SCIENCE CHINA Materials PERSPECTIVES

mater.scichina.com link.springer.com Published online 3 September 2019 | https://doi.org/10.1007/s40843-019-9588-5
Sci China Mater 2020, 63(1): 3–7

Transition metal oxides for water oxidation: All about oxyhydroxides?

Zhichuan J. Xu[1,2,3,4]

To realize a sustainable hydrogen energy infrastructure, techniques to produce hydrogen gas without involving fossil fuels are critical. It has been proposed in last century that producing hydrogen gas by splitting water could be a sustainable way because of plenty of water in this planet. Given electricity from clean energy resources, like solar and wind energy, water electrolysis ideally will be a fossil fuel free process. Water electrolysis is not a new technique. It was firstly observed in the 18th century by Anthony Carlisle and William Nicholson in London, England, and Johann Wilhelm Ritter in Jena, Germany. Later on, Faraday found that the amount of reactants at an electrode was proportional to the passed electric charge, which led to Faraday laws in 1834 and encouraged better electrolzyer design. From 1920s to 1930s, the development of water electrolyzers was relatively fast due to the low cost hydroelectricity as well as the need for ammonia fertilizer manufacture. However, the water electrolysis was given up soon due to the development of coal gasification and steam methane reforming, which were much cheaper in cost for producing hydrogen. Until 1970s, the energy crisis made the water electrolysis concerned again for its critical role in the hydrogen energy infrastructure (the concept hydrogen economy was created by electrochemist Bernhardt in 1970).

At the early 20th century, the industrial water electrolysis was conducted in alkaline water using nickel electrodes and porous separator to separate the anode and cathode. The acidic water electrolysis came late until General Electric invented acidic solid polymer electrolyte (SPE) electrolyzer using proton exchange membrane (PEM), in which platinum and iridium oxide were used as the cathode and anode catalysts, respectively. As compared with industrial alkaline water electrolysis, the PEM electrolyzers are much high in energy efficiency. However, the high cost in catalysts has made the PEM electrolyzers only suitable to niche applications. The alkaline electrolyters can be also made in a similar cell configuration. But there is no anion exchange membrane (AEM) showing comparable properties (especially lifetime) to PEM to date. For industrial alkaline electrolyzers established in 20th century, the cost is much lower than PEM electrolyzers due to the use of nickel as the "bifunctional catalyst", instead of noble metals. One can expect that Ni may persist the metallic phase at the cathode during hydrogen evolution reaction (HER) and become nickel oxide or oxyhydroxide at the anode due to the high working potential of oxygen evolution reaction (OER), at which Ni should be oxidized [1]. The most recent studies have found that in fact the pure nickel oxyhydroxide (NiOOH) is a poor OER catalyst and it is the trace iron impurities in alkaline electrolyte that make the OER activity of NiOOH much higher [2].

In the past decades, extensive research has been given to develop new OER catalysts. This is because the major energy loss in water electrolysis is by slow reaction kinetics of OER at the anode. The OER catalysts under acidic condition cannot avoid the usage of noble metal Ir because Ir is the only metal with relatively higher survival chance under the harsh acidic OER conditions. Recently, it has been reported that the Ir usage can be reduced from using IrO_2 to Ir-based perovskite oxides [3], which is verified by the stability number measurement [4]. Independently, the different researchers have found that under OER condition the surface of Ir-based catalysts finally forms short-range ordered octahedral IrO_xH_y phase (Fig. 1) no matter what structure or composition of the catalysts started with [3–5]. This surface transfor-

---

[1] School of Materials Science and Engineering, Nanyang Technological University, Singapore 639798, Singapore
[2] Energy Research Institute@NTU, ERI@N, Interdisciplinary Graduate School, Nanyang Technological University, Singapore 639798, Singapore
[3] Solar Fuels Lab, Nanyang Technological University, Singapore 639798, Singapore
[4] The Cambridge Centre for Advanced Research and Education in Singapore, 1 CREATE Way, Singapore 138602, Singapore
Email: xuzc@ntu.edu.sg

