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Synergized Multimetal Oxides with Amorphous/Crystalline Heterostructure as Efficient Electrocatalysts for Lithium–Oxygen Batteries

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1. Introduction

Aprotic lithium–oxygen (Li–O₂) batteries (LOBs) have emerged as promising alternative candidate for practical electric vehicle and large-scale energy storage applications by virtue of their high theoretical energy density (~3500 Wh kg⁻¹), low cost, and green active materials (O₂) for the cathode.[1,2] However, LOBs still suffer from the large polarization, low rate capability, and poor cyclability, which mainly originate from the sluggish kinetics of oxygen reduction reaction (ORR) and oxygen evolution reaction (OER), closely related to the formation and decomposition of insulated Li₂O₂ at the cathode.[3–6] An active bifunctional electrocatalyst with high stability is highly required to address these issues faced in the cathode of LOBs.[3,5,7,8]

Various catalysts, including noble metals,[9–11] carbonaceous materials,[7,12–14] and metal oxides,[15–17] have been explored as electrocatalysts for oxygen electrodes of LOBs. Nevertheless, high cost and scarcity of noble metals (such as Pt, Au, and Ru) limit their extensive applications. Due to the advantageous features of low cost, high surface area, sufficient pore volume, and easy functionalization, carbonaceous materials have been widely studied in LOBs. However, carbon tends to be easily oxidized at high potentials during charging process. Moreover, discharge products Li₂O₂ and LiO₂ can react with carbon to form insulating Li₂CO₃ layer, which obstructs electron transfer and impedes further reaction. This results in a voltage polarization during charging process and a degradation in the cycling lifespan.[18–20]

As such, transition metal oxides, especially earth-abundant first-row of 3d metal-based oxides, which are capable of catalyzing the formation and decomposition of discharge-product Li₂O₂ in LOBs, have received increasing attention in LOBs.[15,16,21,22] Compared with unary and binary metal oxides, trimetallic oxides, especially those featured with the introduction of a third metallic element with high valence, can achieve effectively modulated electronic structure, optimizing the adsorption energy of reaction intermediates and thereby promoting the catalytic activity.[23,24] For example, Sargent and co-workers reported that introduction of non-3d metal W with high-valence...
can modulate 3d metal (Fe and Co) oxides, yielding a favorable local chemical environment in line with electronic structure for promoting catalytic activity toward OER in alkaline electrolyte.[25] Li and co-workers also revealed that doping of Mo and V into the Co-based layer double hydroxide could modify the electronic structure of Co that is beneficial for the OER. The doped Mo itself is also an active site for the hydrogen evolution reaction, thus showing high bifunctional electrocatalytic performance in water splitting.[26] Besides, Yu and co-workers synthesized amorphous NiFeMo oxides, which delivered advanced performance for OER due to the formed active oxy(hydroxide) resulting from surface self-reconstruction in the process of OER.[27] However, the incorporation of foreign metallic elements could usually lead to undesired separated and independent phases due to thermodynamic immiscibility of different metallic elements, giving rise to unfavorable electrocatalytic activity. Therefore, the rational design and synthesis of electroactive multimetal oxides remains a great challenge. Furthermore, the dependence relationship between different elements and synergistic effects in electrocatalytic activity are yet to unveil.

In this work, we report a unique trimetallic CoFeCe oxide with amorphous/crystalline heterostructure. With optimal control over the content of Co, Fe, and Ce, highly active CoFeCe oxides with well-balanced thermodynamics and kinetics can be obtained. Typically synthesized structure endows CoFeCe oxide-based LOBs with excellent electrochemical performance (a low overpotential of 0.95 V and a high initial discharge capacity of 12 340 mAh g$^{-1}$), and remarkably enhanced cycling stability (over 2900 h). As revealed by combined experimental analysis and density functional theory (DFT) calculation, four key factors including synergistic interaction between oxide components, amorphous-crystalline domains, unique heterostructure with minimized lattice mismatch, and the enhanced adsorption of intermediate LiO$_2$ are vital to the catalytic activity of CoFeCe oxides. To the best of our knowledge, this is the first time that trimetallic metal oxides with amorphous–crystalline heterostructure are designed to be an effective electrocatalyst for the oxygen cathode of Li–O$_2$ batteries.

