



Nanostructured F doped IrO₂ electro-catalyst powders for PEM based water electrolysis



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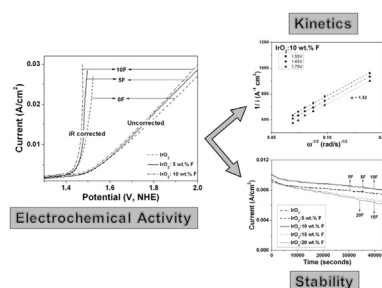
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HIGHLIGHTS

- Nanostructured IrO₂:F electro-catalysts have been wet chemically synthesized.
- IrO₂:10 wt.% F exhibits superior electrochemical activity than pure IrO₂.
- Stability of the IrO₂:F nanomaterials is comparable to pure IrO₂.
- High surface area F doped IrO₂ are promising OER anode electro-catalysts.
- Both half-cell and full cell test data show the superior response of IrO₂:10 wt.% F.

GRAPHICAL ABSTRACT



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ABSTRACT

Fluorine doped iridium oxide (IrO₂:F) powders with varying F content ranging from 0 to 20 wt.% has been synthesized by using a modification of the Adams fusion method. The precursors (IrCl₄ and NH₄F) are mixed with NaNO₃ and heated to elevated temperatures to form high surface area nanomaterials as electro-catalysts for PEM based water electrolysis. The catalysts were then coated on a porous Ti substrate and have been studied for the oxygen evolution reaction in PEM based water electrolysis. The IrO₂:F with an optimum composition of IrO₂:10 wt.% F shows remarkably superior electrochemical activity and chemical stability compared to pure IrO₂. The results have also been supported *via* kinetic studies by conducting rotating disk electrode (RDE) experiments. The RDE studies confirm that the electro-catalysts follow the two electron transfer reaction for electrolysis with calculated activation energy of ~25 kJ mol⁻¹. Single full cell tests conducted also validate the superior electrochemical activity of the 10 wt.% F doped IrO₂.

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1. Introduction

Hydrogen has been universally claimed as a potential next generation energy carrier with the tremendous ability to provide clean, reliable and affordable energy to meet the ever-increasing

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global energy demands [1]. A major barrier limiting the progress towards realization of the hydrogen economy is production, storage and distribution of low cost, carbon-free and ultra-high purity (UHP) hydrogen to meet our sustainability goals. High quality hydrogen can be benignly produced by electrochemical conversion of water using electricity *i.e.*, water electrolysis. The high cost of electricity to date has thus far always hindered the production of electro-catalytic hydrogen [2–4]. Electricity induced splitting of water despite the cost nevertheless, offers no pollutants or the creation of toxic by-products if the electricity is generated *via* renewable energy sources such as the use of photovoltaic cells, wind turbines, geothermal and hydropower. If all of the limitations, and the barriers discussed above are overcome, we can envision the hydrogen fuel and hydrogen technology to provide a very plausible and ecologically sustainable option for energy production if the efficiency of water electrolysis can be significantly improved with considerable reduction in costs [5–9].

The current technologies using proton exchange membrane (PEM) or acid based water electrolysis are very cost intensive. This impedes us from achieving the targeted hydrogen production cost (~\$ 3.0/gasoline gallon equivalent (gge)). High capital costs are encountered due to the expensive noble metal catalysts currently employed combined with the inferior efficiencies and labor intensive fabrication of PEM based electrolyzers [4,5,10–14]. PEM based electrolysis however, display several advantages over alkaline and neutral pH based water electrolysis processes including, but not limited to, high proton conductivity, low gas crossover, compact stack design, higher current densities, high pressure operation and the desired chemical and electrochemical tolerance [6,10,15]. At the anode, the over-potential and the ohmic resistance however results in poor electrochemical activity accounting for the sluggish catalytic performance. The durability of the electro-catalysts is also a major issue under the harsh acidic PEM conditions, thereby making the search for efficient and stable catalysts a high priority and a major imperative need if the much desired progress in this area is to be achieved.

Rutile type noble metal oxides, such as IrO_2 and RuO_2 are well known and accepted as gold standard anode catalysts for the oxygen evolution reaction (OER) in PEM based water electrolysis. Decrease in the noble metal oxide ($\text{IrO}_2/\text{RuO}_2$) loading with improved catalytic activity would enable much reduction in capital costs of PEM electrolyzer cells. It has been reported previously by many researchers [16–27] that addition of cheaper metal oxides or diluents (*viz.*, SnO_2 , Ta_2O_5 , TiO_2 , Nb_2O_5) to the parent noble metal oxide resulting in a binary or ternary metal oxide mixture could reduce the overall noble metal oxide content. However, with the addition of the cheaper diluents results in a reduction in the active surface area and electronic conductivity of the mixed oxides [17,18,24,28–30].

