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Studies on synthesis and characterizations of gadolinium doped ceria as solid electrolyte

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Abstract

Due to need of pollution-free and efficient-power-generation devices, in past few years, pace of research has been rapidly driven by fuel cell technology. The thesis contributes in the same regard, in which conventional solid electrolyte of solid oxide fuel cell is replaced by alternate material (Gd-doped-Ceria-GDC) and its performance has been tested. The process parameters of ceramic route and spray-pyrolysis-technique were optimized to obtain dense 'electrolyte-grade' GDC-bulk and thin-film samples, respectively. In symmetrical cell configuration, GDC-bulk sample showed open-circuit-voltage of 0.84 volts at 500°C. The grain interior conductivity of 13µm GDC-film deposited onto electrode-grade NiO-GDC substrate is ~0.1S/cm at 500°C.

INTRODUCTION

More recently, and particularly in the past two decade, the pace of research has been rapidly driven by the requirements for new clean energy sources, sensors, and high energy density batteries. Because of the promise of important technological devices, a subgroup of anionic conducting materials exhibiting oxygen ion conductivity (solid electrolyte) has been continually developed. However, the conventional oxygen ion conducting solid electrolytes (e.g. Yttria stabilized zirconia – YSZ) requires high operating temperatures (~1000°C) and thereby leads to bottleneck for its commercialization.

The search for alternate materials to replace the conventional solid electrolytes has resulted into exciting discovery of gadolinium doped ceria (GDC). The high ionic conduction of GDC at comparably lower temperature made it an ideal candidate to be used as solid electrolyte for intermediate temperature solid oxide fuel cell (IT-SOFC – operating at 550–650°C) [1, 2]. In order to increase the ionic conductivity at further lower temperature, the thickness of the GDC electrolyte (10-20µm) would be reduced to 10-20µm [3].

EXPERIMENTAL

Using cost-effective ceramic route, the doping level of Gd in ceria was varied to obtain the optimum composition with desirable structural, morphological and electrical properties for solid electrolyte. The process parameters of ceramic route were optimized to obtain the electrolyte-grade solid electrolyte samples [4]. The best suitable composition was further tested for cell performance in a typical fuel cell environment. The optimized doping level was further preferred while studying its film counterpart, which were prepared using spray pyrolysis technique (SPT). The process parameters of SPT were also optimized to obtain the electrolyte-grade samples in thin film form [5]. The films were prepared on ceramic (electrode grade) substrate with the intention to use the formed structure as half cell for SOFC. The electrode/electrolyte structure was further characterized for its interface-quality using electrochemical impedance spectroscopy.

RESULTS AND DISCUSSION

GDC in bulk form: Figure 1 show the XRD of GDC bulk sample prepared with optimum doping level of Gd (10%) and with optimized processing parameters of ceramic route. Formation of phase pure 10%Gd doped ceria with fluorite structure is evident from the XRD pattern. The crystallite size of the sample was of the order of 598nm and the lattice parameter is same as that of JCPDS (PDF No.75-0161) value (5.418Å). SEM of GDC sample showed well grown and globular shaped grains of the size of the order of 5µm (inset of figure 1). Density of the sample was as high as 99% of its theoretical value, which can be clearly seen in its fractured morphology.

OCV measurements: The GDC sample was further tested for OCV in a typical fuel cell environment. Figure 2 shows the measured OCV data which are compared with that of reported OCV data measured for similar conditions. The theoretical OCV data as in [6], decreases with operating temperature. We have obtained the similar variations with low OCV values. However, the OCV values reported for Pt/SDC/Pt [6] and Pt/GDC/Pt [7] increases with the temperature. The OCV values of the present work, though slightly deviated from theoretical one, are higher than the [6] and [7]. The low OCV is most likely due to the poor electrode kinetics of Pt electrodes in this study. Thus the enhanced OCV is expected if highly active electrodes (e.g. Ba- or La-based cobaltite,) are used instead of Pt [8].

