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Short Communication

Preparation, Characterization and Electrochemical Properties of La_2CuO_4@Au as a Novel Bifunctional Oxygen Electrode

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In this paper, a novel bifunctional oxygen electrode, La_2CuO_4@Au, was synthesized using the sol-gel method. Thermogravimetry differential thermal analysis (TG-DTA) was used to analyze the formation mechanism and crystallization temperature. The crystal structure and surface morphologies of La_2CuO_4 were determined by X-ray diffraction (XRD) and scanning electron microscope (SEM), respectively. The CV curves of 0.1M KOH electrolyte saturated with N_2 and O_2 showed that La_2CuO_4@Au had excellent catalytic activity for oxygen reduction reaction (ORR).

Keywords: bifunctional oxygen electrode; La_2CuO_4; X-ray diffraction; sol-gel

1. INTRODUCTION

As efficient energy conversion devices, the successful application of fuel cells will effectively reduce the emissions of environmental pollutants in the process of energy utilization [1–6]. Perovskite composite oxide can be used as an oxidation catalyst, solid electrolyte material, connection material, sensor material and high temperature superconductor material [7–9].

Perovskite composite oxide is a promising bifunctional oxygen electrode catalyst due to its low cost and high electrocatalytic activity [10–11]. Cu-based composite oxides have high catalytic activity for oxidation and reduction, and unique electrochemical properties. La_2CuO_4 composite oxide has a tetragonal structure, and belongs to K_2NiF_4 perovskite type. La_2CuO_4 has good oxygen permeability, catalysis and oxidation performance [12–14]. The conductivity of La_2CuO_4 itself is not high, so researchers adopt the composite method to improve the conductivity.

At present, the preparation methods for perovskite-type composite oxides included the solid state, sol-gel, hydrothermal and glycine nitrate combustion method, and so on [15–16]. The sol-gel method has the advantages of good crystallinity, small particle size and high product purity.

In this paper, La_2CuO_4 was selected as the research object and prepared using the sol-gel method. The mixtures of La_2CuO_4 and Au at a 1:4 mole ratio had high catalytic activity. The synthesized La_2CuO_4@Au was applied to the study of a bifunctional oxygen electrode.

2. EXPERIMENTAL

The required metal salts were weighed according to the stoichiometric ratio and dissolved with deionized water. Then, a proper amount of citric acid and ammonia was added to adjust the solution to a certain *p*H value and it was stirred until a uniform gel was obtained. After further drying, the required catalyst was obtained by sintering at a certain temperature (800 °C, 900 °C, 1100 °C) for 2 h. The mixture of La_2CuO_4 and Au was at a 1:4 mole ratio to obtain La_2CuO_4@Au.

Thermogravimetry differential thermal analysis (TG-DTA, Universal V 3.7A, TA Instruments, USA) was used to analyze the formation mechanism and crystallization temperature of the catalyst. The crystal structure of La_2CuO_4 was determined by X-ray diffraction (XRD, X'pert Pro MPD, Netherlands). The surface morphologies of La_2CuO_4 sintered at different temperatures were measured by scanning electron microscope (SEM, SU8010, Hitachi, Japan). Energy-dispersive X-ray (EDX) analysis of La_2CuO_4@Au was also carried out.

The catalyst film of La_2CuO_4, polytetrafluoroethylene, Au and nickel mesh were pressed into a bifunctional oxygen electrode under a certain pressure. The electrode thickness was 0.5 mm. The bifunctional oxygen electrode was the research electrode, the Pt mesh was the auxiliary electrode, the self-made Ag/AgCl electrode was the reference electrode, and the KOH solution was the electrolyte. The cyclic voltammetry of the oxygen electrode was measured in 0.1 M KOH electrolyte. The scanning range of potential was - 1.0 V ~ 0.4V under N_2 or O_2 saturated conditions. The disk (i_d) current densities ~ potential curves of La_2CuO_4@Au (a) and La_2CuO_4 (b) were tested in 0.1 M KOH solution at four different rotation speeds (400, 900, 1600 and 2500 rpm) during oxygen reduction reaction (ORR).

3. RESULTS AND DISCUSSION

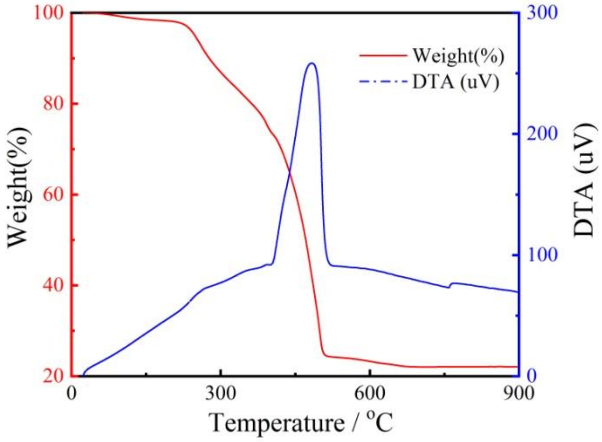


Figure 1. TG-DTA curve of the xerogel to 900 °C.

