available at www.sciencedirect.com

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

Article

Lanthanide-regulated oxygen evolution activity of face-sharing IrO_6 dimers in 6H-perovskite electrocatalysts

Weiqiang Feng, Hui Chen, Qi Zhang, Ruiqin Gao, Xiaoxin Zou *

State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun 130012, Jilin, China

ARTICLE INFO

Article history:

Received 28 February 2020

Accepted 31 March 2020

Published 5 November 2020

Keywords:

Lanthanide

Perovskite

Oxygen evolution reaction

O *p*-band center

Electrocatalyst

ABSTRACT

The development of efficient oxygen evolution electrocatalysts with reduced noble metal uses is a critical challenge for the deployment of various advanced energy conversion technologies. Here, a series of lanthanide-contained 6H-perovskites with a formula of $\text{Ba}_3\text{LnIr}_2\text{O}_9$ (Ln = lanthanides) are investigated as oxygen evolution electrocatalysts, whose active subunits (*i.e.*, face-sharing IrO_6 dimers) can be regulated by the lanthanides in terms of catalytic activity. By using density functional theory (DFT) calculations, we establish the theoretical trend in activity for $\text{Ba}_3\text{LnIr}_2\text{O}_9$ 6H-perovskites, the activity of which is correlated with the difference of adsorption free energy ($\Delta G_{\text{O}} - \Delta G_{\text{OH}}$) between O^* and OH^* reaction intermediates. We further establish a volcano curve between $\Delta G_{\text{O}} - \Delta G_{\text{OH}}$ and the calculated O *p*-band center. Among the $\text{Ba}_3\text{LnIr}_2\text{O}_9$ 6H-perovskites, $\text{Ba}_3\text{LaIr}_2\text{O}_9$ locates at the peak of volcano curve, and correspondingly is the most active electrocatalyst due to the optimal O *p*-band property.

© 2020, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

Published by Elsevier B.V. All rights reserved.

1. Introduction

Accelerating the discovery of new catalysts enabling high activity and cost efficiency is the key to the achievement of many current electrochemical energy conversion technologies toward reducing our dependence on non-renewable resources and mitigating the global warming crisis [1,2]. In this regard, water splitting technologies have been the center subject of the spotlight. The oxygen evolution reaction (OER)—an anode reaction in water splitting—is severely encumbered by the sluggish kinetics involving four-proton/electron-coupled reaction process [3–6]. Proton exchange membrane (PEM) electrolyzer possesses many advantages compared with the alkaline electrolyzer, such as high loading flexibility, high current densities and voltage efficiency [3–5,7,8]. However, the

implementation of these advantages is based on the premise of acid-resistant, highly active oxygen evolution electrocatalysts.

Although some electrocatalysts reported recently are found to be active for OER under harsh acidic operation conditions, the state-of-the-art electrocatalyst is still IrO_2 due to the trade-off between activity and stability. IrO_2 contains high content of expensive, scarce iridium, making it unfeasible for future large-scale commercialization [3–5,9–14]. Therefore, it is urgent to develop highly active, stable and low-cost OER electrocatalysts. An effective protocol of reducing the usage of noble metal content is diluting the noble metal with earth-abundant materials, such as perovskites, pyrochlores and fluorite-like compounds [13,15–18]. Recently, 6H-perovskite SrIrO_3 is demonstrated by our group to contain 27.1 wt% less iridium than IrO_2 , but exhibits higher intrinsic catalytic activity

* Corresponding author. E-mail: xxzou@jlu.edu.cn

This work was supported by the National Natural Science Foundation of China (21771079, 21621001), Fok Ying Tung Education Foundation (161011), the Postdoctoral Innovative Talent Support Program (BX20180120) and the China Postdoctoral Science Foundation (2018M641771), and the 111 Project (B17020).

