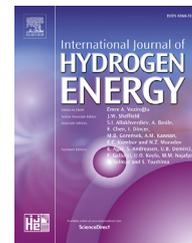




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A novel post-treatment to calcium cobaltite cathode for solid oxide fuel cells

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ABSTRACT

The calcium cobaltite (CCO) cathodes are post-treated by dipping in the hydrogen peroxide (H₂O₂). The electrochemical properties are investigated by the electrochemical impedance spectra (EIS) and current-voltage test in the symmetrical cell and single cell, respectively. The phase structure and morphology of the cathodes are characterized by X-ray powder diffraction (XRD) and scanning electron microscopy (SEM). The experiment results show that the mesopores are created on the surface of the cathode particles and the pore channels of the cathode are cleaned up after leaching with 10 wt % H₂O₂, resulting in a remarkable decreasing of the area specific resistance (e.g. only 42.5% of that for the untreated cathode at 800 °C). The single cell with treated cathode is about 2 times the peak power density of the cell with untreated cathode, signifying the post-treating method may be promising.

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Introduction

Solid oxide fuel cells (SOFCs) are electrochemical devices that are able to directly convert chemical energy into electricity, typically consisting of an electrolyte and two electrodes [1,2]. The electrolyte membrane must be dense to separate the air and fuel compartments and a pure ion conductor, whereas the electrodes must be porous enough to allow gas access to the triple phase boundaries (TPBs) where the electrochemical reactions take place [3–5]. The performance of SOFCs largely depends on the gas transport and electrochemical reaction in the electrodes, therefore, the optimization of the microstructure of the porous electrodes may be necessary [6,7]. On one hand, many fabrication processes have been researched

extensively to maintain sufficient porosity and decrease the mass transport resistance. Adding a pore former is an effective method to form porous structure for gas diffusion to the TPBs [8,9]. The effect of the amount and the particle size ratio of pore former on the porosity of the electrodes were investigated by Wang et al. [10]. The electrodes prepared using ceramic nanofibers fabricated by the electrospinning method have high porosity and percolation, which can promote gas diffusion significantly [11–13]. A phase-inversion technique has been introduced to fabricate hollow fiber electrode support with a thick finger-like layer serving as gas transport channels for efficient mass transport [14–16]. A freeze-casting process was also used to form hierarchically oriented channels/pores in the electrodes to decrease the gas diffusion tortuosity factor [17]. On the other hand, the high-

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temperature sintering for the conventional electrodes usually leads to the sintering and grain growth of the primary particles, resulting in a decrease in electrode specific surface area [18,19]. The electrodes fabricated by the infiltration technique at low temperature are able to remain nano structure with larger surface-to-volume ratio, resulting in an increase of the electrode catalytic activity [20–22]. However, all these techniques mentioned above only can modify and tailor the microstructure of the electrodes before or during sintering process.

The acid/alkali solution etching was performed to investigate the effect of surface segregation of elemental composition on the cathode performance [23–25]. In this work, the sintered calcium cobaltite (CCO) cathodes are post-treated by dipping in the hydrogen peroxide (H_2O_2), and the effect of the H_2O_2 concentration on the microstructure and electrochemical performances of the cathodes are evaluated. The mesopores are created on the surface of the cathode particles and the pore channels of the cathode are cleaned up after treating with H_2O_2 , resulting in a remarkable increase of cathode performance.

Experimental

Polycrystalline $\text{Ca}_9\text{Co}_{12}\text{O}_{28}$ (CCO) was synthesized from a stoichiometric mixture of CaCO_3 and Co_3O_4 by solid state reaction. The mixture was ground and calcined at $900\text{ }^\circ\text{C}$ for 24 h in air. The dense SDC electrolyte pellets of about 1 mm thickness were prepared by pelletizing electrolyte powder and sintered at $1550\text{ }^\circ\text{C}$ for 2 h in air. The symmetrical cells of CCO|SDC|CCO for electrochemical impedance spectra measurement were prepared by painting CCO cathode ink onto both sides of the SDC substrates symmetrically, followed by calcination at $900\text{ }^\circ\text{C}$ for 2 h. The CCO cathode was treated by dipping in H_2O_2 with different concentrations (10, 20 and 30 wt %) for 24 h and then dried at $100\text{ }^\circ\text{C}$ for 2 h to remove moisture. Electrolyte-supported single cells, NiO-SDC|SDC|CCO, were fabricated for single cell performance measurement. The anode NiO-SDC (weight ratio of 6: 4) slurry was hand painted on one side of electrolyte pellet and calcined at $1300\text{ }^\circ\text{C}$ for 2 h. Then, the cathode ink was hand painted on another side of the electrolyte and fired at $900\text{ }^\circ\text{C}$ for 2 h. The treatment of single cell cathode was dipped in the H_2O_2 with optimized concentration. The Ag paste was used as the current collector on the electrode surfaces.

