

## Catalytically Influential Features in Transition Metal Oxides

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**ABSTRACT:** The development of efficient catalysts is critical in advancing electrocatalysis techniques. While tremendous progress has been made on the perspective of optimizing the catalyst–reactant interaction, the influence from other properties has received relatively less attention to date. These properties are normally originated from the intrinsic solid-state properties and can be circumstantially influential on the reaction activity and reaction mechanism. In particular, transition metal oxides (TMOs) possess complex inherent features that enable a wide variety of catalytically influential properties. Therefore, understanding the inherent features in TMOs and mastering the strategies to take full advantage of them will bring opportunities for further advances. Here we provide an overview of the inherent features in TMOs and conceptually discuss how they can alter the catalytic behaviors in electrocatalysis. Perspectives to take full advantage of these features are also proposed for a better design of TMO-based electrocatalysts.

## 1. INTRODUCTION

Exploring better catalysts is one of the central efforts in catalysis studies. The Sabatier principle states that the highest reaction rate occurs when the adsorption of reaction species on the catalytic sites is neither too strong nor too weak. This leads to the construction of a volcano-shaped structure–activity relationship when plotting the reaction rate against descriptors such as the adsorption energy of intermediates. The volcano summit has, therefore, been regarded as the optimal region for the best performance.<sup>1</sup> However, with strategies to freely tune the adsorption energy being intensively reported, the search for a volcano summit is no longer a major obstacle in catalysis.<sup>2,3</sup> Catalysis research at this stage faces a new challenge, that is, whether it is possible to further push the activity of catalyst beyond the summit of the volcano. In other words, it remains mysterious whether the upper limit of the activity is constrained within the established volcano plots.

Since the volcanic structure–activity relationship is built against the surface adsorption, additional opportunities to further raise the activity may hide in the inherent features of the catalysts. Electrocatalysis is different from thermal catalysis, in which the adsorption of reactants and intermediates plays the dominant role in determining the catalysis efficiency. In addition to the adsorption, electrocatalysis involves charge transfer within the electrocatalyst and between reactants and catalyst. Thus, the inherent features of catalysts are influential as well in determining the efficiency. Indeed, some recent studies have highlighted that the electrocatalytic activity of transition metal oxides (TMOs) can be sensibly influenced by the change of inherent features such as charge distribution,<sup>4,5</sup> spin state,<sup>6,7</sup> and magnetic ordering.<sup>8</sup> Catalytic enhancement induced by the change of such features is attributed to two aspects; one is the optimized surface bonding, while the other is the improved intrinsic properties that are beneficial to an increased reaction activity, such as the expedited charge

transfer ability,<sup>4,6</sup> optimized metal–oxygen covalency,<sup>5</sup> and fine-tuned exchange interactions.<sup>7,8</sup> Although these properties cannot directly influence the adsorption of reaction species, they have a significant role in affecting the electron transfer rate within the electrode, which also contributes to the measured activity. Besides, in some cases, these properties may also indirectly influence the surface bonding because of the expedited electron mobility to the surface that compensates the charge at the solid–electrolyte interface, thereby altering the electron transfer barrier during the reactant adsorption.<sup>9</sup> Therefore, mastering the strategies to optimize these properties brings chances to further improve the electrochemical activity of TMOs. The reason that makes TMOs highly sensitive to these strategies is that TMOs exhibit a broad variety of intrinsic features. As strongly correlated electron systems, the spin, charge, and orbital states in TMOs are often coupled to one another because of their multiple degrees of freedom and the electron correlations.<sup>10</sup> Such interactions are highly sensitive to the change of crystal structure and stoichiometry. Therefore, the multiple crystal frames and compositional diversity of TMOs enable a wide variety of inherent features, giving rise to diverse electronic and chemical properties. This makes TMOs highly responsive to the strategies of tuning the inherent features for improved catalytic activity.

Having been reported and highlighted by some recent works, the benefits from these aspects to raise the electrocatalytic activity of TMOs will attract more, well-deserved attention. However, an in-depth description of all the

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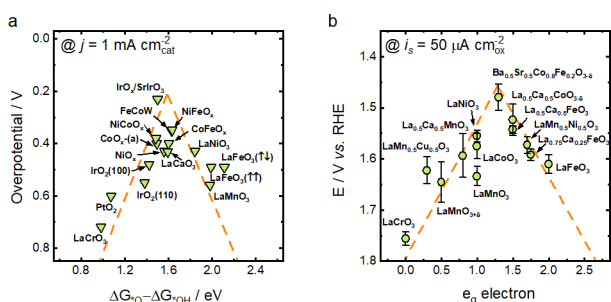
catalytically influential features in TMOs remains elusive. Proper employment of these features is believed to further navigate the activity of TMOs beyond the surface-bonding-dominated volcano summit. Here we aim to **synoptically** introduce state-of-the-art opinions on the volcanic structure–activity relationships of TMOs and conceptually discuss some inherent features that are less discussed but influential on their electrocatalytic activity. Besides, we will also give some perspectives on the establishment of a more logical design paradigm of TMOs, where a wider consideration of the inherent features is integrated toward achieving the maximum potential for catalysis.

