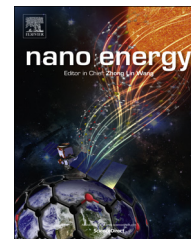Available online at www.sciencedirect.com

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RAPID COMMUNICATION

Calcium-doped lanthanum nickelate layered perovskite and nickel oxide nano-hybrid for highly efficient water oxidation

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Abstract
Perovskite oxides have attracted great attention recently for its high intrinsic activity in oxygen evolution reaction (OER) in electrochemical energy storage and conversion systems. However, their specific activity and durability require substantial enhancement to meet the requirement of the practical applications. Here, we demonstrate for the first time that a layered perovskite-metal oxide nano-hybrid electrocatalyst synthesized through a one-pot combustion process shows remarkably high OER activity in alkaline solution. The hybrid consists of two major phases, i.e. NiO and K_2NiF_4-type layered perovskite $(La_{0.613}Ca_{0.387})_2NiO_{3.562}$, showing synergistically enhanced OER activity and excellent durability under harsh OER operating conditions. The NiO-$(La_{0.613}Ca_{0.387})_2NiO_{3.562}$ hybrid exhibits the lowest Tafel slope ($\sim$42 mV dec^{-1}) and highest mass activity (52.2 mA mg^{-1} @ 1.63 V vs RHE) among all catalysts studied including noble metal oxide RuO_2 and well-known perovskite $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$.
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Introduction

A viable strategy for storing renewable energy (e.g. solar energy and wind energy) is the electrochemical electrolysis of water into oxygen and hydrogen fuels [1-5]. The oxygen evolution reaction (OER) upon water oxidation is an efficiency-limiting process in water oxidation [6-8]. The development of an effective electrode with low overpotential and long-term

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stability for OER is constantly being pursued [9-16]. The optimal oxygen evolution anode materials are RuO_2 and IrO_2, since these oxides exhibit the lowest overpotentials for the reaction at practical current densities [17,18]. However, the high cost of these materials and their poor long term stability in alkaline solution, renders their widespread commercial utilization both uneconomical and impractical. Low-cost transition-metal oxides (hydroxides), such as NiO_x, MnO_x and CoO_x, have therefore become the anodes for water electrolysis [19-25].

Another group of oxides-perovskites have attracted much attention due to their high intrinsic activity toward the OER in alkaline solution [26-28]. $LaNiO_3$ perovskite shows comparable area specific activity and higher durability as compared to the RuO_2 and IrO_2, but the low mass activity of $LaNiO_3$ is an obstacle to its practical application. There has been reported several methods to enhance the activity of the $LaNiO_3$ perovskite [29-31]. Hardin et al. synthesized a nanostructured, phase pure $LaNiO_3$ catalyst with a moderate surface area of $11\ m^2\ g^{-1}$ and supported on nitrogen-doped carbon, which showed nearly 3 times as active as 6 nm IrO_2 toward the OER, despite having nearly 7 times lower surface area [29]. Our previous study showed that the control of crystal structure of the $LaNiO_3$ perovskites played a critical role in determining OER activity [30]. The cubic $LaNiO_3$ perovskite displayed higher OER activity relative to the rhombohedral ones. Benhangi et al. reported that the MnO_2-$LaNiO_3$ hybrid prepared by sonication mixing showed enhanced OER activity due to the synergetic effect between MnO_2 and perovskite [31].

Recently, a series of special perovskite oxides with layered structure (called layered perovskite) attracted attention in OER due to their high activity and stability in alkaline solution [32]. Takeguchi et al. suggested that easily removable oxygen in the Ruddlesden−Popper-type $LaSr_3$-Fe_3O_{10} "layered" perovskite facilitates the redox reaction of the transition metal, thereby leading to enhanced OER activity [33]. Jung et al. improved the OER activity of La_2NiO_4 layered perovskites by doping Ca or Sr into La site [34].

