

Research Article

On a New Point of View Toward the Mechanism of Those Electrochemical Reactions Driven by the External Potential

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Abstract

In the search of electrochemical reaction, uncovering the reaction mechanism plays a decisive role in analyzing the production of diverse products. We believe that all types of electrochemical reaction driven by external potential should follow a general process. In this paper, we propose that in those electrochemical reactions driven by the external potential, the formation of radicals via electron transfer between electrode and the species carrying electric charge serves as the first step, triggering subsequent reactions. This suggestion might be considerable electrochemical interest.

Keywords

Electrochemical Reaction, Reaction Mechanism, Electron-Transfer Step, Radical Reaction, Mechanistic Model

1. Introduction

The using of electrochemistry on synthetic chemistry, energy supply and removal of chemical pollution has a long history beginning with the decomposing water into hydrogen and oxygen by electrolysis using Volta's battery and which is still a hot topic until today. Electrochemistry offers an advantage of having no spent oxidant or reductant for disposal. However, electrochemical processes fell out of favour in the face of conventional chemical reactions because the outcome from electrochemistry was often far from the predictability. Understanding the mechanisms of these processes plays a critical role in designing reaction system to avoid the pitfalls.

Electrons, in electrochemical reaction, are transferred at an electrode singly, not in pairs. The primary reactive species to be generated by electron-transfer is usually considered to be either a delocalized radical-ion or a radical. [1] For various reactions, corresponding processes have been proposed for

understanding the outcome of electrochemical reactions, however, most of them are still in debate. In general, when the primary reactant species are neutral (without an electric charge), it is considered that these neutral species are going to achieve the electron-transfer with electrode in initial reaction step, forming a negatively or positively charged particle. For example, carbon dioxide (CO_2) molecule in CO_2 reduction reaction is considered to accept an electron from cathodic electrode to form $\text{CO}_2^{\cdot-}$ anion in the first step. [2] The standard potential for formation of $\text{CO}_2^{\cdot-}$ anion in an aqueous media is -1.90 V, [3] however, almost all products, including CO, C_1 , C_2 and C_3 , can form under a low potential of -1.0 V in experimental CO_2 reduction reaction. [4] This strongly suggests that the actual process of reducing CO_2 into various valuable products may not involve the formation of $\text{CO}_2^{\cdot-}$ anion.

In addition, it is widely accepted that in electrochemical

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Received: 2 September 2024; **Accepted:** 14 September 2024; **Published:** 29 September 2024



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nitrate (NO_3^-) reduction to ammonia (NH_3), the negatively charged NO_3^- ions are adsorbed on cathode surface in the reduction process for the formation of NH_3 or other products. [5] However, some experiments carried out using surface-enhanced infrared absorption spectroscopic, suggesting that nitrate ion adsorption on electrode surface only occurs

under positive potential. [6] Thus, in our opinion, it might be impossible for anions (NO_3^-) ions to be adsorbed on cathode surface in the reaction process because anions tend to move away from cathode under the external electric field, the cathodic electrode surface might be surrounded by cations and neutral particles during reaction process.

