Proceedings of FUELCELL2005
Third International Conference on Fuel Cell Science, Engineering and Technology
May 23-25, 2005, Ypsilanti, Michigan

FUELCELL2005-74027

DIRECT PREPARATION OF $CE_{0.8}SM_{0.2}O_{1.9}$ POWDERS OXIDIZED WITH H_2O_2 FOR LOW TEMPERATURE SOFCS APPLICATION

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ABSTRACT

A novel method was developed to prepare fine doped ceria (DCO) powders directly. Ceria doped with 20 mol. % of samarium ($Ce_{0.8}Sm_{0.2}O_{1.9}$, SDC) was prepared by in-situ oxidization of hydroxide precipitates with H_2O_2 in the solutions. The resultant powder desiccated at 85℃ overnight was characterized by X-ray diffraction (XRD), thermogravimetry /differential thermal analysis (TG/DTA), and transmission electron microscopy (TEM). The XRD pattern showed that the as-dried SDC powder is single phase with a cubic fluorite structure like that of pure CeO_2. An anode-supported SOFC was also fabricated based on SDC and 20wt. % (62mol. %Li_2CO_3-38 mol. %K_2CO_3) composite electrolyte, $LiNiO_2$ as cathode and NiO as anode, by cold pressing. Using hydrogen as the fuel and air as the oxidant, the I-V and I-P characteristics exhibit excellent performances and the maximum power densities are about 696, 469, 377 and 240 $mWcm^{-2}$ at 650, 600, 550 and 500℃, respectively.

Keywords: samarium doped ceria (SDC); oxidization; H_2O_2; composite electrolyte; low temperature solid oxide fuel cells (LTSOFCs)

INTRODUCTION

Recently, doped ceria (DCO) have received increasing attention as electrolyte material for low temperature solid oxide fuel cells (LTSOFCs) operating at 400-650℃. Low temperature operation of SOFCs will widen the selection of electrodes, interconnect, and manifold materials, improve system reliability, increase the life of SOFCs, and reduce the cost of material processing and cell fabrication. A lower operating temperature also implies faster startup, which make it possible to use SOFCs for automotive applications [1].

However, conventional ion doped ceria electrolyte may have a certain electronic conduction in the reducing environment on the anode side of the fuel cell because of the instability of the ceria. In order to improve the electrical properties and chemical stability, many studies were carried out on ceria-salt composites [2-4]. These materials were prepared usually by mixing different cationic doped ceria, e.g. gadolinium doped ceria (GDC), samarium doped ceria (SDC) and yttrium doped ceria (YDC) with various salts, e.g. carbonates, sulfates, chlorides, and fluorides. The fuel cell based on these composite materials demonstrated excellent performances due to the hybrid conduction of oxygen ion (from DCO phase) and proton (from the interface between the two phases) [5]. These novel electrolyte materials have a promising application in advanced LTSOFCs. In our previous studies, we found that the properties of DCO powders prepared by different methods may have apparent impact on the fuel cell performance [6]. Therefore, it is necessary to develop appropriate method to prepare DCO powders for ceria-salt composite electrolyte material.

DCO powders are typically produced via solid-state reaction started from individual component oxides and /or carbonates, which requires repeated intermittent mechanical mixing and extensive heat treatment at high temperature (such as 1300℃ for 10h). This will introduce impurities such as silicon into the DCO particles, thus severely decrease its ionic conductivities since silicon form an insulation glassy phase in the grain boundaries [7]. In recent years, some wet-chemical

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methods, such as co-precipitation [8], sol–gel [9], and hydrothermal synthesis [10], have been adopted to prepare fine DCO powders. These wet chemistry-derived powders generally show better reactivity than those obtained via solid-state methods, but they still require relatively high temperature to form pure fluorite structure. In this work, we developed a simple method to prepare fine SDC ($Ce_{0.8}Sm_{0.2}O_{1.9}$) powders directly by in-situ oxidization of hydroxide precipitates with H_2O_2 in the solutions. The dried SDC powders were characterized by XRD, TG/DTA, and TEM, respectively. Based on SDC and 20wt. % (62mol. %Li_2CO_3-38 mol. %K_2CO_3) composite electrolyte, an anode- supported SOFC was fabricated, and the performance of the fuel cell were investigated.

