various heating rates (2, 5, 7, 10 °C min⁻¹), the corresponding activation energy plots were in (c, d).

Using the Kissinger method,[31] E_a after hydrogenation at 100 °C was found to be relatively low (69.1 ± 2.9 kJ·mol⁻¹). However this value significantly increased to 106.2 ± 4.0 kJ·mol⁻¹ upon the loss of the γ phase (Table 6-5). Taking into account that there is no significant evolution of the material morphology upon hydrogen

absorption/desorption (Figure 6-13b) it can thus be concluded that the presence of γ -MgH₂ improves hydrogen kinetics. One hypothesis is that it further facilitates hydrogen desorption from the β phase by acting as a pathway for faster hydrogen diffusion.

The high temperature also changed the morphology of products due to the particle sintering of Mg/Ni nanocomposite. As shown in Figure 6-13, at 300 °C, a growth in particle size of Mg was observed (Figure 6-13c, red circle), while Ni particles remained constant. This may indicate a low melting temperature of nanosized Mg, spherical magnesium particles were recrystallised at the edge of the composite. This was confirmed by elemental mapping (Figure 6-13d), the size of big magnesium particles was about 100 nm.

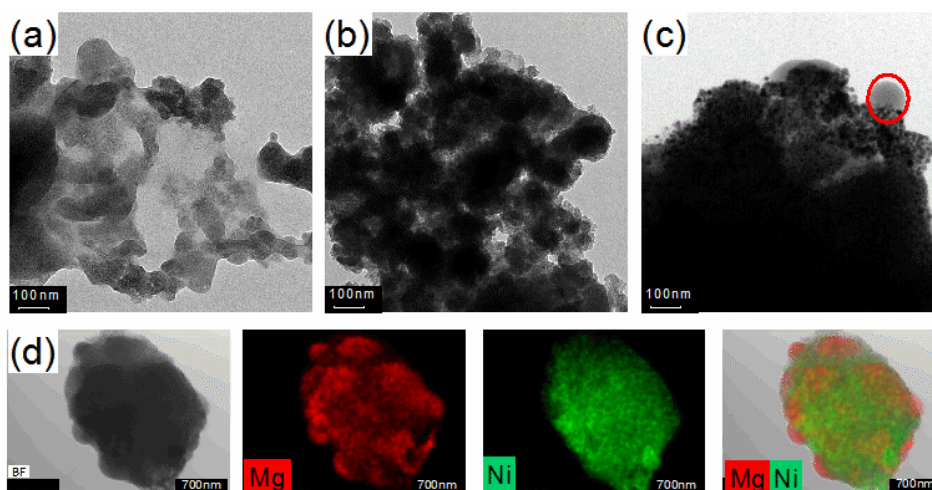


Figure 6-13: The morphologies of Mg/Ni nanocomposites (a) after hydrogenation at 100 °C, (b) cycled at 250 °C and (c) cycled at 300 °C and associated (d) elemental mapping.

Hydrogen absorption and desorption kinetics curves were also measured by PCT to identify the properties of the Mg/Ni nanocomposite prepared with 20 mM TBAB and 5 mA. As the ICP measurement demonstrated, the Mg content is 48 % in this product, so the theoretic storage capacity is around 3.8 mass%.

Absorption was realised at 100 °C and 200 °C while desorption was not possible at these temperatures. However, hydrogen desorption was possible at 200 °C under dynamic vacuum in further investigation (Figure 6-17). Hence, this indicated a low plateau pressure for Mg/Ni nanocomposite at 200 °C. Subsequently, 250, 275 and 300 °C were used for both absorption and desorption. The results shown in Figure 6-14a indicated the kinetics of hydrogen absorption was accelerated with increasing temperatures. At 200 °C, the samples were almost fully absorbed in 3000 s, while when the temperature was higher than 250 °C, the kinetics were much faster (absorption in less than 1000 s). The effect of temperature was more remarkable on the desorption kinetics (Figure 6-14b). Full hydrogen release reduced from 8000 s to 3000 s with a temperature increase from 250 to 300 °C.

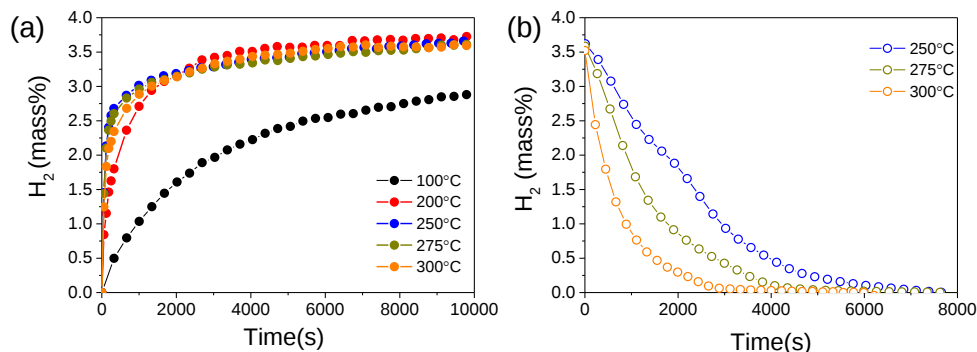


Figure 6-14: Hydrogen (a) absorption and (b) desorption kinetics of Mg/Ni nanocomposite prepared with 20 mM TBAB and 5 mA under different temperature.

However, even with a high content of Ni, the kinetics of hydrogen sorption is slower than catalysts introduced by ball milling, which usually fully absorb and desorb hydrogen in 500 s at 300 °C for example.[32,33] The activation energy of hydrogen desorption ($69.1 \pm 2.9 \text{ kJ}\cdot\text{mol}^{-1}$) is also higher than the one with Nb₂O₅ ($62 \text{ kJ}\cdot\text{mol}^{-1}$). [34,35] Given the small particle size of the Mg produced by electrochemical synthesis

as compared to ball-milled MgH_2 , it seems that factors other than particle size affect the kinetics. These factors could be the ability of Mg surface to split/recombine H_2 , the diffusion through the hydride layer and chemical/structural changes during sorption processes.

6.6.2 Thermodynamics

Pressure-composition-isotherm (PCI) measurements at four temperatures are displayed in Figure 6-15, as well as the corresponding Van't Hoff plots. It is found that the flat absorption plateaus Mg/Ni nanocomposite appeared at 225 °C, and this is similar upon H_2 release. A single plateau pressure was observed upon hydrogen absorption and desorption, which indicated that both γ and $\beta\text{-MgH}_2$ were formed and decomposed at the same time. The reaction enthalpy can be calculated using the Van't Hoff equation. The Van't Hoff plots ($\ln P$ versus $1/T$) of the hydrogen absorption and desorption are shown in Figure 6-15c and d respectively.

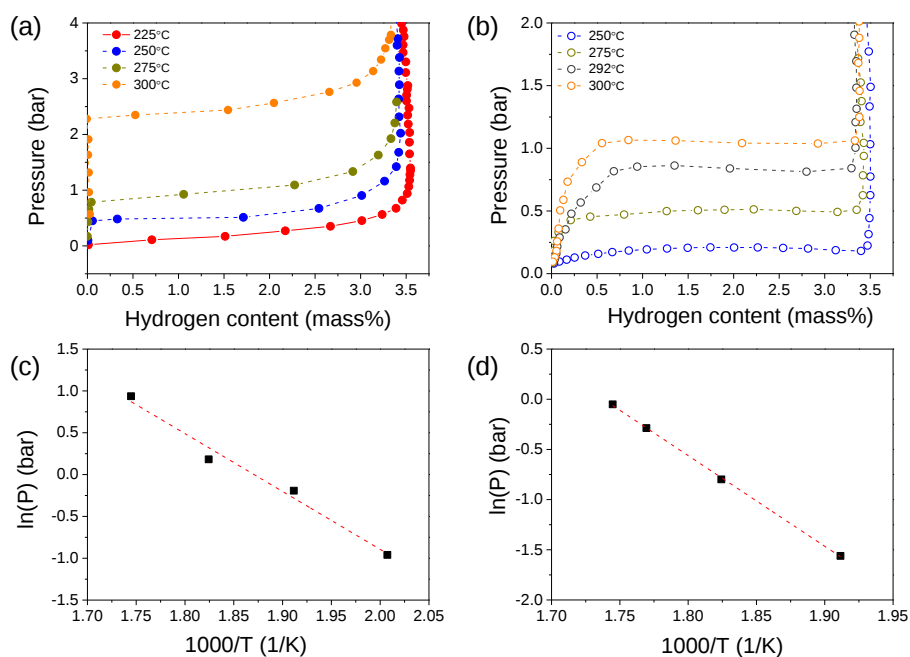


Figure 6-15: PCI hydrogen (a) absorption and (b) desorption of Mg/Ni nano composite with 20 mM TBAB and 5 mA, the Van't Hoff plots are shown in (c,d) respectively.

A reduced ΔH of $57.5 \pm 5.3 \text{ kJ}\cdot\text{mol}^{-1} \text{ H}_2$ was found for the absorption process in comparison to $74.8 \pm 1.0 \text{ kJ}\cdot\text{mol}^{-1} \text{ H}_2$ for the desorption process (Table 6-5). This latter value is close to the widely accepted value of ΔH for bulk Mg and thus once the γ phase is lost, the material behaves along the well-known thermodynamic properties of β -MgH₂. However, the reduced ΔH for the absorption process indicates that the metastable γ phase can lead to a destabilisation of β -MgH₂. But as shown by the low pressure of the absorption equilibrium pressure (e.g. 20 kPa at 225 °C, Figure 6-15a) this reduced enthalpy does not result in a significant improvement of the thermodynamics. Indeed, the reduction in enthalpy is also accompanied by a concomitant decrease in entropy (107.6 ± 10.0 instead of $130.2 \pm 1.8 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} \text{ H}_2$) limiting the overall reduction in desorption temperatures, assuming that the γ phase is retained (Table 6-5).

