ON THE SYNTHESIS AND CHARACTERIZATION OF BISMUTH CONTAINING SUPERCONDUCTORS AS CONTACT LAYER MATERIAL IN INTERMEDIATE TEMPERATURE SOLID OXIDE FUEL CELLS (ITSOFC)

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The melting temperature values (890 - 900°C) of bismuth containing super conducting ceramics prompted us to investigate their properties for possible application as contact layer material between the ceramic cathode and ferritic steel intercell connecting bipolar plate in solid oxide fuel cells operating between 700 and 850°C. $Bi_2Sr_2CaCu_2O_8+x$ (BSCC 2212) and $Bi_2Sr_2CuO_6+x$ (BSCC 2201) were synthesized both by solid state reaction (MO) and citrate complexation (CC) techniques. The physical characteristics such as particle diameter, bulk density, tap density and BET surface area values were measured for the powder. X-ray powder diffraction and differential thermal analysis data were also obtained. The densification data of the powder was also obtained in order to assess the softening characteristics of the pressed pellets upto a temperature of 875°C. Photographs of the surfaces were prepared to show the details on the thermal expansion and the resulting changes in the properties in the temperature range that is applicable to ITSOFC operation. The results obtained on the densification experiments are presented and a discussion is made to draw some useful conclusions on the thermal behaviour of these materials

INTRODUCTION

The Solid Oxide Fuel Cell (SOFC) research and development assumeimportance in today's energy and environment planning [1-10]. Owing to the high operation temperature of SOFC (900-1000°C), several complex and difficult problems are encountered when these cells are on continuous operation. Among the three widely practiced cell designs, the planar design offers greater scope for fabrication and use of cell components with larger apparent geometric area so that realization of high reaction surface area for the electron transfer at the electrode electrolyte interface is possible [II]. In the planar cell design, the state-of-the-art unit cell components viz. nickel-cermet anode, oxide ion conducting solid electrolyte (8%YSZ) and the LSM cathode ($La_{0.65}Sr_{0.3}MnO_3$) are assembled between the steel inter-cell connecting biploar plates to stack several such cells together. Several problems arising due to the atomic diffusion across the interface at the high temperature of SOFC operation had led to research on alternate materials and components for their operation at an intermediate temperature range (700-850°C) without performance loss. New oxide ion conducting solid electrolytes (12-14), ceramic cathodes (15-17) nickel-cermet anodes (18-20) and inter-cell connecting materials (21-22) were investigated earlier fo this purpose. In this research work. experimental characterization of the ceramic high T_C super conducting phases viz. $Bi_2Sr_2CaCu_2O_{(8+X)}$, 2212 BSCC and $Bi_2Sr_2CuO_{(6+X)}$, 2201 BSCC was made to draw information on whether they can be useful as contact layer material between the LSM cathode and ferritic steel inter-cell connector at the interface in the planar ITSOFC. The preliminary experimental results obtained on the densification of these materials are presented and discussed to draw some useful conclusions on their thermal behaviour.

EXPERIMENTAL

Synthesis of ceramic powder

1. Solid state reaction technique

In the solid state reaction technique, appropriate molecular quantities of the starting precursor salts were weighed and mixed well. The resulting mixture was ball milled with acetone and zirconia balls for 24 h under standardized conditions. After drying at 100°C for 2 h, it was once again ground well for homogenization and subjected to sintering at 800°C for 24 h in clean alumina crucibles and in air. After this process, the sintered oxide was crushed and powdered manually in an agate mortar.

To prepare $Bi_2Sr_2CaCu_2O(8+X)$, 100 g of the following starting chemicals were used directly after thorough and intimate mechanical grinding.

40.29g of Bi_2O_3 (ALDRICH, 99.99%)

20.42g of $Ca(NO_3)_2 4H_2O$ (MERCK, 99.9%)

13.76g of CuO (MERCK, 99.9%)

25.53g of $SrCO_3$, (MERCK, 99.9%)

The powder obtained after the sintering procedure was black in colour. This is again ground and stored for further experimental characterization.

To prepare $Bi_2Sr_2CuO_{(6+X)}$ 100g of the following starting chemicals were used directly after thorough and intimate mechanichal grinding.