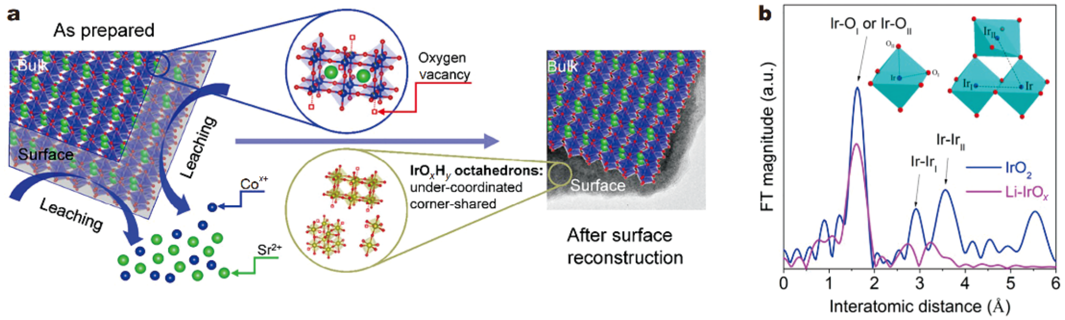

Figure 1 (a) A schematic illustration of the surface reconstruction over the Ir-based perovskite oxide $SrCo_{0.9}Ir_{0.1}O_{3-\delta}$ surface [3]. (b) The evidence of the long range order broken in Li-IrO_x after OER (by Extended XAFS, EXAFS) [5]. Copyright 2019, American Chemical Society.

mation process is often called as surface reconstruction. The X-ray absorption fine structure (XAFS) technique is so far the best choice to characterize the surface transformation under *in-situ* or *operando* conditions [6]. But one should notice that for large catalyst particles, due to the large bulk to surface ratio of large particles, the XAFS may not be sensitive enough to probe the surface information completely. A more detailed review article on surface reconstruction has been provided by Song *et al.* [7].

Because the most materials are able to survive in strong alkaline, the research on developing OER catalysts under alkaline condition is much more active than that under acidic condition. However, although the OER under alkaline is milder than acidic condition, the applied high voltage is still tough to the catalysts. The recent studies have found that most catalysts will go for surface reconstruction under OER. For example, the surface reconstruction under OER has been reported for perovskite oxides. Studying perovskite oxides for OER can be found as early as 1980s [8]. The most recent landmark study is by Shao-Horn *et al.* [9] and it demonstrated a descriptor of anti-bonding electron filling on 3d transition metals (based on molecular orbital theory) for explaining the perovskite oxide catalysts. The descriptor considers the binding strength between the metal cation and the oxygen species (intermediates), based on the model shown in Fig. 2a. It successfully predicted a highly active perovskite oxide $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) for OER under alkaline. A couple of years later, it was further found that BSCF could exhibit much more improved activity if cycled more. This exciting phenomenon was almost discovered at the same time of the birth of lattice oxygen mechanism (LOM) for OER [10,11]. The surface reconstruction of BSCF to amorphous surface layer was found [12]. Later on, Schmidt *et al.* [13] found that nano-sized BSCF could go for self-reconstruction to form cobalt and iron oxyhydroxide at the surface as evidenced by XAFS characterizations. The metals like Ba and Sr with higher solubility in alkaline solution will be leached out from particle surface and the metals like Co and Fe with lower solubility will remain on the surface to give oxyhydroxide (Fig. 2b). The metal oxyhydroxide layer was believed as the real catalyst for OER. Nevertheless, the same group has found that mixing with carbon support could also lead to the surface reconstruction of BSCF [14]. Besides BSCF, the $La_{1-x}Sr_xCoO_3$ with LOM OER ability should also give surface reconstruction to CoOOH although it has not been reported originally [15]. Sr substitution in $LaCoO_3$ up-lifts the lattice oxygen 2p state closer to Fermi level and thus the lattice oxygen is activated. Based on what have been found by Thomas J. Schmidt, it is reasonable to suspect that the Sr can be leached out during LOM OER and the surface transformation to CoOOH should occur. However, it should be noticed that for $LaCoO_3$, the catalyst is quite stable under OER cycling condition. There is no study on whether La can be leached out from $LaCoO_3$ during OER. If La can be leached out, $LaCoO_3$ should go for surface reconstruction as well to produce an oxyhydroxide (CoOOH) surface and thus the increased activity should be observed. However, based on what have been reported in literatures, most likely there is no surface reconstruction for $LaCoO_3$ due to its stable performance under cycling [9,16]. However, one can also argue that the surface reconstruction may be very slight for $LaCoO_3$ and its influence on OER activity is not remarkable.

