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Short communication

Multifunctional non-Pt ternary catalyst for the hydrogen oxidation and oxygen evolution reactions in reversal-tolerant anode

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ABSTRACT

The reversal-tolerant anode (RTA) has been introduced to mitigate the fatal anode degradation by cell voltage reversal under hydrogen fuel starvation in fuel cell electric vehicles (FCEVs). The RTA employs an oxygen evolution reaction (OER) catalyst in the anode to boost water electrolysis rather than carbon corrosion under fuel starvation. Graphitic carbon-supported $IrRu_4Y_{0.5}$ exhibits outstanding performances for hydrogen oxidation reaction and OER. In single cell test, the $IrRu_4Y_{0.5}$ delivers ~ 21% better performance and longer RTA durability (~ 64 min) than Pt/C catalyst. It is anticipated that IrRuY-based alloy catalysts could replace high-priced Pt-based catalysts as multifunctional RTA for FCEVs.

1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) are ideal for maximizing hydrogen utilization, because they quickly and efficiently convert the chemical energy stored in hydrogen (H_2) to electrical energy without emitting greenhouse gases [1–3]. Despite the improvements in fuel cell technology accomplished through much efforts spanning several decades, an increase in the fuel cell market share still faces challenges. These include cost, performance and durability. In the case of fuel cell electric vehicles (FCEVs) that employ PEMFC systems as a power train, there are many transient operational conditions. Several of these conditions can cause fuel starvation, which results in reversal of the cell potential and oxidation of carbon in the anode.

The carbon oxidation reaction (COR, Eq. (1)) in the anode occurs easily to provide protons and electrons required for system operation under fuel starvation conditions by competing the oxygen evolution reaction (OER, Eq. (2)), which is the alternative reaction for the generation of protons and electrons [4].

$$C + 2\,H_2O \rightarrow CO_2 + 4H^+ + 4\,e^- \quad E = 0.21\,V \text{ vs. NHE} \tag{1}$$

$$H_2O \rightarrow O_2 + 4H^+ + 4\,e^- \quad E = 1.23\,V \text{ vs. RHE} \tag{2}$$

If the carbon corrosion persists at a high potential during fuel starvation, the electrochemically active surface area of the catalyst decreases drastically, leading to serious deterioration of the membrane electrode assembly (MEA). To mitigate the fatal anode degradation, some OER catalysts were added into the anode to realize the reversal-tolerant anode (RTA), facilitating water oxidation for the protons and electrons delivered to the cathode, even under fuel starvation [5–11].

Recently, IrRu-based alloy catalyst as the RTA has been proposed owing to its activities for both HOR and OER. Total replacement of the Pt catalyst in the automotive PEMFC with an IrRu-based catalyst was suggested [5,6]. It has been reported that a third element, such as Co, Ce, Ti or Na can be introduced to the IrRu alloy to improve its OER activity [12–14]. However, these elements can readily dissolve under the PEMFC conditions, resulting in the reduction of electrocatalyst's HOR activity.

In this study, yttrium (Y) was selected as the third element for the synthesis of ternary alloy catalysts, because metallic Y was known to increase electrochemical activity in the PEMFC [15–17]. However, it has been known that Y^{3+} ions can hardly be reduced to metallic Y through conventional solution and/or gas reduction methods due to its low reduction potential (2.37 V vs. NHE). In this study, a novel approach such as an electron beam (EB) method was employed *for the first time* to reduce the metal ions to metallic species by using high energy electrons. The enhanced HOR and OER activities were achieved by incorporating Y into the $IrRu_4$ alloy, and its catalytic performance was compared with those of bimetallic $IrRu_4$ alloy catalyst prepared by the EB method, and ternary IrRuY catalysts prepared by the conventional

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