2. Results and Discussion

The preparation of trimetallic CoFeCe oxide is illustrated in Figure 1a. Briefly, the synthesis process involves a facile one-step gentle solvothermal reaction in ethanol without further annealing in order to obtain homogeneous CoFeCe oxides. The X-ray diffraction (XRD) patterns of as-prepared ternary oxides of CoFeCe with different composition are shown in Figure 1b and Figure S1 in the Supporting Information, while that of binary oxide of CoFe is also included for comparison. The diffraction peaks of all samples matched well with those of Fe$_2$O$_3$ (PDF 33-0664). It should be noted that there are no obvious peaks corresponding to cobalt oxide and cerium oxide, which may be attributed to very small size or even amorphous structure of cobalt oxide and cerium oxide. Besides, we checked carefully the changes in the peak position of the XRD pattern for CoFeCe-2 in detail. As shown in Figure S2 and Table S1 in the Supporting Information, compared with the standard diffraction peaks of Fe$_2$O$_3$ (PDF 33-0664), three peaks of CoFeCe-2 ascribed to (113), (024), and (224) of Fe$_2$O$_3$ show a small shift to lower angle. As we all know, the atomic radius of Ce (182 pm) is much larger than that of Co (125 pm) and Fe (126 pm). The peak shift to low angle can be attributed to the doping of Ce into Fe$_2$O$_3$. As shown in the scanning electron microscope (SEM) images (Figure 1c; Figure S3, Supporting Information), the CoFeCe oxides and CoFe oxide possessed typical nanosheets structure, which could expose more catalytic active sites and offer more spaces for the accumulation of discharge products.

![Figure 1.](https://example.com)
The transmission electron microscope (TEM) image (Figure 2a) reveals that the typical CoFeCe-2 oxide is of nanosheets structure with an average thickness of 3–4 nm. The high-resolution TEM (HRTEM) image (Figure 2b) clearly demonstrates the interplanar spacing of 0.267 and 0.155 nm, corresponding to (104) and (214) planes of Fe2O3, respectively. Other two explicit lattice fringe spacings of 0.312 and 0.218 nm, can be indexed to (111) plane of CeO2 and (200) plane of CoO with a clear interface, respectively. Furthermore, in line with crystalline domains, amorphous domains can also be clearly observed, which manifests that the trimetallic oxide of CoFeCe-2 is of hybrid amorphous/crystalline nanostructure. The selected area electron diffraction (SAED) pattern (Figure 2c) further shows the coexistence of (111) plane of CeO2, (200) plane of CoO, and (104) and (100) planes of Fe2O3. The corresponding energy dispersive spectroscopy (EDS) mappings verify that the elements of Co, Fe, Ce, and O distributed uniformly in the as-prepared composite (Figure 2d). DFT calculations were implemented to study the interfaces between the three oxides and the trimetallic crystal structure. In this work, Fe2O3 has a trigonal crystal structure, while CoO and CeO2 possess cubic crystal structure. Three kinds of magnetic structures, including ferromagnetic (FM) state, antiferromagnetic (AFM) state, and paramagnetic (PM) state are taken into consideration. The total energies of different configurations are summarized in Table S2 in the Supporting Information. The DFT calculations reveal that the total energies of AFM state for Fe2O3 and CoO are 0.36 and 0.10 eV per unit lower than those of FM and PM states, respectively. For CeO2, the AFM state exhibits the same total energy with those of FM and PM states, indicating that these three states calculations are effective. Calculation results show that the AFM state is the most stable configuration with the lowest energy. The calculated lattice parameters are listed in Table S3 in the Supporting Information, in good agreement with the experimental results. The CoO and CeO2 have 1.98% and 1.60% lattice mismatch from calculation and experiment results, respectively. Low lattice mismatches convey low interface resistance and facilitate electron transfer between the two phases. This proved the great possibility of constructing CoO–CeO2 heterostructure with high matching degree. During the preparation of trimetallic CoFeCe-2 oxide, the CeO2 can act as a buffer to reduce the mismatch and dislocations between the Fe2O3 and CoO lattices, improving interface stability and electrochemical performance of CoFeCe oxide.