## 2. CURRENT OPINIONS ON STRUCTURE–ACTIVITY RELATIONSHIPS OF TMOs

Owing to the multiple stable oxidation states of metal cations, TMOs exhibit a broad structural variety to form phases composed of varying metal-to-oxygen ratios. **Among the various phases of TMOs, those containing the octahedral units, such as perovskite, spinel, and pyrochlore structures, are found to be advantageous in electrocatalytic applications.**<sup>11</sup> Depending on the type of descriptor, studies exploring the structure–activity relationships of TMOs can be roughly classified into two categories; that is, some use **surface adsorption energy**, while some others use the **inherent features** of TMOs. The surface adsorption energy of key intermediates can be numerically acquired by density function theory (DFT) calculations. A prerequisite of this approach is an in-depth understanding of the reaction pathway, that is, how reactants evolve to become the products. Taking oxygen evolution reaction (OER) as an example, the four-electron transfer steps are recognized to follow the pathway with the  $^*\text{OH}$ ,  $^*\text{O}$ ,  $^*\text{OOH}$ , and  $^*\text{OO}$  ( $^*$  denotes the active site) intermediates, respectively. On the basis of the volcano plot constructed for a wide variety of TMOs (Figure 1a), the descriptor ( $\Delta G_{^*\text{O}} -$

the adsorption energy of  $^*\text{OH}$ ,  $^*\text{O}$ ,  $^*\text{OH}$ , and  $^*\text{NNH}$  are used as descriptors, respectively.

Compared with the paradigms where surface adsorption energy is employed as descriptor, those using the chemical features of TMOs are somewhat simplified. A typical example is the  **$e_g$  occupation**, which was originally proposed for transition metal perovskite family.<sup>17</sup> As shown in Figure 1b, the volcano plot establishes the bridge between the OER potential at  $50\ \mu\text{A cm}^{-2}$  and the number of  $e_g$  electrons in the surface octahedral cation. **The theory behind this plot is that the  $e_g$  filling of surface transition metal cations can greatly influence the binding strength of reaction intermediates to the metal site and thus the activity.** Hence, perovskites in the left and right branch of the volcano exhibit poor OER activity because of the too-strong and too-weak binding affinity to the reaction intermediates, respectively. Additionally, the  $e_g$  theory has been found to be effective in describing the activity of spinel oxides toward ORR and OER.<sup>18</sup> Recently, some other descriptors based on the features of TMOs, such as outer electrons,<sup>19</sup> oxygen 2-p band center,<sup>20</sup> and metal–oxygen covalency,<sup>21</sup> have also been proposed for some specific TMOs, because of their relations to the surface adsorption behavior and the surface reconstruction capability for active site creation. It is obvious to notice that, **although simplified from calculating the adsorption energy, most descriptors based on the chemical features of TMOs are still a hint of the bonding between the surface site and the reaction species.** In other words, it still stays within the Sabatier regime and gives the most straightforward angle of view to survey the catalyst because the reaction always takes place at the surface of the catalyst. However, the process of electrocatalytic reactions is rather complicated. Interpreting it from a single point of view is to some extent insufficient for setting up a comprehensive understanding. Therefore, a step beyond the single perspective of the surface adsorption energy may offer additional opportunities to further promote the intrinsic activity of TMOs beyond the volcano summit.