Table 6-5: Activation energy, ΔH , ΔS of Mg/Ni composite (20 mM TBAB and 5 mA).

Kinetics		Thermodynamics	
E_a (kJ·mol ⁻¹)		ΔH (kJ·mol ⁻¹ H ₂)	ΔS (J·mol ⁻¹ ·K ⁻¹ H ₂)
<u>after H₂ absorption at 100°C</u>	<u>after H₂ cycling at 250 °C</u>	<u>for H₂ absorption</u>	
69.1 ± 2.9	106.2 ± 4.0	57.5 ± 5.3	107.6 ± 10.0
-	-	<u>for H₂ desorption</u>	
-	-	74.8 ± 1.0	130.2 ± 1.8

Such interdependence between ΔH and ΔS has been previously observed upon a significant reduction of Mg particle size, and was attributed to a weaker Mg-H bond and thus a higher level of freedom of the hydrogen atoms in nanosized Mg as compared to

bulk. γ -MgH₂ may induce similar effects, and thus for an effective use of γ -MgH₂ to reversibly store hydrogen, ways to overcome the enthalpy/entropy compensation effect are needed. This could be achieved through the combination of elements or alloys leading to opposite thermodynamic shifts at the nanoscale. [36]

6.7 Behaviour of γ -MgH₂ during hydrogen absorption and desorption

Combining the investigations of current and TBAB concentration variations, at a given reduction current of 5 mA the amount of γ -MgH₂ was not significantly influenced by higher concentrations of TBAB and thus subsequent alterations of the electrode/surfactant interface (Figure 6-16a). However, the amount of γ phase was found to strongly depend on the level of current applied during the electrosynthesis (Figure 6-16b), although either modifying the current or TBAB concentration would lead as-synthesised Mg nanoparticles growing up (Table 6-2 and Table 6-3) . Hence a current of 5 mA was found to be the optimum within our experimental conditions.

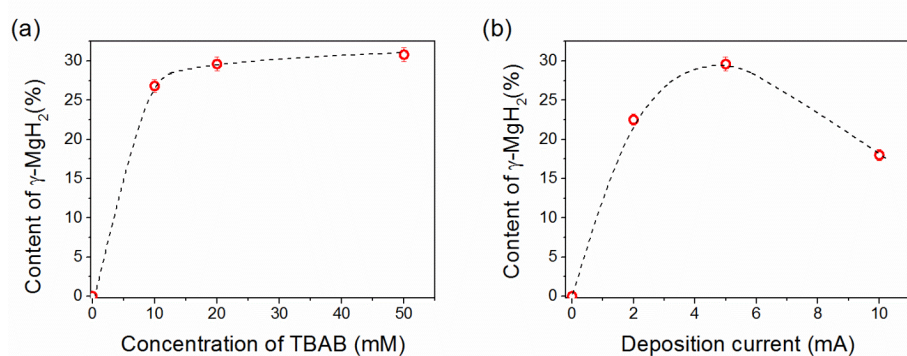


Figure 6-16: Content of γ -MgH₂ of the Mg/Ni nanocomposites prepared with diverse (a) concentrations of TBAB and (b) deposition currents after hydrogenation at 100 °C.

6.7.1 The decomposition of γ -MgH₂ under vacuum

Mg/Ni nanocomposite prepared with 20 mM TBAB and 5 mA current could fully absorb hydrogen at 100 °C and contain a considerable amount of γ -MgH₂. Hydrogen

desorption under vacuum (0.1 kPa) was studied at diverse temperatures (Figure 6-17). It is obvious that MgH_2 began to release H_2 even from 100 °C to produce Mg. The intensity of Mg increased with higher desorption temperature, which implied that hydrogen desorption proceeded gradually. It is impressive that the material was capable of releasing all H_2 at 200 °C, and at 190 °C, there was only a small amount of MgH_2 remaining. Furthermore, as a metastable phase, $\gamma\text{-MgH}_2$ consistently existed until the $\beta\text{-MgH}_2$ desorbed. Such behaviour suggests that the two phases do not decompose separately, but interact with each other. The mechanism of H_2 desorption is thus suspected to first proceed via the decomposition of metastable $\gamma\text{-MgH}_2$ phase triggering the decomposition of the more stable $\beta\text{-MgH}_2$ phase. This process generates stresses that act on the attached $\beta\text{-MgH}_2$ clusters and facilitate following decomposition.[26,37]

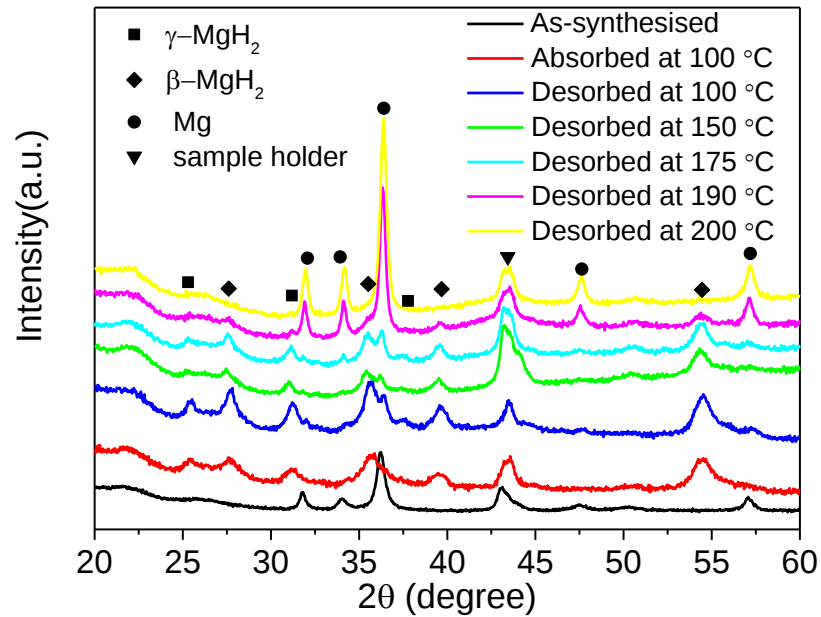


Figure 6-17: XRD patterns of as-synthesised Mg/Ni composite and after various heat treatments.

The evolution of $\gamma\text{-MgH}_2$ and $\beta\text{-MgH}_2$ contents with different desorption temperatures is also summarised in Figure 6-18. These contents were calculated from the XRD

patterns by the Rietveld refinement method. With increasing heat treatment temperatures, the content of Mg increases accordingly. However, the interaction between γ -MgH₂ and β -MgH₂ phase is not so simple, when the temperature is lower than 175 °C, the content of γ -MgH₂ decreases slowly, with the amount of β -MgH₂ almost constant. At a critical temperature around 175-190 °C, γ -MgH₂ abruptly releases H₂, while β -MgH₂ decomposition sharply follows. This phenomenon illustrates that γ -MgH₂ does not simply decompose prior to β -MgH₂, but both phases release hydrogen simultaneously.

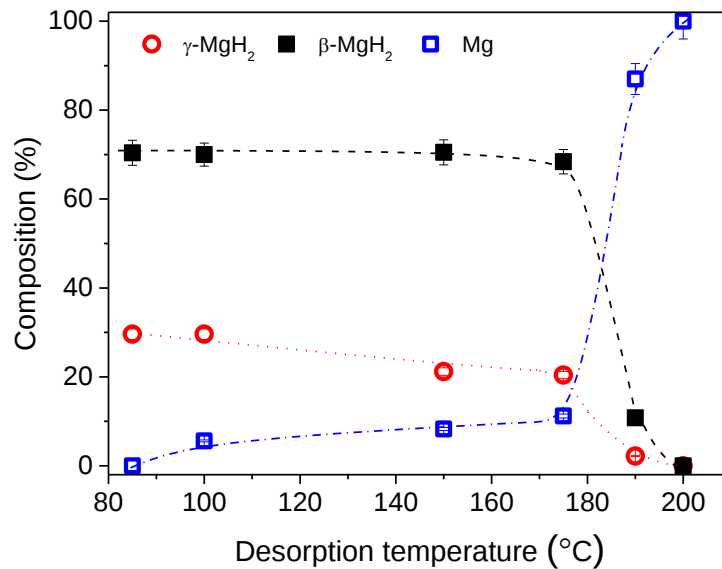


Figure 6-18: The content changing of compositions under vacuum with different desorption temperatures.

6.7.2 The thermal stability of γ -MgH₂

Despite 100 °C hydrogenation, γ -MgH₂ also appeared after hydrogenation at higher temperatures. As shown in Figure 6-19, at 200, 250 and 300 °C, γ -MgH₂ was formed after hydrogenation with 25-30 % content, and there was no Mg left. This confirms that the transformation between γ -MgH₂ and β -MgH₂ does not simply depend on temperature.

