



Contents lists available at ScienceDirect

Journal of Power Sources

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

Nanocarbon/oxide composite catalysts for bifunctional oxygen reduction and evolution in reversible alkaline fuel cells: A mini review

Mengjie Chen ^a, Lei Wang ^b, Haipeng Yang ^{b, **}, Shuai Zhao ^c, Hui Xu ^c, Gang Wu ^{a, *}

^a Department of Chemical and Biological Engineering, University at Buffalo, The State University of New York, Buffalo, NY, 14260, United States

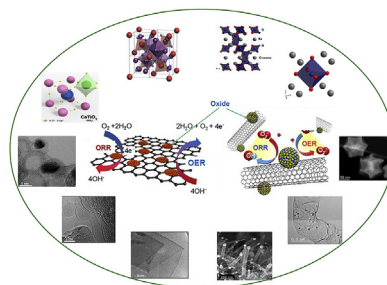
^b College of Materials Science and Engineering, Shenzhen University, Shenzhen, Guangdong, 518060, China

^c Giner Inc., Newton, MA, 02466, United States

HIGHLIGHTS

- The bifunctional ORR/OER catalysts are for reversible alkaline fuel cells.
- The most promising nanocarbon/oxide composite catalysts were discussed.
- A synergistic effect between oxides and nanocarbons was highlighted.
- Perspective and current challenges of nanocarbon/oxide catalysts were outlined.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 20 June 2017

Received in revised form

14 August 2017

Accepted 16 August 2017

Available online xxx

Keywords:

Reversible alkaline fuel cells

Electrolyzers

Oxygen reduction

Oxygen evolution

Bifunctional catalysts

Nanocomposites

ABSTRACT

A reversible fuel cell (RFC), which integrates a fuel cell with an electrolyzer, is similar to a rechargeable battery. This technology lies on high-performance bifunctional catalysts for the oxygen reduction reaction (ORR) in the fuel cell mode and the oxygen evolution reaction (OER) in the electrolyzer mode. Current catalysts are platinum group metals (PGM) such as Pt and Ir, which are expensive and scarce. Therefore, it is highly desirable to develop PGM-free catalysts for large-scale application of RFCs. In this mini review, we discussed the most promising nanocarbon/oxide composite catalysts for ORR/OER bifunctional catalysis in alkaline media, which is mainly based on our recent progress. Starting with the effectiveness of selected oxides and nanocarbons in terms of their activity and stability, we outlined synthetic methods and the resulting structures and morphologies of catalysts to provide a correlation between synthesis, structure, and property. A special emphasis is put on understanding of the possible synergistic effect between oxide and nanocarbon for enhanced performance. Finally, a few nano-composite catalysts are discussed as typical examples to elucidate the rules of designing highly active and durable bifunctional catalysts for RFC applications.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

Recently, substantial attention has been paid on the development of innovative energy storage and conversion technologies, which should be environmental friendly with highly efficiency. Among others, electrochemical energy systems, especially fuel cells

* Corresponding author.

** Corresponding author.

E-mail addresses: yanghp@szu.edu.cn (H. Yang), gangwu@buffalo.edu (G. Wu).

and water electrolyzers, have been studied worldwide over the last decades associated with utilization and generation of hydrogen and oxygen, which are ideally compatible with renewable energy sources and sustainability [1–3]. Recently, a new concept of integrating a fuel cell and an electrolyzer together was introduced to realize periodic energy storage and conversion with reduced cost and increased energy density. This kind of device is so-called reversible fuel cells (RFCs). It is similar to a rechargeable battery. RFCs could provide higher theoretical specific energy (3660 Wh/kg) and packaged specific energy (400–1000 Wh/kg), which are nearly 5 times higher than that of batteries [4]. A reversible fuel cell can be operated in two different modes. One is fuel cell mode and the other is electrolyzer mode. At fuel cell mode, RFCs convert the chemical energy (e.g., H₂ and O₂) into electricity and H₂O with relatively high efficiency in an environmental friendly manner. Oppositely, when RFCs are operated at electrolyzer mode, they can store the electricity generated from solar or wind through water splitting into H₂ and O₂. The fuel cell mode is comparable to the discharging process of a battery for generating electricity, while the electrolyzer mode is the charging process by utilizing electricity for storing energy into chemicals. Therefore, in a RFC, the oxygen electrode should be active and stable for both the oxygen reduction reaction (ORR) and the oxygen evolution reaction (OER) as the cathode in fuel cell and as the anode in electrolyzer mode, respectively. A fuel cell cathode for the ORR needs to shift to the anode for the OER in the electrolyzer. Therefore, it is highly demanded to develop bifunctional catalysts that are active for the ORR and the OER, which represents one of grand challenges in electrocatalysis society [5]. Theoretical simulation predicted that there is no single active site capable of catalyzing both ORR and OER simultaneously [6]. For example, the state-of-the-art catalysts for the ORR are Pt-based catalysts. Nevertheless, Pt is not a good choice for the OER occurring at high potential ranges, during which Pt oxides would form and cover at the surface causing a decrease of activity. The most active and stable catalysts for the OER are Ir and Ru oxides due to their high activity and stability along with good electrical and ionic conductivities. Likewise, they still cannot be used as bifunctional catalysts due to poor activity for the ORR. Therefore, development of PtIr nanocomposite catalysts consisting of active ORR and OER components has become one of the effective solutions to overcome the technical barrier [7]. However, it is highly undesirable to use large amount of these precious metal-based catalysts because they are very scarce and expensive. Pursuing highly efficient PGM-free nanocomposite catalysts simultaneously active for the ORR and the OER therefore becomes highly demanded for the attractive RFC technologies [8–11]. In addition to insufficient catalyst activity, stability remains as a grand challenge due to the fact that most of PGM-free catalysts are not stable in such oxidative ORR/OER environments within a wide electrochemical potential window (0.6–1.9 V). It should be noted that a favorable electrolyte medium is of vital importance for the RFC technology. Compared to acidic media, RFCs operated in alkaline media have many benefits. At first, the alkaline medium provides a relatively less corrosive condition and makes the catalysts more stable [12,13]. In particular, oxides and carbon-based PGM-free catalysts are much more stable in alkaline medium [14,15]. Although these oxygen reactions (ORR/OER) are kinetically sluggish, they would become relatively favorable in alkaline media [2,16–19]. For the OER, the hydroxide is oxidized to generate oxygen and water in alkaline media. For the ORR, two distinct pathways can be observed during the process. The preferred one is that oxygen reacts with water to produce hydroxide directly through a four-electron pathway. The other route goes through two separate two-electron transfer steps and yields hydrogen peroxide that is a harmful intermediate and is undesirable owing to low efficiency.

