



## Molecular Catalysis

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# IrO<sub>2</sub>/Co<sub>3</sub>O<sub>4</sub> supported mesoporous SBA-16: An efficient electro-catalyst for oxygen evolution reaction

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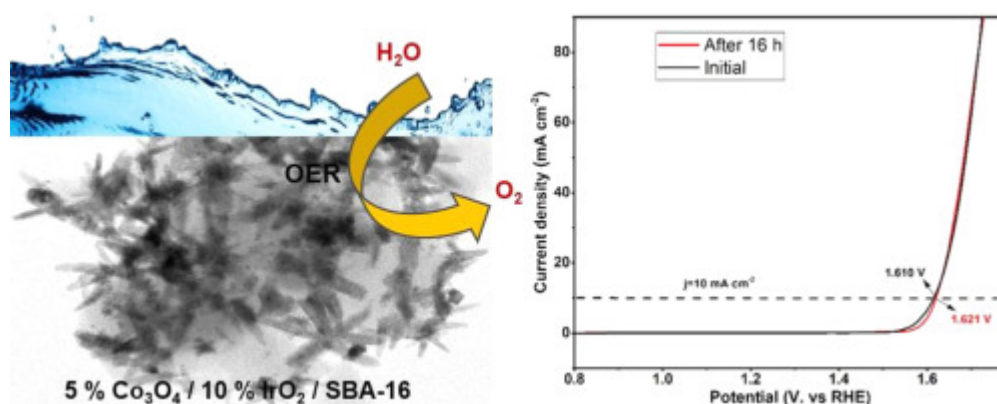
## Highlights

- Modified electrode materials based on mesoporous support with enhanced active site distribution.
- Economical modified electrode for OER reaction.
- Catalyst with surface area of 665 m<sup>2</sup> /g achieved for 5% Co<sub>3</sub>O<sub>4</sub> / 10% IrO<sub>2</sub> / SBA-16.
- 5% Co<sub>3</sub>O<sub>4</sub> / 10% IrO<sub>2</sub> / SBA-16 catalyst showed lesser overpotential of 278 mV with small Tafel slope of 65 mV dec<sup>-1</sup>.
- Outstanding electrocatalytic stability more than 12 h for the catalyst.

## Abstract

A non-conducting mesoporous silica support (SBA-16) with active supported electroactive iridium and cobalt was synthesized by a simple hydrothermal and impregnation method. The synthesized catalysts were represented as 5% IrO<sub>2</sub>/SBA-16, 10% IrO<sub>2</sub>/SBA-16, and 5% Co<sub>3</sub>O<sub>4</sub> / 10% IrO<sub>2</sub>, respectively. All catalysts were characterized by XRD, BET-Surface area, XPS, EDAX, and HR-TEM techniques to study their structural, morphological, chemical and micro structural properties. Small-angle XRD confirmed the mesoporous nature of the material formation, showing major faces at (100), (110), (200), and (220). High-angle XRD confirmed the formation of Co<sub>3</sub>O<sub>4</sub> and IrO<sub>2</sub> phase on the catalyst surface. Nitrogen sorption isotherm showed a ordered material with surface areas of the decreasing order of 5% IrO<sub>2</sub>/SBA-16, 10% IrO<sub>2</sub>/SBA-16, and 5% Co<sub>3</sub>O<sub>4</sub>/10% IrO<sub>2</sub>/SBA-16, respectively. EDAX analysis confirmed the presence of Ir and Co levels in the bimetallic catalysts. The oxidation state of Ir<sup>+4</sup> and Co<sup>3+</sup> were confirmed by XPS analysis. HR-TEM images showed that this material was highly porous and contained active metal particles dispersed throughout the surface. These metal particles play an important role in decreasing lower overpotential and current densities. In particular, the 5% Co<sub>3</sub>O<sub>4</sub> /10% IrO<sub>2</sub>/SBA-16 showed a lower overpotential of 380 mV at a current density of 10 mA. Compared to the activities of all the catalysts, 5% Co<sub>3</sub>O<sub>4</sub> /10% IrO<sub>2</sub>/SBA-16 showed higher activity due to the broad distribution of active sites with frequent electron transfers. Furthermore, during chronopotentiometry testing, a stable potential was maintained for over 12 hours at a constant current density of 10 mA.

