Anisotropic Mg Electrodeposition and Alloying with Ag-based Anodes from Non-Coordinating Mixed-Metal Borohydride Electrolytes for Mg Hybrid Batteries

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Abstract

A highly anisotropic electrodeposition was observed using the hybrid battery electrolyte $\text{Mg}(\text{BH}_4)_2$ with LiBH_4 in diglyme. At low overpotentials high aspect ratio platelet morphologies are observed with a strong fiber texture composed of a $\{10\text{-}10\}$ and a $\{11\text{-}20\}$ component, the first evidence of behavior of this kind in magnesium battery electrolytes. At high overpotentials the deposit aspect ratio is indistinguishable but the texture is shown to be primarily composed of a $\{11\text{-}20\}$ fiber texture. The kinetic parameters relative to the relevant crystallographic faces are extracted from electron microscopy images and compared with the observed bulk rate extracted from the electrochemical data. The use of polycrystalline Ag foil substrates with little preferred orientation at the surface allowed highly polycrystalline nucleation at lower overpotentials than that of platinum, likely due to Ag alloying with Mg. Characterization using focused ion beam (FIB) cross-sections with Auger Electron Spectroscopy (AES) elemental analysis confirm that the deposits are primarily Mg although Mg-Ag alloys of various compositions were observed. It is proposed that the orientation at slow rates of growth is due to the underlying kinetics of adatom diffusion on Mg and that higher rates diminish the phenomenon due to decreased time for adatom diffusion and instead are governed by the rates of adatom formation or more specifically the adatom vacancy formation on the different low-index planes of Mg.

Keywords

Magnesium anode
Crystal growth
Rechargeable magnesium battery
Adatom diffusion
Texture anisotropy

1. Introduction

Magnesium has many of the indicators of a technology that, in principle, might come to displace Li-ion batteries. When compared to Li, Mg is less expensive, more environmentally benign, has a higher volumetric capacity (3833 vs 2062 mAh cm⁻³), and is believed to not be plagued by the formation of dendrites [1]. Commercial production of Mg batteries has been limited due to many problems associated with the high charge density of the Mg²⁺ ion that can generally be categorized as: (1) ion mobility within the cathode [2, 3] (2) anode passivation [4, 5] and (3) electrolyte oxidative stability [6, 7]. Electrolyte development has been arguably the most critical challenge because further studies of prospective cathodes depend upon establishing a stable, non-corrosive electrolyte with a 3 V potential window. The problem of Mg battery electrolyte development has been a Sabatier-like balance of coordination, requiring Cl⁻ coordination strong enough to dissolve the Mg²⁺ ion, yet sufficiently weak (e.g. a μ -Cl complex) to release Mg²⁺ for electrodeposition [8-10]. It is only recently that electrolytes have been developed that are considered ‘non-coordinating’ and non-corrosive [11-13], although questions remain about the specific interactions that might be present due (in part) to the presence of breakdown products. While of great interest, there remain many critical questions to address in these systems, especially ones related to how these (or other newly discovered) electrolyte compositions can be tailored to further improve essential features of electrochemical performance.

Two factors impacting performance in metal anode batteries, the morphology of an electrodeposited metal and the identification of mechanisms to control its evolution in operando, present interesting challenges to progress in research given the complexity of the many features that contribute to them. We have previously shown that passivation anisotropies can

significantly impact the evolution of the morphology of electrodeposited Mg anodes and provide one mechanism of efficiency loss on cycling [5]. Another important mechanism is microvoid formation, which leads to electrical isolation of active material in a manner similar to the electrodes of Li metal batteries that are known to produce dendrites [14, 15].

