Spin Effect on Oxygen Electrocatalysis

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Oxygen involved reactions, including oxygen reduction (ORR) and oxygen evolution reactions (OERs), play a key role in electrochemical energy devices, such as fuel cells and metal–air batteries. Recent theoretical calculations and experimental investigations reveal that the energy loss in ORR/OER is closely related to the triplet O₂ generation/conversion step. However, the spin-related phenomena have long been neglected in understanding of the ORR/OER mechanism. This review highlights recent advances in understanding and application of the spin-related effect in oxygen electrocatalysis. It is demonstrated that the exchange interaction in magnetic catalysts can build a spin-selective channel to filter the electron spins with appropriate orientation in the O₂ generation/conversion step during ORR/OER. It is believed that the introduction of spin effect can establish a more comprehensive understanding of oxygen electrocatalysis and assist designing more reactive oxygen electrocatalysts.

1. Introduction

Energy and environmental issues have spurred continuous innovation in clean and renewable energy technologies,[1–7] such as fuel cell,[8–14] electrolyzers,[15–18] and metal–air batteries,[19–29] in which energy conversion and storage processes are closely related to oxygen electrocatalytic reactions, including oxygen reduction reaction (ORR)[30–33] and oxygen evolution reaction (OER).[34–38] Currently, the bottleneck of the wide application of these new energy technologies lies in the development of earth-abundant and cost-effective electrocatalysts to reduce the energy barrier in ORR/OER, thus reducing the energy loss of the electrochemical devices.[19,39,40]

In the past decade, great progress has been made in elucidating the relationship between their electronic structure and electrocatalytic activity.[19,39–49] Recently, theoretical calculations and experimental investigations revealed that the energy barrier in ORR/OER is closely related to restrictions on the electrons’ spin (e-spin) during the formation and transformation of O₂ molecule.[50–59] This is because the ground state of O₂ is paramagnetic with a triplet state (Figure 1a) and other products and reactants, such as H₂O/OH*, are diamagnetic with singlet states (Figure 1b,c).[60] Therefore, the spin between the reactants or products in ORR/OER reaction are not conserved, where the transition is forbidden by quantum mechanics and requires extra energy or stimulus to drive, such as spin-orbital interactions.[54]

The recent works suggested that the exchange interaction in magnetic catalysts can build a spin-selective channel to filter the “correct” e-spins toward the catalytic interface between the catalyst and the reaction intermediates, which helps to preserve the e-spins during the triplet O₂ generation/conversion step.[55,56,60,61] In the well-known biological photosystem II, it was recognized that the ferromagnetically coupled CaMn₄O₅ center forming a specific spin-selective channel to accept the e-spins with specific orientation from the oxygen intermediate (Figure 2a), which accelerates the formation and release of O₂ from diamagnetic H₂O.[59,62–69] Meanwhile, ferromagnetic couplings in inorganic catalysts with magnetic ordering structure were demonstrated to selectively accumulate/remove appropriate e-spins in the O₂ generation/conversion process (Figure 2b).[57,67–71] These pioneer works highlight the significance of spin-related effect in oxygen electrocatalysis.[72–77]

In this review, we focus on the recent progress in understanding the spin effect on oxygen electrocatalysis. First, we discuss the spin effect on oxygen electrocatalysis in terms of reaction enthalpy and entropy. Then, we reveal the physical origin of the spin effect from the perspective of spin polarization, and give some recent examples of manipulating the spin-selective channel in catalysts. Afterward, we discuss about the design of highly active spin-selective oxygen electrocatalysts. Finally, we propose the major challenges and opportunities in spin electrocatalysis.

2. Spin-Dependent Oxygen Electrocatalysis

2.1. Brief Introduction on ORR/OER Thermodynamics

According to previous theoretical and experimental investigations, the ORR/OER reaction mechanism consists of four concerted proton–electron transfer steps.[19,29,39,40,43,78,79] Considering the intermediates for ORR to be OOH*, O*, and OH*, the four reaction paths in an alkaline environment are
described in Equation (1)–(4), whereas OER proceeds in the reverse direction

\[
\begin{align*}
\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- & \leftrightarrow \text{OOH}^* + \text{H}_2\text{O} + \text{OH}^- + 3\text{e}^- \quad (1) \\
\text{OOH}^* + \text{H}_2\text{O} + \text{OH}^- + 3\text{e}^- & \leftrightarrow \text{O}^* + \text{H}_2\text{O} + 2\text{OH}^- + 2\text{e}^- \quad (2) \\
\text{O}^* + \text{H}_2\text{O} + 2\text{OH}^- + 2\text{e}^- & \leftrightarrow \text{OH}^* + 3\text{OH}^- + \text{e}^- \quad (3) \\
\text{OH}^* + 3\text{OH}^- + \text{e}^- & \leftrightarrow 4\text{OH}^- \quad (4)
\end{align*}
\]

where * denotes a surface catalytic active site. It is worth noticing that although there are also some ORR/OER mechanisms that propose sequential proton–electron transfer pathways, the basic approach is similar and will not be discussed in detail here.