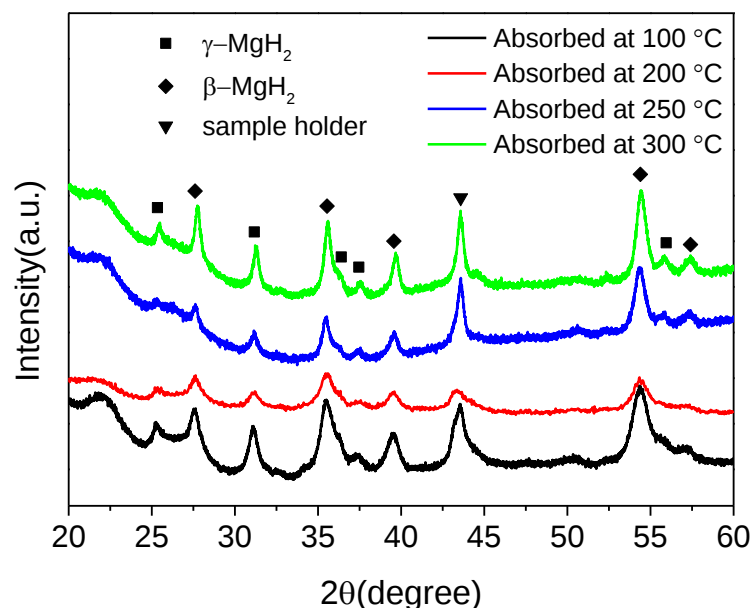


Figure 6-19: XRD patterns of Mg/Ni nanocomposite hydrogenated at different temperatures.

As mentioned, 200 °C dehydrogenation could decompose all the MgH₂ phases under vacuum; however, γ-MgH₂ was still recovered with a following 100 °C rehydrogenation (Figure 6-20). This is the first time that reversible regeneration of γ-MgH₂ is observed. However, after 3 cycles, the amount of γ-MgH₂ decreased and after 5 cycles, there was less γ-MgH₂ in the composite material. Thus the instability of γ-MgH₂ is related to the hydrogen uptake and release cycles. This result can be explained by the effect of strain left in the composite. When hydrogenated at 100 °C, the strain is not released and stops the conversion from distorted γ-MgH₂ to β-MgH₂ further.[38] When γ-MgH₂/β-MgH₂ composite desorbs hydrogen at 200 °C, the higher temperature releases the strain in nanocomposite more effectively, which is why after several 100 °C absorption-200 °C desorption cycles, no more γ-MgH₂ can be formed.[39,40] The strains calculated from XRD patterns of as-synthesised product and the one after 200 °C desorption are 0.75 % and 0.52 % respectively, which confirm the assumption of strain release during cycling.

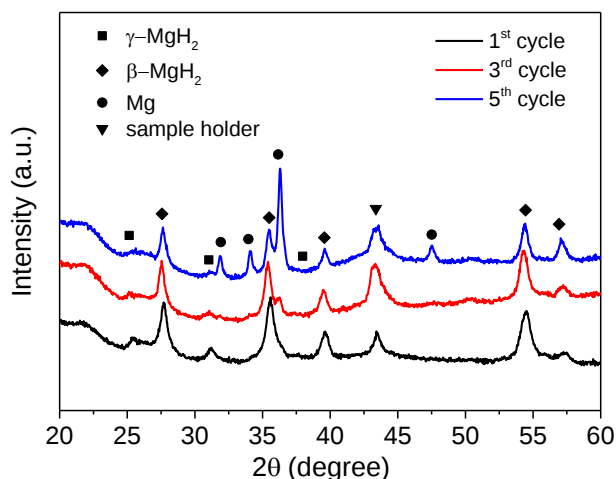


Figure 6-20: XRD patterns of Mg/Ni nanocomposite cycling with 100 °C absorption and 200 °C desorption.

The ball milled MgH_2 was used as a comparison to electrochemical codeposited Mg/Ni nanocomposite. As shown in Figure 6-21, ball milled MgH_2 was not able to desorb H_2 at 200 °C, and even the residual $\gamma\text{-MgH}_2$ did not decompose. Only a high temperature (375 °C) could fully desorb H_2 while H_2 reabsorption at 100 °C was not possible. When ball milled MgH_2 was fully rehydrogenated at 375 °C, the $\gamma\text{-MgH}_2$ vanished. This illustrated that the capability to regenerate $\gamma\text{-MgH}_2$ of ball milled MgH_2 is quite weaker than Mg/Ni nanocomposite prepared via electrochemical codeposition.

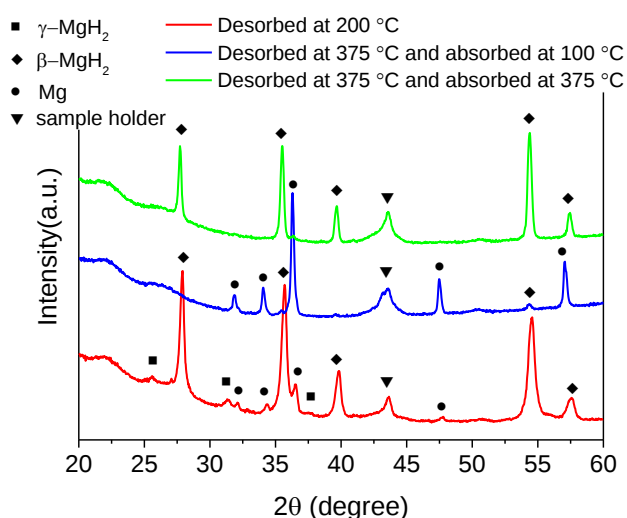


Figure 6-21: XRD pattern of ball milled MgH_2 after H_2 absorption/desorption.

6.8 Discussion

6.8.1 Synthesise Mg/Ni composite via electrochemical codeposition

A route to prepare Mg/Ni composite through electrochemical codeposition was developed and Ni nanoparticles were distributed homogeneously on the surface of larger Mg particles. Conventionally, magnesium-based nanocomposites for hydrogen storage are prepared by ball milling, the catalytic additives include metallic elements such as Ni, Co, Sn, Ge and metal oxides Cr_2O_3 , Nb_2O_5 . [13,41-45] Liu *et al.* synthesised a series of Mg/metal nanocomposites via a co-precipitation method in organic solution by chemical reduction, which showed high catalytic effectiveness of the hydrogen sorption process. The desorption temperature of MgH_2 was around 290-300 °C, which is similar to the value obtained in our investigation. The activation energy of hydrogen desorption was over $100 \text{ kJ}\cdot\text{mol}^{-1}$, and enthalpy of hydrogenation was about $70 \text{ kJ}\cdot\text{mol}^{-1}$ H_2 respectively. [14,46] These two parameters are not as good as the results displayed in this chapter.

The design of the electrochemical system influenced the final morphology and hydrogen storage properties. A magnesium counter electrode only formed a continuous compact product on a working electrode surface; while with Ni instead of Mg, the reduction of overpotential facilitated the codeposition of Mg and Ni. Such phenomenon could help to control the size of particles to some extent and prevent formation of big dendrites as observed in the electrochemical codeposition process. [47,48]

6.8.2 γ - MgH_2 formation and stability in Mg/Ni composite

Metastable γ - MgH_2 usually exists in ball milling MgH_2 sample especially over a long time ($> 20 \text{ h}$). [49] In some literatures, γ - MgH_2 is assumed to decompose at lower temperature than β - MgH_2 . However, the real decomposition mechanism is poorly

understood. [25,26] In our study, γ -MgH₂ can be formed as low as 100 °C with high content, even at higher temperatures, such as 200, 250 and 300 °C, this phase still exists in the hydrogenated samples without the phase transformation from γ -MgH₂ to β -MgH₂ (Figure 6-22a).

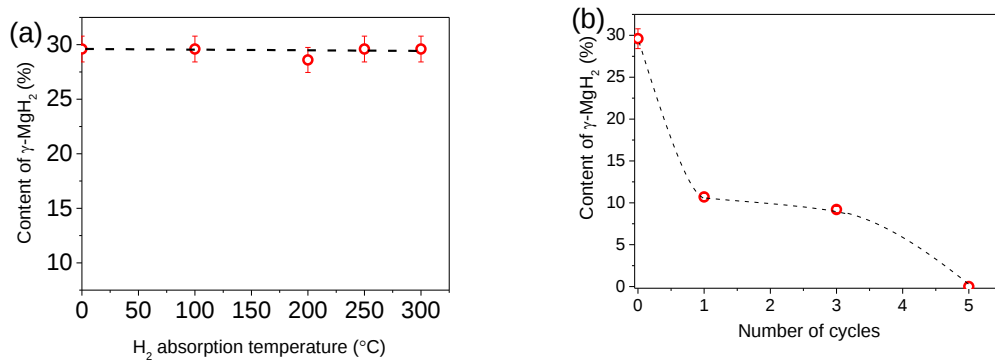


Figure 6-22: The thermal stability of γ -MgH₂. (a) Hydrogenated at various temperatures, (b) hydrogen cycling with 100 °C absorption and 200 °C desorption.

From the structure calculation, β -MgH₂ is with lower total energy corresponding to equilibrium cell volume than γ -MgH₂, so during the hydrogen absorption process, β -MgH₂ is the preferable phase.[50] The explanation for γ -MgH₂ forming when absorbing hydrogen at higher temperatures such as 200, 250 and 300 °C is that the hydrogen is fully absorbed at low temperature (e.g. 100 °C) during temperature increasing process as hydrogenation process with fast reaction rate. It also implies that the strain in MgH₂ cannot be released even under high temperature, as γ -MgH₂ is stable at temperature higher than 300 °C and there is no structural changing. [51] However, the formation of γ -MgH₂ is degraded upon hydrogen cycling even at low temperatures because of strain release at Mg phase (Figure 6-22b).

