Adsorption-energy-based activity descriptors for electrocatalysts in energy storage applications

Youwei Wang¹, Wujie Qiu¹, Erhong Song¹, Feng Gu¹, Zhihui Zheng¹, Xiaolin Zhao¹, Yingqin Zhao¹, Jianjun Liu¹,* and Wenqing Zhang¹,2,*

1 State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, China and 2 Materials Genome Institute, Shanghai University, Shanghai 200444, China

*Corresponding authors. E-mails: jliu@mail.sic.ac.cn; zhangwq@sustc.edu.cn

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ABSTRACT

Energy storage technologies, such as fuel cells, ammonia production and lithium–air batteries, are important strategies for addressing the global challenge of energy crisis and environmental pollution. Taking overpotential as a direct criterion, we illustrate in theory and experiment that the adsorption energies of charged species such as Li⁺ + e⁻ and H⁺ + e⁻ are a central parameter to describe catalytic activities related to electricity-in/electricity-out efficiencies. The essence of catalytic activity is revealed to relate with electronic coupling between catalysts and charged species. Based on adsorption energy, some activity descriptors such as d-band center, e⁻-electron number and charge-transfer capacity are further defined by electronic properties of catalysts that directly affect interaction between catalysts and charged species. The present review is helpful for understanding the catalytic mechanisms of these electrocatalytic reactions and developing accurate catalytic descriptors, which can be employed to screen high-activity catalysts in future high-throughput calculations and experiments.

Keywords: activity descriptors, electrocatalysts, adsorption energy, energy storage applications, overpotential

INTRODUCTION

One of the most central themes of the development of society is increasing energy demands [1]. Under environmental concerns such as pollution and the greenhouse effect, environment-friendly energy storage applications such as Li-ion batteries, metal–air batteries and fuel cells, some of which are mature technologies for practical applications, the others being still under development, are proposed to replace fossil resources (oil, gas and coal) by reversibly converting chemical energy from/into electricity [2]. Among the challenges to improve the electricity-in/electricity-out efficiencies, the high overpotential (defined as the difference between charging and discharging voltages) is one of the most urgent issues for practical applications. Electrocatalysts are applied to lower overpotential in the conversion of low-value molecules (e.g. water, dinitrogen, inactivated metal oxide) into high-value products (e.g. hydrogen, ammonia, activated cations and anions) [3,4]. Thus, electrocatalysis, in the broadest sense, dominates the electrochemical performance.

Compared with the equilibrium voltage of 2.96 V according to the Nernst equation, Li–air batteries (O₂ + 2Li⁺ + 2e⁻ ⇌ Li₂O₂), inducing an outstanding theoretical specific energy of ~3500 Wh/kg, suffer from a high charging voltage of 4.2–4.4 V and a low discharging voltage of 2.5–2.7 V, which lead to low cycle life, low round-trip efficiency and thus poor electrochemical performance [5,6]. Electrocatalysts such as Pt/Au nanoparticles have the ability to decrease charging voltages and increase discharging voltages and thus generate a higher round-trip efficiency with longer cycling life and larger energy capacity [7]. Electrolytic cells have the ability to convert the universal feedstock of water/carbon dioxide into high-value hydrogen/gas, e.g. water splitting is applied to produce pure hydrogen via electrochemical processes (H₂O → 1/2O₂ + 2H⁺ + 2e⁻ in
acidic solution and $2\text{OH}^- = \frac{1}{2}\text{O}_2 + \text{H}_2\text{O} + 2e^-$ in alkaline solution) and then fuel cells provide clean electricity through the reverse reactions [8–13]. However, the electricity-in/electricity-out overpotential from the energy cycle of electrolytic cells and fuel cells leads to a poor electrochemical performance [14]. Therefore, electrocatalysis plays a key role in electricity-in/electricity-out efficiency [15–18]. In addition, $\text{N}_2$ conversion into $\text{NH}_3$ ($\text{N}_2 + 6\text{H}^+ + 6e^- = 2\text{NH}_3$) has recently been considered as a green renewable energy technology [19]. However, though the conversion is an exothermic reaction, about 1.4% of all energy consumed by mankind is attributed to the widely applied Haber–Bosch synthesis of ammonia because the $\text{N} = \text{N}$ triple bond is too stable and needs excess energy to break [20–23]. $\text{V}_3\text{C}_2\text{MXexe}$, a promising material to capture and activate $\text{N}_2$, was reported by mankind is attributed to the widely applied Haber–Bosch synthesis of ammonia because the $\text{N} = \text{N}$ triple bond is too stable and needs excess energy to break [20–23]. $\text{V}_3\text{C}_2\text{MXexe}$, a promising material to capture and activate $\text{N}_2$, was reported to have the ability to catalyze the high-temperature and high-pressure Haber–Bosch process at room temperature with an activation barrier of 0.64 eV; it can thus reduce the electric consumption for ammonia synthesis [24].

There are some challenges in designing high-activity catalysts for electrochemical conversions because accurate models for the material selections are still unavailable. For example, ‘Sabatier principle’ behavior leads to ‘volcano-type’ relationships and ‘Brønsted–Evans–Polanyi’ (BEP) behavior shows linear relationships between catalytic activities and descriptors [25–27]. In other words, the catalytic activities depend on the chosen descriptors. As the apparent activity for a solid catalyst is governed by both the unit activity on each active site (intrinsic) and the number of exposed active sites (extrinsic) [28, 29], the aim of this review is to reveal thermodynamic relationships between catalytic descriptors and intrinsic activity for reducing overpotential. Because the electrochemical reactions mainly occur at the interface between catalysts and charged species, the essence of catalytic activity is revealed to relate to the interfacial electronic coupling. As a parameter to present the electrochemical coupling, adsorption energy is an effective parameter to describe catalytic activities. Because electrochemical reactions usually contain ion–electron pairs ($\text{H}^+ - e^-$ or $\text{M}^{n+} - ne^-$, $\text{M} = \text{Li, Na, Zn…}$ ), we discuss the relationship between adsorption energy and catalytic activities in some typical reactions. Then, based on $d$-band theory, the relationships between catalytic activities and intrinsic physical properties of catalysts, such as $d$-band center, $e_g$-electron number, tolerance factor and charge transfer, are investigated for catalyst design. This review simplifies the complexity of electrochemical catalyst design into some fundamental descriptors of catalysts, which can be used to screen high-activity catalysts in future high-throughput calculations and experiments.

