Reversible and Irreversible Mechanisms of Li-CO₂ Batteries

Yafei Li (liyafei@njnu.edu.cn)  
Nanjing Normal University  
https://orcid.org/0000-0002-6136-863X

Xinxin Zhang  
Nanjing Normal University

Yu Wang  
Nanjing Normal University  
https://orcid.org/0000-0002-8833-9564

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Abstract

Li-CO$_2$ batteries are considered a versatile solution for CO$_2$ utilization. However, their development, including reversibility and efficiency, is impeded by an inadequate understanding of Li-CO$_2$ electrochemistry, particularly the decomposition of carbon and the generation of by-product O$_2$. Here, using Ru (reversible) and Ir (irreversible) as model catalysts and employing state-of-the-art first-principles calculations, the rechargeable/reversible mechanisms of Li-CO$_2$ batteries are disclosed. We find that electrolyte, often neglected or oversimplified in Li-CO$_2$ modeling, plays an essential role in CO$_2$ activation, and C-C coupling affects the generation pathways of discharge intermediates due to the sluggish kinetics. The results rationalize experimental observations, which are also examined by constant-potential modeling. Specifically, by exploring the kinetics of the charging process, we discover that the reversibility of Ru is attributed to its ability to suppress O-O coupling while co-oxidizing Li$_2$CO$_3$ and carbon. In contrast, Li$_2$CO$_3$ decomposition on Ir preferentially produces O$_2$, during which carbon can only be partially decomposed. These findings solve long-standing questions and highlight the necessity of describing the explicit solvent effect in modeling, which can promote further studies on Li-CO$_2$ batteries.

Introduction

Li-CO$_2$ batteries have garnered extensive attention from the scientific community owing to their high potential for CO$_2$ fixation while simultaneously enabling energy storage with a theoretical energy density of 1876 W h kg$^{-1}$.\textsuperscript{1–3} In contrast to Li-ion batteries, their performance is governed by Li − CO$_2$ electrochemistry, which operates according to the following reaction: 4Li + 3CO$_2$ $\leftrightarrow$ 2Li$_2$CO$_3$ + C ($E_0 = 2.8$ V vs. Li/Li$^+$).\textsuperscript{4–7} However, CO$_2$ reduction during the discharging process is kinetically sluggish, which results in large discharging overpotentials, and a high charge voltage is also required to decompose the discharge product, Li$_2$CO$_3$, due to its wide bandgap of 5.03 eV and high thermodynamic stability ($\Delta G_f = -1132.1$ kJ mol$^{-1}$).\textsuperscript{8,9} Moreover, the inadequate decomposition of the discharge product carbon limits energy efficiency and leads to a severe irreversibility problem (e.g., 2Li$_2$CO$_3$ $\rightarrow$ 4Li$^+$ + 4e$^-$ + 2CO$_2$ + O$_2$).\textsuperscript{10–12} Such issues pose massive challenges to the practical applications of Li-CO$_2$ batteries, thereby inspiring the rational design of catalysts that demonstrate high reversibility and low overpotentials.\textsuperscript{13–15}

Uncovering the underlying mechanisms can facilitate the design of efficient catalysts.\textsuperscript{16–21} In recent years, much effort has been expended to reveal the reaction mechanism of Li-CO$_2$ batteries based on experimental characterization and theoretical calculations.\textsuperscript{22–25} For the discharging process, C-C coupling, such as the dimerization of *CO$_2$ (* indicates an adsorption site) and the reaction of *Li$_2$CO$_2$ and *CO$_2$, was regarded as the essential steps for Li$_2$CO$_3$ formation.\textsuperscript{12,20,26} However, the dominant coupling step and reaction pathway are still controversial.

Another important issue is that the oxidative decomposition mechanism of Li$_2$CO$_3$ and carbon remains quite ambiguous. For example, in principle, the as-formed O species can react with carbon, but in the case
of most catalysts, such as Au and Ir, only the decomposition of Li$_2$CO$_3$ has been observed; both O$_2$ and CO$_2$ were found to evolve concomitantly during the charging process.\textsuperscript{3,26–30} Note that the generated O$_2$ may contain aggressive singlet oxygen (\textsuperscript{1}O$_2$), which can attack battery components and cause severe parasitic reactions.\textsuperscript{13,31} In the cases of Ru-based metal catalysts, Li$_2$CO$_3$ and carbon disappear together, and only CO$_2$ is released, corresponding to a reversible process.\textsuperscript{3} However, to date, no satisfactory explanation for such phenomena exists. It is of great significance to gain a mechanistic understanding of the reduction reaction mechanism of CO$_2$ and the subsequent oxidation process in Li-CO$_2$ batteries.

