
Abstract

Low Temperature co-fired Ceramics (LTCC) has proven capability as an effective packaging technology for electronic devices and sensors. It possesses capability to handle mechanical, electrical, thermal and fluidic signals simultaneously. Embedded heaters and channel fabrication is also possible in LTCC, which expands its applications enormously. Due to these advantages, it was felt that LTCC technology can be extended to Fuel cells to fabricate embedded power source. This technology has well developed hermetic sealing process for leak-free gas flows and brazing processes for attaching metallic pins and pipes. The LTCC packages can also be operated at elevated temperatures, which could be as high as 600°C. Solid Oxide Fuel Cells (SOFC) requires high operating temperatures of the order of 1000°C. The high operating temperature causes difficulties in hermetic sealing and interconnects. Considering these difficulties, it was perceived that by reducing the operating temperature of SOFCs to about 600°C, and by devising ways of instilling compatibility with LTCC together with the integration with LTCC process, an overall advantageous situation can be created. This way, the difficulty of sealing could be solved, heater and flow channels can be integrated, the device could be miniaturized and energy wastage can be controlled. The major impediment
for this was SOFC materials that could work at low operating temperature, sinter at LTCC temperatures and are fully compatible with LTCC materials. Therefore, this work focuses on developing SOFC materials with improved properties to reduce the operating temperature range to 400-600°C, while simultaneously making them compatible with LTCC materials and processes.

To carry out the proposed work, some of the known SOFC electrode and electrolyte materials were selected. Gadolinium doped Ceria (GDC) was selected as an oxygen ion conducting electrolyte, having promising conductivity in the temperature range of 600-800°C. This material was synthesized by Glycine Nitrate precursor method. Its synthesis parameters viz. fuel to oxidizer ratio, oven temperature, calcination temperature and calcination dwell time were studied over wide range of parameter values to achieve phase purity, high pellet density and high ionic conductivity. The calcined powders crystallizes pure Fluorite phase and density of 94% was obtained when pellets fired at 1350°C in this study. The optimum conductivity was $4.07 \times 10^{-2}$ S.cm$^{-1}$ at 700°C. These synthesis parameters were statistically studied by Taguchi method. Three different levels of these four parameters were chosen to form a L9 ($3^4$) orthogonal array of experiments. Analysis of Mean (ANOM) and Analysis of Variance (ANOVA) was chosen to find most influential parameters on the basis of total ionic conductivity. Statistical analysis showed fuel to oxidizer ratio is only significant factor. Pellet prepared by optimized statistical condition showed 98% density when fired at 1350°C and ionic conductivity of the order of
0.11 S.cm\(^{-1}\) was obtained at 600°C. This is significant enhancement in ionic conductivity of GDC at 600°C operating temperature implying that GDC can be operated at low operating temperature of SOFC. It was confirmed from ionic transference ratio that this conductivity is totally ionic. This is amongst the highest reported conductivity for GDC.

Yttrium doped Barium Zirconate (BZYO) and Yttrium doped Barium Cerate (BCYO) are selected as proton ion conductors. These oxides are synthesized by sol gel method. To improve ionic conductivity of BZYO was doped with Ytterbium (Yb). Effect of Yb doping along with sol gel synthesis parameters \textit{viz.} effect of pH, combustion temperature, calcination temperature on structural, morphological and electrical properties was studied in detail. The calcined powder showed orthorhombic crystal structures. The pellets were prepared and sintered at 1200-1600°C. However, pellets had cracks, which may be due to lattice stresses caused by Yb doping, which as large atomic radius. The pellet prepared of BZYO showed only 72% density when sintered at 1350°C for 8hrs and low ionic conductivity of the order of \(1.9 \times 10^{-4}\) S.cm\(^{-1}\) at 700°C. BZYO requires high sintering temperature (~1600°C) to obtain high density, which is not suitable for our applications. Hence, BCYO was selected as another proton ion conducting electrolyte.

Yttrium doped Barium Cerate was synthesized by sol gel method, and the effect of pH, gelation temperature, combustion temperature and calcination temperature was studied over wide range of parameter values.
A Cubic perovskite phase was obtained for BCYO powders after calcination. The pellets sintered at 1350°C for 8hrs showed density of 96% of the theoretical density and ionic conductivity of the order of 0.4 S.cm\(^{-1}\) was achieved at 600°C. This is comparable with that reported in the literature.

