First report of vertically aligned (Sn,Ir)O$_2$:F solid solution nanotubes: Highly efficient and robust oxygen evolution electrocatalysts for proton exchange membrane based water electrolysis

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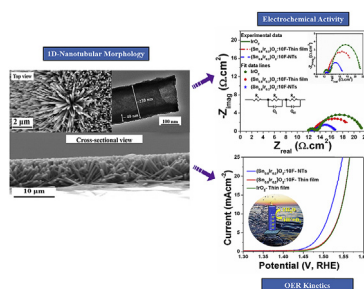[d] Mechanical Engineering and Materials Science, University of Pittsburgh, Pittsburgh, PA 15261, USA
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HIGHLIGHTS

- 1D nanotube (NT) morphology explored for (Sn$_{0.8}$Ir$_{0.2}$)O$_2$:10F as OER electrocatalyst.
- Vertically aligned NTs first synthesized by a sacrificial template assisted approach.
- (Sn$_{0.8}$Ir$_{0.2}$)O$_2$:10F NTs show electrocatalytic activity superior to IrO$_2$ thin film.
- (Sn$_{0.8}$Ir$_{0.2}$)O$_2$:10F NTs exhibit low charge transfer resistance and higher ECSA.
- (Sn$_{0.8}$Ir$_{0.2}$)O$_2$:10F NTs display excellent stability in 1N H$_2$SO$_4$ PEM electrolyte.

GRAPHICAL ABSTRACT

ARTICLE INFO

ABSTRACT

One dimensional (1D) vertically aligned nanotubes (VANTs) of (Sn$_{0.8}$Ir$_{0.2}$)O$_2$:10F are synthesized for the first time by a sacrificial template assisted approach. The aim is to enhance the electrocatalytic activity of F doped (Sn,Ir)O$_2$ solid solution electrocatalyst for oxygen evolution reaction (OER) in proton exchange membrane (PEM) based water electrolysis by generating (Sn$_{0.8}$Ir$_{0.2}$)O$_2$:10F nanotubes (NTs). The 1D vertical channels and the high electrochemically active surface area (ECSA ~38.46 m^{2}g^{-1}) provide for facile electron transport. This results in low surface charge transfer resistance (4.2 Ω cm^2), low Tafel slope (58.8 mV dec^{-1}) and excellent electrochemical OER performance with ~2.3 and ~2.6 fold higher electrocatalytic activity than 2D thin films of (Sn$_{0.8}$Ir$_{0.2}$)O$_2$:10F and benchmark IrO$_2$ electrocatalysts, respectively. Furthermore, (Sn$_{0.8}$Ir$_{0.2}$)O$_2$:10F NTs exhibit excellent mass activity (21.67 A g^{-1}), specific activity (0.0056 mAcm^{-2}) and TOF (0.016 s^{-1}), which is ~2–2.6 fold higher than thin film electrocatalysts at an overpotential of 270 mV, with a total mass loading of 0.3 mg cm^{-2}. In addition, (Sn$_{0.8}$Ir$_{0.2}$)O$_2$:10F NTs demonstrate remarkable electrochemical durability - comparable to thin films of (Sn$_{0.8}$Ir$_{0.2}$)O$_2$:10F and pure IrO$_2$, operated under identical testing conditions in PEM

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water electrolysis. These results therefore indicate promise of $(Sn_{0.8}Ir_{0.2})O_2$:10F NTs as OER electrocatalysts for efficient and sustainable hydrogen production.

1. Introduction

The identification, synthesis and development of high performance oxygen evolution reaction (OER) electrocatalysts for proton exchange membrane (PEM) based water electrolysis with reduced noble-metal (e.g. IrO_2, RuO_2 and Pt/C) content or with non-noble metal electrocatalysts is a major challenge facing the PEM fuel cell area. Added to this is the challenge of the system exhibiting excellent electrocatalytic activity and faster reaction kinetics along with the prolonged stability during electrolysis operation together representing the foremost challenge facing researchers in the OER electrocatalyst research area [1–4]. In an attempt to make major strides, we have exploited the theoretical first principles electronic structure calculations and have identified several highly active OER electrocatalysts with substantial reduction in the noble metal content of IrO_2/RuO_2 (i.e. ~ 70–80 mol. %) [1,4–6]. Accordingly, the solid solution of electrochemically non-active parent oxides with significantly lower noble metal (up to ~ 80 mol % Ir) content such as fluorine (F) doped binary and ternary solid solution oxides, synthesized in 2D thin films architectures have displayed comparable electrocatalytic activity and stability to that of pure IrO_2 [1,5]. The thin film approach for electrocatalyst synthesis is well known and beneficial due to several reasons. In contrast to powder based electrocatalysts, the film composition can be precisely controlled by the metal ions added to the precursor solutions, which is not easily accessible by conventional high temperature based pathways [7]. In addition, the thin film electrocatalysts architecture extensively lack the porous structure which results in facile mass transport of the evolving gases [7]. Also, as thin film electrocatalysts are directly fabricated/grown on the substrate or current collector, it eliminates requirement of any conductive additives or expensive binders, which are predominantly required in the powder based electrocatalysts [8,9].