In this work, we investigate the charge and discharge mechanisms of Li-CO$_2$ batteries by conducting comprehensive first-principles calculations to provide fundamental insights into the issue of reversibility. Ru and Ir are selected as model catalysts because the former has been extensively reported to achieve good reversibility in Li-CO$_2$ electrochemistry, while the latter suffers from irreversibility issues. The modeling results show that the electrolyte can facilitate the activation of CO$_2$, and the disproportionation of *CO$_2$ corresponds to the predominant kinetic barrier for the discharging process. While the two catalysts exhibit the same CO$_2$ discharging process, their charging processes differ essentially. Ru can suppress O-O coupling to form O$_2$ while co-oxidizing carbon and Li$_2$CO$_3$ to generate CO$_2$, thereby ending a complete battery cycle. By contrast, in the case of Ir, Li$_2$CO$_3$ decomposes and releases both CO$_2$ and O$_2$, and carbon can be only partially decomposed into small fragments.

**Results**

To explore rechargeable/reversible mechanisms of Li-CO$_2$ batteries, the typical surfaces of Ru and Ir catalysts, namely, Ru(0001) and Ir(111), were constructed (Fig. 1a). The C-C coupling steps can affect the formation of oxalate intermediates (*C$_2$O$_4$, *LiC$_2$O$_4$, *Li$_2$C$_2$O$_4$), carbonate intermediates (*CO$_3$, *LiCO$_3$, *Li$_2$CO$_3$), and *CO. Although prior experiments have indicated that the addition of high polar electrolytes (e.g., DMSO) can induce the generation of oxalate intermediates,\textsuperscript{32,33} such a phenomenon has only been detected on certain catalysts,\textsuperscript{2,3,22} indicating that a second mechanism for *CO$_2$ dimerization may exist. Meanwhile, the interactions between reaction intermediates and solvent molecules can be strong but are often neglected or oversimplified in the Li-CO$_2$ electrochemistry modeling. Hence, the activation of CO$_2$ (forming *CO$_2$) and the subsequent *CO$_2$-involved C-C coupling steps were first explored with an explicit description of the solvent effect of DMSO.

Different CO$_2$ adsorption sites of the two surfaces were investigated. Figure 1b shows the lowest-energy structure of *CO$_2$ in which the CO$_2$ molecule is chemically adsorbed onto Ru(0001) and Ir(111) with a dual-site adsorption configuration. The adsorption free energies are −0.35 eV for Ru(0001) and −0.30 eV for Ir(111). It is worth mentioning that the solvent effect has resulted in an extension of the C-O bond length with respect to both the Ru(0001) and Ir(111) surfaces, with an increase from 1.250 Å to 1.315 Å for the former and 1.318 Å to 1.325 Å for the latter, indicating an overall stronger CO$_2$ adsorption in both cases (Fig. 1b). The dual-site adsorption presents a longer C-O bond length, which may facilitate the bond
breaking in the subsequent disproportionation reaction. Please also note that in the case of Ru, the configuration of *CO₂ changes from single-site adsorption (forming a Ru-C bond) to dual-site adsorption (forming Ru-O and Ru-C bonds) after considering the solvent effect. These results highlight the essential role of electrolytes in the activation of CO₂ and demonstrate the necessity of describing the explicit solvent effect in Li-CO₂ electrochemistry modeling.

The activated *CO₂ species can undergo direct dimerization to form oxalate or carbonate intermediates, and they are also available to be coupled with the lithiated intermediates, including *LiCO₂ and *Li₂CO₂. To find the most likely reaction path, we performed a kinetic analysis using the double-ended surface walking (DESW) and constrained Broyden dimer (CBD) approaches.³⁴,³⁵ Note that the methods can determine a low-energy pathway linking two minima even without iterative optimization of the path, from which the transition state (TS) can be located readily. As shown in Supplementary Figs. 1 and 2, *CO₂ is more favorable to disproportionate into *CO₃ and *CO for both Ru(0001) and Ir(111). However, the coupling of *Li₂CO₂ and *CO₂ on Ru(0001) tends to generate oxalates, while in the case of Ir(111), the formation of carbonates is still predominant. As mentioned above, polar electrolytes have a significant impact on the formation of discharge intermediates. Therefore, ab initio molecular dynamics (AIMD) simulations were performed to obtain explicit DMSO structures for the Ru(0001) and Ir(111) surfaces (Supplementary Fig. 3),³⁶ and both reaction pathways under solvent conditions were further analyzed.

