A new anodic properties evaluation indicator for the magnesium-based anodes of magnesium-air batteries: The apparent valence

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Summary
Mg-air batteries are promising energy storage systems to deal with the requirement of green usage, high energy density, and sustainable energy. This paper provides an in-depth understanding of the energy loss mechanisms of Mg-based anodes, followed by a proposed new anodic properties evaluation indicator, the apparent Mg valence, based on the reaction mechanism of Mg in aqueous electrolytes. The relationship between apparent Mg valence and the anodic efficiency is elucidated. The paper also provides a brief review of the discharge properties of current Mg anodes using the apparent Mg valence. Some development strategies are suggested to pave the path for the future development of advanced Mg anodes.

KEYWORDS
discharge properties, evaluation indicator, magnesium, Mg anode, Mg-air battery

1 | INTRODUCTION

Burning fuel fossils has allowed the progress of industrialization and modernization during the past century, but has also caused increasing environmental issues. Consequently, the achievement of carbon neutrality requires nonfossil fuel power sources that have a high energy density, and are pollution-free, low cost, reliable, and safe. The Mg-air battery is a good candidate for these next-generation power sources. This battery has quite a simple structure: a Mg-based alloy as an anode, oxygen from the air as the cathode and usually a NaCl solution as the electrolyte. It can work in an open-air environment without any specific requirements like the Li-air battery. The discharge product of this battery is normally Mg(OH)_{2}, which is environmentally friendly and non-toxic for the human body. Compared with other batteries, the Mg-air battery has a high theoretical discharge voltage of 3.1 V and a high energy density of 6800 Wh kg\(^{-1}\) (excluding O\(_2\)), making it a rising star in the battery world.

The broad adaptability of the Mg-air battery permits applications in a diversity of situations. The battery can provide power for outdoor adventure and field rescue. It can also serve as a backup power source for public buildings like schools and hospitals. Because of the good biocompatibility of Mg metal and no harmful discharge products, Mg-based batteries show great potential to power implantable biodevices. For example, Frei et al. showed the discharge performance of a Mg-air battery was sufficient for many electronic contact lens applications. Other future applications include powering electric vehicles and domestic and industrial robots.
Nevertheless, the Mg-air battery suffers from the following two known major issues: (a) the high internal resistance and the accumulation of discharge products lead to a discharge voltage much less than the theoretical value; and (b) the extra energy and mass loss of Mg anodes caused by the anodic hydrogen evolution reaction plus the chunk effect during discharge. The average discharge voltage of reported Mg-air batteries is usually less than 1.6 V and the anodic efficiency is less than 60%. Current evaluations include average discharge voltage, specific capacity, energy density, and anodic efficiency.

This paper proposes a new evaluation metric for Mg anodes, the apparent Mg valence, which has an intrinsic connection with the mechanism of the parasitic anodic hydrogen reaction. An in-depth understanding of the Mg anode energy loss is given herein, followed by a description of the current evaluation system and a discussion of the new evaluation metric. This paper aims to discuss the feasibility of the apparent Mg valence as an evaluation metric for Mg-based anodes and to diversify the evaluation systems of Mg-based anodes. The paper provides a deeper understanding of the causes of the low anodic efficiency and is expected to lead to the development of better Mg anodes.

2 | IN-DEPTH UNDERSTANDING OF ANODE ENERGY LOSS

2.1 | Discharge mechanism of Mg

Li et al. provided compelling evidence for the Mg corrosion mechanism explained in this section, based on prior expositions in prior reviews, although it must be stated that the Mg corrosion mechanism had previously been subjected to considerable controversy. The evidence for this mechanism from Li et al. is provided in the next subsection, and the implications are explained in the third subsection.

