Mg Anode Corrosion in Aqueous Electrolytes and Implications for Mg-Air Batteries

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Aqueous Mg-air primary batteries possess many favorable attributes for energy storage because Mg is affordable, abundant, and lightweight. However, parasitic corrosion of Mg in aqueous electrolytes generates H2 and surprisingly increases with increasing current density during battery discharge (Mg oxidation), limiting the faradaic efficiency of aqueous Mg batteries. In this study, differential electrochemical mass spectrometry and H2 pressure rise measurements were used to characterize Mg corrosion in Mg-air batteries employing aqueous electrolytes with salts (NaCl, NaNO3, NaPO4, and a NaCl/NaPO4 mixture) that provide various degrees of Mg passivation. H2 evolution rates were highest in NaCl electrolytes and lowest in NaNO3 electrolytes. However, NaNO3 salts reduced the H2-evolving corrosion rate at the expense of introducing a nitrate to nitrite corrosion reaction into the battery. The combined Mg corrosion rate in the nitrate-based electrolyte was still lowest among those electrolytes studied. The nitrite to nitrate corrosion reaction also lowered the magnitude of the Mg anodic potential and therefore decreased the overall Mg-O2 battery voltage compared to the NaCl electrolyte. Nevertheless, Mg-O2 batteries utilizing a NaNO3 electrolyte allowed for 60% larger discharge capacity and 50% higher Mg oxidation faradaic efficiency compared to a NaCl electrolyte.

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Increased demand for electrical energy storage has sparked a renewed interest into battery chemistries with theoretical energy densities that are much larger than lithium ion batteries. Among these chemistries, a tremendous amount of recent work has been devoted to metal-air batteries such as Li-O2,1−4 Na-O2,5 and Zn-O2.6 How- ever, much less attention has been paid to Al or Mg-O2 batteries even though Mg and Al are lightweight, abundant, and environmentally friendly.5 Although these batteries are not electrically rechargeable, there is commercial interest in them as standby power sources and as range extenders in electric vehicles because of their inherent safety and long standby lifetimes. Mechanically rechargeable aqueous Mg-O2 batteries, those in which a fully oxidized Mg electrode is replaced as standby range extenders for traditional Li ion battery packs since Mg is typically Mg2+ impermeable, which obviously inhibits Mg dissolution (Equation 1) necessary for Mg-O2 battery operation. Therefore, in a practical battery, a compromise between inhibiting corrosion and allowing Mg dissolution is required. Only a few papers have reported experimental results on operational performance of aqueous Mg-O2 batteries. Among these papers, the effect of nanostructured Mg, porous Mg, and alloyed Mg anodes has been investigated.16−18 In the work reported here, differential electrochemical mass spectroscopy (DEMS) and pressure rise measurements were used to study operating aqueous Mg-O2 cells and fundamentally understand the role of the electrolyte salt on Mg corrosion. The electrolytes studied here included chloride-based electrolytes, which are known to result in substantial Mg corrosion,14,15 phosphate and nitrate-based electrolytes, which are known to suppress Mg corrosion,16,20,21 and mixtures of chloride and phosphate salts, which we hypothesized may allow suppressed susceptibility to corrosion, yet afford facile Mg oxidation during anodic polarization.

Experimental

Materials characterization.—NaCl (99.5%), HN2PO4 (99.9%), and NaNO3 (99%) salts were purchased from Fisher Scientific and used as received. Electrolyte solutions were made by mixing these salts with type 1 ultrapure water at a concentration of either 0.1 mol/L or 0.5 mol/L. Potassium iodide (99.9%), sulfuric acid, standardized hydrochloric acid (0.01 N), standardized sodium thiosulfate (0.1 N), 1 wt% starch in H2O, and ammonium molybdate (99.9%) were all purchased form Sigma Aldrich. Commercial MnO2 cathodes (E-4) were purchased from Electric Fuel Ltd and used as received in the full battery cell configuration. High purity planar Mg sheets (250 µm thick) were purchased from Gallium Source and used in all experiments. From the manufacturers specifications, the impurities in the Mg are

