Understanding Catalytic Mechanisms and Cathode Interface Kinetics in Non-Aqueous Mg-CO$_2$ Batteries

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Abstract: We leverage first-principles density functional theory (DFT) calculations to understand the electrocatalytic processes in Mg-CO$_2$ batteries, considering ruthenium oxide (RuO$_2$) as an archetypical cathode catalyst. Our goal is to establish a mechanistic framework for understanding the charging and discharging reaction pathways and their influence on overpotentials. Interestingly, we discover that Mg adsorption energies are enhanced, leading to the activation of CO$_2$. On the RuO$_2$ (211) surface, we predict that MgC$_2$O$_4$ will form as the discharge product due to its lower overpotential compared to MgCO$_3$. However, MgC$_2$O$_4$ is thermodynamically unstable and expected to decompose into MgCO$_3$, MgO, and carbon (C) as final discharge products. Through Bader charge analysis, we investigate the covalent interactions between intermediates and catalyst sites. We find that CO$_2$ is inactivated due to negligible electron transfer, making the formation of carbonate (CO$_3^{2-}$) and oxalate (C$_2$O$_4^{2-}$) intermediates thermodynamically unfavorable. Moreover, we study the electrochemical free energy profiles of the most favorable reaction pathways and determine discharge and charge overpotentials of 1.30 V and 1.35 V, respectively. Our results underscore the importance of catalyst design for the cathode material to overcome performance limitations in non-aqueous Mg-CO$_2$ batteries.
INTRODUCTION

The growing concern over global warming and its detrimental effects on the environment has intensified the search for sustainable solutions to address the issue of CO$_2$ emissions. $^{1-3}$ The primary contributor to global warming is the burning of fossil fuels, which releases significant amounts of CO$_2$ into the atmosphere. $^{4-8}$ To secure a sustainable future for generations to come and protect the environment, modern society has a crucial responsibility to restore the natural balance. This entails closing the anthropogenic carbon cycle and establishing a sustainable energy flow. To mitigate the impact of CO$_2$ emissions, one approach is the electrification of the transportation sector, aiming to reduce reliance on fossil fuel-powered vehicles. The metal-CO$_2$ batteries offer a promising avenue for the valorization of CO$_2$ through producing green electricity. $^{9-12}$

Li-CO$_2$ batteries have garnered interest as a potential source of high energy density for electrochemical energy storage systems (ESSs), utilizing the power of CO$_2$. $^{13-16}$ However, the limited availability and geographically localized distribution of lithium, along with its high cost, present significant challenges that hinder the widespread adoption of Li-CO$_2$ batteries. $^{17,18}$ Furthermore, the high reactivity of alkali metals, combined with their propensity for dendrite formation during cycling, gives rise to notable safety concerns, diminishes battery cycle life, and imposes practical limitations on their utility. $^{19-21}$ Considering its high volumetric energy density, excellent safety profile, environmental friendliness, and cost-effectiveness, the rechargeable Mg-CO$_2$ battery is regarded as a promising solution for efficient energy storage and effective CO$_2$ utilization. $^{21,22}$

The non-aqueous Mg-CO$_2$ battery demonstrates an encouraging prospective, distinguished by its ability to store energy and recycle CO$_2$. $^{19,22,23}$ However, the development of Mg-CO$_2$ batteries is currently facing significant obstacles, such as limited rate capability, reduced energy efficiency, and shortened cycle life. In addition, despite the conducive factors, there is limited study on Mg-CO$_2$ batteries employing nonaqueous electrolytes or functioning without any assistance from H$_2$O. $^{19}$ Thus far, there are only two published works on Mg-CO$_2$ batteries that require the assistance of water to decrease the elevated voltage hysteresis. $^{22,23}$ A nonaqueous rechargeable Mg-CO$_2$ battery with a Mo$_2$C-CNT cathode reveals the role of catalysts in stabilizing Mg$_2$CO$_3$O$_4$ during the initial discharge stages. However, the presence of electronically insulating MgCO$_3$, MgO, and C as discharge products at later stages hinders catalytic activity, resulting in increased charge overpotential, rapid capacity fade, and limited cyclic performance. $^{19}$ Moisture-assisted nonaqueous Mg-CO$_2$ batteries with CNT cathodes have shown only 50 cycles of operation due to the accumulation of MgCO$_3$ and C, which negatively impacts discharge/charge reversibility and lead to premature battery failure. $^{19}$ Upon thorough examination, it has been determined that the primary obstacles in achieving exceptional non-aqueous Mg-CO$_2$ batteries pertain to four key factors. These include (i) the slow reaction kinetics of CO$_2$RR, (ii) poor reversibility across charging and discharging cycles, (iii) the insulating nature of the final discharge products (MgCO$_3$, MgO, or MgC$_2$O$_4$), which results in an elevated charge overpotential, and (iv) the substantial oxidative decomposition barrier of the final discharge products resulting in their aggregation on the electrode surface, which impacts electrochemical activity and increases interfacial resistance. $^{19}$ Despite extensive research in developing cathode catalysts for alkali metal-CO$_2$ batteries, they cannot be directly applied in Mg-CO$_2$ batteries due to distinct reaction mechanisms between bivalent Mg and CO$_2$, as well as slower redox kinetics in organic electrolytes. Therefore, a major research focus for the realization of Mg-CO$_2$ batteries involves the strategic development of bi-functional cathode catalysts.