The kinetic results involving the solvation effect shown in Fig. 1c and Fig. 1f indicate that the disproportionation pathway (2*CO₂ → *CO₃ + *CO) is more energetically favorable than the dimerization pathway (2*CO₂ → *C₂O₄). For the disproportionation pathway, the energy barriers of Ru(0001) and Ir(111) are 0.76 and 0.83 eV, respectively, which are lower than the dimerization pathway (0.96 and 1.65 eV). In addition, to further catch the solvent network, the slow-growth method was also employed to sample the energy change of the aforementioned optimal reaction pathway (Fig. 1d, 1e, 1g, 1h). The results prove that *CO₂ on the catalysts has a higher propensity towards undergoing disproportionation to form *CO₃ and *CO, which is consistent with the above kinetic results (Fig. 1c, 1f). Note that we also conducted slow-growth simulations up to 50 ps and found similar results. This is not surprising as the high polar electrolytes do not directly participate in the Li–CO₂ reactions, which is different from the typical aqueous electrochemical reactions (e.g., the hydrogen evolution reaction and the reduction of CO₂ and H₂O to CH₃OH). On a different note, the competing coupling of *Li₂CO₂ and *CO₂ to form *Li₂C₂O₄ in DMSO also exhibits a high energy barrier on the Ru(0001) surface (Supplementary Fig. 4). Therefore, the disproportionation of *CO₂ to form *CO₃ and *CO is the dominant pathway for Ru(0001) and Ir(111).

The Li₂CO₃ and carbon formation processes were subsequently investigated using the constant charge method (Fig. 2).²,¹²,²⁴ The relative free energy changes (ΔG) are summarized in Supplementary Table 1. After the disproportionation of *CO₂, *CO₃ can convert to *Li₂CO₃ via two-step lithiation reactions, which are both thermodynamically spontaneous for the Ru(0001) and Ir(111) surfaces (Fig. 2). Subsequently, *Li₂CO₃ desorbs to produce the first Li₂CO₃ species, whereas the previously generated *CO remains on
the catalyst surface. The remaining question is whether CO undergoes disproportionation or participates in subsequent lithiation reactions. According to our calculations, *CO lithiation to form *LiOC is an exothermic reaction, with respective $\Delta G$ values of $-1.43$ eV for Ru(0001) and $-1.54$ eV for Ir(111); in accordance with our expectations, the kinetic barriers of such a lithiation step are small (less than 0.3 eV). By contrast, the disproportionation of *CO to from *C and *CO$_2$ is considerably endothermic, and the kinetic barriers are as high as 2.37 and 2.98 eV for Ru(0001) and Ir(111), respectively. We also calculated the coupling of *CO and *CO$_2$ to form *CO$_3$ and *C but found that the relative kinetic barriers are very high (2.31 and 3.28 eV). These results suggest that the two reactions are difficult to occur. Moreover, the lithiation of *LiOC to *Li$_2$OC is exothermic, and the as-formed *Li$_2$OC can react with CO$_2$ to form *Li$_2$C$_2$O$_3$ and then decomposes into *Li$_2$CO$_3$ and *C species. Such a decomposition step is slightly endothermic by 0.07 eV for Ru(0001) and 0.66 eV for Ir(111).

The theoretical limiting potential ($U_L$) is an important indicator to bridge the experimental activity, such as discharge potential. Based on the free-energy diagrams in Fig. 2, $U_L$ was identified to be 1.43 V for Ru(0001) and 1.54 V for Ir(111). To better simulate electrochemical environments, we performed a constant potential modeling, which can describe the effects of the surface charge of catalysts on electrochemical reactions. The total energy of each reaction intermediate as a function of potential is fitted (Supplementary Figs. 5 and 6), and Fig. 3a and 3b show the fitting results for *LiCO$_3$ and *CO intermediates on Ru(0001) and Ir(111), respectively. We found that the $U_L$ values of Ru(0001) and Ir(111) obtained based on the constant potential method are close to the above constant charge results (Fig. 1c and 1d), and these values are in agreement with experimental observations. These results demonstrate the rationality of our proposed discharge mechanism. Considering the computational cost, the constant charge method was used in subsequent calculations.

