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A Mg/O₂ Battery Based on the MACC Electrolyte

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ABSTRACT: Mg/O₂ cells employing a MgCl₂/AlCl₃/DME (MACC/DME) electrolyte are cycled and compared to cells with modified Grignard electrolytes, showing that performance of magnesium/oxygen batteries depends strongly on electrolyte composition. Discharge capacity is far greater for MACC/DME-based cells, while rechargeability in these systems is severely limited. The Mg/O₂-MACC/DME discharge product comprises a mixture of Mg(ClO₄)₂ and MgCl₃, with the latter likely formed from slow decomposition of the former. The presence of Cl⁻ in these compounds suggests that the electrolyte participates in the cell reaction, or reacts readily with the initial electrochemical products. A rate study suggests that O₂ diffusion in the electrolyte limits discharge capacities at higher currents. Formation of an insulating product film on the positive electrodes of Mg/O₂-MACC/DME cells following deep discharge increases cell impedance substantially, and likely explains the poor rechargeability. An additional impedance rise consistent with film formation on the Mg negative electrode suggests the presence of detrimental O₂ crossover. Minimizing O₂ crossover and bypassing charge transfer through the discharge product would improve battery performance.

INTRODUCTION

Magnesium is an attractive negative-electrode material for battery applications due to its low cost, high energy density, and relative safety in comparison to alkali metals such as lithium.1–10 Furthermore, across the many possible ‘metal/air’ battery chemistries, the theoretical energy density provided by reacting Mg with O₂ is among the highest.11–12 These advantages prompted the study of primary Mg/air batteries using aqueous electrolytes as early as the 1970s.13–17 Despite decades of study since, several challenges remain.18 For example, aqueous electrolytes corrode Mg electrodes because Mg reacts with H₂O spontaneously to form passivating Mg(OH)₂ on the electrode surface.19 Thus Mg/air batteries usually exhibit high interfacial impedance, making practical energy density at most a tenth of what theory suggests.20 Also, the use of air as an O₂ source introduces pernicious impurities such as CO₂.

Relatively few studies have explored the possibility of a rechargeable Mg/O₂ cell based on a non-aqueous electrolyte and a pure O₂ gas source. Shiga et al. reported non-aqueous Mg/O₂ cells that operate at elevated temperatures.21–22 The electrolytes employed included simple Mg salts such as Mg(ClO₄)₂ and Mg(N(SO₂CF₂)₂): dissolved in organic solvents or ionic liquids. Due to their propensity for forming Mg²⁺-impermeable passivation layers, it remains a matter of debate whether these electrolytes are compatible with Mg metal.23 The present authors reported a room-temperature non-aqueous Mg/O₂ battery with an electrolyte based on a modified Grignard reagent.24 This electrolyte was previously shown to allow for efficient Mg deposition/dissolution, and exhibited high oxidative stability,25 but the reversible energy density exhibited by Mg/O₂ cells based on it was low.21–22

It is well-known that Grignard reagents react vigorously with water and are pyrophoric.26 Consequently, the development of less reactive electrolytes is an area of active research. One promising option is the all-inorganic magnesium aluminum chloride complex (MACC) reported by Doe et al.27 MACC is synthesized by reacting a simple Mg salt with a Lewis acid in a non-aqueous solvent such as dimethoxyethane (DME) or tetrahydrofuran (THF). Electrochemical conditioning of the initially synthesized solution activates the electrochemical species responsible for reversible Mg deposition.28–30 Conditioned MACC/DME allows Mg plating and stripping at room temperature with low deposition overpotentials (<300mV vs. Mg/Mg²⁺), high coulombic efficiency (>95%), and high oxidative stability (>3 V vs. Mg²⁺/Mg with a Pt working electrode). In addition, the conductivity of MACC is relatively high (~2 mS/cm)31 when compared to Grignard electrolytes (~0.3 mS/cm).32 Although the exceptional properties exhibited by MACC suggest its promise for use in metal-air batteries, to our knowledge no reports of Mg/O₂ cells based on MACC/DME exist.