Figure 1 provides a schematic of the discharge mechanism of a Mg anode in an aqueous solution, which is equivalent to an anodically polarized Mg corrosion reaction. At the anode of the Mg-air battery, each metal Mg atom is expected to lose two electrons in the anodic partial reaction between the Mg metal and the Mg$^{2+}$ ion. However, recent research has confirmed that Mg loses its outermost electrons one by one. Furthermore, quantum mechanics forbids the simultaneous transfer of two electrons. Thereby, the first step of the anode reaction of an aqueous Mg-based battery is:

\[
\text{Mg} \rightarrow \text{Mg}^{++} + e^-.
\]

This is the rate-determining step.

Due to their high chemical activity, the unipositive Mg$^+$ ions have a short lifetime on the anode surface, as gas-phase studies have indicated that Mg$^+$ reacts with water in milliseconds. A fraction, designated as “$k_1$,” of Mg$^+$ ions lose their other outermost electron via the following reaction, Equation (2).

\[
\text{Mg}^+ \rightarrow \text{Mg}^{+++} + e^-.
\]

These electrons can also provide current to the external circuit. Some of these electrons produced by Equations (1) and (2) may take part in the cathodic partial reaction, Equation (3), which is the cathodic reaction that balances the anodic partial reactions Equation (1) and (2) during Mg corrosion at the open circuit potential.

\[
e^- + \text{H}_2\text{O} \rightarrow \text{OH}^- + \frac{1}{2}\text{H}_2.
\]
The complement of Mg$^+$ ions (the fraction designated as "1 − \(k\)) chemically splits water by Reaction (4) to produce hydrogen and Mg$^{++}$ ions, which precipitate from the aqueous solution as the solid Mg(OH)$_2$, because of its low solubility.

\[
\text{Mg}^++\text{H}_2\text{O} \rightarrow \text{Mg}^{++} + \text{OH}^- + \frac{1}{2}\text{H}_2. \tag{4}
\]

This reaction, Equation (4), does not provide electrons to the external circuit and contributes to the low anodic efficiency of the Mg anode of the Mg-air battery.

Equations (1) to (4) sum to give the overall Mg corrosion reaction at the open circuit potential as follows:

\[
\text{Mg}^+ + 2\text{H}_2\text{O} \rightarrow \text{Mg}^{++} + 2\text{OH}^- + 2\text{H}_2. \tag{5}
\]

### 2.2 Evidence for discharge mechanism

This unipositive Mg$^+$ mechanism predicts that the apparent Mg valence should be less than 2. Li et al.\textsuperscript{15} evaluated the apparent Mg valence for pure Mg and the Mg alloy WE43 subjected to an applied anodic current density in galvanostatic experiments in N$_2$ deaerated 3.5 wt.% NaCl saturated with Mg(OH)$_2$ using Equation (6).

\[
V_{e,\text{anodic}} = \frac{N_{e,\text{anodic}}}{N_W}, \tag{6}
\]

where $N_{e,\text{anodic}}$ is the electron flux associated with the applied anodic current density, mmol cm$^{-2}$ h$^{-1}$, and $N_W$ is the rate of Mg metal loss, mmol cm$^{-2}$ h$^{-1}$. The $N_{e,\text{anodic}}$ was evaluated using Equation (7).

\[
N_{e,\text{anodic}} = \frac{I_a}{F} = \frac{I_{\text{applied}} + I_c}{F}, \tag{7}
\]

where $I_a$ is the anodic current density, which is the summation of the applied anodic current density, $I_{\text{applied}}$ and the current density of cathodic partial reaction (Reaction 3), $I_c$, and $F$ is the Faraday constant. The apparent valence is simply the number of electrons in the anodic reaction for each Mg atom corroded. Li et al.\textsuperscript{15} applied an anodic Mg current density, $I_{\text{applied}}$ in galvanostatic experiments, and measured the anodic hydrogen evolution rate, $N_{t,\text{anodic}}$, the potential of the Mg electrode, and the weight loss of the Mg electrode after the end of each galvanostatic experiment. The cathodic partial reaction was characterized by cathodic polarization curves, which allowed evaluation of the current density of cathodic partial reaction (Reaction 3), $I_c$. The evaluations of the apparent Mg valence by Li et al.\textsuperscript{15} are better than previous evaluations\textsuperscript{17} because of this measurement of the current density of cathodic partial reaction (Reaction 3), $I_c$.