**RELATIONSHIP BETWEEN CATALYTIC ACTIVITY AND ADSORPTION ENERGY**

Electrochemical reactions always involve ions (proton or metal cations) and electrons, $\text{H}^+ - e^-$ or $\text{M}^{n+} - ne^-$. Therefore, before discussing the relationship between catalytic activity and descriptors, we perform the method to calculate the free energy change of the reactions, which involves ion–electron pairs. Taking one step in water electrolysis ($\text{H}_2\text{O} \rightarrow \text{OH}^- + \text{H}^+ + e^-$) at the anode as an example, the free energy change is given by:

$$\Delta G_1 = E_{\text{OH}^+} + (E_{\text{H}^+} - eV_1) - E_{\text{H}_2\text{O}}$$

(1)

Meanwhile, the free energy change of the reaction $\text{H}^+ + e^- \rightarrow \frac{1}{2}\text{H}_2$ at the referenced $\text{H}^+/\text{H}$ electrode is given by:

$$\Delta G_2 = \frac{1}{2}E_{\text{H}_2} - (E_{\text{H}^+} - eV_2)$$

(2)

As a result, the total reaction is an integration of Eq. 1 and Eq. 2:

$$\Delta G = E_{\text{OH}^+} + \left(\frac{1}{2}E_{\text{H}_2} - eU\right) - E_{\text{H}_2\text{O}}$$

(3)

The electromotive potential $U = V_{1} - V_{2}$, which corresponds to the charging voltage vs the $\text{H}^+/\text{H}$ electrode, is determined by shifting the free energies of all intermediates in the whole reaction to $\Delta G < 0$. Also, Eqs. 1–3 demonstrate that the energy change of the $\text{H}^+ - e^-$ pair is equivalent to the energy $\frac{1}{2}E_{\text{H}_2} - eU$, vs the $\text{H}^+/\text{H}$ electrode. This thermodynamic model is widely used to reflect the energy conservation in a multistep electrochemical reaction.

The electrocatalytic processes usually involve the adsorption of reactants on the surfaces of catalysts, break some reactant bonds to form new chemical bonds between the catalyst and reactants, and result in activated intermediates. Because the catalytic activity is attributed to the interfacial electronic coupling, adsorption energy is a good descriptor to identify catalytic activity for surface reactions [30, 31]. Based on the free energies of reactants ($R_1, R_2,...$) and products ($P_1, P_2,...$), the electrochemical reaction and free energy change can be simply taken as:

$$\Delta G(U) = \left(E_{P_1} + E_{P_2} + ...\right) - \left(E_{R_1} + E_{R_2} + ...ight)$$

(4)
where $U$ is the charging/discharging voltage and $E_{R_n^m}$ and $E_{P_n^m}$ are the free energies of the $m$th reactant and $n$th product adsorbed on the catalyst (where * denotes a site on the catalyst surface), respectively. Furthermore, if defining the adsorption energy as $E_{n^{ads}} = E_{n^*} - (e^+ E_{n})$ and assuming that the free energy of a catalyst is invariable through the whole electrochemical reaction, the free energy change can be written as:

$$\Delta G(U) = (E_{P_1} + E_{P_2} + \ldots) - (E_{R_1} + E_{R_2} + \ldots) - (E_{n^{ads}} + E_{n^{ads}} + \ldots)$$

In that way, the whole electrochemical reaction is composed of an intrinsic reaction part, $(E_{P_1} + E_{P_2} + \ldots) - (E_{R_1} + E_{R_2} + \ldots)$, and a catalytic effect part, $(E_{n^{ads}} + E_{n^{ads}} + \ldots)$. As a result, the catalytic effect is directly reflected in the adsorption energy differences of reactants and products.

To present the relationship between the kinetic rate and the thermodynamic free energy change, J. K. Nørskov et al. developed a simple model, in which the activation barrier for the rate-limiting step is assumed to be equal to the largest free energy change of all electrochemical steps [32]. Consider an electrochemical reaction under a voltage of $U$; the rate constant for the reaction can be written as:

$$k(U) = k_0 e^{-\Delta G(U)/k_B T}$$

where $k_0$ is the prefactor related to all details of the ion transfer to the surface and recombination with the electron, $k_B$ is the Boltzmann constant and $T$ is the temperature. In units of current density, the rate constant is:

$$i_k(U) = 2e N_{act} k(U) = 2k_0 e^{N_{act}} e^{-\Delta G(U)/k_B T}$$

where $N_{act}$ is the number of activated sites per surface area. That equation represents an upper bound to the kinetic rate. As a result, the rate-limiting step is the step with the largest $\Delta G(U)$ in the whole electrochemical reaction. In addition, J. Cheng et al. found that a heterogeneous catalytic reaction with multi-step surface processes can be treated kinetically as consisting of two steps, an adsorption step and a desorption step [33]. It can be illustrated that even the hypothetical one-step adsorption/desorption process follows the BEP relation, a volcano curve can be obtained from kinetic analysis including both adsorption and desorption processes. These studies demonstrated that the interfacial adsorption has a
great effect on the kinetic limiting rate. Because the kinetic catalytic activity is also related to thermodynamic $\Delta G(U)$, we just focus on the thermodynamic descriptors and neglect the kinetic effect in this review.