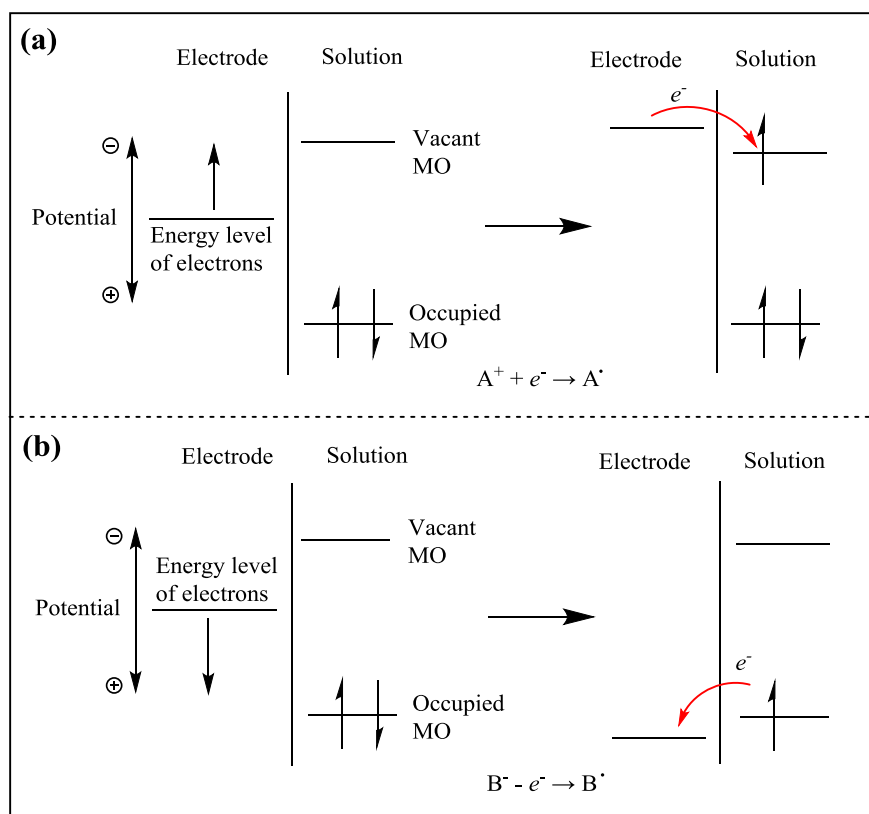


Figure 1. Representation of (a) reduction and (b) oxidation process of a species, A^+ and B^- , in solution for the occurrence of those electrochemical reactions required the applying of external potential. The molecular orbitals (MO) of species A^+ which is reduced into A^\cdot reducing radical on cathode surface are the highest occupied MO and the lowest vacant MO, the MO of species B^- which is oxidized into B^\cdot oxidizing radical on anode surface are the highest occupied MO and the lowest vacant MO as well. These correspond in an approximate way to the E_s^0 of the A^+/A^\cdot and B^-/B^\cdot couples, respectively.

In electrochemical reactions driven by the external potential, the external electric field on electrode exerts an electrostatic force to ions in electrolyte, which makes cations tend to move to cathode and anions tend to move to anode. It has been widely accepted that the primary adsorbed species on surface of electrode are some species with an electric charge (cations adsorbed on cathode and/or anions adsorbed on anode). [7] Therefore, the reactant species in electron-transfer steps (electrochemical reaction step) should be the species with an electric charge. Namely, cations are in favour of achieving electron-transfer with electrode of cathode, and anions are in favour of achieving electron-transfer with electrode of anode.

In the present paper it is shown that on the ground of the above discussion, if we assume that in initial step of electrochemical reaction requiring the driving of external potential, the species with an electric charge is firstly converted to a

reactive radical with an unpaired electron via electron transfer on the electrode as showed in Figure 1 and consider that this reactive radical can react with other radical or spin-paired species for bond forming or bond cleaving in following steps, we can obtain a well understanding of reaction mechanism and illuminating explanation of formation of various products in various types of electrochemical reactions.

In view of the radicals formed from species with an electric charge in initial electrochemical reaction step, we suggest that those radicals formed from positively charged species by accepting a single electron on cathodic electrode have a strong reducing property, it can attack the oxidizing radical on spin-paired species by abstraction or addition. Relatively, radicals formed from negatively charged species by donating a single electron on anodic electrode is a strong oxidizing agent, which can attack the reducing radical on spin-paired

species by abstraction or addition. Notice that radicals formed on anode or cathode also can dimerize to produce a new spin-paired product or intermediate in electrochemical reaction. In the following, several reactions as examples, are concerned, we wish to present a clear line of thought and the facts which have led us to this point of view, hoping that our assumption may be useful to the investigator in area of electrochemistry.

2. Concerning Nitrate Reduction Reaction

We start first with the point of view taken in the electrochemical nitrate reduction, which is a typical reduction reaction driven by the negative potential. There are two reactants: protons (H^+) and NO_3^- ions. The former one is positively charged, and the latter is negatively charged. It seems to us that on cathode surface, it is impossible for NO_3^- ions being absorbed on electrode surface to achieve electrons accepting, and it might be the protons to achieve this forming reactive H^\bullet radicals. As H^\bullet radical is a type of strong reducing agents, [7] which can react with the oxidizing group on NO_3^- , it is our opinion that the processes of NO_3^- reduction to various

