Degradation Mechanisms of Magnesium Metal Anodes in Electrolytes based on $(CF_3SO_2)_2N^-$ at High Current Densities

Hyun Deog Yoo,[†,‡] Sang-Don Han,[‡,§] Gene M. Nolis,[†,‡] Ryan D. Bayliss,[†,‡] Anthony K. Burrell,[‡,§] John T. Vaughey,[‡,§] Jordi Cabana[*,†,‡]

[†] *Department of Chemistry, University of Illinois at Chicago, Chicago, IL 60607, USA.*

[‡] *Joint Center for Energy Storage Research, Argonne National Laboratory, Argonne, IL 60439, USA.*

[§] *Chemical Sciences and Engineering Division, Argonne National Laboratory, Argonne, IL 60439, USA.*

*Corresponding author: jcabana@uic.edu

ABSTRACT: The energy density of rechargeable batteries utilizing metals as anodes surpasses Li-ion batteries, which employ carbon instead. Among possible metals, magnesium represents a potential alternative to the conventional choice, lithium, in terms of storage density, safety, stability, and cost. However, a major obstacle for metal-based batteries is the identification of electrolytes that show reversible deposition/dissolution of the metal anode and support reversible intercalation of ions into a cathode. Traditional Grignard-based Mg electrolytes are excellent toward reversible deposition of Mg, but their limited anodic stability and compatibility with oxide cathodes hinder their applicability in Mg batteries with higher voltage. Non-Grignard electrolytes, which consist of ethereal solutions of magnesium(II) bis(trifluoromethanesulfonyl)imide ($Mg(TFSI)_2$), remain mostly stable near the potential of Mg deposition. The slight reactivity of these electrolytes towards Mg metal can be remedied by the addition of surface-protecting agents, such as $MgCl_2$. Hence the ethereal solutions of $Mg(TFSI)_2$ salt with $MgCl_2$ as an additive have been suggested as a representative non-Grignard Mg electrolyte. In this work, the degradation mechanisms of a Mg metal anode in the TFSI-based electrolyte were studied using a current density of 1 mA cm^{-2} and an aerial capacity of ~0.4 mAh cm^{-2}, which is close to those used in practical applications. The degradation mechanisms identified include the corrosion of Mg metal, which causes loss of electronic pathways and mechanical integrity, the growth of anomalously large Mg deposits, and the decomposition of $TFSI^-$ or Cl^- anions. This study not only represents an assessment of the behavior of Mg metal anodes at practical current density and areal capacity, but also details the outcomes of interfacial passivation, which was detected by simple cyclic voltammetry experiments. This study also points out the absolute absence of any passivation at the electrode-electrolyte interface for the premise of developing electrolytes compatible with a metal anode.

KEYWORDS: magnesium metal anodes, metal rechargeable batteries, passivation, degradation mechanisms, metal deposition

■ INTRODUCTION

The past decade has seen a 'renaissance movement' in metal rechargeable batteries, during which various metals have been tested as potential anodes for the rechargeable batteries.[1-4] The utilization of metal anodes can lead to batteries with superior energy densities compared to Li-ion technologies, where the commonly used graphite anodes have lower specific and volumetric capacity than Li metal. In this context, many contemporary 'post Li-ion' batteries, such as Li-sulfur or Li-oxygen, have a stake in the potential success of Li metal as an anode material. However, the commercialization of Li metal-based batteries is plagued by the various issues with the properties of the anode.[5] Those issues include (1) dendritic growth of Li that leads to short circuit and explosion of the batteries,[6-8] (2) starvation of the electrolyte by repeated decomposition on freshly exposed surface of Li,[9-10] and (3) accumulation of isolated 'dead' Li.[11] Because of these degradation mechanisms, Li metal anodes have failed to reliably operate at high current densities and practical areal capacities.[9-10] Still, active research continues to focus on solving, or at least mitigating, the thermodynamically imperative degradations of Li metal anodes by combining new approaches to system engineering and advances achieved by basic sciences.[12-18]

