

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 MgCl₂, 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 tempera-

tures.²¹⁻²² The electrolytes employed included simple Mg salts such as Mg(ClO₄)₂ and Mg(N(SO₂CF₃)₂)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.^{7, 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, 24}

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 ($<300\text{ mV}$ vs. $\text{Mg}/\text{Mg}^{2+/0}$), high coulombic efficiency ($>95\%$), and high oxidative stability ($>3\text{ V}$ vs. $\text{Mg}^{2+/0}$ with a Pt working electrode). In addition, the conductivity of MACC is relatively high ($\sim 2\text{ mS/cm}$)²⁷ when compared to Grignard electrolytes ($\sim 0.3\text{ mS/cm}$).³¹ Although the exceptional properties exhibited by MACC suggest its promise for use in metal-air batteries, to our knowledge no reports of Mg/O_2 cells based on MACC/DME exist.

A high-capacity Mg/O_2 battery based on MACC/DME is reported here. This room-temperature Mg/O_2 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_2 battery based on a modified Grignard electrolyte.²⁴ The discharge product of the MACC/DME Mg/O_2 cell is found to be a mixture of $\text{Mg}(\text{ClO}_4)_2$ and MgCl_2 , which arises from slow decomposition of metastable $\text{Mg}(\text{ClO}_4)_2$ into MgCl_2 . The presence of Cl points to undesirable electrolyte consumption during discharge-product formation.

In agreement with earlier studies using different electrolytes,²¹⁻²² the rechargeability of the Mg/O_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_2 -saturated electrolyte accelerates film formation on Mg metal, leading to an impedance increase. In a Mg/O_2 cell, such an effect would arise from O_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 mAcm^{-2} (superficial). The results suggest that slow diffusion of O_2 in the electrolyte also contributes to limitations in discharge capacity at discharge currents above 0.1 mAcm^{-2} .

We conclude that efforts to improve the performance of non-aqueous Mg/O_2 cells should aim to (i.) minimize O_2 crossover, (ii.) bypass or improve charge transfer through the discharge product, and (iii.) identify cathode/electrolyte combinations that are highly permeable to O_2 .

METHODS

Experimental. Mg/O_2 cycling experiments were performed using cells designed for metal/ O_2 testing, depicted in the Supporting Information (SI) Fig. S1. Cell fabrication and disassembly closely followed the procedures described earlier by Griffith *et al.*³² Mg/O_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 (26 mg , 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_2 (99.993% , Cryogenic Gases, USA; 2 bar absolute). The separator and carbon were saturated with an electrolyte comprising MgCl_2 (99.99% , Sigma-Aldrich, USA) and AlCl_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 code)³³⁻³⁵ were used to characterize the electronic structures of $\text{Mg}(\text{ClO}_4)_2$ and MgCl_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) method³⁶ was used to treat the core/valence electron interaction. The generalized gradient approximation (GGA) expressed with the formulation of Perdew-Burke-Ernzerhof (PBE)³⁷ was used for the exchange-

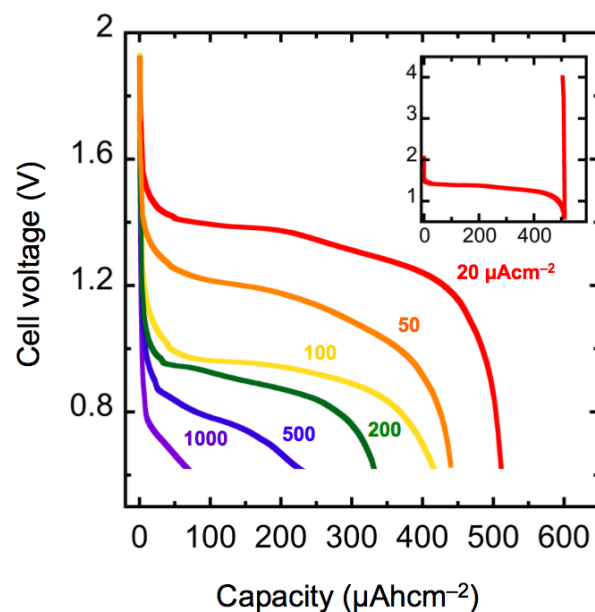


Figure 1. Cell voltage vs. capacity for Mg/O_2 cells at current densities ranging from 0.02 to 1 mA cm^{-2} (superficial). The inset shows a typical discharge/charge cycle at