Because the rate-determining step in an electrochemical reaction can be categorized as ion–electron pair reactions (e.g. the hydrogen evolution reaction, HER), evolution reactions (e.g. the oxygen evolution reaction, OER, or the methane evolution reaction in carbon dioxide conversion into methane) and reduction reactions (e.g. the oxygen reduction reaction, ORR, or the N₂ reduction reaction in ammonia synthesis, NRR), we discuss adsorption energy as a catalytic descriptor in these typical reactions to present the effect of electronic coupling between catalysts and charged species on catalytic activity.

### Hydrogen evolution reaction (ion–electron pair evolution reaction)

Ion–electron pair evolution/reduction reactions usually involve proton/metal cations and electrons, among which HER is widely studied. As shown in Fig. 1a, HER is a classic two-electron-transfer reaction and may occur through either the Volmer–Heyrovsky or Volmer–Tafel mechanisms:

Volmer step : $H^+ + e^- \rightarrow H^*$

Heyrovsky step : $H^+ + e^- + H^* \rightarrow H_2 + *$

Tafel step : $H^* \rightarrow \frac{1}{2}H_2 + *$

Correspondingly, the free energy changes are given by:

$$\Delta G_{Volmer} = E_{H^*} - * - \frac{1}{2}E_{H_2} + \Delta E_{ZPE} - T \Delta S_{H}$$

$$\Delta G_{Heyrovsky} = E_{H^*} + * - E_{H^*} - \frac{1}{2}E_{H_2} - (\Delta E_{ZPE} - T \Delta S_{H})$$

$$\Delta G_{Heyrovsky} = \frac{1}{2}E_{H_2} + * - E_{H^*} - (\Delta E_{ZPE} - T \Delta S_{H})$$

where $\Delta E_{ZPE}$ is the difference in zero-point energy and $\Delta S_H$ is the entropy difference between the adsorbed state and the gas phase. The overall HER
activity primarily depends on the hydrogen adsorption energy \cite{34,35}.

The catalytic activity shows a volcano trend as a function of the adsorption strength between H atoms and adsorbed sites of catalysts in Fig. 1b, which leads to an optimal value of $\Delta G_{H^\ast} \approx 0$ to compromise the reaction barriers and achieve a high HER activity \cite{36}. The volcano-like trends between catalytic activity and hydrogen adsorption energy have been reported for a range of catalyst materials \cite{39–41}. To get the optimal HER activity, the relationship between reaction coordinate and hydrogen free energy is introduced in Fig. 1c, in which a positive value of hydrogen free energy stands for weak hydrogen adsorption and a negative value stands for strong hydrogen adsorption \cite{37}. Too weak chemisorption between hydrogen and the catalysts will limit the Volmer-step rate, whereas too strong binding will suppress the desorption in the Heyrovsky or Tafel steps. As a result, Pt and MoS$_2$ are considered as high-activity catalysts.

Although platinum is considered as a high-activity catalyst for HER by achieving negligible overpotential and high rate in acidic solutions, the scarcity of Pt limits the application \cite{36}. Fortunately, recent studies identified that, although the surface of MoS$_2$ is inactive for HER, the edge sites of Mo(110)) with 50% hydrogen coverage perform near the optimal catalytic activity by $\Delta G_{H^\ast} = 0.08$ eV \cite{37}. For the surface of MoS$_2$, the off-top of HER activity is ascribed to the weakened H–S bonding strength. As the higher energy level of the S 3p orbital is relative to the H 1s orbital, the H adsorption on the basal plane of MoS$_2$ is too weak, leading to $\Delta G_{H^\ast} \approx 2$ eV, and the edge sites enhance the strength of the H–S bond, resulting in a higher catalytic activity. In addition, as shown in Fig. 1d, Co-doping into the MoS$_2$ in-plane can increase the
HER activity, because Co-doping lowers the energy level of dangling bonds of S atoms, offsets the energy mismatch from the H 1s orbital and enhances the adsorption strength between H atoms and edged-S sites [38, 42]. Nevertheless, further increasing the Co-doping concentration will lead to too great an adsorption strength between the H and S atoms, which lowers the HER activity. Besides doping, S-vacancy can also achieve enhanced HER activity by tuning the adsorption strength between H atoms and MoS2 [43]. As a result, the effects of doping or defects on catalytic activity mainly depend on the adsorption strength between the H atoms and the MoS2 catalyst. These results demonstrate that adsorption energy is an effective descriptor for HER activity.

Oxygen/methane evolution reaction

OER is an important part of the electrochemical process. As shown in Fig. 2a, the reactions and free energy changes of OER in water electrolysis are given by:

\[ \Delta G_1 = G_{\text{OH}^+ + \frac{1}{2} \text{H}_2} - G_{\text{H}_2\text{O}(l)} \]

\[ \Delta G_1 = E_{\text{OH}} + E_{\text{OH}}^{\text{ads}} + \left( \frac{1}{2} E_{\text{H}_2} - \epsilon U \right) - E_{\text{H}_2\text{O}(l)} \]

\[ \Delta G_2 = G_{\text{O}^+ + \frac{1}{2} \text{H}_2} - G_{\text{OH}^+} \]

\[ \Delta G_2 = (E_{\text{O}} - E_{\text{OH}}^{\text{ads}}) + E_{\text{O}} + \left( \frac{1}{2} E_{\text{H}_2} - \epsilon U \right) - E_{\text{OH}} \]

