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A LOW-COST PROCESS FOR THE SYNTHESIS OF NANOSIZE YTTRIA-STABILIZED ZIRCONIA (YSZ) BY MOLECULAR DECOMPOSITION

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ABSTRACT

This report summarizes the results of work done during the performance period on this project, between October 1, 2002 and December 31, 2003, with a three month no-cost extension. The principal objective of this work was to develop a low-cost process for the synthesis of sinterable, fine powder of YSZ. The process is based on molecular decomposition (MD) wherein very fine particles of YSZ are formed by: (1) Mixing raw materials in a powder form, (2) Synthesizing compound containing YSZ and a fugitive constituent by a conventional process, and (3) Selectively leaching (decomposing) the fugitive constituent, thus leaving behind insoluble YSZ of a very fine particle size. While there are many possible compounds, which can be used as precursors, the one selected for the present work was Y-doped Na_2ZrO_3, where the fugitive constituent is Na_2O. It can be readily demonstrated that the potential cost of the MD process for the synthesis of very fine (or nanosize) YSZ is considerably lower than the commonly used processes, namely chemical co-precipitation and combustion synthesis. Based on the materials cost alone, for a 100 kg batch, the cost of YSZ made by chemical co-precipitation is >$50/kg, while that of the MD process should be <$10/kg. Significant progress was made during the performance period on this project. The highlights of the progress are given here in a bullet form.

1) From the two selected precursors listed in Phase I proposal, namely Y-doped $BaZrO_3$ and Y-doped Na_2ZrO_3, selection of Y-doped Na_2ZrO_3 was made for the synthesis of nanosize (or fine) YSZ. This was based on the potential cost of the precursor, the need to use only water for leaching, and the short time required for the process.
2) For the synthesis of calcia-stabilized zirconia (CSZ), which has the potential for use in place of YSZ in the anode of SOFC, Ca-doped Na_2ZrO_3 was demonstrated as a suitable precursor.
3) Synthesis of Y-doped Na_2ZrO_3 and Ca-doped Na_2ZrO_3 was achieved using a conventional calcination process. The corresponding surface area was ~1 to 2 m^2/g.
4) By leaching with water, nanosize (very fine) YSZ and CSZ powders were synthesized. The corresponding surface area was ~65 m^2/g. This demonstrates the MD concept, namely macroscopic precursor → leaching → very fine (nanosize) product.
5) Crystallite size was determined by TEM (~5 nm).
6) Anode-supported cells, with YSZ and CSZ made by the MD process, were successfully made by a conventional pressing and sintering process.
7) Single cells were made with as-synthesized YSZ and CSZ as a constituent in anode support.
8) A single cell (LSM + YSZ cathode) was tested at $800^{o}C$ with H_2/air, with maximum power density of ~1.2 W/cm^2.
9) Dense samples of both YSZ and CSZ made by the MD process were fabricated.
10) Preliminary cost analysis, based on materials cost only, showed that the cost of YSZ powder made by the MD process should be considerably lower than that made by either chemical co-precipitation or combustion synthesis. For an anode-supported cell design, for an assumed power density of 0.5 W/cm^2, the cost of YSZ made by the MD process is estimated to be ~$5/kW. By contrast, the cost per kW for chemical co-precipitation or combustion synthesis is ~$70/kW and ~$23/kW, respectively.

Efforts are currently underway to fabricate 5 cm x 5 cm active anode-supported cells with YSZ made by the MD process.

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INTRODUCTION

The standard materials used in the state of the art SOFC are: Ni + YSZ anode, YSZ electrolyte, and LSM + YSZ cathode [1]. Of these, usually YSZ is particularly expensive for three reasons: (1) The cost of yttria, Y_2O_3. (2) The powder must be fine and de-agglomerated so that it is readily sinterable. (3) The powder must be essentially free of impurities – especially free of silica, which can lead to low conductivity. Commercially available YSZ of high quality, and which can be readily sintered, is usually made by chemical co-precipitation. YSZ can also be made using a solid-state process involving calcining mixtures of Y_2O_3 and ZrO_2. However, such a powder is inactive (particle size in the microns), must be subjected to extensive milling and still requires high sintering temperatures. At the present time, commercial vendors charge in excess of $100/kg for sinterable, chemically co-precipitated YSZ powder in batches up to 100 kg. The cost of YSZ in the anode-supported design is in excess of $50/kW assuming an operating power density of 0.5 W/cm^2. The cost of YSZ per kW is also high when using the electrolyte-supported design. Based on these cost numbers, it appears unlikely that co-precipitated powder will meet the SECA cost objectives.

If chemically co-precipitated YSZ powder is used only for the electrolyte in an electrode-supported design, and electrode interlayers, which in the anode-supported design is only ~20 microns thick, the cost of such powder is only about $5.00/kW. This suggests an approach wherein the expensive YSZ is used only in the electrolyte layer and electrode interlayers, while the rest of the YSZ, most of which is in the anode support, is fine, sinterable YSZ, but is inexpensive. These two approaches are compared in Figure 1. Such low-cost YSZ then mainly serves as a filler in the anode. Some developers have used other ceramics, such as Al_2O_3, as fillers in the anode support of anode-supported SOFC. However, long-term compatibility is unknown or uncertain. It would appear that a low-cost zirconia alternative to the currently available YSZ would have a significant impact on the overall cost.

In the Phase I proposal, a molecular decomposition (MD) process for the synthesis of nanosize YSZ was proposed, which has the potential to lower the cost significantly[1]. The process consists of first synthesizing Y-doped Na_2ZrO_3 by calcining a mixture of ZrO_2 and a source of Na_2O, such as NaOH or Na_2CO_3. The raw materials (ZrO_2 and NaOH or Na_2CO_3) are of macro size (microns to several tens of microns). The formed precursor is then simply leached in water to form NaOH (in solution) and form very fine (nanosize) YSZ [2]. Figure 2 shows an overall schematic of the process. Figure 3 shows the mechanics of the process, which involves the in-diffusion of H_2O through the porous, nanosize YSZ formed, reaction at the porous YSZ/Y-Na_2ZrO_3 interface, and the out-diffusion of NaOH in water.

The other processes currently used for the synthesis of YSZ are: (1) Solid-state reaction: This consists of calcining a mixture of Y_2O_3 + ZrO_2 at ~1250^{o}C, followed by ball-milling or attrition milling. (2) Combustion synthesis: This consists of dissolving nitrates of constituents (Y and Zr) into de-ionized water along with a hydrocarbon fuel (e.g glycene), heating to dryness and combusting the mixture [3,4]. Some light milling is required after the combustion process. (3) Chemical co-precipitation: This consists of dissolving nitrates or chlorides of

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[1] A PCT patent application has been filed, and currently it is in the nationalization phase. All claims have been allowed in Australia.

constituents (Y and Zr) into de-ionized water, and introducing a precipitating agent (such as NH_4OH) to precipitate out an intimate mixture of Y_2O_3 and ZrO_2 (or their hydroxides), with NH_4Cl dissolved in water. Subsequent steps involve repeated washing, filtering followed by a calcination step to form YSZ. As the precipitate size is very fine, calcination can be achieved at a relatively low temperature. Several variations of this general concept are in use. Other approaches also involve the formation of a sol, followed by the formation of a gel, and then calcining it. Table I compares the four processes discussed above from the standpoint of powder quality and cost.

The Phase I effort was proposed to develop the MD process for the synthesis of YSZ. Two precursors were proposed; Y-doped $BaZrO_3$ (Y-$BaZrO_3$) and Y-doped Na_2ZrO_3 (Y-Na_2ZrO_3). While satisfactory results were obtained with Y-$BaZrO_3$, much of the focus was shifted to Y-Na_2ZrO_3 for the following three reasons: (1) Y-$BaZrO_3$ is anticipated to be more expensive than Y-Na_2ZrO_3. (2) Unlike Y-$BaZrO_3$, which requires an acid, such as HNO_3 for leaching, Y-Na_2ZrO_3 can be easily leached in water. (3) The leaching and subsequent washing times are fairly short with Y-Na_2ZrO_3, since the YSZ powder formed readily flocculates (soft floccules)

Table I: Comparison of Solid-State, Combustion Synthesis, and Chemical Co-Precipitation with Molecular Decomposition

	Solid-State	Combustion Synthesis	Chemical Co-precipitation	Molecular Decomposition
Raw Materials	Oxides	Nitrates	Nitrates or Chlorides	Oxides
Raw Materials Cost	Low	High	High	Low
Fugitive Constituents (reactant)	None	Glycene	NH_4OH	NaOH
Fugitive Constituent Cost	NA	High	High	Low
First Step	Mixing	Dissolution in Water	Dissolution in Water	Mixing
Second Step	Calcination ~1250^oC	Combustion	Co-precipitation by NH_4OH	Calcination
Third Step	Extensive Milling	Light Milling	Washing/ Filtering	MD Leaching with Water
Fourth Step	NA	NA	Calcination	Washing/ Settling
Fifth Step	NA	NA	Optional Milling	Optional Milling
Powder Quality	Low (Low Surface Area, Impurities due to the milling process)	High (High Surface Area)	High (High Surface Area)	High (High Surface Area)
Cost	Low	Moderately High	High	Potentially Low

in a basic solution – which makes washing straightforward.

In Phase I, very fine (nanosize) YSZ and CSZ powders were synthesized using the MD process. These powders were characterized using XRD, BET, and TEM, which confirmed their very fine size. Samples of both YSZ and CSZ were successfully sintered to a high density. Preliminary measurements of conductivity were carried out. The measured conductivity in both materials (YSZ and CSZ) was comparable to materials of similar microstructures made from commercial materials. Anode-supported cells with YSZ made by the MD process in the anode support, were successfully made and tested. At 800°C, maximum power density of ~1.2 W/cm^2 was achieved. No degradation in performance was observed in the short duration over which testing was done. Preliminary cost analysis for a 30 kg/day batch was made on the basis of materials cost only. The analysis shows that YSZ made by the MD process should be much lower in cost as compared to YSZ made by combustion synthesis or chemical co-precipitation (or sol-gel).

EXECUTIVE SUMMARY

The principal factor, which will determine the commercial viability of SOFC, is the overall cost/kW. One of the significant costs is the cost of SOFC stack, which depends in part on the materials it is made of. The state-of-the-art SOFC is made using YSZ as the electrolyte. In addition to the electrolyte, YSZ is also a constituent in the composite anode (Ni + YSZ) and the composite cathode (e.g. LSM + YSZ). The anode-supported design has been shown to exhibit the highest performance, and has attracted much attention. In the anode-supported design (as well as the electrolyte-supported design), the amount of YSZ used is larger than that in the cathode-supported design[2]. At the present time, many researchers and developers use commercially available powder, which typically sells for > \$100/kg. This commercially available powder is of high quality, and can be readily sintered. However, the cost is high due in part to the high cost of raw materials used to make the powder. The objective of Phase I was to develop a novel process, termed Molecular Decomposition (MD), which can lead to very fine (nanosize) YSZ powder, and has the potential to be a low-cost process. Phase I effort was very successful. The following summary briefly describes Phase I accomplishments.

