DEVELOPMENT AND OPTIMIZATION OF PRECURSOR MATERIALS FOR SOLID OXIDE FUEL CELLS
BY THE NITRATE PYROLYSIS-PROCESS (NPA)

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ABSTRACT
Solid Oxide Fuel Cells (SOFC) will be required to operate at temperatures above 900°C for many years. This will place exacting demands upon ceramic components and ceramic precursor powders. It is shown that the Nitrate Pyrolysis process (NPA) is well suited to synthesis of SOFC precursor materials for electrolyte, cathode, anode and interconnect ceramics. By further mechanical and/or thermal processing, NPA-powders can be optimised for use in processes such as screen printing, dip coating or tape casting. Details of the properties of NPA produced powders and ceramics are given.

1. INTRODUCTION
The development of high performance ceramics and particularly electroceramics has led to a growing demand for improved precursor materials. It has been shown that for applications such as varistors, microwave, PZT and SOFC, materials produced by conventional mixed oxide "solid state" processing have significant limitations [1-6].

The aim of our work has been to develop improved materials by use of "chemical" processes. Initially a programme was conducted to evaluate alternative techniques. This programme included investigation of coprecipitation, sol-gel, microwave synthesis and spray pyrolysis methods. In common with other researchers [6-11], the best results were achieved with spray pyrolysis processing. However the products from standard spray pyrolysis techniques showed some limitations. In previous work, we further developed this technique to establish a new synthesis method, the Nitrate Pyrolysis Process (NPA) [12-14], which produces powders with significantly improved properties for use as electroceramic precursors.

This paper reports on work done to research and develop materials for SOFC using the NPA-process. By working in close contact with other research groups, precursors have been produced for electrolyte, anode, cathode, interconnect and support components. The evaluation of these materials has shown a clear improvement in component fabrication and properties.

2. THE NITRATE PYROLYSIS PROCESS (NPA)
Spray pyrolysis techniques [6-11] are well established and have found some degree of
commercial use in the production of ferrites. However these techniques have not pene-
trated into electroceramics powder manufacture for a number of reasons. The main 
factor is that spray pyrolysis systems use electrical heating and are cost intensive. They 
are limited in throughput and difficult to scale up. Furthermore, cheaper chloride solu-
tions cannot be used as impurity chlorides could adversely affect electroceramic 
properties.

The nitrate pyrolysis process (NPA) [12-14] is based upon a novel spray pyrolysis 
approach. A gas burner provides thermal energy to an aerosol of an aqueous solution 
of metal nitrates [oxidants] and organic compounds [reductants]. This initial energy 
activates an oxidation-reduction reaction allowing continued self sustaining combus-
tion. Each droplet contains sufficient energy for nitrate to oxide conversion and com-
plex metal oxide phase formation. Modification of the oxidant: reductant ratio varies 
the relative free energy and thus, in principle, allows adjustment of the size and mor-
phology of the oxide particles. Reaction times may be reduced to 0.1 - 0.3 seconds 
yielding reactive, homogeneous, phase pure ceramic powders, with a primary particle 
size of 50-100 nm and a mean agglomerate size of 0.5-1µm.

Figure 1: The burner head and solution injection of the nitrate pyrolysis equip-
ment (NPA)

An important advantage of this self sustaining combustion is, that in principle there is 
no limitation to the amount of solution that may be injected. Hence, it is feasible to 
achieve large product throughput capacity with relatively small equipment. Further-
more, the use of solution precursors also allows precise stoichiometry control over a 
very wide range of compositions. Products have low levels of chemical impurities 
determined only by the quality of starting solutions. The powders formed do not come 
into contact with the hot reactor tube which is the major source of impurities in the 
NPA process.
The equipment used for the development of SOFC-materials can provide approximately 5 kg/hour. It is shown in Figure 1 with further technical information in Table I.

### Table I
#### Technical Parameters of the NPA-Process

| Parameter                      | Value                        |
|-------------------------------|------------------------------|
| Reactor size                  | 200*3000 mm                  |
| Solution injection            | 25-45 kg/h                   |
| Powder capacity               | 5-7 kg/h                     |
| Temperature of oper.          | 1000°-1500°C                 |
| Reaction time                 | 0.1-0.3 sec                  |
| Powder morphology             | Porous-Dense                 |
| Surface area [BET]            | 5-25 sqm/g                   |
| Phase purity                  | Given                        |

The NPA-process has proved to be an efficient tool for the synthesis of high quality precursor materials. However, some powders require further mechanical and/or thermal treatment for full optimisation of powder particle size and morphology for use in the various processing techniques for the manufacture of SOFC ceramics.

### 3. SOFC-MATERIALS

Depending on the processing technique and cell design, different powder properties are required to suit different SOFC components. Table II summarises some of the preferred powder properties and the preferred electronic or ionic conductivity of sintered ceramics for each SOFC component. By appropriate post-NPA treatment, most of these parameters have been achieved using powders prepared by NPA processing.

