



Optimization of the rheology and sintering behavior of electrolyte and anode pastes to be used in co-extrusion of solid oxide fuel cells

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Abstract

Typical electrolyte paste including Yttria Stabilized Zirconia (YSZ) and anode paste containing YSZ, NiO, starch/activated carbon (pore former) were prepared. In order to perform co-extrusion process the pastes must have nearly same rheological properties. So, the prepared pastes unified in order to have same rheological characteristics using the Benbow–Bridgwater model. The unification results showed a linear relationship between the required liquid content for paste preparation and weight percentage of NiO powder in unified pastes. Such a linear relationship can be used to predict the required liquid content of the intermediate anode pastes. The unified pastes were extruded as single layer tubes and sintered at various experimental conditions. Micro-structural features of the sintered tubes were investigated using Scanning Electron Microscope (SEM) and optimum sintering temperature and time were found as 1450 °C and 2 h, respectively for full electrolyte densification. Moreover, 30 wt% of carbon may be regarded as the optimum carbon content for creating enough porosity in the anode layers.

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1. Introduction

Today, fuel cells attract lots of attention since they would be very effective in solving the environmental pollution problems that we face when using conventional (fossil) fuels. Different types of fuel cells have been introduced up to now. Among them, more attention has been paid to solid oxide fuel cells (SOFCs) due to their advantageous such as: high efficiency, reliability, modularity, fuel adaptability, and very low levels of NO_x and SO_x gas emission.^{1,2} SOFCs consist of three major layers including electrolyte, anode and cathode. Electrolyte layer is a dense ceramic material that only permits transfer of ions while anode and cathode layers are usually made of porous ceramic and cermet materials, to allow transfer of ions, gases and electrons.

Among two major types of SOFCs namely planar and tubular, the latter type has more advantages than the former^{3,4} such as high power density, lower on-off time.⁵ Also, decreasing the tube diameter and moving toward micro-tubular SOFC

emphasis these advantageous. Many processing routes have been introduced up to now for micro-tubular SOFC fabrication, among which extrusion is the most famous one because of its simplicity.⁶ As, conventional processing methods are based on adding layers on pre-formed anode or cathode layers,⁷ so they would involve many processing and sintering steps that increase the cost of fuel cell production. Co-processing and co-sintering would be served as an efficient method to solve this issue. In this technique electrolyte layer is produced and sintered simultaneously with the anode or cathode layer saving processing time and cost significantly.

On the other hand, co-sintering process does have its own difficulties due to thermo-physical incompatibilities between the materials in each layer. One remedy for such a problem would be using of functionally graded materials which has been suggested previously in co-extrusion of multilayered self supported SOFC.^{8–12} However, co-extrusion requires fine tuning and unification of different pastes in order to fabricate intact tube and use of continuous extrusion.¹³ Unification relies on rheological characterization of the pastes. Many techniques have been introduced in order to determine rheological behavior of paste. The Benbow–Bridgwater technique is one of the most well-known

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methods which is widely used to characterize rheological behavior of pastes.^{14,15} In this method, rheological properties of the paste are calculated using capillary rheometry with ram extruder with different extrusion ratios and extrusion velocities. Powell and Blackburn,¹³ try to unify different pastes, including yttria-stabilized zirconia (YSZ) as electrolyte paste and YSZ-NiO as anode paste, as precursor for co-extrusion process with no report regarding the sintering and structural behavior of different pastes.

In the present work, the rheological parameters of three different pastes, including two anode pastes with different NiO and pore former content and one electrolyte paste, were determined and unified using Benbow–Bridgwater model. Then, the optimum content of the required liquid in each paste preparation were predicted for intermediate anode pastes that were used in the co-extrusion process. Moreover, the microstructure and sintering behavior of the pastes were investigated in order to find the optimum sintering conditions e.g. time, temperature and also the best composition of different layers.