DOI: 10.1016/S1872-2067(20)63628-2 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 41, No. 11, November 2020

for OER in acid [4]. The unique face-sharing IrO₆ octahedral dimers (*i.e.*, Ir₂O₉) are believed to be responsible for the high catalytic activity in this type of perovskites. However, the iridium content is still undesirable in 6H-perovskite SrIrO₃, because besides the Ir₂O₉ dimers, there is another iridium-containing, auxiliary IrO₆ octahedra in this structure. Therefore, it is of great interest to find new 6H-perovskites which contain lower iridium content than SrIrO₃. A further systematical investigation on 6H-perovskites would be conducive to reveal the fundamental relationship of structural motifs and electrocatalytic activity. Such knowledge is also important for the prediction and rational design of efficient electrocatalysts for OER in acid.

In this work, we propose a class of lanthanide-contained, 6H-perovskites with a general formula of Ba₃LnIr₂O₉ (Ln = lanthanides) as OER electrocatalysts, in which the iridium content reduced by 50.11 wt%–51.26 wt% in comparison with IrO₂. We identify Ir₂O₉ octahedral dimers in this class of 6H-perovskites as the active subunits for OER, and their catalytic activities are regulated by the LnO₆ octahedra that directly connects with Ir₂O₉ octahedral dimers. We further find that the catalytic activity is correlated with the difference of adsorption free energy ($\Delta G_0 - \Delta G_{OH}$) between O* and OH* reaction intermediates, and the calculated O *p*-band center. Finally, Ba₃LaIr₂O₉ is identified as the most active catalyst among 6H-perovskites we studied, thanks to its optimal O *p*-band property.

2. Computational methods

The first-principle calculations are conducted by using plane-wave pseudopotential approach within the framework of density functional theory (DFT) as implemented in the *Vienna Ab Initio Simulation Package* (VASP) [19,20]. The generalized gradient approximation formulated by Perdew, Burke, and Ernzerhof (PBE) is used as the exchange-correlation functional [21]. The electron-core interactions are described with the frozen-core projected augmented wave pseudopotentials [20]. A 400 eV cut-off energy for plane-wave basis set is used for all calculations. The convergence threshold for energy is set to 10^{−4} eV and for force is 0.05 eV/Å. 5×5×5 and 5×5×1 Monkhorst-Pack *k*-point grid is employed for the geometric optimization of bulk and slab models, respectively [22]. An 11×11×1 *k*-point grid is employed for projected density of states (PDOS) calculations. The correction of the van der Waals (vdW) interactions is considered by introducing DFT-D2 method [23]. The dipolar correction is included and the symmetrization is switched off for the calculations of the slab models. The crystal orbital Hamiltonian population (COHP) is calculated to analyze the chemical bonding of adjacent Ir atoms in Ir₂O₉ octahedral dimers, which has been implemented in the LOBSTER program [24–26]. Negative -COHP value indicates antibonding states, while the positive -COHP value means bonding states. The Fermi level is set to 0 eV.

O 2*p*-band center (ε_{2p}) relative to the Fermi level was obtained by using the below equation [27]:

$$\varepsilon_{2p} = \frac{\int_{-\infty}^{+\infty} n_{2p}(\varepsilon) \varepsilon d\varepsilon}{\int_{-\infty}^{+\infty} n_{2p}(\varepsilon) d\varepsilon}$$

where ε is the energy referring to $E - E_{\text{Fermi}}$, and $n_{2p}(\varepsilon)$ is the projected density of states (PDOS) for O-2*p* orbital.

All the theoretical models of Ba₃LnIr₂O₉ are assumed as *P63/mmc* space group, according to the structure reported by Doi *et al.* [28]. After optimization, by cleaving these optimized structures through the (001) plane, the corresponding slab models were obtained, with a 20 Å vacuum space to prevent the interaction between periodic images. All slab models have the thickness of six octahedral layers, and the upper 1/3 layers in the model are fully relaxed while the remaining kept frozen during the calculations.