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as follows: 30 ppm Al, 50 ppm Mn, 50 ppm Si, 40 ppm Ca, 30 ppm Fe, 2 ppm Ni, 5 ppm Pb, 50 ppm Zn. Mg was used without any pretreatment to maintain consistency between experiments. Polishing the surface of Mg alloys has been shown to decrease the initial corrosion rate due to removal of contaminants on the alloy surface. However, we obtained significantly different corrosion rates from one polished sample to the next. Therefore, to maintain experiment-to-experiment consistency, we chose to use the Mg as-received (unpolished). Nafion 117 membranes with a 28 mm diameter were used in the H-cell to separate the anode chamber from the cathode chamber. The Mg WE chamber electrolyte was stirred vigorously with a stir bar to ensure uniform mixing. Impedance and linear sweep voltammetry (LSV) experiments were performed using a system similar to the one previously developed by McCloskey et al.25 Battery cells were constructed in a glove box. Gases evolved from Mg reacted with oxygen (from air) to form MgO, which was subsequently removed from the cell. Gases evolved from Mg reacted with water (from water) to form Mg(OH)2, which was subsequently removed from the cell. However, we obtained significantly different corrosion rates from one polished sample to the next. Therefore, to maintain experiment-to-experiment consistency, we chose to use the Mg as-received (unpolished). Nafion 117 membranes with a 28 mm diameter were used in the H-cell to separate the anode chamber from the cathode chamber. The coiled Pt wire (23 cm) counter electrode and a Ag/AgCl reference electrode with glass frit were purchased from BASI Inc. The glass H-cell and the glass bulk electrolysis cell (4 port, ∼30 ml volume) were custom designed and constructed by Adams & Chittenden Scientific Glass (Berkeley, CA). X-ray diffraction (XRD) measurements of the Mg were performed on a Bruker D2 Phaser diffractometer using CuKα radiation. Diffraction patterns were scanned over an angular range of 10–90° (2θ).

**Electrochemical measurements.**—Electrochemical measurements were performed on a Biologic SP-300 potentiostat. When using the H-cell and bulk electrolysis cell, the voltages of both the counter electrode (Pt wire) and working electrode (Mg foil, ∼1 cm2 exposed to electrolyte) were recorded simultaneously vs. a Ag/AgCl reference electrode in the Mg anode portion of the H-cell. All potentials are reported versus Ag/AgCl, except for full cell battery experiments. Impedance and linear sweep voltammetry (LSV) experiments were performed in air in the bulk electrolysis cell with vigorous stirring using a magnetic stir bar. Impedance experiments were performed with an amplitude of 10 mV over a frequency range of 0.1–2 × 106 Hz. LSV experiments were performed by sweeping the Mg working electrode potential from open circuit potential (OCP) at a scan rate of 5 mV/s.

**Differential electrochemical mass spectroscopy (DEMS) and gas pressure rise measurements.**—DEMS and pressure rise measurements were performed using a system similar to the one previously published by McCloskey et al.25 Battery cells were constructed in a 2-electrode cell similar to the configuration previously published.26 The 2-electrode cell battery consisted of a 0.4375” diameter Mg disk (250 μm thick) anode, a 0.5° diameter filter paper separator (QMA grade, Whatman), and a cathode composed of commercial MnO2 E-4 material (12 mm diameter, 0.472”) for electrochemical storage of the battery. The battery cell was assembled in a glove box. Gases evolved from the battery cell were analyzed in the headspace above the cathode of a battery cell in a similar manner to those previously published.24