Magnesium has been the most intensively studied metal anode other than Li metal because of its natural abundance. Furthermore, Mg metal is not susceptible to the previously noted degradation mechanisms. Firstly, the higher electrode potential of Mg (i.e., 0.67 V higher than Li/Li^+) makes it thermodynamically stable with some electrolytes, not through the formation of a kinetically passivating layer, as in the case of Li metal.[19-20] Secondly, due to the faster self-diffusion rate and large coordination number of Mg atoms in metal form, non-dendritic and smooth electrodeposition is favored, compared to the dendritic deposition of Li.[21-22] Furthermore, the overpotential for the Mg deposition is believed to be controlled by the concentration of the metal ion in the electrolyte so that more uniform deposition is obtained.[23] These ideal properties of Mg metal anodes have been demonstrated by the operation of prototype Mg batteries for more than 2,000 cycles at a moderate current density.[24] Furthermore, more than 300 cycles was demonstrated at a high current density of 2 mA cm^{-2} and at a close-to-practical areal capacity of 1 mAh cm^{-2}, whereas the capacity of Li metal cells typically fade in a few cycles at the same conditions.[25]

Traditional Mg metal-based batteries that used Grignard-based electrolytes have demonstrated limited energy density due to the intrinsic properties of electrolytes including (1) the narrow voltage window up to 2.2~2.7 V vs Mg/Mg^{2+} (depending on choice of the current collector) and (2) their nucleophilic nature that leads to the high chemical reactivity with electrophilic cathodes, such as oxides with high voltage.[26] In search for Mg^{2+} salts that are compatible with high-voltage cathode materials, various non-Grignard-type alternatives have been developed.[20,27-31] Among them, electrolytes based on the bis(trifluoromethanesulfonyl)imide (TFSI)-anion stand as some of the most promising candidates.[32-35] Mg(TFSI)$_2$ exhibits good cathodic stability at 0 V vs Mg/Mg^{2+}. The TFSI anion is also known to possess excellent thermal stability that can support high temperature applications,[36] and demonstrates relatively high anodic stability in ionic liquid electrolytes.[37-38] Previous studies have shown that the complexed Mg cations in the TFSI-based electrolytes have a smaller radii than the stable complex for Mg-ions (e.g., $Mg_2Cl_3^+ \cdot 6THF$) isolated in Grignard-based electrolytes, enabling applications in metal hybrid supercapacitors.[39] It is noteworthy that in the case of Mg(TFSI)$_2$ electrolytes with ethereal solutions, the water content must be no more than 3 ppm for the reversible Mg deposition/dissolution to occur with up to 80% Coulombic efficiency.[40] For the TFSI-based electrolytes with nominal water content (i.e. <40 ppm), addition of magnesium chloride ($MgCl_2$) is indispensable to get reversible Mg deposition/dissolution.[40] The possible roles of $MgCl_2$ have been postulated as (1) protecting the Mg metal anode from side reactions with H_2O or $TFSI^-$ anions by the preferential adsorption of Cl^- on the surface of Mg,[33,40] or (2) formation of deposition-active species such as $Mg_2Cl_3^+$ cations in an electrolyte.[35] In some cases, electrochemical conditioning or addition of chemical 'scavengers' of surface passivation products, such as addition of a diorganomagnesium species, further improved the deposition reversibility.[33] In line with such conditioning, Choi *et al.* have tried passing a small current of ~0.2 mA cm^{-2} on the Mg metal anode for about half an hour, which was conjectured to remove surface films (e.g., oxides) in order for reversible Mg deposition and dissolution to happen.[32] All in all, state-of-the-art TFSI-based electrolytes with $MgCl_2$ have voltage windows up to 3.5 V vs Mg/Mg^{2+} and coulombic efficiency of 80~98% for the reversible deposition and dissolution of Mg.[33-34]

The available literature also highlights the slight reactivity of TFSI anions at the surface of a Mg metal, which can be potentially detrimental to the reversible cathodic processes. Theoretical studies have shown the possible breakage of $S–CF_3$ bonds of $TFSI^-$ anions when the anion is adjacent to a Mg metal.[41] Specifically, bonds of $TFSI^-$ anions begin to weaken when $TFSI^-$ is paired with the transient species and partially reduced Mg^+ cation, making the Mg–TFSI species prone to decompose in the vicinity of a Mg anode.[42-43] Chemical reactions that occur at the Mg metal anode during stripping and plating are expected to be more complex if additives such as chlorides participate in those reactions.[44] However, since most of the previous electrochemical tests have been performed under relatively benign conditions, such as small current density (~0.1 mA cm^{-2}) and an areal capacity (0.1~0.2 mAh cm^{-2}), the effects of such side reactions have not yet been thoroughly revealed. Such aspects can be studied in an accelerated way by operating Mg battery cells with TFSI-based electrolytes at high current density and areal capacity. In addition, scale-up experiments are recommended because the larger-scale prototype can not only validate the current understanding that has been built up on the experiments done at smaller scales, but also reveal the effects of passivation reactions on the practical performances of the cells. The scale-up tests in an accelerated condition can provide practical assessments of the current status of the TFSI-based electrolytes and guide the directions toward future development of non-Grignard electrolytes for Mg rechargeable batteries.