### Table II
#### Requirements for SOFC-Materials

| Component     | $T_{\text{sinter}}$ (°C) | $\rho_{\text{final}}$ (% of theoret.) | Average particle size ($\mu$m) | Ionic/electronic conductivity (S/cm) |
|---------------|--------------------------|--------------------------------------|---------------------------|-------------------------------------|
| Electrolyte   | 1500-1700                | > 95                                 | < 1                       | 0.1                                 |
| Cathode       | 1100-1300                | 70-80                                | 1-10                      | > 100                               |
| Anode         | 1100-1300                | 70-80                                | 1-10                      | > 100                               |
| Interconnect  | 1100-1300                | > 95                                 | < 1                       | > 20                                |
| or 1700       |                          |                                       | < 1                       |                                      |

### 3.1 ELECTROLYTE

Pure zirconia is monoclinic up to 1000°C; at this temperature, it transforms to a tetragonal structure with a 9% volume contraction [15]. This would lead to destruction of any fuel cell stack. To overcome this, two- or three-valent cations such as Ca, Mg, La, Y or Yb are added [16, 17, 18]. The use of 8 mol % yttria is preferred for SOFC [19].
Controlled variation of composition is extremely easy by NPA processing and zirconia stabilised with 8 - 10 mol % of yttria and various other dopants has been studied. Powders doped with alumina and magnesia have been synthesised in order to study their influence on the grain size in sintered ceramic. This has established that for YSZ, as in the case of pure alumina, doping with very small quantities of magnesia acts as a powerful control of grain growth during the sintering process.

However most interest has focussed on sinteractivity and oxygen conductivity of electrolyte materials. Fig. 2 shows typical dilatometer data of a pressed pellet of doped YSZ. This confirms that sintering starts at 1000-1100°C and is completed in 3 hours at 1400°C. By processing pressed pellets with binders in this way ceramics with a density of 5.7 g/cm³ have been produced. These powders were prepared by NPA processing without any further processing (see Table IV).

In addition to sintered pellets, 200 - 350 μm YSZ-plates have been sintered from tape cast NPA-powder green bodies by standard techniques. These platelets were translucent and showed similar properties to pellets. The oxygen conductivity was measured in a four probe dc set up with platinum electrodes (Figure 3) in air at temperatures up to 1000°C. The dc-conductivity is > 10 S/m and the activation energy 1.11 eV (Figure 3).

Figure 2: Dilatometric analysis of a YSZ-pellet, doped with 8 mol % yttria and 2 weight % alumina [37, 38]
Figure 3: Four probe dc set up and dc conductivity of YSZ doped with 8 mol % yttria and 2 weight % alumina as a function of temperature.

Figure 4: Temperature dependence of the dc-conductivity of La$_{0.8}$Sr$_{0.2}$MnO$_3$ measured in air.
3.2 CATHODE

A range of lanthanum strontium manganese oxide compositions are preferred as cathode material for SOFC [18; 20-25]. This material is difficult to prepare by the mixed oxide "solid state" process; stoichiometry must be controlled precisely and no residual lanthanum oxide can be allowed as it would deteriorate cathode performance during cell operation. There has been much research into different powder processing techniques which has confirmed that chemically prepared powders can overcome these problems.

Powders as prepared by the NPA-Process showed no free lanthanum oxide, precise stoichiometry, good electronic conductivity and good adhesion on YSZ. However, they proved very difficult to process due to high sinter activity and a coarser powder with reduced surface area has been developed. Table III gives a comparison between NPA-powder as produced and a coarser partially sintered NPA-powder useable for screen printing and other processing techniques. The conductivity of sintered specimens is 130 - 260 S/cm (see Figure 4).

| Physical Data of NPA-Powders                  |
|-----------------------------------------------|
| NPA-Powder         | presintered NPA-Powder          |
| average particle size | 0.5-0.9 μm        | 3 μm  |
| surface area (BET)  | 7-12 m²/g          | 2 m²/g |

A range of Laₙ₋ₓSrₓMnO₃ compositions [x=0.15-0.2] with various dopants have been synthesised and characterised. In general the properties are reproducible and compare favourably with other chemically prepared powder [26] (see Table IV). To date, presintered NPA powders have only produced cathodes with 10-30 % porosity when sintered onto YSZ. Detailed studies will be made to further optimise these materials to ease processing and improve porosity to 40 % in the sintered electrode layer.

3.3 ANODE

A typical anode material consists of 30 - 60 wt % of nickel powder mixed with YSZ by solid state processing [27, 34]. This cermet material shows good conductivity and catalytic properties. Nonetheless, a study has been made to produce improved anode material by the NPA-technique. Starting from nitrate solutions of nickel, yttrium and zirconium, a NiO-YSZ powder with Ni content of 60 wt % was synthesised.

