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Electrochemical Properties assessment of Pr_2CuO_4 submicrofiber cathode for intermediate-temperature Solid Oxide Fuel Cells

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Abstract:

Pr_2CuO_4 (PCO) nanofibers are prepared by electrospinning technique followed by a simple thermal treatment. The morphology and phase evolution are characterized by TG, XRD, FT-IR and SEM, respectively. The well crystallized Pr_2CuO_4 nanofibers are obtained after sintering the fiber precursors at 900°C for 5 hours. The highly porous PCO nanofiber cathode forms good contact with the CGO electrolyte after heat-treated at 900°C for 2 h. The cathode performance of PCO nanofibers is comparably studied with the powder counterpart at various temperatures and under different oxygen partial pressures. The porous microstructure of the nanofiber cathode effectively increases the three-phase boundary, which promotes the surface oxygen

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diffusion and/or adsorption process on the cathode. The nanofiber cathode exhibits a polarization resistance of $0.39 \Omega \text{ cm}^2$ at 700°C in air, which is 30% less than the powder cathode with the same composition. The charge transfer process is the rate limiting step of the oxygen reduction reaction (ORR) on the nanofiber cathode.

Keywords:

Pr_2CuO_4 nanofibers cathode, Intermediate temperature solid oxide fuel cell (IT-SOFC), Electrospinning, Electrode reaction

1. Introduction:

As a new power generation system, intermediate temperature solid fuel cells (IT-SOFCs) have been intensively studied in the last few decades, due to the high energy conversion efficiency, excellent fuel flexibility and environment friendly properties ^[1-2]. One of the major problems encountered in developing IT-SOFC is the slow dynamic oxygen reduction reaction (ORR) on cathode, which accounts for most of the polarization losses in IT-SOFC ^[1]. In order to overcome this problem, material composition modulation is considered as one of the good methods. It includes the exploration of novel mixed ionic and electronic conducting (MIEC) materials and the preparation of composite cathodes ^[3-10]. An alternative strategy concerns to tailor the electrode microstructure to enlarge the TPB length, and therefore promote the electrode reactions. In the last few years, nanofiber materials have been intensively studied and showed potential applications in fabricating electronic and optoelectronic devices, biosensors, and electrochemistry devices ^[11-17]. Very recent studies indicated that nanofiber oxides held great promise as cathode materials for intermediate-

temperature SOFCs, due to their high porosity, large surface area, high gas permeability and small interfibrous pore size ^[18]. For example, Mingjia Zhi and A. Enrico ^[19-20] studied the perovskite nanofiber cathodes, which exhibited interesting electrochemical properties. It is postulated that the 1-D nanofibers provide continuous pathways for both electrons and oxygen ions throughout the bulk cathode. The stacking of nanofiber forms a highly porous network structure, which is expected to facilitate the transport of gas molecules. Li et al ^[21] prepared the $\text{La}_{1.6}\text{Sr}_{0.4}\text{NiO}_4$ (LSN) nanofibers, which exhibited a polarization resistance (R_p) of $0.40 \Omega \text{ cm}^2$ at 700°C in air. The result demonstrates that the LSN nanofiber architecture significantly enhances the ORR activity. Sun et al ^[22] prepared $\text{Nd}_{1.93}\text{Sr}_{0.07}\text{CuO}_4$ nanofiber cathode. EIS analysis gave a polarization resistance of $0.26 \Omega \text{ cm}^2$ at 700°C in air, which is two times smaller than that of the powder cathode with the same composition. This dramatic improvement is attributed to the well constructed microstructure of the fiber cathode, which promotes the surface oxygen diffusion or adsorption processes on the cathode.

Pr_2CuO_4 has already been studied as potential cathode material in IT-SOFC ^[23-29]. Compared with the other Ln_2CuO_4 materials, the Pr_2CuO_4 compound was found to exhibit promising ionic-electronic mixed conductivity (108 S/cm , 800°C) ^[23], relatively high values of oxygen diffusion coefficient D and acceptable chemical stability towards ceria-based electrolyte ^[29]. To further optimize the cathode performances, the PCO nanofiber was synthesized by electrospinning method and tested as SOFC cathode in this work. The electrochemical properties of Pr_2CuO_4

nanofiber cathode was evaluated and compared with the powder counterpart in detail.