We have shown in various publications [16,27,31–34] the viability and efficacy of fluorine as a dopant combined with the use of solid solutions of binary and ternary systems as efficient electro-catalysts for water electrolysis. Specifically, F doped IrO_2 as a thin film electro-catalyst for OER in PEM based electrolysis has been previously reported by us [31]. Fluorine doping resulted in ~20% increase in electrochemical catalytic activity. The stability of the catalysts was also comparable to pure IrO_2 . We also performed first principle theoretical calculations using the *ab-initio* approach [32] that concluded that electrolytic water splitting utilizing F doped IrO_2 could contribute to significantly increasing the catalytic activity. This initial study formed the basis for motivating the development of F doped IrO_2 catalysts in the form of nanomaterials and also conduct detailed studies on the same.

In the present study, research is carried out to synthesize nanostructured F doped IrO_2 electro-catalysts in order to improve

the catalytic activity and the corrosion stability of the doped oxide compared to pure noble metal oxide electro-catalyst. In this article, F doped IrO_2 , denoted as $\text{IrO}_2:x$ wt.% F or $\text{IrO}_2:\text{F}$, with $x = 0, 5, 10, 15$ and 20 have been synthesized using a modification of the Adams fusion approach [35] and tested as an OER electro-catalyst. The catalyst ink is then coated on a porous Ti foil and tested as an anode electro-catalyst for PEM water electrolysis. In order to achieve a better understanding of the fundamental electrochemical reactions or electro-catalytic activity, detailed characterization analyses comprising X-ray diffraction (XRD), transmission electron microscopy (TEM), electrochemical impedance spectroscopy (EIS), Tafel analysis, rotating disk electrode (RDE) experiments, and chronoamperometry (CA) studies have been performed and reported on the synthesized $\text{IrO}_2:\text{F}$ nanostructured powder electro-catalysts.

2. Experimental details

2.1. Electro-catalyst preparation

Iridium tetrachloride [IrCl_4 , 99.5%, Alfa Aesar], and ammonium fluoride [NH_4F , 98%, Alfa Aesar] were used as the precursor sources for Ir and F, respectively. $\text{IrO}_2:\text{F}$ was synthesized using a modification of the Adams fusion method, first reported by Adams et al. [35], and used by other researchers as well [36,37]. The precursors were taken in stoichiometric amounts and completely dissolved in D.I. water generated by the Milli-Q system [18.2 M Ω cm deionized water; Milli-Q Academic, Millipore]. The solution containing the dissolved precursors were mixed with excess sodium nitrate [NaNO_3 , 99%, Alfa Aesar] also dissolved in D.I. water to generate the corresponding nitrate precursors in the dissolved state. The resulting solution mixture was stirred vigorously for 2 h to generate a homogeneous solution following which the water is then carefully evaporated at 60 °C. The mixture is then introduced into a furnace wherein it is heated to 500 °C at a ramp rate of 50 K min⁻¹, and then held at 500 °C for 1 h to form the F doped IrO_2 . The salt mixture is then washed multiple times with D.I. water in order to remove all the undesired excess chloride salts. The resulting homogeneous fluoride containing oxide powder is then dried in an oven at 60 °C for 24 h to form the $\text{IrO}_2:x$ wt.% F electro-catalyst, where x ranges from 0 to 20.

2.2. Physical and chemical characterization

The synthesized electro-catalysts were analyzed by X-ray diffraction using state-of-the-art detector [XRD, Philips XPERT PRO system with CuK_α radiation]. Typical scans were recorded in the 2θ range of 20°–80°. The operating voltage and current were kept constant at 45 kV and 40 mA, respectively. Specific surface area of the catalysts was measured using the Brunauer–Emmett–Teller (BET) technique. The powders were first vacuum degassed and then tested using a Micromeritics ASAP 2020 that employs nitrogen adsorption and desorption for surface area analysis. Correspondingly, multipoint BET surface areas are reported for the synthesized nanostructured powder. The microstructure and particle size of the catalysts was investigated using high resolution transmission electron microscopy (HRTEM). JEOL 4000EX operating at 400 kV was employed for conducting the TEM analysis to evaluate the particle size and nanocrystalline nature. High resolution transmission electron microscopy (HRTEM) analysis was conducted on the samples using JEOL JEM-2100F to further investigate the morphology.

2.3. Electrochemical testing and kinetics studies

Electrochemical characterization was conducted on the samples using a five port jacketed reaction cell [Ace Glass Inc.] assembled

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