correlation energy. Additional calculations were performed using van der Waals-aware functionals.³⁸⁻⁴⁰ The Brillouin zone was sampled with a Γ -centered k -point mesh with density $12 \times 12 \times 6$ for $\text{Mg}(\text{ClO}_4)_2$ and $12 \times 3 \times 12$ for MgCl_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 was used for all geometry optimizations. The ground state energy of the O_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_2 cell at six discharge rates ranging from 0.02 to 1 mA cm⁻² (superficial). The open-circuit (OC) voltage prior to discharge (2.0 ± 0.1 V) is similar to the voltage reported previously for other non-aqueous Mg/O_2 cells.^{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_2^- forms from O_2 at ~ 2 V vs Mg/Mg^{2+} .²⁴ Control experiments in which the cells were not exposed to O_2 showed negligible capacity (Fig. S5), suggesting that the presence of O_2 is necessary for discharge to occur.

The cell based on MACC/DME exhibits a capacity of ~ 400 $\mu\text{Ah cm}^{-2}$ at a discharge rate of 50 $\mu\text{A cm}^{-2}$. (This corresponds to a specific capacity of ~ 38 $\text{mAh g}_{\text{cathode}}^{-1}$.) In contrast, the electrochemical capacities reported previously for a similar Mg/O_2 cell using the 4:1 (PhMgCl)₄- $\text{Al}(\text{OPh})_3/\text{THF}$ modified Grignard electrolyte was much lower, ~ 13 $\mu\text{Ah cm}^{-2}$, at one-tenth the discharge rate (5 $\mu\text{A cm}^{-2}$).²⁴

The large difference in capacities 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 mS cm^{-1} ,²⁵ whereas the conductivity of the conditioned MACC/DME was 2.21 mS cm^{-1} . The latter value agrees with the ~ 2 mS cm^{-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.⁴²⁻⁴³ Taken together, these data support the notion that differences in oxygen permeability between the electrolytes can be associated with the observed differences in capacity at higher operating rates. 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 non-aqueous Li/O_2 cells.⁴⁴

Recharging at 0.02 mA cm^{-2} yielded negligible recharge capacity before the cutoff voltage of 4 V 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 (5 $\mu\text{A cm}^{-2}$).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 OC (*i.e.*, galvanostatically at 0 A) 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 .

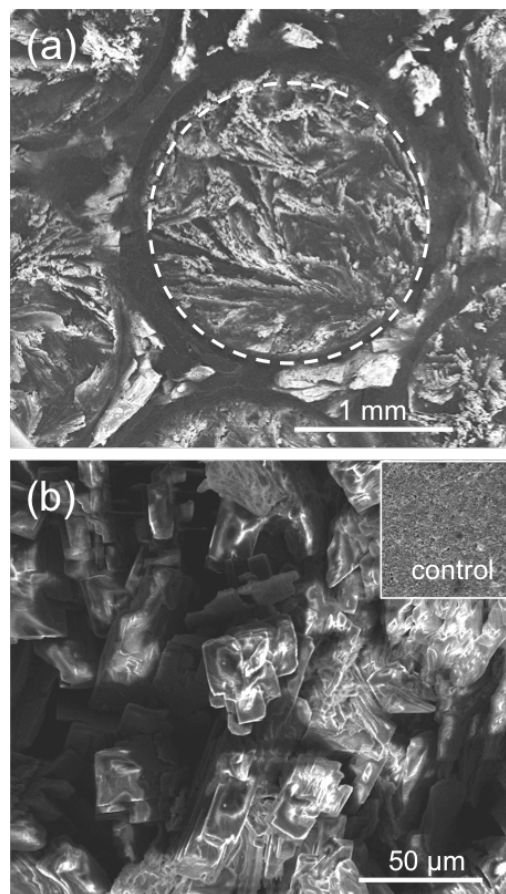
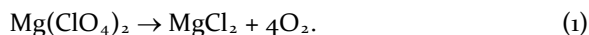


Figure 2. (a) SEM image of the positive-electrode surface on the side closest to the O_2 gas inlet after first discharge (0.05 mA cm^{-2}). The dashed circle represents the boundary of the region that was directly exposed to O_2 through perforations in the Pt-coated current collector. (b) Higher magnification of the electrode after first discharge, with an inset image of a control electrode exposed to O_2 in a similar cell held at open circuit for the same period

