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N-doped $La_2Zr_2O_7$ as an enhanced electrocatalyst for oxygen reduction reaction

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ABSTRACT

Nitrogen shows a positive influence on the ORR activity of certain catalysts, such as N-doped carbon and N-doped ZrO_2. In this paper, we report a method to dope nitrogen into $La_2Zr_2O_7$ nanoparticles by the sol-gel process combined with ammonolysis. XPS results indicate that the nitrogen content in $La_2Zr_2O_7$ is approximately 0.92 at.%. Compared to the ORR activity of $La_2Zr_2O_7$, ORR activity of the N-doped $La_2Zr_2O_7$ is considerably enhanced. Density functional theory (DFT) calculations indicate that the band gap is reduced in N-doped $La_2Zr_2O_7$, which may be one of the factors that contribute to the improvement.

1. Introduction

Aiming at reducing the usage of the precious metal Pt and hence the cost of a fuel cell, the development of non-precious-metal electrocatalysts has thus generated considerable interest. Oxide materials, such as pyrochlores [1] and perovskites [2], are proposed to be good alternatives to Pt-based catalysts. Pyrochlore-structured oxides described by the formula $A_2B_2O_7$ have been evaluated for oxygen electrocatalysis [3–5]. In 0.5 M H_2SO_4, $Bi_2Pt_{2-y}Ir_yO_7$ displays significant catalytic activity for oxygen electroreduction with an onset potential at ca.0.2 V vs. Hg/Hg_2SO_4 [6]. However, the activity of these oxides is still far from being applied in fuel cells.

It has been recognized that doped nitrogen can play an essential role in forming the active sites for oxygen-reduction catalysts and hence increasing their activity towards the oxygen reduction reaction (ORR) [7,8]. Nitrogen-doped materials, such as nitrogen-doped carbon materials [9,10], show significant activity for the (ORR). Shao M. [11] revealed that nitrogen inclusion into graphene reduces the band gap, thus allowing it to catalyze the oxygen-reduction reaction. N-doped ZrO_2, an oxynitride, had shown an enhanced catalytic activity for the ORR compared to that of pure ZrO_2, and its onset potential can achieve 0.8 V vs a reversible hydrogen electrode (RHE) [12]. Therefore, nitrogen doping is believed to be an effective way to greatly improve the electrochemical activity of oxides. As a result, nitrogen insertion into ternary oxides may lead to considerable improvements in ORR activity.

Numerous studies have been attempted to increase the photocatalytic activity of ternary oxides by nitrogen doping [13,17]. Because it is less electronegative than oxygen, the nitrogen 2p (N2p) levels are energetically located above the O2p levels. If oxygen is substituted for nitrogen in oxides, the mixing of the N2p and O2p levels will lead to a narrower band gap [14]. In addition, oxygen vacancies, which can improve the catalytic activity, may be generated in the process of nitrogen doping because N^{3-} and O^{2-} anions differ in their formal oxidation state [15].

However, pyrochlore-structured oxides face the problem that they could be reduced during nitriding, especially when NH_3 is used as the N-source. Therefore, the effects of doped nitrogen on the catalytic activity of pyrochlores have not yet been clarified.

In this study, we selected the ternary oxide $La_2Zr_2O_7$, which is stable during nitriding, and we doped nitrogen into it by a sol-gel process combined with ammonolysis [16–22], aiming to increase its ORR activity by N-doping.

