

D. Processing and Characterization of Structural and Functional Materials for Heavy-Vehicle Applications

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Objectives

- Produce yttria-stabilized zirconia (YSZ) thin coatings using electrophoretic deposition (EPD) technique for solid oxide fuel cells (SOFCs).
- Study the effect of the processing parameters on the porosity of the NiO/YSZ anode substrates.
- Study liquid-phase sintering technique of YSZ.

Approach

- Study the experimental parameters for the EPD process and deposit YSZ thin film coatings using this technique.
- Characterize the coatings using scanning electron microscopy (SEM) and X-ray diffraction (XRD).
- Study the batch preparation, pressing, and sintering parameters for the anode substrate fabrication.
- Examine the anode microstructure by SEM.
- Study the liquid-phase sintering of YSZ dense electrolyte and porous substrate using a sintering aid.

Accomplishments

- Obtained dense and thin YSZ electrolyte coatings on porous cathode substrates.
- Identified the effects of the processing parameters of the die-pressing and sintering technique on the porosity of the anode substrates.
- Acquired dense and porous YSZ according to the requirements using liquid-phase sintering at lower temperatures.

Future Direction

- Optimize the processes to prepare electrodes and electrolyte layers.
 - Fabricate single SOFCs and conduct performance tests.
 - Develop materials for electrolyte with higher conductivities than YSZ.
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Introduction

Low-cost production of the high-quality components for SOFCs by various techniques is of great importance and is the focus of this research project. Techniques that could help to reduce the overall cost of the fuel cell are identifying cost-effective, relatively low-purity raw materials; mass production of cell components; use of inexpensive and simplified fabrication processes; and enhanced cell life.¹⁻⁵ The future of SOFCs greatly depends on the outcome of these techniques. Currently, the cost of the fuel cell is mainly influenced by the number of processing steps during the fabrication process, apart from the direct cost of raw materials. Generally, the SOFC is fabricated in either one of the two most common designs, tubular or planar cell. Electrode-supported planar cells are the most popular and commercially efficient cell design, due to their high power densities.⁶ There are various steps at each stage of the fuel cell fabrication: developing the anode, depositing electrolyte layer, sintering the cell, etc. Each step consumes enormous time and cost. This presents a major hindrance in the commercialization of the fuel cell. The cost and time involved in the fabrication can be reduced a lot by careful selection of process techniques and parameters. In this project, three different cost-effective techniques were used for producing SOFC components. The results of the experimental studies of each technique will be reported.

Electrophoretic deposition (EPD) technique is especially attractive for SOFC application owing to simplicity, low-cost equipment, and ease of deposition of films of controlled thickness on substrates with even complex shape. EPD is a process in which the charged particles in an appropriate solvent move under the influence of the direct electric field toward an oppositely charged electrode and coagulate thereon to form a stable deposit. In the past research and applications, it was used to prepare ceramic laminates^{7,8} and components in electrochemical cells,⁹ etc. It was recently introduced to the area of the manufacturing SOFCs, since thin film electrolytes are highly desired for the fuel cells to work at reduced temperatures and higher efficiencies.

Optimization of the processing parameters by having an experimental design called a factorial design for obtaining data with a minimum expenditure of time and resources and by meticulous

analysis of the data, called analysis of variance (ANOVA) is the key to the low-cost production of the SOFC components. The analysis provides detailed insight into the direct effect of process variables on part's porosity as well as into the intensity of the numerous interactions between variables. This kind of response surface methodology (RSM) helps to determine, on the basis of one experiment, where to move in the next experiment toward the optimal point on the underlying response surface¹⁰. The optimized results will help to reduce cost and time involved in the fabrication process. In this research, the factorial design was used for the production of anode substrates with optimized porosities.

High energy expense in the sintering of the fuel cell components, especially the YSZ electrolyte, is one of the major causes for the cost. Usually the sintering of the YSZ powders needs a temperature higher than 1500°C for many hours to obtain a fully densified electrolyte. Reduction of the sintering temperature will save the energy for sintering and also save the investment on expensive high-temperature furnaces. Previous research has already shown that YSZ can be sintered at a substantially lower temperature by adding a small fraction of low melting-point oxides, for example, bismuth oxide. Bismuth oxide itself is a good oxygen ion conductor. However, the purpose of the research at this time is to achieve desired microstructures with this technique for fuel cell components. The effect of the sintering aid addition on the conductivity of the electrolyte materials will be addressed in the ongoing research.