\[ \Delta G_3 = G_{\text{OOH}^+ + \frac{1}{2} \text{H}_2} - G_{\text{O}^+ + \text{H}_2\text{O}} \]

\[ \Delta G_3 = (E_{\text{OOH}}^{\text{ads}} - E_{\text{O}}^{\text{ads}}) + E_{\text{OOH}} + \left( \frac{1}{2} E_{\text{H}_2} - \epsilon U \right) - E_{\text{O}} - E_{\text{H}_2\text{O}} \]

\[ \Delta G_4 = G_{\text{O}_2 + \frac{1}{2} \text{H}_2} - G_{\text{OOH}^+} \]

\[ \Delta G_4 = E_{\text{O}} + \left( \frac{1}{2} E_{\text{H}_2} - \epsilon U \right) - E_{\text{OOH}} - E_{\text{OOH}} \]

Because metals including Pt usually suffer from oxidation in the OER process and lead to a different type of surface in the OER process, metal oxides present higher catalytic activities than pure metals in the OER process. As shown in Fig. 2b, J. Rossmeisl et al. found a volcano-like trend between OER catalytic activity and \( \Delta G_{\text{O}^+ - \Delta G_{\text{OH}}^+} \), an adsorption energy difference between oxygen and hydroxyl, for metal oxides [44]. Because \( \text{OH}^+ \) and \( \text{OOH}^+ \) normally prefer the same type of adsorbed sites, the correlated adsorption energy of \( \text{OH}^+ \) and \( \text{OOH}^+ \) is very similar. In fact, as shown in Fig. 2c, there is an approximately constant difference of \( \Delta E_{\text{OOH}} - \Delta E_{\text{OH}} \), 3.2 eV, for all the metal oxides. As a result, the chemisorption energy of \( \text{OOH}^+ \) is replaced by that of \( \text{OH}^+ \) plus 3.2 eV and the lower limit for the OER overpotential depends on the chemisorption energy difference between \( \text{O}^+ \) and \( \text{OH}^+ \) by max[\( \Delta G_{\text{O}_2}, \Delta G_{\text{OH}} \)] \( \approx \) \( \max[\{ \Delta G_{\text{O}^+ - \Delta G_{\text{OH}}} \}, 3.2 \text{ eV}-\{ \Delta G_{\text{O}^+ - \Delta G_{\text{OH}}^+} \}] \). Therefore, the OER activity can be described by \( \Delta G_{\text{O}^+ - \Delta G_{\text{OH}}} \) and the optimal activity occurs near \( \Delta G_{\text{O}^+ - \Delta G_{\text{OH}}} = 1.6 \text{ eV} \) to balance \( \Delta G_2 \) and \( \Delta G_3 \). Too large a chemisorption energy difference between \( \text{O}^+ \) and \( \text{OH}^+ \), i.e. \( \Delta G_{\text{O}^+ - \Delta G_{\text{OH}}} >> 1.6 \text{ eV} \), will lead to a high overpotential in Eq. 10 to desorb adsorbed \( \text{O}^+ \), while too small a chemisorption energy difference will result in a high overpotential to desorb \( \text{OH}^+ \). As the OER activity in water electrolysis depends on the adsorption energies of oxygen and hydroxyl, J. Rossmeisl et al. improve the catalytic activity for the OER process by weakening O binding but strengthening hydroxyl binding to the catalysts [45].

In addition, other molecule evolution reactions may be involved in electrochemical processes. For example, there are vast possible products in carbon dioxide conversions, including carbon dioxide, methane, methanol, formate and so on. In this review, we take the methane evolution reaction as an example. J.K. Nørskov et al. performed a theoretical study on the C–H bond activation in one step of methane production, \( \text{H}^+ + \text{CH}_4 \rightarrow \text{CH}_4^+ \) [46]. That particular step involves the desorption of \( \text{H}^+ \) and the formation of the C–H bond. As shown in Fig. 2d and e, the activation energy shows Brønsted–Evans–Polanyi relationships with the adsorption energy of \( \text{H}^+ \) and formation energy of the C–H bond. In addition, a unifying descriptor, the formation energy of the active site motif \( G_{f\text{p}} \), was employed to
**Figure 2.** (a) Catalytic cycle of OER in water electrolysis. (b) Activity trends towards oxygen evolution plotted for metal oxides. The negative theoretical overpotential was plotted against the standard free energy of the $\Delta \Delta G_{\text{O}}^{*} - \Delta \Delta G_{\text{OH}}^{*}$ step. (c) Adsorption energy of OOH$^{*}$ plotted against the adsorption energy of OH$^{*}$ on perovskites, rutile, anatase, Mn$_x$O$_y$, Co$_3$O$_4$, and NiO oxides. (d) Universal scaling for C–H activation of methane ($E_{\text{TS}} = 0.75E_{\text{H}} + 1.09$, mean absolute error (MAE) = 0.11), ethane ($E_{\text{TS}} = 0.75E_{\text{H}} + 0.7$, MAE = 0.13) and methanol ($E_{\text{TS}} = 0.75E_{\text{H}} + 0.54$, MAE = 0.12). (e) The activation energies of C$_1$–C$_3$ alkanes and methanol on Fe(Mg)/MOF-74 plotted as a function of C–H bond energies. (f) 1D volcano plot for the intrinsic rate of methane activation as a function of $G_i$, which is defined as the oxygen activation energy at the active sites. Reprinted from Refs. [44,46] with permission from 1999–2017 John Wiley & Sons and Nature Publishing Group.
predict C–H activation barriers (see Fig. 2f). One approach to improving activity is to tune $G_f$ by changing the physical characteristics of the catalysts and IrO$_2$ and Cu oxides, which lie close to the peak of the volcano of methane activation. Moreover, Petersen and Nørskov also showed another descriptor, adsorption energy of CO, for the overall CO$_2$ reduction into methane and the volcano-like trend between adsorption energy and catalytic activity leading to the major catalyst of copper [47]. In addition to the work in Ref. [46], the importance of Ref. [47] is to demonstrate the fact that the strengthened adsorption energy of CHO relative to that of CO would enable the protonation of CO to CHO at a less negative potential, resulting in a substantially lower overpotential for CO$_2$ reduction into CH$_4$.