A high-capacity Mg/O₂ battery based on MACC/DME is reported here. This room-temperature Mg/O₂ cell exhibits a capacity similar to those of elevated-temperature cells based on simple Mg-salt electrolytes,21–22 yet is much higher than that of the room-
temperature Mg/O\textsubscript{2} battery based on a modified Grignard electrolyte. The discharge product of the MACC/DME Mg/O\textsubscript{2} cell is found to be a mixture of Mg(ClO\textsubscript{4})\textsubscript{2} and MgCl\textsubscript{2}, which arises from slow decomposition of metastable Mg(ClO\textsubscript{4})\textsubscript{2} into MgCl\textsubscript{2}. The presence of Cl points to undesirable electrolyte consumption during discharge-product formation.

In agreement with earlier studies using different electrolytes,\textsuperscript{71-72} the rechargability of the Mg/O\textsubscript{2}-MACC/DME battery was found to be poor. This observation prompted additional characterization using electrochemical impedance spectroscopy (EIS) to identify factors that block reversal of the cell reaction. EIS shows that exposure to an O\textsubscript{2}-saturated electrolyte accelerates film formation on Mg metal, leading to an impedance increase. In a Mg/O\textsubscript{2} cell, such an effect would arise from O\textsubscript{2} crossover to the negative electrode from the positive. In addition, EIS reveals a film resistance on the positive electrode that rises in correlation with depth of discharge, suggesting that the growth of an electrically insulating discharge product impedes cell performance. Ironically, the vastly larger quantity of discharge product produced in cells using MACC/DME (and associated electrode passivation) could explain the limited recharge capacity in comparison to cells based on the modified Grignard electrolyte.

The effects of discharge rate on capacity and discharge voltage were examined from 0.02 to 1 mA cm\textsuperscript{-2} (superficial). The results suggest that slow diffusion of O\textsubscript{2} in the electrolyte also contributes to limitations in discharge capacity.

We conclude that efforts to improve the performance of non-aqueous Mg/O\textsubscript{2} cells should aim to (i.) minimize O\textsubscript{2} crossover, (ii.) bypass or improve charge transfer through the discharge product, and (iii.) identify cathode/electrolyte combinations that are highly permeable to O\textsubscript{2}.

**METHODS**

**Experimental.** Mg/O\textsubscript{2} cycling experiments were performed using cells designed for metal/O\textsubscript{2} testing, depicted in the Supporting Information (SI) Fig. S1. Cell fabrication and disassembly closely followed the procedures described earlier by Griffith et al.\textsuperscript{22} Mg/O\textsubscript{2} cells (EL-CELL Gmbh, Germany) were assembled by sandwiching a glass-fiber separator (0.5 mm thick, EL-CELL Gmbh, Germany) between a planar metallic-Mg negative electrode (99.9%, Goodfellow, USA) and a porous-carbon positive electrode (26mg, SIGRACET GDL 24 BC, Ion Power, Inc., USA). A stainless-steel plate with 1.5 mm diameter perforations (EL-CELL Gmbh, Germany) acted as a positive current collector, and was coated with evaporatively deposited Pt to impede corrosion during testing. The perforations in the plate allowed contact between the carbon and stagnant O\textsubscript{2} (99.993%, Cryogenic Gases, USA; 2 bar absolute). The separator and carbon were saturated with an electrolyte comprising MgCl\textsubscript{2} (99.99%, Sigma-Aldrich, USA) and AlCl\textsubscript{3} (99.999%, Sigma-Aldrich, USA) in DME (99.5%, anhydrous, Sigma-Aldrich, USA), referred to above as MACC/DME. The electrolyte was produced using the precursor materials and conditioned to achieve high performance (cf. Fig. S2, S3, S4) via batch electrolysis (i.e., holding at a negative potential 500 mV below the Mg deposition overpotential until cyclic voltammetry showed the coulombic efficiency for Mg plating/stripping to be > 96%). Discharge experiments were performed at room temperature using a series 4000 battery tester (Maccor, USA). To probe the discharge mechanism, the discharge product was characterized by scanning electron microscopy (SEM), energy dispersive x-ray spectroscopy (EDS), x-ray diffraction (XRD), Raman spectroscopy (RS), Auger electron spectroscopy (AES), and x-ray photoelectron spectroscopy (XPS). Additional details are provided in the SI.