Similar to $LaCoO_3$, spinel $ZnCo_2O_4$ also shows stable OER performance. In fact, most spinel oxides show stable performance upon cycling. This is probably due to two reasons. First, the spinel oxides are made by transition metals completely, which have low solubility in alkaline as

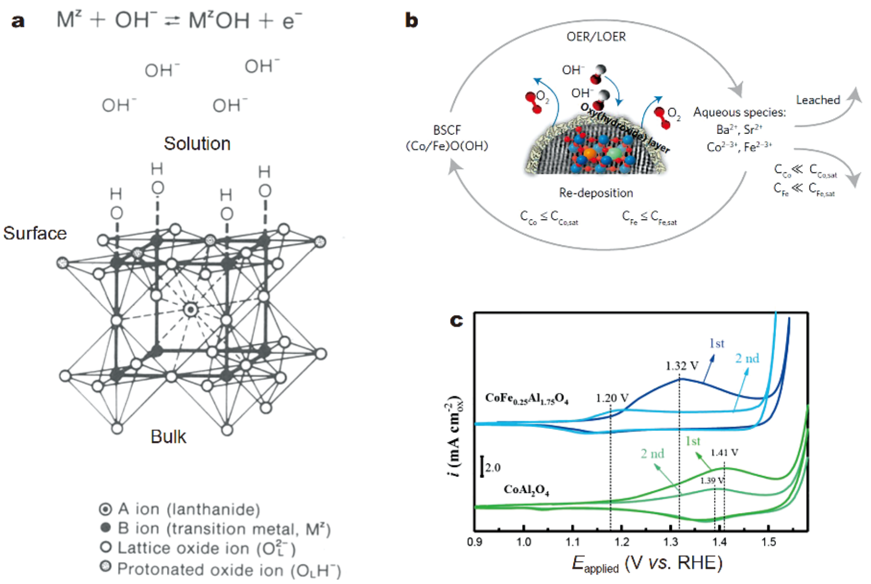

Figure 2 (a) The model of the active surface of the perovskite oxides. The cation B (transition metal) is the active site [8]. Copyright 1984, Electrochemistry Society (ECS). (b) The surface reconstruction on nano-sized BSCF for OER [13]. Copyright 2017, Springer Nature. (c) The Fe substitution enables the easier surface reconstruction of spinel $CoAl_2O_4$ [23]. Copyright 2019, Springer Nature.

compared with those A cations (like Ba, Sr, La, etc.) in perovskite ABO_3. Second, the competition for charges on oxygen anions between metals in octahedral and tetrahedral sites encourages covalency between metal cations and oxygen anions [17]. The relative stable chemistry of spinel oxides makes them follow the adsorbate evolved mechanism (AEM) in most cases [18–20] and thus difficult to break the scaling relationship for better OER [21]. To activate the surface reconstruction of spinel oxides, our group [22] has tried to design the pre-catalyst with activated lattice oxygen. The activation was achieved by substituting Co by Ni in $ZnCo_2O_4$ and the metastable spinel oxide can be made at an optimal substitution level. With the increase of the substitution level, the LOM OER was activated and cycling the catalyst resulted in a significantly improved OER. It also demonstrated that the pure spinel phase cannot be produced at the high substitution level due to the limitation in thermodynamics. Another example is that the surface reconstruction of $CoAl_2O_4$ can be promoted by Fe substitution to form highly active oxyhydroxides with negatively charged oxygen species [23]. Such reconstruction could be terminated by Al leaching at the surface, which caused a Fe-rich spinel sublayer under the oxyhydroxide top layer. The Fe-rich spinel sublayer with lowered lattice oxygen p band state stops the surface reconstruction from reaching deeper, resulting in a stable surface chemistry.