The *Gibbs* free energy of each step for OER is computed according to the equation $\Delta G = \Delta E + \Delta \text{ZPE} - T\Delta S$. The ΔE is the energy differences obtained by DFT calculations. The values of ΔZPE are determined by the vibrational frequencies calculations and the values of $T\Delta S$ are obtained from the standard tables for the gas phase molecules. The entropy for the adsorbate at the surface active site is assumed to be zero and the influence of temperature on the enthalpy is neglected in our calculations. Moreover, an external bias U is imposed on each step by introducing $-eU$ in the calculation of free energy. Then, the reaction free energy of each elementary step can be expressed as following Eqs. (1–4) [19–21,23]:

$$\Delta G_1 = E(\text{HO}^*) - E(^*) - E_{\text{H}_2\text{O}} + 1/2E_{\text{H}_2} + (\Delta \text{ZPE} - T\Delta S)_1 - eU \quad (1)$$

$$\Delta G_2 = E(\text{O}^*) - E(\text{HO}^*) + 1/2E_{\text{H}_2} + (\Delta \text{ZPE} - T\Delta S)_2 - eU \quad (2)$$

$$\Delta G_3 = E(\text{HOO}^*) - E(\text{O}^*) - E_{\text{H}_2\text{O}} + 1/2E_{\text{H}_2} + (\Delta \text{ZPE} - T\Delta S)_3 - eU \quad (3)$$

$$\Delta G_4 = E(^*) - E(\text{HOO}^*) + E_{\text{O}_2} + 1/2E_{\text{H}_2} + (\Delta \text{ZPE} - T\Delta S)_4 - eU \quad (4)$$

where $E_{\text{H}_2\text{O}}$ and E_{H_2} are the computed total energies for H₂O and H₂ molecules, respectively. The free energy of O₂ is obtained from the reaction $\text{H}_2\text{O} \rightarrow 1/2\text{O}_2 + \text{H}_2$ by using the experimental free energy change of 2.46 eV per water molecule. $E(^*)$, $E(\text{HO}^*)$, $E(\text{O}^*)$ and $E(\text{HOO}^*)$ represent energies of the clean surface and oxygen-containing intermediate species adsorbed on the surface, respectively.

3. Results and discussion

The crystal structure of Ba₃LnIr₂O₉ 6H-perovskite adopts space group *P63/mmc*. As shown in Fig. 1(a), there are face-shared Ir₂O₉ octahedral dimers, which are alternatively connected with LnO₆ octahedra in a corner-shared mode along the *c*-axis. Electron location function (ELF) was calculated to analyze the bonding characteristic of Ir–Ir bonds in the Ir₂O₉ octahedral dimers of Ba₃LaIr₂O₉. Fig. 1(b) reveals that there is metallic feature between the Ir–Ir bonds in the Ir₂O₉ octahedral dimers. Additionally, we further investigate the Ir–Ir bonds of Ba₃LnIr₂O₉ by calculating the crystal orbital Hamiltonian population (COHP). As shown in Fig. 1(c), there are two sharp peaks in the bonding state area below the Fermi level, indicating the strong interaction of Ir–Ir bonding in Ir₂O₉ octahedral dimers. The density of states (DOS) (Fig. 1(d)) shows a wide overlap between Ir 5*d* and O 2*p* orbitals, suggesting the strong orbital hybridization of Ir 5*d* and O 2*p* orbital in Ba₃LaIr₂O₉. The DOS is cross the Fermi level,

Fig. 1. (a) Crystal structure of $\text{Ba}_3\text{LnIr}_2\text{O}_9$ series, the yellow and blue arrows point at the face-sharing Ir_2O_9 dimers and LnO_6 octahedra, respectively; ELF image (b) and COHP (c) of Ir–Ir bond in $\text{Ba}_3\text{LaIr}_2\text{O}_9$, (d) Density of states for $\text{Ba}_3\text{LaIr}_2\text{O}_9$.

indicating the metallic behavior of $\text{Ba}_3\text{LaIr}_2\text{O}_9$.