Approach

For the EPD technique, the electrolyte coatings were produced by depositing the charged YSZ particles in a powder suspension under a direct current (dc) electric field. The suspensions were prepared by dispersing the powders in the mixture of two organic solvents, that is, acetylacetone (acac) and ethanol at different ratios ranging from pure acac to pure ethanol. The powder concentrations used were 5, 10, 25, and 40g/L. All the suspensions were subjected to ball milling for 48 h and ultrasonic agitation for 0.5 h before use. Stainless steel with the size of 15 × 15 × 0.3-mm substrates was used for all the depositions for parametric studies. The coatings were also applied on porous cathode substrates

which were made of strontium-doped lanthanum manganite (LSM) produced in our laboratory by slurry casting. The coated specimens were dried at room temperature for more than 20 h and then sintered to obtain a dense electrolyte layer.

In this study, NiO and YSZ, the most preferred anode material for SOFCs, were used as the raw materials along with the pore former graphite. A full 2^4 factorial design was used. The four variables that were considered for the experimental design are graphite (vol %), ratio of NiO to YSZ, compaction pressure, and sintering temperature. The two levels for each variable are listed in Table 1. A total of 16 sets of experiments with two replicates for each set (32 total experiments) were conducted. Powders are weighed according to the design. They were mixed by ball milling along with ethanol for 48 h and then dried. The powder mixture was uniaxially pressed. The green samples were sintered in air for 1 h. The dimensions and weight of the sintered samples were measured using the laboratory calipers and digital balance, respectively. The measured dimensions were used for the porosity calculations.

For the liquid-phase sintering study, 4.5 wt % bismuth oxide powders were added into YSZ powder. The green form of the YSZ laminates was prepared by slurry casting. The slurry was prepared by mixing the powders with polymeric binder, dispersant, plasticizer, and ethanol. To investigate the effect of the liquid-phase sintering on the densification of the YSZ particles with different sizes, the green forms with -325 mesh YSZ powder were cast and dried firstly. A thin layer comprising the suspension of the mixed YSZ powders of 66.7 wt % of -325 mesh, 23.1 wt % of 56 nm and 13.2 wt % of 20 nm in ethanol solution stabilized with poly(dimethyldiallylammonium chloride) (PDDA) was sprayed onto the dried green form YSZ substrate. The coated specimens were sintered at the

Table 1. Level design for the experimental parameters

Independent variable	Treatment level	
	Level 0	Level 1
Graphite (vol %)	40	30
YSZ/NiO weight ratio	50:50	42.5:57.5
Compaction pressure (MPa)	150	125
Sintering temperature (°C)	1350	1200

maximum temperature of 1000°C in air. Figure 1 shows the programmed sintering cycle for the liquid-phase sintering. The microstructure of the sintered specimens was examined with scanning electron microscopy (SEM).

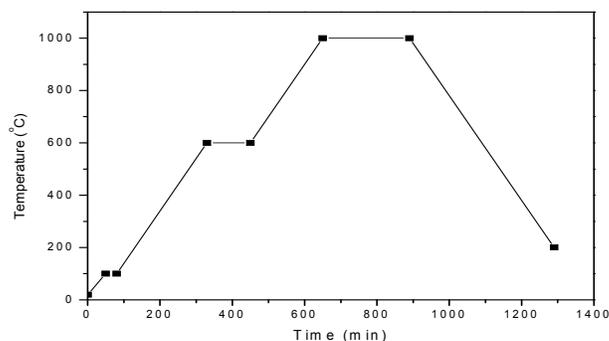


Figure 1. Sintering cycle for liquid-phase sintering of YSZ specimens.

