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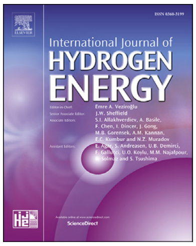

The electrocatalysis of oxygen evolution reaction on $La_{1-x}Ca_xFeO_{3-\delta}$ perovskites in alkaline solution

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ABSTRACT

The electrocatalytic oxygen evolution reaction (OER) on iron based perovskites with composition $La_{1-x}Ca_xFeO_{3-\delta}$ ($0.0 \le x \le 1.0$) in alkaline solution has been investigated. The perovskite samples were synthesized by combustion method. Energy dispersive spectroscopy and X-ray photoelectron spectroscopy were used to determine the bulk and the surface composition, respectively. The X-ray diffraction and iodometric titration method were employed to examine the phases and the oxidation state, respectively. It was observed that incorporation of calcium (Ca^{2+}) ions in the lattice of $LaFeO_3$ decreases the lattice parameters and the cell volume systematically as evaluated by Rietveld method. Furthermore, increase in the degree of Ca^{2+} substitution from 0.0 to 1.0, increases the average oxidation state of iron from Fe^{3+} to Fe^{4+} in addition to creating oxygen vacancies. The evaluation of OER kinetics on a rotating disk electrode setup suggests that incorporation of Ca^{2+} decreases the activity initially ($0.0 \le x \le 0.4$), but further substitution increases the activity. The maximum activity was observed for $x = 1.0$. This change in the OER activity suggests an interplay between the bond lengths and angles, oxygen vacancy and the average oxidation state of Fe.

Introduction

In the present era, there is a growing demand for energy and fuel due to increase in the world population. The entire human population across the world depend mostly on the energy derived primarily from fossil fuels. However, limited availability of these fossil fuels and emission of pollution-causing gasses into the environment has drawn the attention of researchers towards renewable and non-conventional sources of energy and fuels [1,2]. To overcome the energy crisis and minimize the emissions, utilization of hydrogen (H_2) as an energy carrier for mobile and stationery applications is a recommended approach [3,4]. Use of H_2 gas as a fuel for generating of heat by combustion, and electricity by the fuel cell produces only water, which makes it environmental friendly [5]. However, storage and transportation of H_2 gas is critical to use H_2 as a fuel in any future hydrogen-based economy and research done to address the these issues has been discussed in the literature [6,7]. Production of H_2 from steam reforming of methane is a dominant method and produces H_2 in large quantity. However, H_2 gas produced by this steam reforming produces greenhouse gases such as carbon dioxide and carbon monoxide [8].

In this context, production of H_2 by splitting water into H_2 and oxygen (O_2) is one of the cleanest ways available presently

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and it is a practical point of interest [9]. Hence, for several decades, the production of H_2 from water is being researched upon [1,4,10,11]. Electrolytic splitting of water is one of the most convenient methods, in which pure H_2 can be produced along with O_2 in high amounts by passing an electric current through water [1,12]. However, stable, efficient, and cost-effective electrocatalysts are required to electrolyze water. In water electrolysis, anodic reaction in alkaline media, i.e., oxygen evolution reaction (OER) is represented by $4OH^- \rightarrow O_2\uparrow + 2H_2O + 4e^-$, while the cathodic reaction is $2H_2O + 2e^- \rightarrow H_2\uparrow + 2OH^-$. In practice, the efficiency of water electrolysis is restricted by sluggish and kinetically slow anodic reaction, OER [13–15]. This slow OER causes a large anodic overpotential during the electrolysis. For this reason, considerable research has been done to understand the OER mechanism and minimize the energy loss during electrolysis [12–21].

To over come the energy losses during the electrolysis, an effort has been made in the past to use electrocatalysts for enhancing the rate of electrochemical reaction [5,12–15]. The RuO_2 and IrO_2 electrocatalysts frequently used, and have shown the best catalytic activity and stability for OER till date [20]. Other than pure oxides of Ru and Ir, various mixed oxides such as mixtures of IrO_2 and Pt, IrO_2 and TiO_2, IrO_2, and RuO_2 have also been used for the OER [19,21–23]. However, the cost and limited abundance of these metals have lead to difficulty in scaling up the electrolytic process. Consequently, for several decades now, the attention has been directed towards the usage of earth-abundant elements for efficient and stable electrocatalysts for the OER. Several works on efficient electrocatalysis by relatively cheap oxides and hydroxides of transition elements such as Ni, Co, Fe, etc. for OER have been reported [12,15,18,24–26].