We investigate oxygen evolution activities of this class of 6H-perovskites according to adsorbate evolution mechanism (Fig. 2), which is a four-electron transfer pathway for OER proposed by Rossmeisl *et al.* [29,30]. The four-electron transfer pathway for OER in acid can be expressed as below Eqs. of (5)–(8):

where $*$ represents surface active site. The HO^* , O^* and HOO^* are the adsorbed intermediates on the surface active site. ΔG_{OH} , ΔG_0 and ΔG_{OOH} are the Gibbs adsorption energies of these intermediates, respectively. The most thermodynamically unfavorable reaction step for OER is defined as potential-determining step (PDS) (*i.e.*, $\max\{\Delta G_{(1-4)}\}/\text{e}$). The theoretical overpotential is then expressed as the difference between the potential required by PDS and the equilibrium potential, 1.23 V.

We construct the theoretical models by cleaving the (001) plane of $\text{Ba}_3\text{LnIr}_2\text{O}_9$ bulk structure to obtain the corresponding

Fig. 2. Schematic of the adsorbate evolution mechanism for OER in acid.

surface slabs with three possible atom-exposed surfaces (Fig. 3(a)), including the surface with exposed Ln atoms (labelled as surface Ln), the surface with exposed Ir-I atoms (labelled as surface Ir-I) and the surface with exposed Ir-II atoms (labelled as surface Ir-II). Ir-I and Ir-II represent the iridium atoms in IrO_6 octahedra that indirectly and directly connect to the LnO_6 octahedra, respectively. We calculate surface energies of the three possible surfaces (Fig. 3(b)), and find that the surface energies of the surface Ir-I and surface Ir-II are similar and smaller than that of surface Ln. This result indicates that the two iridium-containing surfaces are more favorable to be exposed, compared with the surface Ln. In addition, the surface Ln is found to be unable to adsorb oxygen-involved intermediates, indicating that the surface Ln cannot serve as the catalytic active surface for OER. Thus, we next discuss the catalytic activities of the surface Ir-I and surface Ir-II in a detailed way.

We calculate the theoretical overpotentials of $\text{Ba}_3\text{LnIr}_2\text{O}_9$ series for OER for the surface Ir-I and surface Ir-II. Note that several $\text{Ba}_3\text{LnIr}_2\text{O}_9$ perovskites ($\text{Ln} = \text{Pm}, \text{Eu}, \text{Yb}$) fail to adsorb the oxygen-containing intermediates, and thereby they are not included in our following discussion. We find that: (1) the PDS is the second step (*i.e.*, $\Delta G_0 - \Delta G_{\text{OH}}$) and third step (*i.e.*, $\Delta G_{\text{OOH}} - \Delta G_0$) for the surface Ir-II and the surface Ir-I, respectively; (2) The overpotentials of $\text{Ba}_3\text{LnIr}_2\text{O}_9$ series at surface Ir-II are significantly lower than those of the surface Ir-I (Fig. S1, Table S1 and Table S2 in the Supporting Information). The surface Ir-II of $\text{Ba}_3\text{LnIr}_2\text{O}_9$ 6H-perovskites exhibits excellent catalytic activity due to their small theoretical overpotential (η) of < 0.5 V, which is smaller than that of IrO_2 ($\eta = 0.59$ V) [31]. For example, for $\text{Ba}_3\text{LaIr}_2\text{O}_9$, the overpotential of the surface Ir-II for OER is 0.35 V, while the overpotential of the surface Ir-I for OER is 0.62 V (Fig. 3(c)). The superior activity of the surface Ir-II is due to the optimized adsorption free energy of O^* intermediates, which results in a good balance between the

Fig. 3. (a) Three possible surface models of 6H-perovskite $\text{Ba}_3\text{LnIr}_2\text{O}_9$ series by cleaving the (001) plane. The surface Ln, surface Ir-I and surface Ir-II are presented from the left to the right; (b) Surface energy scatter plot for 6H-perovskite $\text{Ba}_3\text{LnIr}_2\text{O}_9$ series with different lanthanides with respect to surface Ln, surface Ir-I and surface Ir-II, respectively; (c) Gibbs free energy diagrams of $\text{Ba}_3\text{LaIr}_2\text{O}_9$ for OER with additional potential of 1.23 V regarding to the surface Ir-I and surface Ir-II.