To further explore the surface chemical composition and the bonding states of the as-prepared samples, X-ray photoelectron spectroscopy (XPS) measurements were carried out. As shown in Figure 3a and Figure S4a in the Supporting Information, for the high-resolution Co 2p spectra, the peak situated at 784.2 eV can be indexed to Co2+, and the peak at 780.6 eV are ascribed to Co3+. Furthermore, the peak center at 777.4 eV is related to the nonstoichiometric CeO2 resulted from Ce-doping.
(denoted as Ce–CoOₓ), indicating a synergistic interaction between cerium and cobalt atoms. As can be seen in the corresponding histograms of different components, the relative content of Ce–CoOₓ decreases while that of Co²⁺ increases with the increasing of cerium content from CoFeCe-1 to CoFeCe-3. Low-valence Co²⁺ has proven to be propitious to improve the catalytic activity toward the oxygen evolution reaction. For the Fe 2p spectra (Figure 3b; Figure S4b, Supporting Information), two strong doublets at 720.4/710.9 eV and 717.2/707.1 eV are associated with Fe³⁺ and Fe²⁺, respectively. The peak situated at 704.7 eV can be confirmed to be FeOₓ caused by Ce doping (denoted as Ce–FeOₓ), suggesting that there is a synergistic effect between cerium and iron atoms. The relative content of Fe³⁺ increases with the increasing of cerium content from CoFeCe-1 to CoFeCe-3 and the content of Ce–FeOₓ is the highest in CoFeCe-2 as can be seen in the histogram of different components. The Ce 3d spectra in Figure 3c and Figure S4c in the Supporting Information could be deconvoluted into eight peaks, of which two peaks situated at 904.6 and 886.2 eV are assigned to Ce³⁺, and the peaks situated at 901.2 and 882.5 eV correspond to Ce⁴⁺, the others are satellite peaks. The Ce 3d peaks shift toward higher binding energies, while the relative content of Ce⁴⁺ with respect to Ce³⁺ increases from CoFeCe-1 to CoFeCe-3, implying a synergistic effect among cerium, cobalt, and iron atoms. The O 1s spectra (Figure 3d; Figure S4d, Supporting Information) can be fitted to two distinct peaks. The peaks at 529.8 and 531.6 eV could be ascribed to lattice oxygen and oxygen vacancy, respectively. The content of oxygen vacancy increases from CoFeCe-1 to CoFeCe-3, consistent with the Ce⁴⁺ content change among the samples. Notably, a new peak situated at 534.3 is clearly observed for CoFeCe-2, which could be attributed to adsorbed oxygen, suggesting a chemical coupling between oxide components. The specific proportion of constitute element for CoFeCe-X (X = 1, 2, 3, 4, 5) oxides obtained from XPS analysis are presented in Figure S5 in the Supporting Information. XPS results reveal that the content of Co in CoFeCe-2 is highest, reaching up to 25.62 wt%.