The discharge-product composition was characterized using XRD, EDS, AES, and XPS. Figure 3a shows XRD patterns collected from the positive electrode at the end of a discharge at $50 \mu\text{Acm}^{-2}$, and for a control electrode held at OC for the same period. At the end of discharge, peaks associated with MgCl_2 and $\text{Mg}(\text{ClO}_4)_2$ 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 $\text{Mg}(\text{ClO}_4)_2$ can be observed in different locations on parts of the electrode surface covered by discharge product. Similarly, $\text{Mg } KL_{2,3}L_{2,3}$ AES spectra and $\text{Mg } 2p$ XPS spectra collected from different spots on the discharge product show that the binding energies vary with respect to location. Taken together, these data suggest that the discharge product comprises a mixture of $\text{Mg}(\text{ClO}_4)_2$ and MgCl_2 . Anhydrous $\text{Mg}(\text{ClO}_4)_2$ is believed to decompose spontaneously into MgCl_2 and O_2 at room temperature via the reaction:⁴⁵



Thus the nonuniform product observed could be explained by electrochemical $\text{Mg}(\text{ClO}_4)_2$ formation, which is followed by gradual chemical decomposition into

MgCl_2 and O_2 .

DFT Calculations. Density functional theory calculations were performed to evaluate the energetics of $\text{Mg}(\text{ClO}_4)_2$ decomposition via Eq. 1. The calculated enthalpy and free energy of reaction are $\Delta H_r = -42.6 \text{ kJ/mol}$ and $\Delta G_r = -285.7 \text{ kJ/mol}$, respectively, indicating 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/O_2 -MACC/DME cells differs from the mixed MgO/MgO_2 product previously observed in cells based on a modified Grignard electrolyte.²⁴ Nevertheless, the formation of Cl-O complexes has been observed in aqueous Mg/air chemistries using NaCl electrolytes.⁴⁶ Computational studies suggest that conditioned MACC/DME electrolyte contains chloromagnesium cations such as MgCl^+ and Mg_2Cl_3^+ .⁴⁷ In principle, these species could react chemically with electrochemically formed O_2^- to produce $\text{Mg}(\text{ClO}_4)_2$. Such a reaction would be consistent with the observed discharge voltages shown in Fig 1. Both $\text{Mg}(\text{ClO}_4)_2$ and MgCl_2 are expected to be insulators, so sluggish electron transport through them could limit rechargeability.⁴⁸⁻⁴⁹ Indeed, GGA-DFT calculations confirm that MgCl_2 and $\text{Mg}(\text{ClO}_4)_2$ 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.⁵⁰ Most Mg-halogen compounds have Gibbs free energies of formation similar to, or more negative than, that of MgO (MgCl_2 : -592 kJmol^{-1} , MgF_2 : -1071 kJmol^{-1} , MgBr_2 : -504 kJmol^{-1} , MgO : -568 kJmol^{-1}).⁵¹ Thus it is likely that Cl, F, or Br in the electrolyte could be incorporated into the discharge product of a Mg/O_2 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.

