INVESTIGATION OF MULTIDOPED CERIA AS CATHODE MATERIAL FOR LOW TEMPERATURE SOLID OXIDE FUEL CELLS

by

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Dedicated to my husband Dr. Sreekumar & son Sreejit

CERTIFICATE

This is to certify that the thesis entitled **Investigation of multidoped ceria as cathode material for low temperature solid oxide fuel cells,** being submitted by **Ms. Rajalekshmi Chockalingam** to the Indian Institute of Technology Delhi is a record of bona fide research work carried out by her. She has worked under our guidance and supervision and has fulfilled the requirements, which to my knowledge, has reached the requisite standard for the submission of this thesis. The results contained in this thesis have not been submitted in part or full to any University or Institute for the award of any degree or diploma.

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Abstract

State of the art yttria stabilized zirconia (YSZ), high temperature solid oxide fuel cells (SOFC) suffer due to high cost and low reliability. Reducing the operating temperature of SOFC from 800 °C to 550 °C would lower the cell degradation rate and fabrication cost through the use of cheaper metallic interconnections and flexible glass sealants. However, a major issue in reducing the operating temperature below 800 °C is the poor catalytic activity of existing cathode materials for electrochemical reduction of oxygen. Although, the perovskite based cathode materials exhibit high electronic conductivity and catalytic activity for oxygen reduction, the coefficient of thermal expansion of these materials do not match with that of GDC electrolytes. To address this problem, multivalent acceptor doped CeO_2 has been suggested as alternative cathode materials for low temperature SOFC.

The objectives of this thesis are to synthesis phase pure multi-doped ceria for low operating temperature SOFC cathode compositions; praseodymium cerium gadolinium oxide, $Pr_xCe_{0.95-x}Gd_{0.05}O_{2-\delta}$ ($0.15 \leq x \leq 0.40$) and terbium cerium gadolinium oxide, $Tb_xCe_{0.95-x}Gd_{0.05}O_{2-\delta}$ ($0.15 \leq x \leq 0.40$) through solid state and liquid state routes and investigate the structural, thermal, electrical and electrochemical properties. To evaluate the electrical performance of cathodes, two electrolytes $Ce_{0.80}Gd_{0.20}O_{2-\delta}$ $(LiNa)CO_3$ and $Ce_{0.80}Gd_{0.20}O_{2-\delta}$ have been synthesized through co-precipitation method. The total conductivity of the samples has been evaluated by using AC impedance spectroscopy. The ionic and electronic contribution to the total conductivity has been estimated by measuring the ionic transference number.

The values of coefficient of thermal expansion of the composition $Pr_{0.2}Ce_{0.75-x}Gd_{0.05}O_{2-\delta}$ (12.5×10^{-6} K^{-1}) and $Tb_{0.4}Ce_{0.55-x}Gd_{0.05}O_{2-\delta}$ (10.6×10^{-6} K^{-1}) was found to be comparable to that of GDC electrolyte (11.5 x 10^{-6} $K^{-}1$) at 550 °C. $Pr_{0.2}Ce_{0.75-x}Gd_{0.05}O_{2-\delta}$ exhibited an ionic conductivity of 0.008 Scm^{-1} and electronic conductivity of 0.015 Scm^{-1}, whereas for nano-$Pr_{0.2}Ce_{0.75-x}Gd_{0.05}O_{2-\delta}$ showed an ionic conductivity of 0.012 Scm^{-1} and electronic conductivity of 0.030 Scm^{-1} at 550 °C. The increased electronic conductivity observed in nano-$Pr_{0.2}Ce_{0.75-x}Gd_{0.05}O_{2-\delta}$ compared to $Pr_{0.2}Ce_{0.75-x}Gd_{0.05}O_{2-\delta}$ is correlated to band gap reduction. $Tb_{0.4}Ce_{0.55}Gd_{0.05}O_{2-\delta}$ exhibited an ionic conductivity of 0.004 Scm^{-1} and electronic conductivity of 0.010 Scm^{-1}, while nano-$Tb_{0.4}Ce_{0.55}Gd_{0.05}O_{2-\delta}$ showed an ionic conductivity of 0.003 Scm^{-1} and electronic conductivity of 0.005 Scm^{-1} at 550 °C. The lower electronic conductivity of nano-$Tb_{0.4}Ce_{0.55}Gd_{0.05}O_{2-\delta}$ compared to nano-$Pr_{0.2}Ce_{0.75}Gd_{0.05}O_{2-\delta}$ may be due to trapping of electrons.

The single cell with configuration, $Pr_{0.2}Ce_{0.75-x}Gd_{0.05}O_{2-\delta}$-$Ce_{0.80}Gd_{0.20}O_{2-\delta}$ // $Ce_{0.80}Gd_{0.20}O_{2-\delta}$// NiO-$Ce_{0.80}Gd_{0.20}O_{2-\delta}$ delivered a maximum power density of 74 $mWcm^{-2}$ at 550 °C, whereas single cells with nano-$Pr_{0.2}Ce_{0.75}Gd_{0.05}O_{2-\delta}$ cathode with similar configuration delivered a maximum power density of 100 $mWcm^{-2}$ at 550 °C. The single cell with configuration, $Tb_{0.4}Ce_{0.75-x}Gd_{0.05}O_{2-\delta}$-$Ce_{0.80}Gd_{0.20}O_{2-\delta}$//$Ce_{0.80}Gd_{0.20}O_{2-\delta}$//NiO-$Ce_{0.80}Gd_{0.20}O_{2-\delta}$ delivered a maximum power density of 76 $mWcm^{-2}$ at 650 °C and nano-$Tb_{0.4}Ce_{0.75}Gd_{0.05}O_{2-\delta}$ cathode delivered a maximum power density of 96 $mWcm^{-2}$ at 650 °C. The poor performance of TCGO cathode compared to PCGO cathode may be due irregularities in microstructures due processing associated problems. In view of the observed properties, the composition, nano-$Pr_{0.2}Ce_{0.75-x}Gd_{0.05}O_{2-\delta}$ is suggested as a potential cathode material for low temperature SOFC. The other applications of this material are oxygen sensors, bio sensors and energy storage devices.

Contents