As shown in Figure 4a, the 2032-type LOBs consisted of a metal lithium foil anode, a glass-fiber filter (GFC), and a cathode with as-prepared catalysts. From the typical cyclic voltammetry (CV) plots (Figure 4b; Figure S6a, Supporting Information), CoFeCe-2 oxygen electrode demonstrates an ORR onset potential of 2.78 V, which is higher than those of other oxygen electrodes, suggesting a higher electrocatalytic activity of CoFeCe-2 toward ORR. In addition, a small anodic peak indicating the decomposition of Li₂O₂ was situated between 3.2 and 3.6 V. Comparing the enlarged CV curves (inset in Figure 4b and Figure S6a in the Supporting Information), we can see a lower onset potential and higher anodic peak of CoFeCe-2, implying a better electrocatalytic activity toward OER. Figure 4c and Figure S6b in the Supporting Information display first full discharge/charge curves of the LOBs assembled with CoFeCe-X (X = 1, 2, 3) oxide at a fixed current density of 100 mA g⁻¹, the profile of binary CoFe oxide is also included for comparison. The capacities of trimetallic CoFeCe-X (X = 1, 2, 3) oxide are significantly higher than that of CoFe oxide. The CoFeCe-2 electrode delivers a highest discharge capacity of 12 340 mAh g⁻¹ among the as-prepared trimetallic oxide samples. In particular, the CoFeCe-2 cathode shows a lower charge voltage than other comparative samples. In detail, the charge voltage of CoFeCe-2 is only 3.65 V at the specific...
capacity of 3000 mAh g\(^{-1}\), as compared to 4.08 V for CoFe, 4.26 V for CoFeCe-1, and 4.02 V for CoFeCe-3. The significantly low overpotential plays a positive role in improving the battery round-trip efficiency, as well as mitigating the decomposition of electrolyte. The discharge–charge durability of the LOBs based on the as-prepared catalysts was examined under a current density of 100 mA g\(^{-1}\) and at a fixed specific capacity of 1000 mAh g\(^{-1}\). As displayed in Figure 4d and Figure S6c in the Supporting Information, the CoFe electrode merely lasts less than 255 h (12 cycles) with a serious increasing of discharge–charge voltage gap, from \(\approx 2.0\) V at \(< 150\) h to 5.5 V at the terminated 255 h. In contrast, CoFeCe-X (X = 1, 2, 3) electrodes show much improved durability, among which the CoFeCe-2 electrode can successfully sustain for 2900 h (up to 150 cycles) without any decrease in the specific capacities, while maintaining a smaller voltage gap of \(\approx 1.7\) V. Figure 4e shows the rate capability of the CoFeCe-2-based LOBs under the current density of 100, 200, 500, and 1000 mA g\(^{-1}\) and at the fixed specific capacity of 1000 mAh g\(^{-1}\). The CoFeCe-2 demonstrates outstanding recovery ability upon the current density increasing from 100 up to 1000 mA g\(^{-1}\) and then back to 100 mA g\(^{-1}\). Notably, the CoFeCe-2 shows a negligible loss in the discharge/charge capacity after cycling for 560 h upon the current density return back to 100 mA g\(^{-1}\), and maintaining a stable voltage gap of \(\approx 1.30\) V. The electrochemical performance of the trimetallic CoFeCe oxide in this work and those of reported typical metal oxides\(^{[30,35–41]}\) are summarized in Figure 4f and Table S4 in the Supporting Information. The discharge capacity and cycling stability of CoFeCe-2 in this work is among the highest ones.

