Zirconia Powders for Fuel Cell Applications

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Abstract:
Refractron Technologies Corporation (RTC) is currently developing a family of low-cost, high quality, yttria stabilized zirconia (YSZ) powders for use in applications related to Solid Oxide Fuel Cells. The initial development work, which was partially funded by New York State Energy Research and Development Authority (NYSERDA) has been successful and two zirconia powders, a 3 mol% (3YZ) for structural use (interconnect) and a 8 mol% (8YZ) for electrolyte use have been developed. In this effort the batch sizes used were in the range of 20-30 kg. The resultant powders were characterized both for its intrinsic properties as well as for use in SOFC application via a tape cast product. Based on this characterization, the developed powders were found to be comparable to commercially available TOSOH zirconia powders. The price of the developed powder at this volume is projected to be ~$50/kg. It is projected that with further scale up to 250-500 kg batch size the cost can be brought down further.

Process Overview:

RTC zirconia powders are produced using an aqueous-based proprietary process in a batch reactor. The process employs a controlled combination of chemical precursors for zirconia, stabilizers and dopants in a tailored reaction vessel. Ultra-pure precursors are used to produce chemically precise powder compositions. Initial batching conditions are controlled to improve downstream operations and to control powder characteristics. Homogeneous reaction products are subsequently dried and calcined. The combination of calcining and milling is controlled to attain particle size and surface area specifications. Milled powders can be provided in slurry form or they can be dried by several different methods. This batch process is also amenable for introducing other oxides such as alumina during processing to further aid its use in fuel cell applications.

Powder Characteristics:

Two key physical characteristics that are critical for powders are specific surface area (SSA) and particle size distribution (PSD). These properties influence both the rheology of the slip as well as subsequent compaction in the tape casting process. The first part of Table I displays the physical properties of the 3 mole percent yttria doped zirconia powder. For comparison purposes the reported value of the Tosoh powder is also included in this table. The second part of this table compares the chemical analysis. As seen from this table, the properties of the zirconia powder developed here are comparable to Tosoh powder.

Sintering and Strength Characteristics:

The powder was evaluated for sintering characteristics in the form of a tape cast product. The binder package used in this work was a combination of acrylic and carbonate system.

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Tapes of nominal green thickness 250-300 microns were cast using this binder system in a laboratory caster. To compare the sintered densities and other mechanical properties, tapes were also made of a mixture of 80% 3YSE Tosoh powder and 20% 3YE Tosoh[4] powders. Green tapes could be densified to >97% of theoretical density by sintering at 1350°C for 3 hours. Figure 1 shows the theoretical density of different batches of powders sintered at 1350 C for 3 h. The Equibiaxial flexural strength of the sintered tape was characterized using the ASTM procedure C 1499-01 (ring on ring). Figure 2 shows the results of this characterization. The tape made using the RTC 3YZ Zirconia powder yielded a characteristic strength of 1054 MPa with a Weibull modulus of 4.5 in comparison with a characteristic strength of 860 MPa and a Weibull modulus of 6.6 for the Tosoh Tape.

Table 1: Powder Characteristics (3 YZ composition)

Physical Characteristics	Test Method	Refractron	Tosoh
Surface Area (m^2/g)	**BET**	**10.0**	**(7,16)[1]**
Average PSD (microns)	**Laser Scatter.**	**0.6**	**0.6**
Chemical Characteristics	**Test Method**	**Refractron**	**Tosoh**
$ZrO_2 + HfO_2 + Y_2O_3 + Al_2O_3$	**(ICP)**	**>99.9**	**>99.9**
Y_2O_3	**(ICP)**	**5.40**	**5.15**
Al_2O_3	**(ICP)**	**0.25**	**0.25**
SiO_2	**(ICP)**	**≤.02**	**≤.02**
Fe_2O_3	**(ICP)**	**≤.01**	**≤.01**
Na_2O	**(ICP)**	**≤.02**	**≤.04**

