Catalysis Today xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

pH dependence of OER activity of oxides: Current and future perspectives

Livia Giordano[a,c,d,*], Binghong Han[b], Marcel Risch[c], Wesley T. Hong[b], Reshma R. Rao[a], Kelsey A. Stoerzinger[b], Yang Shao-Horn[a,b,c,*]

[a] *Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, United States*
[b] *Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, United States*
[c] *Research Laboratory of Electronics, Massachusetts Institute of Technology, Cambridge, MA 02139, United States*
[d] *Dipartimento di Scienza dei Materiali, Università di Milano-Bicocca, Milano, Italy*

ARTICLE INFO

Article history:
Received 1 August 2015
Received in revised form 1 October 2015
Accepted 4 October 2015
Available online xxx

Keywords:
Electrocatalysis
Oxygen evolution reaction
pH dependence
PCET
RHE

ABSTRACT

Understanding the mechanism of the oxygen evolution reaction (OER) is essential to develop better electrocatalysts for solar fuel generation. Measuring the pH dependence of the OER activity can provide insights on the reaction path that are otherwise difficult to access experimentally, in particular on the coupling of protons and electrons during the reaction. We argue that the use of a pH-dependent reference electrode, such as the reversible hydrogen electrode, is more suitable for these studies as it assures that the overpotential is fixed while varying the pH. We provide criteria for pH dependence when this reference is used and validate the existing results with our measurements on RuO_2 powders. A statistical analysis of the existing results allows us to sketch trends in the reaction order on pH with respect to the number of d electrons, oxidation states, and crystal families, providing the groundwork for future OER mechanistic studies on oxides.

1. Introduction

The transition to renewable energy technologies strongly relies upon storage of the energy produced by intermittent sources, such as solar and wind [1–4]. The electrolysis of water, leading to the production of hydrogen and oxygen, is a viable way to store energy in chemical fuels based on hydrogen equivalents such as hydrogen gas or alcohols. However, this process is currently limited by the oxygen evolution reaction (OER) occurring at the anode [5–13]. Overpotentials on the order of hundreds of mV above the thermodynamic value of 1.23 V are required for the reaction [14,15]. RuO_2 and IrO_2 are considered as the benchmark catalysts for the OER requiring overpotentials of about 300 mV to reach a current density of 10 mA cm^{-2} (per electrode area) [14–16]. For comparing the intrinsic activities of different electrocatalysts, the current can be normalized by oxide area, obtained, e.g. by BET or microscopy [10,16]. Rutile RuO_2 nanoparticles (NPs) show an intrinsic OER activity of ~10 μA $cm^{-2}{}_{ox}$ in acid and ~3 μA $cm^{-2}{}_{ox}$ in alkaline at an overpotential of 0.25 V (1.48 V vs the reversible hydrogen electrode (RHE)). Under the same conditions, the activity of IrO_2 NPs is ~4 μA $cm^{-2}{}_{ox}$ in acid and ~2 μA $cm^{-2}{}_{ox}$ in alkaline [12]. Over the past decades, considerable efforts have been devoted to the search of efficient OER catalysts with alternative compositions to the oxides of precious and rare Ir and Ru metals. Earth-abundant oxides of the first transition metal series have been considered either in rock salt [17], spinel [18], and perovskite [13,19,20] structures as a cost-effective option. Several recent review articles discuss the activity of oxides of various crystal structures and morphologies and thereby provide an overview of the current state-of-the-art activities [7,10,14,15,21].

