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研究課題名(和文) Design of Earth-abundant and Robust Water Splitting Electrocatalysts with Autocatalytic Feedback Mechanisms

研究課題名(英文) Design of Earth-abundant and Robust Water Splitting Electrocatalysts with Autocatalytic Feedback Mechanisms

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研究成果の概要(和文)：Mnは2+から7+までの幅広い酸化状態を持ち、酸化状態を段階的に変化させるとともに、Mn種の個別の酸化還元状態をつなぐ電荷の比例・不均化反応も存在します。Mn酸化物の水分酸化の主な触媒サイクルは、2+、3+、4+の順次酸化還元サイクルであり、正の電位が印加されているときに進行する。しかし、電位が正しすぎると、Mn7+の形でMn酸化物の溶出が起こります。ガイヤール反応はリン酸によって促進される電荷の比例反応であり、Mn2+とMn7+が再結合してMn3+が生成される。新たに生成した価数7+以下のMn種は、OER酸化還元サイクルに再係合し、触媒の安定性に寄与する可能性がある。

研究成果の学術的意義や社会的意義

開発したシステムは、太陽電池や風力発電による再生可能な電力を水素、アモルファス、炭化水素などの化学エネルギーに変換するための水電解槽に不可欠な水の酸化を行うことができます。水酸化の酸化環境は最先端のレアメタル触媒をも腐食させ、太陽光や風力エネルギーの断続性により変動する運転電圧のわずかな変化が腐食の動態を著しく悪化させるため、水酸化の酸化還元力を高めることが重要です。しかし、たった1つの酸化還元反応の導入で触媒の寿命が大きく変化することから、触媒研究におけるネットワーク設計の重要性が明らかになりました。

研究成果の概要(英文)：I discovered how the bottom-up assembly of Mn-redox reactions can realize catalytic systems which are resistant to environmental fluctuations. Mn has a wide range of oxidation states ranging from 2+ to 7+, including incrementally change the oxidation state, as well as charge comproportionation and disproportionation reactions, which connect discrete redox states of Mn species. The main catalytic cycle of water oxidation on Mn oxides is the sequential redox cycle of 2+, 3+, and 4+, which proceeds when a positive potential is applied. However, when the potential is too positive, dissolution of Mn oxide in the form of Mn7+ occurs. The Guyard reaction is a charge comproportionation reaction promoted by phosphoric acid, which recombines Mn2+ and Mn7+ to form Mn3+. The newly formed Mn species with valence states below 7+ might be re-engaged in the OER redox cycles, and thus contribute to the stability of the catalyst.

研究分野：Chemistry

キーワード：Electrocatalysts Redox Hydrogen

様式 C - 19、F - 19 - 1、Z - 19 (共通)

1 . 研究開始当初の背景

A particularly promising setup for hydrogen production is the proton-exchange membrane (PEM) water electrolyzer, which is known for their high current densities, portability, and the usage of noncorrosive electrolytes (Akihiro, N. *et al. Appl. Phys. Express* 2015, 8, 107101.). However, as the proton-exchange membrane creates an acidic environment near the electrode, the only well-established electrocatalysts which exhibit sufficient activity and stability for the oxygen evolution reaction (OER) are oxides derived from iridium (Ir), which is one of the scarcest elements in Earth's crust. It has been estimated that 130 years' worth of annual Ir production would be necessary to cover the 1 TW scale H₂ production using state-of-the-art PEM systems (Ir loading: 1.54 mgIr/cm²) (Kibsgaard, J. *et al. Nat. Energy* 2019, 4, 430). The price of the Iridium (\$47 Million per metric ton) is over 23000 times higher than that of the manganese for example. Therefore, the development of acid-stable non-noble OER catalysts is one of the most critical challenges towards promoting hydrogen production using PEM (1-2), which would lead to industrial scale solar-to-hydrogen conversion. Although extensive research has been carried out to develop 3d transition metal (Fe, Co, Ni, Mn) based OER catalysts, it has been shown over many studies that these materials easily dissolve and deactivate in acidic media, and is the one of the most acute challenges in this field.

2 . 研究の目的

The goal of this research is to develop the autocatalytic feedback mechanisms on manganese oxides during water splitting reaction and provide a roadmap to realize earth-abundant catalysts which can robustly catalyze the OER at ~ 1 A/cm². To this end, I will:

(1) Experimentally identify new strategies to regulate the balance between water splitting reaction and deactivation by optimizing the material and reaction conditions to expand the stable potential window for γ -MnO₂ (> 100 mA/cm²).

(2) Specifically provide the scientific insight, e.g. autocatalytic mechanism, necessary to achieve catalysts operable at 1 A/cm² and above, using in-situ techniques such as Raman, and UV-vis spectroscopy (robustly catalyze the OER at ~ 1 A/cm²).

3 . 研究の方法

The significance of this research is that autocatalysis is a phenomenon which has been known for more than 50 years, but has never been applied for the design of electrocatalyst. My previous study which has identified both the catalytic pathway and the dissolution pathway is critical to finally achieve this goal, because knowledge of both the activation and regeneration pathways are necessary to induce the positive feedback necessary for autocatalysis.