Herein we report degradation mechanisms of a Mg metal anode in a TFSI-based electrolyte during the cycling of the cells under accelerated conditions, at both high current density (~1 mA cm^{-2}) and areal capacity (~0.4 mAh cm^{-2}). A variety of phenomena were noticeable both for the Mg metal anode and the electrolyte, which are not usually seen in milder conditions. First, simple cyclic voltammetry was sufficient to detect a higher degree of passivation of a Mg metal anode in the TFSI-based electrolyte compared to the Grignard-based electrolytes. The outcome of this tendency was further verified by cycling a Mg metal anode at 1 mA cm^{-2} for 400 cycles. These tests demonstrated substantial changes in the electrodes and the electrolyte, including the corrosion of the Mg metal anode leading to loss of electronic pathways and mechanical integrity, the growth of anomalously large Mg deposits on deposition, and the decomposition of $TFSI^-$ or chloride anions along with the deposition of Mg metal. This work proposes systematic methods to assess degradation of a Mg metal anode and an electrolyte with respect to the passivation of the surface of metal anodes. This work also suggests a concise method to detect the passivation layer on the anode through the deviations between the measured potential of Mg metal and 0 V vs Mg/Mg^{2+}, which is often neglected in the evaluation of the electrolytes from the cyclic voltammograms.

■ EXPERIMENTAL

Preparation of Electrolytes. Magnesium(II) bis(trifluoromethylsulfonyl)imide ($Mg(TFSI)_2$, Solvionic, 99.5%) and magnesium chloride ($MgCl_2$, Sigma-Aldrich, 99.99%) salts were used after drying at 150 °C in a vacuum oven. Diethylene glycol dimethyl ether (diglyme, G2, Sigma-Aldrich, spectrophotometric grade) was dried over activated basic Al_2O_3, filtered, and vacuum distilled over liquid Na/K alloy using a Vigreux column. The 0.3 M $Mg(TFSI)_2$ and 0.15 M $MgCl_2$ were mixed together with diglyme in hermetically sealed glass vials and stirred to form homogeneous solutions. Addition of $MgCl_2$ was critical for reversible Mg deposition/dissolution, either because of the formation of active species such as $MgCl^+$ or $Mg_2Cl_3^+$,[33,35] or due to the modification of the electrode-electrolyte interface by the adsorption of free chloride ions.[33,45] Then the electrolyte solution was further dried by contacting with thoroughly dried molecular sieves. All materials were handled in an Ar-filled glove box (<0.5 ppm H_2O and <0.5 ppm O_2). The water content of the electrolytes was verified to be <30 ppm using a Mettler Toledo DL39 Karl Fischer coulometer. Ionic conductivity was determined by measuring the impedance of the electrolytes in a homemade two electrode cell at 25 °C;[46] at least three measurements were made with a fresh sample after each analysis.

Preparation of Electrodes. For Mg metal anodes, a Mg foil (99.95%, GalliumSource LLC, 50 μm thick) was abraded inside the glovebox to expose a fresh metal surface. An activated carbon cloth (ACC-5092-20, Kynol Co., surface area = 2000 m^2 g^{-1}) was dried at 80 °C under vacuum overnight and used as a counter electrode.

Electrochemical and Spectroscopic Measurements. Electrochemical characterization was performed using custom made 3-electrode glass cells. For the characterization of electrolyte, a Pt wire was used as the working electrode (WE) and Mg metal foils were used as reference electrode (RE) and counter electrodes (CE). For the characterization of a Mg metal anode, Mg metal foils served as both WE and RE, and a piece of activated carbon cloth (ACC) attached to a platinum wire was used as the CE. The area of the Mg metal WE in contact with the electrolyte was ca. 2 cm^2. The ACC was punched to a circle with 1.0 cm^2 diameter and corresponding mass of 15.1 mg. Cyclic voltammetry and galvanostatic measurements were performed using a galvanostat/potentiostat (VMP3, Biologic Co.) at room temperature. Samples were imaged by scanning electron microscopy (SEM, S-3000N, Hitachi).

