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Oxygen Plasma Triggered Co-O-Fe Motif in Prussian Blue Analogue for Efficient and Robust Alkaline Water Oxidation

Hao Guan Xu,^{†[a]} Chen Zhu,^{†[a]} Hao Yang Lin,^[a] Ji Kai Liu,^[a] Yi Xiao Wu,^[a] Huai Qin Fu,^[b] Xin Yu Zhang,^[a] Fangxin Mao,^[a] Hai Yang Yuan,^{*[a]} Chenghua Sun,^[c] Peng Fei Liu,^{*[a]} and Hua Gui Yang^{*[a]}

[a] H. G. Xu, C. Zhu, H. Y. Lin, J. K. Liu, Y. X. Wu, Dr. X. Y. Zhang, Dr. F. Mao, Prof. H. Y. Yuan, Prof. P. F. Liu and Prof. H. G. Yang
Key Laboratory for Ultrafine Materials of Ministry of Education, School of Materials Science and Engineering
East China University of Science and Technology
130 Meilong Road, Shanghai 200237, China
E-mails: hgyang@ecust.edu.cn; pfliu@ecust.edu.cn; hyyuan@ecust.edu.cn

[b] Dr. H. Q. Fu
Centre for Catalysis and Clean Energy,
Gold Coast Campus, Griffith University,
Gold Coast, QLD 4222, Australia

[c] Prof. C. Sun
Department of Chemistry and Biotechnology, Faculty of Science, Engineering and Technology,
Swinburne University of Technology,
Hawthorn 3122, Australia

[†] These authors contributed equally to this work.

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Abstract: In the context of oxygen evolution reaction (OER), the construction of high-valence transition metal sites to trigger the lattice oxygen oxidation mechanism is considered crucial for overcoming the performance limitations of traditional adsorbate evolution mechanism. However, the dynamic evolution of lattice oxygen during the reaction poses significant challenges for the stability of high-valence metal sites, particularly in high-current-density water-splitting systems. Here, we have successfully constructed Co-O-Fe catalytic active motifs in cobalt-iron Prussian blue analogs (CoFe-PBA) through oxygen plasma bombardment, effectively activating lattice oxygen reactivity while sustaining robust stability. Our spectroscopic and theoretical studies reveal that the Co-O-Fe bridged motifs enable a unique double-exchange interaction between Co and Fe atoms, promoting the formation of high-valence Co species as OER active centers while maintaining Fe in a low-valence state, preventing its dissolution. The resultant catalyst (CoFe-PBA-30) requires an overpotential of only 276 mV to achieve 1000 mA cm⁻². Furthermore, the assembled alkaline exchange membrane electrolyzer using CoFe-PBA-30 as anode material achieves a high current density of 1 A cm⁻² at 1.76 V and continuously operates for 250 hours with negligible degradation. This work provides significant insights for activating lattice oxygen redox without compromising structure stability in practical water electrolyzers.

Introduction

Amid the growing energy crisis, the utilization of renewable electricity to produce hydrogen through water splitting is widely regarded as a crucial foundation for achieving global carbon neutrality.^[1] In the water electrolysis process, the oxygen evolution reaction (OER) occurring at the anode is considered as the energy barrier limiting overall efficiency due to its sluggish reaction kinetics, compared to the hydrogen evolution reaction (HER) at the cathode.^[2] Although noble metal catalysts, such as IrO₂ and RuO₂, can effectively address the issues of high overpotentials required for OER, their high costs limit the widespread deployment of water electrolysis for hydrogen

production.^[3] Recently, the development of novel anion exchange membrane water electrolyzers (AEMWEs) has further reduced the dependence on noble metal catalysts at the anode. Consequently, there has been a growing interest in exploring the use of abundant and cost-effective non-noble metals, particularly 3d transition metals, as OER catalysts in alkaline media.^[4] However, during actual AEMWE operation, which often involves relatively extreme conditions (e.g., current densities above 1 A cm⁻² and operating temperatures around 55°C), many highly active non-noble metal catalysts fail to be practically implemented in practical membrane electrode assembly (MEA) electrolyzers.^[4c] Therefore, there is an urgent need to develop high-performance non-noble metal catalysts that can maintain exceptional activity and durability under real operating conditions.

Among the developed non-precious metal candidates, anode materials with high valence 3d-transition metal active sites (e.g., Co^{IV}, Fe^V, and Ni^{IV}) exhibit significant intrinsic activity in alkaline OER processes.^[5] This enhanced activity is attributed to the oxidation of metal catalysts to higher valence states, which raises the p-band center of oxygen (O_{2p}) towards the Fermi energy level (E_f) and strengthens the orbital hybridization between the metal d-band and oxygen (M-O bond covalency).^[6] This increases the barrier for electron removal from the metal sites, thus facilitating the involvement of lattice oxygen in the water oxidation process, which involves a direct (O-O) bond coupling.^[5a] This mechanism is known as the lattice oxygen oxidation mechanism (LOM). Compared to the traditional adsorbate evolution mechanism (AEM), LOM breaks the inherent thermodynamic constraints between oxygen-containing intermediates (*OH, *OOH) of the AEM, resulting in a more efficient water oxidation process.

However, the formation of high-valence metal sites requires higher applied potentials due to significant thermodynamic barriers.^[7] To date, extensive researches have focused on constructing high-valence sites, with numerous studies indicating that the similar size compatibility between Fe and Co can facilitate the synergistic generation of high-valence active metal sites and