There have been several advances in the cathode materials to reduce charge-discharge overpotential and improve round-trip energy efficiency of alkali metal-CO$_2$ batteries since the commencement of metal-CO$_2$ battery research over a decade ago. $^{16,18,20,22}$ Carbonaceous materials, including ketjen black (KB), are widely employed as cathode matrices in metal-CO$_2$ batteries due to their favorable attributes such as high electrical conductivity, chemical stability, and adjustable surface area. $^{24-26}$ However, the catalytic performance of nonpolar carbon materials is limited. To address this, recent research has focused on
developing heteroatom-doped and nanostructured carbon materials. The addition of doped pyridinic nitrogen atoms increases energy storage capacity by facilitating the passage of CO$_2$ and Li into the active sites and catalyzing the CO$_2$ reduction reactions (CO$_2$RR) and CO$_2$ evolution reactions (CO$_2$ER) processes. Again, all-solid-state Na-CO$_2$ batteries developed with the improved N-doped nanocarbon showed a discharge capacity (10,500 mA h g$^{-1}$), lower overpotential, longer cycling, and an increased energy density. Despite the large surface area and high electronic conductivity of carbonaceous materials, their low CO$_2$ electrocatalytic activity impedes their effectiveness as cathode catalysts. Consequently, the exploration of transition metal (TM)-based cathodes has emerged as a promising avenue to achieve high-performance metal-CO$_2$ batteries.

Transition metals possess desirable properties, such as incompletely filled d-orbitals, multiple oxidation states, chemical stability, and polyvalence, which endow them with the necessary electrocatalytic activity for cathode interfacial chemistries in metal-CO$_2$ batteries.$^{10,16,27}$ Various TM-based catalysts, including precious metals (Ru nanoparticles on graphene, Ag-graphene),$^{10,16}$ metal carbidexides (N-doped CNT network with IrO$_2$, Ni nanoparticles on N-doped graphene, Cu-doped N-graphene, and Mo$_2$C nanoparticles on CNT matrix, NiO on CNT, TiO$_2$ on CNT),$^{18,28-33}$ co-doped compounds (Ru$_x$Cu$_{1-x}$ on CNT, Ru-Cu-G), have demonstrated improved performance and stability in metal-CO$_2$ batteries.$^{34,35}$ For example, the remarkable catalytic activity of the Ru-based catalyst toward the breakdown of Li$_2$CO$_3$ renders them the most promising catalyst among these material classes. Ni/r-GO (reduced graphene oxide) electrode for Li-CO$_2$ battery exhibited an overpotential of 1.5 V, rate capability of 1000 mA h g$^{-1}$ and reliable cycling performance (around 100 cycles).$^{36}$ In addition, the introduction of Cu into N-doped graphene provided Li-CO$_2$ battery with an overpotential of 0.77 V and cyclic stability of around 50 cycles.$^{15}$ By saturating CNTs with RuO$_2$, Zou's group was able to reduce the Li-CO$_2$ battery's charging potential and so extend the battery's life.$^{37}$ Mixed oxide-based electrocatalysts made of Co$_2$MnO$_4$ nanowires decorated on carbon nanoﬁbres have been employed to improve the decomposition of Na$_2$CO$_3$ in Na-CO$_2$ batteries.$^{38}$ Li-CO$_2$ batteries with a cathode composite of porous ZnCo$_2$O$_4$ nanorods and multi-wall carbon nanotubes (MWCNTs) on a stainless steel substrate possess an improved capacity of 500 mA h g$^{-1}$ and a high cycle performance of 290 cycles at 100 mA g$^{-1}$. Since bivalent Mg reacts differently with CO$_2$ and organic electrolytes and also has slower redox kinetics than monovalent alkali metals, the cathode for alkali-CO$_2$ batteries comprising transition metal-based catalysts cannot be directly used.$^{19}$ Furthermore, the development of Mg-CO$_2$ batteries is still in its early stages, with a limited understanding of cathode catalyst design. Hence, further mechanistic understanding of cathode interfacial chemistry and the role of catalytic cathodes is essential to expedite the advancement of practical Mg-CO$_2$ batteries as sustainable energy storage solutions.

We employ first-principles DFT calculations to investigate the reaction mechanisms of Mg/CO$_2$ chemistry on transition metal oxide (TMO) catalyst, RuO$_2$ (Ruthenium oxide) serving as a cathode catalyst for Mg-CO$_2$ batteries. RuO$_2$ exists majorly in two stable phases such as rutile and anatase RuO$_2$.$^{39-41}$ The choice of rutile RuO$_2$ is inspired by previous experimental and theoretical reports on their improved catalytic performance towards rechargeable Li-CO$_2$ batteries, nitrogen reduction reaction, oxygen evolution/reduction, CO$_2$ reduction, and hydrogen evolution reaction.$^{42-46}$ To the best of our knowledge, there are no studies yet understanding the reaction mechanism and catalytic behavior of TMO, for example, rutile RuO$_2$, for multivalent-CO$_2$ batteries. XRD and HRTEM analysis of previous works report that (211) plane is one of the most commonly observed surfaces with the lowest surface formation energies, hence utilized to perform our computational investigations.$^{47-50}$ We begin our study by evaluating the adsorption energies of the studied RuO$_2$ (211) catalyst with reaction intermediates such as Mg, CO$_2$, MgCO$_2$, MgC$_2$O$_4$, MgO, and MgCO$_3$. Next, we explore the optimal pathway for MgC$_2$O$_4$/MgCO$_3$ nucleation and final discharge products in the Mg-CO$_2$ reaction by analyzing the Gibbs free energies of different nucleation routes for MgC$_2$O$_4$/MgCO$_3$. We found MgC$_2$O$_4$ to be a thermodynamically favorable discharge product on RuO$_2$ (211) owing to their lower overpotential for nucleation compared to MgCO$_3$ however, the energetically preferred MgCO$_3$ nucleations on RuO$_2$ (211) are observed as the final discharge products. We
further elucidate the electrochemical free energies for the most favorable reaction pathway to investigate the role of the studied RuO$_2$ catalyst in improving the electrochemical performance of non-aqueous Mg-CO$_2$ batteries.