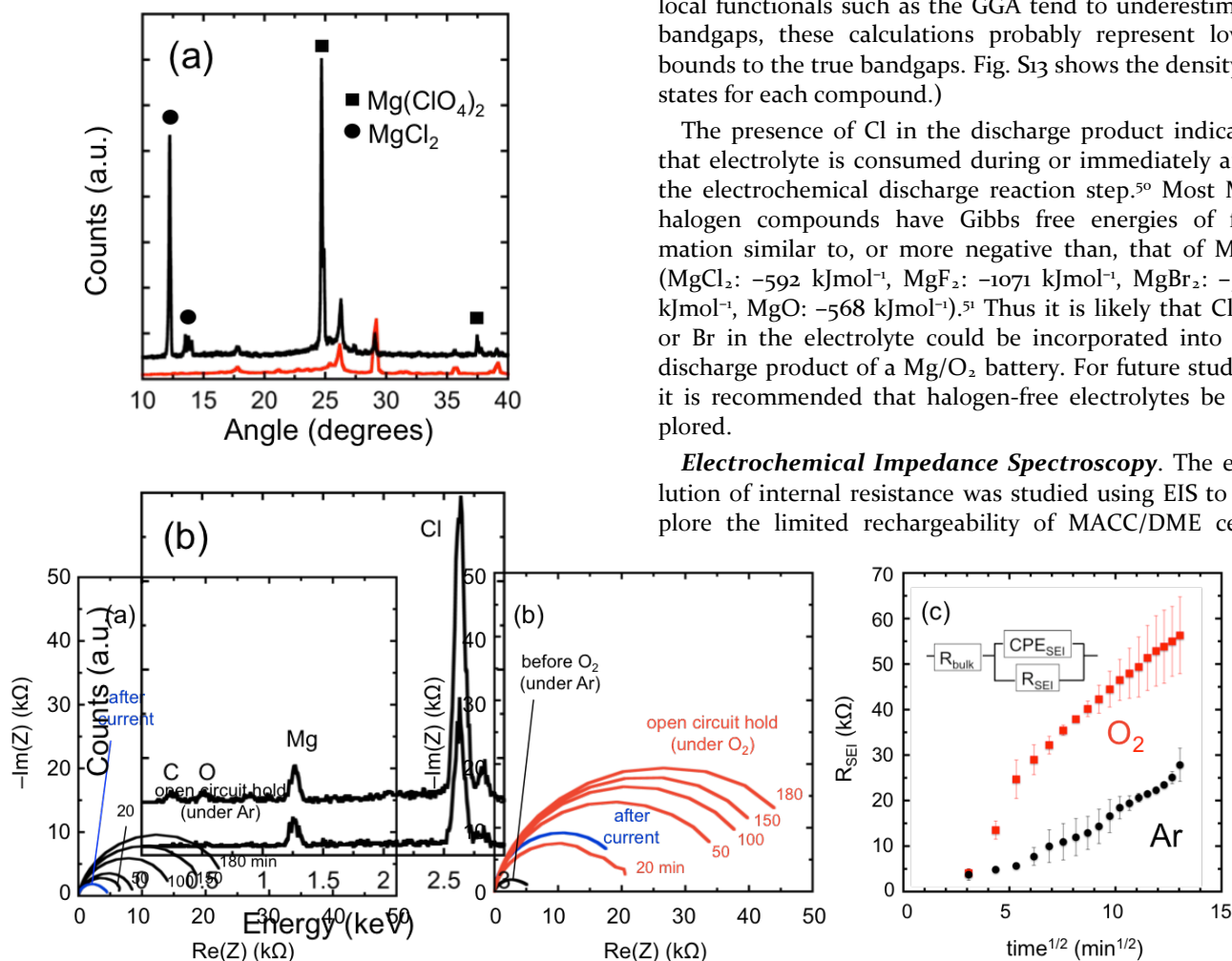


Figure 4. (a) XRD patterns for a Mg/Mg cell discharged in MACC/DME electrolyte under Ar at various times during an OC hold (black) and after passing current (blue). (b) Nyquist plots for a Mg/Mg cell using MACC/DME before O_2 exposure (black) and under O_2 during various times after O_2 exposure (red), and after passing current (blue). (c) Equivalent circuit model fit for R_{SEI} during OC holds for Mg/Mg cells under Ar (black circles) and under O_2 (red squares).

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.

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.⁵² 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 O₂ in the electrolyte were probed using a symmetric Mg/Mg cell exposed to O₂, 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 O₂ exposure, which is similar to the data in Fig. 4a. In contrast to the Ar-only cell, the impedance of the cell exposed to O₂ 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 O₂ exposure.

To quantify the effects of O₂ exposure, an equivalent-circuit model (ECM), illustrated on Fig. 4c, was used to fit the EIS data gathered from both the Ar- and O₂-exposed Mg/Mg cells. In the ECM, R_{bulk} , R_{SEI} , and CPE_{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_{SEI} varies with respect to the square root of time for Mg/Mg-MACC/DME cells under Ar and O₂. An increase in R_{SEI} is expected to correlate with the growth of an SEI-like film. Notably, R_{SEI} increases with time under both Ar and O₂ atmospheres. Nevertheless, the cell exposed to O₂ 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 O₂. Interestingly, R_{SEI} increases approximately linearly with the square root of time in both cases, sug-

gesting a diffusion-limited film-growth process (Figure S7).

The evolution of R_{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 O₂. Comparison experiments, similar to those shown in Fig. 4b, were performed on a Mg/Mg cell using the modified Grignard electrolyte.²⁴⁻²⁵ As shown in Fig. S8, the rate of increase and the absolute value of R_{bulk} were both larger for the modified Grignard electrolyte than for MACC/DME. Lower R_{bulk} values for MACC/DME confirm the earlier mentioned higher conductivity of MACC/DME. Furthermore, the lower rate of increase for R_{bulk} suggests that MACC/DME is more stable with respect to O₂ exposure than the Grignard electrolyte.