**Computational.** Density functional theory calculations (VASP)\textsuperscript{35-35} were used to characterize the electronic structures of Mg(ClO\textsubscript{4})\textsubscript{2} and MgCl\textsubscript{2} and to estimate the enthalpy and free-energy changes associated with the decomposition reaction hypothesized to accompany discharge (described below). Blochl’s projector augmented wave (PAW) method\textsuperscript{36,37} was used to treat the core/valence electron interaction. The generalized gradient approximation (GGA) expressed with the formulation of Perdew Burke Ernzerhof (PBE)\textsuperscript{37} was used for the exchange-correlation energy. Additional calculations were preformed using van der Waals-aware functionals.\textsuperscript{38-40} The Brillouin zone was sampled with a Γ-centered k-point mesh with density 12 × 12 × 6 for Mg(ClO\textsubscript{4})\textsubscript{2} and 12 × 3 × 12 for MgCl\textsubscript{2}. Lattice constants were determined by relaxing the cell shape, volume, and atom positions. A plane-wave cutoff energy of 520 eV and a force tolerance of 0.04 eV Å\textsuperscript{-1} was used for all geometry optimizations. The ground state energy of the O\textsubscript{2} molecule was evaluated using spin-polarized calculations.

**RESULTS AND DISCUSSION**

**Electrochemical Testing.** Figure 1 shows representative discharge curves for the MACC/DME-based Mg/O\textsubscript{2} cell at six discharge rates ranging from 0.02 to 1 mA cm\textsuperscript{-2} (superficial). The open-circuit (OC) voltage prior to discharge (2.0 ± 0.1V) is similar to the voltage reported previously for other non-aqueous Mg/O\textsubscript{2} cells.\textsuperscript{21,24} In an earlier report the authors argued that an OC voltage of ~2.0 V results from the half-reaction associated with superoxide formation at the positive electrode, since O\textsubscript{2}− forms from O\textsubscript{2} at ~2V vs Mg/Mg\textsuperscript{2+}.\textsuperscript{24} Control experiments in which the cells were not exposed to O\textsubscript{2} showed negligible capacity (Fig. S5), suggesting that the presence of O\textsubscript{2} is necessary for discharge to occur.

![Figure 1](image1.png)
The cell based on MACC/DME exhibits a capacity of ~400 μAh cm\(^{-2}\) at a discharge rate of 0.05 mAc\(m^2\). (This corresponds to a specific capacity of ~38 mAh g\(^{-1}\).) In contrast, the electrochemical capacities reported previously for a similar Mg/O\(_2\) cell using the 4:1 (PhMgCl\(_2\))\(\cdot\)Al(OPh\(_3\))/THF modified Grignard electrolyte was much lower, ~13 μAh cm\(^{-2}\), at one-tenth the discharge rate (0.005 mA cm\(^{-2}\)).

The large difference in capacity between cells based on Grignard/THF and MACC/DME owes at least partially to the higher conductivity of the MACC solution and the higher solubility of O\(_2\) in DME. Indeed, O\(_2\) permeability (defined as the product of saturated O\(_2\) concentration and effective diffusivity) is thought to contribute to capacity limitations in Li/O\(_2\) batteries.\(^{32,41}\) The conductivity of the modified Grignard electrolyte examined previously was reported to be 1.24 mScm\(^{-1}\),\(^{31}\) whereas the conductivity of the conditioned MACC/DME was 2.21 mScm\(^{-1}\). The latter value agrees with the ~2 mScm\(^{-1}\) reported by Doe et al.\(^{27}\) Furthermore, the solubility of O\(_2\) in DME has been reported to be 5 times higher than in THF.\(^{32,41}\) Taken together, these data support the notion that differences in oxygen permeability between the electrolytes can be associated with the observed differences in capacity. Additional tuning of the electrolyte composition could raise the capacities observed for Mg/O\(_2\) systems. For example, varying the donor number of the solvent appears to have a significant effect on the capacity of nonaqueous Li/O\(_2\) cells.\(^{46}\)

Recharging at 0.02 mAc\(m^2\) yielded negligible recharge capacity before the cutoff voltage of 4V vs. Mg/Mg\(^{2+}\) was reached (cf. Fig. 1 inset). This response of the Mg/O\(_2\)-MACC/DME cells differs substantially from the behavior observed previously for Mg/O\(_2\)-Grignard/THF cells, which exhibited some rechargeability, albeit at low recharge rates (0.005 mAc\(m^2\))\(^{24}\). Possible explanations for this distinct behavior are discussed in conjunction with the EIS results below.