The reaction free energy (\(\Delta G_0\)) for each step can be calculated using

\[
\Delta G_0 = \Delta H_0 - T\Delta S_0 \quad (5)
\]

where \(\Delta H_0\) and \(\Delta S_0\) are the enthalpy and entropy changes for each step, respectively. In principle, the step with the most positive adsorption free energy changes determines the overpotential of the overall reaction (Figure 3a).\(^{[39,40,80]}\) During the past decades, many research efforts have been devoted to uncovering the correlation of adsorption energies of the ORR/OER intermediates (Figure 3b), including OOH*, O*, and OH*,\(^{[29,39,43,79]}\) which provides a guideline for the exploration and rational design of catalysts to replace the precious metal-based catalysts.

To date, transition metal oxides are considered as the most potential and economical ORR/OER catalysts.\(^{[17,32,36,37,44,45,82–88]}\) Most of these oxides are magnets with net spins (unpaired electrons), in which spin-dependent interactions, such as exchange interaction and/or strong spin-orbit coupling, determine the electronic structure of the oxides\(^{[54]}\) thus the ORR/OER thermodynamics and kinetics.\(^{[56]}\) However, the spin effect on the thermodynamics and kinetics of ORR/OER has long been ignored in understanding of the ORR/OER mechanism.

2.2. Understanding Spin Effect from Reaction Enthalpy

Recent research efforts demonstrated that the spin effect resulted from the magnetic exchange interaction in catalysts can regulate the electron transfer between the orbitals in the catalysts and the chemisorbed reactants.\(^{[56,77]}\) For instance, during the reduction of the triplet state \(\text{O}_2\), the Pauli exclusion principle restricts the transfer of an electron from the orbital of the catalyst to the \(\text{O}_2\) orbitals if there is already an electron of the same spin occupying the \(\text{O}_2\) 2p orbitals (Figure 4).\(^{[56,61,67]}\) In contrast, the exchange interaction in ferromagnetic catalysts enhances the electron transferring with antiparallel spin to the \(\text{O}_2\) orbitals. Therefore, the single-oriented electrons of the ferromagnetic catalyst will reduce the reaction barrier of electron transfer between
the catalysts and the reactants by reducing the Coulomb repulsion. In this case, the reaction enthalpy ($\Delta H$) can be expressed as

$$\Delta H = \Delta H_0 - \Delta H_{\text{spin}}$$

where $\Delta H_{\text{spin}}$ is the spin-dependent change of enthalpy. This formula indicates that ferromagnetic ordering in metal oxides helps moderate the binding energies of the reactants through exchange interactions, and correspondingly their catalytic efficiencies improve. This is in accordance with Sabatier’s principle.

### 2.3. Understandings Spin Effect from Reaction Entropy

In addition to reaction enthalpy ($\Delta H$), the spin effect in ferromagnetic catalysts can also affect the reaction entropy ($\Delta S$) in oxygen electrocatalysis. Note that the entropy of each transferred electron in ORR/OER can be described as

$$S = k_B \ln g$$

where the total number of the possible states ($g$) of the electron depends on the spin degeneracy ($g_{\text{spin}}$) and the configuration degeneracy ($g_c$) mainly originating from orbital degrees of freedom, that is, $g = g_{\text{spin}} \cdot g_c$. To explain the spin effect on reaction entropy, we compare the first electron-hopping step in ORR from a ferromagnetic oxide (with ordered spins) with that from a paramagnetic oxide (with disordered spins, that is, there are both spin-up and spin-down states) (Figure 5). This step involves the electron transfer from the metal d orbital to the triplet O$_2$ p orbital. Assuming the triplet O$_2$ are in $\pi^*$ configuration, according to the Pauli repulsion principle, the electron transferred from the catalyst should be spin-up, which is antiparallel to the spin state of the triplet $\pi^*$ molecule.