In addition to stability against chemical attack by O₂, the possible presence of O₂⁻ ions formed during cell discharge creates a strong oxidizing environment, which might be expected to further decompose electrolytes.⁵³⁻⁵⁵ Stability in the specific presence of O₂ 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/O₂ 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 O₂ results in an impedance increase. This could be attributed to SEI-like film formation on the Mg surface due to O₂ crossover from the positive electrode. The ECM depicted in Figure 4c was sufficient to model the impedance behavior of the Mg/O₂ cells up to this point (i.e., under OC conditions).

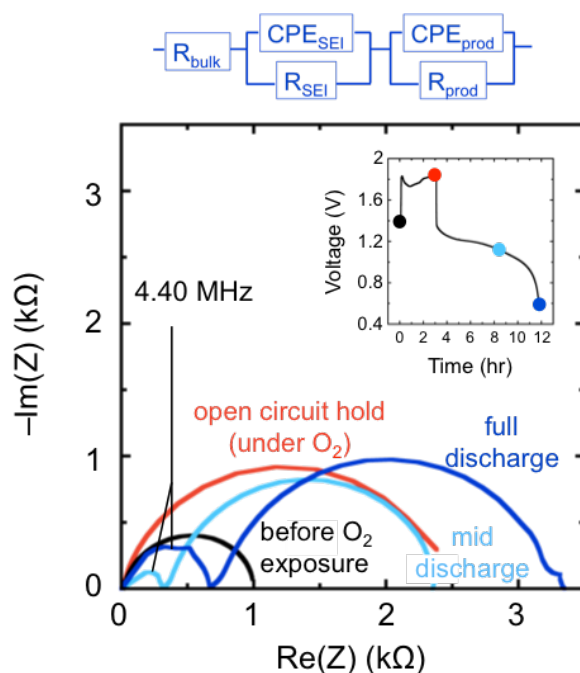


Figure 5. Electrochemical impedance spectra for a Mg/O₂ cell using MACC/DME electrolyte before O₂ exposure (black), after OC hold under O₂ (red), mid-discharge (light blue), and after discharge (blue). The inset indicates the stage of (pre-)discharge at which the EIS data was measured. The ECM used to model the

Upon discharge of the full Mg/O₂ 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/O₂ cells.⁵⁶

An augmented ECM (Fig. 5, top) containing an additional circuit element (parallel CPE_{prod}, R_{prod}) was used to model EIS data during and after discharge. Here, CPE_{prod} and R_{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 these features point to the presence of a solid/liquid interphase.⁵⁷ Figure 5 also highlights that the size of the new semicircle (which scales as R_{prod}) correlates with the depth of dis-

charge. In contrast, the EIS data from Mg/O₂ cells using the modified Grignard electrolyte *do not* show the formation of a new semicircle upon discharge (see Fig. S9). The absence of this feature – which was previously ascribed to the formation of a resistive discharge product – provides insight regarding the greater rechargeability noted for the Grignard electrolyte. In that system a mixed discharge product comprising MgO and MgO₂ was observed.²⁴ Both of these compounds were predicted to be insulators, similar to the MgCl₂ and Mg(ClO₄)₂ products found in the discharged MACC/DME cell.⁵⁸ Nevertheless, the discharge product in the Grignard-based cell covered only a fraction of the electrode surface. This behavior differs from the much higher coverages shown in Fig. 2. Hence, the larger quantity of (insulating) discharge product present in the MACC/DME cell likely contributes to a higher product-film resistance, leading to limited rechargeability relative to the Grignard-based cell.

In summary, EIS measurements on symmetric Mg/Mg cells indicate that SEI-like film formation contributes to impedance at the Mg/electrolyte interface; moreover, the presence of O₂ accelerates the formation of these films. The EIS for full Mg/O₂ 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/O₂ 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/O₂ cells to be discharged at a wide range of current densities, ranging from 0.02 to 1 mA cm⁻². These compare to rates at which Li/O₂ 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 functions of the discharge rate from 28 independently fabricated Mg/O₂ cells. The data shows (Fig. 6a) that discharge rate does not significantly affect capacity at rates below 0.01 mA cm⁻². However, capacity decreases dramatically with increasing discharge rate at rates above 0.02 mA cm⁻². These characteristic features of the capacity vs. rate curve are consistent with the model of Li/O₂ discharge presented by Liu and Monroe, which predicts that the capacity at higher rates falls as a power law with respect to discharge current.⁴¹

The higher-rate data were analyzed using Peukert's law, which is an empirical relation linking discharge capacity, q_{total} , and the discharge current density, i :⁵⁹