**COMPUTATIONAL DETAILS**

Spin-polarized first-principles DFT computations were performed using the Vienna ab initio Simulation Package (VASP). In this work, we used the Perdew-Burke-Ernzerhof (PBE) variety of the generalized gradient approximation (GGA) to account for exchange-correlation potential and the projector augmented wave (PAW) pseudopotential to characterize electron core interactions. Grimme's DFT-D3 technique, necessary for accounting the long-range van der Waal interactions, was used to precisely quantify the binding strength of reaction intermediates to the investigated catalytic cathode. When performing the computations on a plane-wave basis, we set the kinetic cutoff energy to 450 eV. A five-layer slab model of the studied RuO$_2$ (211) surface was constructed using the DFT lattice parameters obtained by bulk optimization. We used conjugate gradient method to relax the atomic geometries until the resulting force and energy were less than 0.025 eV/Å and 1 x 10$^{-4}$ eV, respectively. Using a 3 x 3 x 1 Monkhorst-Pack k-point set, the first three layers were allowed to fully relax during geometric optimization. To prevent interactions across the periodic boundary, 20 Å vacuum space was implemented in the direction perpendicular to the basal plane. Brillouin zone was integrated with a broadening width of 0.05 eV using the Gaussian smearing method. The charge transfer process between the chemical intermediates and the RuO$_2$ (211) substrate was studied via Bader charge analysis. All the studied molecular structures were visualized using VESTA software.

**RESULTS AND DISCUSSION**

**Proposed Mg-CO$_2$ discharge reaction mechanisms**

The nonaqueous Mg-CO$_2$ battery includes a metal Mg anode, a separator, organic electrolytes, a porous cathode, and catalysts (see Figure 1). During discharging, oxidation at the Mg metal anode generates Mg$^{2+}$ which diffuses from the electrolyte to the CO$_2$ cathode, propelled by the potential difference. Dissolved CO$_2$ molecules absorb electrons from the cathode and react with Mg$^{2+}$ to produce solid discharge products at the cathode/electrolyte interface.

![Figure 1. Schematics of non-aqueous Mg-CO$_2$ battery using RuO$_2$ cathode catalyst](https://doi.org/10.26434/chemrxiv-2023-f23m6)
For non-aqueous Mg-CO$_2$ batteries, experimental studies using Mo$_2$C-CNT cathodes have reported the formation of MgC$_2$O$_4$, MgCO$_3$, MgO, and C. Using ex-situ Raman spectroscopy, Liu et al. identified signature peaks at 1060, 1132, and 1200 cm$^{-1}$ that ascribe to MgO, MgCO$_3$, and MgC$_2$O$_4$, respectively, as well as carbon (D peak at 1348 cm$^{-1}$ and G peak at 1576 cm$^{-1}$) and Mg. When a carbon nanotube (CNT) cathode was used, however, the Raman and FTIR spectra reported by Zhang et al. only showed the existence of MgCO$_3$ and C as discharge products. The final discharge product in metal-CO$_2$ batteries has been a subject of ambiguity in previous experimental and theoretical studies. We propose three key mechanisms to initiate reactions that lead to the formation of the final discharge products in Mg-CO$_2$ batteries: (i) selective absorption of Mg atoms at catalytic sites, followed by CO$_2$ absorption, (ii) CO$_2$ absorption followed by Mg absorption, and (iii) two consecutive CO$_2$ absorptions. Figure 2 depicts the suggested routes of the overall reaction process. The reaction pathways rely on the interplay between CO$_2$, Mg, and the catalytic surfaces. The stabilization of MgC$_2$O$_4$ has been observed to have a positive impact on reducing the oxidative decomposition barrier in alkali metal-CO$_2$ batteries. In the pathways studied, Mg or CO$_2$ initially adsorbs onto the catalytically active site. The specific adsorbed MgCO$_2$ species (MgCO$_2$*) formed during this adsorption process is determined by the binding sequences of Mg and CO$_2$ on the catalytic surface (Pathways I, IV, V, and VI). Two CO$_2$ species can co-adsorb via chemical dimerization, leading to the formation of carbonate species (CO$_3^*$ and CO* (Path II)) or oxalate (C$_2$O$_4^{2-}$ (Path III)). MgC$_2$O$_4$ nucleation occurs on the catalyst surface as a result of the oxalate species reacting with Mg. Depending on the ensuing reaction barriers, MgC$_2$O$_4^*$ during the forward discharge process may break down to MgCO$_3$ and CO, or it may remain stabilized on the catalytic surface. CO is commonly formed on the catalytic substrate during the MgCO$_3$ nucleation process. The generated CO could disproportionately result in C and CO$_2$ or lead to the formation of MgCO$_3^*$, MgO*, and C*.