Perovskite-type oxides with a general formula of ABO_3 are considered as potential OER active electrocatalysts due to their high catalytic activity, and the ability to incorporate different metal ions retaining the structure [17]. High structural stability of perovskites permits partial or complete substitution of earth-abundant alkaline earth metals in the A-site and transition metals in the B-site resulting in $A_{1-x}A'_xB_{1-y}B'_yO_3$ [16,27]. This A and B-sites substitution influence the physical properties as well as electrocatalytic properties [17]. Several studies have been carried out on perovskites for OER to understand the parameters influencing the electrocatalytic activity, with further purpose of improving the activity of known materials or predicting new active materials. It has been reported that the OER activity increases along the direction from $LaFeO_3$ to $SrCoO_3$ when both A and B-sites are substituted [16]. This OER activity enhancement was attributed to the broadening of antibonding (σ^* bond) between M-O-M in the lattice [16,28] and increase in the oxidation state of a transition metal (M) present at B-site ion [16]. Further, it was also reported that the OER activity of oxygen deficient $Ca_2Mn_2O_5$ was higher than that of the stoichiometric $CaMnO_3$ [29] highlighting the role of oxygen vacancies as well. Moreover, this suggests that the presence of intrinsic molecular level porosity on the oxygen-deficient sites in $Ca_2Mn_2O_5$ perovskite facilitated the ion transport for OER via oxygen vacancies [29]. Other than oxidation state and oxygen vacancies, the bond angles also influence the activity for OER. It has been observed that substitution of bivalent cation such as strontium (Sr^{2+}) for La^{3+} in the $La_{1-x}Sr_xCoO_3$ perovskite series, in addition to increasing the average oxidation state of Co, has an effect of straightening the octahedral cage, aligning atoms along the Co–O–Co axis resulting in an increase in the activity [30]. This alignment of Co–O–Co bonds and increase in the oxidation state of the Co cations enhances the overlap between the occupied O 2*p* valence bands and unoccupied Co 3*d* conduction band. This overlap in addition to increasing the activity also improves the conductivity as an added feature [30].

Recently, nontoxic and most abundant transition metal iron (Fe) based electrocatalysts have been investigated for the OER. It is reported that the tetravalent iron (Fe^{4+}) ion is the OER active site on the iron type oxides [31–33]. Hence, in the present study, an effort has been made to enhance the oxidation state of Fe present at B-site of perovskites from Fe^{3+} to Fe^{4+}. This will enhance the overlap between occupied 2*p* valence bands and unoccupied 3*d* conduction bands thereby improving the conductivity similar to that for Co as mentioned in the previous paragraph [30,34]. Additionally, the Fe^{4+} ion in the perovskite will have a high-spin d^4 configuration of $t_{2g}^3e_g^1$ [35], i.e., e_g-filling is close to unity for B-site. This ideal close to unity e_g filling balances the adsorption of reactants and desorption of intermediates, which helps in enhancing the electrochemical activity [14,36]. The formation of Fe^{4+} in perovskites can be achieved by substituting a divalent cations at the A-site. In the present work, Ca^{2+} has been substituted for lanthanum (La^{3+}) in the A-site leading to $La_{1-x}Ca_xFeO_3$ perovskite-type oxides and evaluated for their OER activity in alkaline media. Results indicate that the substitution of Ca^{2+} decreased the OER activity initially and further increase in Ca^{2+} substitution enhanced the activity of OER.

Materials and methods

Synthesis of $La_{1-x}Ca_xFeO_3$ perovskites

Lanthanum-calcium ferrites i.e., $La_{1-x}Ca_xFeO_3$ ($x = 0.0$ to 1.0) were synthesized by nitrate combustion method using lanthanum(III) nitrate hexahydrate ($La(NO_3)_3\cdot 6H_2O$), calcium carbonate ($CaCO_3$) dissolved in concentrated HNO_3 and iron(III) nitrate nonahydrate ($Fe(NO_3)_3\cdot 9H_2O$) solutions, and glycine ($C_2H_5NO_2$) as the fuel. The degree of Ca^{2+} cation substitution for La^{3+} cation at the A-site of perovskites ($La_{1-x}Ca_xFeO_3$) was varied from 0.0 to 1.0. The chemicals were used as received without further purification. Solutions were mixed and heated at 250 °C using a hot plate with continuous stirring at 250 rpm. Initially, the solution boiled with frothing and formation of foam. After foam formation subsided, it ignited to burn with a flame yielding a solid product within a minute. These solids were dried at 80 °C for overnight using hot-air oven (Nirmala Scientific Industries, India). The powders of these solids were made by grounding the solid product using mortar and pestle. Later, these powders were calcined in air at 800 °C for 3 h using a furnace (Nirmala Scientific Industries, India). The Fe_2O_3 electrocatalyst was also synthesized with the same procedure.

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