The starting raw materials for the MD process are oxides, mixtures of which were calcined to form the required precursors. For the synthesis of YSZ, two precursors were made, Y-$BaZrO_3$ and Y-Na_2ZrO_3. Typical particle size of the precursors was in the several microns range. The precursors were leached, resulting in nanosize (fine) YSZ powder. The reactions are:

Y-$BaZrO_3$ (solid, macro size) + $2HNO_3 \rightarrow Ba(NO_3)_2$ (in solution) + H_2O + YSZ (nanosize, dispersed)

and

Y-Na_2ZrO_3 (solid, macro size) + $H_2O \rightarrow 2NaOH$ (in solution) + YSZ (nanosize, dispersed)

The specific surface area of the YSZ formed was ~65 m^2/g as measured by BET. XRD confirmed the formation of cubic YSZ. From XRD line broadening, the crystallite size was estimated to be in the 5 to 10 nm range. TEM showed that the crystallite size was ~5 nm. The main emphasis was placed on the Na_2ZrO_3-based process. In Phase I using this process, over several hundred grams of the powder was produced, each batch producing >100 g.

Using CaO-doped Na_2ZrO_3 (Ca-Na_2ZrO_3), calcia-stabilized zirconia (CSZ) was also made. XRD confirmed the formation of cubic zirconia, and XRD line broadening confirmed the formation of very fine (nanosize) CSZ.

Preliminary studies on the sintering behavior were carried out. Both YSZ and CSZ could be sintered to high density (to the stage of closed porosity). Further work is underway on optimizing the sintering behavior. Preliminary work on conductivity measurements was carried out. The measured ionic conductivity is comparable to values obtained on YSZ and CSZ samples made using commercial powders and of similar microstructures.

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[2] In the cathode-supported design, the cost of YSZ as a material is low, as the amount required is small. However, in this design, there is significant cost associated with the cathode support.

Single (button) cells were fabricated with Ni + MD-YSZ and Ni + MD-CSZ as the anode supports (~1 mm thick), with commercial YSZ as the electrolyte (~10 μm thick) and tested. The cell was tested with H_2/air at 800^{o}C. Maximum power density ~1.2 W/cm^2 was measured. No degradation in performance was noted over the duration of the test. With CSZ in the anode support, maximum power density of ~0.7 W/cm^2 was measured at 800^{o}C. Actually, this is an excellent result. This is because the cell was sintered at 1400^{o}C, and the anode support was fully dense. Thus, the only anode porosity was that occurred upon reduction of NiO to Ni, which is too small. In the future, the cells with CSZ will be sintered at lower temperatures to prevent excessive sintering of the anode –a truly desired situation from the standpoint of a single fire process. When sintered at a lower temperature, the performance should improve significantly. This is based on our prior work on NiO + YSZ based anodes.

Preliminary cost comparison of the MD process for a 30 kg/day batch was made with combustion synthesis and chemical co-precipitation (or sol-gel), on the basis of materials cost only. The analysis indicated that the cost of YSZ made by the MD process should be much lower than that by the other two processes, namely chemical co-precipitation and combustion synthesis.

EXPERIMENTAL

Theoretical Basis of the MD Process for the Synthesis of Nanosize Powders: The MD process is based on first synthesizing a precursor by a conventional process, wherein the precursor comprises of the desired constituents in the final product, and a fugitive constituent (or constituents), which can be removed by a leaching process. When the fugitive constituent has been removed, the remaining atoms/ions are beyond the bonding distance. They can thus rearrange to form the requisite stable structure, totally different from the initial one. Also, neither the precursor nor the final product is soluble in the liquid used. This thus leads to the formation of nanosize powders, since Ostwald ripening is precluded from occurring. The theoretical basis of the MD process is briefly described below.

Typical inter-atomic/inter-ionic potential can be given by Lennard-Jones type potential, given by

$$U(r) = -a/r^6 + b/r^{12} \tag{1}$$

Where $U(r)$ is the potential energy, r is the inter-atom/inter-ion distance, and a and b are constants. The negative term corresponds to the attractive term and the positive term corresponds to repulsive term. The equilibrium state corresponds to the minimum in $U(r)$, given by

$$\left(\frac{dU(r)}{dr}\right) = 0 = \frac{6a}{r_o^7} - \frac{12b}{r_o^{13}} \tag{2}$$

where the bond distance is given by

$$r_o = \sqrt[6]{2}\sqrt[6]{b/a} \tag{3}$$

If an external force is applied, the bond distance will be stretched. The maximum force that can be applied while maintaining bonding is given by

$$\left(\frac{d^2U(r)}{dr^2}\right) = 0 = -\frac{42a}{r_m^8} - \frac{156b}{r_m^{14}} \tag{4}$$

which corresponds to the maximum force that can be applied. The corresponding inter-atom/inter-ion distance is given by

$$r_m = \sqrt[6]{26/7}\sqrt[6]{b/a} \tag{5}$$

For values of $r \geq r_m$, the bond is destroyed. For the above potential function, it is seen that

$$r_m / r_o = \sqrt[6]{13/7} \approx 1.1$$

This means that if the distance between the constituent ions, which are to form the final product, in the precursor is greater than r_m for the final product, the new phase formed upon removal of the fugitive constituent, will have no relationship to the precursor phase and structure. As a consequence of this, it is expected that ZrO_2 formed from either $BaZrO_3$ or Na_2ZrO_3 would be the same, and not related to whether the starting precursor is $BaZrO_3$ or Na_2ZrO_3. Experimental work indeed has shown that both of these precursors can be used to form nanosize ZrO_2. Figure 4 shows a schematic.

(a): Preliminary Demonstration of the MD Process for the Synthesis of Very Fine YSZ and CSZ:

Synthesis of Y-$BaZrO_3$ Precursor: For the synthesis of Y-$BaZrO_3$, the following procedure was used. $BaCO_3$, Y_2O_3 and ZrO_2 were weighed and mixed in requisite proportions to form Y-doped $BaZrO_3$, such that Y to Zr ratio was 8:92. Powder mixtures were calcined to form the precursor.

Synthesis of Y-Na_2ZrO_3 Precursor: For the synthesis of Y-Na_2ZrO_3, the following procedure was used. Na_2CO_3, Y_2O_3 and ZrO_2 were weighed and mixed in requisite proportions to form Y-doped Na_2ZrO_3, such that Y to Zr ratio was 8:92. Powder mixtures were calcined to form the precursor. In future work, NaOH will be used instead, since it can be recycled.

Synthesis of Ca-Na_2ZrO_3 Precursor: CSZ is a low-cost alternative to YSZ in the anode support of an anode-supported cell. A potential precursor is Ca-doped Na_2ZrO_3. In order to synthesize Ca-Na_2ZrO_3, mixtures of $CaCO_3$, Na_2CO_3 and ZrO_2 were made in requisite proportions and calcined at 1150°C for 2 hr.

Leaching of Y-$BaZrO_3$ with HNO_3 and Y-Na_2ZrO_3, and Ca-Na_2ZrO_3 with Water: Powder sample of Y-$BaZrO_3$ was boiled in dilute HNO_3 for 2 hr, the powder was washed until the pH was close to 7. The powder was subsequently dried, and XRD traces were obtained. In the case of Y-Na_2ZrO_3 and Ca-Na_2ZrO_3, no acid is needed. The required reagent is simply water. Powder samples were boiled in water and washed.

After the initial work, most of the work was done with Na_2ZrO_3 as the precursor.

(b): Preliminary Studies on the Sintering Behavior of YSZ and CSZ made by the MD Process:

Sintering of YSZ Powder made by the MD Process: Samples of YSZ powder were milled for a short time, pressed, and sintered in air at temperatures as high as 1450°C. In these initial experiments, the emphasis was placed on determining if the powders can be sintered. No special precautions were taken to de-agglomerate the powder samples. In future work, dispersants will be added to ensure de-agglomeration, which should allow sintering at lower temperatures, hopefully as low as 1200°C. Various types of dispersants are possible; those based on steric hindrance or those based on electrostatic interactions.

Sintering of CSZ Powder made by the MD Process: Samples of CSZ powder made by the MD process were milled for a short time, pressed, and sintered in air. In these initial experiments, the emphasis was placed on determining if the powders can be sintered. Density greater than 95% of theoretical was obtained at 1400°C. No special precautions were taken to de-agglomerate the powder samples. Sintering of CSZ made by a conventional solid-state process requires typically 1600°C.

Sintering of NiO + YSZ made by the MD Process for a Prospective Anode Support: Nickel oxide, NiO, was mixed with the YSZ made by the MD process (70 vol.% NiO + 30 vol.%

YSZ). Discs were die-pressed and sintered in air at 1450°C. Subsequently, the sintered anode support was heated to 800°C in an atmosphere containing 10% H_2 + 90% N_2, to reduce NiO to Ni.

(c): Preliminary Studies on the Development of a Rapid Process for Washing the YSZ or CSZ Powder made by the MD Process:

Washing by Flocculation: In the synthesis of very fine powders, it is necessary that the washing/cleaning step be as rapid as possible. If at all possible, the approach should be to avoid filtering, since this adds cost to the overall process [5].

The approach selected here is to adjust the pH in such a way that the powder readily settles down (soft floccules). This can occur provided the zeta potential is close to zero. In the Phase I proposal, it was reported that in the case of YSZ, flocculation and settling occurs readily in low pH (acidic) and high pH (basic) conditions. For a process based on Na_2ZrO_3, it is convenient that the YSZ (or for that matter CSZ) powder formed readily settles down in high pH forming relatively loose agglomerates. These can be readily broken down, by adjusting the pH so that de-flocculation occurs.

The approach to cleaning the powder is as follows. Immediately after boiling Y-Na_2ZrO_3 or Ca-Na_2ZrO_3 in water, the contents are allowed to cool. The powder readily settles down in a few minutes, as the pH is about ~11-12, by virtue of the NaOH present in solution. Suppose the original height of the suspension is H. After settling, suppose most of the YSZ (or CSZ) powder formed is confined to a powder bed of height h, where obviously $h < H$. In this powder bed of height h, there is some sodium, in the liquid portion of this region. Suppose the concentration of sodium in the liquid is C_{Na}^{o}, which depends on the ratio of precursor (Na_2ZrO_3) to water used in the original boiling step. This implies that if one were to decant the liquid corresponding to $(H - h)$, the concentration of sodium remaining in the powder, if one were to simply dry it without any washing, will be given by

$$C_{Na} \sim C_{Na}^{o}\left(\frac{h}{H}\right) \tag{6}$$

If $h << H$, a significant purification (removal of NaOH) can be achieved, in the decanting step. Clearly, the remaining sodium content, as impurity, is still high, and further washing/cleaning is required. This can be achieved by first adding a dilute aqueous acid solution, to adjust pH to near neutral (~7), to disperse, followed by adjusting pH in the basic range by adding a dilute NH_4OH[3] solution after the decanting step. As the pH is now in the basic range, once again flocculation and settling can be achieved (actually within a few minutes), and once again the liquid column can be removed by decanting. If this process is repeated n times, the level of purification achieved will be given by

$$C_{Na}(n) \sim C_{Na}^{o}\left(\frac{h}{H}\right)^{n} \tag{7}$$

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[3] The amount of NH_4OH required is very small, since its purpose to adjust pH, and is not used as a reactant, which is the case in co-precipitation.