2. Experiment:

Pr_2CuO_4 nanofiber was prepared by electrospinning method. In a typical procedure, 10 wt.% Polyvinylpyrrolidone (PVP, molecular weight 0.9 million) solution was prepared by dissolving PVP powder in the mixture of ethanol and water, to which stoichiometric amounts of $\text{Pr}(\text{NO}_3)_3$ and $\text{Cu}(\text{NO}_3)_2$ were added with continues stirring. The total weight percentage of the metal salts is about 3% in the sol. The obtained homogeneous hybrid sol was kept static for 10 hours before being loaded into the electrospinning syringe. The distance between the spinneret (a metallic needle) and the collector (a grounded conductor) was fixed at 17 cm and the high-voltage supply was maintained at 10 kV. A syringe pump was used to disperse the solution at a spinning rate of $1 \text{ mL} \cdot \text{h}^{-1}$. The as-prepared hybrid fiber precursors were dried at 80°C in vacuum for 12 h, and sintered at 950°C for 5 h in air to obtain PCO nanofiber. The cathode ink was prepared by thoroughly mixing the PCO with terpineol for several hours. The symmetrical cell PCO/CGO/PCO was fabricated by manually brushing PCO ink on both sides of the polished CGO pellet to form a square electrode with an effective area of 0.62 cm^2 . The cell was then sintered in air at 900°C for 2 h. Fine platinum gauzes were slightly pressed on both sides of the cell as current collectors. The cathode was first heated at 400°C for 2 h to eliminate organic binders, followed by sintering at 900°C for 2 h in air, according to the modified “fast firing” method.

The thermal behaviors of fibers was examined by a thermogravimetric analyzer

(TGA) (Perkin-Elmer TG/DTA 6300) in the temperature range of 30-900°C in air. The structure and phase purity of the PCO nanofiber was determined by X-ray diffraction (XRD) on a Bruker D8-Advance diffractometer with Cu K α radiation. Infrared spectra were obtained with a Bruker Equinox 55 FT-IR spectrometer using a KBr pellet as background. The microstructure of the nanofiber was observed by scanning electron microscopy (SEM). The electrochemical impedance spectrum (EIS) was recorded over the frequency range from 1 MHz to 0.1 Hz using Autolab PGStat30 potentiostat, with the imposed AC voltage of 10 mV. The measurements were performed at equilibrium potential (OCV) as a function of temperature (500-700°C) and oxygen partial pressure (in an N₂/O₂ mixed atmosphere).

3. Results and discussions

TG-DTG results of the prepared PVP/Pr(NO₃)₃/Cu(NO₃)₂ composite fiber are shown in Fig. 1. In the TG curve, there are three discrete regions of weight loss occurred at about 95, 310 and 430°C, respectively. In the corresponding DTG curve, three peaks could be observed, indicating the change of thermal decomposition mechanism with temperatures. The weight loss below 95°C is probably due to the evaporation of moisture and trapped solvent such as water and ethanol. In the temperature range of 310 °C -430°C, there are continuous weight loss observed in the TG curve, due to the decomposition and burning out of PVP polymers, nitrate and other minor organic constituents introduced from the organic salt stocks. Up to the temperature of 900°C, there is no further weight loss observed, indicating the formation of pure inorganic oxide.

Fig. 1. TG-DTG curve of PVP/Pr (NO₃)₃/Cu (NO₃)₂ composite nanofibers

In order to confirm the TG results, the sample after heat-treated at different temperatures was characterized by XRD. Fig. 2 shows the XRD patterns of the as-prepared hybrid fibers and the samples after being sintered at 450°C and 900°C for 5 h, respectively. It is observed that the hybrid fibers exhibit a broad diffraction peak around 20°, which is the typical pattern of the polymer (Fig. 2a). After heat-treated at 450°C for 5 h, the broad diffraction peak totally disappears, indicating that PVP was decomposed and removed from the hybrid fibers. Meanwhile the diffraction peaks related to Pr₆O₁₁ and CuO phases appear in the XRD patterns (Fig. 2b). When the sintering temperature reaches 900°C, all the observed diffraction peaks are consistent with the data of JCPDS standard card (49-1891), indicating the formation of PCO phase (Fig. 2c).

