CHARACTERISATION OF DOPED CERIA POWDERS
PREPARED BY WET CHEMICAL METHODS

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ABSTRACT

Ceria powders, doped with 20mol% gadolinia, were made by ethylene glycol sol-gel technique, and a reverse strike coprecipitation technique. Particle size analysis of the powders shows the coprecipitated powder to have a bimodal size distribution, with single particles being 0.3-0.4 μm, the agglomerates have an average size of 4-5 μm. The sol-gel powder exhibited a monomodal particle size distribution, with the average size being 12-15 μm. From the large size of the particles, and also an SEM investigation, it has been concluded that the as-calcined sol-gel powder is highly agglomerated. Sintered densities of the pellets indicate that the coprecipitated powder is the more sinterable of the two, obtaining closed porosity, after having been sintered for 10 hours at 1400 °C. The sol-gel pellets only achieved a closed porosity when sintered 10 h at 1600 °C. X-Tek real time x-ray analysis of the sintered pellets revealed that those samples formed using a binder had a more uniform density across the area of the pellet. From initial investigations it appears the coprecipitation technique produces superior powders to those produced by the sol-gel technique employed.

INTRODUCTION

Solid oxide fuel cells are efficient and clean devices for the production of electricity. They consist of an electrolyte material between an anode and a cathode. These individual units are connected together to form a fuelcell stack. Currently, the most predominantly used electrolyte in fuel cell stacks is doped ZrO₂. To achieve useful power outputs ZrO₂ cells are generally operated at approximately 1000°C. This high operation temperature limits the materials that can be used in the remainder of the stack and also in the balance of plant (1). To lower the operation temperature an alternative electrolyte with higher oxygen ion conductivity must be used. Such an alternative is doped CeO₂. Doped CeO₂ electrolytes can achieve comparable conductivities when run at 700°C as those produced by doped ZrO₂ based electrolytes run at 1000°C; for example 4.2 S cm⁻¹ is achievable for (CeO₂)₀.₈(GdO₁.₅)₀.₂ at 700°C (2). By lowering the operation temperature of the fuelcell stack, higher performance materials, that cause adverse reactions at higher temperatures (3), can be used. Also, lower cost “off the shelf” materials may be used in the balance of plant.
Before the potential of CeO₂ electrolytes can be fully realised research must be carried out on finding the optimal fabrication method. This is due to the fact that there are strong interrelationships between structure, properties and processing (3). To achieve the highest performance, electrolyte the powders produced by various methods should be characterised, as production of a fine, agglomerate-free powder is the first step in producing a high quality ceramic (4). This paper will concentrate on the characterisation of powders prepared by two different wet chemical techniques, namely a co-precipitation and a sol-gel method.

EXPERIMENTAL

Powder Preparation

Ceria powders, doped with 20mol% gadolinia were prepared by two different wet chemical techniques. The first method employed was a reverse strike co-precipitation, as detailed by Van herle et al. (2). Stoichiometric amounts of the required metal nitrates, Ce(NO₃)₂·6H₂O (Prochem Inc, IL, USA, 99.9% pure) and Gd(NO₃)₃·6H₂O (Prochem Inc, IL, USA, 99.9% pure) were dissolved in distilled water to form a 1M solution. The nitrate solution was then dripped into a slight excess of 0.06 M oxalic acid, adjusted to pH 6.7-6.9 using dilute ammonia solution, with continuous stirring. The pH was maintained in the range of 6.7-6.9 throughout the nitrate addition by adding small amounts of ammonia solution. Once the entire nitrate solution had reacted with the oxalic acid, the mixture was left to stir overnight. The resulting precipitate was then collected by vacuum filtration. After being washed 5 times with distilled water, followed by 5 times with ethanol, the precipitate was dried over night at 80°C. The precipitate was then calcined for 1 hour at 700°C to convert the oxalate precursor to the oxide material.

The second method employed was an ethylene glycol sol-gel method as detailed by Chen et al. (5). Stoichiometric amounts of the required metal nitrates, Ce(NO₃)₂·6H₂O (Prochem Inc, IL, USA, 99.9% pure) and Gd(NO₃)₃·6H₂O (Prochem Inc, IL, USA, 99.9% pure) were dissolved in distilled water. The required amounts of ethylene glycol and concentrated (69%) HNO₃ were added to the nitrate solution. The resulting mixture was then heated for a total of 80 hours at 80°C until a viscous product was formed. The gel produced was then calcined for 1 hour at 700°C to form the oxide material.

Powder Characterisation

XRD patterns were taken of the calcined powders to determine the phases present. Particle size measurements were taken using a Malvern Mastersizer E laser diffraction system. Particle size was also determined using a Hitachi S4000 SEM; SEM was also used to examine particle shape. BET surface area measurements were performed using a single point nitrogen absorption method. An X-Tek HMX 160 real time X-ray device was used in an attempt to gain information regarding the extent of agglomeration in the powders. This was done by gaining visual representation of the density variations within the powder.
**Pellet Fabrication**

Pellets were fabricated by uniaxial dry powder pressing at a pressure of 14 MPa. Pellets were fabricated by preference without binder, though the powder prepared by the sol-gel method required the addition of 3 wt% oleic acid as a binder. Pellets thus produced were sintered at 1300, 1400, 1500 and 1600°C for either 2 or 10 hours at each temperature, following the sintering regime shown below in Figure 1.

**Pellet Characterisation**

The sintered density of the pellets was measured using the standard Archimedes type method. Sintered pellets were also examined using SEM and an X-Tek HMX 160 real time X-ray device.

