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Electro-analytical performance of bifunctional electrocatalyst materials in unitized regenerative fuel cell system

T. Sadhasivam [a,b], Gowthami Palanisamy [c], Sung-Hee Roh [c], Mahaveer D. Kurkuri [d], Sang Chai Kim [e], Ho-Young Jung [a,b,*]

[a] Center for Energy Storage System, Chonnam National University, 77 Yongbong-ro, Buk-gu, Gwangju, 61186, Republic of Korea
[b] Department of Environment & Energy Engineering, Chonnam National University, 77 Yongbong-ro, Buk-gu, Gwangju, 61186, Republic of Korea
[c] College of General Education, Chosun University, 309 Pilmoon- Daero, Dong-gu, Gwangju, 61452, Republic of Korea
[d] Centre for Nano and Material Sciences, Jain University, Bangalore, 562112, India
[e] Department of Environmental Education, Mokpo National University, 1666 Youngsan Ro, Cheonggye Myeon, Muan, 58554, Republic of Korea

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ABSTRACT

The unitized regenerative fuel cell (URFC) is a round-trip energy conversion device for efficient energy storage systems that offers promising electrochemical energy conversion and environmentally friendly features. The electrocatalyst is a key component for operating URFC unit cell devices. Optimal electrocatalyst materials should be bi-functional with catalytic activity for the oxygen reduction and oxygen evolution reactions (ORR and OER). Over the past few decades, platinum has been recognized as a promising bifunctional electrocatalyst material for the URFC system. However, the ORR and OER activity of Pt is inadequate during the round-trip energy conversion process due to the formation of an oxide layer (PtO_x) and the high onset potential for H_2 evolution. To address these issues, extensive effort has been made to enhance the OER performance without affecting the ORR performance. The most efficient alternative electrocatalyst materials comprise combinations of platinum group metals (PGMs) and their oxides, especially Pt–Ir, Pt–Ir–Ru, Pt–IrO_2, Pt–Ir–IrO_2, and Pt–IrO_2–RuO_2. This comprehensive review emphasizes the potential of various bifunctional electrocatalyst materials for renewable energy generation in the URFC system. Herein, we discuss the limitations of Pt electrocatalysts in the URFC-OER process based on the reaction mechanism. The classification of different bifunctional electrocatalysts is extensively reviewed and highlighted based on the structural, microstructural, fuel cell-ORR, and water electrolysis-OER characteristics, round-trip energy conversion efficiency, inadequacies, and advantages. Taking these features into account, we discuss the possibilities and performance of cost-effective bifunctional electrocatalyst materials for the ORR/OER electro-catalytic process in

* *Corresponding author*. Department of Environment & Energy Engineering, Chonnam National University, 77 Yongbong-ro, Buk-gu, Gwangju, 61186, Republic of Korea.
E-mail addresses: jungho@chonnam.ac.kr, jungho@jnu.ac.kr (H.-Y. Jung).
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advanced URFC systems. This review presents an exclusive vision for the development of bifunctional electrocatalyst materials and should stimulate research on bifunctional electrode-based URFC systems.

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Introduction

The commencement of the industrial revolution was made possible based on the energy supplied by fossil fuel sources, which are still considered as promising energy sources for industrial and transportation applications worldwide [1,2]. However, there are two major issues associated with fossil fuel energy sources: (i) depletion due to higher utilization and (ii) environmental concerns such as toxicity and global warming due to greenhouse effect gases [3–6]. To identify substitutes, recent developments over the past few decades have predominantly focused on alternative, renewable, and sustainable energy storage systems (ESSs) [7–14]. From the viewpoint of alternative and green-energy, polymer electrolyte membrane fuel cells (PEMFCs) are considered as highly promising energy systems because of their superior energy density and the generation of water as a byproduct without any toxic emissions [15–20]. In the PEMFC, hydrogen gas is used as the fuel on the anode side to produce electricity [21,22]. The hydrogen gas is split into protons (H^+) and electrons (e^-) in the anode, which then move toward the cathode through the membrane and external circuit, respectively. The reaction between protons, electrons, and oxygen is completed on the cathode side of the cell by the oxygen reduction reaction (ORR) and water molecules are produced as a final by-product. Despite the many advantages of the PEMFC, the benefits are limited due to the high cost and volumetric/gravimetric capacity involved in the production and storage of hydrogen [23–27]. To augment the advantages of fuel cell technologies, an advanced version of the PEMFC known as the unitized regenerative fuel cell (URFC) system has been identified [28]. The URFC is called as a round-trip energy conversion device, where electricity has generated through hydrogen (and water as a byproduct) in fuel cell mode and electrolysis of water (split into oxygen and hydrogen) processed in regenerative mode to produce the hydrogen. In URFC, the operation of both modes can be performed in a same device. The URFC is a completely clean, green, and renewable energy system [29–36].

As shown in Fig. 1, the water electrolysis (WE) mode and traditional PEMFC structure of fuel cells (FCs) can function in a manner similar to the URFC unit cell system. In WE mode, the water molecules are dissociated into protons, oxygen, and electrons in the positive electrode using the energy supplied by solar/wind sources. The proton and electron are transferred from the positive to the negative side through the polymer electrolyte membrane and external circuit, respectively. In the cathode, the protons combine with the electrons and form hydrogen gas. The produced hydrogen is then stored and can be used as a fuel in the FC mode reaction. In the URFC unit cell system, the reverse reaction of the WE occurs in the FC mode to produce electricity [28,29,33,34]. The operational process of the FC mode in the URFC is similar to that in the typical PEMFC. The electrochemical redox reactions of the WE mode and FC mode are as follows:

Water electrolysis mode reaction:

At anode: $H_2O \rightarrow 2H^+ + 2e^- + 1/2O_2$

At cathode: $2H^+ + 2e^- \rightarrow H_2$

Fuel cell mode reaction:

At anode: $H_2 \rightarrow 2H^+ + 2e^-$

At cathode: $2H^+ + 2e^- + 1/2O_2 \rightarrow H_2O$

Based on the WE and FC reactions, it can be concluded that the URFC system is one of the most promising zero-emission green energy storage systems (no generation of harmful

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