The H-cell configuration is shown in Figure 1. The gases in each side of the cell can be analyzed individually using the mass spectrometer (Stanford Research Systems, RGA200) and an in line pressure transducer (Omega Engineering Inc., PX419). An Al electrode holder was used to hold the Mg foil WE electrode so that the Mg foil is immersed in the electrolyte, but no portion of the Al holder is immersed. The Mg WE chamber electrolyte was stirred vigorously with a stir bar over the course of the experiment to limit mass transport effects. The volume of each chamber of the H-cell was calibrated using a volume expansion technique and the ideal gas law. The volumes of the 3-port chamber (Mg foil and Ag/AgCl reference electrode) and the 2-port chamber (Pt wire counter electrode) of the H-cell were 11.1±0.2 ml and 9.4±0.2 ml, respectively. The uncertainty in the volume arises from the Nafion membrane deflection when the pressure difference between each chamber of the H-cell increases. The volume of the capillaries between the H-cell and the pressure transducer are 1.2 ml. The 3-port and 2-port chamber of the H-cell are each filled with 5 ml of electrolyte during each experiment so that the total headspace of gas above the electrolyte in the 3-port chamber is calculated to be 7.3 ± 0.2 ml. Initially, the headspace above the electrolyte was filled with Ar. As H2 was evolved from the Mg foil submersed in the electrolyte, the pressure transducer measures changes in pressure of the 3-port chamber containing the Mg foil so that the moles of H2 evolved could be quantified directly. Additionally, the gases evolved from Mg could be quantified by pulsed small volumes (500 μL) of gas above the 3-port headspace to a mass spectrometer. Only H2, and no other gas, was found to evolve during any of the measurements reported in this article (see Figure S1 for mass spectrometry gas analysis during anodic and cathodic chronopotentiometry at a Mg electrode). Furthermore, H2 evolution was identical under Ar and O2 headspaces (Figure S2), and therefore electrochemical measurements were performed under an Ar headspace for safety purposes unless otherwise noted.

**NO2− Titration.**—Titration of the NaNO3 electrolyte to detect NO2− was performed in a manner similar to the peroxide titration previously developed by McCloskey et al.25 Briefly, the following three reagents were added, in succession, to an aliquot of electrolyte extracted from the Mg electrode H-cell chamber: 1 mL of 2 wt% KI in H2O, 1 mL of 3.5 M H2SO4, and 50 μL of a molybdate-based catalyst solution. The catalyst solution was prepared by dissolving 1 g ammonium molybdate in 10 mL of 6 N ammonium hydroxide, followed by adding 3 g ammonium nitrate and diluting the solution to 50 mL total using ultrapure H2O. The extracted electrolyte solution turns yellow upon reagent addition due to I2 formation, and the I2 is immediately titrated to a faint straw color using 0.01 N Na2S2O3. This point, ~0.5 mL of a 1% starch indicator is added to the solution, which turns dark blue, and the titration is continued until the solution turns clear. The total time necessary for the peroxide titration after the reagents are added is typically ~1 minute. This titration protocol, originally developed by McCloskey et al. for peroxide quantification in Li-O2 batteries, can be extended to quantify NO2−, which acts in place of peroxide as the oxidizer, as long as it is performed in an inert atmosphere (NO2− spontaneously converts to NO in air). The NO2− titration accuracy was confirmed by making a solution with a known concentration of LiNO2 (5.5 mg/ml) in water (200 μL) and then titrating using the previously described peroxide titration.25 A titration accuracy of >90% was achieved in the control experiment. Titration of the NaNO3 electrolyte in the H-cell was performed by

![Figure 1](image_url)
removing 150 μL aliquots of NaNO₃ electrolyte from the Mg chamber of the H-cell with a syringe. Aliquots were removed and titrated at 15 minute intervals during both OCV and discharge of the Mg anode. The NaNO₃ aliquots were quickly transferred from the syringe into an Ar filled vial (with septum cap) before titration under Ar. The quantity of NO₂ found in the 150 μL aliquot was scaled to the amount that would be found in the whole electrolyte volume assuming the solution was well mixed.

Results

Figure 1 shows a schematic of the electrochemical H-cell that was developed to isolate the Mg electrode from the Pt electrode so that gases evolved/consumed at each electrode could be analyzed individually without influencing one another. The Pt wire counter electrode (CE) is located in the 2-port chamber of the H-cell and the Ag/AgCl reference electrode (RE) and Mg foil working electrode (WE) are located in the 3-port chamber. For the purposes of this study, we focused on the electrochemistry and gas evolution in the Mg WE chamber in order to understand the fundamental Mg corrosion reaction in various aqueous electrolytes. Differential electrochemical mass spectroscopy (DEMS) of the gases evolved in the Mg WE chamber confirmed that H₂ was the only gas evolved at OCV both during reduction and oxidation at the Mg WE (Figure S1).