![Sintering Regime](image)

**Figure 1** Sintering Regime Employed.

**RESULTS AND DISCUSSION**

**Powder Characterisation.**

The XRD patterns obtained from the calcined powders showed both to be single phase, and possessing the cubic fluorite-type structure.

Particle size measurements obtained using a laser diffraction technique revealed that the powder prepared by the coprecipitation method had a bimodal size distribution. The bimodal distribution is explained by the presence of agglomerates as well as single particles. The median size of the single particles present was 0.3-0.4 μm; with the median size of the agglomerates present being 4.3-5.3 μm. In contrast, the particle size distribution of the powder prepared by the sol-gel method was monomodal, with a median particle size, 12-15 μm, which was slightly larger than the agglomerates present in the coprecipitated powder.
Using SEM, large agglomerates can be identified in the coprecipitated powder, Figure 2. It can be seen that the agglomerate consists of a number of generally elongated particles. The morphology of the particles is an artefact of the oxalate precursors, which have a monolithic shape (2). The size of the agglomerates correlates well with the results obtained using laser diffraction. However, the sizes of the particles constituting the agglomerate are considerably larger than the size for single particles determined using laser diffraction. On closer examination of Figure 2, it can be seen that surrounding the agglomerate are considerably smaller particles that do correspond to the single particle size determined using laser diffraction.

![Figure 2 SEM micrograph of coprecipitated powder.](image)

Examination of the SEM micrograph for the sol-gel powder, Figure 3, reveals the presence of large, apparently porous agglomerates. The size of these agglomerates strongly correlates with the laser diffraction results. The large agglomerates appear to consist of numerous, considerably smaller, particles.

![Figure 3 SEM micrograph of sol-gel powder.](image)
Surface area measurements, determined by a single point nitrogen absorption method, indicate that the sol-gel powder has a higher surface area, 17.0 m²/gm⁻¹, than the coprecipitated powder, 14.9 m²/gm⁻¹. This is understandable given the visible porosity of the sol-gel agglomerates, despite them being larger than the co-precipitated particles and agglomerates.

X-Tek real time X-ray visualisation of the density variation in the powders was not satisfactory, as it was not certain if the apparent agglomerates were in fact agglomerates or merely loose clumps of powder. This ambiguity was due to the method in which the powder was prepared and held for X-Tek examination.

**Pellet Characterisation.**

By preference, pellets were fabricated without the addition of a binder. However, due to adherence of the sol-gel powder to the die during pressing, it was necessary to add 3 wt% oleic acid as a binder. Following the addition of the binder no further problems were encountered with respect to the sol-gel powder adhering to the die.

Initially the pellets fabricated from the sol-gel powder appeared to be the more sinterable of the two powders produced, achieving a density of 93% of theoretical after sintering at 1400°C for 2 hours. This is compared with 86% of theoretical density for the coprecipitated sample sintered under similar conditions. However, beyond this point the coprecipitated powder out-performed the sol-gel powder with respect to sinterability. The coprecipitated powder pellets achieving closed porosity (>96% of theoretical density) after sintering for 10 hours at 1400°C. By contrast, the sol-gel pellets only achieved closed porosity after sintering for 10 hours at 1600°C, the maximum sintering condition used in this study. It can be seen in Figures 4 and 5 that at the lowest temperature/time combination employed, the sol-gel pellet, Figure 4, has significantly larger grains and while the pores present are larger than those in the coprecipitated pellet, they are less numerous.

![SEM micrograph, sol-gel pellet, sintered 2 hours at 1300°C.](image)

**Figure 4** SEM micrograph, sol-gel pellet, sintered 2 hours at 1300°C.
Figure 5 SEM micrograph, coprecipitated pellet, sintered 2 hours at 1300°C.

Figure 6 SEM micrograph, coprecipitated pellet, sintered 10 hours at 1600°C.

Figure 7 SEM micrograph, sol-gel pellet, sintered 10 hours at 1600°C.
Examination of the SEM micrographs, Figures 6 and 7, of the pellets sintered at the maximum sintering condition used, 10 hours at 1600°C, show that both samples have no pores present and large grains present. The presence of the large grains indicates that a degree of grain growth has occurred during the sintering process. It should be noted that the sol-gel pellet has significantly larger grains present than the co-precipitated pellet. This would indicate that the sol-gel sample began sintering at a lower temperature than the co-precipitated sample, which concurs with the sintered density results obtained.

X-Tek real time X-ray analysis of the sintered pellets, Figures 8 and 9, show that the co-precipitated pellet has a variable density over the area of the pellet, in contrast the sol-gel pellet has a very uniform density.

Figure 8  X-Tek image, coprecipitated pellet, sintered 10 hours at 1600°C.

Figure 9  X-Tek image, sol-gel pellet, sintered 10 hours at 1600°C.

Although Figures 8 and 9 relate to the samples sintered for 10 hours at 1600°C, the same density differences were observed at all sintering temperatures and times.

In an attempt to determine if the differences in density variation were a powder property a number of pellets were fabricated from the co-precipitated powder, however this time a 3 wt% oleic acid binder was used. By comparing Figures 8 and 10 it can be seen that the use of a binder apparently causes a more uniform density over the area of the pellet.

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CONCLUSIONS

The coprecipitation method appeared to produce a superior powder to that of the sol-gel method. The powder had smaller agglomerates, though it also had a lower surface area. The coprecipitated powder was on the whole more sinterable than the sol-gel powder as it achieved a closed porosity after sintering for 10 hours at 1400°C. The sol-gel powder only achieved closed porosity after sintering for 10 hours at 1600°C.

From initial investigation, it appears that the use of a binder promotes a more uniform density distribution in sintered, uniaxially pressed, pellets.

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