55.42g of Bi_2O_3 (ALDRICH, 99.99%)

35.12g of $SrCO_3$, (MERCK, 99.9%)

9.46g of CuO (MERCK, 99.9%)

The powder obtained after the annealing procedure was black in colour.

2. Citrate complexation technique.

In this technique [23] the exact weights of the starting precursor materials were taken as above and dissolved in distilled water with very small quantity of nitric acid wherever necessary. The rsulting solutions were dissolved in citric acid solution which was already prepared in the molar ratio of 4 moles of citric acid to 1 mole of the metal cations (Bi, Sr, Ca and Cu) in the solution and stirred well. This blue coloured solution was heated at 80°C with continuous stirring. After 3h, ethylene glycol (exactly 1 ml to 1 g of citric acid in the solution) was added in steps (20ml Each time) to the warm solution and stirred well. The volume of ethylene glycol added to the solution was little more than the stoichiometric composition necessary to effect complete reaction with citric acid present in the solution. This solution was heated at 220°C with continuous stirring until most of the solvent evaporated. The viscosity of the hot solution was observed to decrease

with time and stirring became extremely difficult. The colour of the solution turned to deep brown and then to black. While doing this preparation ignition with evolution of deep brown stream of nitrogen containing oxides was observed. The more the HNO_3 in the solution, the more the gas evolution. The black mass obtained after complete evaporation was like a gel and it was dried in an air oven at 230° C for a long time until it became coarse powder. This coarse powder was subjected to calcination in two steps . In the first pre-calcination step, the black coarse material was heated in air at 600°C for 3 h in air on clean platinum crucible. This was carried out in small furnace which contained gas removing device in order to avoid the harmful effects of nitrogen oxides and the burnt organics. The powder obtained after pre-calcination was deep green in colour. In the second calcination step, the deep green powder was annealed at 800° C for 24 h in alumina crucible. The rise in temperature was at the rate of 5°C per minute. The samples after the calcinaion were black in colour and they were ground well prior to further measurements.

Chemical analysis

The powder obtained after calcination has been investigated by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) analysis performed on aqueous solutions of the powder to find the elemental composition of Bi, Sr, Ca, Cu an O. The results obtained are presented in Table 1 and the observed deviations from the intended composition were within the precision of the instrument.

Table -1. The elemental analysis data obtained on the powder samples

Sample	Element	Weight Percentage	
		Calculated	Experimental
$Bi_2Sr_2CaCu_2O_{(8+X)}$ 2212 (solid state technique)	Bi	47.01	44.7
	Sr	19.69	18.7
	Ca	4.525	4.42
	Cu	14.31	13.1
	O	14.45	17.49
$Bi_2Sr_2CaCu_2O_{(8+X)}$ 2212 (citrate technique)	Bi	47.01	42.5
	Sr	19.69	18.5
	Ca	4.525	4.22
	Cu	14.31	12.9
	O	14.45	17.99
$Bi_2Sr_2Cu_1O_{(6+X)}$ 2201 (solid state technique)	Bi	53.22	53
	Sr	22.29	22.2
	Ca	--	--
	Cu	8.12	7.84
	O	16.36	15.68
$Bi_2Sr_2Cu_1O_{(6+x)}$ 2201 (citrate technique)	Bi	53.22	54.9
	Sr	22.29	21.5
	Ca	--	--
	Cu	8.12	7.02
	O	16.36	14.68

DTA, XRD, Particle size, Density and Surface area measurements

The powder samples were subjected to X-ray diffraction analysis with a SIEMENS D5000 apparatus using K_a radiation to ascertain the formation of the desired crystallographic phases and to examine whether there were any additional phases. The results obtained are presented in Fig. 1. The DTA measurements were made in Model STA 409C Instrument. The particle size distribution funtion of the powder was obtained in a computer controlled Model 3.0. MALVERN laser diffraction partcile sizer. The powder was dispersed in methonal and the laser beams with known band widths were used to measure the diameter of the particles. The density values were measured by standard methods as bulk powder and after mechanical tapping in a specific gravity bottle of known volume. The surface area of the powder was determined by BET method using surface are analyser (Quantasorb, QS-14)
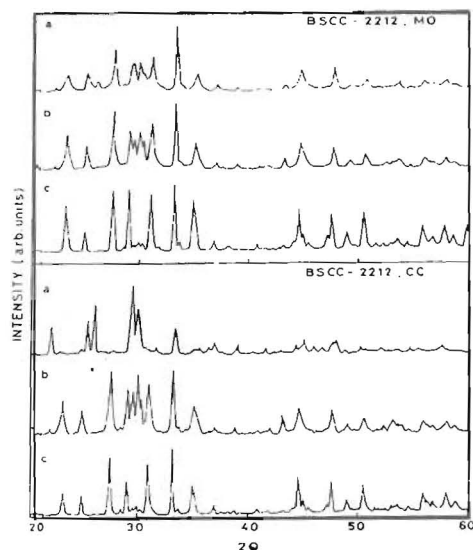