EXPERIMENTAL

SDC powder synthesis

SDC powders ($Ce_{0.8}Sm_{0.2}O_{1.9}$) were prepared by a wet-chemical route as follow. $Ce(NO_3)_3 \cdot 6H_2O$ and Sm_2O_3, as the raw materials, were dissolved in deionized water and dilute nitrate acid to form 1 M $Ce(NO_3)_3$ and $Sm(NO_3)_3$ solution, respectively. Then the $Sm(NO_3)_3$ solution was mixed with the $Ce(NO_3)_3$ solution according to the stoichiometric proportion. An appropriate amount of 3 M NaOH solution was simultaneously dropped into the stirred $Ce(NO_3)_3$-$Sm(NO_3)_3$ mixed solutions at 40℃, where the solution pH value were kept at 8.5 through the reaction. Then, grayish hydroxide precipitates were formed. The desired amount of the 30% H_2O_2 solution was added and the precipitates swiftly changed to brown-red. The final pH value was adjusted at about 6. After that, the precipitate was washed with deionized water by vacuum-filtrating , then the precipitate together with filter paper were desiccated at 85 ℃ overnight. Finally, pale-yellow resultant was obtained. The dried powders and those scraped from filter paper were collected and ground thoroughly for use.

SDC powder characterization

The crystalline phase of the dried sample was characterized by X-ray diffraction (XRD) using graphite monochromatized, Cu K_α radiation. The thermogravimetry /differential thermal analysis were carried out in air using a heating rate 10℃/min. The morphology of the sample was observed by TEM (JEOL, JEM-2000EX). For TEM analysis, sample was prepared in absolute ethanol and evaporated on the copper grid at room temperature.

Fuel cell components and construction

The SDC-carbonate composite electrolyte samples were prepared by mixing SDC with 20wt. % carbonate (62mol%Li_2CO_3:38mol%K_2CO_3) and grinding well. The mixtures were heated at 680℃ for 50min. The resultant materials were grounded again thoroughly for use. The composite anode was composed of NiO (50vol. %) mixed with the electrolyte (50vol. %) and the composite cathode was based on $LiNiO_2$ (50vol. %) with the electrolyte (50vol. %). The composite anode, electrolyte and cathode were uniaxially pressed together at one step to form a sandwich structure. Pellets were pressed under 250MPa and sintered at 600℃ for 30min. A silver paste was coated afterwards on anode surface to act as current collector. The cell size normally is 13mm in diameter and 1-2mm in thickness.

In the measuring procedure, stainless steel was employed for the fuel cell device and silver glue was applied as the sealant. The fuel cell was tested between 500 and 650℃. Hydrogen and air were used as the fuel and the oxidant, respectively. The gas flow rates were controlled between 60-90ml/min under 1 atm pressures.

RESULTS AND DISCUSSION

SDC powder synthesis and characterization

During the synthesis process, NaOH acts as co-precipitator to form homogenous hydroxide precipitate. The pH value of the solution should be adjusted according to the composition. Subsequently, hydrogen peroxide was added to oxidize hydroxide and change it directly to oxide. The chemical reaction may be expressed by Eqs. (1) and Eqs. (2).

$$(1-x)\mathrm{Ce(NO_3)_3} + x\mathrm{Sm(NO_3)_3} + 3\mathrm{NaOH} \rightarrow \mathrm{Ce_{1-x}Sm_x(OH)_3} + 3\mathrm{NaNO_3} \quad (1)$$

$$\mathrm{Ce_{1-x}Sm_x(OH)_3} + (1-x)/2\mathrm{H_2O_2} \rightarrow \mathrm{Ce_{1-x}Sm_xO_{2-x/2}} + (2-x/2)\mathrm{H_2O} \quad (2)$$

Figure 1 shows the XRD patterns of SDC powder sample prepared by the direct oxidization method after dried at 85℃. For comparison, the XRD pattern of SDC power sample synthesized by oxalate co-precipitation method as previously reported [11] is given. Two samples exhibit XRD peaks that attributed to the typical face-centered-cubic fluorite structure. However, the XRD peaks for the SDC sample synthesized by co-precipitation method are very broad, indicating that this sample has low crystallinity. For the sample prepared by direct oxidization method, the XRD pattern is identical to that of pure ceria and all the characteristic diffraction peaks are sharp, indicating that Sm has absolutely entered in the fluorite structure during the preparation process.

