



# Glycine-induced ultrahigh-surface-area $\text{IrO}_2@\text{IrO}_x$ catalyst with balanced activity and stability for efficient water splitting

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## ABSTRACT

Polymer electrolyte membrane water electrolysis (PEMWE) uses intermittent renewable energy and plays a key role in storing energy in the form of hydrogen. However, its widespread application is limited owing to issues associated with oxygen evolution reaction (OER) catalysts, including activity and stability. Thus, it is necessary to develop highly active and durable catalysts in this regard. Herein, an  $\text{IrO}_x@\text{IrO}_2$  catalyst with an ultrahigh surface area (G-450) was synthesized by a simple Adams fusion method and calcined at 450 °C with glycine as an additive. Owing to its micro/mesoporous structure, this catalyst exhibited an ultrahigh specific surface area (SSA) of 403 m<sup>2</sup> g<sup>-1</sup> and an amorphous structure with average oxidation states of Ir(IV). A trade-off between its OER activity and stability was achieved by controlling its SSA and Ir oxidation states via the optimization of the calcination temperature. Surface-rich Ir(III) species and high SSA enhanced the OER activity of G-450 (309 mV overpotential at 10 mA cm<sup>-2</sup>) compared with the  $\text{IrO}_2$  catalyst prepared without glycine (A-450, 351 mV overpotential at 10 mA cm<sup>-2</sup>). Further, the G-450 exhibited an Ir dissolution rate that was 2.5-fold lower than that of the  $\text{IrO}_2$  catalyst prepared at 350 °C (G-350) after 6 h chronopotentiometry at 10 mA cm<sup>-2</sup>, implying a higher stability owing to the presence of Ir(IV) species. Additionally, G-450 was introduced into the anode of the polymer electrolyte membrane (PEM) water electrolyzer single cell and demonstrated higher performance than A-450. The balanced activity and stability of  $\text{IrO}_x@\text{IrO}_2$  enhanced the PEM water electrolyzer performance. Moreover, this facile synthetic method is also applicable to the synthesis of binary oxide compounds and other transition metal oxides.

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## 1. Introduction

Renewable energy technologies have become increasingly important owing to the fact that excessive fossil fuel consumption brings about climate change, which is a serious threat to human existence [1,2]. In this regard, polymer electrolyte membrane water electrolysis (PEMWE), which is an intermittent source of renewable electrical energy, has attracted attention given that it offers the possibility to store energy in the form of hydrogen owing to its rapid transient response and its high current density operation conditions [3–6]. Considering the fact that the oxygen evolution reaction (OER) that occurs at the anode of the water electrolyzer is extremely slow as well as the high cost of most active OER catalysts ( $\text{IrO}_2$  and  $\text{RuO}_2$ ), it is necessary to develop simple and cost effective methods by which highly active and stable OER catalysts can be produced. This has significance in the realization of the widespread commercial application of PEMWE [7–13].

Specifically, several studies have been conducted with the aim of improving the activity of Ir-based catalysts using various methods, including nanostructure morphology control [14], the mixing of metal oxides [15,16], and the manipulation of the crystallinity and oxidation states of Ir [17,18]. According to recent studies, amorphous forms of  $\text{IrO}_x$  mainly composed of Ir(III) and OH species exhibit higher OER activities than rutile-type  $\text{IrO}_2$  [19–21]. However, regarding the trade-off between OER activity and stability, it has been demonstrated that the presence of Ir(III) species favor catalytic activity to a greater extent than the presence of Ir(IV) species, which rather favor stability to a greater extent [22,23]. Further, highly active amorphous  $\text{IrO}_x$ , containing Ir(III), dissolves at orders of magnitude that are higher than that of rutile-type  $\text{IrO}_2$ , which mainly consists of Ir(IV). This is because the mechanism of the participation of lattice oxygen leads to the formation of oxygen vacancies and weak Ir intermediates during the OER [22,23]. Thus, to improve the OER activity of  $\text{IrO}_2$  while maintaining a high stability, (i) stabilizing Ir(III) to overcome Ir dissolution [24] or (ii) structural designs incorporating Ir(IV) to increase the number of active sites is necessary [14,25].

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