Depending upon the ratio $\left(\frac{h}{H}\right)$, one can repeat the washing until a desired level of purification is achieved. The last step is the removal of the powder bed from the reactor and heating above ~100°C to remove water and NH_4OH. This should lead to clean, high purity, very fine powder. As the process is a low temperature one, polymeric additives can readily introduced in the last step to ensure that particles are coated with suitable dispersants – the ones which usually operate on the steric hindrance concept.

(d): Preliminary Work on the Fabrication and Electrochemical Testing of an Anode-Supported Cell made with Anode Support Comprising YSZ and CSZ made by the MD Process:

NiO was mixed with YSZ made by the MD process to form an anode support composition. A disc of approximately 1 mm thickness was pressed. A layer of NiO + YSZ (commercial, co-precipitated) was deposited by slurry coating. Thickness of this layer was about 25 microns. On top of this layer, a layer of YSZ (commercial, co-precipitated) was slurry coated, which after sintering was ~10 microns in thickness. The cell was sintered at 1450°C in air. Subsequently, porous LSM + YSZ (commercial, co-precipitated) cathode interlayer was applied (thickness ~25 microns), and a porous layer of LSM (~50 microns). A schematic of such a cell is shown in Figure 1(b). The cell was fired again at 1150°C. The cell performance was electrochemically evaluated.

Similarly, NiO was mixed with CSZ made by the MD process to form an anode support composition. A disc of approximately 1 mm thickness was pressed. A layer of NiO + YSZ (commercial, co-precipitated) was deposited by slurry coating. Thickness of this layer was about 25 microns. On top of this layer, a layer of YSZ (commercial, co-precipitated) was slurry coated, which after sintering was ~10 microns in thickness. The cell was sintered at 1400°C in air. Subsequently, porous LSM + YSZ (commercial, co-precipitated) cathode interlayer was applied (thickness ~25 microns), and a porous layer of LSM (~50 microns). A schematic of such a cell is shown in Figure 1(b). The cell was fired again at 1150°C. The cell performance was electrochemically evaluated.

(e): Preliminary Cost Analysis and Comparison with Other Processes for the Synthesis of Fine YSZ Powders:

Preliminary cost analysis, on the basis of raw materials cost only, was carried out for a 30 kg/day batch of YSZ. A comparison was also made with chemical co-precipitation and combustion synthesis processes.

RESULTS AND DISCUSSION

(a): Preliminary Demonstration of the MD Process for the Synthesis of Very Fine YSZ and CSZ; Sintering Studies:

Synthesis of Y-$BaZrO_3$,Y-Na_2ZrO_3 and Ca-Na_2ZrO_3: Figures 5(a) and 5(b) show XRD traces of the as-synthesized Y-$BaZrO_3$. Figure 6 shows an XRD trace of Y-Na_2ZrO_3. All peaks could be identified with respective JCPDS files. Figure 7 shows XRD traces of Ca-doped Na_2ZrO_3 precursors with various amounts of Ca doping. Note that over the range of compositions, CaO appears to have been fully dissolved in Na_2ZrO_3.

Synthesis of Nanosize YSZ by MD: Figure 8 shows XRD traces of YSZ formed by MD using Y-$BaZrO_3$ and Y-Na_2ZrO_3 precursors. Note that both traces are virtually identical, and totally different from those of the precursors. Note also that peaks are indeed very broad consistent with very fine (nanosize) crystallite size. The peak positions are consistent with those of cubic YSZ.

TEM Characterization: Figure 9 shows a bright field TEM image of the nanosize YSZ formed by the MD process. The crystallite size is ~5 nm. The agglomerate size in this TEM image is about 50 to 200 nm. The agglomerates are soft, and can be broken with relative ease, down to a few tens of nm (actually by simple dispersion).

Synthesis of Nanosize CSZ by MD: Using Ca-Na_2ZrO_3 as a precursor, nanosize CSZ was synthesized. Figure 10 shows XRD traces of: (a) Ca-Na_2ZrO_3 leached (boiled) in water (—). (b) Ca-Na_2ZrO_3 acid-washed (—). (c) Y-Na_2ZrO_3 boiled in water (—). Note that all of the XRD traces are identical – and all correspond to cubic zirconia. The CSZ powder formed was subsequently heat-treated at several temperatures. The corresponding XRD traces are given in Figure 11. Peaks corresponding to cubic zirconia are clearly seen in the figure. In all subsequent work, water was used as the leaching agent.

Sintering of YSZ Powder made by the MD Process: Figure 12 shows an SEM micrograph of a sample sintered at 1400^{o}C for 2 hr. Note the formation of an equiaxed microstructure with high sintered density.

Sintering of CSZ Powder made by the MD Process: CSZ samples were sintered over a range of temperatures between 1400^{o}C and 1600^{o}C. Figure 13 shows an SEM micrograph of a sample of CSZ (Ca = 0.2) sintered at 1600^{o}C. No special precautions were taken to ensure that the powder was de-agglomerated. The fully dense microstructure seen in the above micrograph, with a very large grain size, suggests that it should be possible to achieve good density at much lower temperatures. As stated earlier, the objective was to see if the powders can be sintered to good density, with minimal of treatment after the MD process.

Anode Support made with NiO and YSZ (made by the MD Process): An SEM micrograph of the reduced anode (NiO converted to Ni) support is shown in Figure 14. Note the uniform microstructure and porosity.

Conductivity of YSZ made by the MD process: Four probe DC conductivity was measured with platinum electrodes. The data are given in Figure 15. The conductivity is comparable to many commercial YSZ materials, especially those made by solid-state processes. No special precautions were taken to clean the powders. In the future, the washing/decanting procedure described will be used, which should lead to conductivity comparable to the best, chemically co-precipitated powders.

(b): Preliminary Studies on the Development of a Rapid Process for Washing the YSZ or CSZ Powder made by the MD Process:

Washing by Flocculation: Preliminary work has been carried out to determine the degree to which settling occurs, and the rapidity with which this occurs. Figure 16 shows a suspension of YSZ powder in a column of water, whose height H is about 3 inches. After adjusting the pH, the powder readily settled down in a few minutes. For this experiment, to allow complete settling (so that a clear column of liquid can be seen), the measuring cylinder was left undisturbed for 3 hr. In actual practice, the time required is much shorter; a few minutes. In such a case, the column will look milky, yet will have a very small amount of powder suspended, rest having settled down. In order to save time, one can dispense with the milky column, in which case one would lose a very small fraction of the powder. The settled height, h, in this experiment was measured to be ~1/64th of an inch. This gives $\left(\frac{h}{H}\right)$ ratio of ~0.0052. Thus, the degree of purification achieved in n washing/settling/decanting steps (no filtering required) is $(0.0052)^n$. It is readily seen that excellent purification can be achieved in about three washing/cleaning steps. The actual number of steps required will depend upon the initial proportion of water to precursor, which determines $\left(\frac{h}{H}\right)$. Also, the preceding assumes the container used for settling/decanting is cylindrical with a fixed cross-sectional area. If such is not the case, the $\left(\frac{h}{H}\right)$ is to be replaced by $\left(\frac{v}{V}\right)$, where V is the initial volume of the suspension, and v is the volume of the settled powder bed.

(c): Preliminary Work on the Electrochemical Testing of an Anode-Supported Cell made with Anode Support Comprising YSZ or CSZ made by the MD Process:

Figure 17 shows voltage and power density vs. current density plots for the very first cell made using YSZ made by the MD process in the anode. In this initial trial, there were a few pinholes in the YSZ film (which was actually made from co-precipitated powder, from a commercial source). As such the OCV is lower than had there been no pinholes. Nevertheless, it can be seen that the cell ASR is quite low (~0.15 Ωcm^2 at 800°C). The corresponding maximum power density is ~1.2 W/cm^2. Had there been no pinholes, and the OCV had been ~1.15 V, the maximum power density would have been ~1.9 W/cm^2. Additional cells are being fabricated. Care is being taken to ensure that no pinholes develop.

Figure 18 shows voltage and power density vs. current density plots for the very first cell made using CSZ made by the MD process in the anode. As seen in the figure, the OCV is 1.15 V, which is excellent, and indicates that there were no pinholes. The cell was sintered at 1400°C, which actually sintered too well. As a result, the anode porosity after reduction was not high enough (about ~25%). For this reason, the power density is lower, about 0.7 W/cm^2. This can be easily corrected, by lowering the sintering temperature. This is also desired from the standpoint of one-step processing, with only one high temperature firing step required.

Additional cells are being prepared in which sintering will be achieved at ~1250°C. This will allow the fabrication of cells with cathode/electrolyte/anode tri-layer in a single firing step.

Sintering of Large Cell with MD-CSZ in the anode: Figure 19 shows a photograph of a cell made with MD CSZ in the anode. The cell is over 3 inches in diameter. This cell was made by die pressing and sintering. In the future, a tape casting process will be developed.

<u>(d): Preliminary Cost Analysis and Comparison with Other Processes for the Synthesis of Fine YSZ Powders:</u>

<u>Estimation of the Cost of 8YSZ Powder made by the MD Process at an Annual Production Capacity of 10,000 kg (~30 kg daily production):</u> A comprehensive analysis of the cost of production of nanosize 8YSZ should include the following cost components:

Raw materials
Energy, materials, and labor costs of production
Depreciation of the plant and capitalized equipment
Maintenance
Interests and fees on loans
Profit

This report covers an analysis of the costs of raw materials required to produce 8YSZ ($Y_{0.148}Zr_{0.852}O_{1.926}$) via the synthesis and decomposition of $Na_2Y_{0.148}Zr_{0.852}O_{2.926}$ as described in the following two reactions:

$$NaOH + 0.074\ Y_2O_3 + 0.852ZrO_2 \rightarrow Na_2Y_{0.148}Zr_{0.852}O_{2.926} \qquad (a)$$

and

$$Na_2Y_{0.148}Zr_{0.852}O_{2.926} + H_2O \rightarrow Y_{0.148}Zr_{0.852}O_{2.926} + 2NaOH \qquad (b)$$

A quantitative flow diagram, shown in Figure 19, was constructed based on the mass balance of the above equations and a daily production rate of 30 kg of 8YSZ. It should be noted that a total amount of 1.98 kg of NaOH is required in the production of 30 kg of 8YSZ. As indicated in Figure 19, it is assumed here that approximately 90 % of NaOH (1.78 kg) will be recycled by concentration and drying of the liquid separated in the decomposition and the decanting step. The balance of 0.2 kg of NaOH is added to the recovered amount to make-up for losses during processing. The exact amount of lost NaOH will depend on the design of the plant and process layout. But the total raw material costs are not likely to change significantly. The flow diagram for CSZ is essentially the same.

Table II lists the raw materials, vendors who quoted the prices, catalog number or grade of the material, material purity, batch size, and cost per batch. The vendors and material grades were selected on the basis of costs for a purity of 99 %. Y_2O_3, however, was available at a purity of 99.9 % and this was the most expensive among the raw materials. The cost of raw materials from Table II and the material balance of Figure 20 yields a raw materials cost of \$192.33 per 30 kg of 8YSZ or \$6.41/kg of 8YSZ. The water required for the decomposition of Y-Na_2ZrO_3 and the leaching of NaOH is not treated as a raw material, but as a material required in the production. As indicated above, raw materials cost is one of several cost elements that are listed above. Each one of these cost elements must be assessed to get the total cost of the 8YSZ powder.