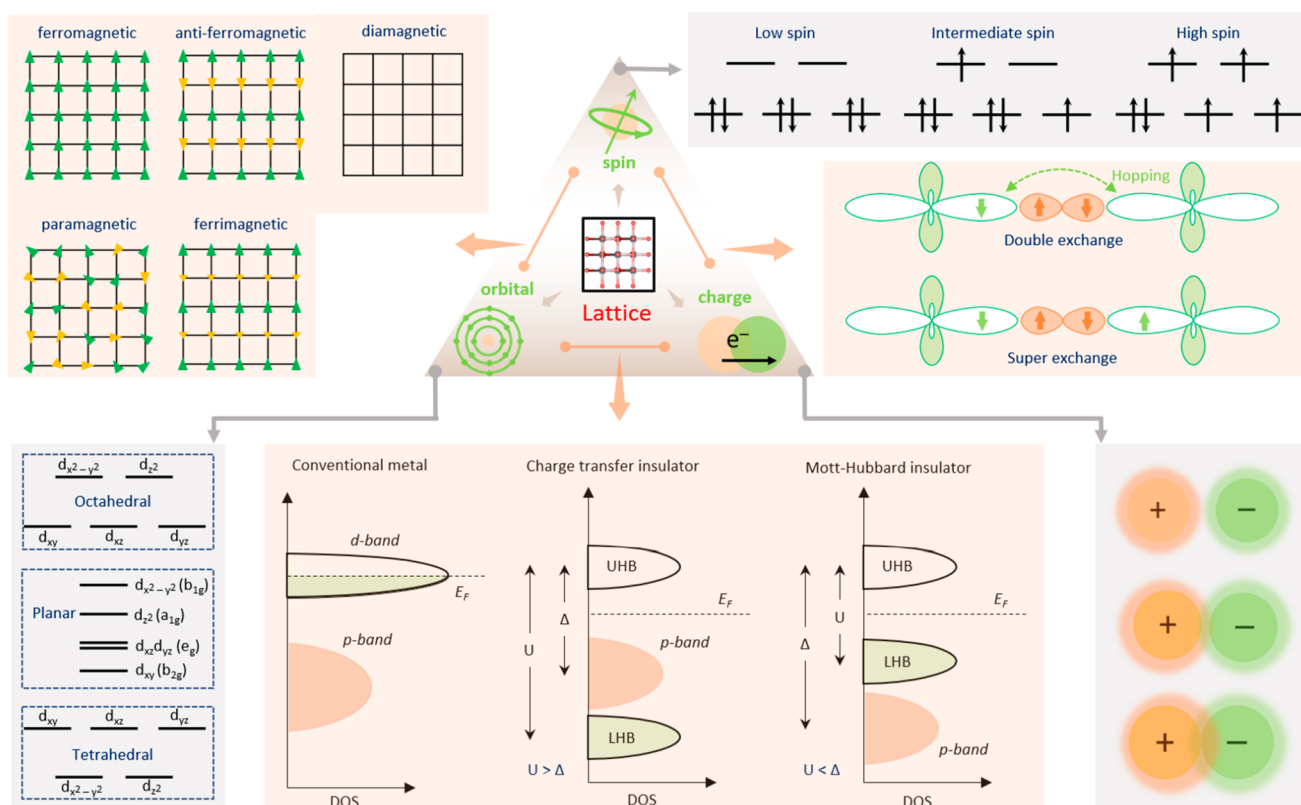


**Figure 1.** Examples of the two common categories of structure–activity relationship established on TMOs. (a) The structure–activity relationship with the descriptor of surface adsorption energy. The data constructing the plot are taken from ref 1. (b) The structure–activity relationship with the descriptor of the chemical features of TMOs. The data constructing the plot are taken from ref 17.

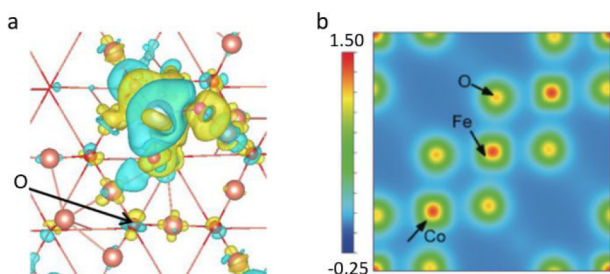
$\Delta G_{^*\text{OH}}$ ) is found to correlate strongly with the experimental overpotential at  $1\ \text{mA cm}^{-2}$ .<sup>1</sup> The TMOs away from the volcano summit (residing in the left and right branch of volcano) exhibit too strong and too weak binding affinity to the oxygen-related intermediates, respectively. Similar to the paradigm of OER, such volcano plots have also been established in oxygen reduction reaction<sup>12</sup> (ORR), chorine evolution reaction<sup>13</sup> (CER),  $\text{CO}_2$  reduction reaction<sup>14,15</sup> ( $\text{CO}_2\text{RR}$ ), and nitrogen reduction reaction<sup>16</sup> (NRR), where