Besides oxides, metal chalcogenides, nitrides, phosphides, and metal-organic frameworks (MOFs) have been extensively studied as well. There is no doubt that chalcogenides, nitrides, and phosphides will go for surface reconstruction to form an oxyhydroxide surface because their low stability under OER condition. The detailed discussion can be found by an Editorial article by Jin [24]. For MOFs, it is interesting that there is no evidence so far for the formation of oxyhydroxide under OER condition [25].

Based on the current studies of oxide catalysts, it is difficult to make a conclusion that all oxides will go for surface reconstruction to an oxyhydroxide surface under OER. Like what is shown in Fig. 2a, the well-defined surface with transition metal cations in octahedral coordination can be the active surface. In this case, the surface does not have the oxyhydroxide phase and the oxide should be the catalyst, instead of a pre-catalyst. Such a surface needs a stable oxide without serious metal leaching or stable bulk chemistry (inactive oxygen anions in lattice). On the other hand, the experimental evidence to support the catalyst surface shown in Fig. 2a is quite limited. Usually, the researchers only paid attention to catalyst surface reconstruction when they observed a significant change in activity during cycling or long term stability test. One hypothesis could be that for all stable oxides, the surface may have a very thin layer of oxyhydroxide during OER, but there is no remarkable influence on the observed activity. This definitely needs direct evidence in future. If that is true, one question will be raised up: why not use oxyhydroxide as the catalyst directly? A follow-up concern is that not all reconstructed surface could give increased activity. That says although the final surface could be metal oxyhydroxides for all oxides after reconstruction, the formed oxyhydroxides could be different in activity even for the same metal oxyhydroxides [26]. It is probably true because different activities have been observed on oxyhydroxides from different pre-catalysts according to the results in literatures. Designing the pre-catalysts may benefit the formation of the reconstructed surface oxyhydroxides with unique electronic structures for better OER.

At the end, a few questions to be addressed in future are summarized.

1) Is the surface reconstruction to an oxyhydroxide surface under OER a general phenomenon for all transition metal oxides? As stated above, a few oxides, like BSCF, have been found going through the surface reconstruction to an oxyhydroxide surface under OER condition. However, the investigation is very limited to several oxides so far. Those oxides with stable performance upon cycling, such as $LaCoO_3$ and $ZnCo_2O_4$, remained unknown about their surface under OER. In addition, for those simple oxides, like CoO, MnO, etc., there is no study to investigate if they will form an oxyhydroxide surface under OER as well. The only known thing is that they usually illustrate lower activity towards OER as compared with perovskite and spinel oxides. One exception is NiO, which is not stable upon cycling and will transform to NiOOH under OER condition. More effort may be needed in future to investigate the surface of all transition metal oxides under OER condition: no matter the oxides to be investigated exhibit stable cycling performance or not, and no matter the oxides exhibit high or low OER activity.

2) Do all oxyhydroxide surfaces give same activity? If the answer is yes, oxyhydroxides should be used directly as the catalyst [27], instead of starting with those pre-catalysts. Based on the reported results to date, the answer most likely will be no. The activity difference among several reconstructed surfaces and directly synthesized oxyhydroxides can be found in literatures [7,26]. For the same oxyhydroxides, it has been found that the reaction pathway depends on oxygen vacancy level, metal-oxygen covalency, cation-doping, and other factors on electronic structure of oxyhydroxides. One may expect that the oxyhydroxide surface with desired electronic structure can be resulted from the carefully selected pre-catalysts.

3) What are key factors to be considered in designing oxide pre-catalysts, which may result in a highly active oxyhydroxide surface? This could be one of the important topics in future for developing OER catalysts based on transition metals. At present, the most researches are maintained at the level of investigating the surface reconstruction and the resulted surface. Few are about how to promote the reconstruction towards the desired surface for OER. Having said that, there is a large space to be filled in future, i.e., to understand the relation between pre-catalyst structure and the resulted surface as well as to establish the design principles of pre-catalysts.