Cost Comparison between Chemical Co-Precipitation, Combustion Synthesis and Molecular Decomposition, on the Basis of Materials Cost: As stated earlier, a comprehensive cost analysis will require number factors to be addressed. However, a preliminary estimate can be obtained on the basis of raw materials cost. Preliminary cost analysis for the MD process is given above. In what follows, illustrative calculation of the costs of the three processes, Molecular Decomposition, Chemical Co-Precipitation (with two types of precursors; nitrates and chlorides) and Combustion Synthesis are given on the basis of materials cost only. Quotes were obtained from vendors, typically for a 1000 kg batch. Tables II, III, IV and V give the results of calculations, based on vendor quotes. Table VI gives cost comparison, again on the basis of raw materials cost. It is readily seen that the materials cost for the MD process, on a per kg basis, is the lowest. Somewhat surprising was the high cost of NH_4OH quoted, which is a typical reagent used for co-precipitation. The high cost of the raw materials in the case of chemical co-precipitation and combustion synthesis, drives the cost high. The actual cost may be even higher. It is not clear, for example, if the cost of YCl_3 of \$6.70/kg in large batches is correct. This needs to be verified. Nevertheless, it is clear that the cost of the powder made by co-precipitation is high due to the raw materials cost. Quotes were obtained for 30 and 100 kg batches of YSZ from three sources. These are given in Table VII. Only the price quoted by one vendor was relatively modest. The powder, in this case, however was made by solid-state calcination – not using either co-precipitation or combustion synthesis. Compacts made could not be sintered to a high enough density at 1450^{o}C using this powder. As is clearly seen, the cost of commercial YSZ is quite high. Based on the preliminary cost analysis conducted here, it is apparent that the high cost of chemical co-precipitation and combustion synthesis is related to high materials cost. At the present time, it is not clear if there is a significant economy of scale – in tonnage quantities. The costs will have to come down by an order of magnitude, before these processes can be cost-effective. It is nevertheless clear that the cost of the MD process will be substantially lower than the other processes.

Table VI also gives the cost of YSZ/kW for an anode-supported stack, based on the following assumptions: (1) The operating power density is 0.5 W/cm^2 at an operating temperature of 750^{o}C, which is an ambitious value. (2) The anode thickness is 0.5 mm, and anode contains ~40 vol.% YSZ. (3) The cell active dimension (cathode) is 15 cm x 15 cm, and the actual outer dimensions are 16 cm x 16 cm. The net active area required per kW is 2000 cm^2, which corresponds to 9 cells. The actual cell area (including the border area) is 2304 cm^2/kW. The corresponding anode volume is 115.2 cm^3, which is equivalent to ~695 gm (assuming a YSZ density of 6.03 gm/cm^3.) That is, the actual amount of YSZ in the anode is ~0.695 kg. We will assume materials loss during the processing to be ~10%. This would mean the YSZ material required for the anode ~760 gm. or ~0.76 kg. per kW. The actual amount will be higher, as this does not include the cost of YSZ for the electrolyte or the cathode (assuming a composite cathode comprising LSM + YSZ). It is evident that cost of YSZ/kW using chemically co-precipitated process is expected to be rather high, and may not meet aggressive cost targets set by SECA. However, the YSZ or CSZ made by the MD process should be able to achieve SECA cost targets.

Table II. Vendors, batch sizes, and costs per batch of raw materials used in the manufacture of nanosize 8YSZ via the synthesis and decomposition of Y-Na_2ZrO_3.

Raw Materials	Vendor	Material Grade	Purity (%)	Batch Size (kg)	Unit Cost ($/kg)
Zirconia (ZrO_2)	Unitec		99	907.2	4.19
Yttria (Y_2O_3)	American Elements	Y-OX-01	99.9	1000	20.0
Sodium Hydroxide NaOH	Fisher Scientific	S318-50	97	50	7.35

Table III. Costs of Raw Materials for Combustion Synthesis using Nitrates and Glycine.

Raw Materials	Vendor	Material Grade	Purity	Batch Size (kg)	Unit Cost ($/kg)	Unit Cost For the Oxide/kg.
Zirconyl Nitrate Hexahydrate ($ZrO(NO_3)_2.6H_2O$)				1000	7.77[♣]	21.39 For ZrO_2
Yttrium Nitrate Pentahydrate ($Y(NO_3)_3.5H_2O$)	Stanford Materials		99.9	1000	7.82	25.26 For Y_2O_3
Glycine (NH_2CH_2COOH)	Alfa Aesar		98.5	1000	13.50	

Table IV. Costs of Raw Materials for Synthesis by Co-precipitation using Nitrates.

Raw Materials	Vendor	Material Grade	Purity	Batch Size (kg)	Unit Cost ($/kg)	Unit Cost For the Oxide/kg.
Zirconyl Nitrate Hexahydrate ($ZrO(NO_3)_2.6H_2O$)				1000	7.77[♣]	21.39 For ZrO_2
Yttrium Nitrate Pentahydrate ($Y(NO_3)_3.5H_2O$)	Stanford Materials		99.9	1000	7.82	25.26 For Y_2O_3
Ammonium Hydroxide (NH_4OH)	Alpha Aesar			35	135.54	

[♣] Not vendor quote; estimated from small batch (1 kg) cost.

Table V. Costs of Raw Materials for synthesis by co-precipitation using chlorides.

Raw Materials	Vendor	Material Grade	Purity	Batch Size (kg)	Unit Cost ($/kg)	Unit Cost for the oxide per kg.
Zirconyl Chloride Octahydrate ($ZrOCl_2.8H_2O$)	Alpha Aesar			1000	3.84[♦]	10.04 For ZrO_2
Yttrium Chloride (YCl_3)	Stanford Materials		99.9	1000	6.70	11.58 For Y_2O_3
Ammonium Hydroxide (NH_4OH)	Alpha Aesar			35	135.54	

Table VI: Comparison of the three processes. Cost/kg and cost/kW.

Process	Zr Source	Y Source	Other Reactants	Total Cost ($/kg)	Cost/kW
Molecular Decomposition	ZrO_2 (0.863 kg)	Y_2O_3 (0.137 kg)	NaOH (recycled)	6.41	$4.86
Combustion Synthesis	$ZrO(NO_3)_2.6H_2O$ (2.376 kg)	$Y(NO_3)_3.5H_2O$ (0.444 kg)	NH_2CH_2COOH (0.617 kg)	30.26	$23.00
Co-precipitation	$ZrO(NO_3)_2.6H_2O$ (2.376 kg)	$Y(NO_3)_3.5H_2O$ (0.444 kg)	NH_4OH (0.619 kg)	105.77	$80.39
Co-precipitation	$ZrOCl_2.8H_2O$ (2.256 kg)	YCl_3 (0.237 kg)	NH_4OH (0.619 kg)	94.10	$71.52

Table VII: Prices of YSZ quoted by vendors for a 30 kg and 100 kg orders.

Name of the Vendor	Trademark for 8YSZ	Quoted price per kg for a 30 kg batch	Quoted price per kg for a 100 kg batch.	Date of quote
Tosoh USA, Inc.	TZ-8Y	$127.00	$118.00	May 27, 2003
American Vermiculite	HSY-8.0	$77.00	$77.00	May 27, 2003
Fuel Cell Materials Division of NexTech Materials	YSZ8-CT	$114.00	$108.0	May 23, 2003
Praxair Surface Tech. Specialty Ceramics		$50.00	$30.00	May 30, 2003

[♦] Not vendor quote; estimated from small batch (1 kg) cost.

CONCLUSIONS

The principal objective of the work proposed in Phase I was to demonstrate the synthesis and densification characteristics of very fine (nanosize) YSZ made by a novel molecular decomposition (MD), a potentially low-cost process. There is reason for optimism that the YSZ powder made by the MD process will be considerably lower in cost, compared to other methods of producing fine powders, such as chemical co-precipitation and combustion synthesis. This is because the raw materials for the MD process are oxides, which are much lower in cost compared to nitrates used in combustion synthesis, or chlorides or nitrates used in chemical co-precipitation. Preliminary cost analysis, based on the materials cost alone, is consistent with this expectation. Specifically, the cost of YSZ based on these two other processes was estimated to be several times that using the MD process.

In addition to the stated objectives of developing very fine YSZ powders by the MD process, other significant results were obtained. These included the fabrication and testing of an anode-supported button cell using YSZ and CSZ made by the MD process as a constituent in the anode. At 800^{o}C, the maximum power density of the cell with MD-YSZ in the anode was about 1.2 W/cm^2. The other significant achievement was the synthesis of calcia-stabilized zirconia (CSZ) by the MD process. The potential use of CSZ in the anode support is expected to have a beneficial effect of further lowering the cost. Single cell performance was ~0.7 W/cm^2. This cell was sintered at 1400^{o}C, and was still very dense. In the future, the sintering temperature will be lowered. This will not only improve performance, but will facilitate the development of a single step firing process. The specific results of Phase I are as follows.

1) Very fine YSZ was made using the MD process, with Y-Na_2ZrO_3 precursor and water as the leaching agent.
2) Very fine CSZ was made using the MD process, with Ca-Na_2ZrO_3 precursor and water as the leaching agent.
3) An approach was developed for rapid washing of CSZ and YSZ powders made by the MD process.
4) Dense samples of YSZ and CSZ were made using the powder made by the MD process.
5) Button cells were made using the YSZ and CSZ powders made by the MD process as a constituent in the anode support of an anode-supported cell. Maximum power density of ~1.2 W/cm^2 at 800^{o}C was demonstrated with MD-YSZ in the anode.
6) Even at a laboratory scale, the process readily makes greater than 100 g at a time.
7) Preliminary cost analysis on the basis of materials cost was conducted. The analysis indicated that the cost of YSZ powder made by the MD process should be much lower than that made by either chemical co-precipitation (or sol-gel) or combustion synthesis. The high cost of commercially available YSZ is consistent with our analysis.