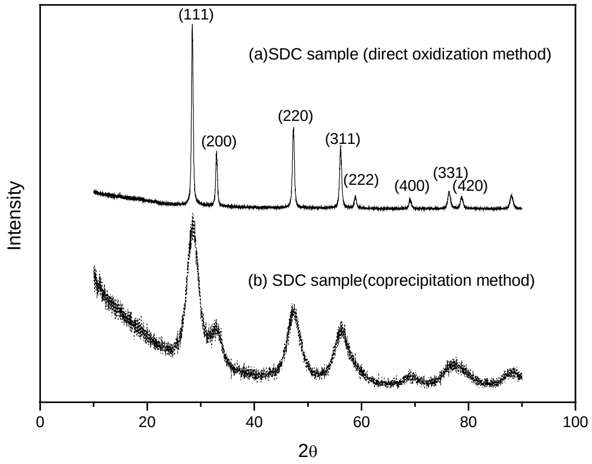

Figure 1. XRD patterns of $Ce_{0.8}Sm_{0.2}O_{1.9}$ powders obtained by direct oxidization method (a) and by co-precipitation method (b)

The TG and DTA curves for the $Ce_{0.8}Sm_{0.2}O_{1.9}$ powder prepared by H_2O_2 oxidization and dried at 85℃ are presented in Figure 2 (a) and (b). The total weight loss up to 801.5℃ for the sample is 13.66%. In TG and DTG profile, two distinct peaks appear at about 94.4℃ and 307.8℃, respectively. Corresponding to TG profile, there is an obvious endothermic peak in DTA profile, accompanied by a weak peak. The first endothermic peak can be attributed to the physical absorbed water molecules at the surface of the powder. According to the XRD data, the second endothermic peak might be attributed to the loss of the structure water molecules.

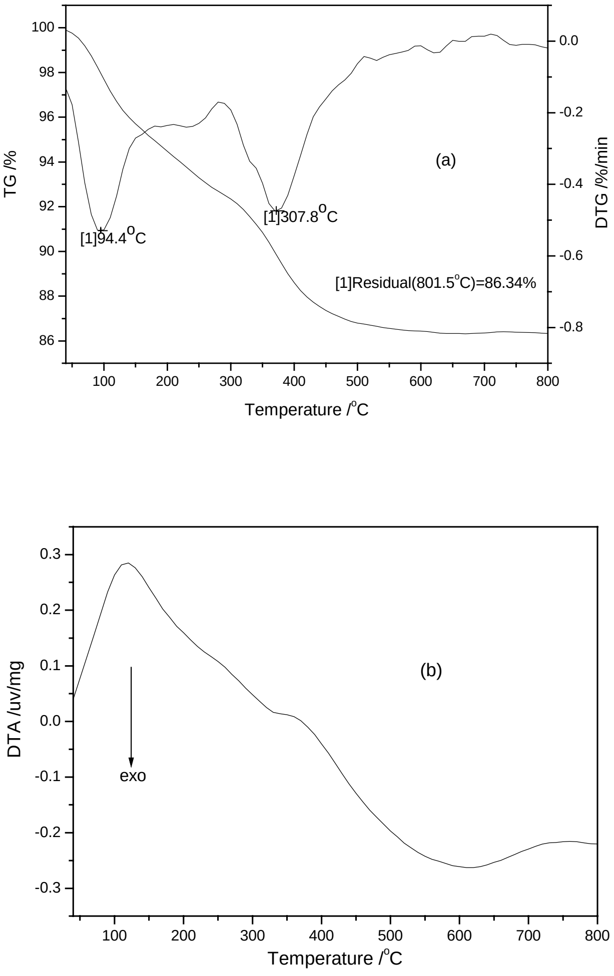

Figure 2. (a) TG and (b) DTA curves for $Ce_{0.8}Sm_{0.2}O_{1.9}$ powders obtained by direct oxidization method and dried at 85 ℃

Figure 3 shows TEM images of $Ce_{0.8}Sm_{0.2}O_{1.9}$ powder prepared by direct oxidization after drying at 85℃. It is quite clear that the partiles agglomerate to form sheet shape. The sample contains ultrafine particles of uniform shape and approximately 5nm in size. The agglomeration might be duo to the presence of the structural water molecules.