**Discharge-Product Characterization.** Figure 2 shows SEM images of positive (carbon) electrodes harvested from Mg/O\(_2\)-MACC/DME cells. Fig. 2a shows an electrode after first discharge, which is covered with discharge product only on the side closest to the O\(_2\) inlet. This product was absent from a control electrode (inset of Fig. 2b) held under oxygen at 0C (i.e., galvanostatically) for the same time period. Higher-magnification images in Fig. 2b reveal that the product comprises faceted particles. The much higher capacity of MgO\(_2\)-MACC/DME cells compared to MgO\(_2\)-Grignard cells is reflected by the much larger amount of discharge product visible on the electrode following discharge. Fig. S10 compares SEM images of carbon electrodes that were imaged after discharge using MACC/DME and the modified Grignard electrolyte. The electrode from the MACC/DME cell exhibits high surface coverage by the product, which extends beyond the boundaries of the perforations in the current collector (these perforations allow direct contact between C and O\(_2\)); in contrast, the electrode from the modified Grignard-based cell exhibits a single incomplete layer of product only on the portion of the carbon surface that was in contact with O\(_2\).

The discharge-product composition was characterized using x-ray diffraction (XRD), energy dispersive spectroscopy (EDS), Auger electron spectroscopy (AES), and x-ray photoelectron spectroscopy (XPS). Figure 3a shows XRD patterns collected from the positive electrode at the end of a discharge at 0.05 mAc\(m^2\), and for a control electrode held at OC for the same period. At the end of discharge, peaks associated with MgCl\(_2\) and Mg(ClO\(_4\))\(_2\) are clearly present in the diffraction pattern from the positive electrode.

Figure 3b presents EDS spectra collected from two different spots on the discharge-product layer. The EDS data qualitatively confirms that the discharge product is rich in Cl, and indicates some degree of spatial nonuniformity. RS, AES and XPS (Fig S11, S12) also confirm the spatial nonuniformity. RS shows that peaks for MgCl\(_2\) and Mg(ClO\(_4\))\(_2\) can be observed in different locations on parts of the electrode surface covered by discharge product. Similarly, Mg K\(_\alpha\), L\(_\alpha\), L\(_\beta\), AES spectra and Mg L\(_\alpha\) XPS spectra collected from different spots on the discharge product show that the bind-

![Figure 2](image-url)
cating that the decomposition of magnesium perchlorate into magnesium chloride should be spontaneous. Additional details regarding the DFT calculations can be found in the SI, Tables S1 and S2.

The discharge-product composition in Mg/O2-MACC/DME cells differs from the mixed MgO/MgO2 product previously observed in cells based on a modified Grignard electrolyte. Nevertheless, the formation of Cl–O complexes has been observed in aqueous Mg/air chemistries using NaCl electrolytes. Computational studies suggest that conditioned MACC/DME electrolyte contains chloromagnesium cations such as MgCl+ and MgCl2+. In principle, these species could react chemically with electrochemically formed O2 to produce Mg(ClO4). Such a reaction would be consistent with the observed discharge voltages shown in Fig 1. Both Mg(ClO4)2 and MgCl2 are expected to be insulators, so sluggish electron transport through them could limit rechargeability. Indeed, GGA-DFT calculations confirm that MgCl2 and Mg(ClO4)2 are both insulators with large bandgaps of 5.6 eV and 5.3 eV, respectively. (Since semi-local functionals such as the GGA tend to underestimate bandgaps, these calculations probably represent lower bounds to the true bandgaps. Fig. S13 shows the density of states for each compound.)

The presence of Cl in the discharge product indicates that electrolyte is consumed during or immediately after the electrochemical discharge reaction step. Most Mg-halogen compounds have Gibbs free energies of formation similar to, or more negative than, that of MgO (MgCl2: –592 kJmol−1, MgF2: –1071 kJmol−1, MgBr2: –504 kJmol−1, MgO2: –568 kJmol−1). Thus it is likely that Cl, F, or Br in the electrolyte could be incorporated into the discharge product of a Mg/O2 battery. For future studies, it is recommended that halogen-free electrolytes be explored.