For the ferromagnetic ordering state, electron transfer occurs through extended long-range ferromagnetic exchange interactions, indicating that $g_{\text{spin}} = 1$ before the electron transfer. Therefore, the reaction entropy contributed by spin degeneracy is $\Delta S_{\text{spin}} = 0$. On the contrary, for the paramagnetic state, due to the existence of both spin-up and spin-down electrons, $\Delta S_{\text{spin}} < 0$, indicating an entropy reduction process, which is thermodynamically and kinetically unfavorable. Therefore, the ferromagnetic ordering in electrocatalysts is beneficial to accelerate the first electron transfer step in ORR by optimizing the reaction entropy.

It is recently revealed that the overpotential in OER is related to restrictions on the e-spins in generating a ground state triplet O$_2$ molecule. Undoubtedly, as discussed earlier, magnetic exchange interactions at the catalytic interface can reduce the energy loss in the O$_2$ generation step by optimizing the entropy and enthalpy through selecting appropriate e-spins. Given that there is a linear relationship between the activation barrier and the reaction free energy (enthalpy and entropy), the spin effect can affect the activation barrier of e-spin steps, thus the kinetics of oxygen electrocatalysis.
3. Physical Origin of Spin Effect on Oxygen Electrocatalysis

As mentioned earlier, the magnetic exchange interaction will change the enthalpy and entropy of the electron transfer at the catalytic interface, thus accelerate the electron transition process. In essence, electron transfer is a quantum transition in which electron delocalizes from one stationary state (donor) and localizes in another stationary state (acceptor) through thermal activation or tunneling.\[92\] For thermal activation, electron exhibits incoherent hopping, lose phase information, and needs to cross the energy barrier.\[56,69\] For tunneling, electron moves from one state to another, maintains a definite phase, and loses negligible energy, guaranteeing a rapid electron transition.\[93\]

The probability of an electron tunneling depends on the relative direction of spins between adjacent atoms, and is proportional to \(\cos(\theta/2)\) (\(\theta\) is the angle between two spins) (Figure 6a).\[94\]

Therefore, the antiferromagnetic interaction results in zero probability of electron tunneling, whereas the ferromagnetic interaction (all spins are aligned in parallel) gives the greatest probability of electron tunneling, facilitating fast tunneling process.

In ferromagnetic materials, subbands with different spins are exchanged and split, and the spin\(\uparrow\) and spin\(\downarrow\) subbands are relatively displaced (Figure 6b), resulting in different electron density at the Fermi level, thus generating spin polarization.\[93,95,96\]

In this case, the spin\(\uparrow\) and spin\(\downarrow\) electrons experience different tunneling barriers, with the spin\(\uparrow\) electrons encountering a relatively lower tunneling barrier than the spin\(\downarrow\) electrons.\[97\]

Therefore, the spin\(\uparrow\) electrons will be screened out through the ferromagnetic coupling between the metal ions, thereby forming a spin-polarized channel for electron transfer (Figure 6c).\[98\]

At the catalytic interface, the filtered spin\(\uparrow\) electron will be transferred to the triplet \(\mathrm{O}_2\left(\sum\mathrm{O}=\downarrow\right)\) molecule. Therefore, the ferromagnetic exchange interaction in catalysts creates a spin-selective channel to filter the “correct” e-spins in ORR/OER (Figure 6d).

4. Manipulating Spin Selectivity in Oxygen Electrocatalysis

As discussed earlier, possessing a spin-selective channel to filter the “correct” e-spins toward catalytic interface is a unique advantage of electrocatalysts with magnetic ordering structure. In this section, some recent examples of manipulating the spin-selective channel to facilitate charge transfer in electrocatalysis are presented.

4.1. Chiral Induced Spin Selectivity

In addition to intermolecular interaction and orbital overlap,\[98\] spin effect also plays a crucial role in the electron transfer of chiral molecules, which are geniuses to create spin-selective channels to filter e-spins toward catalytic interface.\[50,52,53,59,96,99–103\]

Noteworthy is that as electrons move along a chiral molecule, they experience the electrostatic potential of the molecule and the inherent magnetic field produced by themselves, which helps screen spins and produces a spin-polarized current.\[103\]

In particular, right-handed and left-handed molecules generate spin\(\uparrow\) and spin\(\downarrow\) currents, respectively.

Göhler and co-workers\[59\] reported the spin-selective transport of electrons through self-assembled monolayers of double-stranded DNA on gold (Figure 7a). By measuring the spin of the transmitted electrons with a Mott polarimeter, they found that the spin polarizations of DNA molecules exceeds 60% at room temperature, and the spin filtration efficiency of the
DNA depends on the length of DNA molecule and its organization structure. This work demonstrates the potential of applying self-assembled monolayers of chiral molecules as very effective spin filters in spintronic applications at room temperature.