Next, we moved our focus to the charging process. Compared with the discharge reaction, the charging mechanism is relatively complex and ambiguous. According to whether the discharge products Li$_2$CO$_3$ and carbon can be completely decomposed, the charging process can be divided into reversible and irreversible reactions. It was previously reported that both chemical and electrochemical pathways may exist for the decomposition of Li$_2$CO$_3$. For most reported catalysts, only the decomposition of Li$_2$CO$_3$ was observed during the charging process while carbon is partially decomposed. Meanwhile, for exceptional catalysts such as Ru, no satisfactory explanation on the underlying mechanism of the oxidation of Li$_2$CO$_3$ and carbon has been provided. In this regard, we proposed two possible mechanisms and performed corresponding calculations, as discussed later.

The discharge product carbon is a complex system; in principle, its decomposition is the gradual transformation of large fragments into small fragments. According to our calculations, the decomposition of carbon on Ru is much more energetically favorable than that on Ir, and as the number of C atoms in the carbon fragments decreases, the energy barrier for removing C atoms typically increases. For example, we investigated the kinetics of removing a C atom from C$_{13}$ and C$_6$ clusters
(Supplementary Fig. 7). The results show that the decomposition barrier of the C\textsubscript{13} cluster is 0.38 and 0.94 eV for Ru(0001) and Ir(111), respectively. In the case of the C\textsubscript{6} cluster, the barriers are significantly higher, being 1.45 eV for Ru(0001) and 1.98 eV for Ir(111). Note that after the carbon six-membered ring is broken, the subsequent barrier is moderate; for instance, the barrier of removing a C atom from a C\textsubscript{5} cluster is 1.05 eV for Ru(0001) and 1.21 eV for Ir(111) (Supplementary Fig. 7).

However, the decomposition of carbon and Li\textsubscript{2}CO\textsubscript{3} might be not simply oxidized separately but a co-oxidation process.\textsuperscript{27} Thus, we further include the contributions from Li\textsubscript{2}CO\textsubscript{3} in carbon decomposition. Herein, the C\textsubscript{6} cluster is adopted as the representative model because its decomposition exhibits the largest energy barrier compared with other carbon fragments (Supplementary Fig. 7). For the charging process, *Li\textsubscript{2}CO\textsubscript{3} first loses two Li and then generates *CO\textsubscript{3} via two delithiation steps (Fig. 4a, 4b). These steps are relatively easy to occur on both Ru(0001) and Ir(111) by applying moderate charging voltage. The further decomposition of *CO\textsubscript{3} to *CO\textsubscript{2} and *O is also energetically favorable, displaying a moderate barrier of 0.51 eV and 0.50 eV on Ru(0001) and Ir(111), respectively.

The remaining question is how *O is oxidized. Two possible reaction pathways for *O oxidation were studied. In the first pathway, *O couples with one another to generate O\textsubscript{2}, corresponding to the irreversible charge; in the second pathway, *O attacks carbon to form carbon oxides, which enables a complete battery cycle. It was found that the as-formed *O species can facilitate the carbon decomposition on both the Ru(0001) and Ir(111) surfaces (Fig. S8). Meanwhile, in accordance with our expectations, the reaction of *O with the C\textsubscript{6} cluster to form *CO and *C\textsubscript{5} on Ru(0001) exhibits a moderate energy barrier (0.86 eV), whereas in the case of Ir(111), the value is as high as 1.60 eV (Supplementary Fig. 8). To further investigate the oxidative decomposition of carbon, the reaction energy barriers with respect to the DMSO solvent were also computed (Fig. 4c). A slight decline in the respective energy barriers was observed, validating the feasibility (infeasibility) of oxidative decomposition of carbon on Ru (Ir).