![Figure 2](image2.png)

**Figure 2** Plot of apparent Mg valence, $V_{e,\text{anodic}}$, and the value of $k$, vs applied current density for the applied current densities that produced data with acceptably low measurement errors in the galvanostatic experiments of Li et al.\textsuperscript{15} The average value of the apparent Mg valence was 1.2 ± 0.1 consistent with expectations of the unipositive Mg$^+$ corrosion mechanism, and was independent of the applied anodic current density, $k = (1 - X)/(1 + X), X = N_{t,\text{anodic}}/N_{e,\text{a}}$. The average value of $k = 0.2$ was in good agreement with the average value of $V_{e,\text{anodic}} = 1.2$

The value of $k$ was evaluated by Li et al.\textsuperscript{15} using Equation (8):

\[
k = \frac{1 - X}{1 + X}, X = \frac{N_{t,\text{anodic}}}{N_{e,\text{a}}}, \tag{8}
\]

where $N_{t,\text{anodic}}$ is the measured anodic hydrogen evolution rate by Equation (4). Equation (8) is clear from inspection of the unipositive Mg$^+$ mechanism as outlined above. The average value of $k = 0.2$ was in good agreement with the average value of $V = 1.2$.

Equations (1), (2), and (4) indicate that increasing anodic polarization should increase the amount of Mg$^+$ produced, and consequently, the amount of anodic hydrogen evolved and the amount of weight lost. There should be a relationship between the amount of anodic hydrogen evolved and the amount of weight loss as given by Equation (9):
the measurement of the current density of the cathodic reaction, Equation (3), is exponentially decreased to essentially zero. The hydrogen production at the Mg anode in the Mg-air battery is increasingly produced by Mg$^+$ ions chemically splitting water by reaction Equation (4) and decreasingly by the hydrogen evolution reaction Equation (3), which is the cathodic reaction for Mg corrosion at the open circuit potential.

The effective consumption of metal Mg should go through Reactions (1) and (2), which provide energy conversion and electrons for the external circuit. In contrast, Reaction (4) does not produce any electrons to the external circuit and is wasteful consumption. The macrophenomenon of Reaction (4) is hydrogen gas released from the anode surface. Some hydrogen may also be evolved by Reaction (3) and this is also a wasteful reaction if it occurs on the Mg anode of a Mg-air battery. Chen et al. reported two different discharge morphologies, the blocky discharge and the fasciculate Mg(OH)$_2$, which refer to the two different reactions. The Mg(OH)$_2$ produced by Reactions (3) and (4) is generated on the very surface of the Mg anode, and has a blocky morphology. The Mg$^{++}$ ions from Reaction (2) meet OH$^-$ in the solution to form Mg(OH)$_2$ and then adhere to the anode surface, presenting the fasciculate morphology. The wasteful consumption of Mg via Reaction (4) has been proved by Chen et al. as the only reason for the energy loss of an ultra-high purity (UHP) Mg anode in the Mg-air battery. Reaction Equation (4) is known as the anodic hydrogen reaction and as the negative difference effect (NDE).

For the research of Li et al. the value $k = 0.2$ predicts that $N_{H,m}/N_W = 0.4$. Figure 3 plots the hydrogen evolution rate, $N_{H,m}$ vs weight loss rate, $N_W$, for pure Mg and WE43 in $N_2$ deaerated 3.5 wt. % NaCl saturated with Mg(OH)$_2$ in the galvanostatic experiments of Li et al. The experimental data was in good agreement with the expectations from Equation (9).

Figures 2 and 3 indicate that the weight loss rate, the hydrogen evolution rate, and the applied anodic current density were all interrelated in these experiments of Li et al. exactly as expected by the Mg$^+$ corrosion mechanism, providing compelling evidence for this Mg corrosion mechanism. The major advance of the work of Li et al. was the measurement of the current density of the cathodic partial reaction (Reaction 3), $I_c$, so that these measurements are better than prior measurements where the cathodic current density was not considered.