Fig. 4. The negative theoretical overpotential as a function of the $\Delta G_O - \Delta G_{OH}$ for $\text{Ba}_3\text{LnIr}_2\text{O}_9$ series.

second and the third steps involved in the OER. By contrast, the adsorption free energy of O^* intermediates for the surface Ir-I is too strong compared with the surface Ir-II, leading to a higher potential needed for the third step for OER.

Considering the similar properties of lanthanides, $\text{Ba}_3\text{LnIr}_2\text{O}_9$ is an ideal material system to reveal the underlying effects on the activity regularity. We correlate the overpotentials of surface Ir-II and surface Ir-I of $\text{Ba}_3\text{LnIr}_2\text{O}_9$ with $\Delta G_O - \Delta G_{OH}$, a catalytic activity descriptor for OER. For the surface Ir-I, there is not a volcano plot relationship between $\Delta G_O - \Delta G_{OH}$ and catalytic activity (Fig. S2 in the Supporting Information), suggesting that lanthanides do not have a regular influence on the surface Ir-I active sites. In contrast, for the surface Ir-II, a volcano plot is well constructed on the basis of theoretical overpotentials and activity descriptor, $\Delta G_O - \Delta G_{OH}$. As shown in Fig. 4, the $\text{Ba}_3\text{LnIr}_2\text{O}_9$ all locate at the right side of the volcano plot, which suggests that the PDS is the second step—the deprotonation of OH^* immediate to form O^* immediate. The left side of the volcano plot suggests the PDS is the third step (*i.e.*, the formation of OOH^* intermediate). It can be seen that the $\text{Ba}_3\text{LaIr}_2\text{O}_9$ locates at the top peak of this volcano plots, suggesting the optimal catalytic activity for OER is realized by $\text{Ba}_3\text{LaIr}_2\text{O}_9$. This result further demonstrates that the catalytic activity of the surface Ir-II can be regulated by varying lanthanides in the LnO_6 octahedra to achieve the optimized $\Delta G_O - \Delta G_{OH}$. Among the series of $\text{Ba}_3\text{LnIr}_2\text{O}_9$, it is believed that the most promising candidate catalyst for OER is $\text{Ba}_3\text{LaIr}_2\text{O}_9$.

In order to reveal the influence of electronic properties of $\text{Ba}_3\text{LnIr}_2\text{O}_9$ on $\Delta G_O - \Delta G_{OH}$, we calculate the O p -bands of $\text{Ba}_3\text{LnIr}_2\text{O}_9$. As shown in Fig. 5, a volcano curve trend is presented by the calculated O p -band center relative to Fermi level *versus* negative $\Delta G_O - \Delta G_{OH}$. The $\Delta G_O - \Delta G_{OH}$ decreases with the O p -band center closer to Fermi level in the left side of the volcano curve, while the $\Delta G_O - \Delta G_{OH}$ increases in the right side of the volcano curve when the O p -band center closer to the Fermi level. The above results indicate that a good electrocatalyst in $\text{Ba}_3\text{LnIr}_2\text{O}_9$ requires an O p -band center neither too far nor too close to the Fermi level, which gives an

Fig. 5. The volcano curves of the negative $\Delta G_O - \Delta G_{OH}$ versus the calculated O p -band centers relative to Fermi level for $\text{Ba}_3\text{LnIr}_2\text{O}_9$ series.

optimized $\Delta G_O - \Delta G_{OH}$, and thereby a good electrocatalytic activity. It is worth noting that $\text{Ba}_3\text{LaIr}_2\text{O}_9$ locates at the top peak of the volcano curves. This material has a moderate O p -band center and the minimum $\Delta G_O - \Delta G_{OH}$ value, which refers to the optimal activity for OER.