Results

Effect of the Solvent on the Preparation of YSZ Coatings by EPD

To produce dense, homogeneous green forms of the coatings with EPD, a dilute, well-dispersed, and stable colloidal suspension is of great importance. In this case the stable suspension was obtained by absorbing free protons on the surface of the particles, while the free protons were produced by the reaction between acac and ethanol. Figure 2 shows the weight gains as a function of the fraction of ethanol in its mixture with acac. It can be noticed that deposits were obtained in all the different mixtures. The weight gain in pure acac is obviously much higher than in any other mixtures in constant current deposition mode (curve a). However, this advantage is much less in constant voltage mode (curve b). If we examine the voltage required for pure acac in Figure 3, it is ten times more than the lowest one. We can suggest that the amount of the free proton is much less in pure acac than in any other mixtures and even in pure ethanol. High electrical energy input led to the high yield. At the constant voltage mode, even though the input power in pure acac is the lowest, the deposition yield was still the highest one. In constant voltage mode, the power inputs in all the mixtures are higher than either in pure acac and ethanol. Nevertheless, the deposition yields were gradually decreased with the

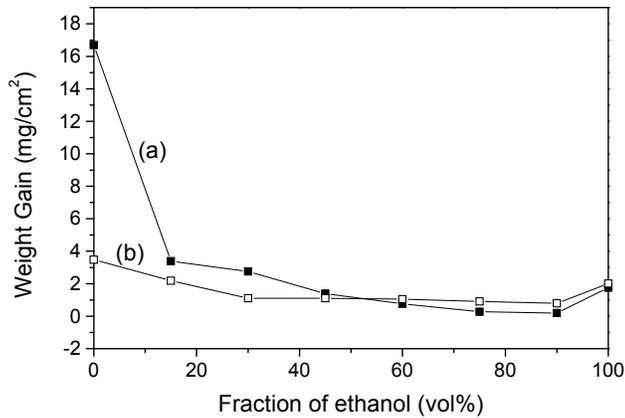


Figure 2. Weight gains as functions of the volume fraction of ethanol in its mixture with acac. Depositions were carried out at (a) a constant current density of 0.20 mA/cm² and (b) a constant voltage of 50 V. Deposition time was 120 s with a powder concentration of 5 g/L.

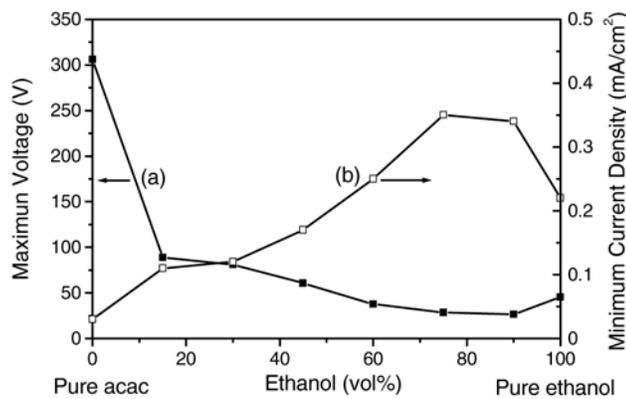


Figure 3. Current and voltage as functions of the mixing ratios of ethanol and acac during the 120-s depositions. (a) Maximum voltage required to maintain a constant current density of 0.20 mA/cm², and (b) minimum current density when a constant voltage of 50 V was applied.

increase of the fraction of ethanol in the mixture. It is recommended that in these mixtures, there are free protons in addition to those absorbed by the YSZ particles. The moving of these free protons partially contribute to the total electric current; the deposition rates were hence lower than the expectations.

The microstructures were examined with SEM. Figure 4 shows the micrographs taken from the surfaces of the deposited green forms at the constant voltage of 50 V. Figure 4(a) and (c) show poorly packed green forms from the suspensions with pure acac and pure ethanol. The poor packing resulted from the large agglomerates in the suspensions. This means that in the solvents of either pure acac or pure ethanol, the YSZ particles were not well dispersed because of the low free proton levels. Figure 4(b) shows a homogeneous packed deposit in the suspension with 45 vol % ethanol/55 vol % acac as the solvent. The particle sizes are much smaller than in the other samples. Therefore, the deposition behavior was further studied for suspension in the solvent with the mixing ratio of ethanol and acac 1:1.