### 2.3 Consequences of discharge mechanism

In the Mg-air battery, the anodic reaction is accelerated by the current drawn from the battery, so that the anodic reactions, particularly Equation (1), are accelerated as compared with Mg corrosion at the open circuit potential, and the speed of the cathodic reaction, Equation (3), is exponentially decreased to essentially zero. The hydrogen production at the Mg anode in the Mg-air battery is increasingly produced by Mg$^+$ ions chemically splitting water by reaction Equation (4) and decreasingly by the hydrogen evolution reaction Equation (3), which is the cathodic reaction for Mg corrosion at the open circuit potential.

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The energy loss for a Mg-based alloy as an anode for the Mg-air battery is more complicated than for pure Mg, as shown in Figure 1. Alloying pure Mg with other elements tends to form two phases. Most of these second-phase precipitates are nobler than Mg. During the discharge process, these precipitates have a lower dissolution priority than the Mg matrix because of the difference in the standard potential. The stimulation from the precipitate particles causes the surrounding Mg to dissolve preferentially. As the discharge progresses, the precipitates lose support from the surrounding Mg and then drop out from the anode. Supporting evidence is provided by the lamellar surface of Mg anodes containing the LPSO phases after discharge. These precipitates that have dropped out of the anode also cause wasteful mass and energy loss. Further support was provided by Ma et al., who detected Mg$_2$Al$_2$ particles in the discharge products of a Mg-Al anode. The precipitates in the Mg matrix also lead to the chunk effect. The exfoliation of precipitates removes some Mg from the anode, which is wasteful Mg consumption. Therefore, the energy loss for a Mg alloy as an anode for the Mg-air battery comes from four parts: (a) any cathodic hydrogen evolution at the Mg
Thus, future researchers indicate that the ideal when it is used also in the calculation of energy density. Generally, a higher discharge voltage is better. However, due to the high internal resistance, the average discharge voltage of published Mg anodes is typically lower than 1.6 V, which is much lower than the theoretical value of 3.1 V. Voltage stability is also an important aspect of the discharge voltage. The desired Mg anode should have a stable discharge voltage that has a high value. Nevertheless, some Mg-based anodes show large voltage fluctuations, particularly at large current densities. Thus, future researchers are encouraged to characterize the Mg anode using both the average discharge voltage and its variance.

The specific discharge capacity, $C$, is the electric charge produced by a given mass of Mg metal, and is evaluated using Equation (10):

$$C \text{ (mAh g}^{-1}\text{)} = \frac{I t A}{\Delta W},$$

where $I$ is the current density (mA cm$^{-2}$) produced by the battery (or applied during a battery test), $t$ is the discharge time (h), $A$ is the anode surface area (cm$^2$), and $\Delta W$ is the Mg metal mass loss during the discharge (g). In Equation (10), the current density is designated as $I$, and this designation is used also in Equations (11) to (13). However, this current density can also be designated as $I_{\text{battery}}$, and is so designated in Section 4 when it is useful to distinguish between battery evaluations and the galvanostatic experiments of Li et al. that elaborated the Mg corrosion mechanism in Section 2.2.

The energy density, $\epsilon$, is evaluated by the multiplication of the specific capacity and the average discharge voltage, $U$, and can be obtained, as shown in Equation (11):

$$\epsilon \text{ (mWh g}^{-1}\text{)} = UC = \frac{U I t A}{\Delta W}.$$  

The anodic efficiency, $\eta_{\text{anode}}$, is a significant indicator of the energy conversion efficiency of Mg-based anodes, and is the ratio of the specific capacity, $C$, to the theoretical capacity, $C_{\text{thero}}$:

$$\eta_{\text{anode}} = \frac{C}{C_{\text{thero}}} \times 100\%,$$

where the theoretical capacity, $C_{\text{thero}}$, is the electric charge produced by the complete energy conversion of the Mg anode, and is given by Equation (13):

$$C_{\text{thero}} \text{ (mAh g}^{-1}\text{)} = \frac{e N_A}{3.6} \sum f_i n_i M_i,$$

where $e$ is the charge of an electron, $N_A$ is the Avogadro constant, $f_i$ is the weight fraction of alloy element $i$, $n_i$ is the number of electrons that can be provided by the element $i$, and $M_i$ is the molar mass of element $i$.