Absorption/desorption cycling at 250 and 300 °C (Figure 6-23) showed impressive results. No γ -MgH₂ can be detected in XRD patterns, which means the strain is released faster at higher temperatures. Consequently, in order to utilise the enhancement from γ -

MgH₂, the hydrogen absorption and desorption could and must be proceeded with relatively low temperature to keep the strain of microstructure. This is different from most of the results reported before where hydrogenation was usually taken at 300 °C or higher temperature to ensure full absorption.[52,53]

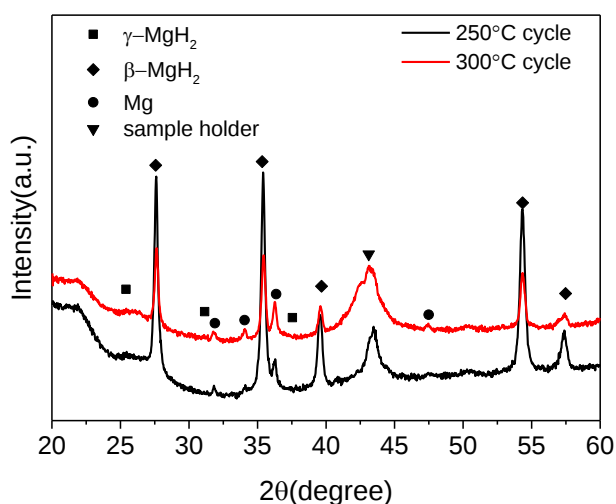


Figure 6-23: XRD patterns of Mg/Ni composite cycled at high temperatures.

6.9 Conclusion

With the purpose of tuning the thermodynamics and kinetics of magnesium, forming Mg-transition metal nanocomposite is a promising method. In this chapter, *in-situ* electrochemical codeposition is developed to synthesise Mg/Ni nanocomposite to improve the hydrogen storage properties of Mg-based material.

Mg(BH₄)₂ is used as a magnesium precursor, and the electrolysis condition is found to be crucial to deposit Mg/Ni nanocomposite with the proper nature. Material of the sacrificial anode, concentration of supporting electrolyte TBAB and deposition current would change the morphology, elements distribution and hydrogen storage properties of final products. With the best combination of electrolysis components, 20 mM Mg(BH₄)₂, 20 mM TBAB, Ni counter electrode and 5 mA current, well distributed Ni nanoparticles

(~3 nm) grew uniformly on ~30 nm Mg particles. On the other hand, external addition of catalysts such as Nb₂O₅ and Ni are not able to produce an ideal mixture with Mg deposits.

The Mg/Ni composites absorbed hydrogen at low temperature (100 °C) and a metastable γ -MgH₂ phase was formed with considerable content. The decomposition of γ -MgH₂ is more complicated than reported before, as it decomposes along with β -MgH₂ rather than individually at lower temperature. Only with a little amount of γ -MgH₂ or the inhomogeneous distribution between γ - and β -MgH₂, will two hydrogen desorption peaks be presented. The former one should be the combination of γ - and β -MgH₂ decompositions, and the latter is β -MgH₂ alone. The thermal stability of γ -MgH₂ is impressive, it will not transform to another phase with hydrogen pressure even when the temperature increases to 300 °C. The hydrogen absorption and desorption cycling releases the strain in structure and the ability to regenerate γ -MgH₂ degrades. This effect is more drastic at high temperature.

The activation energy of hydrogen desorption increasing after 250 °C cycling compared with direct hydrogenation at 100 °C demonstrated the thermal instability of the Mg/Ni nanocomposite, while the excellent cyclability at high temperature indicated that the samples would be stable. The hydrogen absorption enthalpy of Mg/Ni nanocomposite with 20 mM TBAB and 5 mA significantly decreased to a relatively low 57.5 kJ·mol⁻¹ H₂, however, the desorption enthalpy is with “standard” 74.8 kJ·mol⁻¹ H₂ which is close to the MgH₂ without any modification because of the loss of γ -MgH₂. The improved kinetic and thermodynamic properties demonstrate that electrochemical codeposition provides novel tools to achieve an effective alteration of magnesium-based hydrogen materials preparation.

One drawback in the current electrochemical system is that the impurities adsorbed on the final product resulted in the low hydrogen capacity even when the Mg in composite was fully hydrogenated. It requires more stable surfactants to substitute the TBAB to form electrolyte, while the effect of stabilisation for the nanocomposite must be maintained. Maybe cationic surfactants with a longer alkyl chain such as hexadecyltrimethyl ammonium bromide (CTAB) could be washed off by solvent more easily thus decreasing the amount of adsorbed impurities on metal clusters.[39] The other disadvantage is the particle size of magnesium deposits is still too big to achieve fast hydrogen sorption kinetics even with Ni as a catalyst. One possible approach to solve this issue is to apply sonoelectrochemical deposition, the sonicate of the working electrode will forcibly strip Mg deposits and prevent further growth, thus smaller Mg nanoparticles can be produced.

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CHAPTER 7 ELECTROCHEMICAL SYNTHESIS OF COMPOSITES WITH MAGNESIUM AND CARBON-BASED MATERIALS

7.1 Introduction

Carbon materials were widely used in nanoconfinement of magnesium to achieve better hydrogen storage properties especially kinetics due to their excellent thermal conductivity and large surface area. The options of carbon materials include carbon nanotubes (CNT), high surface area graphite (HSAG), graphene, etc.

Currently, magnesium nanoconfinement with carbon materials is usually prepared via mechanical milling and thermal decomposition.[1,2] Xia *et al.* synthesised monodispersed magnesium hydride nanoparticles on graphene which led to impressive hydrogen sorption kinetics that hydrogen could fully desorb in 30 min at 250 °C.[3] Herein we propose to utilise the electrodeposition method to prepare Mg/carbon composite to promote the hydrogen storage properties. The surfactants will be removed from the electrolysis system to avoid any by-products generated during reaction. As reported before, highly dispersed Pd nanoparticles supported on graphene were successfully prepared by a one-step electrochemical codeposition approach.[4] Cu-graphite and Cu/Ni-multiwalled carbon nanotubes composites can also be synthesised by the electrodeposition method, [5,6] so a similar approach should be possible with Mg.

In another aspect, electrochemical deposition also can lead to thin film structures, and in Chapter 4, it has been shown that Mg film could be readily deposited at Ni substrate, which consisted of small Mg particles.[7-9] Therefore, to further investigate/extend the potential of the electrodeposition method, we will aim at electrochemically depositing nanosized Mg film on conductive polymer substrates (e.g. polypyrrole (PPy)), that is

easy to recover for additional H₂ characterisation. Taking this concept further, a multilayered sandwich PPy-Mg-PPy structure could be grown to increase the H₂ capacity. Conductive polymer PPy can be electropolymerised in organic electrolyte to avoid moisture, oxygen and acid reacting with magnesium.[10] Depositing metal on PPy film is widely reported, copper, nickel and gold nanoparticles could be electrochemically reduced on PPy surface.[11-14] However, covering the metallic layer with another PPy film has never been investigated.

In this chapter, carbon nanotubes (CNT) or high surface area graphite (HSAG) was used as the substrate suspended in the electrolyte, which were supposed to be deposited with magnesium to form Mg/carbon composites. The morphology and hydrogen storage properties of the products were investigated. Furthermore, a Mg-PPy sandwich structure was also prepared with the aim of investigating the hydrogen sorption properties.

7.2 Experimental section

7.2.1 Chemicals

Magnesium ribbon, platinum mesh, nickel plate and titanium foil were purchased from Goodfellow, tetrahydrofuran (THF) was purchased as HPLC grade from Fisher Scientific and dried using a LC Technology SP-1 solvent purification system. Di-*n*-butylmagnesium (MgBu₂) in heptane, pyrrole monomer and tetrabutylammonium hexafluoro-phosphate (TBAPF) were from Sigma-Aldrich. Carbon nanotubes (CNT) and high surface area graphite (HSAG) were also purchased from Sigma-Aldrich.

7.2.2 Magnesium deposited on carbon suspension

In a typical experiment, 20 mM MgBu₂ was mixed with 1 mg·mL⁻¹ CNT or HSAG in 18 mL THF to form the electrolyte. A 0.5 mA·cm⁻² current was applied to reduce Mg

with a Pt mesh (2 cm^2) acting as a working electrode and a Mg ribbon as a counter electrode. The electrolysis proceeded for 20 h to generate 9 mg of Mg and achieved Mg/CNT or HSAG ratio of 1:2. The concentration of CNT was also changed to 2, 5, 10 $\text{mg}\cdot\text{mL}^{-1}$ to check the effect of the carbon amount. At the end of the electrosynthesis process, the composites were centrifuged and washed with THF then dried under vacuum to remove residual solvent and impurities.

7.2.3 Magnesium/PPy multilayer structure preparation

Polypyrrole film was first deposited on a Ti electrode in an electrolyte containing 0.1 M pyrrole monomer and 0.1 M TBAPF in 18 mL THF solution. Ni plate and Ti foil were used as counter and working electrodes (2 cm^2) respectively. The electropolymerisation was done at $4\text{ mA}\cdot\text{cm}^{-2}$ for 2 min. The PPy film was then washed with THF several times. The electrolyte for Mg deposition on PPy film contained 30 mM MgBu_2 in 18 mL THF. The deposition process of Mg was then carried out with a Mg ribbon as a counter electrode, and a $0.5\text{ mA}\cdot\text{cm}^{-2}$ deposition current was applied for 1 h to form Mg film on PPy layer. To generate a sandwich structure, the conditions above were repeated.