## Graphical abstract



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## Introduction

In light of the global energy demand and the need for clean and renewable energy, there is a strong focus on research in the field of renewable energy. Over the next decades, renewable energy produced from carbon-neutral sources is seen as a strategy that can overcome all environmental challenges [1]. Electrochemical water electrolysis (EWE) is recognized as an essential method for the production of renewable hydrogen and oxygen for human consumption and fuel for a different application [2]. Electrochemical water electrolysis is performed through two processes: hydrogen evolution reaction (HER) at the cathode and oxygen evolution reaction (OER) at the anode. OER is a four-electron-proton bonding process that forms O–O bond that can be initiated by a low overpotential catalyst. Both of these half-cell reactions are irreversible and restrained by charge transfer [3]. This is catalyzed by an efficient electrocatalyst with the key properties of providing low onset overpotential and low overpotential at standard current densities. In most cases, RuO<sub>2</sub> and IrO<sub>2</sub> are the two important metal oxides that catalyze the OER reaction [3]. Nevertheless, when compared to the easy-to-evolve hydrogen evolution (HER) reaction, the main challenge that arises in the water electrolysis process is the anodic oxygen evolution reaction, which suffers from slow kinetics and excessive overpotential [2]. Therefore, the storage of renewable hydrogen fuels is vulnerable by the sluggish kinetics of the oxygen evolution reaction (OER), and the development of efficient OER catalysts is essential for the development of H<sub>2</sub> storage technologies. Furthermore, the development of high-performance heterogeneous electrocatalysts with cost-effectiveness is a great challenge in the oxygen evolution reaction (OER). In particular, the catalyst containing high active sites with low overpotential, high reaction kinetics, and high durability are the superior properties of OER catalysts [4,5]. Therefore, the development of efficient catalyst with high performance in water oxidation is an increasing interest in the field of research. Moreover, the reaction medium is also believed to play an important role in achieving high catalytic activity. Due to the material instability in acidic media, higher catalytic activity is observed in basic media than in acidic media [6]. However, there were few materials that showed activity in acidic media and showed high electrocatalytic activity, but their stability is questionable [7], [8], [9]. It is known that IrO<sub>2</sub> and RuO<sub>2</sub> are considered good anode materials for OER. Ru is less stable at high oxidation potentials, but provides high performances, and IrO<sub>2</sub> is more stable [10]. However, due to the high cost and the lack of regenerative ability of the material, it has not been put to practical use. Based on these factors, the introduction of high surface area mesoporous SBA-16 silica support may play an important role in improving the active site distribution and providing more active sites for adsorption of water molecules. Furthermore, the inclusion of active metal ions into the high surface area support is an alternative method to the preparation of inexpensive modified electrodes in the OER reaction. These modified electrode materials based on mesoporous

supports were used for catalytic purposes [11], [12], [13]. Since their discovery, these materials are being used in various research fields such as catalysis, sensing, energy storage, and biomedical [12]. Mesoporous materials are porous materials with regular and tuneable pore sizes from 2 to 50 nm [12]. The use of mesoporous inert silica has been limited by its non-conductivity in electrode reactions. Similarly, carbon supports are also corroded in OER reaction at high anodic potentials when used as electrocatalysts in metal-air batteries [3]. Apart from this drawback, these materials can provide the host active iridium metal oxide with excellent surface area and stability, which is advantages over using bulk iridium oxide to obtain high OER activity. In this study, SBA-16 mesoporous silica was used as a high surface area support and therefore one of the most attractive materials in the family of mesoporous silica to be used as catalytic support because of its large surface area and 3-D cubic structure with spherical pores connected via smaller pore opening. It also has a thick wall and its hydrothermally stable. Thus, SBA-16 play an important role in the preparation of working electrode for the electrochemical OER reaction because it offers maximum active sites and stabilize to hold high-cost IrO<sub>2</sub> while also minimizing particle size and enhances electron transfer by the metal support interaction [12,14]. In recent years, the noble metal-based catalyst has a significant interest in OER activity, particularly iridium oxide shows high catalytic activity due to its low overpotential [15,16]. Moreover, many researchers have reported different IrO<sub>2</sub>-supported catalysts for OER reactions in order to increase efficiency [15], [16], [17], [18], [19], [20]. However, the evolution per oxygen molecule required the transfer of 4 electrons. Obviously, OER is a more complicated reaction because its slow kinetics require high energy to break the activation barrier, which is the reason for the inefficiencies of the water electrolysis cell. Therefore, there are plenty of opportunity for efficiency improvement through catalyst development in the OER. The transition metals Co, Fe and Ni were extensively studied as electro catalysts and these materials were high active in acidic media and therefore comparable with noble metal oxides. However, comparison with acidic environment, use of transition metals in alkaline medium, reduces entire cost of the devices [21]. Therefore, on the basis of these considerations, transition metal Co was incorporated into the noble metal Ir and creates a bimetallic active site to improve the electron transfer. A limited report exists on IrO<sub>2</sub>-supported silica catalyst and further to the best of our knowledge no published results investigated the electrochemical properties of Co<sub>3</sub>O<sub>4</sub>/IrO<sub>2</sub> supported SBA-16 material. In this study, we used a nonconductive high surface area SBA-16 support with iridium and cobalt nanoparticles embedded on it, which demonstrated high electron conductivity. 5% IrO<sub>2</sub>/SBA-16, 10% IrO<sub>2</sub>/SBA-16, and 5% Co<sub>3</sub>O<sub>4</sub> / 10% IrO<sub>2</sub>/ SBA-16 mono and bimetal-based cobalt and iridium supported catalyst were prepared via hydrothermal and impregnation method. These materials were characterized by various physicochemical techniques and evaluated their electrochemical properties.