**Mg and CO$_2$ adsorption on RuO$_2$ (211)**

We investigated the catalytic mechanism of RuO$_2$ (211) during discharge and charge processes by DFT calculations in order to better guide the cathode catalyst design for Mg-CO$_2$ batteries. Proceeding with the studied substrate, the calculated lattice parameter for the five-layer stochiometric rutile RuO$_2$ (211) was a = 9.684 Å and b = 13.696 Å. The atomic positions of the three bottom layers of the RuO$_2$ slab are fixed, while the positions of the remaining atoms are relaxed to their minimum energy state. To determine the adsorption energy, we used the following formula: $E_{ads} = E_{Mg/CO_2} + E_{surf} - E_{Mg/CO_2+surf}$ where $E_{Mg/CO_2}$, $E_{surf}$ and $E_{Mg/CO_2+surf}$ are the DFT energies of the reactants, the studied RuO$_2$ (211) surface, and the reactant.
adsorbed RuO$_2$ (211) surface. Multiple adsorption sites were examined for the adsorption of Mg and CO$_2$ on the studied catalytic surface, and the optimized adsorption configurations and energies are presented in Figure S1-S6 and Table 1.

Table 1. Reactant adsorption energies ($E_{\text{ads}}$), overpotentials ($\eta$) for nucleation of MgC$_2$O$_4$/MgCO$_3$, computed equilibrium potential ($U_{\text{eq}}$), discharge ($U_{\text{dis}}$) /charge ($U_{\text{chg}}$) potential and computed total overpotential ($\Delta E$) for most favorable electrochemical free energy pathway

<table>
<thead>
<tr>
<th>$E_{\text{ads}}$ (Mg) (eV)</th>
<th>$E_{\text{ads}}$ (CO$_2$) (eV)</th>
<th>$\eta$ (MgC$_2$O$_4$) (V)</th>
<th>$\eta$ (MgCO$_3$) (V)</th>
<th>$U_{\text{eq}}$ (V)</th>
<th>$U_{\text{dis}}$ (V)</th>
<th>$U_{\text{chg}}$ (V)</th>
<th>$\eta_{\text{dis}}$ (V)</th>
<th>$\eta_{\text{chg}}$ (V)</th>
<th>$\Delta E$ (V)</th>
</tr>
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<tbody>
<tr>
<td>-3.31</td>
<td>-1.10</td>
<td>0.03</td>
<td>0.67</td>
<td>1.42</td>
<td>0.12</td>
<td>2.77</td>
<td>1.3</td>
<td>1.35</td>
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We found that both Mg and CO$_2$ reactants can be bonded spontaneously with the RuO$_2$ substrate with the calculated binding energies of -3.31 eV and -1.10 eV, respectively. Our findings reveal that the most stable adsorption site for Mg adsorption is the hollow site atop the Ru and O atoms, whereas for CO$_2$ adsorption, the favorable site is on the top of the Ru atom (see Figure S1 and S2). The shortest bond distance between Mg and CO$_2$ adsorbed RuO$_2$ substrate are 2.14 Å and 2.27 Å. After a detailed examination of CO$_2$ adsorbed structure, we found that the O of CO$_2$ (2.27 Å) is closer to the substrate compared to that of C of CO$_2$ (3.35 Å). Strong adsorption of CO$_2$ and subsequent activation is an important step because of CO$_2$'s strong thermodynamic stability. We found that after CO$_2$ adsorption on the RuO$_2$ substrate, the bond angle between two C=O bonds is 179 degrees, and the C=O bond distance is 1.168 Å, which are similar to a gaseous CO$_2$ molecule. These observations indicate that the adsorbed CO$_2$ is inactivated and hence the first reaction step of possible studied pathways is the Mg adsorption. A similar kind of behavior is found in Li-CO$_2$ battery electrocatalysts as well. 11,53,54

To further investigate the electronic structure of the RuO$_2$ (211) catalyst, we perform projected density of states (DOS) calculations before and after the adsorption of reaction intermediates. The electrical conductivity of the studied RuO$_2$ (211) catalyst is depicted in Figure S7, which shows that the material has a metallic character with significant electron states around the Fermi level. Notably, the Ru-4d states' contribution to the catalyst's metallic behavior is highlighted by the PDOS analysis (Figure S7). In addition, the electrical conductivity is preserved after adsorption, as shown by a comparison of the PDOS before and after intermediate adsorption. Figure S7 shows that after Mg adsorption, the Mg peak is significantly reduced, indicating a robust charge transfer with the substrate. In contrast, for CO$_2$ adsorption, there is no significant change in the DOS near the Fermi level and could separate the peaks of C-2p of CO$_2$, indicating no obvious charge transfer for CO$_2$ intermediate adsorption. Moreover, MgCO$_3$ adsorption is found to exhibit stronger hybridization compared to MgC$_2$O$_4$, expected to enhance adsorption phenomenon, charge transfer and minimize the overpotential for overall battery performance.

Mechanisms of MgC$_2$O$_4$/MgCO$_3$ nucleation

While carbon-based cathodes normally provide MgCO$_3$ as the end discharge result, Mo$_2$C-CNT cathodes can trigger MgC$_2$O$_4$ nucleation in the early stages of battery discharge, as shown by experimental findings from non-aqueous Mg-CO$_2$ battery investigation.19 However, earlier experimental studies have failed to definitely identify the ultimate discharge product in Mg-CO$_2$ batteries.19,23 We have chosen MgC$_2$O$_4$ and MgCO$_3$ nucleation as the focus of our investigation on discharge products to acquire a more in-depth understanding of the reaction mechanisms occurring on the investigated RuO$_2$ (211) surface. We studied both the open circuit ($U= 0$ V) and equilibrium potential ($U_0$ (MgC$_2$O$_4$) = 1.98 V and $U_0$ (MgCO$_3$) = 2.13 V) Gibbs free energies of the intermediates involved in the nucleation of MgC$_2$O$_4$ and MgCO$_3$ to understand more about the catalyst's efficiency in this regard. The non-aqueous Mg-CO$_2$ batteries

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demonstrate an inherent propensity to adhere to a four-electron pathway, which comprises of four elementary steps within diffusion cathodes.