3 | CURRENT EVALUATION SYSTEM FOR Mg ANODE

Mg-based anodes are currently evaluated using the following four metrics: (a) the average discharge voltage and its stability, (b) specific capacity, (c) energy density, and (d) anodic efficiency. The average discharge voltage indicates the electrochemical activity of the Mg-air battery, and is also used in the calculation of energy density. Generally, a higher discharge voltage is better. However, due to the high internal resistance, the average discharge voltage of published Mg anodes is typically lower than 1.6 V, which is much lower than the theoretical value of 3.1 V. Voltage stability is also an important aspect of the discharge voltage. The desired Mg anode should have a stable discharge voltage that has a high value. Nevertheless, some Mg-based anodes show large voltage fluctuations, particularly at large current densities. Thus, future researchers are encouraged to characterize the Mg anode using both the average discharge voltage and its variance.

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4 | THE APPARENT VALENCE OF Mg ANODE

The above section introduced the current evaluation system for the discharge performance of an Mg-based anode. This section explains that the Mg apparent valence provides another estimation method for Mg anodes. The discharge mechanism in Section 2 indicates that the ideal Mg anode would have a 100% energy conversion rate if the rates were zero for Reactions (3) and (4). The anodic reaction would then be the same as the theoretical reaction (14), in which case the apparent valence of Mg anode would be 2.

$$\text{Mg} \rightarrow \text{Mg}^{++} + 2e^{-}.$$  

However, the energy conversion rate is typically less than 60%, meaning that the apparent valence of the Mg anode is less than 2. Thus, the apparent Mg valence, $V$, can be used to evaluate the discharge performance of an Mg anode, since $V$ varies from 0 to 2. It is convenient to use a separate designation, $V_{e,\text{ibattery}}$ for the apparent valence of the Mg anode of the Mg-air battery because it is convenient to evaluate this apparent valence in a manner slightly different to the evaluation of the apparent valence in the galvanostatic experiments of Li et al.

The apparent Mg valence, $V_{e,\text{ibattery}}$ for the Mg anode of the Mg-air battery is evaluated using Equation (15), and the $N_{e,\text{ibattery}}$ is evaluated using Equation (16),

$$V_{e,\text{ibattery}} = \frac{N_{e,\text{ibattery}}}{N_W},$$

$$N_{e,\text{ibattery}} \approx \frac{I_{\text{battery}}}{F},$$

where $I_{\text{battery}}$ is the applied current density used in the evaluation of battery performance as explained in
Section 3, and makes the implicit assumption that \( I_{\text{battery}} \) is a good approximation for \( I_a \), the anodic current density. This assumption is equivalent to the assumption that the current density of the cathodic partial reaction (Reaction (3)), \( I_c \), is small or negligible. \( I_c \) is assumed to be small or negligible during battery discharge because the cathodic hydrogen evolution reaction, Equation (3) decreases exponentially with increasing applied anodic current density.

The \( N_W \) can be obtained using Equation (17)

\[
N_W = \frac{f W_l}{M_{\text{Mg}}},
\]

where \( W_l \) is the mass loss rate, mg cm\(^{-2}\) h\(^{-1}\), \( M_{\text{Mg}} \) is the molar mass of Mg, and \( f \) is the weight fraction of Mg in alloy. The apparent Mg valence evaluated by Equation (15) is the number of electrons produced by the Mg anode in the external circuit for each Mg atom dissolved in the Mg-air battery.