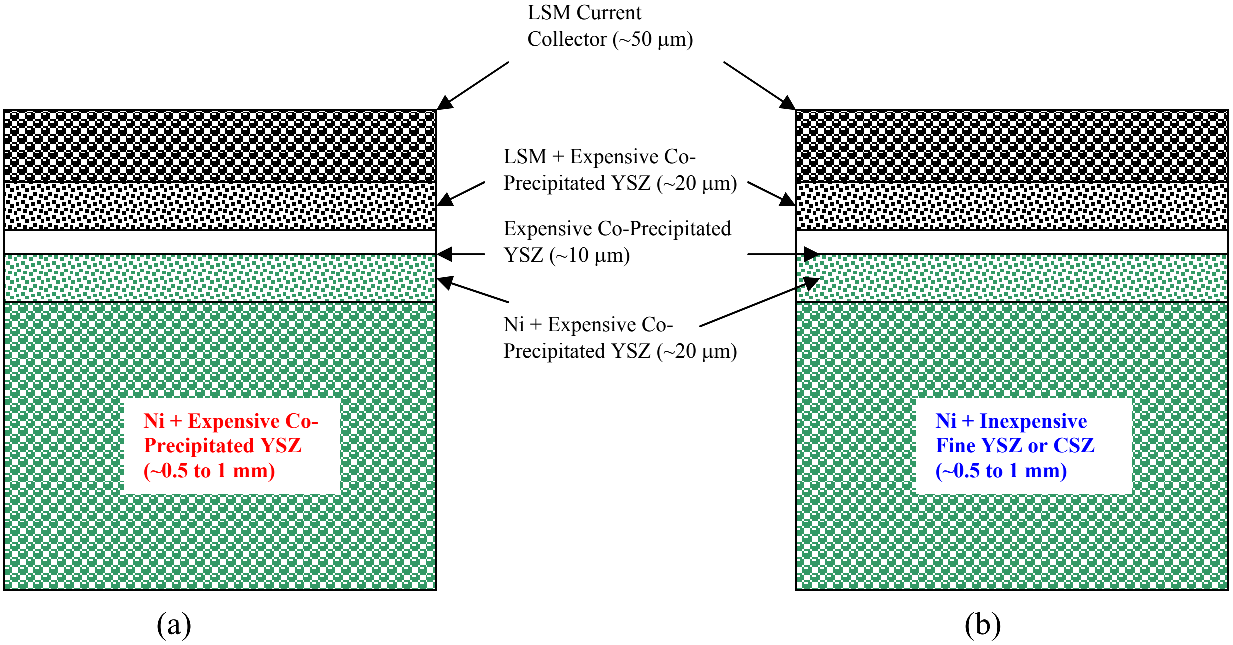

Figure 1: Schematics of anode-supported cells: (a) Currently used approach in many designs. The cost is high due to expensive YSZ in the thick anode support. (b) Proposed approach: A low-cost, yet sinterable, active YSZ is used in the anode support. The zirconia in the anode support can also be calcia-stabilized zirconia (CSZ), which should further lower cost.

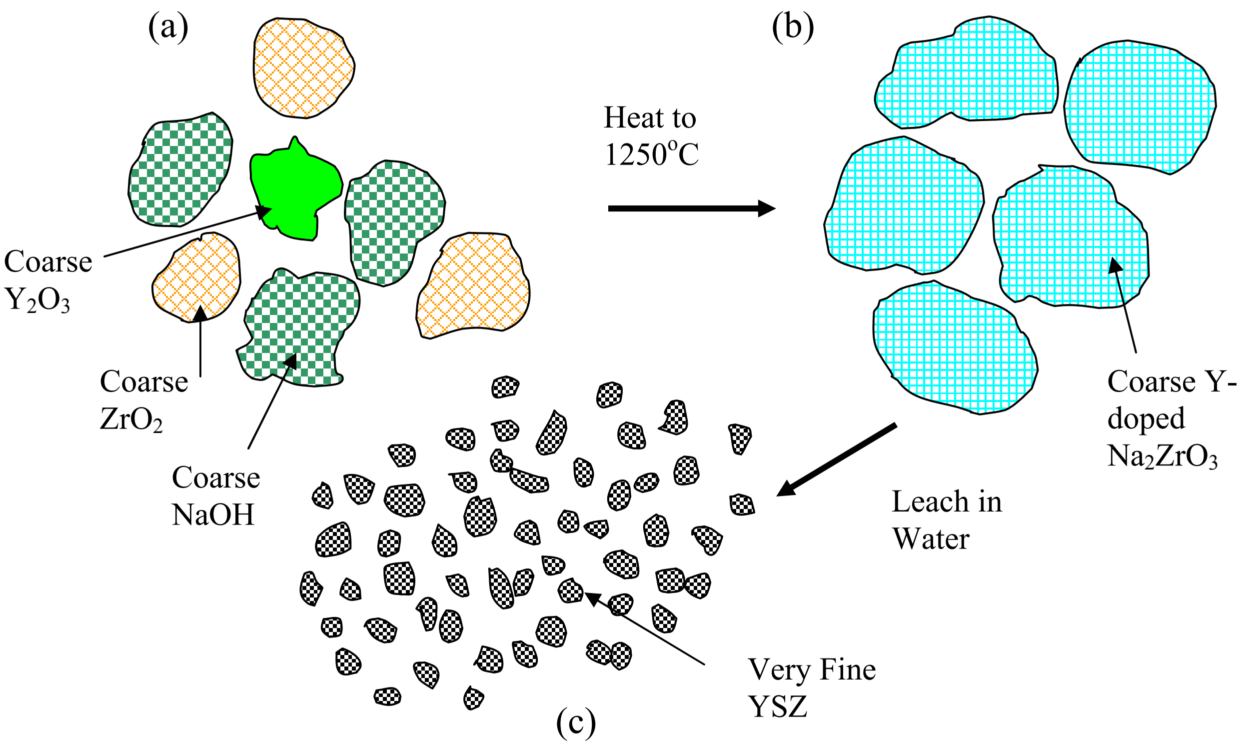

Figure 2: A schematic of the MD process: (a) Mixing of raw materials; Y_2O_3, ZrO_2, and NaOH, all of particle sizes in the micron to tens of microns range. (b) Calcination to form Y-Na_2ZrO_3, of several tens of microns in size. (c) Leaching in water to form nanosize YSZ.

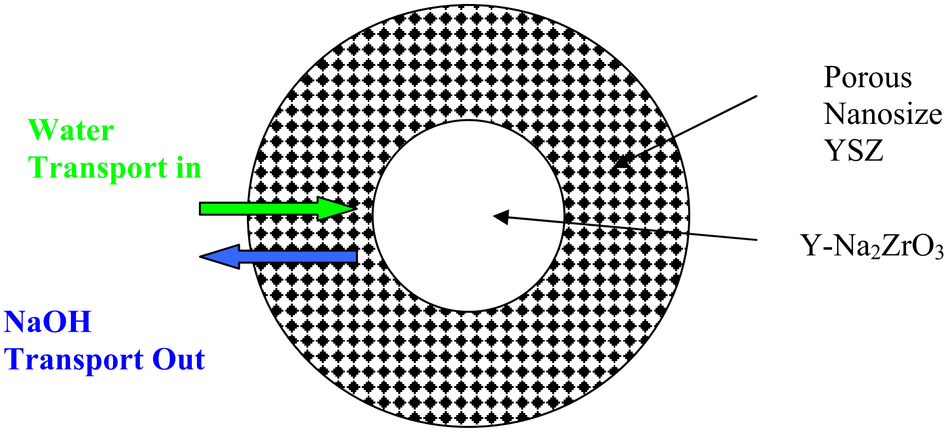

Figure 3: A schematic showing the mechanics of leaching of microscopic (or macroscopic) particles of Y-Na_2ZrO_3, leading to the formation of nanosize YSZ.

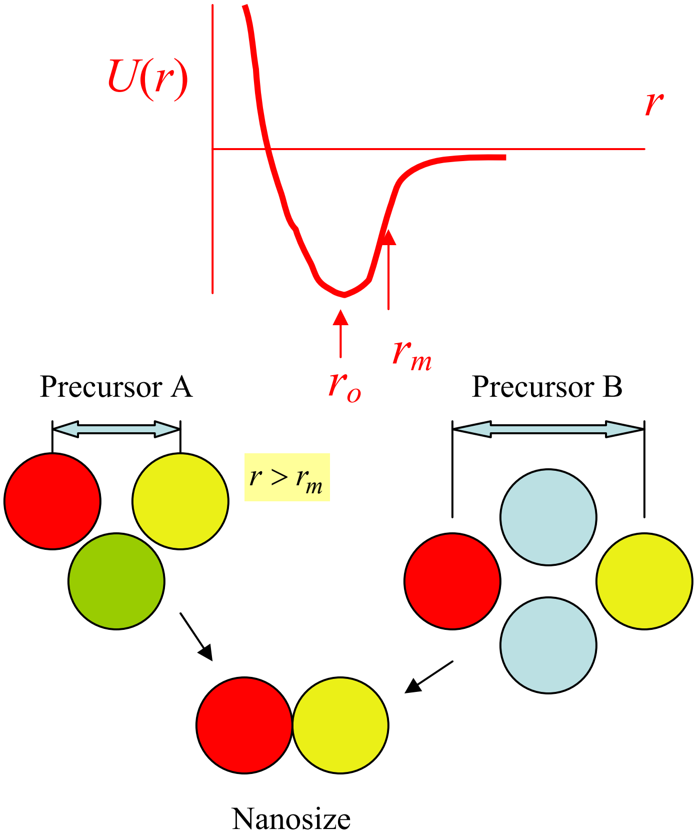

Figure 4: A schematic showing the plot of potential energy, $U(r)$, vs. r. The minimum occurs at $r = r_o$. The inflexion occurs at $r = r_m$. As long as the distance between the final constituent ions (ions which form the final product, here red and yellow) in the precursor is greater than r_m of the final product, there is no relationship between the structure of the final product and the precursor. Thus, as long as this condition is satisfied, both precursor A and B give the same final product. Indeed, both $BaZrO_3$ and Na_2ZrO_3 give the same final, nanosize ZrO_2.

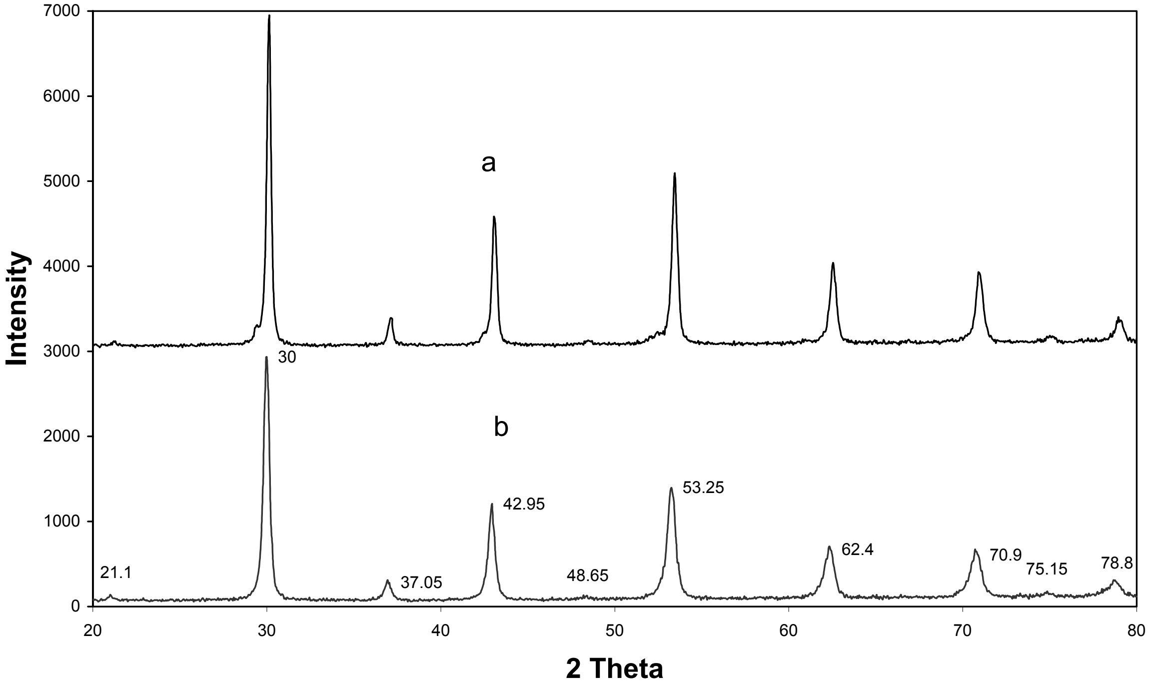

Figure 5: XRD traces of Y-doped $BaZrO_3$. (a) Starting powders were $BaCO_3$, Y_2O_3 and ZrO_2. (b) Starting powders were $BaCO_3$ and YSZ.