Fig.1 is the TG-DTA analysis of a dried 10 mg xerogel sample (La_2CuO_4). From the TG curve, the dehydration and decomposition of solvent water, citric acid crystal water and citrate in the gel show a gradual loss of weight on the TG curve at 100-270°C. The TG and DTA curves show a serious weightlessness and a large exothermic peak between 300-520°C, respectively. This is due to the oxidative combustion of citric acid or its decomposition products [13–14]. The weight no longer decreases after 700°C. Therefore, the calcination temperature of the catalyst should be higher than 700°C.

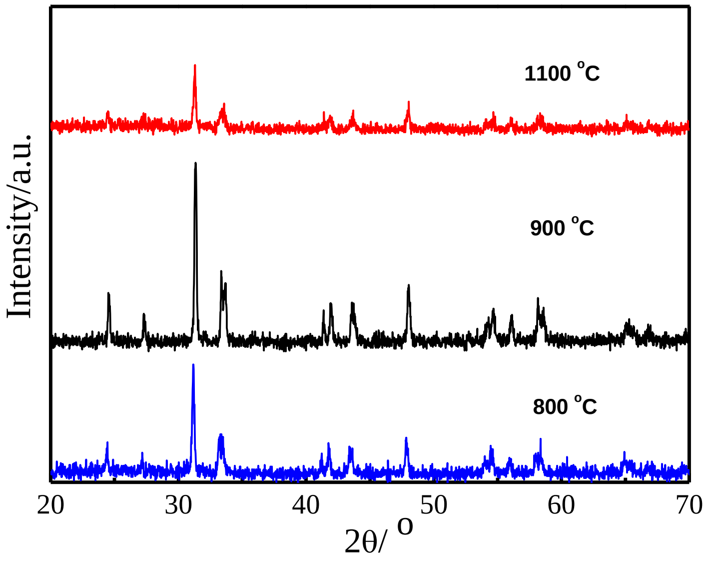


Figure 2. The crystal structure of La_2CuO_4 sintered at different temperatures.

The longer the calcination temperature is, the more likely the particles are to agglomerate. Because the pure perovskite phase can be obtained after sintering for 2h, the calcination time was fixed to 2h. XRD patterns of La_2CuO_4 sintered at different temperatures (800 °C, 900 °C, 1100 °C) are shown in Fig. 2. The XRD results show that a complete perovskite crystal can be formed after sintering at 800 °C or 900 °C for 2 h, and the product is almost pure, without impurity phase [14]. The higher calcination temperature of La_2CuO_4 at 1100 °C may result in the loss of some oxides and a change of the crystal structure.

Fig. 3 shows the SEM pictures of La_2CuO_4 sintered at different temperatures (800 °C, 900 °C, 1100 °C). The morphology of La_2CuO_4 prepared at 800 °C is fluffy and cotton-like. The higher the calcination temperature, the more easily the particles agglomerate. There is a certain degree of sintering phenomenon when the sample is calcined at the high temperature of 1100 °C. The larger particle sizes of the prepared catalyst will reduce the active surface area of the electrochemical reaction [17]. According to the results of XRD, we chose the sample sintered at 800°C as the research object.