2. Experimental

2.1. Preparation of catalysts

The synthesis of N-doped $La_2Zr_2O_7$ was performed by a sol-gel process combined with ammonolysis [22]. In a typical sol-gel

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synthesis, 1.07 g of $ZrO(NO_3)_2 \cdot xH_2O$ (99.99%, Aladdin) were added into a 30 mL aqueous solution containing 1.3 g of $La(NO_3)_3 \cdot 6H_2O$ (99.9%, Aladdin), 3.36 g of citric acid (purity higher than 99.5%, Sinopbarm Chemical Reagent Co., Ltd.) and 4 g of ethylene glycol (purity higher than 99%, Sinopbarm Chemical Reagent Co., Ltd.). Then, the solution was heated with constant stirring at 80 °C. When a moist white paste formed, it was transferred into a vacuum oven at 80 °C to become a white xerogel, and then it was crushed and fired for 3 hours at 650 °C in air to form a fine white powder. For nitriding, 0.3 g of the amorphous oxide was annealed in gaseous ammonia (NH_3, 98. 888%) at a flow rate of 200 $mL \cdot min^{-1}$, and the sample was heated to 950 °C at a heating rate of 10 $°C \cdot min^{-1}$. After 24 h, the sample was cooled to room temperature under an ammonia atmosphere to prevent re-oxidation, which resulted in a slightly yellow powder. For comparison, the amorphous oxide was sintered under the same conditions except that the NH_3 atmosphere was changed to an argon (Ar, 99.999%) atmosphere, which yielded white powders.

2.2. Characterization of the catalysts

X-ray powder diffraction (XRD) analysis of the catalysts was performed by a Rigaku-D/MXIII diffractometer with Cu Kα radiation ($\lambda = 1.5406$ Å). X-ray data were collected in the scanning angle range of 20 to 100° at a speed of $5° \cdot min^{-1}$. X-ray photoelectron spectra (XPS) were obtained on a VG Scientific ESCALAB 210 electron spectrometer with Mg Kα radiation. Fourier transform infrared (FT-IR) absorption spectra were recorded using a 60-SXB IR spectrometer from 399 cm^{-1} to 2000 cm^{-1} and a resolution of 2 cm^{-1}. The FTIR sample preparation is mainly by pressing the mixture of sample and KBr, and then testing the pressed pellet by FTIR. Transmission electron microscopy (TEM) images were obtained with a JEOL JEM-2010 microscope operating at an accelerating voltage of 200 kV. The powdered catalysts were sonicated in anhydrous ethanol (purity higher than 99%, Sinopbarm Chemical Reagent Co., Ltd.) for 30 min in an ice bath. Then, a drop of the solution was deposited onto a carbon-coated copper mesh and left to dry in air.

2.3. Electrochemical measurements

The electrochemical tests were performed in a standard three-electrode system controlled with a CHI660 C station (CH Instruments, Inc., USA) using a Pt gauze and Hg/HgO in 6 M KOH as the counter electrode and the reference electrode, respectively. In these tests, the Hg/HgO reference electrode was calibrated in H_2-saturated 0.5 M KOH by measuring the hydrogen oxidation/evolution currents on 20 wt%Pt/C-RDE and defining the potential of zero current as the reversible hydrogen electrode (RHE) potential. The working electrodes were prepared by casting catalyst-containing inks onto a rotating disk electrode (RDE) of 5-mm diameter with a geometric area of 0.196 cm^2. The RDE was polished with 0.05 μm Al_2O_3 slurry to a mirror finish and then rinsed well with pure water and ethanol, alternately, to obtain an effectively clean GC electrode surface [23]. The electrolyte used throughout the work was an aqueous solution of 0.5 M KOH, prepared from pelletized KOH and high-purity water. Prior to electrochemical experimentation, the electrolyte was purged in the electrochemical cell with bubbled O_2 for at least half an hour to achieve saturation.

The catalyst inks were prepared by 1 h of sonication of an appropriate amount of the synthesized samples, Vulcan XC-72 (Cabot Corporation) and Nafion® ionomer solution (5 wt%, DuPont) in an ice bath, yielding inks with final concentrations of 5 $mg_{sample} \cdot mL_{ink}{}^{-1}$, 1 $mg_{xc72} \cdot mL_{ink}{}^{-1}$ and 20 $\mu L_{Nafion} \cdot mL_{ink}{}^{-1}$. The samples were mixed with Vulcan xc72 at a 5:1 mass ratio of sample and carbon to eliminate the electronic conductivity limitations within the electrodes [24]. Then 10 μL of the catalyst ink is deposited onto a glassy carbon (GC) electrode and dried in air at room temperature with a final composition of 255 $\mu g_{oxide} \cdot cm_{disk}{}^{-2}$, 51 $\mu g_{xc\ 72} \cdot cm_{disk}{}^{-2}$.