**Figure 3.** (a-b) The computed Gibbs free energies of various possible reaction pathways for MgCO$_3$/MgC$_2$O$_4$ nucleation at open circuit potential (c) Schematics of MgCO$_3$ nucleation reaction (Path VI) on RuO$_2$ (211) catalyst. Color code: Magnesium: Orange; Oxygen (CO$_2$): Blue; Carbon: Brown; Ruthenium: Silver and Oxygen (RuO$_2$): Red. The optimized structures for other pathways are provided in Figure S1-6

Figure 3 depicts the Gibbs free energy profiles of the reaction pathways concerning MgCO$_3$ and MgC$_2$O$_4$ nucleation on RuO$_2$ (211). It is noteworthy that all intermediate steps that involve Mg atoms with electron transfer exhibit an exothermic nature at $U = 0$ V. Although the first CO$_2$ adsorption to form MgCO$_2$ (Path I, IV, V, and VI) is exothermic at $U = 0$ V, the consecutive CO$_2$ adsorption phenomenon to produce oxalate (C$_2$O$_4$ (Path III)) intermediate species is energetically uphill with positive Gibbs free energies of 1.066 eV at $U = 0$ V. Moreover, the Gibbs free energies to produce CO$_3$+CO is also very close to the thermoneutral value, say, $\Delta G = -0.06$ eV, compared to free energies for Mg adsorption intermediates. The formation of the C$_2$O$_4^{2-}$ or CO$_3$ + CO intermediate is proposed to occur through the chemical dimerization of two CO$_2$ intermediates without the need for additional electron transfer. Therefore, to enable the efficient reduction of CO$_2$ and initiate dimerization, the studied electrocatalyst should adsorb and significantly activate the inert CO$_2$ molecule. As depicted in Figure 3, it is evident that the initial adsorbed Mg plays a crucial role in activating the inert CO$_2$ molecule. As depicted in Figure 3, it is evident that the initial adsorbed Mg plays a crucial role in activating the inert CO$_2$ molecule.
MgCO₃+CO (ΔG = -1.459 eV) or MgO+CO₃+C (ΔG = 1.357 eV), which in turn further undergo Mg adsorption with electron transfer to generate MgCO₃ with ΔG = -1.957 eV (Path I) and ΔG = -4.774 eV (Path V). It is worth noting that, in contrast to the nucleation of MgC₂O₄ via C₂O₂ dimerization pathway with an energy barrier of ΔG = 1.066 eV (C₂O₂*), the adsorbed MgCO₂* would undergo reaction with CO₂ to produce MgC₂O₄* (see Figure 3) with ΔG = 0.03 eV (Path IV). Importantly, after Mg adsorption on RuO₂ (211) substrate, the O=C=O bond angle of the inert linear CO₂ molecule (180 degree) would twist the O=C=O bond configuration to nearly 124 degrees, closer to O=C=O conformation in MgC₂O₄ illustrating CO₂ activation characteristics with surface Mg adsorption behavior and moreover, similar kind of behavior in found in Li₂CO₃ batteries also.⁵³,⁵⁴

**Figure 4 (a-b).** Calculated Gibbs free energy change for the elementary steps of the most favorable pathway for MgC₂O₄/MgCO₃ nucleation at both open circuit and equilibrium potentials

Now, at equilibrium potentials, U = U₀ (MgCO₃) = 2.13 V and U = U₀ (MgC₂O₄) = 1.98 V, the Gibbs free energy profiles in Figures S8, S9 and 4 demonstrate a transition from exothermic and downhill behavior to an endothermic nature for all intermediate steps involving Mg adsorption and electron transfer at U = 0 V. In addition, while the second and third CO₂ adsorption step involving the formation of reaction intermediates such as MgCO₂* (Path I and V), MgCO₃ + CO* (Path I) and MgC₂O₄ (Path IV) are still exothermic at equilibrium potentials, the second CO₂ adsorption step to form MgO + CO₃ + C (Path V) is endothermic with positive free energy change. Overall, the lowest rate-determining step for MgCO₃ and MgC₂O₄ nucleations are found to be path VI and path IV, making them the most viable pathways for MgCO₃/MgC₂O₄ nucleations (See Figure 4). Furthermore, when equilibrium potentials are employed, the variations in free energy for MgCO₃ and MgC₂O₄ nucleation are -0.631 eV and -1.736 eV, respectively. The free energy changes of the rate-governing steps at equilibrium potentials were calculated to determine the overpotentials for nucleation of MgCO₃ and MgC₂O₄ on the studied RuO₂ (211) surface, according to η₀ = - ΔGf / (n.e). The data presented in Table 1 and Figure 4 indicate that the overpotential for the free energy change of MgC₂O₄ nucleation is significantly lower (0.063 V) than that of MgCO₃ (0.67 V), confirming that the nucleation of MgC₂O₄ as a discharge product using RuO₂ (211) cathode catalyst is thermodynamically favorable in the overall reaction process for Mg-CO₂ batteries.