The morphology arising from electrodeposition is defined by an overpotential, which is a complex combination of properties including mass diffusion, electrolyte equilibria, charge transfer processes, as well as traditional nucleation and growth concepts like surface energy and adatom diffusion. Rates for charge transfer and mass diffusion can be extracted from electrochemical data, but nucleation and growth parameters can be much more difficult to analyze and as a result are frequently developed via theoretical modeling or estimations taken from fundamental UHV studies of metal growth. Nucleation has been modeled using electrochemical data, but such treatments typically embed gross simplifications (e.g. assuming hemispherical nuclei) and only report on their number without capture of the crystallographic features of their growth [16-18]. One study of Mg electrodeposition exists that examines morphology in growth under practical conditions and concludes that it is dominated by surface energetics at slow rates, but diffusion at high rates [1]. While surface energy is undoubtedly important, it is also understood in many systems that it is the dynamical attributes of adatom diffusion on different crystallographic planes that are critical for the development and evolution of morphology during growth [19-21]. It arises as an important need, then, to ascertain how the effects of adatom diffusion and nucleation interplay within the evolution of texture in Mg electrodeposition and how these features change at different applied potentials. The present study addresses these concerns for an exemplary “non-coordinating” electrolyte system.

The choice of substrate is important when studying deposition morphologies due to such factors as underpotential deposition (UPD), epitaxial growth, and alloying. Electrolyte development studies commonly use Pt as a substrate due to its stability towards corrosion, but more practical materials have also been examined that show different behavior [22]. Most Mg electrolytes have a large overpotential for deposition on Pt, which causes sparse nucleation in growth regimes near the onset potential. Electrolyte additives provide one means to modify this behavior. We have previously shown that the overpotential for the deposition of Mg from a $\text{Mg}(\text{BH}_4)_2$ electrolyte decreases in the presence of a LiBH_4 additive due to the UPD of Li on the Pt [23]. An intriguing alternative to Pt is Ag, in part due to its high theoretical range of operating potential. The binary phase diagram further suggests that Ag could be a prospective alloying anode material for Mg batteries [24], yet no studies have examined it for such a purpose (see Tables S1-S4). Silver also has an unexpected benefit for morphology studies due to an even lower overpotential for deposition than Pt (<50 mV for Ag compared to >500 mV for Pt, vide infra), a feature that we show allows a more uniform habit of nucleation and growth at values of applied potential lying closer to the thermodynamic limit.

Herein we describe data that reveal the important role played by the texture-sensitive dynamics of adatom diffusion and the potential-dependence of nucleation in the evolution of texture during Mg electrodeposition on a base Ag electrode. The study highlights the discovery and analysis of a distinctly different anisotropic growth mode than has previously been seen in Mg electrolytes and a marked activity towards alloy formation due to the interdiffusion of Ag into the accreting Mg deposit. The electrolyte used is $\text{Mg}(\text{BH}_4)_2$ with LiBH_4 in diglyme, a well-studied electrolyte that has been proven to work well in Li-Mg hybrid batteries [25-27]. The use of a Ag electrode enhances the efficiency of this electrolyte system, further reducing the

overpotential for the onset of growth and fostering dense heterogeneous nucleation in conjunction with the significant interdiffusion of Ag. The latter feature leads to a complex speciation of the Mg deposit that evolves from a Mg rich speciation at the growth surfaces to specific alloy/intermetallic compositions at its base. The attributes of the growth dynamics seen experimentally are well described by kinetic nucleation theories and texture-dependent adatom/vacancy diffusion rates of Mg.

2. Experimental

LiBH_4 and $\text{Mg}(\text{BH}_4)_2$ were purchased from Sigma-Aldrich and used without further purification. Anhydrous diglyme was purchased from Sigma-Aldrich and further purified by distilling over calcium hydride and subsequently storing over activated molecular sieves to decrease water content to less than 10 ppm according to Karl-Fischer titration analysis. The electrolyte 0.1 M $\text{Mg}(\text{BH}_4)_2$ + 1.5 M LiBH_4 in diglyme was used for all the electrochemical experiments, unless otherwise stated. All electrochemical experiments were performed in an argon-filled MBRAUN LABstar glovebox with $\text{O}_2 < 2$ ppm. Electrochemical experiments were performed using either CH Instrument 650 B or 660 D model instruments. Mg foil (99.95%, 0.05 mm thick, GalliumSource, LLC), stainless steel foil (304, 0.1 mm thick, Alfa Aesar), Pt foil (Grade 1, 0.1 mm, thick Johnson Matthey), and Ag foil (99.998%, 0.1 mm thick, Alfa-Aesar), were used as the working electrodes. Roughening of the Ag foil was performed according to an established protocol [28]. For all experiments, freshly abraded Mg ribbons formed the counter and reference electrodes. All potentials are referenced to Mg/Mg^{2+} (-2.37 V vs. SHE).