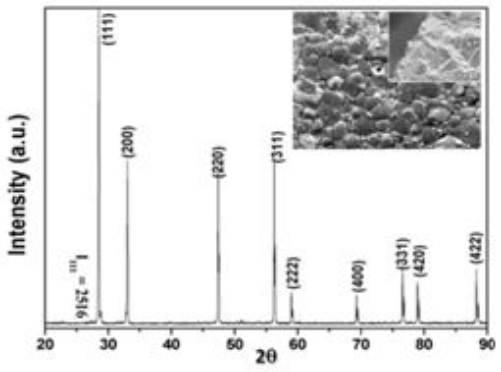

Figure 1: XRD of GDC sample prepared with optimum doping level (10%) and with optimized processing parameters of ceramic route. Inset: SEM of surface and cross section of GDC sample.

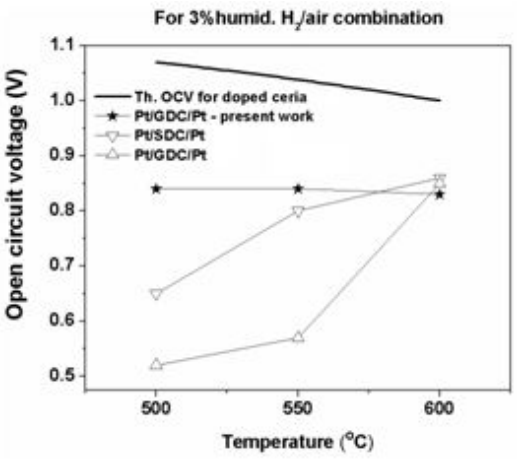

Figure 2: Comparison of OCV of Pt/GDC/Pt cell with Pt/SDC/Pt [6] and Pt/GDC/Pt [7] as a function of temperature. Theoretical (Th.) OCV curve of doped ceria [6] is also shown in figure.

GDC thin film on NiO-GDC: XRD of GDC film (not shown) prepared with optimized preparative parameters of SPT on NiO-GDC substrate confirms the phase formation. The film thickness was large enough (~13μm) to screen the peaks originating from substrate. Figure 3 shows the SEM of GDC films on NiO-GDC substrate annealed at 1000°C. Density of the GDC film was as high as 98% of its theoretical value, which is attributed to the presence of nano-granules in the films with avg. grain size 83-85nm (AFM image – inset of figure 3). SEM of GDC/NiO-GDC interface clearly depicts that the film and substrate is well in contact and the interface is gas-tight (a desirable).

Electrical performance of GDC/NiO-GDC structure: A typical trend of three semicircles was observed in impedance spectra of structure. The analysis of these spectra revealed the quality of interface formed between GDC film and NiO-GDC substrate. From table 1, it is clear that the interface showed insignificant impedance to overall electrical properties of structure and can be said to have good interface for its prospective use in SOFCs.

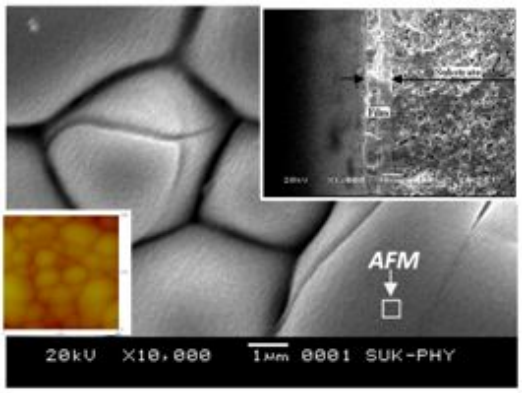

Figure 3. SEM of GDC/NiO-GDC structure annealed at 1000°C/8h. Insets: Top-right: SEM of GDC\NiO-GDC interface and Bottom-left: AFM of GDC film.

Table 1. Grain interior (g) and grain boundary (gb) conductivities of substrate and structure at 500°C.

Sample	σ_g (S/cm)	σ_{gb} (S/cm)	E_g (eV)	E_{gb} (eV)
NiO-GDC	0.107	0.9×10^{-3}	0.81	0.90
GDC/NiO-GDC	0.103	0.5×10^{-3}	1.02	0.93

CONCLUSIONS

Combining both the studies together one could prepare good quality half cell of SOFC which could be further coated with suitable cathode to form a cell. Thus formed cell can be easily co-sintered at comparatively lower temperature as the spray synthesized electrolyte has the desired density. This low-temperature co-sintering ability of cell, thus, avoids formation of un-desirable phases at the interface and provides reliable solution during its construct.

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