2. Experimental procedure

In order to perform co-extrusion process, multiple anode pastes and an electrolyte paste must be obtained with the unified rheological behavior. In order to unify pastes, the rheological properties of different pastes must be investigated using the Benbow–Bridgwater analysis method. So, the rheological behavior of the anode pastes with different amounts of NiO was determined. Moreover, different amounts of pore former are used in the anode pastes in order to govern the effect of pore former on their rheological behavior. In addition, the effect of the solvent content on the rheological properties of the electrolyte paste (YSZ paste) was investigated. After unification of the pastes, sintering behavior of the anode and electrolyte pastes was determined. To do so, the detailed experimental procedure is provided below.

2.1. Materials

The electrolyte paste was prepared using Yttria Stabilized-Zirconia (8 mol% Yttria Stabilized Zirconia, Inframat Advanced Materials Co., USA). The anode pastes prepared using YSZ, black nickel oxide (NiO, Acros Organics Co., USA) and activated carbon or starch as a pore former. In preparation of all pastes, different organic additives were used as a binder system such as cyclohexanone (Merck, Germany) as solvent and polyvinyl butyral (PVB, Sigma-Aldrich Co., USA) as binder, stearic acid (Merck, Germany) as surfactant and dibutyl phthalate (DBP, Merck, Germany) as plasticizer.

2.2. Paste preparation

In preparation of electrolyte paste, the dry powder (YSZ, PVB and Stearic Acid) was mixed using a jar mill for 2 h with ball (5 mm diameter YSZ balls) to powder ratio (BPR) of 10. The amount of PVB to stearic acid was fixed to 6:1 wt% in all paste preparation procedures. After dry mixing, the solvent

and plasticizer were added to the mixed electrolyte powder to form the final paste. The plasticizer content fixed to 2 wt%, however, the solvent content changed in order to obtain pastes with different solid loads. The materials were mixed for 1.5 h using a shear mixer.

In order to characterize and optimize the rheological properties of the anode pastes, various pastes with different amounts of NiO and pore former content were fabricated. The amount of NiO content was changed in the anode pastes because they have to be used in SOFC with graded and multi-layer structure, i.e. four anode layers and one electrolyte layer, in which each anode layer contain different amount of NiO. In addition, the effect of the amount of pore former and its type (in this case starch and activated carbon) on the anode paste rheological properties were investigated.

In anode paste preparation, YSZ, NiO and pore forming agent powder, with different proportions was mixed by wet attrition for 5 h (BPR = 40). After mixing, the powder was dried in oven for 8 h and then screened (60 mesh). The resulted powder mixture was then dry mixed with PVB (6 wt%) and stearic acid (1 wt%) using a jar mill for 2 h (BPR = 10). Finally, the solvent and plasticizer (2 wt%) were added to the powder to prepare the anode paste. Different amount of solvent was used in order to produce pastes with different solid loads.

All pastes were deaerated and left to age in plastic bag for 4 h before extrusion in order to eliminate all time dependent variations between different pastes.

2.3. Paste rheological characterization

Rheological characterization of pastes was performed using capillary rheometry with ram extruder. The barrel diameter was 20 mm and interchangeable dies were used with 4 mm diameter and length of 4, 16 and 32 mm. The die entry angle was 90° and different extrusion velocities of 0.2, 0.8, 2 and 4 mm/s were used. The rheological data were then calculated using Benbow–Bridgwater equation^{14,15} which can be presented as follows:

$$P = P_1 + P_2 = 2(\sigma_0 + \alpha V) \ln \left(\frac{D_0}{D} \right) + 4 \left(\frac{L}{D} \right) (\tau_0 + \beta V) \quad (1)$$

in which P is the total pressure drop, P_1 and P_2 are the pressure drop due to convergent flow and plug flow (die-land flow), respectively. D_0 is the barrel diameter, D is the die diameter and L is the die land length. V is the extrudate velocity, σ_0 is here termed the paste yield value, τ_0 the initial die wall shear stress and α and β are velocity factors that represent the velocity dependence of the bulk yield stress and wall shear stress, respectively.

From the experimental data the extrusion parameters of Eq. (1) are calculated. The yield value (σ_0) calculated by extrapolating extrusion pressure versus L/D curve at zero velocity to region of $L/D=0$. Let $L/D=0$, the velocity factor α can be calculated using extrusion pressure versus velocity curve. Next, from the slope of the extrusion pressure versus L/D line at zero

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