Electrochemical Impedance Spectroscopy. The evolution of internal resistance was studied using EIS to explore the limited rechargeability of MACC/DME cells. Figure 4(a) shows Nyquist plots for a symmetric Mg/Mg cell with a 0.5 mm thick glass-fiber separator soaked with MACC/DME electrolyte and operated under Ar. The cell was kept at OC for a total of 3 hours, during which an impedance spectrum was gathered every 10 minutes to examine temporal changes in the resistance of the Mg/electrolyte interface. The first EIS measurement (corresponding to time = 0 min) was recorded less than 5 minutes after the cell was assembled.

Figure 3. (a) XRD patterns of a discharged cathode (black) and a control cathode (red). Unlabeled peaks correspond to the carbon positive electrode. (b) EDS spectra collected in spot mode from two locations on the discharge product.

DFT Calculations. Density functional theory calculations were performed to evaluate the energetics of Mg(ClO4)2 decomposition via Eq. 1. The calculated enthalpy and free energy of reaction are DH = –42.6 kJ/mol and DG = –285.7 kJ/mol, respectively, indi-
A Nyquist plot produced from the Mg/Mg cell under Ar shows a single depressed semi-circle. Depressed semicircles are often observed in battery impedance studies and are commonly attributed to electrode surface roughness. The radius of the semi-circle grows as a function of time, indicating an impedance increase arising from the formation of a partially passivating phase on the electrode surfaces. This behavior is similar to that observed for solid-electrolyte interphase (SEI) formation in Li-ion battery negative electrodes. After the 3h OC hold, 0.075 mAh cm\(^{-2}\) of charge (a 1.5 hour discharge at 0.05 mA cm\(^{-2}\)) was passed through the cell and another impedance spectrum was recorded (shown as the blue curve in Fig. 3a). The interfacial impedance decreased substantially after current was applied, suggesting electrochemically-driven dissolution of an SEI-like layer from the Mg electrode surfaces.

Contributions to the impedance associated with dissolved O\(_2\) in the electrolyte were probed using a symmetric Mg/Mg cell exposed to O\(_2\) rather than Ar, during the OC hold, for which Nyquist plots are shown in Fig. 4b. The black curve represents an impedance spectrum collected before O\(_2\) exposure, which is similar to the data in Fig. 4a. In contrast to the Ar-only cell, the impedance of the cell exposed to O\(_2\) is larger, and grows more rapidly. The subsequent passage of 0.075 mAh cm\(^{-2}\) at 0.05 mA cm\(^{-2}\) results in an impedance decrease, but the cell does not return to its state before O\(_2\) exposure.

To quantify the effects of O\(_2\) exposure, an equivalent-circuit model (ECM), illustrated on Fig. 4c, was used to fit the EIS data gathered from both the Ar- and O\(_2\)-exposed Mg/Mg cells. In the ECM, \(R_{\text{bulk}}, R_{\text{SEI}},\) and CPE\(_{\text{SEI}}\) represent the bulk resistance associated with the electrolyte, and the Mg electrode's interfacial resistance and equivalent capacitance, respectively. (A more complex ECM was also considered, which included uncompensated resistance and cell capacitance elements. This was found to increase the variances in the parameters without improving goodness-of-fit; additional details can be found in the SI.)

Figure 4c shows how \(R_{\text{SEI}}\) varies with respect to the square root of time for Mg/Mg-MACC/DME cells under Ar and O\(_2\). An increase in \(R_{\text{SEI}}\) is expected to correlate with the growth of an SEI-like film. Notably, \(R_{\text{SEI}}\) increases with time under both Ar and O\(_2\) atmospheres. Nevertheless, the cell exposed to O\(_2\) exhibits a more rapid rate of increase, and higher overall interfacial resistance, possibly due to oxidation of the Mg surface caused by the presence of O\(_2\). Interestingly, \(R_{\text{SEI}}\) increases approximately linearly with the square root of time in both cases, suggesting a diffusion-limited film-growth process (Figure S7).

The evolution of \(R_{\text{bulk}}\), which is associated with the resistance of the electrolyte, and given by the high-frequency intercept of the Nyquist curve with the real axis, was investigated to gain insight into the relative stability of MACC and Grignard electrolytes under O\(_2\). Comparison experiments, similar to those shown in Fig. 4b, were performed on a Mg/Mg cell using the modified Grignard electrolyte. As shown in Fig S8, the rate of increase and the absolute value of \(R_{\text{bulk}}\) were larger for the modified Grignard electrolyte than for MACC/DME. Lower \(R_{\text{bulk}}\) values for MACC/DME confirm the earlier mentioned higher conductivity of MACC/DME. Furthermore, the lower rate of increase for \(R_{\text{bulk}}\) suggests that MACC/DME is more stable with respect to O\(_2\) exposure than the Grignard electrolyte.