## 3. INHERENT FEATURES OF TMOs AND THEIR INFLUENCE ON ELECTROCATALYTIC ACTIVITY

**In TMOs, the d-electrons of transition metals play the major role in shaping the electronic structure of TMOs.** The d-orbitals in most of the transition metals are partially filled and have three fundamental features, that is, the **orbital, charge, and spin**.<sup>10</sup> The first-order expression of the three features is dominated by the crystal structures. First, for a given crystal, the coordination and **ligand** environments determine how the d-orbitals of transition metals split (Figure 2). For example, **in an octahedral crystal field, the five d-orbitals split into three low-lying  $t_{2g}$  orbitals and two high-lying  $e_g$  orbitals, while two low-lying e orbitals and three high-lying  $t_2$  orbitals are formed in a tetrahedral one.** Second, the charge of transition metals is also constrained within a certain range after situating in a **specific crystal frame**. However, the charge on metal cations can be fine-tuned via strategies such as fabrication of hybrid structures and metal substitution. Recent studies have revealed that the charge redistribution in TMOs can induce an observable change in catalytic activity. For example, the charge redistribution on zirconium and copper cations after anchoring  $\text{ZrO}_2$  on  $\text{Cu}_2\text{O}(111)$  substrate (Figure 3a) is responsible for the catalytic enhancement for methane oxidation, as it creates an optimized electron transfer pathway for  $\text{CH}_4$  dissociation.<sup>4</sup> Similarly, the OER activity of  $\text{Li}_{0.5}\text{Zn}_{0.5}\text{Co}_2\text{O}_4$  is boosted by



**Figure 2.** Schematic of the inherent features in TMOs. The lattice of TMOs defines the first-order features of spin, charge, and orbital degrees of freedom. These features couple to one another, creating some other features within the TMO lattice, that is, the electronic band structure, the magnetic ordering, and local exchange interactions. The abbreviations of UHB, LHB,  $E_F$ ,  $U$ , and  $\Delta$  represent the upper Hubbard band, the lower Hubbard band, the Fermi level, the on-site Coulomb interaction, and the charge transfer energy between the oxygen p-orbitals and metal d-orbitals, respectively.



**Figure 3.** Examples of the strategies to fine-tune the charge distribution in TMOs for improving the catalytic activity. (a) The charge density difference of anchoring  $\text{ZrO}_2$  on  $\text{Cu}_2\text{O}(111)$  substrate. The isosurfaces in yellow and cyan represent the charge redistribution. Reproduced with permission from ref 4. Copyright 2021 Elsevier. (b) The charge density on [001] direction of  $\text{Li}_{0.5}\text{Zn}_{0.5}\text{Fe}_{0.125}\text{Co}_{1.875}\text{O}_4$ . Reproduced with permission from ref 5. Copyright 2019 John Wiley & Sons.

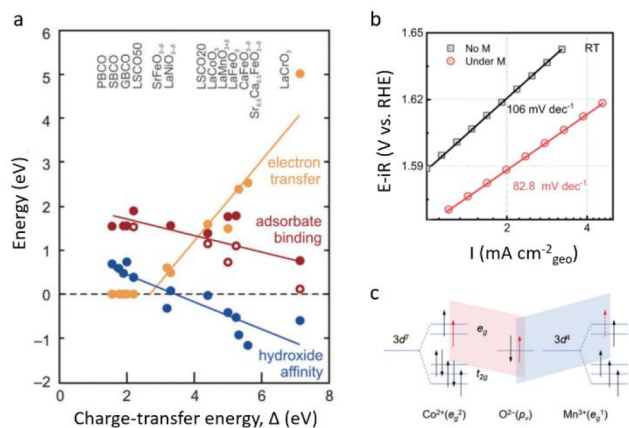
substituting Co with a trace amount of Fe, as it allows the shift of oxygen charge toward the cobalt center (Figure 3b) and results in enlarged Co–O covalency.<sup>5</sup> Finally, after specifying orbital and charge, the possible spin state can then be speculated. As shown in Figure 2, considering a  $\text{Co}^{3+}$  cation located in an octahedral field, three possible spin states exist, that is, low-spin state, intermediate-spin state, and high-spin state. Recent studies have demonstrated that the change of spin state is also crucial in manipulating the catalytic activity.<sup>6,7,22</sup> However, the explicit effect of cation spin state

on the catalytic performance needs to be analyzed case-by-case. For example, spinel  $\text{ZnCo}_2\text{O}_4$  benefits from high-spin state cobalt cations ( $\text{Co}^{3+}$ ) for catalyzing OER, because the propagation of spin channel promotes spin-selected charge transfer. In comparison, no such spin channel can be propagated in  $\text{ZnCo}_2\text{O}_4$  that is composed of low-spin state  $\text{Co}^{3+}$ , which exhibits inferior activity.<sup>6</sup> However, spinel  $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$  benefits more from a low-spin state  $\text{Ni}^{3+}$  for catalyzing urea oxidation reaction (UOR). In  $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ , the octahedrally coordinated cobalt cations are in low-spin state ( $t_{2g}^6e_g^0$ ). Compared to high-spin state  $\text{Ni}^{3+}$  ( $t_{2g}^5e_g^2$ ), the low-spin state  $\text{Ni}^{3+}$  ( $t_{2g}^6e_g^1$ ) can construct more unobstructed charge transfer pathway to boost the conductivity.<sup>22</sup>