**MgC₂O₄ splitting reactions**

For Li₂CO₃ batteries, experimental studies have confirmed that Li₂C₂O₄ is observed as the final discharge product when Mo₂C/CNTs and Ru(bpy)₃Cl₂ are used as cathode catalysts.¹³ However, in the case of Au catalysts used as the cathode in Li-CO₂ batteries, in situ Raman characterization has detected oxalate species (C₂O₂*) during the initial discharge processes. Nonetheless, the oxalate peaks are quickly replaced by growing signals of carbonate and carbon during subsequent reductions.⁵⁵ The only reported work on non-aqueous Mg-CO₂ battery claims that the discharge process on Mo₂C-CNT cathodes initiates

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the formation of MgC$_2$O$_4$, which is later followed by the production of insulating MgCO$_3$, MgO, and C at the final stage of discharge.\textsuperscript{19} Hence, to understand the final discharge products in non-aqueous Mg-CO$_2$ batteries using RuO$_2$ (211) cathode catalyst, we investigated MgC$_2$O$_4$ splitting reactions employing two disproportionation reactions (denoted as (1) and (2) in Figure S10).

Based on the findings illustrated in Figure S10, the reaction of MgC$_2$O$_4$ splitting into MgCO$_3$ and CO demonstrated a negative free energy change of -1.02 eV. In contrast, the formation of MgCO$_2$ and CO$_2$ exhibited a lower negative free energy change of -0.63 eV. Consequently, the formation of MgCO$_3$ and CO is predicted to be thermodynamically favorable on the investigated RuO$_2$ (211) catalyst. Furthermore, in the nucleation process of Li$_2$CO$_3$ on various catalytic surfaces, an intermediate CO species have been identified, which subsequently undergoes disproportionation to yield C and CO$_2$, as depicted in Figure S10.

To explore the potential formation of MgCO$_3$ alongside C and CO$_2$ through CO splitting, our study investigated the Gibbs free energy of CO disproportionation, which was calculated to be 3.46 eV. Notably, the rate-controlling step of the initial splitting reactions (1) and (2) exhibited free energy changes of -1.02 eV and 3.46 eV, respectively. In contrast, the second splitting reactions (1) and (2) displayed free energy changes of -0.63 eV and 3.06 eV, respectively. While the first splitting reaction, leading to the formation of MgCO$_2$ and CO nucleation from MgC$_2$O$_4$, is thermodynamically favorable, the subsequent CO disproportionation reaction to produce C and CO$_2$ is found to be energetically uphill. This suggests that MgC$_2$O$_4$ can indeed split into MgCO$_3$ and CO, but the subsequent decomposition into C and CO$_2$ is hindered. It is worth noting that the Gibbs free energy calculations for the formation of MgCO$_3$, along with MgO and C through MgCO$_2$ and CO, accompanied by electron transfer, reveal a free energy barrier of 2.30 eV at U = 2.13 V, in contrast to the energetically unfavorable formation of C and CO$_2$. Thus, it can be concluded that while the intermediate MgC$_2$O$_4$ formation is thermodynamically favorable, it will undergo further decomposition and electron transfer reactions to eventually form the final discharge product, MgCO$_3$, along with MgO and C (denoted as (3) in Figure S10).

![Figure 5](https://doi.org/10.26434/chemrxiv-2023-f23m6) ORCID: https://orcid.org/0000-0003-4073-3770 Content not peer-reviewed by ChemRxiv. License: CC BY 4.0

**Figure 5** Computed charge transfer for various reactant adsorbed RuO$_2$ surface. The inset shows the charge density difference (DCD) schematics of Mg, CO$_2$, MgC$_2$O$_4$ and MgCO$_3$ adsorbed on RuO$_2$ (211).

**Charge transfer analysis**

We further conducted charge transfer analysis using Bader charge method to comprehensively understand the chemical interactions and binding mechanisms between the reaction intermediate species and the studied RuO$_2$ (211) catalytic cathode. The positive charge transfer values in Figure 5 illustrate that charge is getting transferred from the intermediate to the catalytic surface. For the adsorption of CO$_2$
molecule on RuO$_2$ (211), a negligible charge of \(-0.05\) \(|e|\) is transferred from the RuO$_2$ surface to the inert CO$_2$ molecule. The elongation of bond length and bending of CO$_2$ molecule is attributed to the enhanced chemical interaction and improved charge transfer between the substrate and CO$_2$, very vital to activate the inert CO$_2$ and facilitate dimerization. However, the observed minimalistic charge transfer between CO$_2$ and RuO$_2$ majorly illustrates the inactivation of the adsorbed inert CO$_2$ molecule, thereby expected to increase the energy barrier for the generation of CO$_3^+ + CO$ and C$_2$O$_4^{*}$ intermediate species formation compared to Mg adsorption, well corroborated with Gibbs free energy calculations. In contrast to CO$_2$, for the Mg reactant, a significant amount of charge transfer (1.54 \(|e|\)) occurs from the reactant to the catalytic surface, accountable for predicted increased adsorption energies (-3.31 eV). The enhanced charge transfer behavior for Mg, would in-turn elucidate the favorable accumulation of initial Mg adsorption and further mediate the activation of CO$_2$ to facilitate the activation of C-C coupling process to produce MgC$_2$O$_4$/MgCO$_3$ nucleations. Additionally, the RuO$_2$ (211) surface exhibited charge transfer values of 0.271 \(|e|\) and 0.359 \(|e|\) for the nucleation of MgC$_2$O$_4$ and MgCO$_3$, respectively. The observed improved charge transfer for MgCO$_3$ nucleation illustrate improved adsorption characteristics, which is expected to exhibit superior catalytic activity, possibly decrease the free energy during the formation of final discharge products in Mg-CO$_2$ batteries. Furthermore, charge density difference (DCD) analysis was conducted on the RuO$_2$ substrate with representative MgCO$_3$ adsorption, as depicted in Figure 5 and S11. The electron transfer between the RuO$_2$ substrate and MgCO$_3$/RuO$_2$ interface is well supported by the charge depletion and charge accumulation, as evidenced by the charge transfer analysis.