In addition to stability against chemical attack by O\(_2\), the possible presence of O\(_2\) ions formed during cell discharge creates a strong oxidizing environment, which might be expected to further decompose electrolytes. Stability in the specific presence of O\(_2\) and its electrochemical products appears to be just as important as electrochemical stability against oxidation by the positive electrode – or even more important. These effects are illustrated by the full Mg/O\(_2\) cell EIS data shown in Figure 5. During an initial OC hold under Ar, the Nyquist plot resembles that of the symmetric Mg/Mg cells (Fig. 4a): there is only one apparent depressed semicircle. Similar to the symmetric Mg/Mg cells, exposure to O\(_2\) results in an impedance increase. This could be attributed to SEI-like film formation on the Mg surface due to O\(_2\) crossover from the positive electrode. The ECM depicted in Figure 4c was sufficient to model the impedance behavior of the Mg/O\(_2\) cells up to this point (i.e., under OC conditions).

Upon discharge of the full Mg/O\(_2\) cell (Fig. 5, blue and light blue curves), a second depressed semicircle in the Nyquist plot appeared, presumably due to the formation of a new resistive interface in the cell. This likely owes to the formation of the discharge-product layer. Similar EIS data (showing a new semicircle after discharge) have been observed previously during discharge of Li/O\(_2\) cells.

An augmented ECM (Fig. 5, top) containing an additional circuit element (parallel CPE\(_{\text{prod}}, R_{\text{prod}}\)) was used to model EIS data during and after discharge. Here, CPE\(_{\text{prod}}\) and \(R_{\text{prod}}\) represent the equivalent capacitance and resistance associated with the discharge-product layer. This layer's characteristic frequency is 4.40 MHz, with equivalent capacitance on the order of 1 pF. Both of

![Figure 5](image-url)
In summary, EIS measurements on symmetric Mg/O\textsubscript{2} cells indicate that SEI-like film formation contributes to impedance at the Mg/electrolyte interface; moreover, the presence of O\textsubscript{2} accelerates the formation of these films. The EIS for full Mg/O\textsubscript{2} cells shows that growth of the discharge-product introduces a new and sizable interfacial resistance. The additional impedance contribution associated with the formation of a new interphase, arising from the low electrical conductivity of the discharge product and its high coverage on the electrode, likely explains the poor rechargeability of Mg/O\textsubscript{2} cells using MACC/DME.

**Rate Dependence.** In addition to energy density and rechargeability, rate capability is another important performance metric for batteries. The MACC/DME electrolyte allowed Mg/O\textsubscript{2} cells to be discharged at a wide range of current densities, ranging from 0.02 to 1 mA cm\textsuperscript{2}. These compare to rates at which Li/O\textsubscript{2} cells have been tested, offering the possibility for a direct comparison of Li and Mg chemistries.

Figure 6 shows discharge capacity and cell voltage at 50% depth-of-discharge as a function of discharge rate from 28 independently fabricated Mg/O\textsubscript{2} cells. The data shows (Fig. 6a) that discharge rate does not significantly affect capacity at rates below 0.01 mA cm\textsuperscript{2}. However, capacity decreases dramatically with increasing discharge rate at rates above 0.02 mA cm\textsuperscript{2}.

The higher-rate data were analyzed using Peukert’s law, which is an empirical relation linking discharge capacity, \( q_{\text{total}} \) and the discharge current density, \( i \):

\[
\ln \left( \frac{q_{\text{total}}}{q_{\text{ref}}} \right) = (1 - k) \ln \left( \frac{i}{i_{\text{ref}}} \right)
\]