Besides, the interplay among charge, spin, and orbital degrees of freedom can induce extra inherent features of TMOs, that is, the band structure, magnetic ordering, and exchange interactions. As shown in Figure 2, because of the nature of strongly correlated electron systems, the coupling between electrons and crystal orbitals outlines the band structure of TMOs, which can be illustrated by the calculated density of states (DOS) patterns. Generally, unlike the conventional metal band where the d-state is narrow and consecutive across the Fermi level, the d-electrons in most TMOs, because of strong electron correlation, are localized and exhibit insulating behavior, which can be understood within the context of a Zaanen–Sawatzky–Allen scheme.<sup>23</sup> In this scheme, the TMOs may be classified as either charge-transfer insulators or Mott–Hubbard insulators. The dis-



tion between the two regimes are the relative values of  $U$  and  $\Delta$ , where  $U$  refers to the d–d Coulomb repulsion and  $\Delta$  stands for the charge-transfer energy between oxygen p-orbitals and cation d-orbitals. The d–d Coulomb repulsion raises the energy of the lowest unoccupied state, such that the d band splits into the lower Hubbard band (LHB) and the upper Hubbard band (UHB). The charge transfer insulators are those where  $U$  is much higher than  $\Delta$ . In this regime, the lowest-energy charge migration route is a transition from oxygen ligand to metal site, i.e.,  $d_i^n L^m \rightarrow d_i^{n+1} L^{m-1}$ , where d and L represent the metal site and oxygen ligand, respectively. The Mott–Hubbard insulators are, however, those where  $U$  is much less than  $\Delta$ . In this case, d electrons are completely localized on metal cations because of the presence of the strong Coulomb repulsion. The charge transfer route is expected to be the hopping of d-electron from one metal cation to another, i.e.,  $d_i^n d_j^n \rightarrow d_i^{n-1} d_j^{n+1}$ , where i and j indicate different metal sites. It is obvious that the band structure of TMOs is an indicator of the charge transfer property, which is highly relevant to the reaction kinetics. However, whether it is pertinent to the reaction mechanism and to what degree it affects the reaction activity are still not clear. A pioneering work by Y. Shao-Horn’s group found that decreasing the charge-transfer energy of perovskite oxides can effectively change their OER activities and alter the OER mechanism from electron-transfer-limited to proton–electron-coupled and to proton-transfer-limited reactions (Figure 4a).<sup>9</sup> The explicit

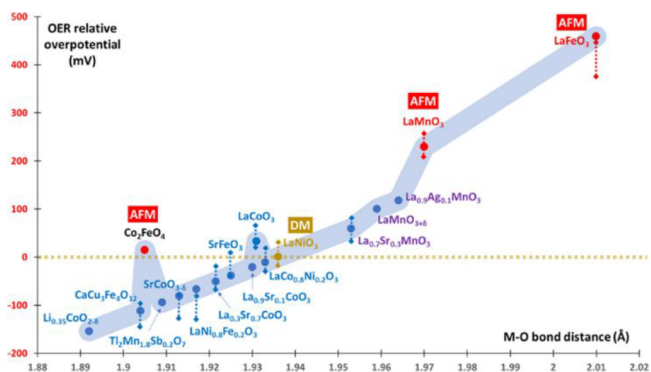


**Figure 4.** Examples of the strategies to alter the catalytic activity by manipulating the band structure, magnetic ordering, and local exchange interactions in TMOs. (a) The change of band structure of TMOs results in the change of charge transfer energy and therefore the change of electron transfer, adsorbate binding, and hydroxide affinity. Reproduced with permission from ref 9. Copyright 2017 Royal Society of Chemistry. (b) The spin direction of ferromagnetic  $\text{CoFe}_2\text{O}_4$  is aligned in higher degree under an external magnetic field, which results in enhanced OER activity. Reproduced with permission from ref 8. Copyright 2021 Springer Nature. (c) The design of double exchange  $\text{Co}^{2+}(\text{e}_g^1)\text{--O--Mn}^{3+}(\text{e}_g^1)$  to facilitate electron transfer during electrocatalysis. Reproduced with permission from ref 37. Copyright 2021 Royal Society of Chemistry.

evidence demonstrated in their work enlightened the explorations into the band-structure-related feature of TMOs, as both the reaction mechanism and reaction activity can be finely tuned through the manipulation of charge-transfer energy. However, the band-structure investigations of other TMO families and electrocatalytic reactions remain blank,

which may become one of the hotspots in future catalysis research.