The understanding of reaction mechanisms is the key for optimization of OER oxide catalysts [10]. The turnover frequency is proportional to the kinetic current density, *i*, and depends exponentially on the overpotential η, which is herein defined as the difference between the applied potential and the standard potential of the OER (1.23 V on the reversible hydrogen electrode, RHE, scale) [10,22]. In addition to the overpotential, the turnover frequency depends on the activities of the reactants and products, most notably a_{H+} in acid and a_{OH-} in alkaline. The activity of these species is commonly measured by the pH $= -\log(a_{H^+})$, and the study of the pH dependence of the OER activity can therefore provide useful insight on the kinetics and intermediates of

---

* Corresponding authors at: Massachusetts Institute of Technology, Cambridge, MA 02139, United States.
E-mail addresses: lgiordan@mit.edu (L. Giordano), shaohorn@mit.edu (Y. Shao-Horn).

http://dx.doi.org/10.1016/j.cattod.2015.10.006
0920-5861/

Please cite this article in press as: L. Giordano, et al., pH dependence of OER activity of oxides: Current and future perspectives, Catal. Today (2015), http://dx.doi.org/10.1016/j.cattod.2015.10.006

the reaction. The oxygen evolution half-reaction is a four-electron, four-proton reaction:

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \quad \text{(in acid solution)} \tag{1}$$

$$4OH^- \rightarrow O_2 + 4e^- + 2H_2O \quad \text{(in alkaline solution)} \tag{2}$$

The three parameters most important to describe the OER kinetics – current, potential, and pH – relate akin to equations of state in thermodynamics [23]:

$$\left(\frac{\partial E}{\partial \mathrm{pH}}\right)_i = -\left(\frac{\partial E}{\partial \log(i)}\right)_{\mathrm{pH}} \cdot \left(\frac{\partial \log(i)}{\partial \mathrm{pH}}\right)_E \tag{3}$$

where additionally, the temperature and pressure need to be held constant. These partial derivatives are also important for understanding the mechanism. Only the slowest step in the catalytic cycle is experimentally accessible by steady-state measurements, and thus these derivatives are usually associated with potential and pH dependence of the rate-determining step (RDS) or of a preceding pre-equilibrium. Consequently, changes in the Tafel slope $b = (\partial E/\partial \log(i))_{\mathrm{pH}}$ and the reaction order $\rho = (\partial \log(i)/\partial \mathrm{pH})_E$ have played an important role in identifying mechanistic transitions across potentials, pH, and among different catalysts, where these quantities are related by the equation: $i = k_0(a_{H^+})^{-\rho}10^{\eta/b}$ [24].

Despite the promise of pH-dependent measurements in elucidating the reaction mechanism, it is difficult to find consistent studies on reaction orders for oxides. In this perspective, we report a survey of the literature and show that different reaction orders are in some cases reported for the same chemistry, highlighting the role of the electrochemical measurement setting and conditions (i.e. electrolyte composition and choice of the overpotential) in extracting the OER activity at different pH values. Although we have surveyed data in the pH range 0–15.5 (Table S1), we focus our analysis on pH-dependent OER activities of oxides reported in two limiting pH regions, 0–1.5 and 12.5–14, where the buffering capacity of water is high [25] and no additives are required to stabilize the pH. We show the importance of measuring the effect of pH on the OER current density at fixed overpotentials using the RHE as a reference, which has a significant influence on the results but is largely ignored by a number of previous studies. Although the reported reaction orders are quite diverse and depend on potential and pH ranges, by converting previous OER measurements to an RHE scale we report some general trends in reaction order as a function of d-electron number, oxidation state, and crystal family in the high pH region. These findings and experimental considerations provide a groundwork and motivation for future pH-dependent studies for OER mechanism research.

2. Reaction mechanism and pH dependence

The reaction order of OER activity in pH indicates how the OER kinetics depends on the proton activity. A zeroth-order reaction would imply no dependence, while a first-order reaction indicates a linear dependence on the proton activity and as such a linear dependence of log(i) on pH. Fractional reaction orders are expected when the mechanism consists of complex chain reactions or when there is a competition between direct product formation and side reactions. Side reactions can be due to the presence of unstable species or secondary phases or their generation during the reaction.