Here \( k \) is the Peukert coefficient, \( i_{\text{ref}} \) is a reference current density (in this case, 1 mA cm\textsuperscript{2}), and \( q_{\text{ref}} \) is the capacity at \( i_{\text{ref}} \). The Peukert exponent, \( k \), describes the ability of a battery to retain its capacity with increasing rate, and can be compared across different battery chemistries. An ideal battery would have \( k = 1 \), meaning that the cell capacity is unchanged as a function of discharge rate. (For reference, \( k \) values for Li-ion batteries fall within the range of 1.6 \pm 0.1\textsuperscript{,} while those of Pb/acid cells are nearer 1.4\textsuperscript{.)} Since drawing a current is associated with energy dissipation, \( k > 1 \). The capacities observed above 0.02 mA cm\textsuperscript{2} for Mg/O\textsubscript{2} cells using MACC/DME follow a power-law dependence on the discharge current. The calculated Peukert exponent is 1.9, with a reference capacity of 91 \( \mu \text{Ah cm}^{-2} \) at 1 mA cm\textsuperscript{2}. This \( k \) value agrees well with the assumption that battery performance is limited by liquid-phase \( \text{O}_2 \) diffusion, which manifests as a Peukert exponent of 2. Compared to the Li/O\textsubscript{2}: chemistry, for which \( k = 1.6 \textsuperscript{,} while Mg/O\textsubscript{2} cells appear to exhibit lower rate capability. The transition from \( k = 1.6 \) (below 0.01 mA cm\textsuperscript{2}) to \( k > 1 \) (above 0.02 mA cm\textsuperscript{2}) is commonly observed for metal/O\textsubscript{2} batteries\textsuperscript{.}

Figure 6(b) shows the cell potential at 50% depth-of-discharge as a function of discharge rate. Following an analysis similar to that of Viswanathan et al.\textsuperscript{,} the present data reveals a Tafel slope of 4.9 V\textsuperscript{−1} and an exchange-current density of 1.6 \( \mu \text{A cm}^{-2} \) (superficial). Compared to Li/O\textsubscript{2} cells operated at the same rates (Tafel slope 11 \pm 1 V\textsuperscript{−1} and exchange current density 7 \pm 3 \( \mu \text{A cm}^{-2} \)), the present Mg/O\textsubscript{2} cells have a lower exchange-current density, suggesting that kinetic overpotentials are higher.

**CONCLUSION**
A non-aqueous Mg/O₂ cell based on the MACC/DME electrolyte was demonstrated and found to exhibit high discharge capacity but poor rechargeability. The discharge product was characterized using several techniques, and was determined to be a mixture of crystalline Mg(ClO₄)₂ and MgCl₂. This combination is consistent with a discharge reaction that proceeds via initial reduction of O₂ to O₂⁻, followed by chemical formation of Mg(ClO₄)₂, and its (slow) partial decomposition into MgCl₂ and O₂. The presence of Cl in the discharge product suggests that the electrolyte participates in the discharge reaction. The MACC/DME cell yielded significantly higher capacity than a similar cell based on a modified Grignard/THF electrolyte. This behavior is consistent with the larger quantity of discharge product visible on the surface of the MACC/DME positive electrode, which appears to cover most of the electrode surface, and with the higher oxygen solubility and conductivity of the MACC/DME system.

The low recharge capacity of the MACC/DME system motivated an impedance study on Mg/Mg symmetric cells and on full Mg/O₂ cells as a function of O₂ exposure and applied current. EIS measurements showed that the formation of an SEI-like film on Mg electrodes is accelerated by O₂ exposure. The application of current reduces the cell impedance, possibly by driving removal of the SEI-like layer. In full Mg/O₂ cells the formation of the discharge product layer apparently contributes substantially to cell impedance, and coincides with the appearance of a new semicircle in EIS measurements. This behavior reflects the insulating nature of the Mg(ClO₄)₂/MgCl₂ discharge product and the relatively large amount of product formed in the MACC/DME system. In contrast, a much smaller amount of discharge product was generated in a prior study using a modified Grignard electrolyte. These differences could explain the low rechargeability of the MACC/DME cells in comparison to the Grignard-based systems. Redox mediators and cell designs that minimize O₂ crossover could be employed to promote rechargeability while maintaining large discharge capacities.

Finally, Mg/O₂ cells were discharged over a wide range of rates. The calculated Peukert exponent of 1.9 points to an O₂-diffusion-limited discharge regime at rates higher than 0.02 mA cm⁻². Compared to Li/O₂ cells, for which k = 1.6, the Mg/O₂ cells examined here appear to exhibit lower rate capability.

ASSOCIATED CONTENT
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The authors declare no competing financial interest.

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