7.3 Magnesium deposited on carbon suspension

The challenge of Mg/carbon composite synthesis is to distribute magnesium nanoparticles homogeneously onto the carbon substrate. Typically, in the electrochemical reduction method, the magnesium precursor and the carbon materials are dispersed in electrolyte. When the reaction starts, metallic magnesium could be formed directly on the electrode surface rather than on the carbon surface only. However, because of the conductive nature of carbon, it is expected that Mg will be deposited on the carbon materials every time the latter touches the working electrode. MgBu_2 would then be reduced at the carbon surface.

7.3.1 Magnesium nanoparticles deposited on CNT and HSAG

The morphologies of magnesium deposited in a $1 \text{ mg}\cdot\text{mL}^{-1}$ CNT suspension are shown in Figure 7-1. The bright-field mode shows the clear CNT morphology and different types of magnesium deposits. Small nanoparticles, irregular rods and well-developed hexagonal crystal illustrated that the magnesium growth in the electrodeposition system is not uniform, but some Mg was also deposited on the CNT.

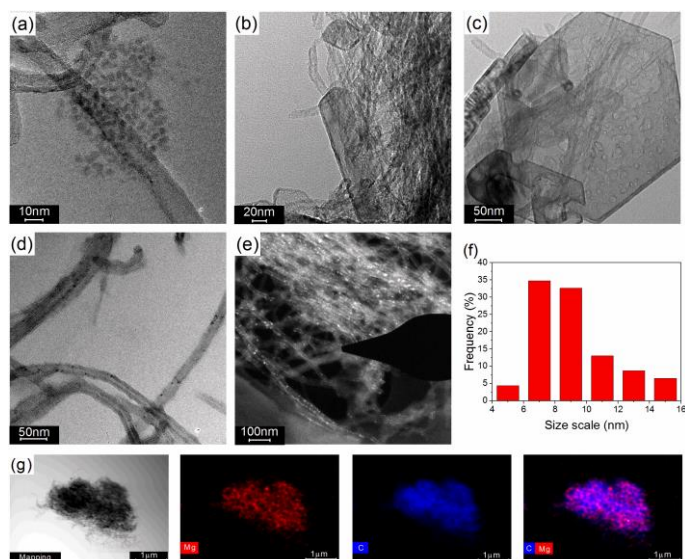


Figure 7-1: Magnesium deposited on CNT, (a-d) bright-field of TEM, (e) dark-field of TEM, (f) the size distribution of magnesium on CNT, (g) elemental mapping.

Figure 7-1d presents the magnesium deposited on CNT (because of the similarity in atomic weight, it is hard to distinguish magnesium from carbon).[15] However, the obvious Mg/C distribution can be observed from dark field image (Figure 7-1e), the size distribution of small magnesium crystallites (bright spots) on CNT is shown in Figure 7-1f, which is 4 to 15 nm. Elemental mapping further proves that the distribution of Mg and C is uniform (Figure 7-1g).

For HSAG, the amount of magnesium deposits was less compared to CNT (Figure 7-2), and the bright spots under the dark-field mode corresponding to Mg particles led to a

particle size of 6 to 16 nm. As reported, the specific of carbon nanotubes is over 1000 $\text{m}^2\cdot\text{g}^{-1}$, while that of high surface area graphite is 400 ~ 500 $\text{m}^2\cdot\text{g}^{-1}$. [16,17] The distinct morphologies demonstrated that CNT is a better carbon substrate than HSAG, as there is more active area exposed for CNT and thus more Mg deposits can adhere on the surface of CNT.

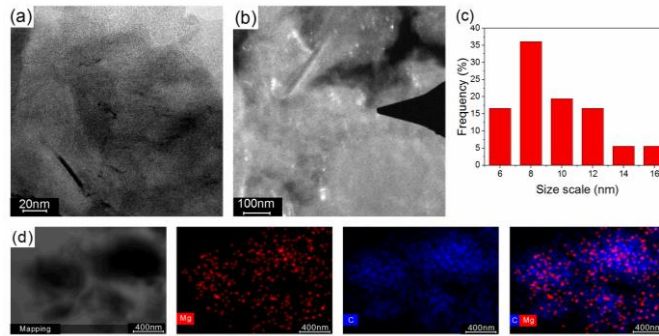


Figure 7-2: Magnesium deposited on HSAG, (a) bright-field of TEM, (b) dark-field of TEM, (c) the size distribution of magnesium on HSAG, (d) elemental mapping.

The XRD patterns of as-prepared Mg/C composites showed a typical hexagonal magnesium phase in Figure 7-3. However, there is no magnesium hydride phase detected after hydrogenation at 100 °C, which means that magnesium hardly absorbs hydrogen at low temperature. Hence transition metals or other catalysts (e.g. Fe, Ti, V) are needed to facilitate the hydrogen sorption at low temperatures. [18,19]

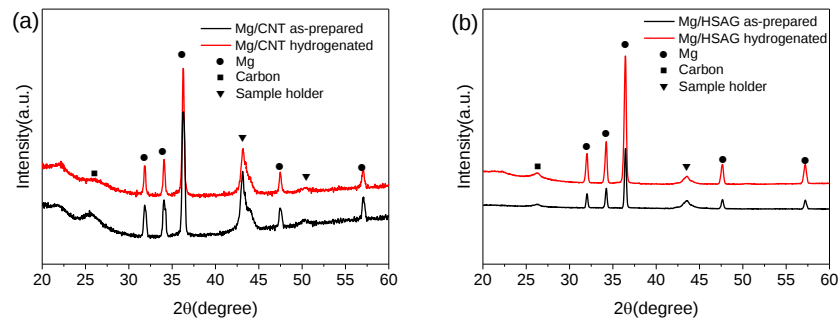


Figure 7-3: XRD patterns of magnesium deposited on (a) CNT and (b) HSAG before and after 100 °C hydrogenation.

Determination of H₂ release from mass spectra (Figure 7-4) also does not show an obvious signal corresponding to the release of hydrogen before 300 °C, and the temperature of the main H₂ desorption is over 400 °C. This is near the hydrogen desorption temperature of bulk MgH₂. This main peak was assigned to the large Mg particles (50-200 nm) produced along the Mg/CNT or Mg/HSAG composite materials. The small hydrogen desorption peaks around 150 °C were ascribed to the hydrogen sorption of nanosized Mg formed on carbon surface.

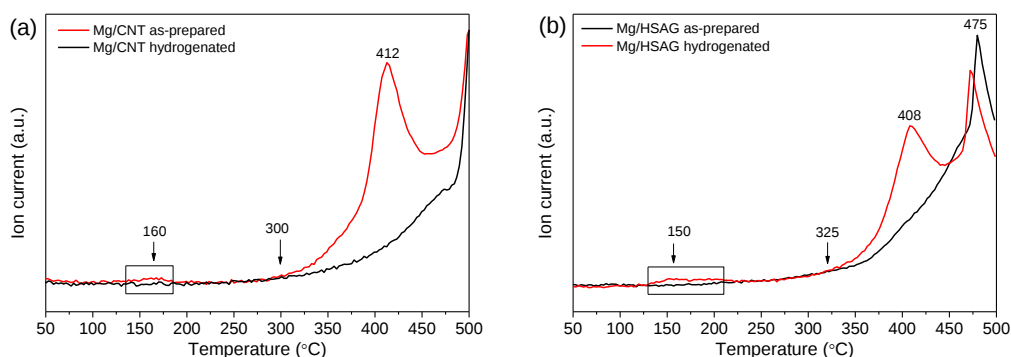


Figure 7-4: hydrogen release profiles of (a) Mg/CNT and (b) Mg/HSAG composites before and after 100 °C hydrogenation. The hydrogen peak at 475 °C for the product with HSAG should be ascribed to the functional groups on the graphite surface.

7.3.2 Effect of CNT concentration in electrolyte

As the hydrogen storage properties of Mg/C composites codeposited with low concentration (1 mg·mL⁻¹) carbon substrates were poor, the amount of CNT was varied in an attempt to increase the amount of Mg attached on the CNT surface. The electrolyte was thus modified with 2, 5 and 10 mg·mL⁻¹ CNT and 9 mg of Mg was electrochemically deposited. It is supposed that the high concentration of CNT would cover the surface of working electrode densely and there was more surface area for magnesium to adhere, which inhibited the subsequent growth of magnesium on the electrode.

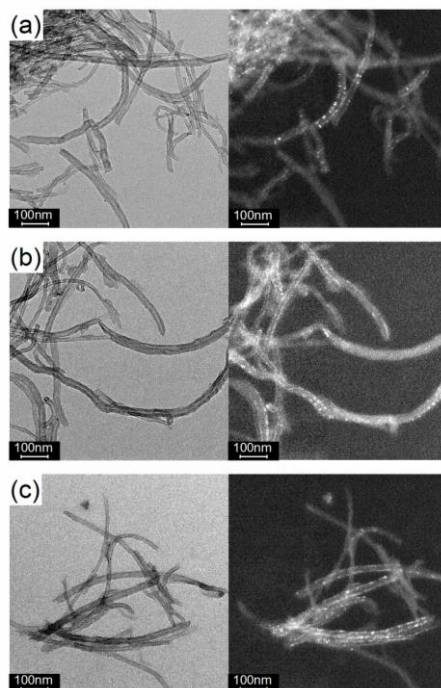


Figure 7-5: TEM images of as-prepared magnesium on (a) 2, (b) 5, and (c) 10 mg·mL⁻¹ CNT.

