Journal of Power Sources 218 (2012) 307–312

Contents lists available at SciVerse ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Nanostructured Gd–CeO_2 electrolyte for solid oxide fuel cell by aqueous tape casting

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HIGHLIGHTS

- Fabrication of GDC electroyte for SOFC by tape casting.
- Optimization of electrolyte slurry formulation.
- Reproducibility of green scrap tapes.
- Densification by novel flash sintering technique.

ARTICLE INFO

Article history:
Received 19 March 2012
Received in revised form
29 June 2012
Accepted 1 July 2012
Available online 7 July 2012

Keywords:
Aqueous tape casting
GDC
Electrolyte
SOFC
Flash sintering

ABSTRACT

Gadolinia-doped ceria ($Ce_{0.9}Gd_{0.1}O_{1.95}$, GDC) electrolyte was fabricated by aqueous-based tape casting method for solid oxide fuel cells (SOFCs). The ceramic powder prepared by combustion synthesis was used with poly acrylic acid (PAA), poly vinyl alcohol (PVA), poly ethylene glycol (PEG), Octanol, 2,4,7,9-tetramethyl-5-decyne-4,7-diol ethoxylate and double distilled water as dispersant, binder, plasticizer, defoamer, surfactant and solvent respectively, to prepare stable GDC slurry. The conditions for preparing stable GDC slurries were studied and optimized by sedimentation, zeta potential and viscosity measurements. Green tapes with smooth surface, flexibility, thickness in the range of 0.35–0.4 mm and 45% relative green density were prepared. Conventional and flash sintering techniques were used and compared for densification which demonstrated the possibility of surpassing sintering at high temperatures and retarding related grain growth.

1. Introduction

Nanostructured materials with enhanced desired characteristics have attracted great attention for many niche applications in recent years. The nanostructured ceramics with improved ionic conductivity have recently become one of the popular fields of research since they can be used in emerging energy conversion devices such as SOFCs [1].

SOFCs have gained widespread attention due to their high-energy conversion efficiency and low pollution. However, high temperature operation would incur materials selection issues; expensive balance of plant (BoP) and fabrication cost are the barriers towards the commercialization of SOFC. Therefore, lowering the operating temperature of SOFCs and developing the low-cost and environmentally friendly fabrication techniques are the focus of recent studies [2].

High-ionic conducting solid oxide electrolytes based on rare earth doped ceria have been intensively investigated [3]. In order to reduce the operation temperature from 1000 °C to lower temperatures, gadolinium doped ceria (GDC) solid solution formed by replacing the Ce^{4+} sites of the CeO_2 lattice by Gd^{3+} cations, has been considered as a candidate solid electrolyte material for intermediate and low temperature SOFCs [4,5].

In the case of electrolyte-supported cells, the fabrication of the electrolyte is dominated by tape casting which is a well established and cost-effective method in the electroceramics industry and is scalable for mass production [6]. Tape casting often uses a slurry containing ceramic powder, solvent, binder, plasticizer, and additives

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http://dx.doi.org/10.1016/j.jpowsour.2012.07.005

such as de-foamer, surfactant and dispersant [7]. Traditionally, tape casting was done using organic solvents. Due to environmental, health, safety and economic reasons, aqueous-based tape casting method using water as solvent is adopted to replace the traditional organic-based tape casting method [5]. Despite these advantages, several critical challenges should be overcome which include slow drying rate of the tape, high crack sensitivity, flocculation and poor wetting of the slip due to the high surface tension of water [8,9]. Therefore, one of the main challenges in aqueous tape casting is to formulate a suitable suspension composition to avoid the defects which may occur during the drying process.

Ceramic powder as main constituent of slurry plays an important role in suspension composition. Colloidally stable nano-sized powder suspensions are known to have a markedly lower volume loading compared to suspensions with larger particle sizes [10]. There are a wide variety of processes for the synthesis of ceramic powders, which provide different properties such as particle size, shape, surface area and morphology. For particles in the nanometres range, adhering layer becomes significant and the maximum volume loading for a stable suspension is decisively lower. As a consequence of this, the green bodies resulting from nano powders usually have low green densities and are difficult to sinter to dense ceramics [11,12].

A number of sintering methods rely on the assistance of applied electric field, such as microwave sintering, electric discharge compaction (EDC), and spark plasma sintering have been used for superfast densification of ceramic powders despite each of these techniques has some limitations [13–15]. Recently, flash sintering emerged as a potential technique for fast sintering is under exploration. This is achieved by a sudden sintering event when the sample reaches a certain temperature under a given applied electrical field, thus enhancing the sintering rate and retarding grain growth [16–20].