In this study, we demonstrated a NiO and Ca-doped La_2NiO_4 layered perovskite hybrid electrocatalyst for OER. The hybrid was synthesized by a one-pot solution combustion process. Crystal structure and morphology of the hybrid were characterized. The synergetic effect on the enhancement of OER activity was discussed. $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF), $LaNiO_3$, $(La_{0.6}Ca_{0.4})_2NiO_{4-\delta}$, NiO, RuO_2 and NiO-$(La_{0.6}Ca_{0.4})_2NiO_{4-\delta}$ prepared by wet impregnation were also prepared and tested for comparison. The specific OER activity of nano-hybrid electrocatalyst surpasses all the other electrocatalysts studied including noble metal oxide (RuO_2) and the well-known perovskite BSCF [35]. Moreover, the hybrid electrocatalyst shows excellent stability during OER in alkaline media.

Experimental

Powder synthesis

The nano-structured NiO–Ca-doped La_2NiO_4 layered perovskite hybrid was synthesized through a one-pot combustion process. Lanthanum nitrate $La(NO_3)_3$, calcium nitrate $Ca(NO_3)_2$, and nickel nitrate $Ni(NO_3)_2$ were applied as the raw materials for the metal ion sources. All metal nitrates were added based on the required molar ratio of $La_{0.6}Ca_{0.4}NiO_{3-\delta}$, followed by the introduction of EDTA and citrate acid as complexing agent. The molar ratio between metal ions, EDTA and citrate acid was 1:1:2. Excessive ammonia was needed in the system. All series of the components were dissolved in distilled water separately and were heated to 120 °C under stirring until the solution gelatinized. The mixture was then calcined in the oven at 260 °C to trigger auto combustion. After combustion, the ash was collected, ground, and calcined at 850 °C in air for 5 h.

NiO-$(La_{0.6}Ca_{0.4})_2NiO_{4-\delta}$ was also fabricated by wet impregnation for comparison. Equal molar $(La_{0.6}Ca_{0.4})_2NiO_{4-\delta}$ and $Ni(NO_3)_2$ were mixed in 5 ml ethanol under ultrasonic vibration, followed by drying at room temperature for 24 h. The NiO-$(La_{0.6}Ca_{0.4})_2NiO_{4-\delta}$ electrocatalyst was obtained by calcinating the dry mixture at 850 °C in air for 5 h.

Sample characterization

The crystal structure of the samples was determined by X-ray diffraction (XRD, Model D8 Advance, Bruker, Germany) with filtered CuKα radiation (40 kV and 40 mA). The experimental diffraction pattern of the NiO-$(La_{0.613}Ca_{0.387})_2$-$NiO_{3.562}$ hybrid was collected by step scanning in the 2θ range of 10-90° with intervals of 0.01°. Refinements of the XRD patterns were conducted using DIFFRACplus Topas 4.2 software. During the refinements, general parameters, such as the scale factor, background parameters, and the zero point of the counter, were optimized. Because too many parameters were involved in the refinement, Le Bail refinement was used to determine the space group and lattice parameters of the NiO-$(La_{0.613}Ca_{0.387})_2NiO_{3.562}$ hybrid first. Rietveld refinement was then conducted to determine the position of each atom in the lattice and the concentration of each phase.

The morphology of the samples was studied by field emission scanning electron microscopy (FESEM, JEOL 7001) and transmission electron microscopy (TEM, JEOL JEM-2100F). The chemical state of O was analyzed by XPS (Kratos Axis ULTRA). The Brunauer-Emmett-Teller (BET) surface area of the powders was measured using N_2-adsorption measurements on a Micromeritics TriStar II 3020, after degassing the samples for 24 h at 250 °C prior to the test.

Electrochemical characterization

For the purpose of lifting electronic conductivity restrictions within the thin film electrodes, the as-synthesized sample electrocatasts were mixed with as received carbon (Super C65) from TIMCAL C'NERGY at mass ratio of 1:1. The electrocatalyst suspension was prepared by sonication of electrocatast (10 mg), carbon (10 mg), ethanol (1 mL) and Nafion solution (5 wt%, 100 μL) for 30 min. An aliquot of 5 μL of mixture suspension was drop-casted onto a glassy carbon disk electrode (4 mm diameter, 0.126 cm^2 area) and left under a glass jar for drying for 3 h.

Voltammetric experiments were conducted on a Biologic VMP2/Z multichannel potentiostat. Cyclic votlammetry (CV)