**Figure 6.** Electrochemical free energy change during discharging/charging for the most favorable pathway using RuO$_2$ (211) catalyst

**Electrochemical free energy analysis**

To explore the overall electrochemical performance, we investigated the cathode reaction using the four-electron reaction mechanism during the discharging (CO$_2$RR)/charging (CO$_2$ER) process of Mg-CO$_2$ batteries. The performance assessment of the Mg-CO$_2$ battery relies on the calculation of discharge overpotential ($\eta_{dis}$), charge overpotential ($\eta_{chg}$), and total overpotential ($\Delta E_{total}$) using the following equations: $\eta_{dis} = U_{eq} - U_{dis}$, $\eta_{chg} = U_{chg} - U_{eq}$, and $\Delta E_{total} = \eta_{dis} + \eta_{chg}$. The equilibrium potential ($U_{eq}$) serves as the driving force for spontaneous charging and discharging reactions, with a lower overpotential indicating enhanced battery performance. The discharging potential ($U_{dis}$) and charging potential ($U_{chg}$) are determined as the minimum and maximum electrode potentials, respectively, to ensure that all steps in the optimal pathway exhibit energetically downhill behavior. This approach provides a quantitative measure
for evaluating the electrochemical performance on the RuO$_2$ (211) surface. The results are illustrated in Figure 6 and the detailed calculation methodology is given in SI.

Figure 6 portrays the electrochemical free energy plot, highlighting the spontaneous and downhill nature of reactions at $U = 0$ V wherein all reaction steps in the plot exhibit negative $\Delta G$ values, say, $\Delta G < 0$ V, affirming their thermodynamic favorability. The electrochemical free energy of all the reaction stages in the discharging reaction decreases until the electrode potential turns out to be 0.124 V. As a result, the studied RuO$_2$ (211) surface has a discharge overpotential of 1.30 V (dis). Moreover, further increase in the electrode potential render the electron transfer reaction during the discharge to be thermodynamically uphill. This suggests that the last step of the electron transfer reaction comprising MgCO$_3$ with CO and MgCO$_3$ with MgO and C adsorption is critical in regulating the discharge rate. Since the electrochemical free energy of each step in the reaction process decreased at a potential of 2.773 V, an overpotential of 1.35 V now exists during charging. The rate-controlling step during the charging process involves the decomposition of MgCO$_3$ along with MgO and C accompanied with electron transfer. Total overpotential $\eta_{\text{total}}$ is commonly employed to evaluate catalytic activity in the field of bifunctional catalysis for CO$_2$RR/CO$_2$ER, with a smaller value suggesting a greater degree of activity. The calculated total overpotential for overall electrochemical reaction process of non-aqueous Mg-CO$_2$ battery using RuO$_2$ (211) catalyst is 2.65 V.

![Image](https://doi.org/10.26434/chemrxiv-2023-f23m6) ORCID: https://orcid.org/0000-0003-4073-3770 Content not peer-reviewed by ChemRxiv. License: CC BY 4.0

Figure 7. Comparison of the computed overpotentials of various cathode catalyst materials for Mg-CO$_2$ and Li-CO$_2$ batteries

Figure 7 presents the discharge and charge overpotentials obtained from computational simulations of Li-CO$_2$ batteries. The previous studies on Mg-CO$_2$ batteries include only adsorption strength calculations as a descriptor to understand the reaction mechanism during the charging/discharging process. Nevertheless, in this study, we proposed the various possible reaction pathways during the reaction of CO$_2$ cathode with Mg anode and moreover, for the first time, comprehensively investigated the entire electrochemical reaction mechanism during the CO$_2$RR/CO$_2$ER. We compared the results of this study to that of Li-CO$_2$ batteries (see Figure 7) because computational and experimental studies on non-aqueous Mg-CO$_2$ is very scarce. While the calculated Mg-CO$_2$ discharge-charge overpotential using RuO$_2$ (211) is lower than that of $\alpha$-Mo$_2$C (001), $\beta$-Mo$_2$C (001), it is comparable to that of Ti$_2$C and Zr$_2$C for Li-CO$_2$ batteries respectively. $^{11,56}$
CONCLUSION

In summary, our study employs first-principles DFT calculations to investigate the intricate electrocatalytic processes involved in reaction intermediates within Mg-CO$_2$ batteries, with a particular focus on ruthenium oxide (RuO$_2$) as a representative cathode catalyst. Our findings reveal intriguing aspects, such as the enhanced Mg adsorption energies that activate inert CO$_2$, resulting in the discharge product MgC$_2$O$_4$ with lower overpotential compared to MgCO$_3$ on the RuO$_2$ (211) surface. While MgC$_2$O$_4$ is thermodynamically favored as a discharge product, our investigation suggests its subsequent decomposition into MgCO$_3$, MgO, and C. Bader charge analysis highlights the negligible electron transfer for CO$_2$, rendering it inactive and making the formation of carbonate (CO$_3$)/oxalate (C$_2$O$_4$) intermediates via C-C coupling thermodynamically unfavorable. Remarkably, our results demonstrate significant electron transfers from the catalytic surface to the MgC$_2$O$_4$/MgCO$_3$ products illustrating improved adsorption characteristics. These findings have the potential to enhance catalytic activity and reduce the free energy in the formation of final discharge products in Mg-CO$_2$ batteries. Additionally, we carefully examine the electrochemical free energy profiles of the most favorable reaction pathways, quantifying discharge, and charge overpotentials as 1.3 V and 1.35 V, respectively. Overall, these findings underscore the critical importance of deliberate catalyst design for cathode materials in addressing performance limitations encountered in non-aqueous rechargeable Mg-CO$_2$ batteries.