Received 30 July 2019; accepted 23 August 2019;

1 Schalenbach M, Zeradjanin AR, Kasian O, *et al.* A perspective on low-temperature water electrolysis—Challenges in alkaline and acidic technology. Int J Electrochem Sci, 2018, 13: 1173–1226

2 Klaus S, Cai Y, Louie MW, *et al.* Effects of Fe electrolyte impurities on $Ni(OH)_2$/NiOOH structure and oxygen evolution activity. J Phys Chem C, 2015, 119: 7243–7254

3 Chen Y, Li H, Wang J, *et al.* Exceptionally active iridium evolved from a pseudo-cubic perovskite for oxygen evolution in acid. Nat Commun, 2019, 10: 572

4 Geiger S, Kasian O, Ledendecker M, *et al.* The stability number as a metric for electrocatalyst stability benchmarking. Nat Catal, 2018, 1: 508–515

5 Gao J, Xu CQ, Hung SF, *et al.* Breaking long-range order in iridium oxide by alkali ion for efficient water oxidation. J Am Chem Soc, 2019, 141: 3014–3023

6 Wang M, Árnadóttir L, Xu ZJ, *et al. In situ* X-ray absorption spectroscopy studies of nanoscale electrocatalysts. Nano-Micro Lett, 2019, 11: 47

7 Jiang H, He Q, Zhang Y, *et al.* Structural self-reconstruction of catalysts in electrocatalysis. Acc Chem Res, 2018, 51: 2968–2977

8 Bockris JOM, Otagawa T. The electrocatalysis of oxygen evolution on perovskites. J Electrochem Soc, 1984, 131: 290–302

9 Suntivich J, May KJ, Gasteiger HA, *et al.* A perovskite oxide optimized for oxygen evolution catalysis from molecular orbital principles. Science, 2011, 334: 1383–1385

10 Grimaud A, Diaz-Morales O, Han B, *et al.* Activating lattice oxygen redox reactions in metal oxides to catalyse oxygen evolution. Nat Chem, 2017, 9: 457–465

11 Rong X, Parolin J, Kolpak AM. A fundamental relationship between reaction mechanism and stability in metal oxide catalysts for oxygen evolution. ACS Catal, 2016, 6: 1153–1158

12 May KJ, Carlton CE, Stoerzinger KA, *et al.* Influence of oxygen evolution during water oxidation on the surface of perovskite oxide catalysts. J Phys Chem Lett, 2012, 3: 3264–3270

13 Fabbri E, Nachtegaal M, Binninger T, *et al.* Dynamic surface self-reconstruction is the key of highly active perovskite nano-electrocatalysts for water splitting. Nat Mater, 2017, 16: 925–931

14 Fabbri E, Nachtegaal M, Cheng X, *et al.* Superior bifunctional electrocatalytic activity of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$/carbon composite electrodes: Insight into the local electronic structure. Adv Energy Mater, 2015, 5: 1402033

15 Mefford JT, Rong X, Abakumov AM, *et al.* Water electrolysis on $La_{1-x}Sr_xCoO_{3-\delta}$ perovskite electrocatalysts. Nat Commun, 2016, 7:

11053
16 Duan Y, Sun S, Xi S, *et al.* Tailoring the Co 3d-O 2p covalency in $LaCoO_3$ by Fe substitution to promote oxygen evolution reaction. Chem Mater, 2017, 29: 10534–10541
17 Sun S, Sun Y, Zhou Y, *et al.* Shifting oxygen charge towards octahedral metal: A way to promote water oxidation on cobalt spinel oxides. Angew Chem Int Ed, 2019, 58: 6042–6047
18 Wei C, Feng Z, Scherer GG, *et al.* Cations in octahedral sites: A descriptor for oxygen electrocatalysis on transition-metal spinels. Adv Mater, 2017, 29: 1606800
19 Zhou Y, Sun S, Song J, *et al.* Enlarged Co-O covalency in octahedral sites leading to highly efficient spinel oxides for oxygen evolution reaction. Adv Mater, 2018, 30: 1802912
20 Li H, Sun S, Xi S, *et al.* Metal–oxygen hybridization determined activity in spinel-based oxygen evolution catalysts: A case study of $ZnFe_{2-x}Cr_xO_4$. Chem Mater, 2018, 30: 6839–6848
21 Man IC, Su H, Calle-Vallejo F, *et al.* Universality in oxygen evolution electrocatalysis on oxide surfaces. ChemCatChem, 2011, 3: 1159–1165
22 Duan Y, Sun S, Sun Y, *et al.* Mastering surface reconstruction of metastable spinel oxides for better water oxidation. Adv Mater, 2019, 31: 1807898
23 Wu T, Sun S, Song J, *et al.* Iron-facilitated dynamic active-site generation on spinel $CoAl_2O_4$ with self-termination of surface reconstruction for water oxidation. Nat Catal, 2019, 334
24 Jin S. Are metal chalcogenides, nitrides, and phosphides oxygen evolution catalysts or bifunctional catalysts? ACS Energy Lett, 2017, 2: 1937–1938
25 Zhao S, Wang Y, Dong J, *et al.* Ultrathin metal–organic framework nanosheets for electrocatalytic oxygen evolution. Nat Energy, 2016, 1: 16184
26 Huang ZF, Song J, Du Y, *et al.* Chemical and structural origin of lattice oxygen oxidation in Co–Zn oxyhydroxide oxygen evolution electrocatalysts. Nat Energy, 2019, 4: 329–338
27 Xiong X, Cai Z, Zhou D, *et al.* A highly-efficient oxygen evolution electrode based on defective nickel-iron layered double hydroxide. Sci China Mater, 2018, 61: 939–947

Acknowledgements This work was supported by Singapore Ministry of Education Tier 2 (MOE2017-T2-1-009) and Singapore National Research Foundation under its Campus for Research Excellence And Technological Enterprise (CREATE) programme, through Singapore Berkeley Research Initiative for Sustainable Energy (SinBeRISE), Cambridge Center for Carbon Reduction in Chemical Technology (C4T), and eCO2EP programmes. The author thanks Dr. Shengnan Sun for proof reading.

Conflict of interest The author declares no conflict of interest.

Zhichuan J. Xu is an associate professor in the School of Materials Science and Engineering at Nanyang Technological University (NTU). He received the PhD training from Lanzhou University, Institute of Physics (CAS), and Brown University. He worked at the State University of New York at Binghamton as a research associate and then in Massachusetts Institute of Technology as a postdoctoral researcher in the Electrochemical Energy Lab. His major research interests are electrocatalysis and energy storage materials.

过渡金属氧化物析氧催化都是通过氧氢氧化物实现的吗?

徐梽川[1,2,3,4]

摘要 本文首先简单回顾了电解水的发展历史以及碱性和酸性条件下电解水的电极材料特点. 对于碱性条件下的电解水，电极材料以过渡金属氧化物为主. 近年来，人们对于过渡金属氧化物的析氧反应开展了大量的研究，特别关注钙钛矿、尖晶石、氧氢氧化物等催化剂. 析氧反应条件苛刻, 一些氧化物催化剂会发生表面重构, 转化为过渡金属氧氢氧化物. 因此, 对这些氧化物来讲, 真正的催化剂表面是一个氧氢氧化物的表面. 另一方面，一些氧化物在析氧反应中表现出较强的稳定性，一般认为这些氧化物的表面不会发生重构，因而没有氧氢氧化物的生成. 一些已知的基于氧化物结构的活性描述参数也对该观点提供了实验和理论支持. 最后，本文提出尚待回答的一个问题：在析氧反应中是否所有的过渡金属氧化物都会发生表面重构而生成一个氧氢氧化物的表面？不管以上问题的答案是什么，该如何设计预催化剂实现重构后的高活性表面将成为未来关注的热点之一.