Mixed protonic-electronic conducting perovskite oxide as a robust oxygen evolution reaction catalyst

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ABSTRACT

Large-scale utilization of hydro, solar, or wind-based electrochemical water splitting relies on the availability of low cost, highly active oxygen evolution reaction (OER) catalyst. Transition metal-containing perovskite oxide is attractive in this regard. The OER on such perovskite oxide in an alkaline solution is nonetheless often limited by proton transfer step. To overcome such limitation, here we apply mixed protonic-electronic conductor $BaCo_{0.8-x}Fe_xZr_{0.1}Y_{0.1}O_3$ (x = 0, 0.2, and 0.4) as an OER catalyst. Among these three, $BaCo_{0.8}Zr_{0.1}Y_{0.1}O_3$ ($BC_{0.8}ZY$) in particular shows the lowest OER overpotential, the lowest Tafel slope, the highest OER mass activity, and the highest OER specific activity, which surpass those of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) benchmark. Using O_2-temperature programmed desorption, impedance spectroscopy, and O1s X-ray photoelectron spectroscopy, we attribute such superior OER performance to the highest oxygen desorption capacity, the lowest charge transfer resistance, and the highest hydroxide species content for $BC_{0.8}ZY$. We also demonstrate that the OER current of $BC_{0.8}ZY$ exhibits a first-reaction order dependence to the solution pH between 12.5 and 14, which confirms its proton transfer rate-determining step.

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1. Introduction

Hydrogen production *via* efficient electrochemical water splitting using renewable solar or wind-based electricity offers a sustainable pathway towards clean energy future [1,2]. Water splitting is therefore one of the most important processes in many energy storage and conversion devices [3–6]. The high overpotential of the oxygen evolution reaction (OER) in the anode side of these devices nonetheless limits their water splitting performance [7]. The presence of a highly efficient OER electrocatalyst is thus necessary to enable lower OER overpotential and accelerate OER kinetics [8]. IrO_2 and RuO_2 are currently the most active OER catalysts benchmark. However, their high costs have hindered their large-scale

application [9]. This has led to an extensive search for the low cost and stable OER catalyst alternative that can lower the operation cost in long run.

Perovskite oxides with an ABO_3 composition formula, where A is a rare-earth or alkaline-earth metal and B is a transition metal, are attractive candidates since they are relatively inexpensive and display high electrocatalytic activity for various reactions [10–14]. Their high OER activities in an alkaline solution at room temperature have also been confirmed recently [15–17]. In this context, Shao-Horn et al. proposed an OER activity descriptor based on molecular orbital principle and identified BSCF as an active OER catalyst with an even higher intrinsic activity than IrO_2 [18]. During repetitive OER cycling however, BSCF experiences rapid amorphization, which is accompanied by the leaching out of Sr^{2+} and Ba^{2+} from its surface and an increase in the OER currents and pseudo-capacitive [19,20]. This reveals an operational durability issue for BSCF especially in specific OER applications where the capacitive current enhancement over increasing operation time is not desirable.

The OER in an alkaline solution is generally thought to occur *via* four consecutive proton-coupled electron transfer (PCET) steps on the surface of the metal cation centers, during which the proton and the electron are transferred simultaneously [21,22]. Three PCET mechanisms may take place, proton transfer (PET) or electron transfer (EPT), a one-step mechanism in which proton and electron transfer are concerted, and concerted proton and electron transfer (CPET). The balanced equation for PET is $A+HB \leftrightarrow B^- +AH^+ \leftrightarrow B^- +AH$. The balanced equation for EPT on the other hand, is $A+HB \leftrightarrow A+BH \leftrightarrow B^- +AH$ while the balanced equation for CPET is $A+HB \leftrightarrow B^- +AH$. The onset potential of OER referenced to reversible hydrogen electrode (RHE) potential should be independent of the solution pH if such coordinated PCET mechanism indeed prevails [23]. However, recent findings showed that several metal oxide-based OER catalysts exhibit pH-dependent OER performances on RHE reference electrode, which suggests the decoupling of proton and electron transfer (DPET) [24]. The DPET for OER involves OH and OOH intermediates, which are not present in the suggested mechanisms. Because of the DPET, in the catalysis process, the pH of the intermediates may play a very active role. For these oxide catalysts, the proton transfer and the electron transfer occur in sequence where the proton transfer step becomes the rate limiting step [25]. The reaction order by which the proton is transferred becomes dependent on the relative stability of the reaction intermediates. Moreover, in such a case, to obtain an optimum reaction performance, the adsorption energy and the desorption energy of the reaction intermediates on the metal oxide surface should be neither too strong nor too weak, respectively [26].