products are a sequence of radical reactions with H radicals as illustrated in Figure 2. We assume that NO_3^- is initially converted into N-centred $\text{O}-\text{N}^{\bullet}=\text{O}$ radical (NO_2) by abstraction of O^{\bullet} from NO_3^- by H^{\bullet} radical (H^{\bullet} formed from H^+ by accepting an electron from electrode). An O-centred $\text{O}^{\bullet}-\text{N}=\text{O}$ radical (NO_2) may then be formed by displacement of electrons of this N-centred $\text{O}-\text{N}^{\bullet}=\text{O}$ radical. Following this, a radical dimerization reaction with H^{\bullet} radical may occur on NO_2 forming nitrite (HNO_2), which can be converted to a new N-centred $\text{N}^{\bullet}=\text{O}$ radical (nitrogen monoxide (NO), one side product and important intermediate in electrochemical NO_3^- -to- NH_3) by abstraction of $\text{O}-\text{H}$ from $\text{HO}-\text{N}=\text{O}$ by H^{\bullet} radical. In addition, the NO_2 may also react with H_2O forming HNO_3 and NO as shown in Figure 2 (blue line). If N-centred $\text{N}^{\bullet}=\text{O}$ radical undergoes a radical dimerization reaction with H^{\bullet} radical forming a spin-paired intermediate ($\text{HN}=\text{O}$), another side product (NH_2OH) and useful product (NH_3) may then be formed via stepwise reactions with reducing H^{\bullet} radicals. However, if two N-centred $\text{N}^{\bullet}=\text{O}$ radicals encounter and dimerize, a spin-paired intermediate ($\text{O}=\text{N}-\text{N}=\text{O}$) will form, N_2H_4 or N_2O molecule might be produced through radical reactions with H^{\bullet} radicals, but the O on N_2O might be removed by further reactions with H^{\bullet} radicals forming N_2 in final step.

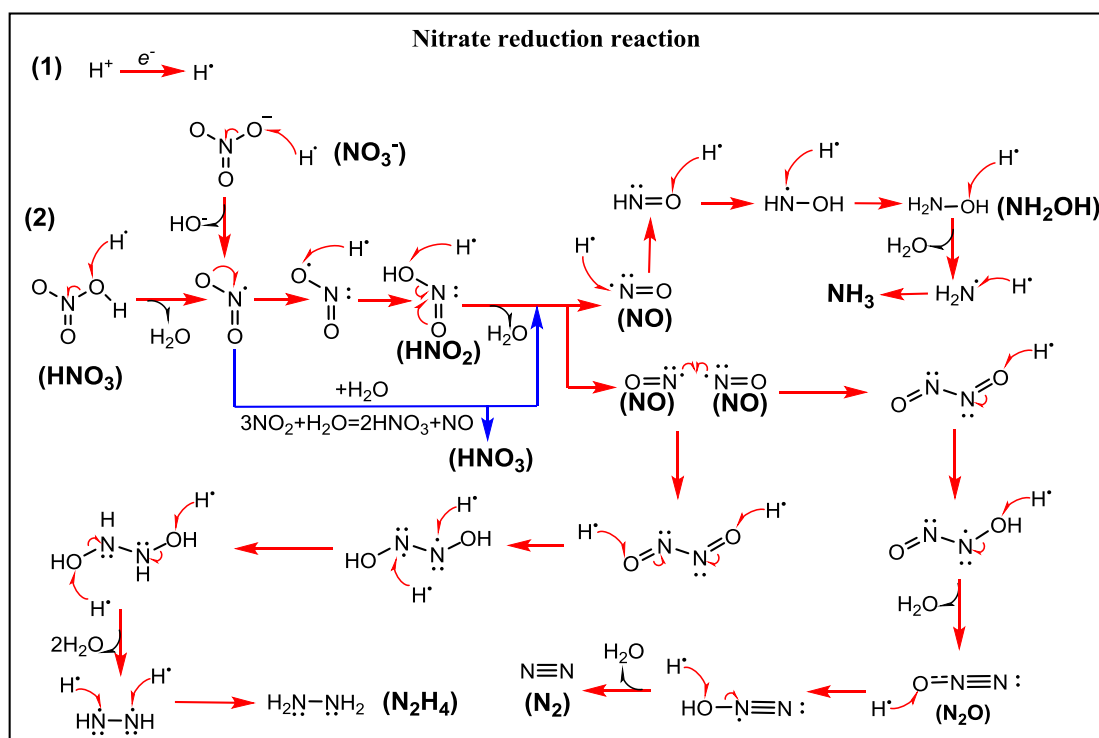


Figure 2. The proposed reaction pathways for nitrate reduction reactions; (1) proton (H^+) is converted into H^\bullet radicals via electron-transfer step, (2) the possible reaction pathway for electrochemical nitrate reduction reaction on cathodic bias; NO_3^- ions are converted into various products by H^\bullet radicals, which are formed via electron-transfer to proton from cathode under negative potential.