The Mg corrosion rate is strongly influenced by the electrolyte employed. Figure 2 shows the cumulative H₂ evolved (normalized to the surface area of Mg foil exposed to electrolyte) from the Mg WE chamber of the H-cell in four aqueous electrolytes, selected given their use in previous reports on Mg-O₂ batteries and Mg corrosion studies, and during anodic chronopotentiometry (Mg oxidation). A fifth aqueous electrolyte, 0.5 M Na₂SO₄, was also characterized (Figure S3), but was found to result in substantially higher H₂ evolution than phosphate-based electrolytes and was therefore not further explored. Four consecutive 20 min., 3.2 mA cm⁻² anodic steps, in which each step is followed by a 20 min OCV, were performed. In a typical experiment, the initial pH of the NaCl and NaNO₃ electrolytes was 5 and increased to ~8 during the course of data collection. The HNa₂PO₄ and NaCl/HNa₂PO₄ mixed electrolytes initially started at pH 8 and increased to pH 9. For 0.5 M HNa₂PO₄, 0.5 M NaCl/0.05 M HNa₂PO₄ mixture, and 0.5 M NaNO₃ electrolytes, negligible H₂ evolution (Mg corrosion) was observed at OCV when compared to the pure 0.5 M NaCl electrolyte, suggesting that these electrolytes salt passivate the Mg surface more effectively than NaCl. For all four electrolytes, the H₂ evolution increases once the galvanostatic oxidation of Mg begins (i.e. Mg anodic dissolution) and returns to the OCV H₂ evolution rate (i.e. inherent Mg corrosion) at the end of the galvanostatic oxidation. The seemingly thermodynamic-defying increase of H₂ evolution during anodic Mg dissolution, termed the negative difference effect (NDE), is consistent with previous reports, and is observed to occur to varying extents in the various electrolytes. Consistent with previous reports, the NaNO₃ electrolyte appears to almost completely inhibit corrosion, both at OCV and during oxidation, given the extremely small H₂ evolution observed. However, we will show later that the suppressed H₂ evolution is at the expense of the introduction of a second corrosion reaction. The Mg voltage, H₂ evolution rate (ν), and faradaic efficiency of productive Mg²⁺ dissolution (i.e. that not due to the corrosion reaction) in each electrolyte are shown in Table I. The OCV in NaCl is close to that expected for the standard potential of Mg, Mg²⁺ + 2e⁻ = Mg (ν = 1.61 vs. Ag/AgCl). The mixture of HNa₂PO₄ and NaCl/HNa₂PO₄ mixture, and 0.5 M NaNO₃ electrolytes, negligible H₂ evolution during anodic Mg dissolution, termed the negative difference effect at the end of the galvanostatic corrosion (ν = 1.35 vs. Ag/AgCl, see Figure S4 and S5). The very large overpotential during discharge

![Figure 2](https://example.com/figure2.png)

**Figure 2.** H₂ evolution from a Mg working electrode (1.2 cm² surface area) in 0.5 M NaCl (green), 0.5 M NaCl / 0.05 M HNa₂PO₄ (blue), 0.5 M HNa₂PO₄ (red), and 0.5 M NaNO₃ (orange) electrolytes. Four consecutive anodic chronopotentiometric scans (20 min at 3.2 mA cm⁻²) are shown in between holding the electrode at OCV for 20 minutes.

Table I. Comparison of Mg Anode Properties in Different Electrolytes.

| Electrolyte          | OCV (V) | Discharge* H₂ Potential (V) | OCV H₂ Evolution (rOCV, μmol min⁻¹ cm⁻²) | Discharge* H₂ Evolution (rdischarge, μmol min⁻¹ cm⁻²) | Mg²⁺ Faradaic efficiency (%) |
|----------------------|---------|-----------------------------|----------------------------------------|--------------------------------------------------|-----------------------------|
| 0.5 M NaCl           | −1.61   | −1.58                       | 0.79                                   | 1.39                                             | 40                          |
| 0.5 M NaCl/0.05 M    | −1.58   | −1.54                       | 0.04                                   | 0.73                                             | 31                          |
| HNa₂PO₄              | −1.52   | 2.3                         | 0.01                                   | 0.35                                             | 66                          |
| 0.5 M HNa₂PO₄        | −1.4    | −1.35                       | 0.01                                   | 0.08                                             | 93**                        |

*Mg²⁺ faradaic efficiency defined as \(\frac{\text{ipplied} - \text{ipplied}}{\text{applied}} \times 100\); \(\text{ipplied} = (\text{rdischarge} - \text{rOCV})Fz, \text{ipplied} = 3.2 \frac{nA}{cm^2}\).