■ RESULTS AND DISCUSSION

Figure 1a shows a cyclic voltammogram of the TFSI-based Mg^{2+} electrolyte using a Pt wire as the working electrode at a scan rate of 25 mV s^{-1}. It shows reversible Mg deposition/dissolution on an inert surface of Pt with a Coulombic efficiency of 93% and an overpotential of 0.26 V for the deposition. This plot is commonly used to characterize Mg electrolytes in terms of the reversibility/kinetics for Mg deposition/dissolution and the anodic stability window of the electrolytes. Although the cyclic voltammogram provides a convenient way to demonstrate the reversible deposition and dissolution of Mg, insight into the anodic stability is often obscured by the relatively large current for the dissolution and deposition of Mg. The magnified view of the data shown in Figure 1b reveals that a significant faradaic process occursed starting at 2.4 V vs a Mg RE as shown by the abrupt increase in the slope of current. Figure 1c shows a second magnified view, this time around 0 V vs a Mg RE. It displays an unusual result in that the dissolution begins at –0.1 V vs Mg RE, whereas thermodynamics do not allow the dissolution of Mg metal at a potential less than 0 V vs Mg/Mg^{2+}. In fact, similar results were also observed in an all-phenyl-complex (APC) Mg electrolyte, albeit with a smaller difference (–0.04 V vs Mg RE), as well as in a Ca^{2+}-based electrolyte..[47] This observation was ascribed to a drift in the potential of the reference electrode. To assess its actual potential vs Mg/Mg^{2+}, the open circuit potential of a freshly deposited Mg was measured against Mg RE (Figure 1d). The open circuit potential of the freshly deposited Mg metal was measured at –0.1155 V vs Mg RE. This observation means that the potential of Mg RE was inherently shifted to about 0.1 V higher than Mg/Mg^{2+}, possibly due to the spontaneous formation of a passivation layer on its surface upon immersion into the electrolyte. Such passivation layer can raise the potential of the Mg RE if the layer contains immobile anions, e.g., by specific adsorption of Cl^{-} or $TFSI^{-}$ on the surface. Considering the deviation between the potential of Mg RE and the Mg/Mg^{2+} couple, the corrected electrode potentials vs Mg/Mg^{2+} reported henceforth were obtained by adding +0.1 V to the measured potential vs Mg RE.

The cyclic voltammograms suggest the formation of a passivation layer on Mg metal in the electrolyte. As multivalent metal ions have been shown negligible mobility within the passivation layer, the dissolution of Mg must occur via breakdown and repair of the passivation film in those cases,[48] which can ultimately become a degradation mechanism upon repeated cycling. For Li metal anodes, repeated breakdown and repair of such passivation film accelerates growth of dendrites on Li metal,[8] starvation of the electrolyte solution by the continued exposure of fresh Li surface,[9-10] and formation of isolated 'dead' Li that impedes further electrochemical reactions.[11] On the other hand, one of the premises of utilizing a Mg metal anode is the absence of any surface film which impedes the movement of multivalent ions.[19] The formation of passivation films on Mg has been shown to be effected by additives such as chlorides,[35] borohydrides,[49] or organometallic compounds that can result in chemically degradation..[33] The addition of chloride was found not to be completely effective in these conditions.

To delve into the degradation mechanism of a Mg metal anode, we employed a 3-electrode cell test with Mg metal foils as the WE and RE. Activated carbon cloth (ACC) was used as the CE operating through the adsorption and desorption of Mg^{2+} ions on its surface. Note that alternative Mg | Mg configurations may not reveal some realistic features that originate from the asymmetry of cathodic and anodic reactions of these complete Mg cells. This issue is primarily due to the high capacity and rate capability of the ACC, which enables experiments at high current density of 1 mA cm^{-2} and areal capacity of ~0.4 mAh cm^{-2} on the WE. Figure 2a shows optical images of the Mg metal WE and the electrolyte after Mg deposition and dissolution in cells represented by the voltage profiles in Figure 2b (at 25 μA cm^{-2}). The color of the electrolyte was colorless at the initial state (top of Figure 2a), but it turned to a yellowish color after the Mg deposition on the Mg metal anode (bottom of Figure 2a); upon subsequent Mg dissolution, the color of the electrolyte returned to its original colorless state. The change in color may be related to the formation of chlorinated compounds, since the chlorine ligands must be separated from $Mg_xCl_y^{z+}$ ions that are active during the Mg deposition. The red circles in Figure 2a denote hemispherical deposits with diameter of ~0.1 mm on the surface of a Mg metal WE after cycling. Although they are not dendritic, such relatively large deposits indicate non-homogenous Mg deposition on the surface of a Mg metal anode.