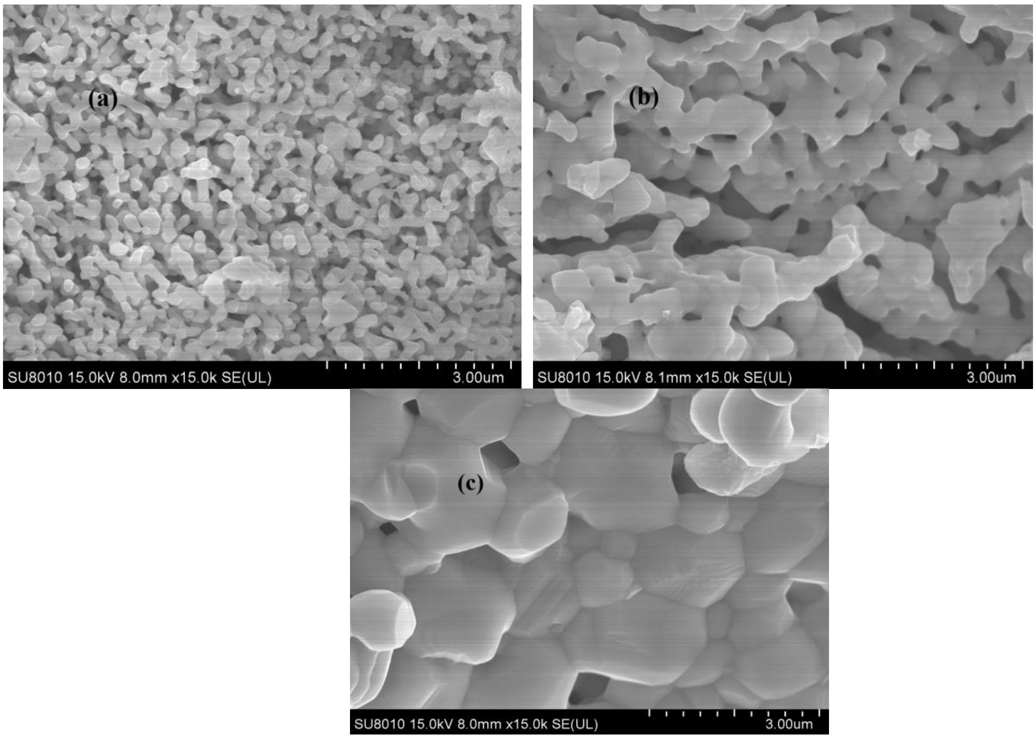


Figure 3. The SEM pictures of La_2CuO_4 sintered at different temperatures (a) 800 °C, (b) 900 °C, (c) 1100 °C.

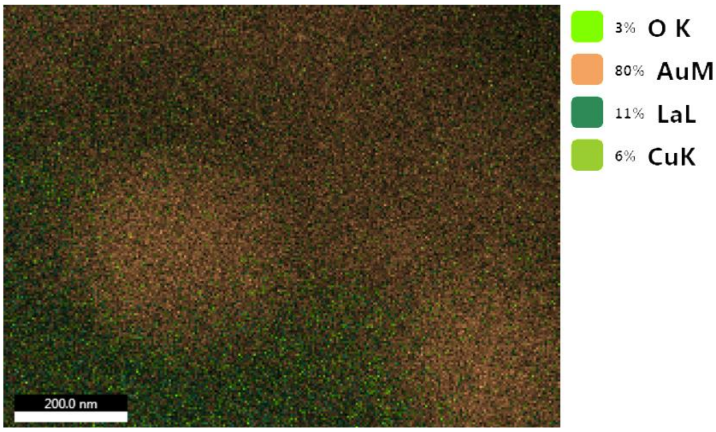


Figure 4. The EDS Mapping analysis of La_2CuO_4@Au.

Fig. 4 is the EDS Mapping diagram of La_2CuO_4@Au. There was 11 % La, 6 % Cu, 3 % O and 80 % Au in the La_2CuO_4@Au. The mole ratio of La_2CuO_4 and Au was 1:4, which is consistent with the proportion of the experimental raw materials.

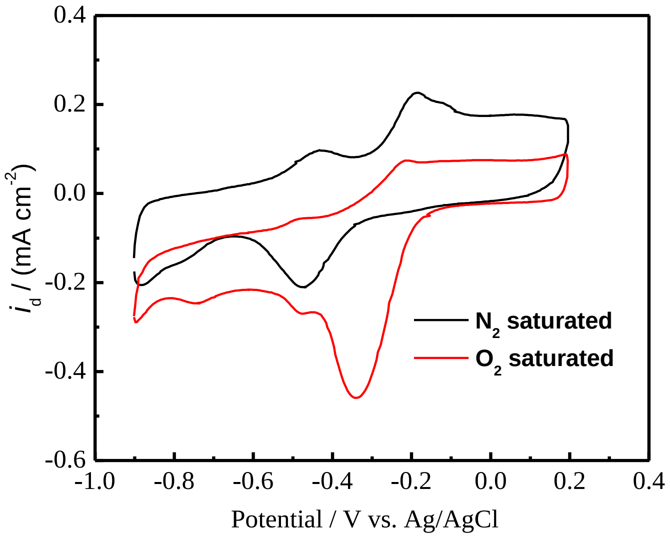
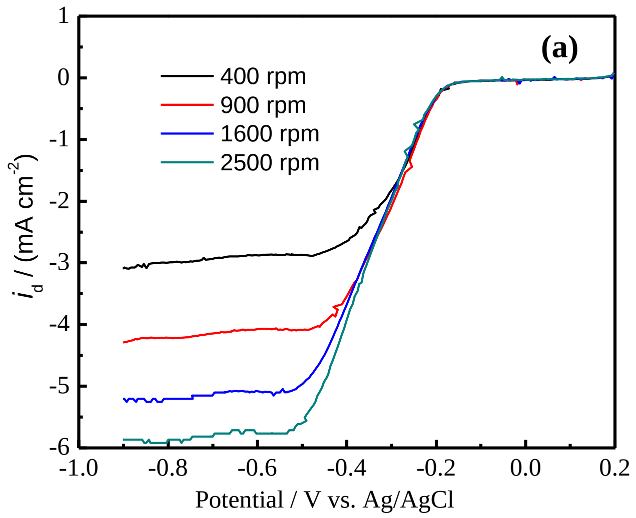


Figure 5. The cyclic voltammetric (CV) curves of the bifunctional oxygen electrode in 0.1 M KOH electrolyte. The scanning range of potential is - 1.0 V ~ 0.4V under the N_2 or O_2 saturated conditions.