Finally, the adsorbed *CO species over Ru(0001) can react with another *O to form *CO\textsubscript{2}. Although the energy barrier of the *CO oxidation reaction is slightly high, it becomes more favorable as the coverage of *O and *CO increases (Fig. 4d). This is also consistent with previous reports that CO oxidation on Ru will be more active under high gas pressure.\textsuperscript{44,45} On a different note, the dimerization of *O to form O\textsubscript{2} on Ru(0001) is virtually impossible on account of the massive changes in free energy of 3.90 eV (Fig. 4a). In the case of Ir(111), the *O intermediate preferentially couples with another *O species to generate O\textsubscript{2}, which is attributed to a moderate kinetic barrier (0.53 eV). Overall, the above modeling results demonstrate that Li\textsubscript{2}CO\textsubscript{3} and carbon can be co-oxidized on Ru to conclude a complete battery cycle, while Ir can only partially decompose carbon into small fragments together with oxidizing Li\textsubscript{2}CO\textsubscript{3} into CO\textsubscript{2} and O\textsubscript{2}. Therefore, our observations are in good agreement with the aforementioned experimental phenomena.\textsuperscript{3,28}

To gain a fundamental understanding of the difference in the oxidation of carbon on Ru(0001) and Ir(111), the surface charge distributions of *C adsorbed on the two metal surfaces were assessed through
a Bader charge analysis. As shown in Supplementary Fig. 9, a considerable amount of electronic charge is transferred from both metal surfaces to the *C species. The electron transfer value of the Ru(0001) surface (1.39 e) significantly exceeds that of the Ir(111) surface (1.02 e), corresponding to a substantially stronger Coulomb interaction between C and Ru(0001). In addition, the continuous formation of the *O intermediate on the Ru(0001) surface results in the former being widely distributed on the latter, which also facilitates reactions between *O and *C to generate CO$_2$.

**Discussion**

In conclusion, using comprehensive first-principles calculations, the complete reversible and irreversible mechanism pathways of Li-CO$_2$ batteries were disclosed for the first time. The modeling results highlighted that the electrolyte may play an essential role in the activation of CO$_2$; both Ru and Ir prefer to undergo the direct disproportionation of *CO$_2$ to *CO$_3$ and *CO during the discharge process. The constant-potential calculations verified the rationality of our reaction mechanism. Moreover, we elucidated the reversible co-oxidation process of the discharge products carbon and Li$_2$CO$_3$ on Ru(0001) as well as the rationale for the partial decomposition of carbon and the generation of O$_2$ on Ir(111). Our findings provide a solution to long-standing questions and impart ample guidance in the development of reversible Li-CO$_2$ batteries.

**Methods**

**First-principles calculations.** All first-principles calculations were performed using the Vienna ab initio simulation package (VASP) with the projector augmented wave method and Perdew–Burke–Ernzerhof (PBE) generalized gradient approximation exchange-correlation functional.$^{46–48}$ The cutoff energy was set to 400 eV after a series of tests, and the criteria were set as $10^{-5}$ eV for energy and 0.05 eV/Å for force. The Brillouin zone was sampled using a Monkhorst–Pack 3 × 3 × 1 k-point grid, and the Grimme-D3 approach was applied to describe the dispersion interactions.$^{49}$ The reaction pathways and transition states were located using the double-ended surface walking (DESW) and constrained Broyden dimer (CBD) methods, as implemented in the LASP software.$^{34,35}$ All transition states have been verified by using vibrational frequency calculations (only one imaginary frequency). Note that these methods can determine a low-energy pathway linking two minima even without iterative optimization of the path, from which the transition state (TS) can be located readily.

**Structure models.** The lattice parameters of bulk Ru and Ir are optimized to be $a = b = 2.719$ Å, $c = 4.297$ Å, and $a = b = c = 3.872$ Å, respectively, which are consistent with experimental values. Two metal typical surfaces, i.e., Ru (111) and Ir (111), were constructed using 2 × 4 × 1 supercells, respectively. A vacuum region of 15 Å thickness along the z direction was chosen to eliminate the interactions between neighboring surfaces; five explicit DMSO molecules fill the gap to provide the experimental density of $\rho = 1.1$ g/cm$^3$. The top layer, the adsorbates, and all DMSO molecules are allowed to relax while the remaining atoms are fixed during the calculations. For the Ru (111) and Ir (111) surfaces, we first perform
10 ps AIMD simulations to obtain explicit DMSO structures. Then, adsorbates were placed on the metal surfaces for further study of the CO$_2$ electrochemical processes.