Copper Zinc oxide (CuZnO) and Samarium and Strontium doped Cobaltite (SSC) were selected as anode and cathode materials respectively. Both the oxides were synthesized by Glycine nitrate precursor method. CuZnO powder shows Rhombohydral crystal structure after calcined at 600°C. Pellet fired at 900°C shows 14% shrinkage and 30% porosity. Area Specific Resistance (ASR) values was 8.55Ωcm\(^2\) and ionic conductivity of the order of 5x10\(^{-3}\)S.cm\(^{-1}\) at 700°C. SSC was selected as cathode material. SSC was found to have crystallized in Body Centered Cubic (BCC) crystal structure. The sintered pellet at 1100°C shows 14% shrinkage and porosity of the order of 25%. The ASR and ionic conductivity at 600°C are 10Ω.cm\(^2\) and 7.6x10\(^{-3}\)S.cm\(^{-1}\). These materials were used to make them compatible with LTCC through sintering aids and later to fabricate SOFC button cell.

In order to reduce sintering temperature, different sintering aids were added to GDC and BCYO electrolyte. Bismuth oxide (Bi\(_2\)O\(_3\)) was added as sintering aid in GDC showed significant enhancement in sinterability and ionic conductivity. Pellet sintered at 850°C shows shrinkage of 3.1% by adding 2 wt% Bi\(_2\)O\(_3\) showed 98% density and ionic conductivity of 0.1 S.cm\(^{-1}\) at 600°C operating temperature. However, low
shrinkage of the pellet compared to LTCC made this composite difficult to use in the present application. With BCYO, such addition of sintering aid did not show any improvement but showed deterioration in conductivity. In order to make these electrolyte materials compatible with LTCC, various glasses were used as sintering aid for GDC as well as BCYO electrolyte. The aim was to achieve close to LTCC shrinkage (~13%) direction at 875°C sintering temperature without deteriorating ionic conductivity properties. This goal was achieved in case of GDC oxygen ion conducting electrolyte. Bismuth based alkali phosphate glass \((x(Bi_2\text{O}_3-K_2\text{O})-y(V_2\text{O}_5-P_2\text{O}_5))\) (BKVP) was found suitable to achieve shrinkage of ~9% when fired at 1000°C by adding 25 wt% of this glass to GDC. The ionic conductivity measured at 600°C was 0.034 S.cm\(^{-1}\). This ionic conductivity was about double as compared to GDC powder used as host material for these experiments. The physical and chemical compatibility of GDC-glass composite electrolyte was studied by preparing screen printable thick film paste and co-firing and after printing on LTCC single tape of thickness 250µm. The fired substrate showed negligible warpage. Cathode material SSC was also made compatible with GDC and LTCC by adding 40 wt% BKVP glass.

A button cell was fabricated using GDC-glass composite electrolyte, SSC-glass composite cathode and CuZnO as anode material. The cell performance measured at 500°C showed open circuit voltage of 5.6mV and short circuit current of 40mA. The maximum power output was 1.5µW with fill factor calculated 0.67. The obtained powder density was 2.84µW.cm\(^{-2}\). The sealing experiments were performed by integrating
electrolyte pellet with platinum electrode. This cell was then enclosed in the fabricated LTCC structure and then sealed using DuPont 9616 glass paste. The reliability of sealing was tested under thermal cycling up to 600°C. This fuel cell package showed structural stability and no cracks or any physical damage was observed.

Overall, this work has successfully developed SOFC electrode and electrolyte materials which can be sintered at ~1000°C or lower, with ionic conductivity properties which are better than reported till date. Different electrolyte materials and electrodes with high ionic conductivity and mixed ionic conductivity have been developed. Physical and chemical compatibility of these SOFC component materials was demonstrated. This work contributed towards initial materials development for integration of SOFC in LTCC structures. Optimization of materials for co-firing of SOFC with LTCC and miniaturization of SOFC may be the future development for this work.

**Keywords:** LTCC, SOFC, integration, GDC, BCYO, SSC, CuZnO, compatibility, impedance analysis, glass ceramic composite electrolyte, glass ceramic composite electrodes