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References


Supporting Information

Understanding Catalytic Mechanisms and Cathode Interface Kinetics in Non-Aqueous Mg-CO$_2$ Batteries

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Calculation methodology

The given expression, $\rho_b = \rho_{\text{adsorbed state}} - (\rho_{\text{adsorbent}} + \rho_{\text{cat}})$, is utilized to quantify the disparity in charge density for intermediate species adsorbed RuO$_2$ (211). Here, $\rho_{\text{adsorbed state}}$, $\rho_{\text{adsorbent}}$, and $\rho_{\text{cat}}$ correspond to the charge density associated with the catalyst in the presence of adsorbed reaction intermediates, the charge density of the isolated intermediate species, and the charge density of the catalytic surface, respectively.
Figure S1. Top and side views of the most stable geometric configuration of MgCO$_3$ nucleation (Path I)

Figure S2. Top and side views of the most stable geometric configuration of MgCO$_3$ nucleation (Path II)
Figure S3. Top and side views of the most stable geometric configuration of MgCO₃ nucleation (Path V)

Figure S4. Top and side views of the most stable geometric configuration of MgCO₃ nucleation (Path VI)
Figure S5. Top and side views of the most stable geometric configuration of MgC$_2$O$_4$ nucleation (Path III)

Figure S6. Top and side views of the most stable geometric configuration of MgC$_2$O$_4$ nucleation (Path IV)
Figure S7. The projected density of states of various reaction intermediate (CO₂, Mg, MgC₂O₄ and MgCO₃) adsorbed RuO₂ (211) surface. The Fermi level is denoted by dotted line.

Figure S8. Computed Gibbs free energies of various reaction intermediate pathways for MgCO₃ nucleation at U = 2.13 V.
Figure S9. Computed Gibbs free energies of various reaction intermediate pathways for MgC_2O_4 nucleation at U = 1.98 V

Figure S10. Computed Gibbs free energies of MgC_2O_4 splitting reactions
Figure S11. Snapshot of top views of charge density difference (DCD) for Mg, CO$_2$, MgC$_2$O$_4$ and MgCO$_3$ adsorbed RuO$_2$ (211)

**Standard Gibbs Free energies and equilibrium voltages**

The complete chemical reaction for the nucleation of MgCO$_3$ and MgC$_2$O$_4$ can be stated as

1. $2\text{Mg (s)} + 2 \text{CO}_2 (\text{g}) \rightarrow \text{MgCO}_3 (\text{s}) + \text{MgO (s)} + \text{C (s)}$  
2. $\text{Mg (s)} + 2 \text{CO}_2 (\text{g}) \rightarrow \text{MgC}_2\text{O}_4 (\text{s})$  

The standard Gibbs free energies of MgCO$_3$ (s) and MgC$_2$O$_4$ (s) can be calculated based on the chemical reactions provided.

\[
\Delta G^0_f (\text{MgCO}_3)_s = G^0 (\text{MgCO}_3)_s + G^0 (\text{MgO})_s + G^0 (\text{C})_s - 2 G^0 (\text{Mg})_s - 2 G^0 (\text{CO}_2)_g
\]  

\[
\Delta G^0_f (\text{MgC}_2\text{O}_4)_s = G^0 (\text{MgC}_2\text{O}_4)_s - G^0 (\text{Mg})_s - 2 G^0 (\text{CO}_2)_g
\]
The values of $\Delta G^0_f (\text{MgCO}_3)$ and $\Delta G^0_f (\text{MgC}_2\text{O}_4)$, was determined through standard free energy calculations, resulting in -8.55 eV and -3.98 eV, respectively. As per the Nernst equation,

$$U_0 (M) = -\Delta G^0_f / ne \quad (5)$$

The equilibrium potential values for MgCO$_3$ and MgC$_2$O$_4$ were determined to be 2.13 V and 1.98 V, respectively, based on the number of transferred electrons and electronic charge represented by n and e.

**Electrochemical free energy change during the discharging and charging process**

The electrochemical free energy change of the catalyst was determined by analyzing the most favorable pathway during the discharging/charging process using the given expression.

$$(\Delta G_E (\text{Mg-CO}_2)) = E_{\text{total}} - \{E_{\text{prev}} + n_{\text{Mg}} (\mu_{\text{Mg}}) + n_{\text{CO}_2} (\mu_{\text{CO}_2})\} \quad (6)$$

$E_{\text{total}}$ and $E_{\text{prev}}$ denotes energy of the total system and of the previous step. $n_{\text{Mg}}, n_{\text{CO}_2}, \mu_{\text{Mg}}$ and $\mu_{\text{CO}_2}$ denotes the number of Mg, CO$_2$ and chemical potential of Mg and CO$_2$.

Discharge overpotential ($\eta_{\text{dis}}$) = $U_{\text{eq}} - U_{\text{dis}}$, \quad (7)

Charge overpotential ($\eta_{\text{chg}}$) = $U_{\text{chg}} - U_{\text{eq}}$, \quad (8)

Total overpotential ($\Delta E_{\text{total}}$) = $\eta_{\text{dis}} + \eta_{\text{chg}}$, \quad (9)