Apart from the activity of $\text{Ba}_3\text{LnIr}_2\text{O}_9$, the thermodynamic stability is another important prerequisite factor for consideration. Therefore, we calculate the decomposition enthalpy of $\text{Ba}_3\text{LaIr}_2\text{O}_9$ into the corresponding binary compounds. The decomposition enthalpy is defined as the energy difference between the decomposed products and the $\text{Ba}_3\text{LaIr}_2\text{O}_9$ perovskite. The positive value of decomposition entropy means the endothermic reaction and thus difficult decomposition of $\text{Ba}_3\text{LaIr}_2\text{O}_9$. $\text{Ba}_3\text{LaIr}_2\text{O}_9$ has good thermodynamic stability with fairly large positive value of 3.79 eV. This result suggests that the $\text{Ba}_3\text{LaIr}_2\text{O}_9$ is screened to be a promising candidate for OER, and its catalytic performance is worth exploring experimentally.

4. Conclusions

We have presented a new family of lanthanide-contained, 6H-perovskites with largely reduced iridium content as electrocatalysts for OER in acid. The face-shared Ir_2O_9 octahedral dimers in this class of 6H-perovskites are the active subunits for OER, and their catalytic activities can be regulated by the LnO_6 octahedra. Among 6H-perovskites we studied, $\text{Ba}_3\text{LaIr}_2\text{O}_9$ is identified as the most promising candidate toward OER, with small theoretical overpotentials. Experimental efforts should be encouraged to synthesize this prospective, highly active oxygen evolution electrocatalyst.

References

- [1] A. Grimaud, K. J. May, C. E. Carlton, Y.-L. Lee, M. Risch, W. T. Hong, J. Zhou, Y. Shao-Horn, *Nat. Commun.*, **2013**, 4, 2439.
- [2] Z. W. Seh, J. Kibsgaard, C. F. Dickens, I. Chorkendorff, J. K. Nørskov, T. F. Jaramillo, *Science*, **2017**, 355, eaad4998.
- [3] C. Shang, C. Cao, D. Yu, Y. Yan, Y. Lin, H. Li, T. Zheng, X. Yan, W. Yu, S. Zhou, J. Zeng, *Adv. Mater.*, **2019**, 31, 1805104.

Graphical Abstract

Chin. J. Catal., 2020, 41: 1692–1697 doi: 10.1016/S1872-2067(20)63628-2

Lanthanide-regulated oxygen evolution activity of face-sharing IrO₆ dimers in 6H-perovskite electrocatalystsWeiqiang Feng, Hui Chen, Qi Zhang, Ruiqin Gao, Xiaoxin Zou*
Jilin University

A family of lanthanide-contained, 6H-perovskites are investigated theoretically as electrocatalysts for OER in acid. The face-shared Ir₂O₉ octahedral dimers in this class of 6H-perovskites are the active subunits for OER, and their catalytic activities can be regulated by the lanthanide-containing octahedra.