**Oxygen/nitrogen reduction reaction**

As the reverse process to OER, ORR in fuel cells ($O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$) involves either four proton–electron transfers to form water or two proton–electron transfers to produce hydrogen peroxide. As shown in Fig. 3a, a simple dissociative mechanism to form water is given by:

$$\frac{1}{2}O_2 + \ast \rightarrow O^\ast (12)$$

$$\Delta G_0 = G_{O^\ast}(U) - E_{O_2} = E_{O^\ast} - \frac{1}{2}E_{O_2} = E_{ads}^{O^\ast} (13)$$

$$O^\ast + H^\ast + e^- \rightarrow OH^\ast (14)$$

$$\Delta G_1 = G_{OH^\ast}(U) - G_{O^\ast + \frac{1}{2}H_2}(U)$$

$$= (E_{ads}^{OH^\ast} - E_{ads}^{O^\ast}) + E_{OH} - E_O$$

$$- \left( \frac{1}{2}E_{H_2} - \epsilon U \right) (14)$$

$$OH^\ast + H^\ast + e^- \rightarrow H_2O + \ast (15)$$

$$\Delta G_2 = G_{H_2O}(U) - G_{OH^\ast + \frac{1}{2}H_2}(U)$$

$$= E_{H_2O} - E_{OH} - E_{ads}^{OH^\ast} - \left( \frac{1}{2}E_{H_2} - \epsilon U \right) (15)$$

As shown in Fig. 3b–c, theoretical volcano-like trends between ORR catalytic activity and oxygen or/and hydroxyl adsorption energy for metal catalysts are observed in fuel cells [32,48]. For metals, such as Ni, which binds O and OH strongly, the activity is limited by the proton transfer to oxygen and hydroxyl. For metals, such as Au, which binds O and OH weakly, although the proton transfer is fast, oxygen is less stable on the surfaces of catalysts than it is in the gas phase and thus no transfer of protons and electrons to oxygen on the surfaces of catalysts occurs at the beginning of the ORR process. Compared with strong binding, weak binding leads to a fast attenuation in ORR activity. Even the catalyst Pt, which is near the top of the volcano-like trend in metals, still has a nonzero overpotential of 0.3–0.4 V [32,48]. Pt$_3$M (M = Ni, Fe, Co, Ti, Sc, Y) bimetallic alloy, as a Pt-based catalyst, can further reduce the overpotential by increasing the oxygen adsorption energy by 0.2–0.3 eV related to that of a pure Pt catalyst [49–51].

Some groups have also elucidated the mechanism of O$_2$ reduction into Li$_2$O$_2$ on the surface of catalysts in the discharging process, which is a two-step reaction [53,54]:

$$Li^+ + O_2^\ast + e^- \rightarrow LiO_2^\ast$$

$$\Delta G_1 = G_{LiO_2^\ast} - G_{Li+O_2}$$

$$= E_{LiO_2} - (E_{Li} - \epsilon U) - E_{O_2} + E_{abs}^{LiO_2} - E_{abs}^{O_2}$$

$$Li^+ + LiO_2^\ast + e^- \rightarrow Li_2O_2^\ast (s)$$

$$\Delta G_2 = G_{Li_2O_2^\ast} - G_{LiO_2^\ast+Li}$$

$$= E_{Li_2O_2} - (E_{Li} - \epsilon U) - E_{LiO_2} + E_{abs}^{Li_2O_2} - E_{abs}^{LiO_2}$$

The whole process neglects the disproportionation reaction, 2LiO$_2$ → Li$_2$O + O$_2$, in solutions, where catalysts have little effect.

Y. Lu et al. demonstrated that the intrinsic ORR activity of polycrystalline Pd, Pt, Ru, Au and glass carbon surfaces in Li–air batteries is primarily correlated to oxygen adsorption energy and generates a volcano-like trend [55], which is in good agreement with the trend of nanoparticle catalysts [56,57]. As shown in Fig. 3d, G.K.P. Dathar et al. performed a theoretical study by calculating the catalytic activity of Au, Ag, Pt, Pd, Ir and Ru for catalyzing the Li-ORR of the first step [52]. They found that the catalytic activity exhibits a volcano-like trend with oxygen adsorption energy and that Pt and Pd perform high Li-ORR catalytic activities, which is in close agreement with Y. Lu et al.’s work [55]. According to the free energy change of the first step,
Figure 3. (a) Catalytic cycle of ORR in fuel cells. Trends in oxygen reduction activity plotted as a function of (b) O adsorption energy and (c) both O and OH adsorption energies in fuel cells. (d) Volcano-like relationships between catalytic activity and adsorption energies in Li–air batteries. (e) 2D volcano plots of limiting potentials for N₂ reduction as a function of the potential limiting steps with two cases for the potential limiting step for the fcc (111) surface of reactive materials. (f) Comparison of HER and NRR limiting-potential volcanoes. The HER and NRR overpotentials as a function of the N⁺ adsorption energy descriptor on the (111) surface are shown in blue and black, respectively. Reprinted from Refs. [22,32,52] with permission from 2017 American Chemical Society and 1999–2017 John Wiley & Sons.
the discharging voltage shows a direct relationship with the adsorption energy difference of O₂ and LiO₂. Too strong oxygen–metal interaction (e.g. Au, Ag) hinders O₂ activation to bond with lithium, whereas too weak oxygen–metal interaction (e.g. Au, Ag) hinders O₂ activation to bond with Li⁺. Based on density functional theory (DFT) calculations, H. Kim et al. found that Pt₃Co exhibits remarkably high ORR and OER catalytic activities, which are ascribed to the high Li and low LiO₂ adsorption energies, compared to pure Pt [58]. However, the equilibrium potential of the discharging voltage for the overall reaction is given by:

\[
U_{\text{discharge}} = \left(-E_{\text{Li}_2\text{O}_2} - \Delta N_{\text{Li}}\mu_{\text{Li}} - \frac{1}{2}\Delta N_{\text{Li}}\mu_{\text{O}_2}\right) / \Delta N_{\text{Li}}
\]  

where \(\mu_{\text{Li}}\) and \(\mu_{\text{O}_2}\) are the chemical potentials of Li and O₂, respectively, \(E_{\text{Li}_2\text{O}_2}\) is the free energy of bulk Li₂O₂, and \(\Delta N_{\text{Li}}\) is the number of Li atoms required to form the bulk Li₂O₂. Equation 18 shows that the equilibrium potential undergoes almost no obvious change for the discharging production of bulk Li₂O₂.

Besides ORR, electrochemical reactions may involve other molecule reduction reactions, such as the N₂ reduction reaction in ammonia synthesis. In N₂ reduction reactions of the ammonia synthesis process, we consider a possible reaction to follow an associative Heyrovsky mechanism, where the nitrogen molecules are hydrogenated by protons and electrons:

\[ \text{N}_2 + \text{H}^+ + e^- \rightarrow \text{NH}_3 + \text{H}_2 \]

\[
\Delta G_1 = G_{\text{NH}_3 + \text{H}^+ + \text{N}_2} - G_{\frac{1}{2}\text{H}_2 + \text{N}_2}\]
\[ = E_{\text{NH}_3} + E_{\text{H}^+} - \left(\frac{1}{2}E_{\text{H}_2} - \epsilon U\right) - E_{\text{N}_2}\]
\[ + E_{\text{N}_2}^{\text{ads}} - E_{\text{H}_2}^{\text{ads}} \]  

\[
\Delta G_2 = G_{\text{NH}_3 + \text{H}^+ + \text{N}_2} - G_{\frac{1}{2}\text{H}_2 + \text{N}_2 + \text{H}^+}\]
\[ = E_{\text{NH}_3} + E_{\text{H}^+} - \left(\frac{1}{2}E_{\text{H}_2} - \epsilon U\right) - E_{\text{N}_2}\]
\[ + E_{\text{N}_2}^{\text{ads}} - E_{\text{H}_2}^{\text{ads}} \]  

Theoretical works have shown that the reductive adsorption of \(\text{N}_2\text{H}^+\) is one of the rate-determining steps, while desorption of \(\text{NH}_2\text{H}^+\) for the (211) surface and the adsorption difference of \(\text{NH}_2\text{H}^+\) and \(\text{N}^+\) for the (111) surface of reactive metals are the other rate-determining steps [24,59]. As a result, the overpotential depends on the free energy difference by \(\Delta G_1, \Delta G_5, \Delta G_6\). As shown in Fig. 3e–f, J.K. Nørskov et al. demonstrated a volcano-like trend between nitrogen adsorption energy and catalytic activity on fcc (111) surfaces of reactive metals using DFT calculations [22,59]. Those results demonstrate the same fact as Li–air batteries: that too-weak binding between metal and nitrogen limits the adsorption of N₂ as N₂H⁺ in the early reaction period, whereas too-strong binding suppresses the protonation of NH⁺ into NH₂⁺ or further NH₂⁺ into NH₃. For metal catalysts, those near the top of the volcano can reduce the overpotential to about 0.5 V.
As theoretical and experimental studies have demonstrated, adsorption energy is an effective descriptor for catalyst design. The relationship between adsorption energy and catalytic activity is helpful for the initial selection of catalysts and the key to mapping the relationship is to establish the quantitative relationship between the intrinsic electronic properties of materials and catalytic descriptors.

### SOME DESCRIPTORS RELATED TO ADSORPTION ENERGY

Addressing the relationship between catalytic activity and descriptors is the central theme to tailor electrochemical properties in catalyst design. The principle for mapping the relationships is to choose the right descriptors, such as band-gaps in photovoltaic applications and ZT (including electric conductance and thermal conductance) in thermoelectric materials. In this section, we discuss some other catalytic descriptors related to intrinsic properties of catalysts.