In this powder, NiO must be reduced to metallic Ni during the operation of the fuel cell. Figure 5 shows the thermogravimetric analysis of a powder sample in a hydrogen atmosphere (97 % N₂; 3 % H₂). This shows that weight loss and hence reduction starts at 400°C - 500°C and is complete at 700 - 800°C. The overall weight loss is 14.3 % (theoretical 14.1 %). Due to the very fine Ni-distribution, powder is air-sensitive and 4 wt % re-oxidation takes place at room temperature.
Anode ceramics have extremely high conductivity, which cannot be measured without special equipment. Therefore, to gain some measure of conductivity, reduced powder specimens were pressed and studied by SEM analysis (see Figure 6). Scans were made on a sample without sputtering the surface with gold or carbon and compared to a standard gold sputtered sample. The resultant scans showed a homogeneous contrast over the whole surface of the specimen with no difference detectable between the sputtered and non sputtered samples. Therefore it can be concluded that this material has a highly uniform Ni doping and an extremely high conductivity, even as pressed powder.

3.4 INTERCONNECT

It is commonly accepted that for most SOFC stack designs a material is required to act as an interconnect between two triple layers, in order to allow serial switching. For a variety of reasons doped lanthanum chromites have become preferred materials for this cell component. However, dependent upon cell design - tubular, planar or monolithic - interconnect requirements vary. The critical factor is the sintering temperature, where, particularly for planar and monolithic designs, a temperature of 1250-1400°C is required. For full densification, lanthanum chromites must usually be sintered at > 1700°C which is clearly incompatible with this application [28-30]. It is well known that by adding 0.2 - 16 mol % B₂O₃ or 2 - 40 mol % Bi₂O₃ [35, 36] to La₁₋ₓSrₓCr₁₋ₚMgₚO₃ (0 ≤ x ≤ 1, 0 ≤ p ≤ 1) the interconnect can be sintered to 93-97 % of theoretical density in 5 hours at 1300°C. However this is a rather high dopant level and interdiffusion of boron and bismuth might take place during operation leading to reduced cell performance.

Figure 5: Thermogravimetric analysis of NiO-YSZ
Figure 6: SEM analysis of a pressed powder sample of Ni-YSZ powder obtained after reduction. The sample was not sputtered with gold or carbon.

Figure 7: Sinter density of Lanthanum Calcium Chromium oxide as a function of B$_2$O$_3$-content. The maximum function was a result of a screening study to find the optimum dopant level. The triangle shows the sinter density achieved with NPA-powder with the optimum dopant level.
Therefore it was considered essential to produce more sinteractive powders and investigate the properties of NPA-lanthanum chromite powders with only small amount of B$_2$O$_3$. In an initial screening, study powders with varying B$_2$O$_3$ content were prepared by a small scale microwave synthesis [31-33]. They showed a maximum of sinter density in the region of 2 to 10 mol% (0.45 to 2 wt%) (see Fig. 7). Using this information La$_{1-x}$Ca$_x$CrO$_3$ with $0.1 \leq x \leq 0.2$ was synthesized with 0.45 wt% B$_2$O$_3$, pressed and sintered at 1350°C for 3 hours. The specimen had a density of 6.2 g/cm$^3$ (98% of theoretical) and an electronic conductivity of 21-26 S/cm at 1000°C.

In further work other lanthanum chromite compositions with very low levels of sinteractive dopants, compared to reported values [35,36], have been produced by the NPA method. These materials also demonstrate substantially improved sinteractivity. However, to avoid potential dopant interdiffusion problem, work continues to develop dopant-free sinteractive lanthanum chromites for use as a SOFC interconnect material.

4. CONCLUSION

The work reported confirms that the NPA process can be used as a powerful and flexible tool in the development and subsequent production of Solid Oxide Fuel Cell materials. The materials for the electrolyte, cathode, anode and interconnect components have been successfully synthesized and optimised for different processing techniques. In each case, NPA powders have demonstrated substantially improved technical and processing properties compared to conventional "solid state" precursors.

The development of these basic materials has now reached an advanced status; further work will focus on the interaction of cathode, electrolyte and anode. This will be in terms of assessment of thermal expansion coefficient and interdiffusion of main elements and impurities during the long term operation of Solid Oxide Fuel Cells constructed from NPA produced powders.

| Table IV  | Powder Properties and Electronic/Ionic Conductivity of NPA-Powders |
|-----------|-------------------------------------------------------------------|
| Electrolyte (Zirconia + 8 mol% Yttria) + 2wt % Alumina | Cathode La$_{0.82}$Sr$_{0.18}$MnO$_{3-x}$ |
| d50[microns] | < 1 | 1-3[10*] |
| BET-surface [m$^2$/g] | 8-10 | 2-10 |
| Begin-surface [m$^2$/g] | 1150°C | 1100°C |
| End of Sintering | 1400°C | 1400°C |
| Sintertemperature | 1400-1450°C | 1150-1350°C |
| Density [g/cm$^3$] | 5.73 | > 6.0 dense samples |
| Phase Analysis | cubic | monoclinic |
| Conductivity [S/cm] | 0.1 | 150-260 (dense) |

* in preparation
Anode

Ni(60)YSZ(40) as NiO-YSZ

|                | NiO-YSZ (cubic) | monoclinic |
|----------------|-----------------|------------|
| Phase Analysis |                 |            |
| Conductivity [S/cm] |             | > 20       |

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