- [4] L. Yang, G. Yu, X. Ai, W. Yan, H. Duan, W. Chen, X. Li, T. Wang, C. Zhang, X. Huang, J.-S. Chen, X. Zou, *Nat. Commun.*, **2018**, 9, 5236.
- [5] Y. Lin, Z. Tian, L. Zhang, J. Ma, Z. Jiang, B. J. Deibert, R. Ge, L. Chen, *Nat. Commun.*, **2019**, 10, 1–13.
- [6] L. Huang, Y. Zou, D. Chen, S. Wang, *Chin. J. Catal.*, **2019**, 40, 1822–1840.
- [7] J. Lim, S. Yang, C. Kim, C. W. Roh, Y. Kwon, Y. T. Kim, H. Lee, *Chem. Commun.*, **2016**, 52, 5641–5644.
- [8] T. Fujigaya, Y. Shi, J. Yang, H. Li, K. Ito, N. Nakashima, *J. Mater. Chem. A*, **2017**, 5, 10584–10590.
- [9] X. Li, W. Xue, R. Mo, S. Yang, H. Li, J. Zhong, *Chin. J. Catal.*, **2019**, 40, 1576–1584.
- [10] O. Diaz-Morales, S. Raaijman, R. Kortlever, P. J. Kooyman, T. Wezendonk, J. Gascon, W. T. Fu, M. T. M. Koper, *Nat. Commun.*, **2016**, 7, 12363.
- [11] Y. Chen, H. Li, J. Wang, Y. Du, S. Xi, Y. Sun, M. Sherburne, J. W. Ager, A. C. Fisher, Z. J. Xu, *Nat. Commun.*, **2019**, 10, 572.
- [12] P. E. Pearce, C. Yang, A. Iadecola, J. Rodriguez-Carvajal, G. Rousse, R. Dedryvère, A. M. Abakumov, D. Giaume, M. Deschamps, J.-M. Tarascon, A. Grimaud, *Chem. Mater.*, **2019**, 31, 5845–5855.
- [13] Z. Zhou, W. Q. Zaman, W. Sun, L. Cao, M. Tariq, J. Yang, *Chem. Commun.*, **2018**, 54, 4959–4962.
- [14] S. Geiger, O. Kasian, M. Ledendecker, E. Pizzutilo, A. M. Mingers, W. T. Fu, O. Diaz-Morales, Z. Li, T. Oellers, L. Fruchter, A. Ludwig, K. J. J. Mayrhofer, M. T. M. Koper, S. Cherevko, *Nat. Catal.*, **2018**, 1, 508–515.
- [15] C. C. L. McCrory, S. Jung, I. M. Ferrer, S. M. Chatman, J. C. Peters, T. F. Jaramillo, *J. Am. Chem. Soc.*, **2015**, 137, 4347–4357.
- [16] H.-S. Oh, H. N. Nong, T. Reier, A. Bergmann, M. Gliech, J. Ferreira de Araújo, E. Willinger, R. Schlögl, D. Teschner, P. Strasser, *J. Am. Chem. Soc.*, **2016**, 138, 12552–12563.
- [17] H. N. Nong, H.-S. Oh, T. Reier, E. Willinger, M.-G. Willinger, V. Petkov, D. Teschner, P. Strasser, *Angew. Chem. Int. Ed.*, **2015**, 54, 2975–2979.
- [18] S. Park, Y. Shao, J. Liu, Y. Wang, *Energy Environ. Sci.*, **2012**, 5, 9331–9344.
- [19] G. Kresse, J. Furthmüller, *Phys. Rev. B*, **1996**, 54, 11169–11186.
- [20] G. Kresse, D. Joubert, *Phys. Rev. B*, **1999**, 59, 1758–1775.
- [21] J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.*, **1996**, 77, 3865–3868.
- [22] H. J. Monkhorst, J. D. Pack, *Phys. Rev. B*, **1976**, 13, 5188–5192.
- [23] S. Grimme, *J. Comput. Chem.*, **2006**, 27, 1787–1799.
- [24] V. L. Deringer, A. L. Tchougréeff, R. Dronskowski, *J. Phys. Chem. A*, **2011**, 115, 5461–5466.
- [25] S. Maintz, V. L. Deringer, A. L. Tchougréeff, R. Dronskowski, *J. Comput. Chem.*, **2013**, 34, 2557–2567.
- [26] S. Maintz, V. L. Deringer, A. L. Tchougréeff, R. Dronskowski, *J. Comput. Chem.*, **2016**, 37, 1030–1035.
- [27] J. H. Montoya, A. D. Doyle, J. K. Nørskov, A. Vojvodica, *Phys. Chem. Chem. Phys.*, **2018**, 20, 3813–3818.
- [28] Y. Doi, Y. Hinatsu, *J. Phys. Condens. Matter*, **2004**, 16, 2849–2860.
- [29] I. C. Man, H.-Y. Su, F. Calle-Vallejo, H. A. Hansen, J. I. Martínez, N. G. Inoglu, J. Kitchin, T. F. Jaramillo, J. K. Nørskov, J. Rossmeisl, *ChemCatChem*, **2011**, 3, 1159–1165.
- [30] F. Shi, X. Zhu, W. Yang, *Chin. J. Catal.*, **2020**, 41, 390–403.
- [31] J. Rossmeisl, Z.-W. Qu, H. Zhu, G.-J. Kroes, J. K. Nørskov, *J. Electroanal. Chem.*, **2007**, 607, 83–89.