Fig. 2. XRD patterns of various nanofibers samples: (a) PVP/ $\text{Pr}(\text{NO}_3)_3$ / $\text{Cu}(\text{NO}_3)_2$ composite nanofibers; (b) calcination at 450°C ; (c) calcination at 900°C

The Rietveld refinement result reveals that PCO crystallizes in tetragonal structure with the space group $I4/mmm$ (Fig. 3). The cell parameters are $a=b=3.960(6) \text{ \AA}$, $c=12.225(0) \text{ \AA}$, which are in good agreement with the literature [29]. This result proves that the pure phase PCO nanofiber material is successfully prepared by the electrospinning method followed by a simple thermal treatment.

Fig. 3. Experimental (red circles) and calculated (black continuous line) XRD patterns (and their difference, blue line at the bottom) for Pr_2CuO_4 . Green vertical bars indicate the positions of the Bragg peaks of the phases contained in the sample

The evolution process of PCO fiber with temperature is further studied by the FT-IR spectra, and the results are presented in Fig. 4. Clearly the spectra of pure PVP fiber and PVP/ $\text{Pr}(\text{NO}_3)_3/\text{Cu}(\text{NO}_3)_2$ hybrid fibers are almost identical (Fig.4a and b). The PVP shows the characteristic vibration bands of the stretching vibration of hydroxyl group ($\nu\text{O-H}$), C-H bond ($\nu\text{C-H}$), carbonyl group ($\nu\text{C=O}$), C-H bond ($\delta\text{C-H}$), and C-N bond or C-O bond ($\nu\text{C-N}$ or $\nu\text{C-O}$) at around 3462, 2955, 1664, 1428 and 1283 cm^{-1} , respectively. These bands are weakened or disappeared, and new band appears around 510 cm^{-1} after sintered at 900°C for 5 h (Fig.4c). This new band is due to the contribution of the stretching vibration of Cu-O_{II} linkages in the basal planes ^[30]. This result indicates that crystallized Pr_2CuO_4 is formed at 900 °C, which is in good agreement with the XRD conclusions.

Fig. 4. The FT-IR spectra of PVP (a), Pr(NO₃)₃/Cu(NO₃)₂/PVP composite fibers (b), composite fibers after calcined at 900°C for 5 h(c).

The morphology evolution of the electrospun material was followed with SEM. Fig. 5a shows the SEM image of the PVP/Pr(NO₃)₃/Cu(NO₃)₂ hybrid fibers. The nanofiber morphology is evidently observed. The diameter of the nanofiber is about 1 μm. The surface of the fiber is smooth because of the amorphous nature of the polymer. After sintering at 900°C for 5 h (Fig. 5b), the surface of the nanofiber becomes coarse and the diameter shrinks to 400-500 nm, due to the burning out of the PVP organic components and the crystallization of PCO material. Fig. 5c shows the surface image of the PCO nanofiber cathode on CGO electrolyte. It is observed that the nanofiber morphology remains un-changed after sintering at 900°C for 2 h. These nanofibers are cross-linked together to form a three-dimensional porous framework (Fig. 5c inlet). The cross- section image shows that the nanofiber cathode with

thickness $\sim 24 \mu\text{m}$ forms good contact with the CGO electrolyte (Fig. 5d). The porosity of the nanofiber cathode (P) can be calculated by the following relation [19], **Erreur ! Source du renvoi introuvable.**, where m and A are the cathode mass and area (given the PCO loading 4 mg cm^{-2}), L is the cathode thickness, and ρ is the theoretical density of PCO ($\sim 7.1 \text{ g cm}^{-3}$). The value of P is 71.3%, which reveals that a highly porous cathode was successfully prepared without adding any pore-formers. It is speculated that this highly porous three dimensional nanofiber framework will supply a transport “highway” for both oxygen ions and electrons throughout the whole cathode. As a result, the TPB sites are extended efficiently to the whole electrode and the oxygen reduction reaction will be enhanced.

Fig. 5. SEM images of: (a) PVP/PCO composite fibers; (b) fibers calcined at 900°C; (c) the surface of the PCO nanofiber cathode supported on CGO electrolyte surface;

(d) cross-section image after sintering at 900°C for 2 h.