In order to further analyze the catalytic activity and durability of the CoFeCe-2, the morphology, structure, and composition changes after first discharge–charge cycle have been studied by using SEM, XRD, and XPS (Figure 5). After the first discharge, the surface of the CoFeCe-2 electrode is completely covered by discharge products with layered structure (Figure 5a). Propitiously, all layered discharge products disappear and the initial
The nanosheet structure of the CoFeCe-2 is re-exposed after the first charge (Figure 5b), which promotes the further reaction in the subsequent discharge–charge processes. As demonstrated in Figure 5c, there is no difference in the diffraction peaks of the CoFeCe-2 electrode after the first discharge process from those of the electrode after the first charge process. Besides, the diffraction peaks situated at 55° and between 40° and 45° can all be assigned to the characteristic peaks of carbon paper, which acted as a current collector. The other diffraction peaks are in well agreement with the standard XRD pattern of FeO3, and no peaks related to Li2O2 or Li2CO3 can be observed after the first discharge. The Li 1s XPS spectra (Figure 5d) confirm that the discharge product on the CoFeCe-2 electrode is Li2O2, which is completely decomposed after first charge. It should be noted that the formed Li2O2 on the CoFeCe-2 electrode as confirmed by XPS is amorphous since no discernable peaks related to Li2O2 can be observed in XRD pattern (Figure 5c). The results indicate that the CoFeCe-2 electrode possesses high electronic conductivity and structural stability toward the formation and decomposition of Li2O2. Figure 5e displays the electrochemical impedance spectra (EIS) of CoFeCe-2 electrode after first discharge and charge and the equivalent circuit from the simulation of Nyquist plot included. The EIS results of other CoFeCe-X (X = 1, 3, 4, 5) and CoFe electrodes are included in Figure S7 and Table S5 in the Supporting Information. All the samples show very similar ohmic resistance (Ro) either after the first discharge or after the first charge but hierarchically different charge transfer resistance (Rct). Specifically, the CoFeCe-2 electrode shows Ro of 298.77 Ω after the first discharge and 153.34 Ω after the first charge, which are smaller than those of other oxide electrodes. The smaller charge transfer resistance in CoFeCe-2 implies the improved kinetics of ORR/OER on the CoFeCe-2 electrode in the LOBs.

To further explore the structural stability of CoFeCe-2 with extended cycling, the Li–O2 battery with this electrode after cycling for 2000 h was carefully disassembled and examined using ex situ XPS and SEM. By comparing the XPS spectrum (Figure S8, Supporting Information), it can be seen that the CoFeCe-2 maintains same components after cycling for 2000 h. The relative contents of Ce–CoOx and Ce–FeOx are decreased, the contents of Co2+ and Fe3+ are increased, and those of Ce4+ and oxygen vacancy show feeble changes after extended cycling. As can be observed in the SEM images (Figure S9, Supporting Information), the CoFeCe-2 remains nanosheets structure after cycling for 2000 h. The results suggest that the trimetallic CoFeCe-2 oxide demonstrates good structural stability during the long-term discharge–charge cycling in the Li–O2 batteries.