镧系元素调控6H相钙钛矿中共面IrO₆二聚体的产氧活性

冯尉强, 陈 辉, 张 琪, 高瑞芹, 邹晓新*

吉林大学化学学院无机合成与制备化学国家重点实验室, 吉林长春130012

摘要: 随着全球气候变暖的加剧和化石能源的日益枯竭, 开发清洁无污染的可再生能源变得越来越重要. 作为一种清洁无污染、能量密度高的能源载体, 氢气被认为是极具应用前景的化石燃料替代品. 电解水技术所得氢气纯度高, 可以利用风

能、太阳能、水能等可再生电能, 是未来大规模工业产氢的理想路线之一. 电解水过程包括阳极析氧反应和阴极析氢反应两个半反应. 其中, 阳极析氧反应具有更缓慢的反应动力学, 成为水裂解过程的主要限速反应, 影响整个电解水器件的效率. 质子交换膜电解水技术是目前最先进的电解水技术. 寻找在酸性条件下实现高效产氧反应速率的电催化剂对于开发下一代质子交换膜电解水技术具有重要意义. 目前, 铱的氧化物是在酸性条件下高效、稳定的催化剂. 但是, 其价格昂贵且资源储量低, 不适合大规模应用. 因此, 寻找低贵金属含量的高活性产氧催化剂迫在眉睫.

本文以一系列含有镧系元素的6H相钙钛矿结构的 $\text{Ba}_3\text{LnIr}_2\text{O}_9$ 作为研究对象, 探究了其在酸性条件下的产氧电催化性能(Ln代表镧系元素). 我们发现, 镧系元素可以调控 $\text{Ba}_3\text{LnIr}_2\text{O}_9$ 结构中共面的 IrO_6 八面体活性亚结构单元. 基于密度泛函理论(DFT)计算, 我们建立了 $\text{Ba}_3\text{LnIr}_2\text{O}_9$ 系列结构的理论催化活性趋势, 并发现其活性受反应中间吸附产物(吸附氧 O^* 和吸附羟基 OH^*)的吸附自由能之差($\Delta G_{\text{O}} - \Delta G_{\text{OH}}$)的调控. 进一步, 为了从电子结构方面揭示 $\Delta G_{\text{O}} - \Delta G_{\text{OH}}$ 对催化活性的作用规律, 我们计算了 $\text{Ba}_3\text{LnIr}_2\text{O}_9$ 系列的氧 p 带中心, 并利用计算的氧 p 带中心和 $\Delta G_{\text{O}} - \Delta G_{\text{OH}}$ 建立了典型的火山型曲线. 其中位于火山型曲线顶点的 $\text{Ba}_3\text{LaIr}_2\text{O}_9$ 具有优化的氧 p 带中心和最佳的催化活性. $\text{Ba}_3\text{LaIr}_2\text{O}_9$ 是这类 $\text{Ba}_3\text{LnIr}_2\text{O}_9$ 结构当中最有潜力的产氧催化剂.

综上, 本文通过DFT计算方法, 研究了一系列低贵金属含量的 $\text{Ba}_3\text{LnIr}_2\text{O}_9$ 钙钛矿的电催化产氧活性, 并筛选出了其中活性最优的 $\text{Ba}_3\text{LaIr}_2\text{O}_9$ 作为有潜力的OER电催化剂. 这种通过DFT计算设计高效催化剂的方法有望加快实现各种新能源转换技术用催化剂的更新换代.

关键词: 镧系元素; 钙钛矿; 析氧反应; 氧 p 带中心; 电催化剂

收稿日期: 2020-02-28. 接受日期: 2020-03-31. 出版日期: 2020-11-05.

*通讯联系人. 电子信箱: xxzou@jlu.edu.cn

基金来源: 国家自然科学基金(21771079, 21621001); 霍英东教育基金(161011); 博士后创新人才支持项目(BX20180120); 中国博士后科学基金(2018M641771); 111计划(B17020).

本文的电子版全文由Elsevier出版社在ScienceDirect上出版(<http://www.sciencedirect.com/science/journal/18722067>).