*3.2 mA cm⁻² discharge.

**Based on H₂ corrosion reaction only.
indicates the pure HNa2PO4 electrolyte passivates the Mg surface too strongly, presumably by introducing a very resistive layer between the metal and the electrolyte interface. The NaNO3 electrolyte displays the smallest H2 evolution and the highest apparent faradaic efficiency for Mg2⁺ dissolution. Unfortunately, the Mg OCV and discharge voltage are reduced in the NaNO3 electrolyte, hence the overall battery cell voltage would be decreased compared to the NaCl and HNa2PO4 electrolytes.

If only considering the gas evolution results (Figure 1 and Table I), the corrosion protection provided by the pure 0.5 M NaNO3 electrolyte without any NaCl seems to be the most favorable electrolyte for an aqueous Mg-O2 battery since it evolves the smallest quantity of hydrogen (least corrosion) and hence displays the highest apparent Mg2⁺ faradaic efficiency.16 However, the electrolyte salt choice also affects the electrochemistry of the battery, which can be seen more clearly by examining the apparent Tafel plots and Nyquist plots for Mg in each electrolyte, as shown in Figures 3 and 4, respectively.

Figure 3 shows apparent (not iR corrected) Tafel plots for the Mg foil working electrode in the same electrolytes as in Figure 1. The voltage was scanned cathodically (Mg or H⁺ reduction) and anodically (Mg oxidation) at a rate of 5 mV/s. The Tafel slope for anodic dissolution of Mg in NaCl electrolyte remains small even at modest current densities, a desirable feature of Mg anodes in Mg-O2 batteries. However, the Mg voltage quickly increased as the anodic current increased in the HNa2PO4 electrolyte, yielding a large (almost vertical) Tafel slope and indicating the difficulty of Mg2⁺ dissolution through the passivating layer on the Mg surface at larger current densities, in agreement with the results in Table I for HNa2PO4. Interestingly, mass spectroscopy measurements during Mg oxidation in the 0.5 M HNa2PO4 electrolyte revealed H2 evolution from the Mg occurred even at potentials as large as 2.2 V (Figure S4 and S5). This result implies that the potential at the Mg surface and the electrolyte surface are significantly different in 0.5 M HNa2PO4 due to the presence of a high impedance passivating film (which is confirmed in Figure 4, as will be discussed later).

Figure 3 clearly shows the higher OCV of the Mg electrode in the NaNO3 electrolyte compared to the NaCl and HNa2PO4 electrolytes. The higher Mg potential in the NaNO3 electrolyte is unfavorable for a Mg-O2 battery, as it results in a lower discharge voltage. Additionally, for the NaNO3 electrolyte during Mg anodic dissolution, an intermediate Tafel slope is evident compared to the HNa2PO4 and NaCl electrolytes. NaNO3 inhibits OCV H2 evolution, and still appears to minimize the H2 evolution at moderate current densities. However, the different OCV and H2 evolution for the NaNO3 electrolyte suggest

Figure 3. (a) Apparent Tafel plots in the bulk electrolysis cell for 0.5 M NaCl (green data), 0.5 M NaCl / 0.05 M HNa2PO4 (blue data), 0.5 M HNa2PO4 (red data), and 0.5 M NaNO3 (orange data) electrolytes with a Mg foil working electrode, Pt wire counter electrode, and Ag/AgCl reference electrode.

Figure 5. Nitrite titration results displaying the quantity of nitrite (NO₂⁻) formed in the Mg chamber of the H-cell in 0.5 M NaNO3 electrolyte during OCV and 3.2 mA/cm² discharge.
that a different corrosion reaction than Eq. 5 may be occurring in this electrolyte, as will be shown later in Figure 5.