#### d-band center

Molecular-level theoretical studies of heterogeneous catalysts such as d-band theory have been established to understand the complex processes in electrochemical reactions [60,61]. d-band theory highlights the relationship between band structures of catalysts and adsorption energy, which theoretically explains the intrinsic catalytic mechanism. For example, when 2p electrons of an O2 adsorbate interact with s electrons of the metal, the strong covalent bonding states lead to low activity as the O2 adsorbate is dissociated and in a 2− state, i.e. the oxygen ions have a charge of minus two. However, when the O2 molecule absorbs a noble metal with d electrons, the electronic coupling of 2p electrons to d electrons leads to different strengths of chemical bonds. If the d bands of noble metals are well below the Fermi level, the antibonding states of p-d coupling are completely filled with d electrons and there is little charge transfer from the noble metals to the O2 adsorbate. The small charge transfer leads to weak binding (small adsorption energy) and is not enough to break the O=O bonds. As a result, the O2 adsorbate is still low activity. For example, the binding of O2 to a gold surface is weaker than the O=O bond in O2 molecules, so that the O2 molecules will not dissociate on gold at all, i.e. the gold has low activity to dissociate O2 molecules [60]. Though the result is unique and noble for gold, it also means that gold has no catalytic activity for O2 at all. For those noble metals with d bands across the Fermi level, electrons transfer from the d band to the bonding state of p-d coupling, which enhances the strength of the chemical bonds between the O2 adsorbate and the noble metals. As the charge transfer increases, the strong binding between the noble metals and the O2 molecules breaks the O=O bond into O–O bonds, leading to activated intermediates of adsorbed O2. If the broken O=O bonds of molecular O2 accept charge, which means that the O 2p is in the 0–1− state, i.e. the charge of the oxygen ions is higher than minus one but lower than zero valence, the activity of molecular O2 is improved and the noble metals show high catalytic activity. However, when the charge transfers from noble metals to O2 molecules lead to the O 2p being close to the 2− state, the O2 molecules completely dissociate on the noble metals and the activity of the intermediates is lower. These results demonstrate the fact that the catalytic activity of noble metals on O2 molecules increases and then decreases as the adsorption energy increases.

Because the chemical adsorption energies are given by the coupling of O 2p to the d electrons, some descriptors can be associated with the catalyst activity. B. Hammer and J.K. Nørskov discussed the relationship between adsorption activity and the d-band center of metal catalysts [61]. As shown in Fig. 4, based on experimental data [62] and DFT calculations, they found that the adsorption energy shows a linear relationship with the position of the d-band center relative to the Fermi level and that chemisorption energies increase towards the left of the periodic table of elements in the 4d transition metal series. This relationship provides a path for locating high activity compositions from the large potential chemical space.

#### Tolerance factor and eg-electron number

d-band theory has provided a molecular-level understanding of the relationship between adsorption energy and d-band center. These quantitative structure—activity relationships show the desired catalytic behavior for structural and/or elemental descriptors. Recently, as shown in Fig. 5, W. T. Hong et al. reviewed the oxygen-evolution catalytic activity in perovskite oxides and plotted the relative catalytic activity with different descriptors [63]. They demonstrated how statistical learning can be used to address ambiguities in the OER activity descriptors. Based on factor analysis [64], they reduced the 14 descriptors into five major descriptors: charge-transfer energy [65,66], Madelung potentials, metal–oxygen bond length [67,68], ϵg electrons [69,70] and d electrons [71]. The five major descriptors can also be explained by adsorption energy. While the metal–oxygen bond length and...
tolerance factor mainly show the structural effects on the adsorption energy between adsorbates and the catalyst surface, the $d$ electrons and $e_g$ electrons reflect the effect of element compounds.

Alloying is a good strategy to explain the structural descriptor of the tolerance factor. The addition of another metal to a metallic surface, which changes the electronic structure of the alloy surface from that of the pure metallic surface alone, possibly changes the metal–oxygen bonding geometries and tunes the energy levels of bonding and antibonding states [61]. The structural effect of alloying on metal–oxygen bond length can be ascribed to the strain due to the lattice parameter difference. Specifically, when the metal surface undergoes a compressive or tensile strain, the overlap of the $d$ band will either increase or decrease, which changes the $d$ bandwidths and thus the adsorption energy between alloy and oxygen. The shift of the $d$ band on alloying has a great effect on the catalytic activity, which may lead to higher catalytic activity than pure metal [50, 51, 58, 72, 73].

Figure 4. Comparison of DFT-based oxygen chemisorption energies, $E(O/$surface$)-E(O_2)-E($surface$)$, experimental values and model estimates of the bond strengths for the various close-packed transition and noble metal surfaces. The calculated adsorption energies correlate well with the $d$ band center $\epsilon_d$. Reprinted from Ref. [61] with permission from Elsevier.

Figure 5. Confidence band plots of trends in relative OER activity for $d$ electrons, $e_g$ electrons, tolerance factor and charge-transfer energy. The full set of data (training and test) is plotted. A LOESS smoothing curve of the data is shown in white to visualize the trend, with 5000 nonparametrically bootstrapped smoothers used to determine the 68%, 95% and 99.7% confidence bands (lighter shade indicates larger confidence interval). Reprinted from Ref. [63] with permission from 2017 American Chemical Society.
$d$ electron number, another descriptor to describe the energy level of the $d$ band, shows the effect of elements on the ability of the surface to bond oxygen. In particular, the $e_g$ electron, the specific symmetry of $d$ orbitals, shows a volcano-like trend with catalytic activity [69,70]. Because the adsorption strength between the $O_2$ adsorbate and the catalyst surface depends on the occupancy of the bonding and antibonding states, the $e_g$ occupation has a great effect on the energy level of the $d$ band and thus acts as a good descriptor. In addition, the $t_{2g}$ occupation, another symmetry component of $d$ orbitals, is also a descriptor for the same reason. The difference between $e_g$ and $t_{2g}$ occupation is that one comes from occupied valence band states and the other from occupied conduction band states. Thus A. Vojvodic and J.K. Nørskov proposed the occupancy of $e_g$/$t_{2g}$ as a descriptor [76].

The effects of structural and elementary descriptors on catalytic activity can be explained in the $d$-band framework and thus related to adsorption energy. Furthermore, because structural and elementary descriptors are experimentally quantified compared with adsorption energy, they are useful for discovering new catalyst materials and ensuring a leap forward in electrochemical performance.