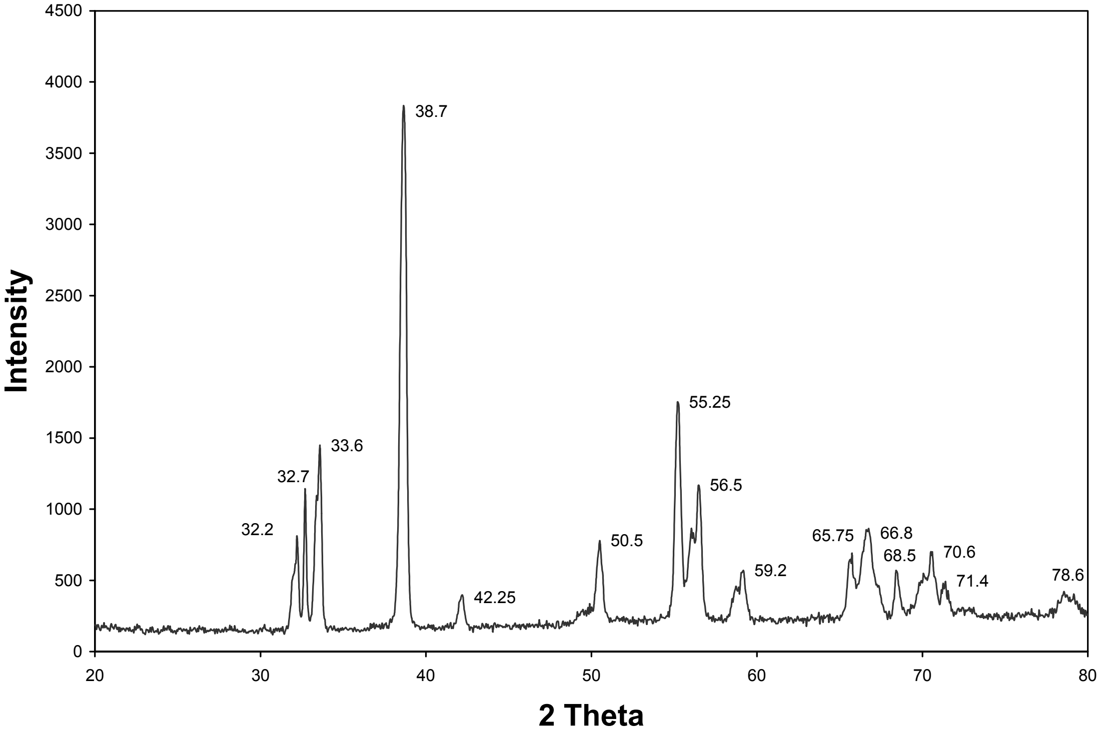

Figure 6: An XRD trace of Y-Na_2ZrO_3. All peaks are identified with JCPDS file for Na_2ZrO_3.

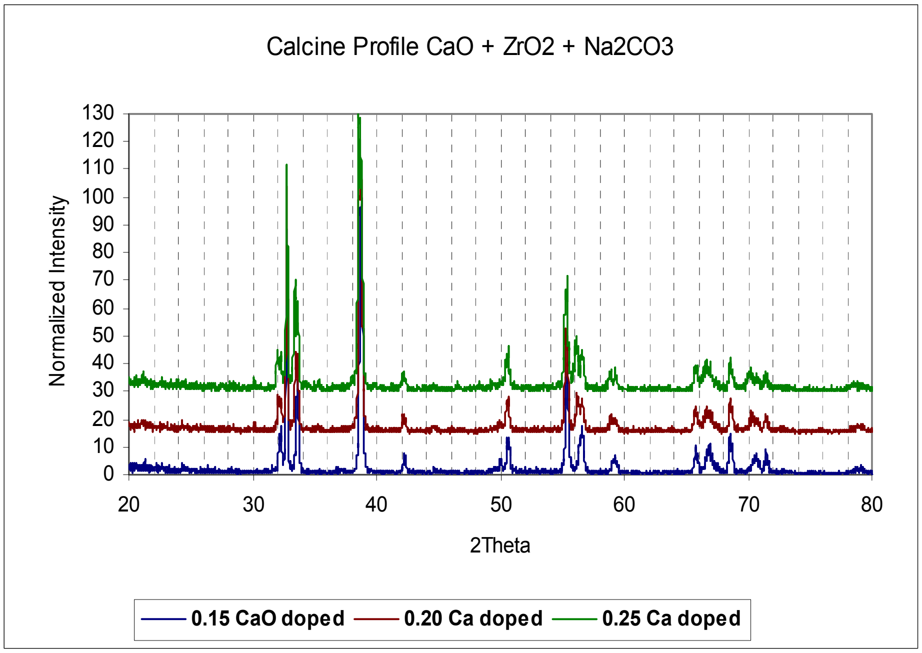

Figure 7: XRD traces of Ca-doped Na_2ZrO_3 precursors with various amounts of Ca doping. Note that over the range of compositions, CaO appears to have been fully dissolved in Na_2ZrO_3. All peaks are identified with JCPDS file for Na_2ZrO_3.

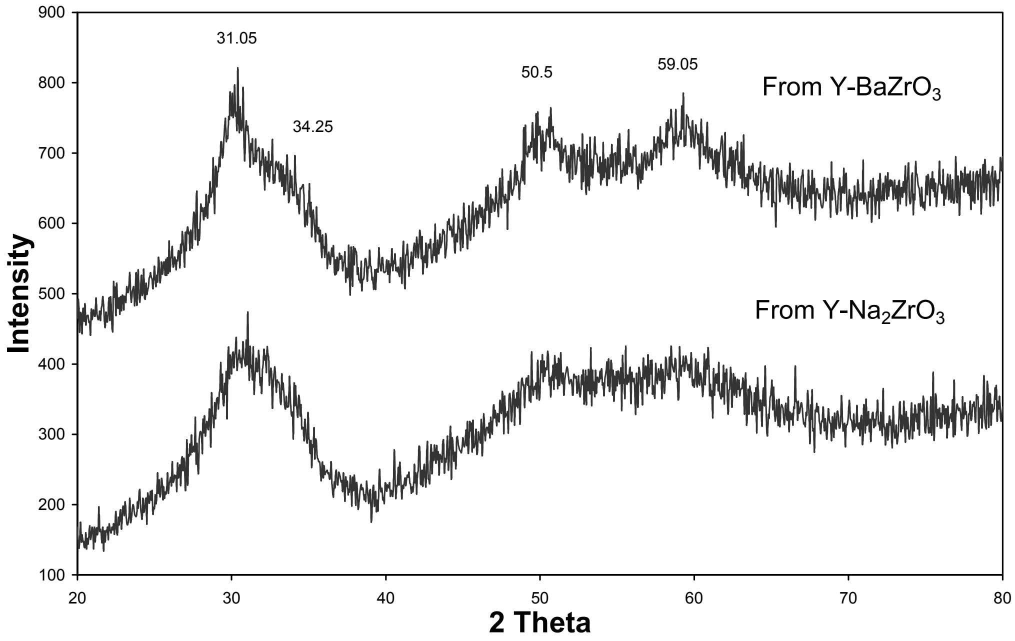

Figure 8: XRD traces of nanosize YSZ formed from Y-$BaZrO_3$ and Y-Na_2ZrO_3 precursors. Note that both traces are virtually identical, and totally different from those of the precursors. Note also that peaks are indeed very broad consistent with very fine (nanosize) crystallite size. The peak positions are consistent with those of cubic YSZ.

Figure 9: A bright field TEM image of the nanosize YSZ formed by the MD process. The crystallite size is ~5 nm. The agglomerate size in this TEM image is about 50 to 200 nm. The agglomerates are soft, and can be broken with relative ease, down to a few tens of nm.

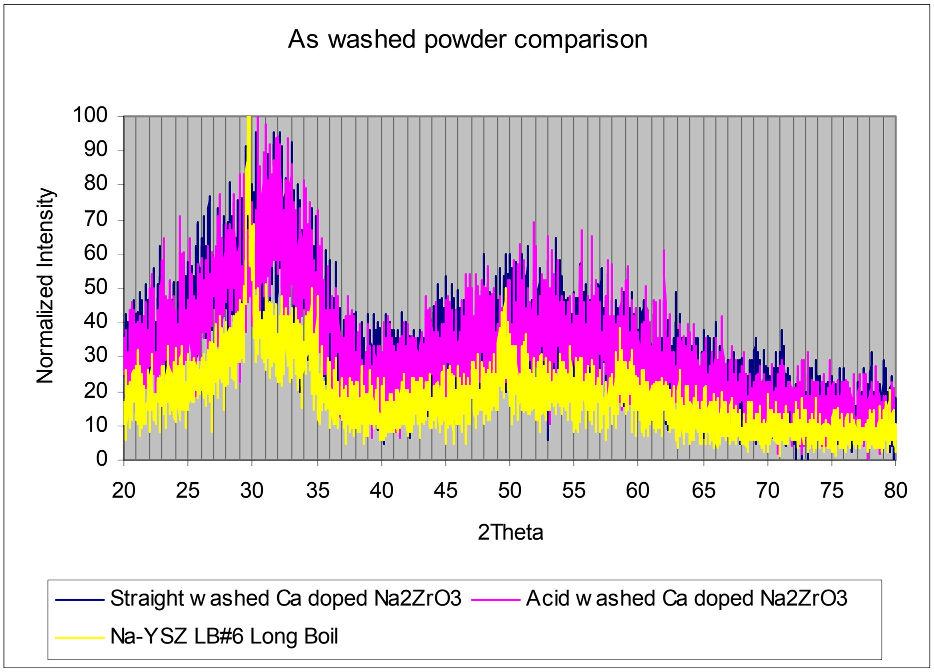

Figure 10: XRD traces of: (a) Ca-Na_2ZrO_3 leached (boiled) in water (——). (b) Ca-Na_2ZrO_3 acid-washed (——). (c) Y-Na_2ZrO_3 boiled in water (——). Note that all of the XRD traces are identical –and all correspond to cubic zirconia.