A trade-off exists between the ability of an electrolyte to passivate the Mg surface (decrease corrosion and H2 evolution) and allow Mg2+ dissolution through the passivating layer during discharge. The effect of the passivating layer was examined by inspecting the Nyquist plots at OCV for each electrolyte as shown in Figures 4a, 4b. Figure 4a shows the Nyquist plot for the Mg working electrode during OCV prior to discharges in the same electrolytes as in the previous figures. The ability of the electrolyte to form a passivating layer on the Mg surface is directly related to the resistance (intercept on the x-axis) from the Nyquist plot. In the Mg corrosion literature, the high frequency semicircle is ascribed to the charge transfer resistance at the Mg surface and the low frequency semicircle to the mass transfer resistance (diffusion of Mg2+) through the solid film (corrosion product) on the Mg.27,28 A weak passivating film existed on the Mg surface in NaCl, leading to facile Mg2+ dissolution at large current densities and simultaneously large Mg corrosion rates. In contrast, the pure HNa2PO4 and NaNO3 electrolyte exhibited clear evidence of a significant mass transfer resistance, consistent with the higher slopes for anodic Mg2+ dissolution observed in the apparent Tafel plots in Figure 3.29 The NaCl electrolyte displayed the smallest resistance (highest corrosion) and the NaNO3 electrolyte displayed the highest resistance (lowest corrosion).

Figure 4b shows the Nyquist plot for Mg in each electrolyte after 3 consecutive 20 min. discharges (3.2 mA/cm²). The resistance in the NaNO3 electrolyte did not change significantly after discharging, hence the passivating layer seems to be unaffected by discharge. Interestingly, in the HNa2PO4 electrolyte, the resistance increased significantly after discharge, indicating that a stronger passivating film is formed on Mg during discharge. Post-mortem XRD on electrodes indicate substantial Mg(OH)2 surface coverage occurs during corrosion in NaCl electrolytes (see supporting information Figure S6). Although no surface species were observed in the phosphate-based electrolytes using XRD, a thin, highly compact, undetectable surface layer likely formed given the large impedance rise.

Figures 3 and 4 indicate the importance of the role of the passivating film formed on the Mg surface in limiting OCV Mg corrosion and also in allowing Mg2+ dissolution during Mg oxidation (battery discharge).19,30 As mentioned previously, the NaNO3 electrolyte seems to inhibit Mg corrosion, while simultaneously allowing Mg2+ dissolution during battery discharge. Unfortunately, as indicated previously, the OCV and limited H2 evolution behavior suggest that another corrosion reaction may be occurring. In fact, the nitrate (NO3−) to nitrite (NO2−) reaction is known to occur at low overpotentials in aqueous electrolytes as shown in Equation 7.

\[ NO_3^- + H_2O + 2e^- \rightarrow NO_2^- + 2OH^- \quad (U^0 = 0.01(V vs. SHE)) \] [7]

In order to test the hypothesis that Eqn. 7 is the dominant cathodic corrosion reaction (instead of H2 evolution) on Mg in the NaNO3 electrolyte, a nitrite titration was performed on the electrolyte as shown in Figure 5. Figure 5 shows the results of the NO2− titration performed on the NaNO3 electrolyte as a function of time during Mg OCV and Mg dissolution (discharge). The Mg electrode rested at OCV for the first 60 minutes of the experiment, followed by a 3.2 mA/cm² Mg oxidation (discharge). Aliquots of the NaNO3 electrolyte were removed at 15 minute intervals and titrated to measure the concentration of NO2− that was formed. Figure 5 shows that the concentration of NO2− in the electrolyte increased with time during both OCV and Mg dissolution, indicating the nitrate to nitrite corrosion reaction (Equation 7) was indeed occurring over the course of the experiment. Interestingly, the rate of NO2− production (0.15 µmol cm² min⁻¹) in the electrolyte was almost twice as large as the rate of H2 evolution (0.08 µmol cm² min⁻¹) in the NaNO3 electrolyte from Table I. Hence, the dominant corrosion reaction in the NaNO3 electrolyte was NO3− to NO2− (Equation 7) instead of H2 evolution (Equation 5), although some H2 evolution still occurs. Nevertheless, the total corrosion rate of both reactions in NaNO3 is smaller compared to the overall corrosion rate in the HNa2PO4 and NaCl electrolytes, hence NaNO3 is still a relatively favorable electrolyte for Mg-O2 batteries. The Mg2+ faradaic efficiency drops from 93% to 77% when including nitrite corrosion reaction with the H2 corrosion reaction, which is still more efficient than the other salts studied.