Effect of the Parameters in the Factorial Experiments

The obtained porosity values after sintering are shown in Table 2, which will be used as the inputs for the ANOVA subsequently.

The effects of the processing parameter on the porosity of the sintered anode pellets were analyzed by the ANOVA method. It was understood that the porosity of the anode increased slightly with the increasing of the NiO component in the mixture, and the increasing rates were in accordance with the level of the pressure used to make the pellets. The sintering temperature was found to be one of the very significant factors in the porosity control. The

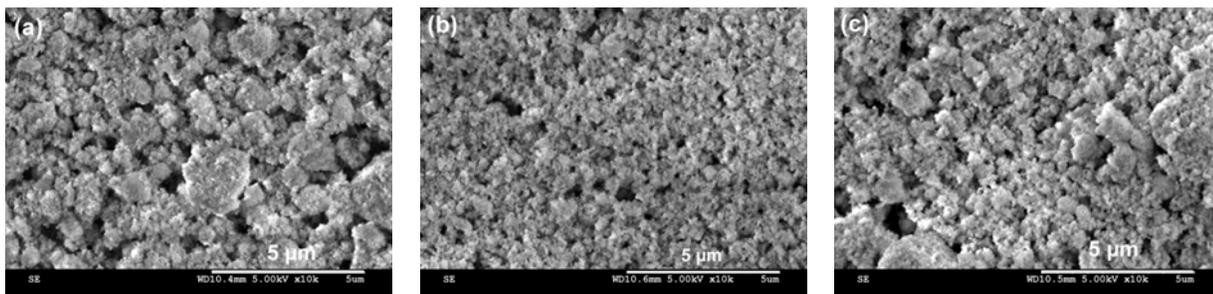


Figure 4. Micrographs of the dried green forms deposited on stainless steel substrates at a constant voltage of 50 V for 120 s. The depositions were conducted in the suspensions of 5 g/L YSZ in solvents of (a) pure acac, (b) 45 vol % ethanol/55 vol % acac, and (c) pure ethanol for 120 s.

Table 2. Porosity values of sintered NiO/YSZ samples

Design No.		1	2	3	4	5	6	7	8
Porosity (%)	Set 1	6.85	40.62	8.00	41.41	10.85	42.94	10.68	40.38
	Set 2	7.09	41.80	8.39	41.41	10.47	42.57	10.03	40.92
Design No.		9	10	11	12	13	14	15	16
Porosity (%)	Set 1	9.58	34.38	9.38	33.80	11.16	35.15	9.31	33.83
	Set 2	9.75	33.68	10.23	34.13	9.68	35.08	9.69	35.77

porosity of the anode sintered at 1200°C was four times more than that sintered at 1350°C. The effect of the amount of graphite used as the pore former was shown to be significant, too. The porosity of the anode increased as the graphite amount increased within the experimental range.

Effect of the Sintering Temperature in Liquid-Phase Sintering

A comparison of the effect of the sintering temperatures on the densification of YSZ was made.

Figure 5 shows the micrographs of the specimens sintering at 1000°C and 1100°C, respectively. From images in Figure 5(a) and (b) that were magnified to 20,000 times, it seems that both specimens that sintered at 1000 and 1100°C are fully sintered. From the images in Figure 2(c) and (d), which were taken at a lower magnification from the same specimens mentioned above, it is shown that there are still many pores over the samples. This set of images demonstrates that the densification at 1000°C and 1100°C did not make significant difference.