Fig. 1. X-Ray diffraction pattern of powders - a comparative representation showing the evolution of crystalline phases - a. after annealing at 800°C for 24 h; b. after annealing at 850°C for 2h; c. after annealing at 850°C for 168 h.

Preparation of compact pellets and sintering :

For the prepartion of the circular pellets (8mm diametre, 5mm height, 1g of powder) 1-2 drops of 2% solution of PVA was employed as the binding vehicle. A homogeneous mixture of the powder and binder was made and subjected to uniaxial compression in suitably designed and surface prepared die assembly with a hand operated laboratory model hydraulic pressing machine at a pressing pressure of 298 MPa for 1min. duration. The circular pellets were subjected to varying sintering conditions wih a view to investigate their shrinkage in volume and to know the densification behaviour as a function of the sintering
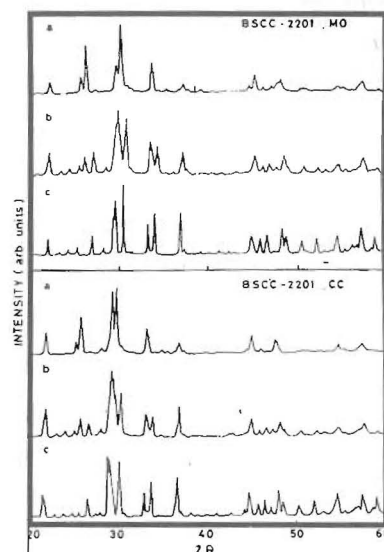

Fig.1. X-Ray diffraction pattern of powders - a comparative representation showing the evolution of crystalline phases - a. after annealing at 800°C for 24 h; b. after annealing at 850°C for 2h; c. after annealing at 850°C for 168 h.

temperature. The sintering procedure involved a programmed annealing from room temperature to the final temperature at the rate of 2°C per min., 2 h dwelling time and 3°C per min. cooling rate to the room temperature in air. The final temperature of sintering was set at different levels namely, from 700°C to 850°C at 25° intervals. Each sintering experiment was carried out on 2 identically prepared pellets for which the necessary physical dimensions, namely, height, and radius were measured as an average of 5 measurements both before and after subjecting them to sintering experiments with an electronic digital micrometer.

RESULTS AND DISCUSSION

Powder Characteristics

The colour of the powder was black for all the four samples investigated. The elemental analysis results obtained on the powder after calination at 800°C for 24h when compared with the calculated values from the molecular weights of the starting materials taken for synthesis, as shown in Table 1, indicated that the oxygen content in the powder was found to be more in the case BSCC 2212 after calcination whereas it was less for BSCC 2201 synthesized by both the techniques. The XRD analysis data, as shown in Fig. 1, indicated that the evolution of different crystalline phases as a function of annealing temperature which was completed only after continuous calcination of the powder for long duration. Evidence for the existence of other phases was noticed in both phases

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and it was more for the powder obtained by citrate complexation. Enrichment of purity in the phases formed was made possible by repeated milling and calcination of the powder. The powder morphology varied only a little. The particle size data, the bulk and tap density data and the BET surface area values obtained on the powder are presented in Table. 2. The bulk density and the tap density values, of the powder did not vary significantly although different methods were adopted for their synthesis. The particle size distribution function obtained from these powders was uniform. The particle diameter values of these powders viz. 5-10 μm was enough to fabricate the pellets straight away for further measurements. The differential thermal analysis and thermogravimetric analysis transients obtained for these powders are shown in Fig.2. The melting temperature values of BSCC 2212 and BSCC 2201 were found to be 836°C and 896°C respectively for the MO powders. The DTA curves showed broad endothermic peaks upto a temperatue of 800°C which could be related to the onset of oxygen loss observed in the TGA curves. Reversible oxygen loss and gain was observed in heating and cooling cycles respectively.