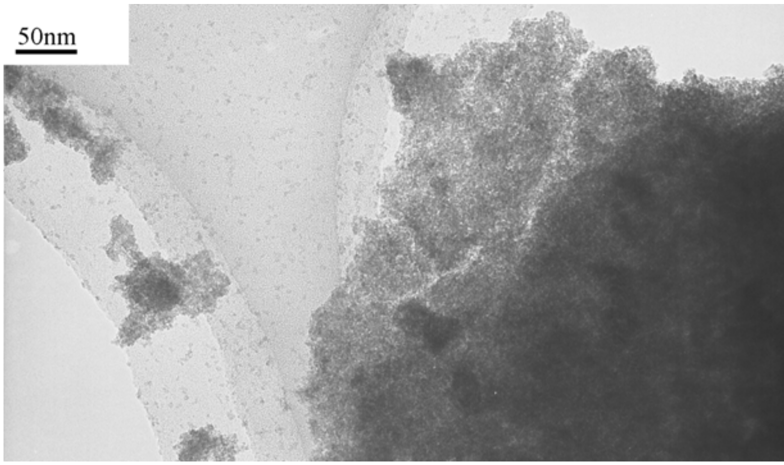

Figure 3. TEM photograph of $Ce_{0.8}Sm_{0.2}O_{1.9}$ particles prepared by direct oxidization and dried at 85 ℃

The fuel cell performance using the direct prepared $Ce_{0.8}Sm_{0.2}O_{1.9}$ and 20wt. %(62mol%Li_2CO_3: 38mol%K_2CO_3) composite electrolyte were further investigated. Figure 4 shows typical I-V and I-P characteristics for the fuel cell at various temperatures. An open circuit voltage (OCV) of about 0.97V was achieved at 500℃. The OCV is lower than the theoretical OCV resulting from the relative high porosity, implying the electrolyte layer was not dense enough. Maximum power density were about 696, 469, 377 and 240 mWcm^{-2}, respectively, when the cell was operated at 650, 600, 550 and 500℃. Figure 4 also shows that the fuel cell exhibited serious diffusion polarization at higher current density. This might be caused by the microstructure of the electrodes. Further improvement in preparation technique of the fuel cell is required.

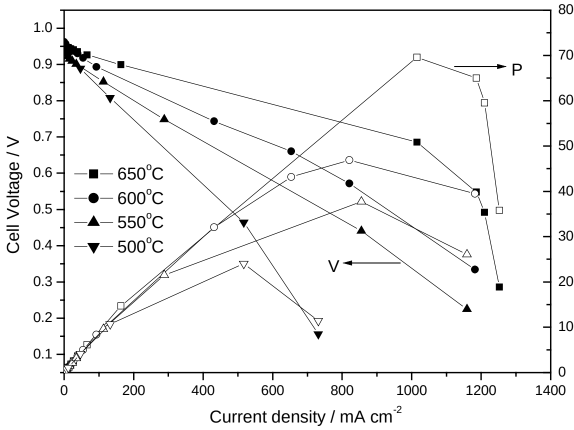

Figure 4. Fuel cell performance for using the SDC-20wt. % (62mol. %Li_2CO_3-38 mol. %K_2CO_3) composite electrolyte at various temperatures

CONCLUSIONS

Nanosized powders of $Ce_{0.8}Sm_{0.2}O_{1.9}$ were prepared by in-situ oxidization of hydroxide precipitates with H_2O_2 in the solution at 40℃. The fine oxide particles directly prepared were inclined to form sheet-shaped agglomeration. The fuel cell using the SDC-carbonates composite electrolyte displayed excellent performance. This work shows a possibility to fabricate cost-effective LTSOFC with inexpensive electrolyte materials because of the novel method preparing oxide powders.

ACKNOWLEDGMENTS

This work was supported by China National Hydrogen project (contract number: G2000026410, 2001AA515080).

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