To test Mg-O2 battery performance in NaCl and NaNO3 electrolytes, a 2-electrode battery cell with an O2 headspace was constructed and tested. Figure 6a shows the Mg-O2 battery cell voltage as a function of time during a 5 mA/cm² discharge in NaCl and NaNO3 electrolytes. The battery employed a Mg anode, a Whatman filter paper separator, a commercial MnO2 air cathode (Electric Fuel Ltd.), and a fixed volume of O2 headspace above the cathode. The OCV of the cell in NaCl and NaNO3 electrolytes was 1.65 V and 1.45 V, respectively, illustrating the lower overall battery cell voltage in the NaNO3 electrolyte compared to NaCl. Additionally, the voltage plateau during discharge was lower in the NaNO3 electrolyte compared to the NaCl electrolyte. However, the NaNO3 discharged to a capacity of ~10 mAh before failure compared to ~6 mAh for the NaCl electrolyte, presumably caused by the lower corrosion rate in NaNO3 compared to NaCl. In Figure 6b, the cumulative gas in the pure O2 headspace.
is plotted versus time for the same battery cells as in Figure 6a. At OCV, the quantity of gas in the headspace increased with time in the NaCl electrolyte ($\text{H}_2$ evolution from Mg corrosion) and decreased in the NaNO$_3$ electrolyte. During Mg discharge, the gas pressure in the headspace of the cell with the NaCl electrolyte continued to increase as more $\text{H}_2$ was evolved (Mg corrosion) than $\text{O}_2$ was consumed by the MnO$_2$ cathode. In contrast, during Mg discharge in a NaNO$_3$ electrolyte, the gas pressure in the headspace of the cell decreased with time as $\text{O}_2$ was consumed by the MnO$_2$ cathode. These results clearly indicate that choice of electrolyte salt in an aqueous Mg-O$_2$ battery can have a substantial effect on the discharge capacity of the cell.

Moreover, $\text{H}_2$ evolution clearly changes as the discharge proceeds due to the change in electrolyte pH and Mg surface film formation during cell operation.

In conclusion, the electrolyte salt choice in Mg-O$_2$ batteries significantly affects the electrochemistry and gas evolution/consumption during discharge and OCV. A novel electrochemical H-cell with mass spectroscopy and pressure rise capabilities was used to study the fundamental corrosion of Mg in various aqueous electrolytes. HNa$_2$PO$_4$ and NaNO$_3$ electrolytes reduced the $\text{H}_2$ evolution corrosion reaction relative to a saline electrolyte, with NaNO$_3$ maximizing Mg$^{2+}$ dissolution from the productive faradaic reaction appropriate for Mg-O$_2$ batteries at significant current densities. Unfortunately, the NaNO$_3$ electrolyte also displayed a lower OCV voltage and introduced a NO$_3^-$ to NO$_2^-$ corrosion reaction to the battery, as verified by NO$_2^-$ titrations. However, even when accounting for both the NO$_2^-$ and $\text{H}_2$ corrosion reactions, the NaNO$_3$ electrolytes still exhibit faradaic Mg$^{2+}$ efficiencies more than 20% higher than NaCl and HNa$_2$PO$_4$. The formation of passivating surface films formed on Mg play a crucial role in corrosion and in Mg$^{2+}$ dissolution during battery discharge and an ideal electrolyte for Mg-O$_2$ batteries would inhibit corrosion without inhibiting Mg$^{2+}$ dissolution. A potentially interesting direction of future research is the use of either mixed aqueous/noneaqueous or pyric/protic electrolytes, where it may be possible to more carefully optimize the tradeoff in corrosion inhibition and anodic Mg$^{2+}$ dissolution.

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