Furthermore, the conducting supports were eliminated in this work because the silica support was not affecting the catalytic performance [11]. According to TEM results, the active species were highly abundant on the external surface without aggregation, resulting in a high catalytic activity, and further, the combination of two metals in the catalyst has shown high activity than the single site IrO<sub>2</sub> catalyst. Furthermore, the OER activity results of mono metallic IrO<sub>2</sub> suggest that the increase in activity is due to the addition of cobalt oxide to the iridium oxide, which has more active sites for interelectrode electron transport. It further reduces the kinetic barrier by providing an interface and exposing the active site to reactive intermediates. In addition, most of the active particles of this bimetallic catalyst are 10-20 nm in size and are all involved in the electrocatalytic activity. Therefore, it may all play an important role in the OER reaction. The electrocatalytic properties of mesoporous silica, based on IrO<sub>2</sub> and Co<sub>3</sub>O<sub>4</sub> were investigated using cyclic voltammetry, linear sweep voltammetry, and EIS.

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## Section snippets

### Chemicals

Tetra-ethyl-ortho-silicate (TEOS, 99% pure), Pluronic F127 (EO<sub>106</sub> PO<sub>70</sub> EO<sub>106</sub>), and n-Butanol were purchased from Sigma Aldrich. SRL chemicals Ltd supplied 35% hydrochloric acid (HCl). Aldrich chemicals Ltd supplied the iridium trichloride (IrCl<sub>3</sub> nH<sub>2</sub>O), and Cobalt chloride (CoCl<sub>3</sub> n H<sub>2</sub>O). During the experiment, Millipore distilled water was used. All chemicals were utilized in their natural state, with no further purification....

### Preparation of mesoporous SBA-16 support

The hydrothermal approach was employed to prepare mesoporous SBA-16...

### XRD

Fig. 1(a) represented low angle XRD spectrum of Si-SBA-16, 5% IrO<sub>2</sub> / SBA-16, 10% IrO<sub>2</sub> / SBA-16 and 5% Co<sub>3</sub>O<sub>4</sub> / 10% IrO<sub>2</sub> / SBA-16 catalysts. The low angle XRD spectrum of Si-SBA-16 shows peak at  $2\theta=0.85$  corresponding to the major plane 110 of mesoporous cubic natured material with cage-type mesopores (Im3m symmetry) [24]. Furthermore, the succeeding catalysts, namely 5% IrO<sub>2</sub>, 10% IrO<sub>2</sub>, and 5% Co<sub>3</sub>O<sub>4</sub> / 10% IrO<sub>2</sub> shows strong diffraction peak at  $2\theta=0.94^\circ$ ,  $0.92^\circ$ ,  $0.84^\circ$  respectively. A small peak...

## Conclusions

The Ir and Co oxide nanoparticles supported mesoporous catalyst were prepared by hydrothermal and impregnation method, which is an efficient method for the preparation of inexpensive anode materials for OER reaction. HR-TEM images with particle size distribution curve indicated that a large number of smaller particles were located on the external surface of the catalyst, which providing more active sites for electron transport. The mesostructured silica supports play a crucial role because it...

## CRedit authorship contribution statement

**Sudhakar Pichaikaran:** Investigation, Formal analysis, Writing – original draft.

**Shanmugam Kotteswaran:** Investigation. **Mathew K Francis:** Data curation, Formal analysis. **P. Balaji Bhargav:** Supervision, Writing – review & editing, Funding acquisition.

**Wang Bo:** Writing – review & editing. **Nafis Ahmed:** Conceptualization. **Balaji C:** Writing – review & editing....

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper....

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