Figure 2c shows the voltage profiles of Mg deposition (black) and dissolution (red) on a Mg metal anode for 400 cycles. The Mg metal anode exhibits relatively stable potential of Mg dissolution/deposition up to around 300 cycles with an overpotential of 0.23 V, while capacity fade is observed upon cycling, which is related to the degradation of the CE, not the Mg metal WE. The potential for Mg dissolution (red) rises notably to 0.4–0.9 V vs Mg/Mg^{2+} beyond 300 cycles. The increase in overpotential may be associated with the loss of electronic pathways under the percolation threshold. After 400 cycles, the cycled Mg metal anode was broken and precipitated in the electrolyte as shown in Figure 2d. A more detailed examination of the broken pieces of anode revealed that the corroded parts became brittle and porous (bottom of Figure 2d). Although Mg metal is relatively stable in air, the shattered Mg metal debris were high surface area and sparked under mechanical friction upon exposure to air. In addition, the color of the electrolyte turned very dark, being completely different from the original colorless state. These results indicate that repeated cycling leads to the degradation in the electrolyte as well as on the electrode. Most probably, the electrolyte may have suffered from continuous reduction on freshly exposed Mg metal and nucleophilic attacks from chlorinated compounds that are produced during the deposition of Mg metal. Also, the darkened electrolyte solution may incorporate various products from the decomposition of TFSI anions.

Figure 3 shows the SEM images of Mg metal anodes before cycling and after 400 cycles at 1 mA cm^{-2}. The fresh Mg metal was planar with scratches resulting from the scraping of the surface prior to cycling (Figure 3a). After cycling, however, the overall surface of the Mg metal became porous (Figure 3b). The porous structure may be attributed to an incomplete reversibility of Mg dissolution/deposition (~93%), which ultimately consumes a portion of Mg metal in the electrolyte solution. Moreover, lumps of hemispherical deposits were observed on some specific parts of the surface (Figure 3c). The size of hemispherical deposits ranged from <10 μm to ca. 400 μm. The small deposits tend to be found on the surface overall, while the larger deposits tend to agglomerate on specific spots (i.e., on top of another hemisphere as shown in Figure 3d), yielding to lumps of deposits. These anomalously large deposits suggest that the deposition happened on extremely localized spots where the effective current densities weremuch larger than applied. At such extremely high current densities, the Mg deposits tend to show larger curvatures, where the extreme case is the hemispheres.[50]

The EDS analysis of the cycled Mg metal anode showed C, O, F, Cl, and S besides Mg (Figure 4a), where the percentage of each F, C, S, and Cl element amounts to 5~7 at.% and the percentage of O was 19.2 at% (Figure 4b). The elements C, O, F, and S signify the decomposition of TFSI ($N(SO_2)_2(CF_3)_2$) anions on the Mg metal surface. The element Cl suggests that chlorine plays specific roles during the deposition/dissolution of Mg metal,[44] such that the breakage of a Mg–Cl bond required for the deposition of Mg metal leaves chloride products precipitated on the surface. Additonally, the decomposition species from $TFSI^-$ anions forms a significant part of the passivation film on the Mg metal anode that undergoes repeated breakdown-and-repair mechanism during the cycling.

Figure 5 summarizes the proposed degradation mechanisms of Mg metal anodes based on the observations above. First, the surface of Mg metal is passivated by $TFSI^-$, Cl^-, and trace amount of H_2O that block significant portions of surface area. As the passivation film limits the accessible sites for the deposition, each site experiences much larger effective current density. The large effective current density in specific locations results in anomalously large and sparsely distributed hemispherical deposits, in accordance with the theoretical expectation of larger curvature of Mg deposits when current density reaches several mA cm^{-2}.[50] Second, the passivation of the Mg metal surface results in an inefficient process of dissolution-deposition of Mg. Therefore, some amount of Mg is irreversibly lost from the anode for every cycle of charge-discharge, leading to a morphology that is irregular, porous, and brittle upon repeated cycling at high current density and areal capacity. We conclude that type of passivation of the surface of Mg metal and its limitations are behind all the degradation mechanisms of the anode in TFSI-based Mg^{2+} electrolytes.