The cyclic voltammetric (CV) curves of the bifunctional oxygen electrode were determined to further analyze the electrochemical performance of the oxygen electrode, as shown in Fig. 5. The scanning range of potential was - 1.0 V ~ 0.4V in 0.1 M KOH of electrolyte under N_2 or O_2 saturated conditions, respectively. CV is scanned to be stable under saturated N_2 condition to obtain the background current curve. The initial reaction potential and limiting current density were obtained by comparison with the data under saturated O_2. From Fig. 5, the CV curves of 0.1M KOH electrolyte saturated with N_2 and O_2 show that La_2CuO_4@Au has excellent catalytic activity for oxygen reduction reaction (ORR) [18]. The reason for this phenomenon may be that La_2CuO_4 coated with Au greatly improves its ORR activity.



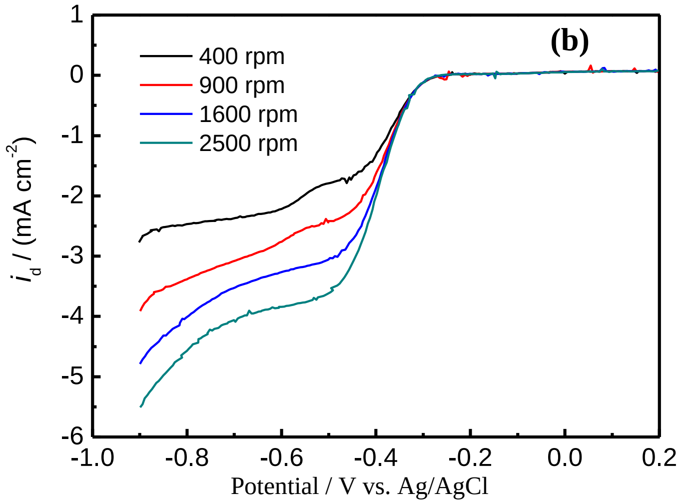


Figure 6. The disk (i_d) current densities ~ potential curves in 0.1 M KOH solution at four different rotation speeds (400, 900, 1600 and 2500 rpm) of La_2CuO_4@Au (a) and La_2CuO_4 (b) during oxygen reduction reaction (ORR).

Table 1. The initial potential and half-wave potential (2500 rpm) in this work and literatures.

Bifunctional oxygen electrodes	Initial potentials and half-wave potentials
La_2CuO_4@Au	-0.20 V, -0.35 V, in this work
La_2CuO_4	-0.27 V, -0.33V, in this work
$La_{0.8}Sr_{0.2}MnO_3$	-0.26 V, -0.34 V, [18]
$La_{0.8}Sr_{0.2}MnO_3$	-0.26 V, -0.32 V, [19]

The disk (i_d) linear sweep voltammetry curves of La_2CuO_4@Au (a) and La_2CuO_4 (b) were tested in 0.1 M KOH solution at four different rotation speeds (400,900,1600,2500 rpm) during oxygen reduction reaction (ORR). It can be observed from Fig. 6(a) that the reduction peak occurred in the voltage range of – 0.4 V ~ – 0.5 V at low rotation speed, which was caused by the reduction reaction of oxygen dissolved in a large number of mesopores in the sample. The diffusion speed of oxygen on the electrode surface increases, which results in a higher diffusion current density and is accompanied by a smaller peak shape with the increase of rotation speed [17–18]. The values of the initial potentials and half-wave potentials of La_2CuO_4@Au (a) are both greater than La_2CuO_4 (b) and literatures [18-19] under the same condition (Table 1). This may be due to the introduction of metallography to increase the catalytic activity of the electrode.

4. CONCLUSIONS

In this study, a novel bifunctional oxygen electrode, La_2CuO_4@Au, was synthesized using the sol-gel method. TG-DTA results showed that the calcination temperature of the catalyst should be higher than 700°C. The XRD results showed that a complete perovskite crystal can be formed after sintering at 800 °C or 900 °C for 2 h. Combined with the results of SEM, we chose the sample sintered at 800°C as the research object. The CV curves of 0.1M KOH electrolyte saturated with N_2 and O_2 showed that La_2CuO_4@Au had excellent catalytic activity for oxygen reduction reaction (ORR).

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