**Charge transfer**

Besides structural and elementary descriptors, charge transfer is also an important part in electrochemical reactions and improves the catalytic activity (see the last column in Fig. 5). The principle of charge transfer is to remove charge from stable bonds in reactants and lower the activation barrier of the rate-limiting step. In particular, if we consider the effect of charge transfer on free energy change, the relationship can be written as:

$$\frac{\partial G}{\partial e} = \left( \frac{\partial E_{P1}}{\partial e} + \frac{\partial E_{P2}}{\partial e} + \ldots \right)$$

$$- \left( \frac{\partial E_{R1}}{\partial e} + \frac{\partial E_{R2}}{\partial e} + \ldots \right)$$

$$+ \left( \frac{\partial E_{P1}^{abs}}{\partial e} + \frac{\partial E_{P2}^{abs}}{\partial e} + \ldots \right)$$

$$- \left( \frac{\partial E_{R1}^{abs}}{\partial e} + \frac{\partial E_{R2}^{abs}}{\partial e} + \ldots \right)$$

(25)

where the first two terms represent the free energy changes of products and reactants, and the last two terms represent the change of adsorption energy accompanied by charge transfer. As a result, charge transfer has a great effect on catalytic activity.

*J. Liu et al.* performed first-principles thermodynamic calculations to study the catalytic activity of X-doped graphene ($X = $ B, N, Al, Si, and P) materials as potential cathodes to lower the charging overpotential [78,79]. They found that Li-adsorbed sites on B-doped graphene, as the electron-withdrawing center, enhance charge transfer from Li$_2$O$_2$ to the cathode and thus reduce the O$_2$ evolution barrier. Furthermore, they took surface acidity (defined as the energy change of catalysts with charge transfer) as a descriptor of charge transfer to study the electrocatalytic activity in the charging process [77,80,81]. They elucidated that the O-rich Co$_3$O$_4$ (111) surface with a relatively low surface energy, promoting charge transfer from the Li$_2$O$_2$ particles to the underlying surface, has a high catalytic activity to reduce overpotential and the O$_2$ evolution barrier [80]. Furthermore, as shown in Fig. 6, based on a three-phase interfacial model of ‘Li$_2$O$_2$/catalysts/O$_2$’, they found that the O$_2$ evolution and Li$^+$ desorption energies show linear and volcano relationships with the surface acidity of catalysts, respectively, resulting in a volcano relationship between the charging voltage and surface acidity [77]. Moreover, T.S. Zhao followed the same strategy and discovered a new catalyst, RuO$_2$ [82].

The charge-transfer strategy is complex for fuel cells or water electrolysis because the reactants and products are pH-dependent [83,84]. Y. Shao-Horn et al. investigated the role of charge transfer on catalytic activity in an alkaline environment by varying Sr substitution of La$_{(1-x)}$Sr$_x$MnO$_3$ [85] and found that OER activity of perovskite catalysts can be enhanced by reducing the charge-transfer energy [63,65]. In addition, a previous review has highlighted the effects of covalent bonds (charge
transfer) and non-covalent electrostatic interaction (no charge transfer) on catalytic activity [14].

Theoretical and experimental studies have been exploring how to identify charge transfer as a catalytic descriptor. However, theoretical and experimental studies related to charge transfer are still rare. Moreover, it is hard to identify the quantitative relationship between catalytic activity and charge transfer, leading to a challenge to overcome. Furthermore, the integration of high-throughput experiments and calculations can be employed to speed up the material design and shorten the development cycle, in which effective descriptors play an important role in discovering new materials.

OUTLOOK
The development of electrocatalyst design for clean energy conversion has drawn increasing interest from the material research society. There have been outstanding reviews identifying the key limitations of known catalysts materials and proposing successful strategies, such as interfacial properties and activity/active-site control, to improve the efficiency of clean energy conversion [14,29]. One of the main conclusions is that chemisorption between adsorbates and catalysts dominates the catalytic activity. In this review, we have highlighted a simple strategy to improve catalytic activity, which is to reduce activation barriers of electrochemical reactions by tuning interfacial electronic coupling between the adsorbate and catalyst surface.

Based on thermodynamics, the complexity of electrochemical catalyst design is simplified into free energy changes of electrochemical reactions. Though adsorption energy is an effective descriptor for catalytic activity, the major problem with adsorption energy is that it is a physical quantity for theoretical calculations but a poor control variable for experiments. As a result, researchers choose other descriptors, such as $\epsilon_0$ and tolerance factor, to screen catalysts. The intrinsic relationships between adsorption energy and other descriptors are explained based on $d$-band theory. Fundamental understanding of structure–activity relationships between catalytic activity and the physical properties of catalyst materials is helpful in choosing effective descriptors and developing efficient multiscale computational models for an accurate description of catalyst materials. High-throughput calculations and experiments can be employed to speed up the screening of catalyst materials and shorten the development cycle in future studies.

However, even solving the intrinsic problem of activity, catalysts still face the vital requirements of stability and safety before practical applications. For example, carbon, a widely used cathode material because of its high conductivity and large surface area, is observed to be stable below 3.5 V during the charging and discharging processes of Li-air batteries. However, carbon undergoes an oxidizing decomposition to form Li$_2$CO$_3$ above 3.5 V, which leads to a relatively high charging potential over 4 V and thus fading capacity [86]. In contrast, pure metal electrodes, such as a nanoporous gold electrode, prevent carbon decomposition and generate an excellent electrochemical performance with 95% capacity in 100 cycles [87]. These stability and safety issues should also be considered before a catalyst that has been screened to show high catalytic activity is put into application. In other words, this review only focuses on the problem of activity in catalyst screening and further work on stability and safety is still needed to put high-activity catalysts into application.

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