To further understand physical properties of trimetallic CoFeCe oxide and elucidate the possible effect of CoFeCe oxide on the nucleation and growth of Li2O2, first-principle calculations were performed based on DFT. The calculation results (Figure 6a) show that FeO3 and CeO2 exhibit semiconducting behavior with 0.90 and 0.98 eV bandgap, respectively. In contrast, CoO demonstrates metallic character with excellently electronic conductivity. The presence of CoO enhances the electronic conductivity of CoFeCe oxide. Based on the XRD results in Figure S2 in the Supporting Information, the CoFeCe model is built further with doping strategy. Ce and Co are substituting for Fe in Fe2O3 (Figure S10a,b, Supporting Information). Two different doping contents of Ce and Co (8% and 16%) are taken into consideration. The density of states (DOS) calculations (Figure S10c,d, Supporting Information) reveal that CoFeCe exhibits metallic behavior with electronic density of states cross the Fermi-level. The main content of total DOS near Fermi-level is Co partial DOS (PDOS) and O PDOS, indicating that Co and O bonding contribute to the metallic behavior. Moreover, CoFeCe with 16% Co doping presents better electronic conductivity than that of 8% Co doping, indicating that Co can effectively improve the conductivity of CoFeCe. The adsorption of intermediate LiO2 is a critical factor to influence the characteristic of Li2O2 during discharge process, the adsorption energy of LiO2 on different constituents of CoFeCe oxide was calculated (Figure 6b). The calculation results show that CoO (111) plane and CeO2 (110) plane display larger adsorption energies of −4.01 and −3.84 eV than that of FeO3(001) plane (−2.92 eV). These results verify that the presence of CoO and CeO2 can improve the adsorption of LiO2, promoting the subsequent formation of amorphous Li2O2 and in turn affecting the whole catalytic activity of Fe2O3-based material. Furthermore, the charge density difference was calculated to distinctly analyze the charge variation during the adsorption process of LiO2 (Figure 6c,d). When LiO2 is adsorbed onto the (001) plane of FeO3 (110) plane of CeO2, the charge would rather be distributed around Li atom than O atoms, indicating Li atoms in Li2O2 are key contributors to the electron gain and loss during the ORR on FeO3 and CeO2. By contrast, bigger increased charged areas are mainly observed between Co site and O atoms in Li2O2 (marked in yellow), indicating that the massive Co∗∗ plays a very important role in the electron-withdrawing ability of CoFeCe oxide to Li2O2. To reveal the underlying mechanism of the enhanced reactivity of CoFeCe, the adsorption energy of Li2O2 on (001) plane for FeO3, (110) plane for CeO2, and (111) plane for CoO is further calculated (Figure S11, Supporting Information). Adsorption energy calculations reveal that the absolute value of Gibbs free energy change for Li2O2 formation can be ordered as: CoO (2.04 eV) < CeO2 (2.55 eV) < FeO3 (2.68 eV). This result indicates that both CeO2 and CoO can reduce the overpotential and facilitate the formation of uniform Li2O2 by promoting the adsorption of LiO2. In summary, CoO enhances efficiently the overall electronic conductivity and strong LiO2 adsorption; CeO2 improves the lattice matches upon the formation of CoO–CoO heterostructure, reducing energy barrier for charge transfer, and while the adsorption of LiO2 is also promoted. These factors enable trimetallic CoFeCe oxide with well thermodynamics and kinetics for the formation of decomposable amorphous Li2O2.

3. Conclusion

In conclusion, we rationally construct trimetallic CoFeCe oxide with amorphous/crystalline heterostructure on carbon paper acting as a cathode for the LOBs. The LOBs with thus-deriv ered CoFeCe cathode manage to deliver a low voltage gap of only about 0.95 V, a considerable initial specific capacity of 12 340 mAh g−1 at 100 mA g−1 and an enhanced cycling stability of more than 2900 h at a fixed specific capacity of 1000 mAh g−1 and a current density of 100 mA g−1. The high electrocatalytic
activity of CoFeCe oxide can be attributed to the following reasons: 1) the unique amorphous/crystalline heterostructure with minimized lattice mismatch is in favor of reducing energy barrier for charge transfer during the catalytic reactions; 2) the coexistence of amorphous and crystalline domains exposes more intrinsic highly active sites; 3) the presence of CoO provides high electrical conductivity; 4) the adsorption of key intermediate LiO$_2$ is enhanced on the surface as revealed by the DFT calculation, leading to the formation of amorphous Li$_2$O$_2$ that is prone to be decomposed. Given the high performance and facile fabrication, the designed trimetallic oxide holds a great potential to be a promising electrocatalyst for the LOBs. This design strategy can be expanded to prepare other multimetal oxides and applied in other fields of energy harvesting, conversion, and storage.

4. Experimental Section

**Synthesis of CoFeCe Oxide on Carbon Paper**: A piece of 2 × 4 cm carbon paper was cut off, and washed with deionized water and absolute ethanol sequentially for 3 to 6 times to remove impurities. The washed carbon paper was then dried at 60 °C for later use. 0.55 g FeCl$_3$·6H$_2$O, 0.35 g CoCl$_2$·6H$_2$O, and 0.1 g CeCl$_3$·7H$_2$O were dissolved in 35 mL absolute ethanol under vigorous magnetic stirring for 15 min to obtain a homogeneous mixed solution. Then, the mixed solution and the cleaned carbon paper were transferred into a 50 mL Teflon-lined stainless-steel autoclave, sealed, and heated at 160 °C for 900 min. The resultant carbon paper was washed with deionized water and absolute ethanol for several times to remove excess unreacted reagents, and then was dried at 35 °C for 10 h, being noted as CoFeCe-2. For comparison, CoFeCe-1 and CoFeCe-3 were synthesized by adding 0.05 and 0.15 g of CeCl$_3$·7H$_2$O, respectively, to the solution dissolved with 0.1 g CeCl$_3$·7H$_2$O. Besides, CoFeCe-4 and CoFeCe-5 was also prepared with different ratios of FeCl$_3$·6H$_2$O to CoCl$_2$·6H$_2$O (0.35 g/0.55 g and 0.2 g/0.7 g, respectively) while keeping the mass of CeCl$_3$·7H$_2$O (0.1 g) unchanged, aiming to explore the influence of cobalt and iron contents on the structure and performance of composites.