Naaman and co-workers reported filtering the e-spins by coating the photoelectrode with chiral organic semiconductors. Their magnetic conducting atomic force microscopy measurements showed that the chiral semiconductor has a strong spin-selective ability, so the electrons transferred to the electrode are spin polarized. In this case, the formation of H₂O₂, a byproduct in OER, is symmetrically forbidden. Notably, during water splitting, two OH⁻ species must combine to form a triplet oxygen molecule, in which an electron from each OH⁻ is transferred to the electrode, leaving OH⁻ with one unpaired electron. The spin-selectivity by chiral molecules causes the spins of two unpaired electrons in OH⁻ to align parallel to produce a triplet O₂, whereas the spins of-Co²⁺ in the adjacent two layers are arranged in reverse, forming the spin↑ and spin↓ conduction channels through spin polarization (Figure 8b,c). They claimed that the specific spin-selective channel can help the extraction of electrons with specific spin orientation, facilitating the generation the triplet O₂ molecules (Figure 8d).

4.2. Magnetic Ordering Structure Induced Spin Selectivity

We emphasize earlier that the spin-selective channel generated by ferromagnetic interactions in catalysts plays a key role in the triplet O₂ generation and conversion steps in ORR/OER. It should be noted that not only ferromagnets but also materials with ferromagnetic ordering structure can be ideal spin-selective catalysts. Xu and co-workers reported a layered antiferromagnetic inverse spinel oxide LiCoVO₄ (Figure 8a). In each Co–O layer, the spins of Co²⁺ are arranged in parallel, whereas the spins of Co²⁺ in the adjacent two layers are arranged in reverse, forming the spin↑ and spin↓ conduction channels through spin polarization (Figure 8b,c). They claimed that the specific spin-selective channel can help the extraction of electrons with specific spin orientation, facilitating the generation the triplet O₂ molecules (Figure 8d).

Figure 6. a) Schematic diagram of the spin orientations of adjacent ions. b) Schematic diagram of band splitting of ferromagnetic catalyst due to exchange interaction. c) Electron-tunneling process in spin-polarized channel for ORR and OER. Reproduced with permission.[56] Copyright 2018, Elsevier Inc. d) Schematic diagram of spin filtering effect.
4.3. Magnetic Field Introduced Spin Selectivity

In addition to the intrinsic magnetism of the catalysts, the introducing of an external magnetic field can also induce the spin selectivity in ORR/OER. This is because the magnetic field can cause the spin flip of the magnetic ions in catalysts and the reaction intermediates with net spins, therefore optimizing the reaction path and improving the reaction efficiency.\(^{105-108}\)

Galán-Mascarós and co-workers\(^{109}\) investigated the effect of external magnetic fields on the OER performance of non-magnetic, ferromagnetic, and antiferromagnetic catalysts (Figure 9a–d). The magnetic field enhancement was observed in the ferromagnetic and antiferromagnetic catalysts, which should be attributed to the influence of the external magnetic field on the \(\text{O}_2\) generation step. That is, the magnetic field promotes the parallel alignment of net spins in intermediates and

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Figure 7. a) Schematic diagram of using monolayer of DNA as a spin filter. Reproduced with permission.\(^{59}\) Copyright 2011, American Association for the Advancement of Science. b) Schematic diagram of production of \(\text{H}_2\text{O}_2\) and \(\text{O}_2\) on achiral and chiral molecules, respectively. Reproduced with permission.\(^{50}\) Copyright 2017, American Chemical Society. c) Schematic diagram of chiral molecules chemisorbed on \(\text{Fe}_3\text{O}_4\) nanoparticles to facilitate photoelectrochemical water splitting. Reproduced with permission.\(^{100}\) Copyright 2018, American Chemical Society.