**Slow-growth simulations.** The slow-growth method was used to sample the free-energy change during the disproportionation reaction.$^{50,51}$ Nose-Hoover thermostat was adopted to keep temperature at 300 K.$^{52}$ The corresponding increment speed of the CV was within the range between 0.0003 and 0.0004 CV/step, and the simulation time ranged from 5 to 10 ps depending on the length of the reaction pathways. We performed several independent slow-growth simulations for each step, and all results revealed that the disproportionation pathway ($2^\text{CO}_2 \rightarrow ^*\text{CO}_3 + ^*\text{CO}$) is more energetically favorable than the dimerization pathway ($2^\text{CO}_2 \rightarrow ^*\text{C}_2\text{O}_4$). In addition, we also conducted slow-growth simulations up to 50 ps and found no impact on determining the dominant pathway.

**Free energy calculations.** The free energy change ($\Delta G$) for each elemental step was calculated by

$$\Delta G = \Delta E + \Delta E_{ZPE} - T\Delta S$$

where $\Delta E$, $\Delta E_{ZPE}$ and $\Delta S$ are the total electronic energy difference, zero-point energy difference and entropy change ($T = 298$ K), respectively. For adsorbates, all 3N degrees of freedom were treated as harmonic vibrations, while the contributions from the catalyst surfaces were neglected. For CO$_2$, the adsorption energy can be calculated according to the following equation,

$$E_{\text{ads}} = E_{\text{total}} - E_{\text{slab}} - E_{\text{adsorbate}}$$  \hspace{1cm} (1)

where $E_{\text{total}}$ represents the electronic energy of the total system, $E_{\text{slab}}$ is the energy of the adsorbate-free slab, and $E_{\text{adsorbate}}$ represents the energy of the adsorbate moiety.

**Declarations**

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**Author contributions**

Y.L. designed the research, X.Z, Y.W. demonstrated the initial idea and collected all the data. X.Z, Y.W. and Y.L. wrote the paper and all authors commented on it.

**Competing financial interests**

The authors declare no competing financial interests.
Additional information

Supplementary information accompanies this paper at http://www.nature.com/naturecommunications

Correspondence and requests for materials should be addressed to Y. W or Y.L.

Data availability

The authors declare that the data supporting the findings of this study are available within the paper and its supplementary information files

Code availability

The computational codes used in this work are available from the corresponding author on reasonable request.

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Figures
**Figure 1**

**Adsorption, disproportionation, and dimerization of CO$_2$ on Ru and Ir catalysts.** (a) Structures and possible adsorption sites of the Ru(0001) (left) and Ir(111) (right) surfaces. (b) The most stable CO$_2$ adsorption configurations of Ru(0001) and Ir(111) in vacuum (upper) and DMSO solvent (bottom). C, O, S, H, Ru, and Ir are represented by gray, red, yellow, white, green, and dark cyan spheres, respectively. (c, f) Energy barriers of C–C coupling on (c) Ru(0001) and (f) Ir(111), in which the DESW and CBD methods are employed. The inserts are geometric structures of the initial state (IS), transition state (TS), and final state (FS). (d, e) Free energy profiles of the (d) CO$_2$ disproportionation and (e) dimerization pathways on Ru(0001). (g, h) Free energy profiles of the (g) CO$_2$ disproportionation and (h) dimerization pathways on Ir(111).
**Figure 2**

Free energy diagrams of CO₂ reduction (discharging process) on the (a) Ru(0001) and (b) Ir(111) surfaces. Insets display geometric structures of free slabs, adsorbates, and key transition states that are highlighted by dashed boxes.
Figure 3

**Constant-potential energy profiles.** (a, b) Total energy of the absorbed *LiCO₃ and *CO species of (a) Ru(0001) and (b) Ir(111) as a function of potential. (c, d) Free energy changes of discharge elementary reactions of (c) Ru(0001) and (d) Ir(111) based on the constant potential method.
Figure 4

Energy profiles of oxidative decomposition of Li$_2$CO$_3$ and carbon. (a, b) Calculated energetic profiles of the charging process of (a) Ru(0001) and (b) Ir(111). (c) Energy barriers for the oxidative decomposition of a C$_6$ cluster to form *C$_5$ and *CO on Ru(0001) and Ir(111). (d) Energy barriers for *CO oxidation under different *CO and *O coverages.

Supplementary Files

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