The evolution of morphologies of as-prepared Mg/CNT composites is not significant with CNT concentration modification as shown in Figure 7-5, but the distribution of Mg nanoparticles on CNT is not uniform in these three composites as present in the dark-field mode. This implies that the reduction process of MgBu₂ on CNT strongly depends on the conductivity of carbon nanotubes, so in order to obtain homogeneously distributed Mg deposits, the firm connection between CNT and the electrode surface must be established.

The influence of CNT concentration to hydrogen absorption properties for Mg/CNT composites was characterised by XRD (Figure 7-6). In the as-prepared samples, the signal of CNT is stronger as the concentration increases. This effect of CNT concentration is apparent after hydrogen absorption at 300 °C. The strongest peaks of MgH₂ appear in the sample with 10 mg·ml⁻¹ CNT, which suggests that a high

concentration of CNT is capable of improving the hydrogen absorption property to some extent, assuming the Mg deposits are confined by high concentration of CNT effectively.

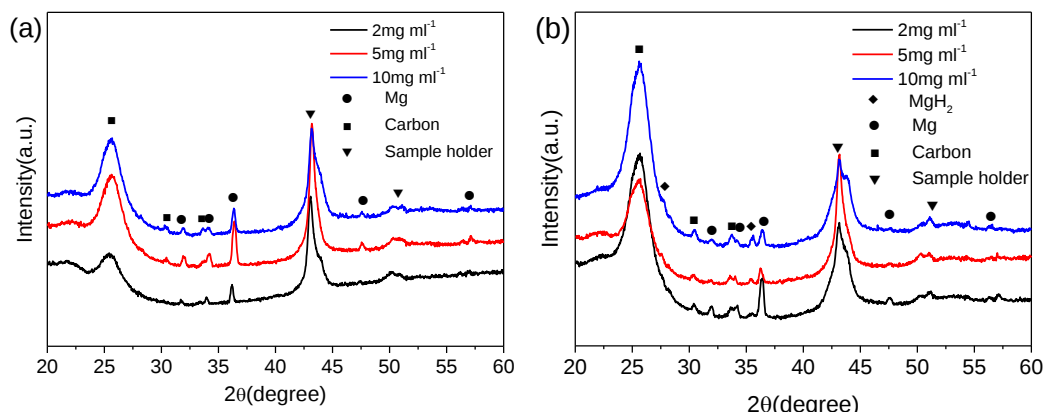


Figure 7-6: XRD patterns of magnesium deposited on different amounts of CNT (a) as-prepared and (b) after hydrogenation at 300 °C.

The mass spectra of samples with different concentrations of CNT after hydrogenation at 300 °C demonstrated that the hydrogen release only occurred at high temperature (Figure 7-7). Comparing the onset of hydrogen desorption, Mg deposited with 10 mg·ml⁻¹ CNT could start to release hydrogen at 350 °C, which is 25 °C lower than the one with 2 mg·ml⁻¹ CNT.

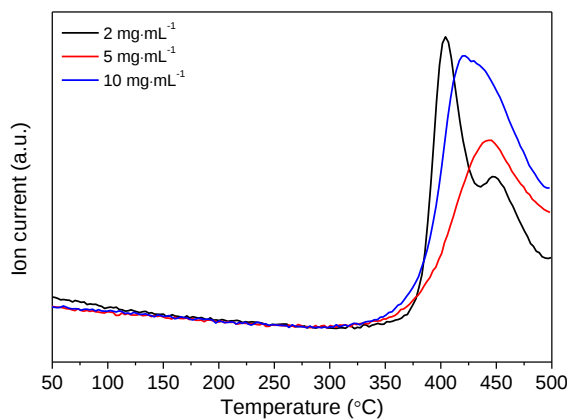


Figure 7-7: The hydrogen release profiles of samples with different concentrations of CNT after cycling at 300 °C.

7.4 Magnesium/PPy multilayered sandwich structure

A multilayer structure of magnesium with catalytic metals such as Pd, Ni was intensively investigated to improve hydrogen storage properties. These thin films with nanoscale features achieved shorter hydrogen diffusion distance, and the coating with a Pd layer prevented their oxidation.[20,21] For electrochemical deposition, conductive polymers can be used as a substrate to form Mg layer. A multilayer structure can then be generated by alternative polymer and magnesium films. This approach was thus investigated with the aim of stabilising Mg thin film while protecting these against oxidation.

7.4.1 Electropolymerisation of PPy film

Figure 7-8 showed the electropolymerised monolayer PPy film. The surface consists of PPy clusters and the thickness is uniform along the cross-section. This film is more smooth than reported before,[22] and this is important when considering the idea of growing subsequent layers. Compared with Mg/metal multilayer prepared by physical/chemical vapour deposition with several nanometers thickness, electrodeposition has to generate a much thicker PPy layer to cover Ti substrate completely. With shorter deposition time, thinner PPy film could be formed but some part of the Ti foil electrode surface was partially covered.

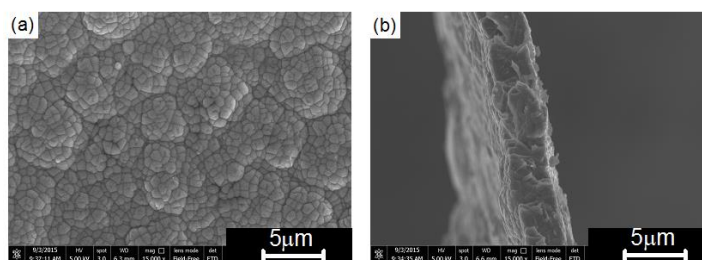


Figure 7-8: SEM images of the electropolymerised PPy monolayer, (a) surface and (b) cross-section.

To confirm the formation of PPy, FTIR characterisation was carried out. The FTIR spectrum is displayed in Figure 7-9a, a vibration of pyrrole ring appears at 1544 cm^{-1} . The band at 1030 cm^{-1} is assigned to the in-plane deformation vibration of pyrrole ring; and the bands at 1315 cm^{-1} and 920 cm^{-1} are attributed to C-N bond and C-H wagging respectively.[23,24] TGA-DSC and mass spectra (Figure 7-9b and c) of PPy film show that the thermal stability of the PPy film is not so high. A rapid mass loss occurs at around $200\text{ }^{\circ}\text{C}$, which is attributed to the thermal decomposition of PPy chains.[25] The C_3H_6 fragment shown in mass spectra should be ascribed to the surfactant TBAPF used in PPy electropolymerisation process, which is strongly adsorbed in the PPy film.

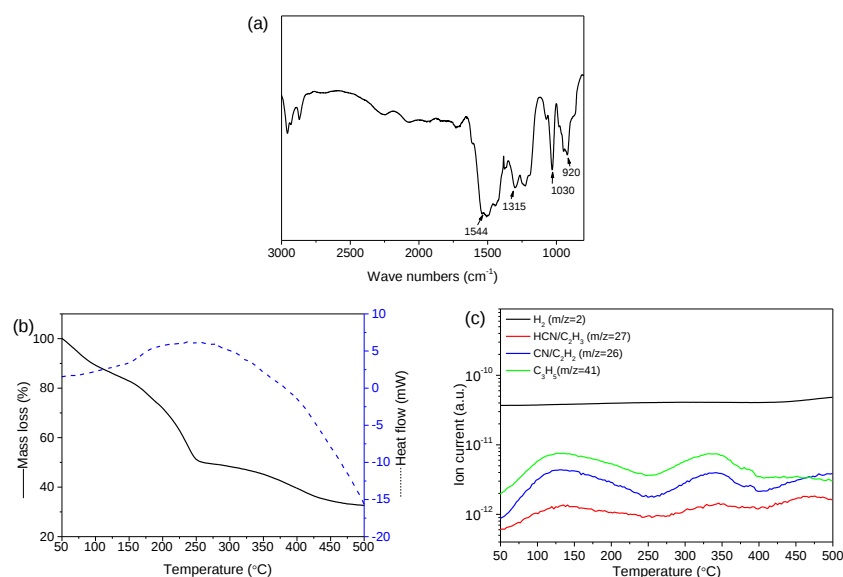
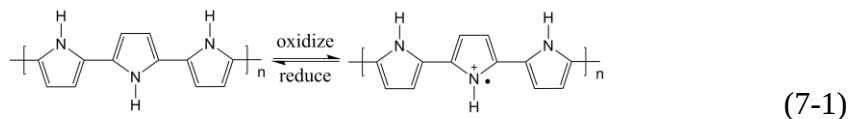


Figure 7-9: (a) FTIR of deposited PPy film, (b) TGS-DCS and (c) mass spectra of as-prepared PPy film decomposition.