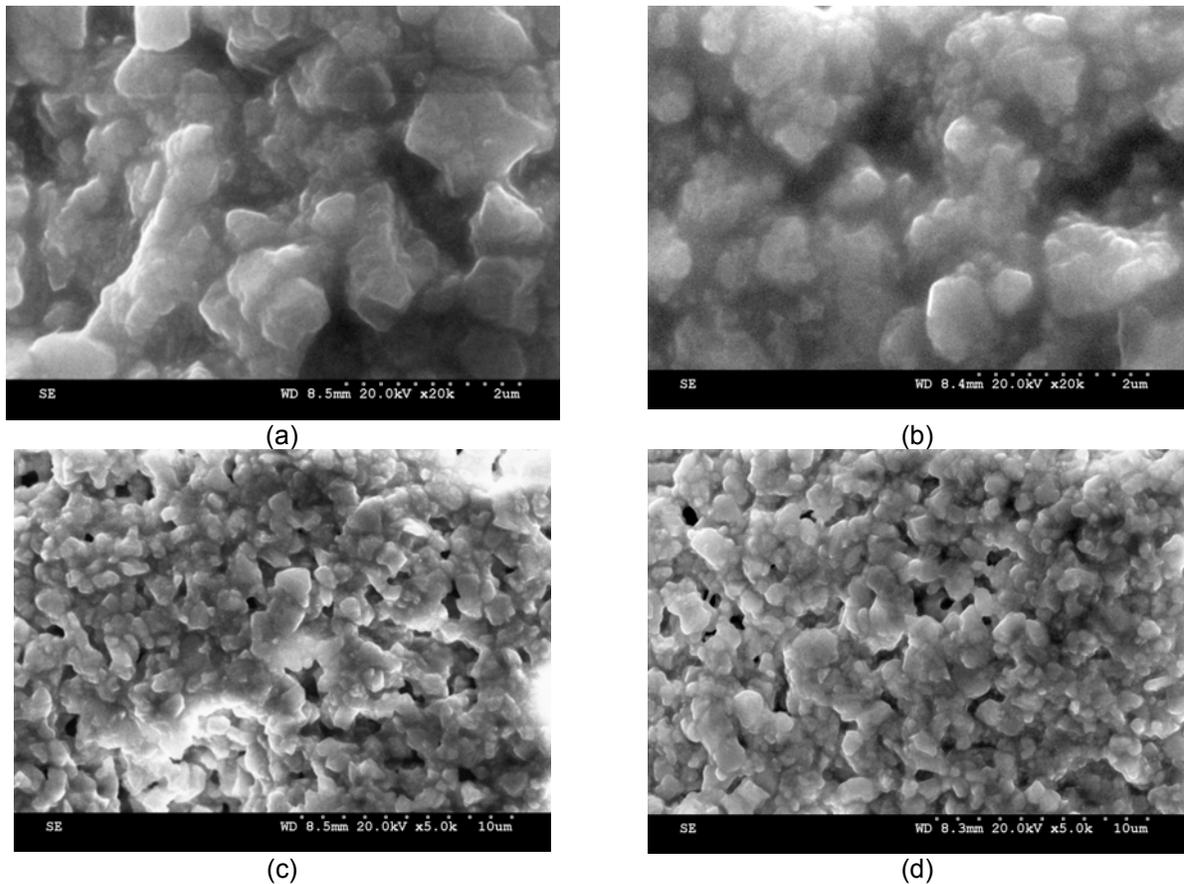


Figure 5. Micrographs of liquid-phase sintered YSZ with addition of 4.5 wt % of bismuth oxide sintered at different temperatures, (a) and (c) 1000°C; (b) and (d) 1100°C for 4 h.

Therefore, a temperature of 1000°C was chosen for all the sintering thereafter. On the other hand, this experiment revealed a potential to produce porous YSZ frame structure at lowered temperatures using liquid-phase sintering.

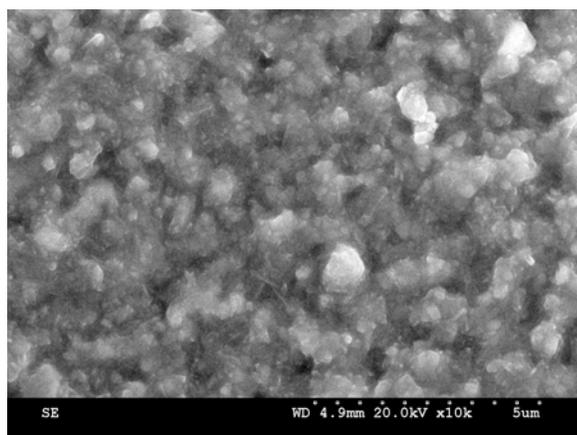
Effect of the YSZ Particle Size in Liquid-Phase Sintering