Several electrochemical reactions occurring at the catalyst surface consist of the transfer of one proton and one electron. Fig. 1 shows two such reactions in alkaline solution: the adsorption and discharge of a hydroxyl group (Fig. 1a) and the removal of an adsorbed hydrogen atom (Fig. 1b). These are two examples of proton-coupled electron transfer (PCET) reactions. The PCETs are common reactions not just in electrocatalysis and photocatalysis but also in biological systems [27–31]. Specifically in electrocatalysis, the study of PCET has benefited from the work of Saveant and coworkers, who derived the expressions for the potential-dependent rate constants [32] and demonstrated how protons and electrons can be carried concertedly for long distances in aqueous environments via a Grotthuss-type PCET allowed by the hydrogen-bond network [33].

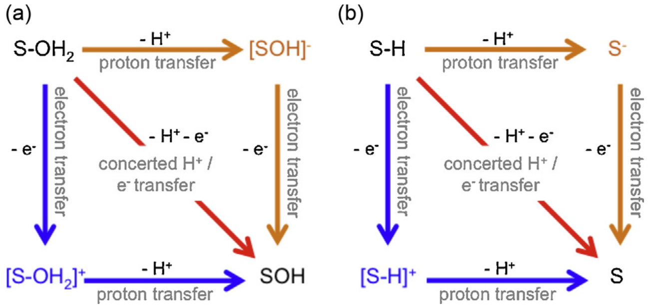

Fig. 1. Square reaction scheme for (a) OH adsorption and (b) H removal from the oxide surface (S) showing the sequential and concerted proton-coupled electron transfer reactions [26]. (For interpretation of the references to color in text, the reader is referred to the web version of this article.)

The PCET follows a concerted reaction path (CPET) in most cases [27] (red lines in Fig. 1), where the proton and the electron are transferred simultaneously. Two factors have been reported to favor the concerted mechanism. First, the concerted reaction mechanism prevents the formation of charged reaction intermediates (the off-diagonal orange and blue intermediates in Fig. 1), which are usually high in energy [26]. Second, the electron and proton reaction coordinates are cross-coupled in such a way that they are concertedly transferred [28].

However, systems containing transition metal (TM) centers, such as transition metal molecular catalysts or transition metal oxides, can sustain some degree of charge buildup accommodated by a change in the TM oxidation state [27]. The decoupling of proton and electron transfers is then possible for these systems. In the case of the single PCET reactions reported in Fig. 1, the proton and the electron can thus transfer sequentially, and the reaction proceeds through a charged intermediate. Although the study of the actual reaction rates, including the electron and proton tunneling probability and the explicit description of the solvent, is required for a complete description of the reaction, usually the order by which the proton and the electron are transferred can be deduced from the relative stability of the reaction intermediates [34,35]. For the proton transfer, this is associated with the acid dissociation constant, K_a, that is the equilibrium constant for the deprotonation of a site. Most often, the negative logarithm pK_a is used, where the site is deprotonated if pH ≫ pK_a and protonated if pH ≪ pK_a. The acid–base chemistry of active sites thus becomes particularly relevant as $\Delta G^\circ_{\mathrm{dep}} = 2.303\,RT\,\mathrm{p}K_a$, where $\Delta G^\circ_{\mathrm{dep}}$ is the standard free energy of deprotonation. The driving force of the electron transfer is determined by the adiabatic redox potential of the active site, the solvation energy of the charged state, and the applied potential.

Considering the reaction in Fig. 1a as an example, proton and electron transfer must have comparable thermochemical or kinetic barriers for concerted proton and electron transfer. In systems with pK_a of the active site comparable to pH of the solution, it can be expected that protons exchange easily with the electrolyte. Likewise, if the OER overpotential is similar to the redox potential of the active site, electron transfer will be facile. On the other hand, for relatively low pK_a (high acidity) of the active site, deprotonation is favorable and might occur first, particularly if the redox potential of the active site prevents electron transfer. In this case, a negatively charged intermediate is traversed in the reaction path. If the active