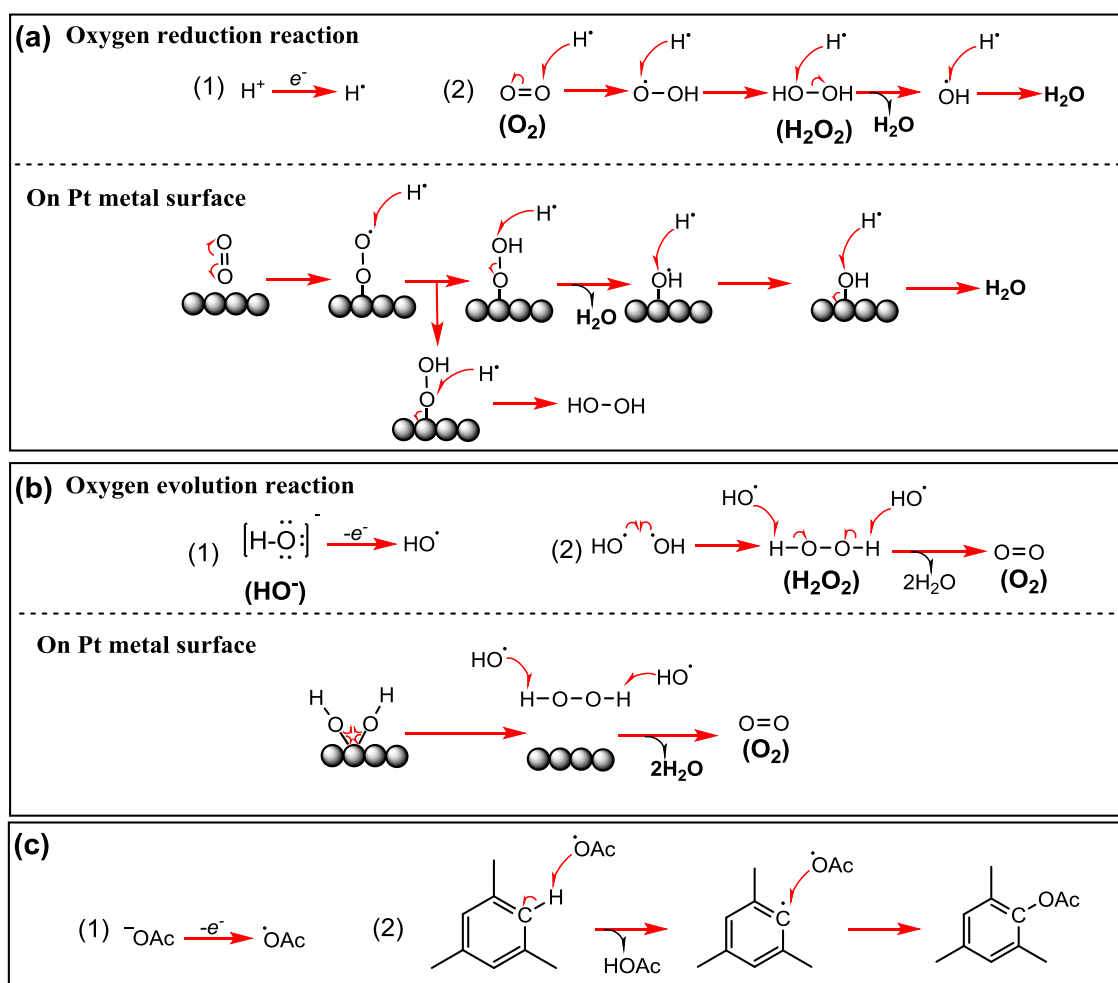


Figure 3. The proposed reaction pathways for oxygen reduction reaction and oxygen evolution reaction; a) reaction pathways for oxygen reduction reaction; O_2 molecules are converted into hydrogen peroxides or water by H^\bullet radicals, and Pt metal as catalysts can increase the reaction rate by activating O_2 into reactive radical state, b) reaction pathways for oxygen evolution reaction; this reaction starts with the conversion of HO^- ions into oxidizing HO^\bullet radicals by electron-transfer to anode, two HO^\bullet radicals may undergo dimerization forming hydrogen peroxide, which is then converted into O_2 molecule by abstraction of H^\bullet groups by another two HO^\bullet radicals. On Pt electrocatalysts surface, part HO^\bullet radicals formed via electron-transfer are in-situ bonded on surface atoms forming HO-Pt , which may be converted into O_2 molecule with stepwise reactions with HO^\bullet radicals. c) reaction pathways for α -substitution of methylbenzenes in acetic acid media, this reaction starts with ^-OAc ion conversion into $^\bullet\text{OAc}$ radical with strong oxidizing property, the reducing H^\bullet agent on a position of methylbenzenes forming α -substitution product with a further radical dimerization.

As it is impossible for NO_3^- ions to be absorbed on cathode during reaction process, and the conversion of a NO_3^- ion into NH_3 requires eight H^\bullet radicals, it is our opinion, furthermore, that those catalysts that can promote the formation of H^\bullet radicals will be beneficial for the reduction of NO_3^- ions to NH_3 . It is intriguing that, in practice, Pd metal is experimentally proved to be effective for the formation of H^\bullet radicals, [8] and that Pd metal cathode also can support a high selectivity of reduction of NO_3^- to NH_3 . [9, 10] Thus, it might be that the study of electrocatalysts for conversion of NO_3^- ions into NH_3 should focus on the improvement of formation of H^\bullet radicals (avoiding dimerization of H^\bullet radicals to form H_2 side-products), rather than the relationship between catalysts and NO_3^- ions.

3. Concerning CO_2 Reduction Reaction (CO_2RR)

There are two reactants in this reaction: protons (H^+) and CO_2 molecules. The assumption of formation of $\text{CO}_2^{\bullet-}$ anion in the initial step of electrochemical CO_2RR is doubtable as discussed above. Here, we have assumed that the electron-transfer may be achieved by protons, rather than CO_2 molecule. Protons receive electrons from cathode forming reducing H^\bullet radicals. As CO_2 molecules are inert and H^\bullet radicals are easy to dimerize to form H_2 , catalysts are required for this reaction to convert CO_2 molecules into active state for reaction spontaneously occurring. It is experimentally proved that Cu metal is active in this reaction and can produce a wide