XRD experiments utilized a PANalytical Philips X'pert MRD system equipped with a Cu K- α source at 0.15418 nm located in the Frederick Seitz Materials Research Laboratory (FS-MRL) at the University of Illinois at Urbana-Champaign. XRD 2 Θ - Ω scans were taken at a scan rate of 1.2° min⁻¹ for all samples. Pole figures of the {10-10}, {10-11}, and {11-20} peaks for depositions at -200 and -500 mV on Ag foil were taken at 5° s⁻¹. XRD results were analyzed using JADE XRD analysis software and the MTEX toolbox for Matlab [29].

SEM experiments used a JEOL 7000F analytical SEM that is housed at the FS-MRL facilities. Samples were rinsed with diglyme and allowed to dry in the glovebox before removing for imaging. All experiments utilized a 15 keV accelerating voltage and working distance of 10 mm.

FIB and AES analysis were performed by Evans Analytical Group using a Helios 650 FIB and a Physical Electronics 680 AES. The sample was exposed to atmosphere before FIB and again before AES analysis. FIB preparation included the addition of a protective conductive layer to retain the original definition of the exposed growth surfaces. AES analysis was performed using a 10 keV accelerating voltage and 29 nA sample current. The sample was tilted 30° with respect to the incoming electron beam and sputtering was done with a 2 kV argon ion beam. Sputter depth for AES was calculated assuming a sputter rate of 5.8 nm min⁻¹ for SiO₂.

3. Results and Discussion

3.1 Electrodeposition from Mg(BH₄)₂/LiBH₄ Electrolytes at Ag and Pt Anodes

Figure 1a shows a cyclic voltammogram (CV) obtained from a solution containing 0.1 M Mg(BH₄)₂ + 1.5 M LiBH₄ in diglyme on a roughened Ag foil. The high concentration of LiBH₄ relative to Mg(BH₄)₂ was used to improve kinetics and increase current density and coulombic

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4 112 efficiency as observed by others [30] and previously in our work [23]. The voltammetry obtained
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9 114 shown in Figure 1b. The reversible deposition of Mg on Pt is known to exhibit a large
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11 115 electrodeposition overpotential with a near 100% coulombic efficiency whereas there appears to
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14 116 be about a 30 mV overpotential for the electrodeposition of Mg on a roughened Ag foil with a
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16 117 97% coulombic efficiency. Previously our group showed that Li UPD is implicated in the
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19 118 overpotential and high current density of Mg deposition achieved with this electrolyte on Pt [23].
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21 119 Li has been shown to undergo UPD on Ag at -280 mV and Li-Ag alloying begins at -440 mV
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24 120 [31, 32], making it unlikely that Li is the cause for the observed low overpotential in this case.
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26 121 Simple voltage models outlined in Table S5 indicate Mg-Ag alloying may be the cause. The
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29 122 lower overpotential for deposition that is achievable on roughened Ag, nonetheless, allowed us
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34 124 growth without the use of a Mg substrate that would otherwise complicate texture analysis.

3.2 Potential Dependence of the Morphologies of Anisotropic Growth

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39 126 In order to evaluate the effect of deposition parameters on the Mg deposit, we measured
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47 129 current-time transient for the -500 mV sample but analogous experiments carried out in the same
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54 132 The image shows the presence of hexagonal platelets growing perpendicular to the Ag substrate.
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57 133 The sharp, high aspect ratio crystals appear in stark contrast to the smaller, roughly
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Figure 3b. While potentiostatic measurements were chosen for emphasis of features, galvanostatic deposition measurements on roughened Ag foil made to account for differences in charge passed and material deposited notably show similar behavior (Figure S1). As an exemplar, a similar platelet morphology is observed for a case where the potential was held at -200 mV for 16 h (Figure S2). Hexagonal platelets are also formed on SS and Mg substrates when a potential hold at -200 mV is applied and on a Pt substrate when a low current density is applied (Figure S3). This morphological phenomenon is unusual for Mg electrodeposition at low rates as the texture is usually random or {0001} oriented [1, 5], so we sought to understand this behavior in more detail using XRD and AES to better define the texture and elemental composition of the deposits.