Figure 4 presents the apparent Mg valence, \( V_{e,\text{battery}} \), of UHP Mg, AZ80 (a representative Mg-Al anode) and ZK60 (a representative Mg-Zn anode) at different applied current densities during battery testing. The apparent Mg valence of UHP Mg was 0.95 at a low current density of 0.5 mA cm\(^{-2}\), and increased with increasing current density. The highest apparent valence of UHP Mg was 1.26 at 40 mA cm\(^{-2}\). This increase in the value of the apparent Mg valence, \( V_{e,\text{battery}} \), with increasing current density is due to the progressive decrease of the cathodic hydrogen evolution reaction, Equation (3). This is clear from a comparison of Figures 4 and 3, and a comparison on the definitions of \( V_{e,\text{battery}} \) and \( V_{e,\text{anodic}} \).

The apparent Mg valence of AZ80 and ZK60 in Figure 4 also increased with increasing current density, just like the apparent valence of UHP Mg for the same reason. However, the value of the apparent valence of AZ80 and ZK60 was obviously less than for UHP Mg, particularly for ZK60. For example, the apparent valence of AZ80 was only 0.61 at 2.5 mA cm\(^{-2}\), and the peak apparent valence was only 0.92 for ZK60 at 40 mA cm\(^{-2}\).

Both Mg alloys AZ80 and ZK80 had values of apparent Mg valence much lower than those of UHP Mg for all values of applied current density. The low values at low current densities and the increase with increasing current density are attributed to the same cause as for UHP Mg: that is that there was a significant cathodic hydrogen evolution rate, by Equation (3), on the surface of the Mg anode during the discharge process. The generally low values of apparent Mg valence are attributed to the effects of the precipitates on the Mg matrix. Precipitates cause the following: (a) the microgalvanic effect between the precipitate and the Mg matrix, which results in a significant amount of cathodic hydrogen evolution on the precipitate by Reaction (3), (b) a severe chunk effect due to the undermining and dropping out of precipitate particles from the Mg anode, leading to extra mass loss of Mg, and (c) there is probably an influence on the partitioning factor "\( k \)" which characterizes the amount of Mg\(^{\text{II}}\) that reacts by Equation (2) or by Equation (4).

The expected relationship between anodic efficiency and apparent Mg valence, \( V_{e,\text{battery}} \), can be determined by a rearrangement of Equations (6) and (12) to be:

\[
\frac{V_{e,\text{battery}}}{2} = \frac{\eta_{\text{anode}}}{100\%}.
\]

Figure 5 evaluated this relationship. Figure 5A shows that the cross-plot of values of anodic efficiency, \( \eta_{\text{anode}} \), for UHP Mg and apparent Mg valence, \( V_{e,\text{battery}} \), produced a linear plot. This provides experimental verification for the equivalence of apparent Mg valence, \( V_{e,\text{battery}} \), and anodic efficiency, \( \eta_{\text{anode}} \). Figure 5B evaluates this relationship for AZ80 and ZK60 by providing a cross-plot of the values of anode efficiency, \( \eta_{\text{anode}} \), and apparent Mg valence, \( V_{e,\text{battery}} \), as the data points compared with the expected relationship by the drawn line. For AZ80 and ZK60 the values of anodic efficiency, \( \eta_{\text{anode}} \), were slightly less than the theoretical expectation. The difference range was 1% to 4%. This difference is attributed to precipitates in these alloys. The calculation of anodic efficiency assumes that all elements participate in the energy conversion to provide electrons, while the calculation of apparent valence only counts the weight
fraction of Mg in the alloy. As mentioned in Section 2, precipitates drop out of the anode without participation in energy conversion. Therefore, the calculated anodic efficiency is less than $V_{e,ibattery}/2$. It is also noticed that the difference range is less than the alloying fraction of anodes.