As is stated above, sintering experiments were conducted for the samples with substrate and coating layered structure. The substrate comprises YSZ particles of a larger size (~325 mesh), while the coating consists of YSZ particles of mixed sizes. The purpose of doing it this way is to explore the possibility of producing a dense YSZ layer on a porous YSZ substrate using one liquid-phase sintering process. The knowledge of solid-state sintering advises that small particles have higher densification rates than the large particles during sintering because of two main reasons. First, large particles have lower packing density than the small particles. The material comprised with large particles needs more diffusion energy and time to reach densification than one with small particles. Secondly, small particles, especially nano particles, have higher chemical potentials than large particles. As a result, the material with small particles possesses higher diffusion rates than one with large particles. This will further enlarge the difference of the densification during sintering between materials with different particles sizes. These factors will also take effect in liquid-phase sintering.

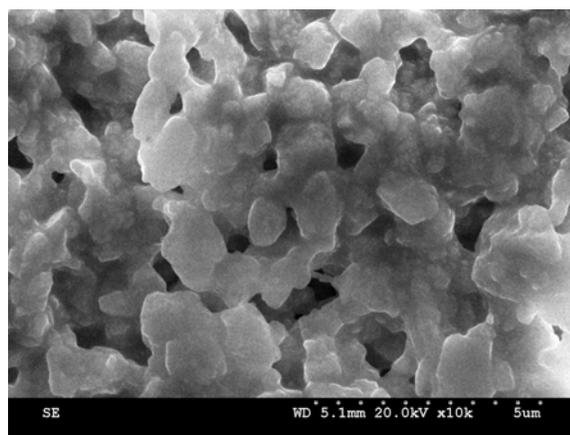
Figure 6 shows the SEM images taken from the top and bottom surfaces of a coated specimen after liquid-phase sintering at 1000°C for 4 h. This observation proved that it is effective to produce dense coating on porous substrate by using different particle sizes in the two different parts of the structure during liquid-phase sintering. This method can be employed in production of SOFC sandwich structures, which will reduce the manufacturing cost substantially by simplifying the fabrication process and saving sintering energy.

Conclusions

Three cost-effective techniques used to produce SOFC components were investigated. In the EPD for preparation of YSZ electrolyte coatings, microstructure suggested that deposits obtained in the suspensions with ratio of ethanol to acac at about 1:1 outcome homogeneously packed green form that forms dense coatings after sintering even through depositions can be achieved in any of the mixing compositions. For the anode factorial experiments, the effects of these parameters were examined against the porosities of the sintered anode samples. The sintering temperature and graphite usage were found to have very significant effects, while the ratio of NiO/YSZ and the pressing pressure were found to have less significant effects on the porosity of the anodes. The effects are planned to be further analyzed by ANOVA. Experiments demonstrated that liquid-phase sintering is an energy-efficient process, and Bi₂O₃ is an effective low melting point material to perform liquid-phase sintering of YSZ.



(a)



(b)

Figure 6. Micrographs of the (a) coating and (b) substrate sintered at 1000°C for 4 h in liquid phase in one process.

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- "Property Control of Cathodes and Anodes Produced by Slip Casting for Planar Solid Oxide Fuel Cells," *Ceramic Engineering and Science Proceedings*, **26**(4), 185–90 (2005).
- "Influence of Processing Parameters on Porosity of NiO-YSZ Solid Oxide Fuel Cell Anode Material," *Ceramic Engineering and Science Proceedings*, **26**(4), 177–83 (2005).
- "Exploration of Combustion CVD Method for YSZ Thin Film Electrolyte of Solid Oxide Fuel Cells," accepted for publication in *Mixed Ionic Electronic Conducting Perovskites for Advanced Energy Systems*, eds. N. Orlovskaya and N. Browning, Kluwer Academic Publication, 2005.
- "Exploration of Electrophoretic Deposition of YSZ Electrolyte for Solid Oxide Fuel Cells," K8.2, *MRS Proceedings*, Volume **835**, eds. P. Knauth, C. Masquelier, E. Traversa, and E. D. Wachsman, December 2004.