■ CONCLUSIONS

The stability of a Mg metal anode upon long-term cycling at high current density was studied in a non-Grignard, TFSI-based Mg electrolyte. The incomplete reversibility of the Mg deposition and dissolution resulted in continuous corrosion of the Mg metal anode that led to formation of porous and brittle structures with loss of electronic pathways and mechanical integrity. Relatively large hemispherical deposits were found in some specific locations. They may be due to the passivation film that limited the area of accessible sites for Mg deposition. At the origin of these abnormalities lies a passivation layer on the Mg metal surface, which is possibly composed of various decomposition products of $TFSI^-$ anions, chlorides, and trace amount of H_2O. Deposition of active $Mg_xCl_y^{z+}$ species led to the formation of chlorinated compounds with yellowish color in the electrolyte. After extensive cycling, brittle and porous Mg metal debris formed, which flashed upon exposure to air. This work signifies the degradation of Mg batteries in the presence of even small imperfection of the reversibility, such as through the formation of a passivation film, can lead to the detrimental results to the electrodes and electrolytes. This work also suggests a concise way to detect the formation of a passivation film on a metal anode through the deviation between the immersion potential of the metal anode and the potential of freshly deposited Mg, which is 0 V vs Mg/Mg^{2+}.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: jcabana@uic.edu (J. Cabana).

Notes

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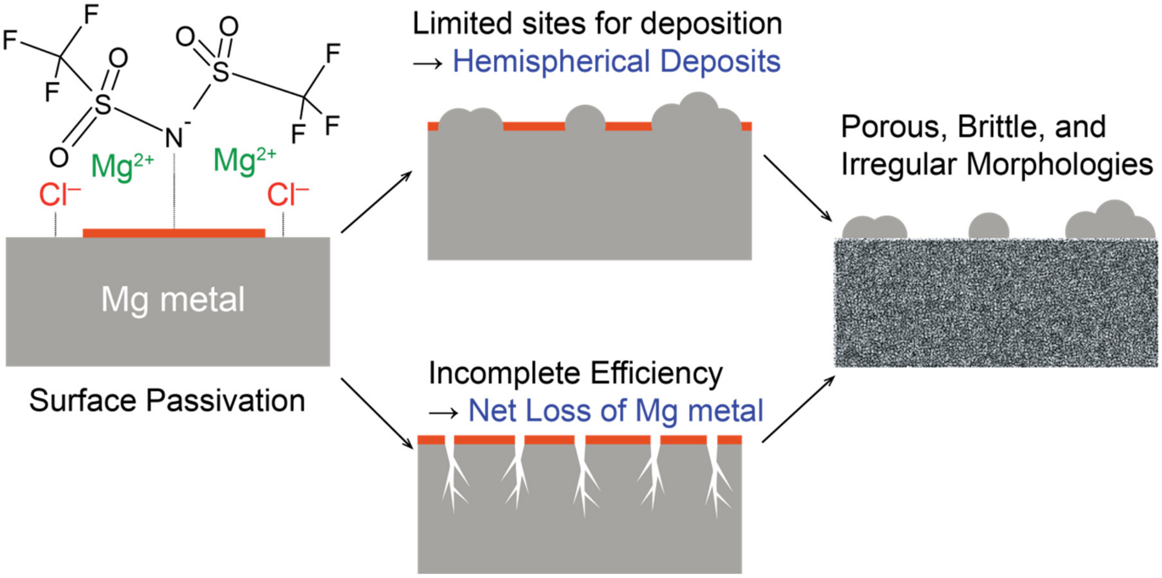
Table of Contents Graphic


Mg²⁺
Mg²⁺
Cl⁻
Cl⁻
Mg metal
Surface Passivation
Limited sites for deposition
→ Hemispherical Deposits
Incomplete Efficiency
→ Net Loss of Mg metal
Porous, Brittle, and
Irregular Morphologies