

Short communication

A study on sintering aids for $\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$ electrolyte

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Abstract

In this study, an addition of Co oxide or Cu oxide to $\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$ (SDC) was studied to improve the sinterability of SDC. It has been found that both Co and Cu oxide are very effective as sintering aids, and the SDC sintering temperature can be reduced from 1400 °C without aids to below 1000 °C with only 1 at.% of either Cu oxide or Co oxide. As compared to the pure SDC, a slight decrease of ionic conductivity was observed in SDC with Cu sintering aid. There is no obvious effect on electrochemical property of SDC with Co sintering aid under 2.5 at.%. © 2006 Elsevier B.V. All rights reserved.

Keywords: SDC electrolyte; SOFC; Sintering aids; Cobalt oxide; Copper oxide

1. Introduction

Ceria-based ceramic materials doped with Sm and/or Gd have been acknowledged to be the most promising electrolytes for solid oxide fuel cells operating below 600 °C due to their high ionic conductivity and good compatibility with electrodes, especially with high performing Co-content cathodes. Maximum power density of anode supported thin ceria-based electrolyte cells has been reported over 880 mW cm⁻² at 600 °C with H₂ fuel [1,2]. However, the ceria electrolytes are difficult to densify below 1400 °C [3–6]. If a dense ceria-based electrolyte can be prepared at lower temperatures it can be co-sintered with the electrode components, which simplifies the fabrication process and reduces the cost, helping with porous electrode microstructure control and avoiding phase diffusion and chemical interaction problems.

In order to sinter doped ceria materials at a lower temperature, several methods have proven effective, which could be classified into two categories:

- 1) Using ultra-fine powders at submicron and nanometer size by special synthesis, such as hydrothermal synthesis [7,8], oxalate co-precipitation [9,10], chemical combustion vapour

synthesis [11,12] or intensive mechanical milling [13]; the decrease of a starting particle size enables the densification at a lower heating temperature because of the increased driving force (specific surface area) of sintering. However, a small pore size between ultra-fine particles produces a high capillary force in the powder compact which is the origin of low packing density and cracks formed during drying and firing [14,15].

- 2) Adding a sintering promoter or aid in a limited amount [3,13]. It has been reported that Mn₂O₃ and Co₃O₄ promotes grain growth of doped ceria even at initial stages of sintering, while Ga₂O₃ promoted rearrangement of particles. The sintering temperature could be decreased from 1600 to 1400 °C by adding 1 at.% of such aids [3].

In this paper, we studied the influence of Co and Cu oxides as sintering aids on sintering behavior, conductivity, phase and microstructure of SDC.

2. Experimental

2.1. Sample preparation

Table 1 lists the starting chemicals and ceramic powder materials used in this study. Firstly, both Co and Cu nitrates were separately dissolved in ethanol at 1.0, 2.5 and 5.0 at.%, through

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Table 1
Properties and supplier of starting materials

Material	Composition	Properties	Supplier
Co additive	$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	Formula weight (FW) 291.04	Alpha Aesar, Lot#23282
Cu additive	$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$	FW 241.60	Alpha Aesar, Lot#K10N42
Electrolyte	$\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$ (SDC)	FW 172.6; D50: 0.40 μm ; surface area: 7.0 $\text{m}^2 \text{g}^{-1}$	Praxair Lot#03-P4687DM
Cathode	$\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ (SSCo)	D50: 0.80 μm ; surface area: 5.16 $\text{m}^2 \text{g}^{-1}$	Praxair
Anode	NiO type F + SDC	D50: 1.0 μm ; surface area: 4.0 $\text{m}^2 \text{g}^{-1}$	Novamet (SDC from Praxair)

a ball milling process, using nalgene bottles with \varnothing 5 mm YSZ balls, before adding SDC powder. After adding SDC powder, ball milling was carried out for 40 h, with subsequent drying at 50 °C for 8 h and separation of powders for thermal decomposition at 500 °C for 5 h in air. The obtained seven types of powders, including one blank SDC powder (without Co or Cu additive), were pressed at 40–50 MPa into pillars of \varnothing 5 mm about 10 mm length and pellets of \varnothing 20 mm about 2.0 mm thick. The pillar samples were used for shrinkage-sintering studies using a Setsys 16/18 TMA (Setaram). The sintered pellet samples after surface polishing were used for XRD analysis and electrochemical characterization. Both NiO–SDC anode and $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ cathode were applied on the polished samples and co-sintered at 1000 °C for 2 h in air. Measurements were performed in fuel cell operating conditions, i.e., at 600 °C with 97% H_2 + 3% H_2O as anode gas and air as cathode gas, both at flow rates of 100 ml min^{-1} . Cyclic voltammetry curves were measured using a Solartron 1480 at a scan rate of 0.5 mV s^{-1} .