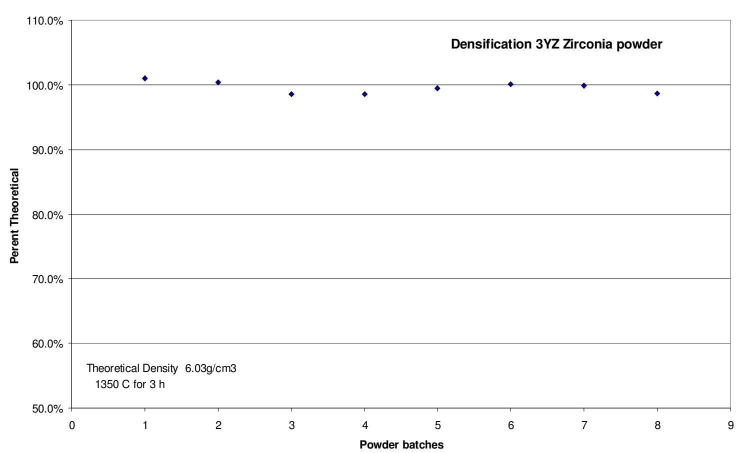

Figure 1. Densification of different batches of 3YZ Zirconia powders

[4] Multiple grades (3YS-E, 3Y-E)

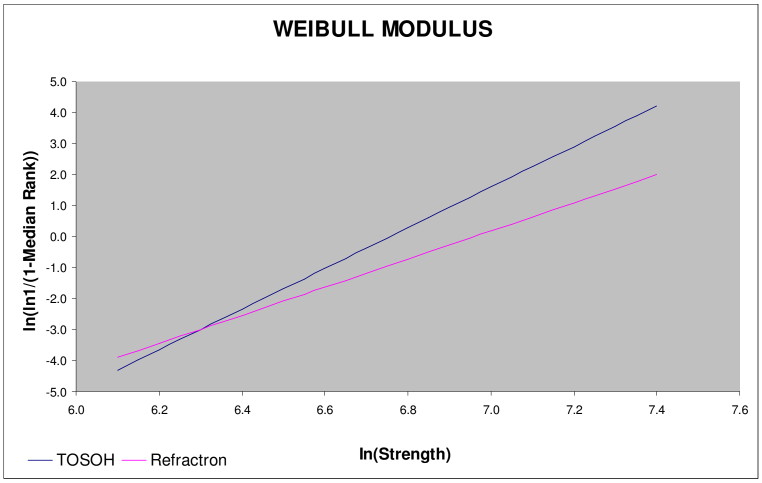

Figure 2 Equibiaxial flexural strength determination of RTC and Tosoh samples

To check the reproducibility of the process, several different batches were made during this study ranging in size from 25-50 kg. Powders from each of the batches were evaluated in a production tape caster. Ten kg batches were used for this work and 250-300 micron thick tapes were cast. As before, the green tapes were evaluated for densification by sintering at 1350°C for 3 hours. The sintered tapes were characterized for Equibiaxial flexural strength and this characterization is shown in Table 2 listing the characteristic strength and Weibull Modulus for each test.

Table 2 Comparison of strength characterization of multiple batches

Batch	# Specimens		Characteristic Strength, MPa	Weibull Modulus
	Tested	Valid		
ECS-6	30	28	1455	5
ECS-7	30	25	1478	6.2
ECS-9	27	23	1395	6.2
ECS-10	28	21	1130	7.3
ECS-11	30	22	1314	6.2
ECS-13	30	21	1262	8.3
ECS-15	28	26	1220	7.5

Although initial development work was carried out for producing 3-mol percent yittria doped powder, work was later extended to make 8 mol percent yittria doped powders for use in electrolyte application. Powders with characteristics similar to that shown in Table 1 were produced with this. The powder was evaluated as before for densification and strength via a tape cast route. Figure 3 shows the densification study on this powder. Here the green tapes were densified at different temperatures held for 3 hours. Good densification (>97%) was achieved at 1350-1400°C. Figure 4 shows the strength characterization of this powder, which yielded a characteristic strength of 396 MPa and a Weibull Modulus of 4.8. The strength of the 8 YZ tapes was significantly less than that of 3 YZ tapes.