At present, a variety of PGM-free materials have been studied as a bifunctional catalysts including various transition metal oxides and nanocarbons. Transition metal oxides are able to shift among cationic oxidation states, which provides active redox sites and tolerates the oxidative condition during ORR and OER [16,20]. Moreover, transition metal oxides have some extra abilities, with which precious metals could not compete. For example, transition metal oxides are able of being doped with secondary and third metals, which creates the opportunity to develop complex oxide catalysts, such as perovskite and spinel oxides, simultaneously active for the ORR and the OER. However, their insufficient electrical conductivity and low surface area largely limit them to be used for practical catalysts. In addition, relative to their high activity for the OER, these oxide catalysts often suffer from low ORR activity. Consequently, highly conductive and ORR-active materials are demanded to integrate with oxides to achieve the intrinsic high OER activity and improve ORR performance.

Another promising materials are carbon nanomaterials, which often own high electrical conductivity and high active surface area for electrocatalysis [19,21–25]. In addition, they can be easily doped by heteroatoms and transition metals with enhanced catalytic activity [26]. Especially, the doped pyridinic nitrogen sites in carbon-based catalysts could serve as adsorption sites of O₂ to promote ORR by 4-electron route in alkaline media. The graphitic nitrogen in carbon planes can change the electronic structure of carbon inducing catalytic activity [27–29]. In addition to being used as catalysts, carbon materials could serve as supports to improve the conductivity of oxide catalysts and promote the dispersion of oxide nanocrystals [30,31]. Commonly used carbon materials are carbon blacks, carbon nanotubes, and graphene [32]. However, due to the thermodynamic instability of carbon, carbon itself cannot be considered as a stable OER catalyst candidate even in alkaline media.

To overcome their weaknesses and combine their advantages, the most effective solution is to develop nanocarbon/oxide composite catalysts for the challenging bifunctional oxygen catalysis. Currently, it is not fully understood the active site structure in such nanocomposite catalysts during ORR and OER. But it is a consensus that the porous morphology and large electrochemical surface area often lead to better catalytic activity. Importantly, optimal combination of oxides and nanocarbon can provide a great opportunity to achieve outstanding stability [33]. In this mini review, we discuss the rules of design and synthesis of nanocarbon/oxide composite catalysts with an emphasis on their possible synergistic effect. Recent progress is summarized to provide insightful structure-property correlations.

2. Nanocarbon/oxide nanocomposite catalysts

Although transition metal oxide has been considered as one kind of promising bifunctional catalyst, it is difficult to achieve their intrinsic electrocatalytic activity due to their low electrical conductivity and low surface area, primarily limiting kinetic reaction rates and power density in the reversible fuel cells [34–36]. One effective solution is to integrate transition metal oxides with conductive materials by promoting conductivity or changing their electronic structure [37,38]. Carbon material is a promising candidate, not only because it could provide high electrical conductivity, but also its high surface areas can be applied as effective catalyst supports [1,12,35,39]. Furthermore, the oxide catalysts are relatively more active towards OER due to the difference of optimal active sites between these two reactions. Oppositely, carbon materials with appropriate heteroatom doping often exhibit high ORR activity in alkaline media, but not good for the OER. Therefore, substantial research is focused on synthesis of nanocarbon/oxides

Download English Version:

<https://daneshyari.com/en/article/7726103>

Download Persian Version:

<https://daneshyari.com/article/7726103>

[Daneshyari.com](https://daneshyari.com)