7.4.2 Preparation of PPy-Mg-PPy sandwich structure

For magnesium deposited on PPy film, the process is quite different from the previous deposition on normal metal electrodes. Polypyrrole generally displays a yellow or green colour in the reduced form and a blue or violet colour in the oxidized state. [26] The oxidized PPy film is highly conductive (10^2 to $10^3\text{ S}\cdot\text{cm}^{-1}$) and the reduced form is

nearly insulating (10^{-15} to 10^{-5} S·cm⁻¹). [27] The transformation between reduced and oxidized forms is shown as followed: [28]



As magnesium requires a negative voltage to be reduced from Mg²⁺, PPy will also transform from an oxidized form to a reduced form if the potential is too low. How to balance these two processes is thus the key step to generating an ideal Mg layer on PPy film. Here the concentration of MgBu₂ was modified to achieve magnesium reduction and maintain the oxidized form of PPy. It is found that 20 mM MgBu₂ was not able to deposit a significant amount of Mg, and the original black PPy film turned to green. This means the low concentration of MgBu₂ demands quite low reduction potential as the Nernst equation demonstrated, [29] and PPy film is thus transformed from an oxidized form to a reduced form, the decrease of conductivity inhibited the subsequent deposition. 30 mM MgBu₂ was a suitable concentration for this electrodeposition, magnesium was able to deposit on PPy film without significantly changing the conductivity of PPy film.

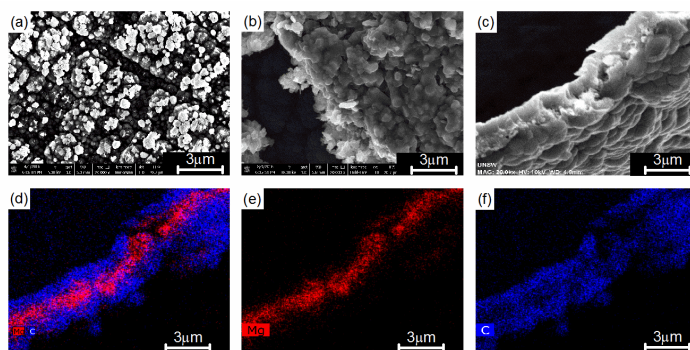


Figure 7-10: SEM images Mg deposited on PPy with (a) 10 min and (b) 1 h. (c-f) correspond to cross-section image and elemental mappings of PPy-Mg sandwich structure with three layers.

Figure 7-10 corresponds to the SEM images of the Mg deposited on the PPy film with different times and the PPy-Mg-PPy sandwich structure generated layer by layer. It is obvious that with longer deposition time, the surface of PPy was covered by more Mg until a continuous magnesium layer was formed. In the PPy-Mg-PPy structure, the Mg layer consisted of magnesium nanoparticles with about 1 μm thickness (Figure 7-10c and d). The XRD patterns in Figure 7-11 demonstrated the formation of a hexagonal magnesium phase, and this magnesium layer was found to remain stable after the deposition of a PPy layer to form a sandwich structure.

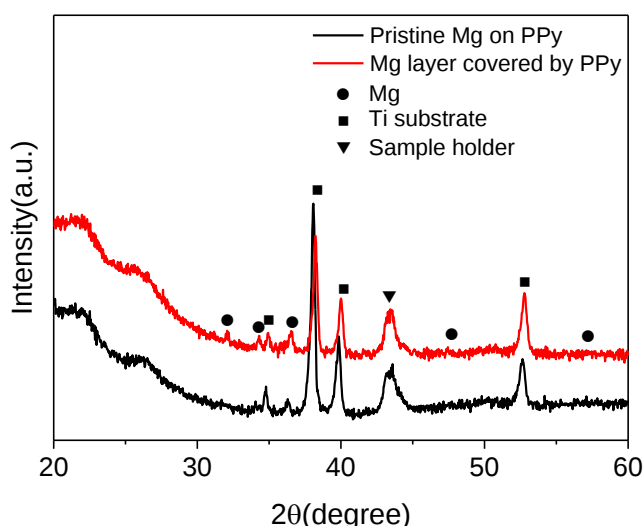


Figure 7-11: XRD patterns of pristine magnesium deposited on PPy film and Mg layer covered by second PPy to form sandwich structure.

PPy-Mg sandwich structure with more layers was also prepared as shown in Figure 7-12. It is observed that the layer structure is not quite uniform due to the complex process of deposition. In particular, the growth of a second PPy layer was inhibited on the Mg layer at some sites (Figure 7-12a). This morphology suggests that the uniformity of an individual layer determines the morphology of the next layer. With proper control, more layers with ideal structure could be prepared as Figure 7-12b displayed.

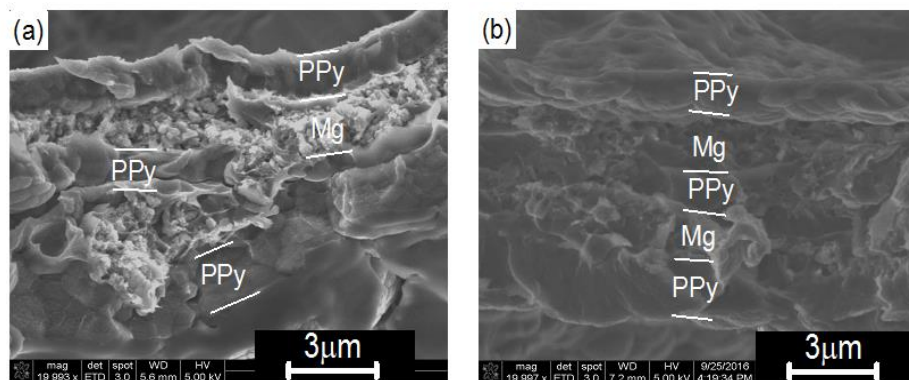


Figure 7-12: SEM images of PPy-Mg sandwich structure with five layers.

7.4.3 Hydrogen storage properties of PPy-Mg sandwich structure

The hydrogen sorption properties of such structure are hard to determine because of the initial decomposition of the PPy film due to lack of thermal stability. However, an initial assessment of the desorption behaviour was revealed for the following investigation.

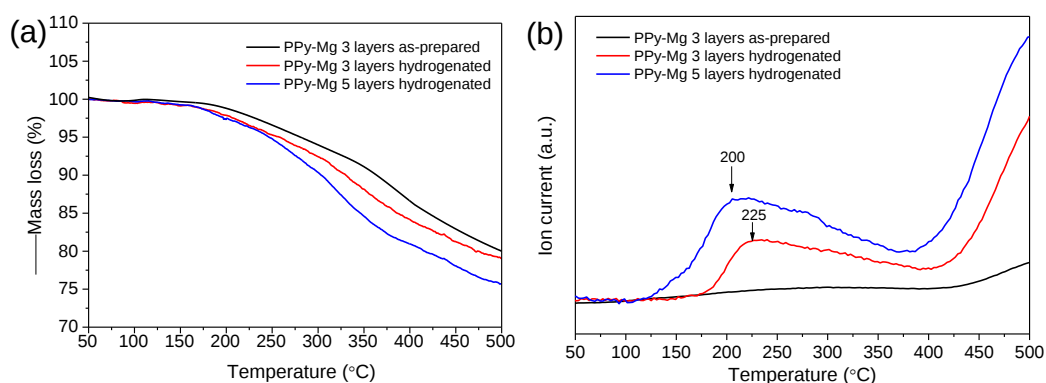


Figure 7-13: (a) TGA and (b) mass spectra of hydrogen release profiles of sandwich PPy-Mg depositions before and after being hydrogenated at 100 °C.

The TGA curves corresponding to the PPy-Mg sandwich structures in Figure 7-13a displayed big weight loss either before or after hydrogenation because of the decomposition of PPy film. Mass spectra in Figure 7-13b showed clear hydrogen desorption peaks of hydrogenated samples which can be distinguished from an as-

prepared one. The temperatures are also impressive, 3 layers PPy-Mg composite displayed peak temperature at 225 °C, and the 5 layers composite showed even lower temperature at 200 °C. This difference between the PPy-Mg sandwich structure before and after hydrogenation implies that the hydrogen sorption properties are significantly improved by PPy supported layers.

7.5 Discussion

Magnesium/carbon material composites were prepared by electrochemical codeposition with soluble Mg precursor MgBu_2 and suspended CNT or HSAG in THF solvent. Compared with Mg/C composites synthesised by ball milling, the hydrogen storage properties of the electrochemical codeposited composites were poor. The main drawback of the electrodeposition route is that the interaction between carbon suspension and electrode is potentially too weak, and Mg then prefers to be reduced on the electrode surface rather than carbons. However in the ball milling process, magnesium is mixed with carbon additives with high energy to enhance the interaction between them, while the desorption temperature of magnesium hydride with carbon materials modification usually desorbs hydrogen higher than 350 °C, [19,30-32] which is still far from practical application. It is also found that with a high concentration of CNT, Mg/CNT composite could achieve better hydrogen storage properties, as Mg active species has less chance to be reduced on electrode.

The previous literature demonstrates that the type and specific area of carbon materials significantly influence the hydrogen sorption properties of MgH_2/C composites.[30,33] Furthermore, in order to enhance the hydrogen storage properties of the composite, it is necessary to introduce catalysts.[34-37] These findings implied that it is possible to

improve the electrochemically deposited Mg/C composite by changing the carbon sources and adding extra catalytically nanoparticles.

The Mg-PPy multilayered sandwich structure is hindered by the instability of PPy. In order to improve this, different conductive polymers such as PANi (polyaniline)[38] and PEDOT (poly(3,4-ethylenedioxythiophene)) [39] can be tried to substitute for PPy. Other additives, for example, chitosan [40] or carbon [41] are able to stabilise polymers under relatively high temperatures (~ 300 °C). If the magnesium deposited on thermal stable polymers still realises a low sorption temperature, the influence of PPy decomposition can be minimised to maximise the cyclability of the Mg/conductive polymer composite with a multilayered sandwich structure.