2.2. Sample characterization

Powder characterization was performed using a Mastersizer 2000 (Malvern Instruments Ltd., UK) for particle size analysis and by using a SA3100 Surface Area Analyzer (Beckman Coulter™) for surface area analysis. The density of experimental pellets was measured by Archimedes' method at room temperature.

Table 2
Composition, particle size and surface area of powders and sintering temperature, density and grain size of samples used in this study

Powder composition	Appearance	Mean particle size ^a (μm)	BET surface area ($\text{m}^2 \text{g}^{-1}$)
blank-SDC	Yellow	0.18	7.15
5.0 at.%Co-SDC	Green	0.17	8.25
5.0 at.%Cu-SDC	Dark green	0.17	8.39

Sample	T_s (°C) (for 5 h)	Density (g cm^{-3})	Grain size (μm)
blank-SDC	1400	6.948	1–2
1.0 at.% Co	1000	6.865	0.5–1
2.5 at.% Co	1000	6.750	0.5–1
5.0 at.% Co	1000	6.633	0.5–1
1.0 at.% Cu	1000	7.004	SDC: 0.5–1
2.5 at.% Cu	1000	7.009	Cu-compound ^b
5.0 at.% Cu	1000	6.981	>10 μm

^a Water as dispersant, 4 min ultrasonic agitation.

^b New phase appeared on the pellet surface with Cu sintering aids, named Cu-compound.

Table 2 gives the composition, particle size and surface area of powders, and sintering temperature, density and grain size of samples in this study. It can be seen that there is a slight increase of the BET surface area of SDC with sintering aids after the powder processing. The increase of BET surface area of SDC after Cu or Co addition and pre-treatment at 500 °C indicated the formation of fine Co or Cu oxides on the SDC particle surface. The density of experimental pellets slightly decreased with the increase of aids content; over 93% theoretical density of the SDC was reached.

3. Results and discussion

3.1. Powder pre-treatment condition

Thermal decomposition of SDC powders with 5 at.% $\text{Co}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ or $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ was analysed from room temperature to 800 °C in air flowing at 20 ml min^{-1} by TGA and DTA. As shown in Figs. 1 and 2, both Co and Cu nitrates are fully decomposed before 300 °C and the fastest decomposition rate happens at 231 °C for $\text{Co}(\text{NO}_3)_3$ and 251 °C for $\text{Cu}(\text{NO}_3)_2$. The DTA results also show the different temperatures for desorbing the adsorbed water in each nitrate.

Based on the TGA results, all SDC powders with nitrates at designed content (0, 1, 2.5 and 5 at.% of Co or Cu) were treated for thermal decomposition at 500 °C for 5 h in air.

3.2. XRD results

The lattice constant was determined using a D8-02 X-ray diffractometer (Bruker AXS GmbH) with Cu K α radiation at room temperature. The spectra were acquired from 2θ angles of

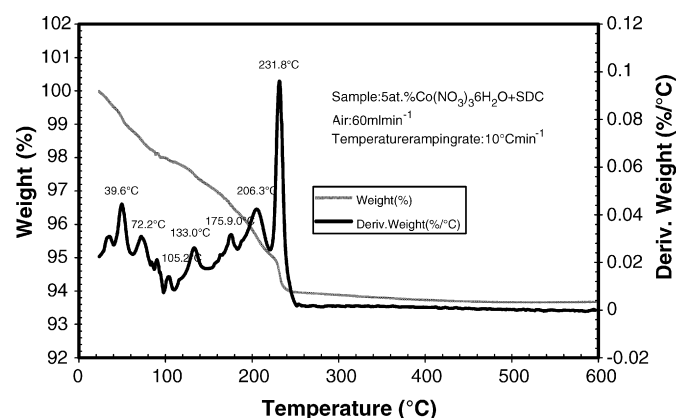


Fig. 1. TGA of SDC powders with 5 at.% $\text{Co}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$.

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