range of products. We have assumed that in our previous publication, [11] Cu with single unpaired can activate CO_2 molecules into reactive C-centred radicals ($\text{O}=\text{C}^\bullet\text{-O-Cu}$), followed by various radical reactions with H^\bullet radicals and/or other type of radicals to form various products. See the detailed reaction processes for the formation of various products in our previous publication, [11] we will not discuss more in this work. Besides nitrate reduction reaction and CO_2 reduction reaction, we wish to discuss more reactions. The following treatments are several other types of electrochemical reactions.

4. Concerning Oxygen Reduction Reaction (ORR)

O_2 molecules and protons (H^+) are reactants in ORR. We believe that it is the proton that achieves electron-transfer with cathode forming reactive H^\bullet radicals in the initial step. Then, the O_2 is gradually reduced into hydrogen peroxide or water by H^\bullet radicals (Figure 3a). The radical addition of H^\bullet radical to an O_2 molecule leads to the formation of a $\text{O}^\bullet\text{-OH}$ radical, which is then converted into spin-paired hydrogen peroxide molecule (HO-OH) by dimerization with a H^\bullet radical. With further stepwise reactions of radical abstraction and radical dimerization with H^\bullet radicals, an O_2 molecule is gradually converted into two H_2O molecule.

Free H^\bullet radicals tend to dimerize into H_2 molecule and solubility of O_2 usually is low in electrolyte, these make the kinetics of ORR reactions much slow, and an efficient electrocatalyst is required to adsorb and activate O_2 molecule. [12] It is experimentally confirmed that Pt or Pd metals are active in this reaction. [13] Recent experimental studies have confirmed that O_2 molecule can react with surface atom of Pt metal. [14] This makes us assume that surface atoms of Pt metal might have the potential to adsorb and activate O_2 molecule into reactive O-centred radical ($\text{O}^\bullet\text{-O-Pt}$), which can make the reaction with H^\bullet radicals more convenient and faster. As shown in Figure 3a (on Pt metal surface), O_2 interacts with Pt to give reactive $\text{O}^\bullet\text{-O-Pt}$ intermediate, which then reacts with H^\bullet radical by dimerization to give H-O-O-Pt . Hydrogen peroxide (H-O-O-H) might be generated when H-O-O^\bullet group is abstracted by H^\bullet radical from H-O-O-Pt . Yet, if H-O^\bullet group of H-O-O-Pt is abstracted by H^\bullet radical forming H_2O and $\text{O}^\bullet\text{-Pt}$ intermediate, O_2 in this reaction pathway will be converted into H_2O with further reaction with H^\bullet radicals.