The electrocatalytic property of perovskite oxide is closely associated with its reduction-oxidation (redox) behavior, which in turn, is determined by its transition metal constituent [27]. Cobalt-based perovskites for example are reported to be more OER active than iron-based perovskites [28,29]. It is thus of interest to determine the effect of the relative content of cobalt and iron on the room temperature OER performance of perovskite-based mixed protonic-electronic conductors (MPECs) with compositions of $BaCo_{0.8-x}Fe_xZr_{0.1}Y_{0.1}O_3$ (x = 0, 0.2, and 0.4), which we denote as $BC_{0.8}ZY$, $BC_{0.6}F_{0.2}ZY$, and $BC_{0.4}F_{0.4}ZY$, respectively, in an alkaline solution. We hypothesized that the use of such MPEC materials may overcome the proton transfer limitation observed in OER using oxide catalyst. Among these three compositions, $BC_{0.8}ZY$ displayed the highest OER performance. In comparison to BSCF, which showed an overpotential (η, i.e., the difference between the applied potential and the standard potential of OER of 1.23 V versus RHE) of 0.5 V at current density of 10 mA cm^{-2} (per electrode area), a Tafel slope of 101 mV dec^{-1}, a mass activity of 18.63 mA mg$^{-1}_{oxide}$, and a specific activity of 2.11 mA cm$^{-2}_{oxide}$, $BC_{0.8}ZY$ displayed a lower overpotential (η) of 0.42 V at a 10 mA cm^{-2} current density, a lower Tafel slope of 83 mV dec^{-1}, a higher mass activity of 69.44 mA mg$^{-1}_{oxide}$, and a higher specific activity of 5.74 mA cm$^{-2}_{oxide}$. We attribute such superior performance of $BC_{0.8}ZY$ to its high amount of hydroxide species, its low charge transfer resistance, and its high oxygen desorption capability. In addition, $BC_{0.8}ZY$ also exhibited strong pH-dependent OER activity against RHE reference electrode, which reflects non-zero reaction order in pH and thus, a proton transfer rate-determining step for OER using this oxide in an alkaline environment.

2. Experimental

2.1. Catalysts syntheses

Using a combined ethylenediaminetetraacetic acid-citric acid (EDTA-CA) complexing sol-gel method, $BaCo_{0.8-x}Fe_xZr_{0.1}Y_{0.1}O_3$ (x = 0, 0.2, and 0.4), denoted as $BC_{0.8}ZY$, $BC_{0.6}F_{0.2}ZY$, and $BC_{0.4}F_{0.4}ZY$, respectively, were synthesized [30]. Stoichiometric amounts of $Ba(NO_3)_2$, $Fe(NO_3)_3 \cdot 9H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, $Zr(NO_3)_4 \cdot 5H_2O$, and $Y(NO_3)_3 \cdot 6H_2O$ were mixed in de-ionized water followed by the addition of a solution mixture of EDTA and CA as complexing agents. The molar ratio of total metal ions to EDTA and CA is 1: 1: 2. Solution pH was adjusted to 6 by adding an aqueous ammonium hydroxide solution for complete complexation. To get transparent gel, the solution was heated with slow evaporation of water on constant stirring. Solid precursor was later gained by pretreating gel at 250 °C for 5 h in the furnace. The precursor was calcined at 1000 °C for 10 h with a ramping rate of 5 °C min^{-1} in air and cooled to room temperature naturally to obtain the perovskite powder.

2.2. Catalysts characterization

The crystal structures of the synthesized catalysts were determined by powder X-ray diffraction (XRD, Rigaku Smartlab 3 kW) using filtered Cu-Kα radiation (λ of 1.5406 Å) operated at a 40 kV tube voltage and a 40 mA current by step scanning in 2θ of 10−90° with an interval of 0.02°. Rietveld refinement of catalyst XRD patterns was performed using GSAS program to obtain more detailed structural information [31]. The specific surface areas of the catalysts were quantified by nitrogen adsorption-desorption tests on a BELSOR-II instrument at 77 K using the Brunauer-Emmett-Teller (BET) method. Scanning electron microscope (SEM) was performed on QUANTA-2000. Transmission electron microscopy (TEM) was performed using a Philips Tecnai T30F field emission instrument operated at a 200 kV voltage, which is equipped with a 2k-CCD camera. The surface oxidation states and the elemental composition of $BC_{0.8}ZY$, $BC_{0.6}F_{0.2}ZY$, $BC_{0.4}F_{0.4}ZY$, and BSCF were analyzed by an X-ray photoelectron spectrometer (XPS PHI 5000) using an Al-Kα X-ray. Temperature-dependent oxygen and water desorption capacity of the catalyst powder were tested by combined thermogravimetric analysis (STA 449F3) and mass spectrometry (QMS 403D) at a increasing rate of 10 °C min^{-1} in Ar.

2.3. Electrochemical tests

Electrochemical tests were carried out on a rotating disk electrode (RDE) of glassy carbon (GC, 5 mm-diameter, 0.196 cm^2 electrode area) as a working electrode at room temperature. Electrocatalysts were added with carbon black (Super P Li) to provide a conductive medium to facilitate the utilization of the perovskite electrocatalysts. To form a homogeneous dispersion, catalysts inks were prepared by sonication of perovskite oxide powder (10 mg), carbon black (10 mg), ethanol (1 mL) and Nafion (5.0 wt. %, 0.1 mL) for 1.5 h. To get a nominal catalyst loading of 0.232 mg$_{cat}$ cm^{-2} for the catalyst-modified RDE after complete drying at room temperature, a 5 μL of homogeneous ink was dropcasted onto the GC substrate. A Pt wire was used as the counter electrode and an Ag|AgCl (3.5 M KCl) electrode was used as the reference electrode. A CHI 760E bipotentiostat was utilized to control and monitor the electrochemical measurements. During the measurements, a 0.1 M potassium hydroxide (KOH) aqueous electrolyte solution (pH of 12.7) was purged with an ultra-pure oxygen (99.999% purity) to maintain the O_2|H_2O equilibrium at 1.23 V versus RHE. Therefore, the tested datas were obtained in O_2-saturated 0.1 M KOH. Prior to the OER activity measurements, the catalyst-modified RDE was electrochemically activated by potential cycling with a 100 mV s^{-1} scan rate between 0.2 V and 1.0 V vs Ag|AgCl (3.5 M KCl) at least five times while approximate reduplicative curves were obtained. LSV was carried out in the range of 0.2−1.0 V versus Ag|AgCl (3.5 M KCl) at a 5 mV s^{-1} scan rate using a catalyst-modified RDE at a rotation rate of 1600 rpm.