Besides organic-based tape casting of commercially produced $Ce_{0.1}Gd_{0.9}O_{1.95}$ powder [21,22], aqueous-based tape casting of $Ce_{0.8}Gd_{0.2}O_{1.9}$ synthesized by a co-precipitation method [23] and commercially produced $Ce_{0.1}Gd_{0.9}O_{1.95}$ powder [5] have been reported.

We have earlier reported the combustion synthesis of rare earth doped ceria nano powders [24,25]. In this investigation, aqueous-based tape casting of $Ce_{0.1}Gd_{0.9}O_{1.95}$ powder prepared by combustion synthesis was used for fabricating the SOFC electrolyte. The characteristics of tape casting ceramic slurry, green and sintered tapes were also studied.

2. Experimental

2.1. Starting materials

$Ce_{0.9}Gd_{0.1}O_{1.95}$ (GDC) powders were synthesized by the nitrate-fuel combustion method. Citric acid was used as an organic fuel and high purity (>99.9%) cerium nitrate [$Ce(NO_3)_3 \cdot 6H_2O$] and gadolinium nitrate [$Gd(NO_3)_3 \cdot 6H_2O$] were used as precursor reagents. The details of the method have been reported elsewhere [24]. For preparing the slurry, distilled water was used as the solvent. Poly acrylic acid (PAA) with molecular mass of 1800 g mol^{-1} was used as an electrosteric dispersant. Poly ethylene glycol (PEG) with molecular mass of 200 g mol^{-1} was used as the plasticizer. Poly vinyl alcohol (PVA) with molecular mass of 70,000–100,000 g mol^{-1} was used as the binder. Octanol was selected as defoamer and 2,4,7,9-tetramethyl-5-decyne-4,7-diol ethoxylate as surfactant. The pH value of the suspensions was adjusted by analytical grade $NH_3 \cdot H_2O$ and HNO_3.

2.2. Zeta potential analysis

Zeta potential values of the GDC powder suspensions (0.01 vol.%) prepared in the absence and presence of PAA were measured with Zeta Meter 3.0 at various pH values adjusted by adding KCl (0.1 mol l^{-1}) or KOH (0.1 mol l^{-1}). The suspension was ultrasonically agitated and stirred for 20 min to achieve equilibrium between powder surface and dispersant.

2.3. Sedimentation measurements

The pH level of a suspension of 0.01 wt.% GDC with 1 wt.% PAA was adjusted by $NH_3 \cdot H_2O$ and HNO_3. Then, the suspensions were poured into 50 ml graded measuring cylinders and ultrasonically agitated for 30 min. Reading of the sediment volume was recorded for 8 days.

2.4. Viscosity measurements

Viscosity of slurries with different solids loading was measured using SV-10 Sine wave vibro viscometer which employs a tuning forks vibration system and resonance feature as sensors.

2.5. Slurry preparation and tape casting

GDC powders were dispersed in distilled water containing optimum content of dispersant and defoamer with the pH adjusted within the range of 9–10 by 1 h ball milling in a poly ethylene jar with 5 and 10 mm diameter ZrO_2 balls. The plasticizer was added and the mixture was ball milled for 24 h. Then, the binder and surfactant were added to the slurry and ball milled for another 24 h to achieve good homogeneity. Before the addition of binder, the PVA was dissolved in distilled water (PVA/water ratio: 0.16) by heating the solution to 75 °C for 6 h and stirred to ensure a complete dissolution. Then, the temperature was decreased to below 35 °C while stirring.

The laboratory-scale tape casting machine with single doctor blade and moving substrate was used. A casting speed of 100 mm min^{-1} and gap height of 1 mm were set. The suspensions were cast onto a silicone-coated mylar carrier film. The details of the slurry compositions used in tape casting are given in Table 1. After tape casting, the heating bed was adjusted on 25 °C without blowing air and the tapes were left to dry for 24 h. The green tape thicknesses were in the range of 350–400 μm. The green density of the dried tapes was determined by a geometrical method. The thickness was measured using a micrometre accurate to 0.001 mm and the weight of the samples was measured using a laboratory scale accurate to 0.01 mg.

Table 1
The compositions of aqueous GDC slurries.

Slurry	Powder (wt.%)	Solvent (wt.%)	Binder[a] (wt.%)	Plasticizer (wt.%)	Dispersant (wt.%)	Surfactant (wt.%)	Defoamer (wt.%)	Viscosity (mPa s)
A	37.9	31.7	25.8	3.8	0.8	–	0.1	245
B	47.0	13.2	32	6.8	0.8	0.1	0.1	2950
C	44.6	16.2	30.1	8.1	0.8	0.1	0.1	1100

[a] The binder was prepared by dissolving PVA in distilled water (PVA/water ratio: 0.16).