The electrochemical impedance spectra (EIS) of the symmetrical cells were measured using a CHI 604e electrochemical workstation from 650 to $800\text{ }^\circ\text{C}$ under open circuit conditions in the frequency range (100 KHz to 0.1 Hz) with a signal amplitude of 10 mV. The area specific resistances (ASRs) of the cathodes were calculated by analyzed the impedance data with the ZSimpWin 3.10 software. During the single cells test, the 3 wt % H_2O humidified hydrogen was fed into the anode side at a flow rate of 50 ml min^{-1} and ambient air acted as the oxidant. The current-voltage curves of the cells were monitored in the temperature range $650\text{--}800\text{ }^\circ\text{C}$ using a Keithley 2420 digital source meter. The EIS of single cells were acquired in the frequency range from 100 KHz to 0.01 Hz.

Phase identification of the cathode powders was performed with diffractometer (Rigaku, Smartlab) with Cu K_α radiation ($\lambda = 0.15418\text{ nm}$). Rietveld refinement was performed on the XRD data using the EXPGUI software [26–30]. The morphology of the cathodes and the particle surface was observed by scanning electron microscopy (JEOL, JSM-6360 LV) and field-emission scanning electron microscope (Ultra55 FE-SEM, ZEISS), respectively.

Results and discussion

The typical impedance spectra of the CCO|SDC|CCO cells treated with different concentration H_2O_2 are shown in Fig. 1. The low-frequency intercept of the plotted impedance normalized to zero by subtracting the serial ohmic resistance on the real axis corresponds to the ASR of the cathode. As can be seen, the ASR values for the CCO cathodes treated with H_2O_2 (especially with 10 wt % H_2O_2) are much lower than those for the untreated cathode. For example, ASR value for the CCO cathode treated with 10 wt % H_2O_2 is $0.17\text{ } \Omega\text{ cm}^2$ at $800\text{ }^\circ\text{C}$, and only 42.5% of that ($0.40\text{ } \Omega\text{ cm}^2$) for the untreated cathode. However, when H_2O_2 concentration increases to 20 and 30 wt %, the ASR values also increase to 0.21 and $0.27\text{ } \Omega\text{ cm}^2$, respectively. The electrochemical measurements are also performed at various p_{O_2} values ranging from 0.05 to 1 atm for the untreated and 10 wt % H_2O_2 treated CCO cathode at $750\text{ }^\circ\text{C}$ (date shown in Fig. S1). The low frequency resistance (R_L) is significantly influenced by the working oxygen concentration (p_{O_2}). This indicates that the R_L is maybe related to oxygen gas diffusions process [31,32]. The ASR represents the overall cathodic resistance related to the diffusion (low frequency response) and charge transfer (high frequency response) processes, respectively [33]. The results of EIS fitting are listed in Table 1. As can be seen, the low frequency resistance (R_L) is larger than the high frequency resistance (R_H) for all the samples. This indicates that the R_L related diffusion process probably limited the oxygen reduction reaction rate at cathode [34,35]. The low frequency diffusion resistance (R_L) is significantly decreased from 0.68 to 0.24, 0.27 and $0.34\text{ } \Omega\text{ cm}^2$ treated by 10, 20, 30 wt % H_2O_2 , respectively, at $750\text{ }^\circ\text{C}$. It is thus clear that treatment with H_2O_2 can effectively enhance the diffusion process. The reduced high frequency resistance (e.g. R_H from 0.24 to $0.13\text{ } \Omega\text{ cm}^2$ at $750\text{ }^\circ\text{C}$) indicates that the charge transfer process also can be improved by treating by 10 wt % H_2O_2 . This positive effect becomes slight with increasing the concentration of H_2O_2 to 30 wt % (e.g. R_H from 0.24 to $0.21\text{ } \Omega\text{ cm}^2$ at $750\text{ }^\circ\text{C}$).

XRD analysis (data shown in Fig. 2) is performed on the CCO powders before and after H_2O_2 treating to determine whether there are any bulk phase changes during the treatment. The data show that the as-prepared CCO powder is a single phase and in good agreement with $\text{Ca}_9\text{Co}_{12}\text{O}_{28}$ (JCPDS card no. 21–0139). For H_2O_2 -treated CCO powder, the impurity peak belongs to CaCO_3 (JCPDS card no. 17–0763) was observed in addition to the main peaks belong to $\text{Ca}_9\text{Co}_{12}\text{O}_{28}$ phase. In the XRD pattern of H_2O_2 -treated CCO powder further calcined at $900\text{ }^\circ\text{C}$ for 2 h, Co_3O_4 phase (JCPDS card no. 42–1467) was discovered except for the $\text{Ca}_9\text{Co}_{12}\text{O}_{28}$ phase. The detailed information of phase structure and lattice parameters analyzed

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