Figure 8. a) Crystal structure of a typical cubic spinel oxide. b) Crystal structure of \(\text{LiCoVO}_4\) with spin isosurface. Ions with yellow color isosurface indicates spin\(^+\), whereas ions with blue color isosurface indicates spin\(^-\). c) Spin distribution map of \(\text{LiCoVO}_4\) along the [001] direction. d) Spin-selective electron transfer in layered antiferromagnetic \(\text{LiCoVO}_4\). Reproduced with permission.\(^{57}\) Copyright 2020, Wiley-VCH GmbH.
products, such as \(O\ldots O\) and \(O=O\). We take NiO, an antiferromagnetic catalyst, as an example (Figure 9e). Notably, OER at high pH occurs through the interaction of two O atoms adsorbed on two surface metal sites of oxides, during which the spins of the two O atoms would be either in parallel or antiparallel. When the spins of the two Ni atoms are in antiparallel, the intermediate \(O\ldots O\) and the product \(O=O\) will be in singlet-state configurations with high energy. Under the external magnetic field, the spins of Ni atoms will be aligned in a parallel fashion, thus the intermediate \(O\ldots O\) and the product \(O=O\) will turn to be triplets with low energy. Their theoretical computation verified that this spin-selected reaction pathway induced by magnetic field is indeed thermodynamically favored.

5. Rational Design Oxygen Electrocatalysts based on Spin Effect

Aforementioned examples highlight the role of manipulating the spin-selective channels in promoting ORR/OER. However, strong magnetism of the magnetic catalyst does not guarantee high reactivity because both spin and space conditions are required for electron transfer at the catalytic interface between the catalyst and the reactants/intermediates. For example, in ZnMn\(_2\)O\(_4\), although the spin selection is satisfied, the orbitals of Mn 3d above the Fermi level are the 3d\(_{xy}\) and 3d\(_{yz}\) orbitals, which have weak \(\pi-\pi\) interactions with the adsorbed OH\(^-\), thus restricts the interfacial electron transfer.\(^{[69]}\)

In the past few decades, considerable research efforts have been made to propose appropriate descriptors to describe the binding energy of ORR/OER intermediates on the metal and oxide surfaces, and various volcano-shaped relationships have been established to predict the most active ORR/OER catalysts (Figure 10).\(^{[39,40,43,76]}\) In fact, all the catalysts at the top of the volcano plots possess ideal space condition for electron transfer at the catalytic interface. For example, the pioneer work by Shao-Horn and co-workers\(^{[44,45]}\) suggest that the \(e_g\) orbitals of transition metal in perovskite interact with the 2p orbitals of the oxygen to stabilize the ORR/OER intermediates, and \(e_g\) filling \(\approx 1\) is optimum for the best activity (Figure 10b).

We would like to point out here that for the catalysts at the top activity of the volcano plots, if the reaction enthalpy and entropy are further optimized by spin effect, the catalyst activity is highly expected to be improved beyond the volcano peak, surpassing precious metal-based catalysts.\(^{[56,67]}\)

6. Conclusions and Perspectives

This review highlights recent advances in understanding and application of the spin effect in oxygen electrocatalysis. It demonstrates that spin effect can build a spin-selective channel to filter the “correct” e-spins for \(O_2\) generation/conversion step in ORR/OER, thus optimize the entropy and enthalpy of electron transfer at the catalytic interface between the catalyst and the reactants/intermediates. Undoubtedly, incorporating spin effect can establish a more comprehensive understanding of oxygen electrocatalysis, and help design more active oxygen electrocatalysts. Future research directions in this field include but are not limited to the following: 1) simple and operable methodology, such as heteroatom doping, strain control, or size limitation, should be developed to tailor the magnetic ordering structure of electrocatalysts, thus effectively adjust the spin-selective channel to filter the “correct” e-spins toward the catalytic interface.
2) Regulating the spin-orbit coupling in heavy metal oxides, such as iridium oxide,\cite{43} to achieve spin-selectivity. Similar to chiral induced spin selectivity, which is essentially the interacting between electron momentum and its spin, the spin-orbit coupling in heavy metal oxides can cause d-band splitting, thus generate spin-polarized currents. 3) In addition to magnetic fields, external fields such as light, electricity, and heat can be combined to regulate the charge, spin, and orbital coupling of the catalyst and/or the spin arrangement of the reaction intermediates. 4) Spin-polarized density functional theory calculations should be used to accurately describe the spin-related catalytic phenomena and provide more reliable predictions for catalyst designing.\cite{58}

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**Conflict of interest**

The authors declare no conflict of interest.

**Keywords**

ferromagnetic interaction, oxygen evolution reactions, oxygen reduction reactions, spin selectivity, spin-selective catalysts

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\[ \text{Figure 10. a) OER activity trends as a function of } \Delta G_{\text{O}_2^-} - \Delta G_{\text{O}_2^+} \text{ in metal oxides. Reproduced with permission.}\]  
\[ \text{b) ORR activity trends as a function of } \epsilon_g \text{ orbital in perovskite-based oxides. Reproduced with permission.}\]

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