3.3 Composition Dependences Resulting from Mg-Ag Interdiffusion

Analyses by XRD and AES were performed to determine the nature of the interactions occurring between the Mg and Ag and the extent that alloy and/or compound formation occurs between them. Figure 4 presents exemplary XRD patterns of Mg deposited for 16 h on roughened Ag from the $\text{Mg}(\text{BH}_4)_2$ electrolyte. The 2Θ - Ω scans for the -200 mV and -500 mV deposits are presented in Figure 4a. Full patterns are given in the SI (Figure S4). Individual peaks are labeled according to their material assignments: Ag (black squares), Mg (blue diamonds), and Ag_xMg_y (green circles). Analyses of the XRD patterns suggest that only pure Mg phases are deposited during the potential holds at -200 and -500 mV, with no suggestion of a co-deposition occurring with Li. There is, however, strong evidence for, in addition to Mg, the formation of Ag-Mg phases within these data. The relevant phase diagram shows there are a number intermetallic compounds and alloy compositions known to exist for the Ag-Mg binary system including the intermetallic compounds: Ag_3Mg , AgMg , $\text{Ag}_{17}\text{Mg}_{54}$, AgMg_3 , and AgMg_4 [24]. The

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4 158 formation of such Ag-Mg phases may help explain the lower overpotential observed in the cyclic
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6 159 voltammogram, as alloys would likely form at a potential more positive than the potential for
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9 160 bulk deposition of Mg. Our results show that, over time, the initial peak splitting characteristic of
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14 162 to oxidizing of the Mg-Ag alloy (shown in Figure S5). Figure 4b shows the 38° region in more
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19 164 file databases. The peak splitting in the -200 mV sample in Figure 4b is indicative of a mixture
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24 166 whereas the -500 mV sample overlays almost perfectly with the AgMg peak at 38.5°. Cross
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26 167 sectioning and elemental analysis using FIB and AES was used to better understand the extent of
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29 168 alloying and clarify how these binary microstructural compositions might be dispersed within
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34 170 The AES results of Mg deposited on a roughened Ag foil using a 2 h potential hold at
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36 171 -200 mV are presented in Figure 5. Figure 5a is a false color SEM image of the sample after FIB
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54 178 Figure 5b and resulted in Ag:Mg ratios of >9:1 in the Ag substrate and 1:3 within the central
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56 179 region of the Mg deposit. Full data, sampling locations, depths and elemental mapping are
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6 182 reveal a much more Mg rich composition, a finding consonant with the presence hcp pure phase
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11 184 composition is high) that progressively transitions to a composition of an intermetallic in the
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31 192 (given that the substrate presents an essentially infinite supply of Ag, and thus
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33 193 thermodynamically should present at equilibrium as a Ag-rich composition). From the AES
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38 195 deposit and can be explained by the known rapid diffusion coefficient of Ag in Mg [33]. As seen
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48 199 Ag as a mediating alloy anode for Mg. We note that the asymmetrical diffusion of Ag into Mg
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51 200 also suggests that the observed platelet morphology is due to properties that are intrinsic to Mg
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53 201 and not alloying. Control experiments compel the conclusion that Ag alloying cannot be the
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55 202 cause of the platelet morphologies since they can be elicited for growth on other substrates, as
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well (Figure S3). With these understandings of the effects of nucleation and alloying, it is possible to analyze the morphology of Mg at low and high overpotentials.

The evolution of texture in the electrodeposition of Mg is depicted in Figure 6. A magnified SEM image of a platelet formed at -200 mV is shown in Figure 6a. The true crystallographic orientation of the individual crystals like that formed in Figure 6a is not discernable from the SEM images because the probable orientation planes of {10-10} and {11-20} form identical angles with the hexagonal {0001} plane. A quantitative interpretation of the orientation of the Mg deposits can be obtained by using the XRD data shown in Figure 6b to determine the texture coefficients (Figure 6c). Only the low index planes of {10-10}, {0001}, {10-11}, and {11-20} corresponding to the XRD peaks at 32.2°, 34.4°, 36.6° and 57.4° were analyzed because they are the most important for crystal growth and although the data in Figure 6b are normalized to the (101) peak, the raw data was used to calculate coefficients. Texture coefficients are numerical values of the observed XRD peak intensities normalized to the standard diffraction pattern of Mg via the equation:

$$TC_{(hkl)} = \frac{\frac{I_{(hkl)}}{I_{0(hkl)}}}{\frac{1}{n} \sum \left(\frac{I_{(hkl)}}{I_{0(hkl)}} \right)}$$

where TC , $I_{(hkl)}$, $I_{0(hkl)}$, and n are the texture coefficient, the experimental peak intensity, the standard diffraction peak intensity, and the number of peaks used for the calculation, respectively. A texture coefficient of 1 corresponds to a random orientation whereas a texture coefficient above 1 corresponds to a preferred orientation. Pole figures were also performed but the results are less obvious and are more difficult to analyze due to the overlapping textures and polycrystalline nature of the deposits. Nevertheless, the pole figures are provided in Figure S10

of the supporting information. The very low texture coefficient of the basal {0001} plane, for both samples, indicates an orientation of the Mg crystals away from the {0001} plane, as is evident from Figure 6a but is less obvious from SEM images of the Mg deposit after deposition at -500 mV. The other texture coefficients reveal the -200 mV sample is oriented away from the {10-11} plane but is oriented towards both the {10-10} and the {11-20} planes. The -500 mV sample is oriented away from the {10-11} plane but has a preferred orientation towards the {11-20} plane. Together the texture information indicates that at low overpotential there is a {10-10} and {11-20} combined texture but high overpotentials change to primarily a {11-20} texture. The exchange of preferred orientations could be due to a multitude of factors, but as we will show this is actually indicative of the underlying kinetics of the reaction.

3.4 Modeling of Nucleation and Growth and Correlations to Mg Morphologies

The well-defined platelet morphologies obtained at -200 mV provide an experimental basis for establishing growth rates in two directions. Figure 7 contains an example of a measurement of a platelet and the resulting statistics for a 30 and 120 minute deposition. Only platelets with distinct edges and nearly vertical orientations were used for analysis as indicated by Figure 7a (further examples and calculation assumptions are available in the SI and in Figure S11). The average aspect ratio remains nearly identical at about 5.3 for both 30 min and 120 min depositions (actual step edges from cross-sections can be found in Figure S12). Assuming a constant rate of growth, the observed rates of growth are 0.33 nm s^{-1} in the $\langle 10-10 \rangle$ and $\langle 11-20 \rangle$ directions and 0.062 nm s^{-1} in the $\langle 0001 \rangle$ direction. The electrochemical growth rate falls between the observed values at 0.26 nm s^{-1} and indicates that the growth rates derived from SEM images are relatively accurate.

The macroscopic dimensions in principle reflect the intrinsic atomic level growth dynamics of step edges and terraces that develop due to adatom formation, diffusion and incorporation into kink sites during nucleation and growth. Calculated Mg adatom activation energies have been previously computed from numerical simulations and provide a good estimate of the actual diffusion energy according to the Arrhenius like equation:

$$D = D_0 e^{-E_a/kT}$$

where D , D_0 , E_a , k , and T correspond to the diffusion constant, the pre-exponential factor, the activation energy, the Boltzmann constant, and the temperature, respectively [34]. The pre-exponential factor has been determined to be roughly identical for many metal atoms, often varying by only a factor of 2 for different crystallographic planes of the same element [35]. The ratio of the diffusion constants for different planes of Mg can therefore be interpreted as just the ratio of the exponential factor as summarized in Figure S13 and Table S7.

The important results of the analysis of the ratios of the diffusion energy barriers in the context of this work are summarized in Figure 8. A diffusion anisotropy exists on both the preferred texture planes observed in the Mg electrodeposition experiments, namely the {10-10} and {11-20} planes. Both planes contain channels that allow fast diffusion of adatoms along one axis, but the fast direction is opposite for the two planes. On the {10-10} plane the diffusion rate perpendicular to the <0001> direction is ~800x faster than the rate parallel to the <0001> direction, depicted in Figure 8a. On the {11-20} plane the diffusion rate perpendicular to <0001> direction is ~100x slower than the rate parallel to the <0001> direction, depicted in Figure 8b. Combined, the surface diffusion anisotropies lead to a ratio of anisotropies of ~8 compared to the measured aspect ratio of 5.3. Two factors could be bringing down the observed ratio. First, the pre-exponential factor is assumed to be negligible, but may be contributing to the observed ratio.