Densification and thermal expansion :

The green pellets fabricated from the powder under identical conditions were subjected to different annealing conditions to understand their thermal characteristics. The results obtained are presented in Tables 3 and 4 for BSCC 2212 and BSCC 2201 respectively. The photographs of the pellets taken before and after annealing at different temperature conditions are presented in Fig.3. From the expansion values obtained on BSCC 2212 pellets it was inferred that the relative percentage expansion due to annealing was almost linear upto a temperatue of 800°C
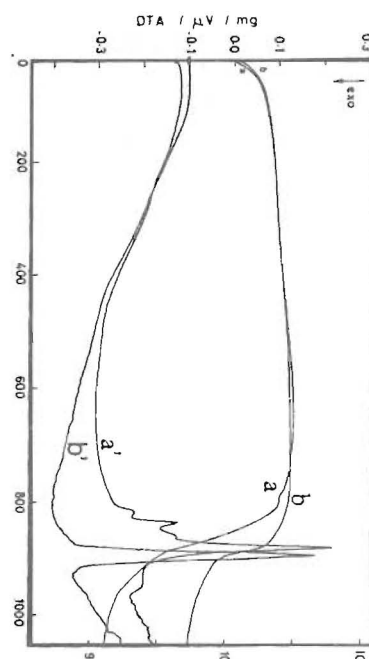

Fig.2. The DTA and TGA transients - a and a'. BSCC 2212 ; b and b'. BSCC 2201 powders.

and it increased beyond this abruptly upto 850°C. When the relative expansion values obtained on BSCC 2201 as a function of annealing temperatue was compared with that of BSCC 2212, it was evident that the relative expansion was lesser for the former than the latter. Another observation made from these tables and the photographs was that there was a competition between the densification of the pellets and phase enrichment involving recrystallization and resulting in volume expansion and cracks. There was a wide difference observed in the relative expansion behaviour of the BSCC 2201 pellets fabricated from powder synthesized by the two methods. A more detailed study of annealing at many temperature values at an interval of 5°C was considered necessary to throw more light on this phenomena.
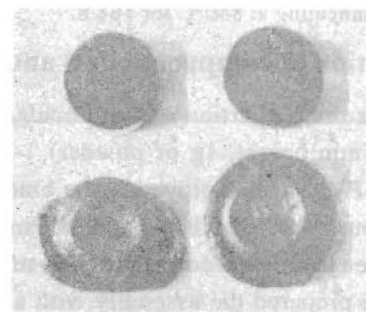
Table 2. The physical characteristics obtained on the powder samples

Sample	Particle dia. (μm)	Bulk density (g.cm⁻³)	Tap density (g.cm⁻³)	BET Surface area (m².g⁻¹)
$Bi_2Sr_2CaCu_2O_{(8+x)}$ 2212 (Solid state)	7.4	2.215	3.356	8.31
$Bi_2Sr_2Cu_1O_{(6+x)}$ 2201 (Solid state)	6.5	2.456	3.611	7.62
$Bi_2Sr_2CaCu_2O_{(8+x)}$ 2212 (citrate)	3.6	2.963	3.568	9.54
$Bi_2Sr_2Cu_1O_{(6+x)}$ 2201 (citrate)	4.5	2.764	3.349	12.83

Fig.3. The photographs of the BSCC 2212 (solid state reaction) pellets showing the evolution of expansion and cracks as a function of annealing temperature a) as prepared b) annealed at 825°C/2 h c) annealed at 850°C/2 h d) annealed at 860°C/2 h.