3. Results and discussion

Detailed XRD studies were performed on the as-synthesized compound, and the pattern is compared with that of the parent $La_2Zr_2O_7$ in Fig. 1. Because pyrochlore is a superstructure of a fluorite-like array of atoms, superlattice diffraction peaks of the (331) and (511) peaks are the characteristic peaks of the pyrochlore structure to distinguish it from the fluorite defect structure [25]. As shown in Fig. 1, the (331) peak exists in the pattern of N-doped $La_2Zr_2O_7$ and $La_2Zr_2O_7$, so both of them possess the pyrochlore structure. Compared with the peaks for $La_2Zr_2O_7$, although there is no apparent difference in Fig. 1a, the XRD reflections of the N-doped $La_2Zr_2O_7$ shift toward lower 2θ angles, as shown in Fig. 1b. According to the equation of $\lambda = 2d^* \sin\theta$ (θ is the diffraction angle, and d is the interplanar distance), the interplanar distance of the (222) peak for N-doped $La_2Zr_2O_7$ is 0.3148 nm, which is larger than that of 0.3136 nm for $La_2Zr_2O_7$. The enlargement of this parameter indicates that nitrogen is inserted into the $La_2Zr_2O_7$ structure.

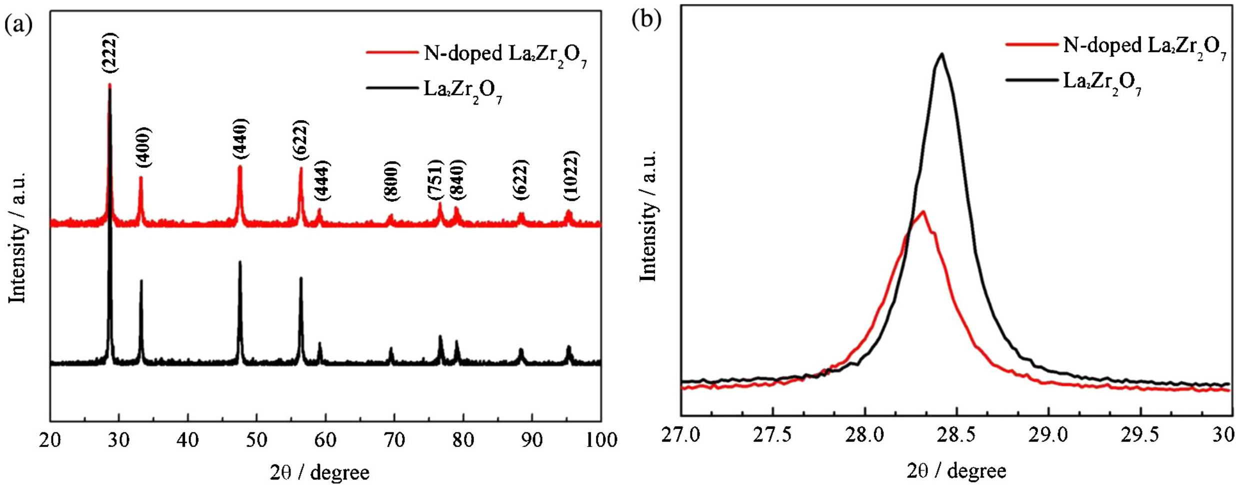

Fig. 1. XRD plots of N-doped $La_2Zr_2O_7$ and $La_2Zr_2O_7$ over the 2θ range of: (a) 20-100° and (b) 27-30°.