Second, the ratios of vacancy and surface diffusion anisotropies are opposite, with a vacancy diffusion anisotropy ratio of 4. The change in texture at -500 mV is due to the relatively fast diffusion on the {11-20} plane. Average surface diffusion rates are faster on the {11-20} plane than on the {10-10} plane. The minimum diffusion rate for both surface diffusion and vacancy diffusion are also faster for the {11-20} plane compared to the {10-10} plane, making the {11-20} plane the preferred plane at high overpotentials or fast deposition rates.

Additional insight into the kinetics at each overpotential can be gained from the results of fitting the current-time transients for the -200 and -500 mV samples, from Figure 2, to nucleation and growth models (Figure S14); only the first 1000 seconds were modeled. The equation, shown here, is adapted from work done by Scharifker, Radisic, and their respective coworkers [16, 36].

$$I_{TOTAL} = I_{SP} + I_{3D-DC}$$

$$I_{TOTAL} = C \exp(-k_{ads}t) + p_1 t^{-1/2} \left(1 - \exp \left\{ -p_2 \left[t - \frac{1 - \exp(-p_3 t)}{p_3} \right] \right\} \right)$$

where I_{SP} is the current due to a surface process (e.g. adatom formation) and I_{3D-DC} is the current due to the 3D nucleation and diffusion controlled growth. The fitted parameters along with the calculated kinetic values are presented in Table 1. Of great importance to this discussion are the values for A , the nucleation rate per active site and N_0 , the number density of active sites. Relatively speaking, the electrodeposition at -200 mV with a slower nucleation and a larger number of active sites behaves more like a progressive process whereas, the electrodeposition at -500 mV with a faster nucleation and a fewer number of active sites behaves more like an instantaneous process. At faster nucleation rates the plane with the faster adatom diffusion rates would be dominant, however, at slower nucleation rates a plane with slightly slower adatom

diffusion rates has a greater probability of forming together with the faster plane. High rates are necessary for Mg batteries to be competitive with Li-ion batteries, but the highly anisotropic growth and few active sites at high current densities creates a favorable environment for the formation of microvoids that decrease the performance of metal anodes.

Further proof that it is the adatom diffusion rates that are defining the deposition texture can be found from Cl^- additive experiments. Outlined in Figure 9, we observed that the distinct anisotropy seen in this report changes to a $\{0001\}$ orientation parallel to the substrate when a Cl^- additive is present. Grignard reagents contain a significant amount of halides and achieve similar results to those shown in Figure 9. Our previous results and those of Matsui show a $\{0001\}$ orientation when depositing Mg from a Grignard solution [1, 5]. Schmickler has shown via DFT calculations that Au-Cl complexes diffuse much faster than Au adatoms alone [37]. The change in morphology due to addition of Cl^- indicates that either adsorbed Cl^- is inhibiting Mg adatom diffusion or Cl^- complexes Mg^{2+} to form adsorbed complexes compared to a relatively non-coordinating environment provided by the borohydride anion.

4. Conclusion

In a putatively non-coordinating electrolyte, one comprising the borohydride anion in diglyme, we have shown that the morphology and texture of Mg deposits are strongly $\{11-20\}$ and $\{10-10\}$ oriented due to the underlying rate anisotropies of adatom surface diffusion and adatom vacancy diffusion on the low index planes of Mg. Chloride additive studies further support the adatom surface/vacancy diffusion hypothesis as a consequence of the distinctly different textures that result compared to the non-chloride modified electrolyte. This study suggests a foundation for future studies of Mg battery electrolytes, particularly for the investigation of additive packages and mediating electrodes that might be exploited to control the

growth behaviors in the electrochemical deposition of Mg. The origin of the low overpotential and the performance of Ag as well as its potential utility for use as an alloy anode remain undetermined and future studies, both in experiment and theory, will be needed to address these issues.

5. Acknowledgements

This work was supported as part of the Joint Center for Energy Storage Research (JCESR), an Energy Innovation Hub funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences. The authors thank Mauro Sardela and Elvan Ekiz-Stumphy for their helpful discussions regarding the XRD and pole figures.