4 . 研究成果

In order to realize sustainable water oxidation under fluctuations, we have focused on the rich redox chemistry of manganese oxide. Manganese has a wide range of oxidation states ranging from 2+ to 7+, and is capable of not only redox reactions which incrementally change the oxidation state, but also charge comproportionation and disproportionation reactions, which connect discrete (faraway) redox states of Mn species (Figure 1). The main catalytic cycle of water oxidation on Mn oxides is the sequential redox cycle of 2+, 3+, and 4+, which proceeds when a positive potential is applied (Figure 1a, blue reactions, OER on-cycle reactions). However, when the potential is too positive (> 1.8 V), dissolution of Mn oxide in the form of MnO₄⁻ (Mn⁷⁺) occurs (Figure 1b, brown reaction, OER off-cycle reactions). Mn⁷⁺ is the terminal-end valence state of Mn, representing the degradation of the catalyst once formed. This dissolution occurs even when the excess voltage is in the order of millivolts, and therefore, the catalyst corrodes irreversibly in the presence of voltage fluctuation unless another redox reaction is added to the network (Figure 1c, green reaction). This reaction, known as the Guyard reaction, is a charge comproportionation reaction promoted by phosphoric acid, which recombines Mn²⁺ and Mn⁷⁺ to form Mn³⁺. As one key redox state of Mn for OER, Mn³⁺ could be oxidized into Mn⁴⁺ or disproportionate into Mn⁴⁺ and Mn²⁺ in the subsequent OER cycles. In either way, the newly formed Mn species with valence states below 7+ might be re-engaged in the OER redox cycles, and thus contribute to the stability of the catalyst sustainability of the OER reaction.

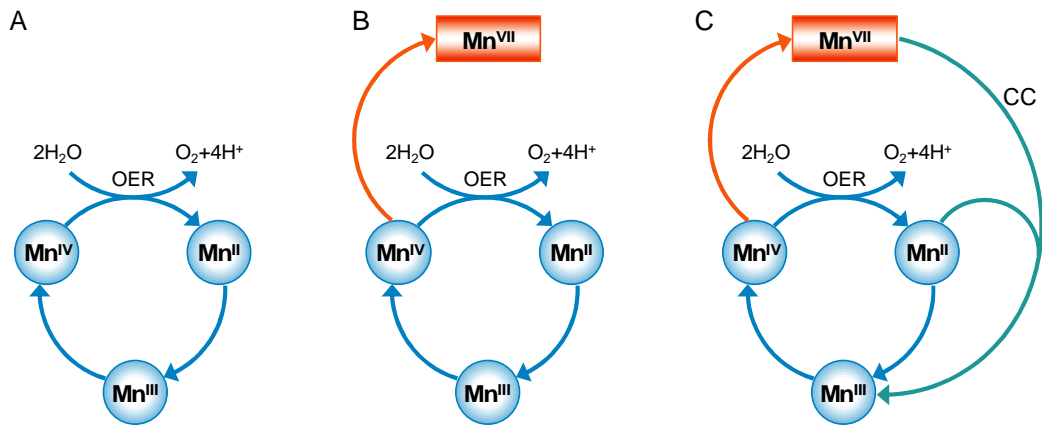


Figure 1. Schematic diagram of the chemical reaction network of water oxidation on MnO_2 for its catalytic reaction redox (A), dissolution reaction (B), and repair processes (C).

As a result, I have discovered that adding phosphoric acid into the electrolyte can suppress MnO_4^- generation until 1.87 V, thus suppressing the corrosion. A stable OER performance with a current density of 100 mA/cm^2 for more than 1000 h (>1 month) was achieved. Further optimization by using the platinum-coated titanium mesh as the substrate, with a geometric surface area 10 times higher than that of a flat FTO substrate, a current of 1000 mA/cm^2 was achieved. A lifetime of over 500 hours at 1 A cm^{-2} was further performed. Both results are under preparation for publication.

< 引用文献 >

Li, A., Ooka, H., Bonnet, N., Hayashi, T., Sun, Y., Jiang, Q., Li, C., Han, H., Nakamura, R. Stable Potential Windows for Long Term Electrocatalysis by Manganese Oxides in Acidic pH. *Angew. Chem., Int. Ed.* 2019, 58, 5054-5058.

Li, A., Kong, S., Guo, C., Ooka, H., Adachi, K., Hashizume, D., Han, H., Xiao, J., Nakamura, R. Enhancing the stability of cobalt spinel oxide towards sustainable oxygen evolution in acid. *Nat. Catal.*, 2022.

5. 主な発表論文等

〔雑誌論文〕 計0件

〔学会発表〕 計0件

〔図書〕 計0件

〔産業財産権〕

〔その他〕

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6. 研究組織

| | 氏名 (ローマ字氏名) (研究者番号) | 所属研究機関・部局・職 (機関番号) | 備考 |
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7. 科研費を使用して開催した国際研究集会

〔国際研究集会〕 計0件

8. 本研究に関連して実施した国際共同研究の実施状況

| 共同研究相手国 | 相手方研究機関 |
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