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Stabilizing role of Mo in TiO_2-MoO_x supported Ir catalyst toward oxygen evolution reaction

Eom-Ji Kim[a], Jaewook Shin[a,b], Junu Bak[a], Sang Jae Lee[a], Ki hyun Kim[a], DongHoon Song[a], JeongHan Roh[a], Yongju Lee[a], HyoWon Kim[a], Kug-Seung Lee[c], EunAe Cho[a,b,*]

[a] Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology (KAIST), 291 Daehak-ro, Yuseong-gu, Daejeon 34141, Republic of Korea
[b] Advanced Battery Center, KAIST Institute for NanoCentury, Korea Advanced Institute of Science and Technology (KAIST), 291 Daehak-ro, Yuseong-gu, Daejeon 34141, Republic of Korea
[c] Pohang Accelerator Laboratory (PAL) Pohang, 790-784, Republic of Korea

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ABSTRACT

To accomplish the goals of cost reduction and durability improvement of polymer electrolyte water electrolysis (PEMWE), we report a titanium oxide and molybdenum oxide composite (TiO_2-MoO_x) as a support for the iridium (Ir) nanoparticle catalyst (Ir/TiO_2-MoO_x) toward oxygen evolution reaction (OER). Incorporation of Mo (V) and Mo(VI) into TiO_2 significantly enhances the electrical conductivity of TiO_2. During the synthesis of Ir nanoparticles on TiO_2-MoO_x, Mo(V) is oxidized to Mo(VI) with suppressing oxidation of Ir(III) to Ir(IV). Consequently, Ir/TiO_2-MoO_x forms higher fraction of the OER-active Ir(III) species on Ir surface enhancing OER activity of Ir catalyst. During OER, the chemical interaction between Mo and Ir keeps in Ir(III) and lessens the dissolution of Ir(III), improving the durability of Ir/TiO_2-MoO_x. Thus, Ir/TiO_2-MoO_x exhibits superior OER activity and durability. The single cell test results demonstrate that, as an anode catalyst, Ir/TiO_2-MoO_x can improve the performance and durability of the PEMWE cell than Ir black.

1. Introduction

With the increase in global attention to climate change, the capacity of renewable power sources installed worldwide has increased. For efficient utilization of intermittent renewable energy, surplus electricity needs to be properly stored. As an energy storage technology [1], polymer electrolyte membrane water electrolysis (PEMWE) has attracted a great deal of attention owing to its ability to operate at a high current density over wide load range, to respond rapidly to load changes, and to produce high purity hydrogen [2]. However, the commercialization of PEMWE is hindered due to the high fabrication cost and low durability, mostly related to the strongly-corrosive environment of the anode. In addition to the harsh condition, the sluggish oxygen evolution reaction (OER) limits anode materials to precious iridium (Ir)-based catalysts [3–6], whose catalytic activity and durability should be improved for implementation of PEMWE. To achieve the goal, nanostructured Ir-based catalysts have been extensively studied [7–10]. Although those catalysts have exhibited better OER activity than that of Ir, cost and durability issues have not yet been resolved [11–13].

One novel strategy to improve the activity and durability of Ir nanoparticles is to incorporate supports [14]. With support, nanoparticles can be finely dispersed and prevented from agglomeration [15]. Carbon black is a well-known support material with high electrical conductivity [16]. However, under harsh PEMWE anode conditions, carbon black corrodes, forming carbon dioxide ($C + 2H_2O \rightarrow CO_2 + 4H^+ + 4e^-$, 0.207 V_{RHE}) [17]. Alternatively, corrosion-resistant oxides have been introduced with dopants to enhance their electrical conductivity [18,19]. Thus, niobium-doped TiO_2 (Nb-TiO_2) and antimony-doped tin oxide (Sb-SnO_2) have been reported to enhance mass activity of Ir nanoparticles [20–23]. However, the durability of the supported catalysts still remains a challenge [21,24–27] since Nb and Sb are thermodynamically unstable and dissolve under PEMWE anode conditions [28,29]. Therefore, it is necessary to develop a new support material that can ensure durability and activity of Ir nanoparticles for OER.

Ir nanoparticle catalysts are prepared either as metallic Ir or thermally-oxidized IrO_2. During PEMWE operation, metallic Ir is electrochemically oxidized to form amorphous IrO_x [5,30]. Compared to IrO_2, IrO_x is known to have higher catalytic activity towards OER [5] owing

* Corresponding author at: Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology (KAIST), 291 Daehak-ro, Yuseong-gu, Daejeon 34141, Republic of Korea.
E-mail address: eacho@kaist.ac.kr (E. Cho).

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