Beside the electronic band structures, the magnetic ordering induced by the long-range spin orientation in TMOs is also an important inherent feature that should not be ignored. Although some TMOs exhibit diamagnetic feature (such as low-spin state  $\text{ZnCo}_2\text{O}_4$ ), most TMOs show certain magnetic features under ambient conditions. While ferromagnetism, antiferromagnetism, and ferrimagnetism are feasible in some cases, under ambient conditions, paramagnetism is the most common magnetic ordering in TMOs, where the spin directions in metals are random. The influence of magnetic ordering on the superconductivity<sup>24</sup> and optical properties<sup>25</sup> of TMOs has been long studied, however, its role in navigating the electrocatalytic activity has attracted attentions only recently. The pioneering works of Gracia et al. have theoretically highlighted that TMOs with antiferromagnetic ordering show much poorer OER activity than TMOs with ferromagnetic ordering (Figure 5).<sup>26,27</sup> This leads to the design



**Figure 5.** Theoretically calculated OER overpotential of TMOs with respect to that of  $\text{LaNiO}_3$ . The red labels represent TMOs in antiferromagnetic ordering. The labels in other colors represent TMOs in ferromagnetic ordering. Reproduced with permission from ref 26. Copyright 2019 American Chemical Society.

of TMOs with aligned magnetic ordering for better OER activity. Thereafter, Garcés-Pineda et al.<sup>28</sup> and Ren et al.<sup>8</sup> (Figure 4b) report that the OER activity of some TMOs can be directly enhanced under an applied external magnetic field, where the magnetic ordering of ferromagnetic TMOs was aligned in a higher degree. Although an exhaustive explanation for the enhancement remains mysterious, a possible reason on spinel  $\text{CoFe}_2\text{O}_4$  may be the expedited reaction kinetics for the first electron transfer step. With rising attention being paid to the usage of applied external magnetic field, more reactions, such as ORR<sup>29</sup> and  $\text{CO}_2\text{RR}$ ,<sup>30</sup> have been found to benefit from the aligned ferromagnetic spin ordering. However, it is worth noting that the external magnetic field also induces some other effects, which may affect the observed activity. For example, the field may lead to the decreased electrical resistivity of ferromagnetic oxides as well as the enhanced mass transport near the electrode surface. Therefore, the conclusion of a spin-dominated catalytic enhancement should be cautiously validated. Pertinent control experiments and data analysis must be conducted to exclude the possible influence from these “non-spin” effects.<sup>8,31,32</sup>

In addition to the external magnetic field, manipulating the exchange interactions within the crystal lattice can also be used to tune the local spin ordering in TMOs. As shown in Figure 2,

the double-exchange and superexchange effect result in completely different spin ordering between two metal cations connected through the same oxygen ligand. According to the Goodenough–Kanamori rules,<sup>33,34</sup> the superexchange effect creates strong antiferromagnetic coupling between two nearest-neighbor cations through the connected oxygen anion. This is because the Pauli exclusion principle forces both spins in the d and p hybridized orbitals to be oriented antiparallel. However, when the M–O–M bond angle is 90°, weak ferromagnetic ordering occurs when the two cations hybridize with different p-orbitals of the oxygen anion. The double-exchange effect usually arises between ions on a different oxidation state. The key to realize the double-exchange effect is the hopping of electron from one cation to another, which, based on Hund's rules, gives rise to ferromagnetic spin ordering of the two cations.<sup>35</sup> Since the double-exchange system generally shows better charge transfer ability than the superexchange one, strategies of introducing double-exchange interaction in electron-transfer reactions have been proposed in order to boost the catalytic activity. Successful examples can be found in the work by H. Liu et al.<sup>36</sup> and Z. Zhuang et al.,<sup>37</sup> where double-exchange  $\text{Mn}^{3+}\text{--O--Mn}^{4+}$  and  $\text{Co}^{2+}(\text{e}_g^2)\text{--O--Mn}^{3+}(\text{e}_g^1)$  (Figure 4c) serve as active centers for HER and ORR, respectively.

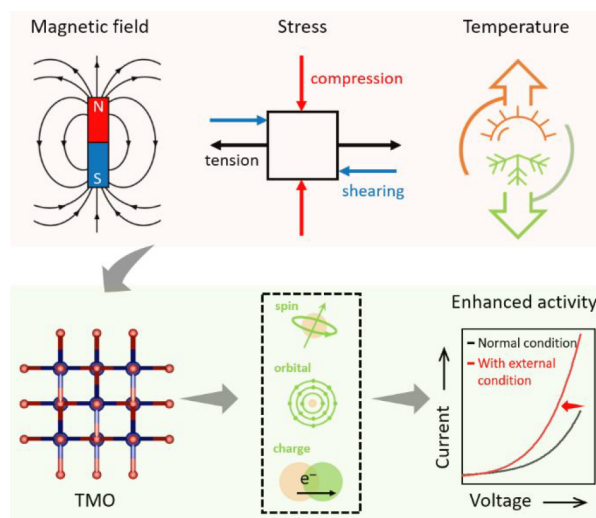
#### 4. PERSPECTIVES ON DESIGN OF TMOs WITH INTEGRATED CONSIDERATION OF INHERENT FEATURES