Figure 6 reviews the best discharge properties of Mg-based anodes for Mg-air batteries from the literature. Raw data and references are shown in Table S1.

for all Mg anodes. Unfortunately, most current Mg-based anodes have an apparent valence lower than 1.26. The Mg-Zn (−X) alloy system has low apparent valence values from 0.62 to 0.98. In contrast, Mg-Ca (−X) and Mg-Li (−X) alloy systems have higher apparent Mg valence values: 1.04 to 1.44 for Mg-Ca (−X) and 1.09 to 1.53 for Mg-Li (−X). There are also some studies using modified commercial Mg alloys as anodes. The Mg-Al alloy system has the largest portion with the development of AZ and AP series. The AZ80 and modified alloys present the highest apparent valence from 1.05 to 1.48 among all commercial alloys. So far, only a few Mg-based alloys have an apparent Mg valence higher than that of UHP Mg. The highest was for Mg-14Li-1Al-0.1Ce, which had an apparent valence of 1.53 at 2 mA cm$^{-2}$. Li et al$^{35}$ reported a Mg-9Al-1In anode subjected to a 24 h annealing treatment at 400°C, which had an apparent Mg valence of 1.49 at 40 mA cm$^{-2}$. The Mg-0.1Ca-0.2In alloy showed a high apparent valence of 1.44 at 5 mA cm$^{-2}$. Other noticeable anodes that have an apparent Mg valence higher than UHP Mg are as-rolled Mg-6Al-1Zn-0.5La, $^{37}$ AZ80-1La-0.5Gd$^{38}$ and AP65-0.2Ce-0.2Y.$^{39}$

5 | CLOSING DISCUSSION AND PERSPECTIVES

The Mg-air primary battery has attracted increasing attention and interest in recent decades due to its promising application potential. The parasitical anodic hydrogen reaction during the discharge process is an important issue leading to the low energy conversion efficiency of Mg anodes. Based on the reaction mechanism of anodic hydrogen evolution, this paper proposed a new
evaluation indicator for Mg-based anodes, the apparent Mg valence, which varies between 0 and 2. The ideal Mg anodes should have an 100% energy conversion efficiency and an apparent Mg valence of 2. The apparent Mg valence can serve as an indicator individually to reflect the energy conversion efficiency and the anodic hydrogen reaction rate.

So far, the apparent valence of current Mg anodes is less than 1.6. This paper also suggests the following strategies for the future Mg-based anodes to achieve a higher apparent Mg valence: (a) choosing the alloying element prudently and controlling the volume fraction of precipitates in the Mg matrix; and (b) using electrolyte additives to suppress the anodic hydrogen reaction. The former can be achieved via microalloying and heat treatment methods. Noticeable work has been done by Deng et al\textsuperscript{36,40} on the development of micro-alloyed Mg-Ca anodes. Electrolyte additives have also been used to improve the discharge properties of Mg-based anodes.\textsuperscript{41,42} For example, Wang et al\textsuperscript{43} reported that the addition of 2,6-dihydroxybenzoate into the NaCl electrolyte reduced the hydrogen evolution volume of the Mg-0.15Ca anode. This strategy is, therefore, a promising method to improve the apparent valence of Mg anode.

6 CONCLUSION

- The apparent Mg valence base on the unipositive Mg\(^+\) mechanism provides a new evaluation metric for the Mg-air battery, which is directly related to the anode efficiency.
- The low apparent valence and low anode efficiencies at low current densities was attributed to the cathodic hydrogen evolution reaction occurring on the Mg anode during battery discharge.
- The generally low values of apparent Mg valence are attributed to the effects of the precipitates on the Mg matrix. Precipitates cause the following: (a) the micro-galvanic effect between the precipitate and the Mg matrix, which results in a significant amount of cathodic hydrogen evolution on the precipitate, (b) a severe chunk effect due to the undermining and dropping out of precipitate particles from the Mg anode, leading to extra mass loss of Mg, and (c) there is probably an influence on the partitioning factor “\(k\)” which characterizes the amount of Mg\(^+\) that reacts with water chemically and produces no electrons in the external circuit.

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**SUPPORTING INFORMATION**

Additional supporting information can be found online in the Supporting Information section at the end of this article.

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