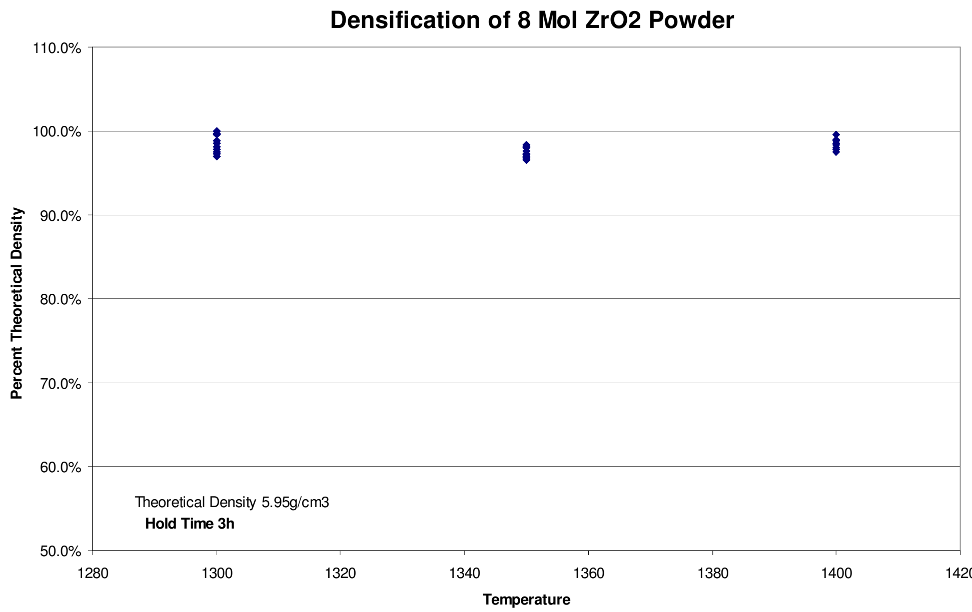

Figure 3 Densification of 8-mol percent yittria doped RTC Zirconia powder

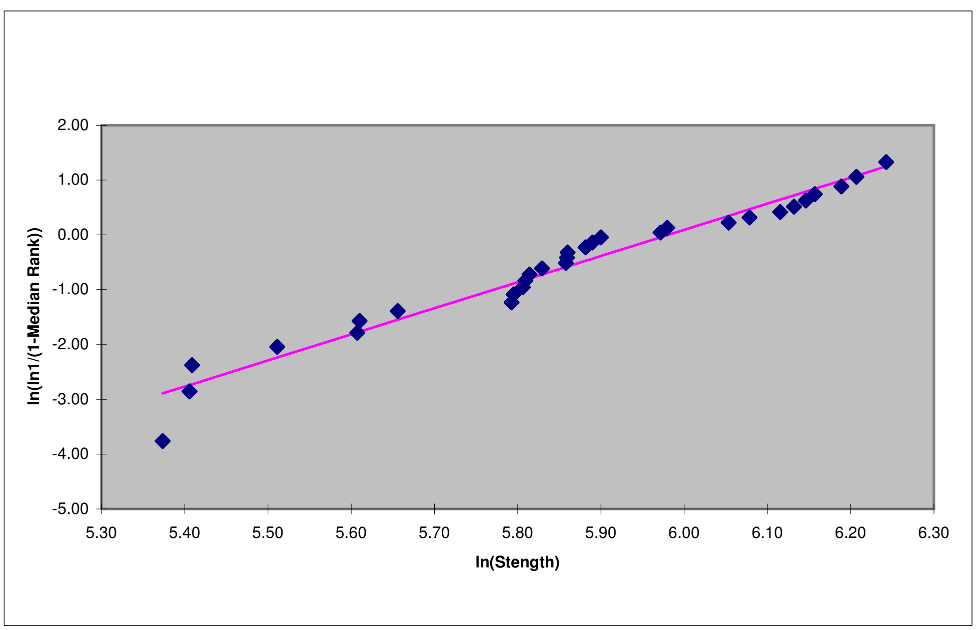

Figure 4 Equibiaxial strength characterization of 8-mol percent yittria doped RTC Zirconia powder

Ionic Conductivity:
Ionic conductivity of the two powders was measured using impedance spectroscopy studies at Alfred University. Samples for this work were prepared by isostatically pressing the powders at 20 ksi followed by sintering at 1425°C for 4 hours. The resultant sample was sliced with a diamond wheel. Measurements were made over a range of temperature and the value presented in Table 3 is the value at 800°C.

Table 3 Ionic Conductivity measurements of 3-Mol and 8- Mol yittria doped Zirconia powders at 800°C

	Sample 1	**Sample 2**
3 YZ	**2.75 S/m**	**2.70 S/m**
8 YZ	**7.80 S/m**	**10.10 S/m**

Summary:
RTC is developing a series of Zirconia powders for SOFC applications. The developed powders have characteristics similar to commercially available TOSOH powders and the price of the developed powder at this volume is projected to be ~$50/kg. Current manufacturing efforts are focused to further optimize the process and to produce repeat batches of 250-500 kg size at a lower cost.