The above two sections have briefly introduced the current understandings of the surface-bonding-dominated structure–activity relationships in TMOs and conceptually elucidated how some inherent features can further influence their electrocatalytic activity. **It is worthwhile to emphasize that the surface bonding is still the pivotal factor that determines the first-order catalytic nature of TMOs, as electrochemical reactions take place at the interface between the solid catalyst and the electrolyte.** However, electrochemical reactions are complicated, and their sensitivity to the electric conductivity, spin/charge transfer route, and magnetic coupling offers additional opportunities for the activities to be increased beyond the volcano summit. In this regard, attention should be paid to the inherent physics in TMOs. To integrate these aspects in the future design of TMOs, some perspectives are proposed.

**First, using dopants to create a local M–O–M bond with enhanced charge transfer ability is expected to boost the intrinsic electrocatalytic activity.** Most TMOs are intrinsically insulating under ambient conditions; therefore, the charge transfer ability within the lattice needs to be improved to maximize the involvement of the active sites. A common approach that has been intensively employed in experiment is to couple TMOs with conductive supports, such as carbon-based materials. While this indeed improves the measured conductivity of the electrocatalysts, however, the enhancement from this approach to the intrinsic activity of TMOs is limited. The improvement of charge transfer around the active surface sites cannot be guaranteed. In other words, electrons must be freely transferred around the surface sites before they can hop to the conductive carbon supports. **The creation of a local M–O–M bond with enhanced charge transfer ability, such as a local double-exchange coupling, can significantly address this issue and improve the intrinsic activity of TMOs.** To achieve this, the selection of a suitable dopant is the key. It is worth

noting that it is not necessary for the dopant to serve as an active site; a sole function in boosting the charge transfer ability is also significant toward enhanced intrinsic catalytic activity.

**Second, the recently observed catalytic enhancement under external magnetic field hints at a strategy of utilizing external conditions to influence the inherent features of TMOs and thus the catalytic activity.** Generally, the inherent features in many TMOs are sensitive to the change of external environment, such as pressure, stress, temperature, and magnetic/electric field (Figure 6). For example, the temper-

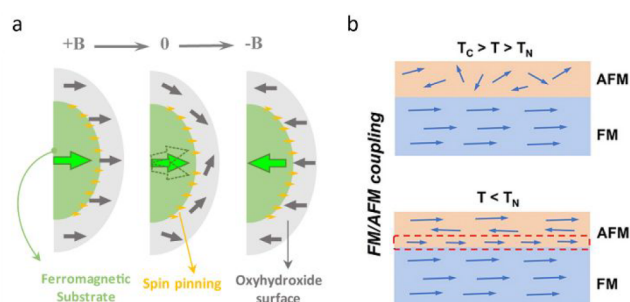


**Figure 6.** Schematic of the activity enhancements of TMOs under applied external conditions. The applied external conditions, such as magnetic field, stress, and temperature, may alter the inherent features of TMOs, such as spin, charge, and orbital degrees of freedom. TMOs under these conditions may exhibit enhanced catalytic activity than those under normal conditions.

ature-induced change of magnetic ordering is a common phenomenon in most TMOs. The phase change of TMOs under high temperature and pressure is also conventional to achieve unusual properties such as superconductivity.<sup>10</sup> Before the recently emerged approach of applying external magnetic field, the strategies of applying external conditions, however, did not attract significant attention in electrocatalytic applications. The effect of these strategies on electrocatalytic reactions has raised attention only recently.<sup>38</sup> Since, in many cases, slight changes in the external conditions are sufficient to induce a substantial change of inherent features, these strategies are believed to hold enormous potential and may be of significance in future catalyst design. One difficulty is that the catalytic mechanism under external conditions is rather complicated, as the inherent features of TMOs are coupled to one another. Therefore, a change in one feature may give rise to changes of the entire electronic structure. To uncover an in-depth mechanistic understanding, tremendous efforts need to be devoted.