Based on the work conducted to date, for further enhancing the electrocatalytic activity of these reduced noble metal containing 2D thin film solid solution electrocatalysts, we have embarked on the challenge to tailor the material length scales into one-dimensional (1D) nanoscale motifs. Accordingly, 1D vertically aligned nanotubular (VANT) architectures of electrochemically active systems have been generated in an attempt to improve the reaction kinetics and correspondingly, the nanotubular structures exhibit superior electrocatalytic activity towards the water splitting reaction [2,10–12].

In recent years, 1D nanostructures with nanotube (NT) as well as nanowire (NW) based morphologies have been widely studied for the application of electrocatalysts such as Pt NTs [8], nitrogen-containing carbon nanotubes (NCNTs) [13], Pt-Ru/Co NWs [14], Co_4N NWs [9], Pt–Ni–TiO_2 NTs [15] etc. in the water splitting and direct methanol fuel cell (DMFC) research area. Assembling the nanoparticles of electrocatalyst into tubular nanostructures offers various added benefits such as high active surface area, high aspect ratios (length-to-width ratio), dense catalytic sites - which expedite the catalytic activity for surface electrochemical reactions [2,8,16]. For example, Pt nanostructures with 1D nanotubular architectures have demonstrated ~ 1.4 times higher electrochemical active surface area than Pt black; leading to significantly improved catalytic activity (4.4 fold) towards oxygen reduction reaction [8,17]. In addition, 1D vertically oriented nanostructures offer sufficient porosity between the adjacent 1D nanostructures which facilitates mass as well as charge transport including superior electrocatalyst-electrolyte contact due to the easy accessibility of electrolyte molecules into the deep portion of the electrode/catalyst surface, which ultimately bolsters the electrocatalytic performance [2,11,16,18,19]. Besides, due to the presence of vertical

channels, the 1D vertically aligned motifs expedite the facile charge transport pathway between the catalyst surface and the current collector by directing effective channels in the catalyst electrodes which decreases the surface charge transfer resistance (R_{ct}) and thus, enhancing the electronic conductivity i.e. reaction kinetics on the electrocatalyst surface [8,9]. Moreover, the1D nanostructures also offer the unique prospect of developing the electrocatalyst nanostructures directly grown on the current collectors - without any requirement of conductive additives or binders [8,9].

It has been reported that the electrocatalysts with similar composition yet different morphologies significantly influence the electrocatalytic activity due to alteration of the charge transport properties, electrochemically active surface area and diffusion of reactants and products during the reaction process [20,21]. Therefore, in the present study, we have explored the 'nanotube (NT) structured-1D morphology for the solid solution $(Sn_{1-x}Ir_x)O_2$:10F (x = 0.2) electrocatalyst'; comprising earth abundant tin oxide (SnO_2), fluorine (F) and ultra-low noble metal (Iridium, Ir) content, for the very first time to the best of our knowledge. Accordingly, we have studied and compared the electrochemical performance for OER of the solid solution metal oxide based electrocatalysts of different architectures (nanostructured 2D thin film and 1D nanotubes) and correlated their materials length scale parameters to the electrocatalytic properties. We have already studied the system as an optimum 2D thin film composition [$(Sn_{0.8}Ir_{0.2})O_2$:10F] for OER in PEM based water electrolysis in our previously published report [1]. Thus, herein, a versatile sacrificial template-assisted approach has been employed to fabricate $(Sn_{0.8}Ir_{0.2})O_2$:10F VANTs on titanium (Ti) substrate. In order to generate 1D nanomaterials, various methods such as physical vapor deposition [22], thermal decomposition [23], and vapor-liquid-solid deposition [24,25] etc. have been reported. Among these techniques, the template-assisted or template-directed approach is simplistic, cost-effective and well known for the reliable fabrication of uniformly arranged one-dimension architectures, offering efficient control over size and shape of the various nano-structured materials [26–28]. Accordingly, in the present study, 1D $(Sn_{0.8}Ir_{0.2})O_2$:10F VANTs are synthesized via ZnO nanowires as a sacrificial template-assisted approach. The as-synthesized 1D $(Sn_{0.8}Ir_{0.2})O_2$:10F VANTs exhibit superior electrocatalytic activity toward OER with lower surface charge transfer resistance (R_{ct}), lower Tafel slope, higher electrochemical active surface area (ECSA), higher specific activity and turnover frequency (TOF) than the corresponding 2D thin film architectures of $(Sn_{0.8}Ir_{0.2})O_2$:10F and state-of-the art IrO_2 electrocatalysts. This research outlines the synthesis of vertically aligned nanotubes, structural and detailed electrochemical characterization of the $(Sn_{0.8}Ir_{0.2})O_2$:10F nanotubular electrocatalyst.

2. Experimental methodology

2.1. Synthesis of electrocatalysts

2.1.1. Vertically aligned nanotubes (VANTs) of $(Sn_{1-x}Ir_x)O_2$:10 wt% F (x = 0.2)

2.1.1.1. *Synthesis of ZnO based nanowires (NWs) as sacrificial template.* Synthesis of $(Sn_{1-x}Ir_x)O_2$:10F VANTs has been achieved using ZnO NWs as a sacrificial template. ZnO NWs were grown on titanium (Ti) foil (substrate) by the hydrothermal method [2,18,29–31]. Prior to growing the NWs, the Ti foil (0.5 cm × 2 cm, Aldrich) was thoroughly cleaned by ultra-sonication in a mixture of acetone, ethanol and deionized water (18 MΩ cm, MilliQ Academic, Millipore). 5.5 mM of zinc acetate solution in ethanol (anhydrous, 200