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

Here k is the Peukert coefficient, i_{ref} is a reference current density (in this case, 1 mA cm⁻²), and q_{ref} is the capacity at i_{ref} . The Peukert exponent, k , describes the ability of a battery to retain its capacity with increasing rate, and can

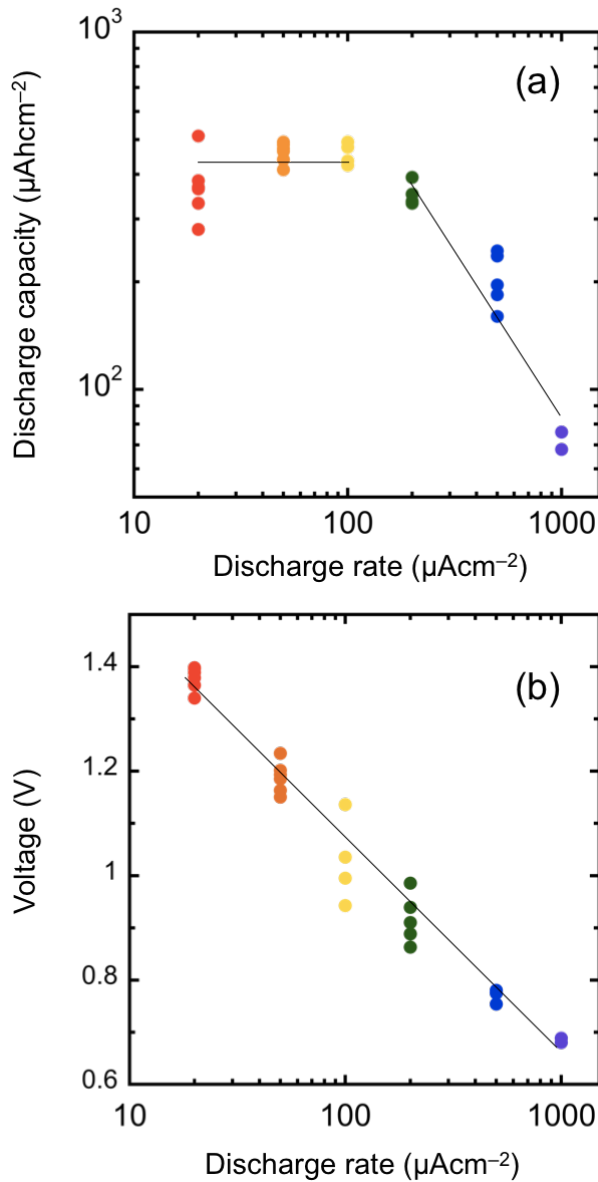


Figure 6. (a) Capacity per geometric electrode achieved at the 0.6V cutoff potential as a function of discharge rate. Capacity falls as a power law with respect to discharge rate at rates higher than 0.02 mA h cm⁻². (b) Cell voltage at 50% depth-of-discharge as a function of discharge rate.

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 ± 0.1 ,³² whereas those of Pb/acid cells are nearer 1.4.⁶⁰) Since drawing a current is associated with energy dissipation, $k > 1$. The capacities observed above 0.02 mA cm^{-2} for Mg/O₂ 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^{-2} . This k value agrees well with the assumption that battery performance is limited by liquid-phase O₂ diffusion, which manifests as a Peukert exponent of 2.⁴¹ Compared to the Li/O₂ chemistry, for which $k = 1.6$,³² Mg/O₂ cells appear to exhibit lower rate capability. The transition from $k = \sim 1$ (below 0.01 mA cm^{-2}) to $k > 1$ (above 0.02 mA cm^{-2}) is commonly observed for metal/O₂ batteries; Liu and Monroe's model suggests that this transition occurs when the discharge current drives product formation sufficiently fast that O₂ is unable to diffuse all the way across the positive electrode.^{41, 61}

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.*,⁶² the present data reveals a Tafel slope of 4.9 V^{-1} and an exchange-current density of $1.6 \mu\text{A cm}^{-2}$ (superficial). Compared to Li/O₂ cells operated at the same rates (Tafel slope $11 \pm 1 \text{ V}^{-1}$ and exchange current density $7 \pm 3 \mu\text{A cm}^{-2}$), the present Mg/O₂ 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.²⁴ 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

Cell assembly, electrolyte and cell testing, additional characterization details, density functional theory details. Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemmater.xxxxxxx

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Notes

The authors declare no competing financial interest.

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