**Third, proper design of heterojunction structures is also an operational strategy.** As illustrated in Figure 2, the crystal lattice defines some fundamental features of TMOs. Therefore, creation of a heterojunction, where two or more different crystals meet at an interface, may bring chances to create an advantageous charge-transfer route and ion diffusion because of the interfacial effect such as band bending.<sup>39</sup> These features

may not be realized in a single crystal. Although heterojunction structures have emerged as a type of material with advanced catalytic activities, to date the efforts are mainly devoted on the bonding of intermediates on the interface region. More subtle manipulations of the charge transfer route and ion diffusion at the interface may further promote their activity. Besides, with the help of external magnetic field, some unique spin-related effects can also be achieved at the interface between TMOs with different magnetic ordering. For example, a spin pinning effect can be created at the core@shell interface in which the core material is ferromagnetic and the shell is paramagnetic/antiferromagnetic. Under an external magnetic field, a strong magnetic anisotropy field can be produced at the core@shell interface, which can align the spin in the shell to ferromagnetic state. Taking advantage of this strategy, the core-shell structures of  $\text{Co}_{2.75}\text{Fe}_{0.25}\text{O}_4@\text{Co}(\text{Fe})\text{O}_x\text{H}_y$ <sup>31</sup> (Figure 7a) and  $\text{Fe}_3\text{O}_4@\text{Ni}(\text{OH})_2$ <sup>40</sup> (Figure 7b) have been successfully designed as remarkable OER catalysts.



**Figure 7.** Schematic of two core@shell models with spin pinning effect at the interface between ferromagnetic substrate and paramagnetic shell. (a) The core@shell model of  $\text{Co}_{2.75}\text{Fe}_{0.25}\text{O}_4@\text{Co}(\text{Fe})\text{O}_x\text{H}_y$  for OER. Reproduced with permission from ref 31. Copyright 2021 Springer Nature. (b) The core@shell model of  $\text{Fe}_3\text{O}_4@\text{Ni}(\text{OH})_2$ . Reproduced with permission from ref 40. Copyright 2021 John Wiley & Sons.

Fourthly, the consideration of reaction kinetics is essential for a comprehensive optimization of reaction performance. Conventional mechanistic studies mainly focus on the free energies of each elementary step. While this gives explicit insights into the reaction thermodynamics, the impact of reaction kinetics is not reflected in such a regime. In electrochemical reactions, electrons are transferred between the active sites and the surface adsorbed species, in which an activation barrier needs to be surmounted. Therefore, ascertaining the kinetic rate for each electrochemical step is necessary for setting up a well-described reaction mechanism. A possible approach to computationally investigate the elementary rate constant is the microkinetic models, in which the kinetic rate constant is given by  $k = A \exp\left(\frac{-G_A}{RT}\right)$ , where  $A$ ,  $R$ ,  $T$ , and  $G_A$  represent the frequency factor, the universal gas constant, the temperature, and the activation barrier, respectively. The challenge of this approach is that the determination of activation barrier requires the search for the transition states on a potential-energy surface, which is computationally very intensive. The development of this approach necessitates the establishment of more economical computational technologies to locate the transition-state energy. In addition to considering the transition state, the charge transfer between active sites and the surroundings in

the electrode materials is also necessary to be considered for a thorough mechanistic understanding.

Finally, integrating the surface adsorption energy and the inherent features of TMOs into one single descriptor should give more explicit design principles for better catalyst design. Though it is encouraging that increasing attention is being paid in exploring the inherent physics of TMOs, to date research in these aspects still remains at an early stage. A major obstacle is that quantifying the inherent features, such as the exchange and correlation effects, in TMOs is rather difficult. This makes numerically establishing the correlation between inherent features and reaction activity, which is of significance in outlining a rough prospect to stimulate deeper explorations, seems unachievable at this stage. A breakthrough on this point may rely on further development of DFT-based techniques, where a suitable parameter can be extracted to ideally represent the target inherent feature. After successfully extracting a suitable parameter to describe the inherent feature, incorporating it with the surface-adsorption-related descriptor to develop a new one should give more accurate design principles. It is worth noting that the incorporation of inherent features and adsorption energy may not be a simple process of summing up the inherent features. As surface adsorption energy is much more relevant to the reaction performance, its proportion in the integrated descriptor may be much higher than that of the inherent features. Therefore, the procedure of identifying the subtle percentage of each type of feature is crucial. Machine learning and related artificial intelligence techniques may be of great assistance in accelerating this process.

## 5. CONCLUSIONS

In summary, although to what extent have TMOs been exploited as electrocatalyst is rather difficult to measure, one thing is clear: that the potential of TMOs is so enormous that their upper limit for catalytic applications is far from being reached. The theories and technologies of conventional design regime based on surface-adsorption-related descriptors are mature and great achievements have been made accordingly. However, the complexity of inherent features in TMOs, and their unneglected influence on catalysis offer additional opportunities to further drive the activity of TMOs beyond the volcano summit. Explorations in these aspects may be hotspots in future catalysis research.

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### Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

### Notes

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