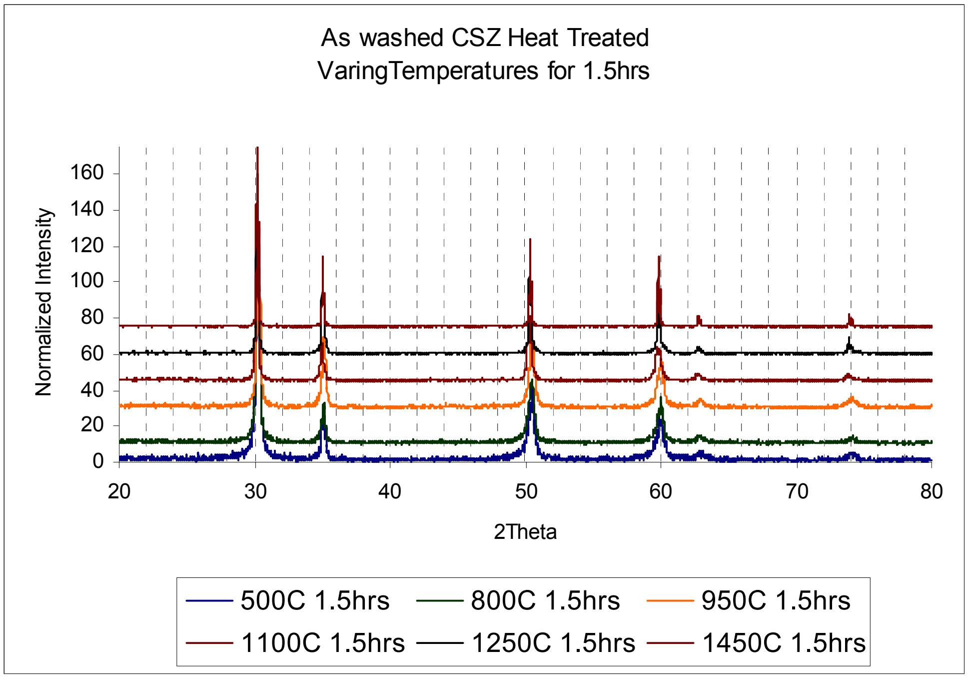

Figure 11: XRD traces of nanosize CSZ after thermal treatment at temperatures as high as 1450°C. Note that the XRD traces are consistent with cubic zirconia.

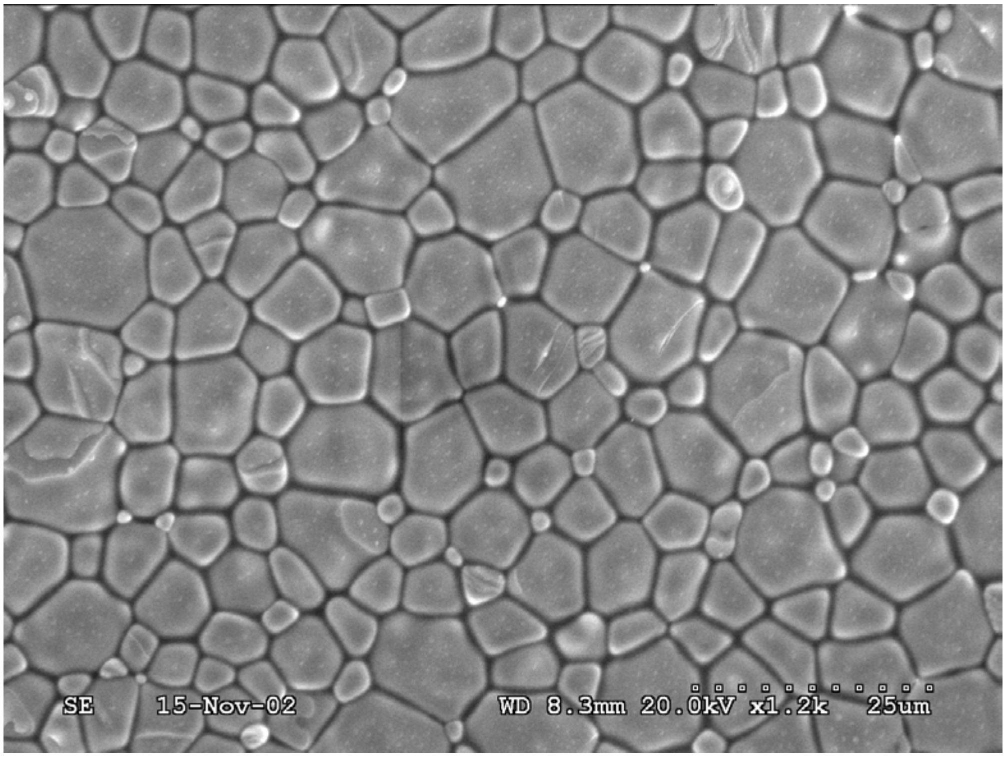

Figure 12: An SEM micrograph of a sintered sample of YSZ made by the MD process. The sample was sintered at 1400^{o}C.

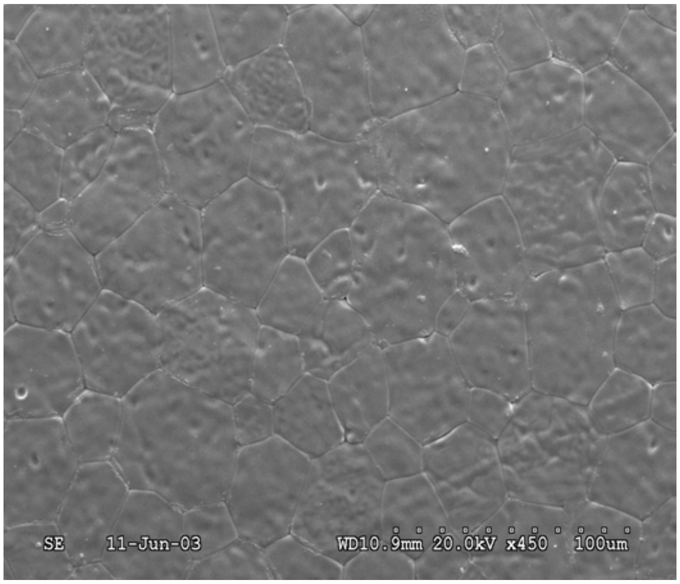

Figure 13: An SEM micrograph of a sample of CSZ (Ca = 0.2) sintered at 1600°C. No special precautions were taken to ensure that the powder was de-agglomerated. The fully dense microstructure seen in the above micrograph, with a very large grains size, suggests that it should be possible to achieve good density at much lower temperatures. As stated earlier, the objective was to see if the powders can be sintered to good density, with minimal of treatment after the MD process.

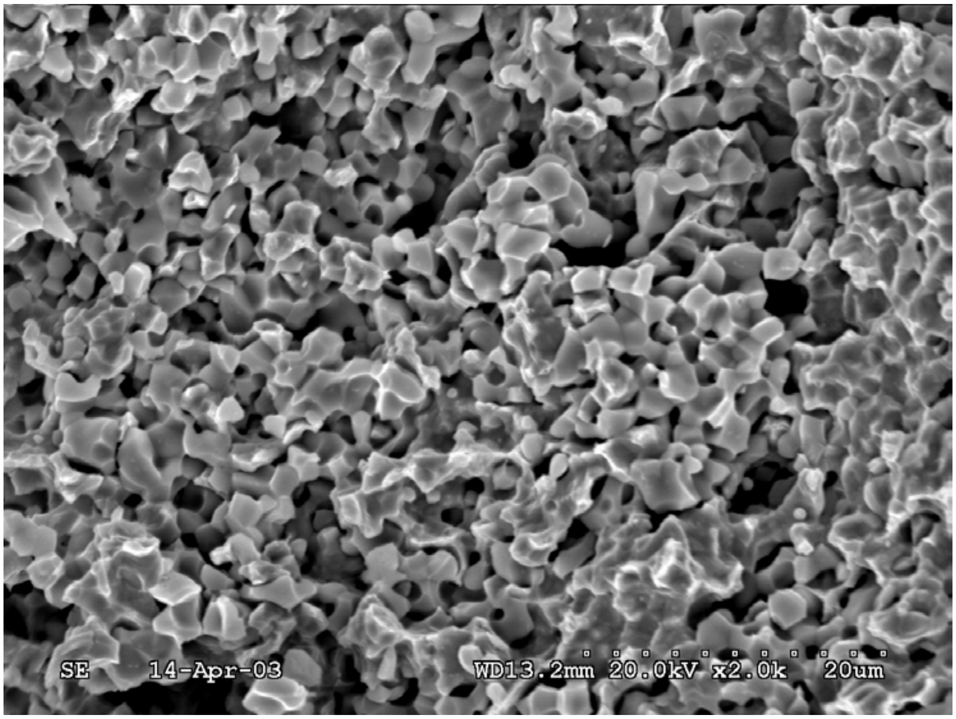

Figure 14: An SEM micrograph of a reduced sample of 70% NiO + 30% YSZ (made by the MD process). Note the equiaxed microstructure and uniform porosity. The sample was sintered at 1450°C.

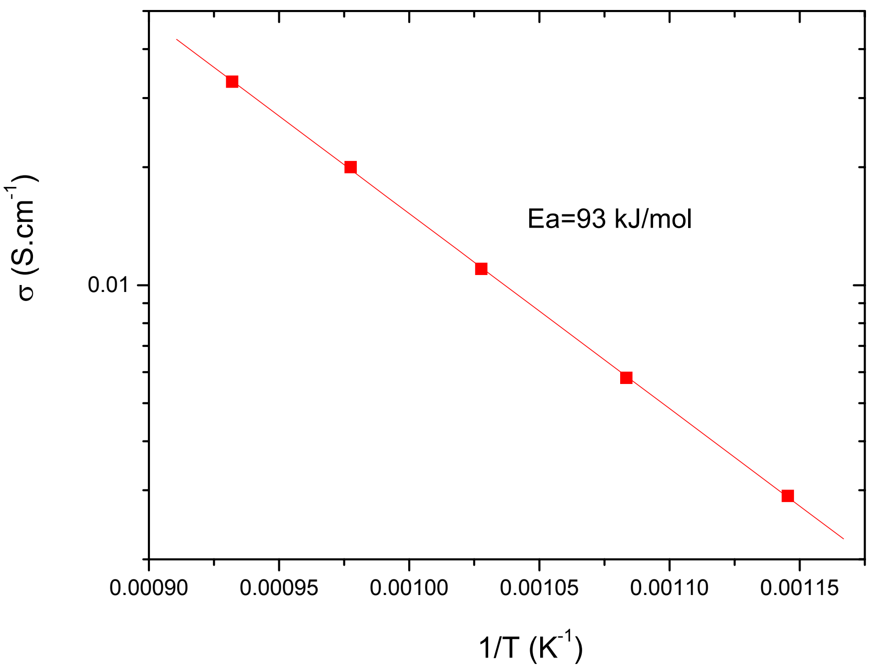

Figure 15: Conductivity as a function of temperature of YSZ sample made by the MD process. The measured conductivity is comparable to a typical commercial material, made by solid-state process.

Figure 16: (a) YSZ powder made by the MD process in suspension in water in a measuring cylinder. (b) After the powder had settled down. In Phase I, as much as 100 g of powder was made in a single experiment at each time, using simple lab-ware.