5. Concerning Oxygen Evolution Reaction (OER)

The following treatments focus on the electrochemical reactions driven by the positive potential. OH^- ions are only one reactant in OER and are negatively charged. Thus, it must be that under positive potential, OH^- ions lose electrons forming reactive O-centred radicals (HO^\bullet), which is a strong oxidizing agent. [15] As shown in Figure 3b, two free HO^\bullet radicals

dimerize to give a spin-paired hydrogen peroxide (HO-OH). Due to the strong oxidation of HO^\bullet , the HO-OH might be converted into O_2 molecule by abstraction of two H groups by another two free HO^\bullet radicals in final step.

It should be noticed that part noble metals as electrocatalysts (such as Pt) can improve the kinetics of this reaction. Recently, it is detected that OH is adsorbed on Pt surface at positive potential by using in-situ vibrational spectroscopy, in-situ X-ray absorption spectroscopy, and ex-situ X-ray photoelectron spectroscopy. [14, 16, 17] This makes us assume that OER on Pt metal surface follows the pathways as showed in Figure 3b (on Pt metal surface), two HO^\bullet radicals formed via electron-transfer step are in-site bonded on Pt surface forming H-O-Pt-O-H intermediate, which might result in the formation of H-O-O-H (the formation of O-O bond). Then, the H group of H-O-O-H might also undergo an attack by oxidizing HO^\bullet radical to give an O_2 and two H_2O molecules.

Besides the H^+ and HO^\bullet can be converted to relative reducing or oxidizing radicals on electrode by a single electron transfer, and then involving in sequence of radical reactions for formation of products in electrochemical reaction, we also assume that other types of positively or negatively charged species in electrolyte could achieve it as well. For example, methylbenzenes can be oxidized to a α -substitution product on anodic bias in acetic acid. [18] It is our assumption that in initial step, OAc^- with negative charge is converted to an oxidizing O-centred radical (OAc^\bullet) by removing a single electron to anode (Figure 3c), then C-centred radical could be made by abstraction of H from α position of methylbenzenes by OAc^\bullet radical. In final step, α -substitution product could then be formed by dimerization with another OAc^\bullet radical.

6. Conclusions

Thus far, we have already discussed several reaction processes of electrochemical reactions driven by external potential—based on our assumptions—including reduction reaction on cathodic bias and oxidation reaction on anodic bias. From reactant species to final products in these electrochemical reactions, the pathways are clear and straightforward. We hope that some experiments will carry out to proof those assumptions in our future work.

In addition, we believe that the electrocatalysts play a normal catalytic role in electrochemical reaction, such as activation of spin-paired reactant and/or supporting the dimerization reaction of radical (the formation of new chemical bond). [11, 19-21] The assumption of mechanism of electrochemical reaction as discussed above may be considered as different interpretations in the description of the process of electrochemical reactions. The viewpoint of conversion of ions into strong reducing or oxidizing radicals via electron-transfer, as well as the assumption of the radical reactions in process for formation of various products as above discussed, are hoped to find applications more widely to problems on the mechanism of electrochemical reactions.

Abbreviations

MO	Molecular Orbitals
OER	Oxygen Evolution Reaction
ORR	Oxygen Reduction Reaction
CO ₂ RR	CO ₂ Reduction Reaction

Acknowledgments

I would like to thank my mom for her encouragement for the publication of this work.

Author Contributions

Youyi Sun is the sole author. The author read and approved the final manuscript.

Conflicts of Interest

The authors declare no conflicts of interest.

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Research Field

Youyi Sun: Catalytic reaction mechanism, electrochemical reaction, renewable energy storage, electrochemical reaction mechanism, catalytic ammonia synthesis, Fischer-Tropsch reaction.