**Materials Characterization**: XRD patterns were performed to analyze the crystal structure of CoFeCe oxide (Bede Scientific Ltd., UK; Cu Kα radiation). Morphology and microstructure of the resulting CoFeCe oxide were investigated on SEM (Hitachi SU8010) and TEM (Tecnai F20). The chemical state and binding environment of elements in CoFeCe oxides were analyzed by XPS (VG ESCALAB MKII).

**Electrochemical Measurements**: CoFeCe oxide was in situ grown on the carbon paper with a mass loading of about 0.6 mg cm$^{-2}$. 1 m lithium bis(trifluoromethane sulfonamide, LiTFSI) was fully dissolved in ethylene glycol dimethyl ether (TEGDME) to make the electrolyte. The 2032-type
coin battery involved a metal lithium foil anode, a GFC (Whatman) soaked in electrolyte, and a cathode. All measurements were performed in a sealed self-prepared glass bottle filled by O₂ with ultrahigh purity to test their electrochemical properties. The fixed specific capacity and current density were normalized by the calculated mass of typical catalyst.

Density-Functional Theory Calculations: Plane-wave periodic DFT calculations for this work were performed by using the Vienna ab initio simulation package (VASP).[42,43] The generalized gradient approximation (GGA)[44] of Perdew–Burke–Ernzerhoff (PBE)[45] was employed to describe the exchange–correlation potential and solve the Kohn–Sham equations. The Hubbard U correction was used to modify the tight-binding error and enhance the description of the strong correlation of transition metal–electrons. The U values were chosen according to the previous theoretical studies, 3.9 eV for Fe,[46] 3.7 eV for Co,[47] and 5 eV for Ce.[48] The plane-wave cutoff energy was 500 eV and the K-point meshes in structural relaxation of FeO₉, CoO, and CeO₂ were 9 × 9 × 5, 13 × 13 × 13, and 9 × 9 × 9, respectively. The crystal structures were fully relaxed until geometry optimization energy converged to 1 × 10⁻⁵ eV per atom and residual forces to 0.01 eV Å⁻¹ on each atom. Spin orbital coupling (SOC) was adopted. The magnetic of Fe₂O₃, CoO, and CeO₂ compounds were taken into consideration and FM state, AFM state, as well as PM state were calculated. First-principles calculations show that the AFM configuration was the most stable state with the lowest energy among these three configurations. When building the slab modeling, the vacuum layer was set 15 Å to avoid the interactions between the periodic layers.

The adsorption energies of LiO₂ and Li₂O₂ were calculated as follows

\[ \Delta E_1 = E_{\text{oxides}} - \{E_{\text{LiO}} + E_{\text{oxides}}\} \] (1)

\[ \Delta E_2 = E_{\text{oxides}} - \{E_{\text{LixO}} + E_{\text{Li}}\} \] (2)

where \( E_{\text{oxides}} \), \( E_{\text{LiO}} \), \( E_{\text{LixO}} \), and \( E_{\text{Li}} \) represent the total energy of LiO₂ adsorbed on oxides, Li₂O₂ adsorbed on oxides, oxides, LiO₂, and Li, respectively.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
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Research data are not shared.

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