In order to understand the effect of material morphology on the performance of cathode, the Nyquist plot of both PCO nanofiber electrode and the powder one are comparatively presented in Fig. 6. There is only one impressed arc that could be found in the spectrum of fiber cathode at 650°C. For the powder cathode however, two consecutive depressed arcs are found. Normally the intercept value of the impedance arc with the real axis at high frequency corresponds to the resistance of the electrolyte and lead wires, and the value between the high-frequency intercept point of the x-axis and the low-frequency one is attributed to the total polarization resistance (R_p) of the test cell. The R_p is widely used to describe the resistant terms that related to the electrode processes. The ASR can be calculated by the expression of $ASR = 1/2 R_p \cdot S$, whereas S is the area of the cathode. The ASR value of PCO nanofiber cathode is $0.39 \Omega \text{ cm}^2$ at 700°C in air, about 30% less than the PCO powder cathode [25]. The Arrhenius plots of the polarization resistances for both the powder and the fiber cathode are presented in Fig. 6 inset. The activation energy (E_a) calculated from the Arrhenius plot is 1.27 eV for the nanofiber cathode, which is comparable to the E_a value of PCO powder cathode ($E_a = 1.48 \text{ eV}$). Thus, it is supposed that the enhancement of the cathode performance is probably due to the fine microstructure of the PCO nanofiber cathode, but not to the change of the oxygen reduction mechanism.

Fig. 6. The Nyquist plot of PCO powder and nanofiber cathodes that measured at 650°C in air; (inlet) Arrhenius plots of the polarization resistances of PCO powders and nanofibers electrodes in air. The electrolyte contribution has been subtracted from the impedance.

Fig. 7 shows the impedance spectra of Pr_2CuO_4 nanofiber cathode measured at 700°C under different oxygen partial pressures ($p\text{O}_2$). It is observed that the polarization resistance (R_p) decreases gradually with the increase of oxygen partial pressure, indicating that the oxygen concentration plays an important influence on the ORR process. In order to further determine the mechanism of the oxygen reduction reaction on the fiber electrode, the oxygen partial pressure dependence of R_p at $600\text{--}700^\circ\text{C}$ is shown in Fig. 7. Generally, the relationship between R_p and the oxygen partial pressure can be described according to the following equation ^[31],

$$R_p = R_p^o (p\text{O}_2)^{-n}.$$

From the equation, the value of n decides the type of species involved in the electrode reactions ^[32, 33] as follows:

Specifically, for metal oxide electrodes on solid electrolytes, $n = 1$ can represent the gaseous diffusions and adsorption of oxygen molecules; $n = 1/2$ is the oxygen adsorption-desorption process, which includes oxygen diffusion at the interface of gas/cathode and surface diffusion of related intermediate oxygen species; $n = 1/4$ can be attributed to the charge transfer process on the electrode, occurring at the interfaces of current collector/electrode; $n = 3/8$ corresponds to the charge-transfer reaction at the triple-phase boundary (TPB), and $n = 0$ relates to the oxygen ion transfer from the TPB to the electrolyte. According to the results of Fig. 8, all the n values are in the vicinity of $3/8$ at different temperatures, which corresponds to a charge-transfer reaction at the triple-phase boundary. Therefore in this study, the major rate-limiting step for the fiber cathode is the charge transfer reaction in the whole range of measurement oxygen partial pressure. The rate-determining step of the PCO powder cathode has been found to be the charge transfer process ^[25]. In this sense, we proved that the modification of the microstructure of the PCO cathode can have an impact on the cathode performance, but have no effect on the oxygen reduction mechanism.

Fig. 7. Impedance diagrams of LSN nanofiber cathode at 700°C under various oxygen partial pressures.

Fig. 8. Oxygen partial pressure dependence of R_p of PCO cathode at 600-700°C.

4. Conclusions

The Pr_2CuO_4 nanofibers were successfully synthesized by electrospinning method and used as prospective cathode for IT-SOFC. The rate limiting step for the ORR on PCO nanofiber electrode was the charge transfer process, the same as the powder electrode. The lowest area specific resistance obtained for PCO nanofiber cathode at 700°C was $0.39 \Omega \text{ cm}^2$ in air. The three-dimensional porous morphology of the nanofiber cathode promotes the ORR process, but has no effect on the ORR mechanism.

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