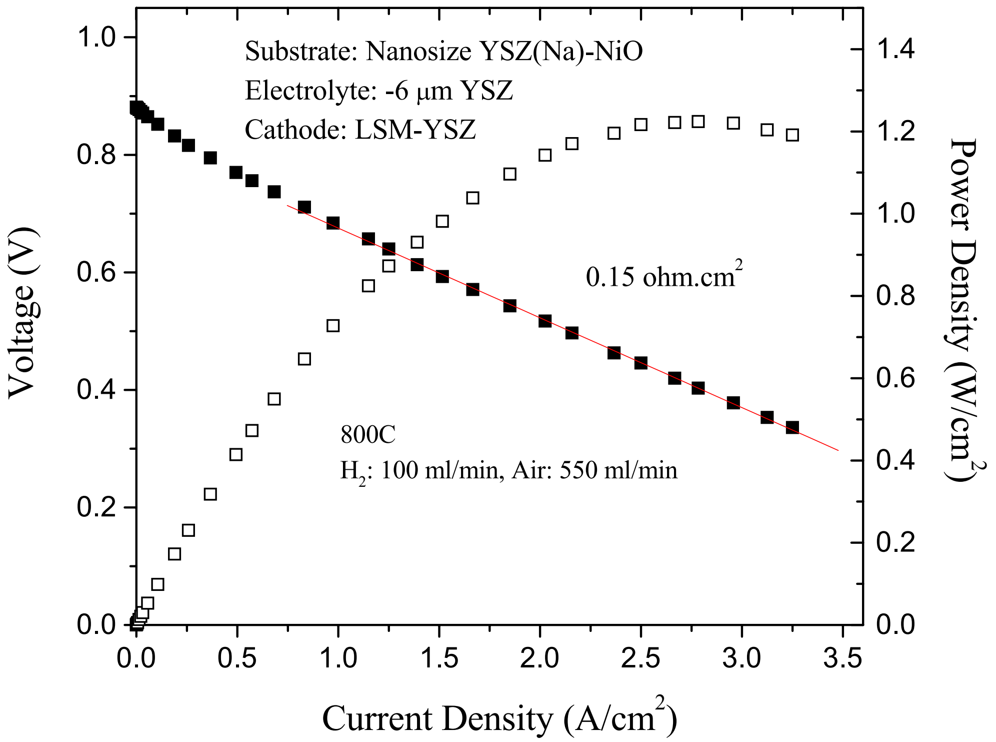

Figure 17: Voltage and power density vs. current density plots for the very first cell made using YSZ made by the MD process in the anode. In this initial trial, there were a few pinholes in the YSZ film (which was actually made using co-precipitated powder, from a commercial source). As such the OCV is lower than had there been no pinholes. Nevertheless, it can be seen that the cell ASR is quite low (~0.15 Ωcm^2 at 800°C). The corresponding maximum power density is ~1.2 W/cm^2. Had there been no pinholes, and the OCV had been ~1.15 V, the maximum power density would have been ~1.9 W/cm^2. Additional cells are being fabricated.

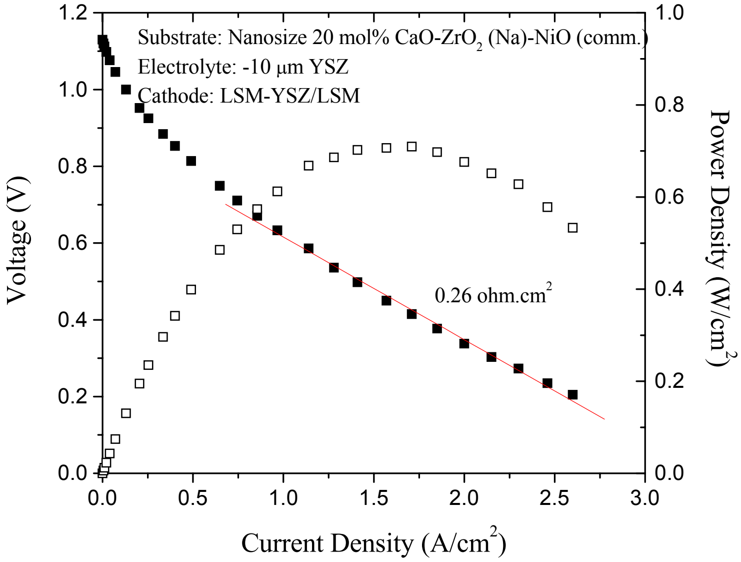

Figure 18: Performance curves for a cell made with MD CSZ in the anode. Note an excellent OCV, indicating that there were virtually no pinholes. The power density was ~0.7 W/cm^2 in this initial test. The anode porosity (after reduction of NiO to Ni) was only about 25%, due to excellent sintering characteristics at 1400°C. Either pore formers will be added in the anode, or sintering temperature will be lowered. This material has a very good potential to make a one-step sintering process by lowering the sintering temperature.

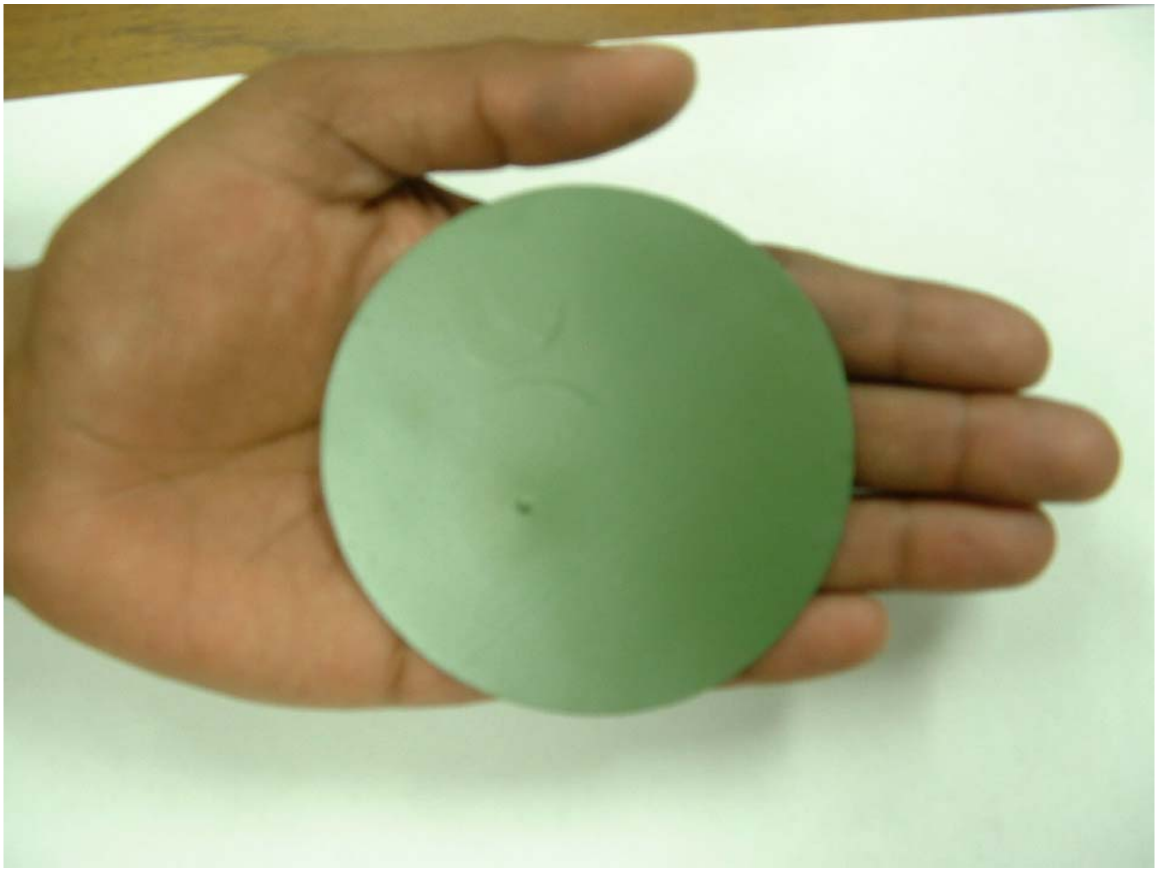

Figure 19: A photograph of an anode-supported cell made with MD-CSZ in the anode support. The cell is over 3 inches in diameter. This cell was made by, die pressing and sintering. In the future, a tape-casting process will be developed.

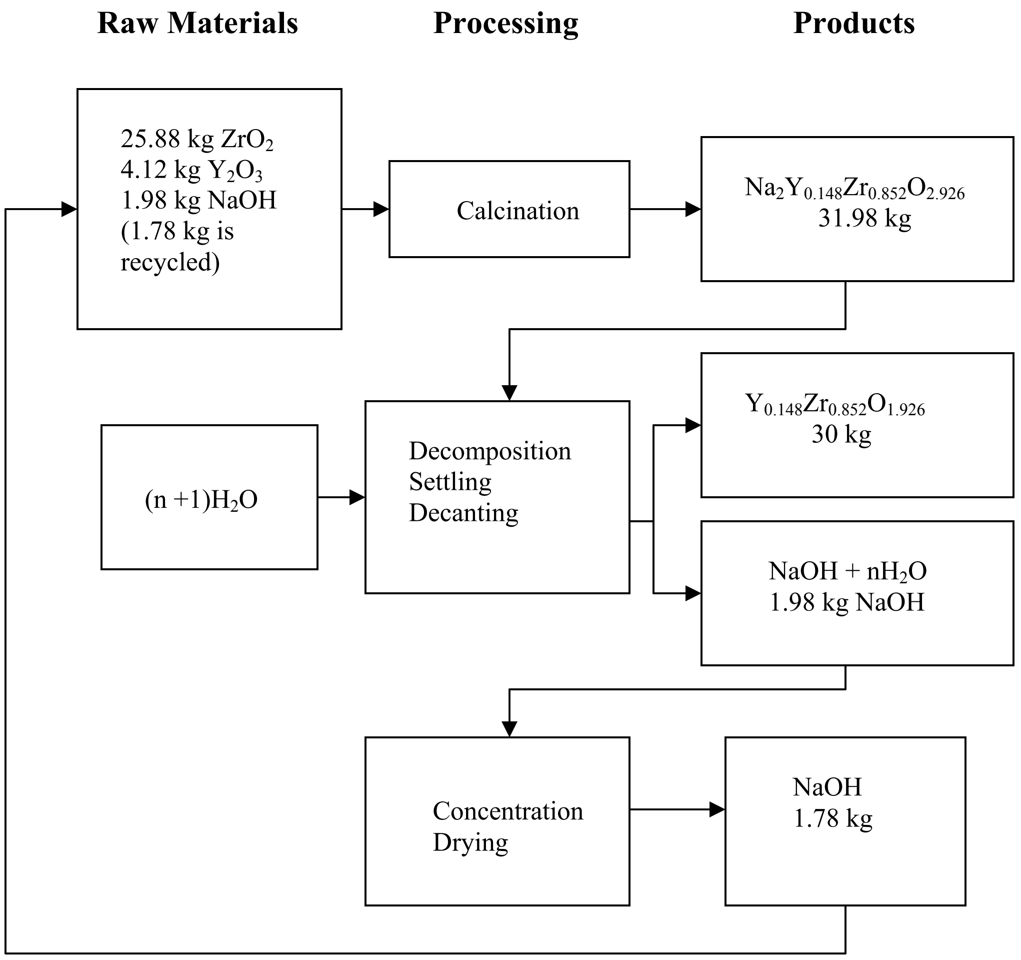

Figure 20: Quantitative flow diagram for the manufacture of 30 kg/day of 8YSZ by the MD process. The one for the synthesis of CSZ is virtually identical.

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LIST OF ACRONYMS AND ABBREVIATIONS

CSZ:	Calcia-stabilized zirconia
DC:	Direct current
LSM:	Sr-doped $LaMnO_3$
MD:	Molecular Decomposition
SECA:	Solid-state Energy Conversion Alliance
SEM:	Scanning electron micrscopy
SOFC:	Solid oxide fuel cell
TEM:	Transmission electron microscopy
XRD:	X-ray diffraction
YSZ:	Yttria-stabilized zirconia