The hydrogen storage properties of Mg thin films are affected by the synthetic conditions and thickness.[21] Generally, thicker Mg films would desorb hydrogen at higher temperature,[42,43] however, the defects and stress induced in a thicker layer also decrease the desorption temperature in some cases.[21] The layer structure inhibits significant volume changing or recrystallisation during hydrogen absorption and desorption so the cycling ability could be improved.[44] For electrochemical preparation, thinner (< 100 nm) films of conductive polymer and magnesium are needed to be generated by better controlling, more layers can then be synthesised as magnetron sputtering and laser depositing methods. Thus the hydrogen storage properties of a Mg/conductive polymer multilayered sandwich structure could be promoted.

7.6 Conclusion

Carbon-based materials were used to form a Mg/C composite to achieve better hydrogen storage properties of Mg, while the results demonstrated that electrochemical codeposition is not a proper route at present. The products were not able to absorb

hydrogen at 100 °C, and were not fully hydrogenated even at 300 °C. The hydrogen storage improvement with high concentration of CNT implied the strategy to inhibit Mg direct reduction on the electrode surface is necessary. One possible improvement is the combination of CNT with pyrrole to form a conductive polymer/CNT layer on the electrode.[45] The direct deposition of Mg nanocrystallites on the electrode surface can then be inhibited by a conductive polymer layer; furthermore, CNT will be connected to the electrode surface to achieve higher conductivity. Such a strategy could lead to Mg/C composites with better hydrogen sorption properties.

Another route was developed to form a Mg-PPy sandwich structure to realise the excellent hydrogen sorption kinetics as the Mg-metal layers reported before. The preparation of a multilayer structure involved complex processes and was sensitive to the conditions of electrolysis. The PPy-Mg multilayer structure was well controlled and from TGA-MS curves, the hydrogen desorption temperature decreased to 200-225 °C, which was impressive for Mg-based hydrogen storage materials. The poor thermal stability of PPy hindered precise measurement of hydrogen capacity of such a composite, conductive polymers with better thermal stability are required to optimise this interesting novel approach. Nevertheless, a new electrolysis system especially the electrolytes used for polymer and Mg depositions needs to be explored to prepare thinner layers alternatively, for example, changing the supporting electrolyte to realise a polymer layer thinner than 100nm.[12]

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CHAPTER 8 CONCLUSIONS AND FUTURE PERSPECTIVES

The trend of energy transition towards renewable resources urgently requires an efficient and reliable energy storage system to withstand the imbalance between power production and demand induced by the intermittent nature of renewable energy. Currently, batteries are the most practical choice. However, the concerns about batteries such as relatively low energy density, lifespan, and restricted operating conditions appeal for alternative sustainable storage systems with high energy density. Hydrogen is a very promising option due to its universal abundance, high energy capacity, versatility in production, and zero-emission at the point of use. However, the lack of a practical hydrogen storage method currently restrains its widespread utilisation. Storing hydrogen in solid state metal hydride materials is a safe, compact and efficient route. Nevertheless, there are some major challenges of metal hydride materials such as limited hydrogen density, poor effective reversibility, high thermodynamic requirements, and slow reaction kinetics. Light metal hydride MgH_2 has advantageous high hydrogen capacity above 7.6 mass%, yet suffers the drawbacks of low recyclable capacity under mild conditions as well as some thermodynamics and kinetics hurdles.

With the purpose of improving the hydrogen storage properties of magnesium, nanosizing and adding catalysts are the most popular measures to choose. Different from synthetic methods used before, electrochemical deposition of magnesium, conducted under mild conditions and which could form various types of products with proper modifications, was the method developed in this thesis. The thermodynamic and kinetic properties of magnesium hydride were improved via various effective morphology control and catalyst introduction approaches. Hydrogen absorption and desorption at relatively low temperatures were also realised in this thesis.

Firstly, to establish an available electrochemical deposition system to prepare magnesium nanostructures, various magnesium precursors and surfactants/stabilisers were used to test the solubility, electrochemical stability and the influence of functional groups. The final deposits with different conditions demonstrated that most of the combination of di-*n*-butylmagnesium and cationic surfactants just formed a compact magnesium film on working electrode. However, TBATFMS achieved suspended nanoparticles due to the counterion weakening the interaction between electrolyte and electrode. Nevertheless, anionic surfactant SDBS produced big dendrite deposits and non-ionic polymer PMMA generated Mg matrix consisting of nanoparticles.

In order to investigate the morphology and hydrogen storage properties of magnesium thin films deposited on substrates, catalytic (Ni) and non-catalytic (Ti) substrates were used as working electrodes to reduce MgBu_2 and $\text{Mg}(\text{BH}_4)_2$. The morphologies of the final products demonstrated that reduction overpotential and diffusion rate of electroactive species led to diverse deposit growth modes. MgBu_2 deposited on Ni with the smallest particle size (68 ± 11 nm) showed the best hydrogen storage properties, which achieved low hydrogen desorption activation energy (37.8 ± 0.7 kJ·mol⁻¹ H₂). The kinetics of hydrogen desorption of Mg deposited on Ni foam was surface-controlled at low temperature (150 °C) while at a higher temperature (e.g. 200 °C), the rate-limiting step was controlled by diffusion. The synergetic of the catalytic substrate and small particle size improved the hydrogen sorption properties of magnesium in an impressive manner.

As the metal substrates are too heavy, the magnesium thin film could only realise quite low hydrogen capacity, thus a new electrochemical system to generate isolated magnesium particles was designed to get rid of the substrates. Cationic, anionic, non-ionic stabilisers and their combinations were used to modify the system and investigate

the evolution of morphologies and hydrogen storage properties. In the products with single stabilisers, different morphologies of magnesium deposits were shown, while only PMMA exhibited high hydrogen capacity after hydrogenation at 100 °C. The combination of cationic and anionic stabilisers improved the hydrogen storage properties to some extent, the desorption temperature decreased to 317 °C for TBATFMS/SDBS combination, but the conversion rate from Mg to MgH₂ was still low at 100 °C. However, the triple compositions electrolyte consisting of TBATFMS, SDBS and PMMA showed impressive improvements. The hydrogen capacity reached 4 mass% after hydrogenation at 100 °C, meanwhile the desorption temperature was only 336 °C. In addition, the sample from triple compositions was capable of absorbing hydrogen at a temperature lower than 100 °C, even room temperature, although the hydrogen capacity was limited due to the slow kinetics.

Catalyst introduction had proven to be a very effective way of drastically improving the hydrogen storage properties of magnesium, but the electrochemical route taken to prepare composites of Mg and catalysts had not been studied before. The attempt to establish an *in-situ* codeposition system to prepare Mg/Ni nanocomposites was achieved with Ni sacrificial anode and soluble magnesium precursor Mg(BH₄)₂. The final products could absorb considerable amount of hydrogen at 100 °C and exhibited a high content of metastable γ -MgH₂, which is a phase induced from high pressure and usually observed in the ball milling route with low content. The modifications of deposition current and concentration of surfactant TBAB were investigated and the results demonstrated that with proper conditions, the Mg/Ni nanocomposite was able to fully convert into MgH₂ at 100 °C with 30.6 % γ -MgH₂. Such a mixture of MgH₂ phases can fully release hydrogen lower than 200 °C under dynamic vacuum, and the desorption temperature on TGA is only 285 °C, which is over 100 °C lower than bulk magnesium.

Furthermore, the formation and regeneration of γ -MgH₂ was investigated, and it was found that the ratio of γ -MgH₂ kept stable even when hydrogenated at 300 °C, while it decreased fast during hydrogen absorption and desorption cycles at lower temperature. The release of strain in the Mg/Ni composite during cycling was regarded as the reason for the disappearance of γ -MgH₂, and this was confirmed by the strain values calculated for Mg/Ni composites as-synthesised and after hydrogen desorption.

Preliminary investigations were also performed into composites of magnesium and carbon-based materials. Magnesium was codeposited with carbon nanotubes (CNT) and high surface area graphite (HSAG) suspended in electrolyte to form Mg/C composite, while the hydrogen storage properties were not improved compared with bulk magnesium. This illustrates that the strategy still needs significant modification. Another attempt to prepare Mg/C composite is to form Mg-PPy multilayer structure. The PPy and Mg films were alternatively generated by the electrochemical deposition method and showed remarkable hydrogen sorption properties.

Electrochemical deposition is still a novel method of preparing magnesium-based hydrogen storage materials, the mechanism and factors to control the system are not fully understood at present. Future investigations should focus on four broad areas.

1. Testing more types of magnesium precursors and surfactants/stabilisers to summarise the effect of the electrolysis system on the properties of magnesium deposits. These include the morphology and particle size distribution of final products, as well as the hydrogen storage properties.
2. Synthesising magnesium nanoparticles with a proper stabiliser to realise the smallest amount of stabiliser adsorbed on final product to maximise the hydrogen capacity,

meanwhile keeping the nanostructure of deposits stable during hydrogen absorption-desorption cycling.

3. Changing the Ni counter electrode in the codeposition system to other metallic sacrificial anodes to prepare different types of Mg/metal nanocomposites. This strategy could be used to investigate the catalytic effect of different metals to magnesium and the potential to generate γ -MgH₂.

4. Depositing magnesium nanoparticles with substrates or on decorated electrode to improve the distribution.

In comparison with previous synthetic methods, the electrochemical deposition approach provides a means of modifying magnesium nanostructures with a remarkable evolution of morphologies and hydrogen storage properties. The thorough investigation could realise a step forward in the solution of the energy storage problem.