Table 3. Changes observed in the density of the circular pellets - 2212 phase

Sample	Density before sintering (g.cm^{-3})	Sintering conditions	Density after sintering (g.cm^{-3})	Expansion / densification (%)
Solid state technique	4.355	700	4.343	0.257
	4.422	725	4.396	0.587
	4.620	750	4.548	1.558
	4.731	775	4.640	1.932
	4.728	800	4.525	4.296
	4.543	825	3.919	13.738
	4.589	850	3.533	23.009
Citrate Complexation	4.582	700	4.537	0.982
	4.399	725	4.321	1.773
	4.593	750	4.512	1.763
	4.450	775	4.342	2.426
	4.494	800	4.324	3.782
	4.255	825	3.596	15.480
	4.283	850	2.984	30.320

Electrical conductivity

The electrical conductity values measured on the rectangular pellets revealed that at 800°C for BSCC - 2212 and BSCC - 2201 the conductivity values were 46 and 7 Scm^{-1} respectively. It has to be emphasized that no efforts were made to strongly densify the sample to obtain relative density values (D_{th}) which can be expected after ITSOFC assembling conditions. The relative densities were 50% and 65% respectively for BSCC-2212 and BSCC - 2201. As a rule of thumb the conductivity of any contact layer material should be more than 10 Scm^{-1}.

Thermal compatibility

It is desirable that the material to work as a suitable layer in IFSOFC boundary conditions has a melting point just a little above 800°C, the operation temperature of ITSOFC.

An analysis of the results obtained from this work revealed that the materials investigated satisfy this requirement well. Long term annealing experiments with suitably designed test specimens need to be carried out on these materials to assess their compatibility with the adjoining cell components under typical ITSOFC operation conditions. The order of suitability for contact layer application based on the available results : BSCC 2201>BSCC 2212.

CONCLUSION

The following general conclusions were drawn from the present research work.

1. The density values just after compaction of the powder prior to the annealing step indicated that the 2201 phase registered consistently above 5 g.cm^{-3} whereas the 2212 phase registered only above 4 g.cm^{-3}.

Table 4. Changes observed in the density of the circular pellets - 2201 phase

Sample	Density before sintering (g.cm^{-3})	Sintering conditions	Density after sintering (g.cm^{-3})	Expansion / densification (%)
Solid state technique	5.068	700	5.090	0.570
	5.060	725	5.116	1.104
	4.896	750	4.960	1.137
	5.117	775	5.095	--0.445
	5.071	800	5.058	--0.591
	5.064	825	5.101	0.732
	5.025	850	5.077	1.036
Citrate Complexation	5.152	700	4.999	2.969
	5.178	725	5.034	2.780
	5.165	750	5.076	1.723
	5.180	775	5.122	1.119
	5.170	800	5.092	1.508
	5.158	825	5.016	2.753
	5.073	850	4.303	15.178

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2. There was no significant change in the density values between that of the same phase prepared by solid state technique and citrate comlexaion technique.

3. The high temperature annealing of the compacted pellets had indicated almost a periodic decrease in volume upto 775°C, whereas above this temperature, an increase in volume was observed upto 850°C for the 2212 phase prepared by both the techniques.

4. For the 2201 phase prepared by solid state technique, the volume of the pellets showed a periodic decrease in volume as a function of annealing temperature upto 850°C. For the 2201 phase prepared by citrate complexation technique, the volume was found to increase at 850°C.

5. Melting of the pellets and shape changes due to annealing were observed beyound 850°C.

6. The DTA experiments indicated a melting point of 838°C for the 2212 phase (solid state technique) and 836°C for the 2212 phase (citrate). For the 2201 phase (solid state technique), it was 896°C.

7. The 2212 phase began to soften more easily at temperature above 850°C, whereas the 2201 phase began to soften only above 850°C. This observation holds good for powder prepared by both the techniques.

It has been shown by experimental measurements that the super conducting ceramic materials, namely BSCC 2212 and BSCC 2201 offer desirable thermal properties for applicaion as thin contact layer material and the kinetics of the processes involving recrystallization of the phases combined with softening of the bulk resulting in the volume expansion and shape changes need to be investigated in detail by insitu experimental measurements for a better understanding of the phase enrichment observed on both BSCC 2212 and BSCC 2201 ceramics at temperatue above 800°C.

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REFERENCES

1. H.P. Buchkremer, U.Diekmann, L.G.J.de Haart, H.Kabs, U.Stimming and D.Stoever, in: *Proc. 5 th Int.Symp.Solid Oxide Fuel Cells (SOFC-V)*, eds. U.Stimming, S.C.Singhal, H.Tagawa and W.Lehnert, The Electrochemical Society, Pennigton, NJ, 1997, p. 160.