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		-200 mV	-500 mV
Fitted Parameters	C (A cm⁻²) (10⁻⁵)	92.86 ± 0.19	306.9 ± 0.8
	k_{ads} (s⁻¹) (10⁻⁴)	86.6 ± 2.0	138 ± 7
	p_1 (A s^{1/2} cm⁻²) (10⁻⁴)	175.4 ± 0.3	320.0 ± 1.3
	p_2 (s⁻¹) (10⁻⁴)	38.0 ± 0.3	29.9 ± 0.8
	p_3 (s⁻¹) (10⁻³)	25.1 ± 1.1	32 ± 10
Kinetic Parameters	A (s⁻¹) (10⁻³)	25.1	32.0
	D (cm² s⁻¹) (10⁻⁶)	2.59	8.64
	k'	0.19	0.19
	N_0 (cm⁻²)	2485.77	587.63

Table 1. Nucleation and growth model parameters for the electrodeposition of Mg on roughened Ag.

Figure Captions

Figure 1: (a) A cyclic voltammogram (1st cycle) at 20 mV s^{-1} of a roughened Ag foil working electrode in $0.1 \text{ M Mg(BH}_4)_2 + 1.5 \text{ M LiBH}_4$ in diglyme. (b) A cyclic voltammogram (1st cycle) at 20 mV s^{-1} of a Pt disk working electrode in $0.1 \text{ M Mg(BH}_4)_2 + 1.5 \text{ M LiBH}_4$ in diglyme.

Figure 2: Current-time transients of the 2 h electrodeposition of Mg on roughened Ag foil from a $0.1 \text{ M Mg(BH}_4)_2 + 1.5 \text{ M LiBH}_4$ in diglyme electrolyte at -200 (dashed) and -500 (solid) mV.

Figure 3: SEM images of Mg deposited on roughened Ag foil resulting from the current-time transients at -200 mV (a) and -500 mV (b) shown in Figure 2.

Figure 4: (a) XRD patterns of -200 mV (red), -500 mV (blue), and the Ag substrate (black). Peaks are labeled according to Mg ($\diamond$), Ag ($\square$), and Mg-Ag alloy ($\bullet$). (b) Standard diffraction pattern overlays of discrete, possible Mg-Ag alloys (dotted lines) on top of -200 and -500 mV deposit XRD patterns (solid lines).

Figure 5: (a) FIB-SEM cross-sectional image of Mg deposited on Ag at -200 mV for 2 h with elemental compositions colored for Mg_3Ag (blue), Ag (orange), and Pt-C (gray). (b) AES spectra corresponding to the elemental mapping in (a).

Figure 6: (a) SEM image of Mg deposited from a $0.1 \text{ M Mg(BH}_4)_2 + 1.5 \text{ M LiBH}_4$ in diglyme electrolyte at -200 mV, showing a Mg platelet. (b) Comparison of the XRD patterns shown in Figure 4 with a standard Mg diffraction pattern. All patterns were normalized to the (101) peak. (c) Texture coefficients of the 16 h depositions with the standard diffraction pattern coefficients equal to 1.

Figure 7: (a) SEM image depicting the method of measurement for aspect ratios. (b) Histograms of the calculated aspect ratio and (c) the calculated length after 30 min (black) and 120 min (red) of deposition at -200 mV on roughened Ag foil.

Figure 8: Schematic of adatom diffusion anisotropies on the relevant planes. Red arrows indicate the preferred diffusion direction and blue arrows indicate the slower diffusion direction.

Figure 9. A comparison of the effects of a chloride additive on the morphology of the electrochemical deposit: (a) an electrolyte with 1.5 M LiBH₄ + 0.1 M Mg(BH₄)₂ (black) compared to an electrolyte with 1.5 M LiBH₄ + 0.1 M MgCl₂ (red) in diglyme on roughened Ag foil; (b) the XRD patterns of deposits from the Cl additive (black) and normal electrolytes (red) on roughened Ag; (c) SEM image of the Mg deposit resulting from the electrodeposition of Mg in 1.5 M LiBH₄ + 0.1 M MgCl₂ at -200 mV for 16 h; (d) magnified SEM image of the center of (c).

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9