2. T. Ishihara, H. Matsuda and Y. Takita, *J. Amer.Chem.Soc.* **116** (1994) 3801.

3. M. Feng and J.B. Goodenough, Eur. *J. Solid State Chem.*, **31** (1994) 663.

4. Yoshihiro Ohno, Susuma Nagata and Hiroyaki Sato, *Solid State Ionics*, **9 & 10** (1983) 1001.

5. Rasit Koe and H.U.Anderson, *materials Science*, **27** (1992) 5837.

6. B.C.H.Steele, *Solid State Ionics*, **86 - 88** (1996) 1223.

7. S.T.Anma, M.Muthuraman, and K.C.Patil, J..Mater. Chem.,7(12),2499-2503; *Solid State Ionics*, **111** (1998) 45.

8. H.S.Maiti, A.Chakraborthy and M.K.Paria, *Proc. 3rd Int.Symp. Solid Oxide Fuel Cells (SOFC-III)*, ed. S.C.Singhal and H.Iwahara, The Electrochemical Society Pennington, NJ, 1993, p. 190.

9. R.Dhosi, V.L.Richards, J.D.Charter, X.Wang and M.Krumplet, *J.Electrochem.Soc.*, **146-4** (1999)1273.

10. D.Simwonis, H.Thulen, F.J.Dias, A.Naoumidis and D.Stoever, *J. Mater.Processing* Tech., 92-93 (1999) 107.

11. *l. Arul Raj* and V.K.Venkatesan, Int.*J. Hydrogen Energy*, **13** (1988) 215.

12. W.Bakker, K.Huang, J.Goodenough, A.Khandkar and S.Elangovan,, Fuel Cell Seminar Abstracts, Palm Springs, CA, **16 - 19** November 1998, pp. 250.

13. P.Huang and A.Petric, J.Electrochem.Soc., **143-5** (1996)1644.

14. T.Ishihara, M.Honda, T.Shibayama, H.Minami, H.Nishiguchi and Y.Takita, *J.Electrochem.Soc.*, **145-9** (1998) 3177.

15. E.Syskakis, W.Jungen and A.Naoumidis, *Proc.Int.Conf.Material by Powder Technology*, Dresden, **23-26** March 1993, pp.707.

16. T.Tsai and A.Barnett, in: *Proc. 5 th Int.Symp.Solid Oxide Fuel Cells (SOFC-V)*, eds. ' U.Slimming, S.C.Singhal, H.Tagawa and W.Lehnert, The Electrochemical Society, Pennigton, NJ, 1997, p.369.

17. G.Stochniol, H.Gruebmeier, A.Naoumidis and H.Nickel, in: *Proc. 4 th Int. Symp.Solid Oxide Fuel Cells (SOFC-IV)*, eds. M.Dokia, O.Yamamoto, H.Tagawa and S.C.Singhal, The Electrochemical Society, Pennigton , NJ, 1995, p. 995.

18. R.Maric, S.Ohara, T.Fukui, T.Inagaki and J.Fujita, *Electrochemistry-Solid State Letters*, (1998)201.

19. P.Costamagna, P.Costa and E.Arato, *Electrochim.Acta*, **43-48** (1998) 967.

20. M.Mori, T.Yamamoto, H.Itoh, H.Inaba and H.Tagawa, *J.Electrochem.Soc.*, **145-4** (1998)1374.

21. W.J.Quadakkers, H.Greiner, M.Hansel, A.Pattanaik, A.S.Khanna and W.Mallener, *Solid State Ionics*, **91** (1996)55.

22. H.Schmidt, B.Bruckner and K.Fischer, *Proc. 4 th Int. Symp.Solid Oxide Fuel Cells (SOFC-IV)*, eds. M.Dokia, O.Yamamoto, H.Tagawa and S.C.Singhal, The Electrochemical Society, Pennigton , NJ, 1995, p.869.

23. Maggio P..Pechini, *US Patent No:* 3,330,697, July 11, 1967.

24. N.Q.Minh and T.Takahasi, in *Science and Technology of Ceramic Fuel Cells*, Elseveir Science, Netherlands, 1995, pp.129.