ABSTRACT

The technological interest of high temperature ceramic nanocomposites in the power generation automotive industries has attracted an extensive research due to the performance of solid oxide fuel cell (SOFCs) electrolyte at high temperatures. However, the ionic conductivity and chemical stability of the material have been limited due to the poor polarization of the material at high temperatures. Recently, the proton conducting perovskite electrolytes possess superior conductivity at an intermediate temperature range of about 400-700ºC (IT-SOFCs), reducing the material strain defects. The rare earth (RE) elements were substituted into the proton conducting perovskite matrix to further enhance the ionic conductivity and to maintain the chemical stability. Grain growth is an important parameter while sintering the ceramic material at high temperatures, which affects the microstructure and density of the material. The novel microwave sintering technique has been exploited due to its rapid sintering of material which effectively controls the grain growth.

Nanocrystalline $BaCe_{0.8}Y_{0.1}$(BCY):$(RE)_{0.1}O_{3-\delta}$ (RE=Yb,Nd,Sm) high temperature proton conductors were synthesised by the modified Pechini route. Powder XRD results show that materials sintered at 1300ºC exhibit orthorhombic crystalline structure with the particle size in the range of nanometer scale. BCY:Sm sample possesses higher lattice strain (ε)

co-efficient of 2.8 X 10^{-3}. SEM micrograph shows bimodal distribution of dense particles with an observable pores in the sub-micrometer scale. The maximum theoretical density of about 95% was achieved for the BCY:Sm sample. I-V and I-P results show a higher open cell voltage (OCV) of 1.03V and the maximum power density of 446 $mWcm^{-2}$ for the BCY:Sm sample compared to other samples indicating that the material is highly stable at higher current density. From the Nyquest impedance plot, the grain boundary bulk resistance was measured to be 52 kΩ and thus the bulk conductivity (σ) of 6.124 X 10^{-4} $S.m^{-1}$ was observed for the BCY:Sm sample at an operating temperature of 700ºC.

Nanocrystalline $BaZr_{0.8}Y_{0.1}:(RE)_{0.1}O_{3-\delta}$(RE=Tb,Nd,Ce) high temperature proton conductors were synthesised by the modified Pechini route. Powder X-ray diffraction analysis shows that the BZY perovskite exhibit cubic crystalline structure with nanometre size particles. SEM micrograph resembles the homogeneous particles distribution in the sub-micrometre scale with lesser pore size. The maximum power density of 77.59 $mWcm^{-2}$ and higher OCV of 1.05V were measured for the BZY:Ce sample from the I-V and I-P measurement . The Nyquest impedance plot reveals the grain boundary resistance of 2.38 kΩ for BZY:Ce sample and the bulk conductivity of about 4.20 X 10^{-4} $S.m^{-1}$ at 700°C.

Ni-$BaCe_{0.8}Y_{0.2}O_{3-\delta}$ proton conducting composite anode was synthesized by the modified Pechini route followed by suspension method to obtain a NiO-BCY composite powder. The prepared NiO-BCY composite powder was reduced to Ni-BCY proton conducting composite anode by

sintering at 700°C for 2 h under hydrogen atmosphere. Powder XRD results show that the Ni phase exhibits cubic and BCY perovskite exhibits orthorhombic crystalline structure and the mean crystallite size of the phases was in the nanometre range. From the SEM micrograph, the homogeneous particles distribution and highly porous microstructure were observed for the reduced Ni-BCY composite anode. The 40% porosity was measured for the reduced Ni-BCY composite anode compared to NiO-BCY sample (31%). From the I–V and I-P measurement, maximum OCV and the maximum power density were measured for the Ni-BCY composite anode as 1.09 V and 486 $mWcm^{-2}$ respectively. From the AC impedance Nyquest plot, the grain boundary resistance of 13.21 Ω and the bulk conductivity (σ) of 4.545 $S.m^{-1}$ were measured for the reduced Ni-BCY composite anode.

Zirconia toughened alumina (ZTA) nanocomposites with different zirconia contents (5-20 mol. %) were prepared by sol-gel method. The prepared composites were sintered at 1300ºC by both conventional and microwave techniques. The crystallinity, average grain size, microstructure and densification of the samples prepared by conventional and microwave sintering methods were compared. X-ray diffraction analysis shows that the microwave sintered samples possess higher tetragonallity and also exhibit reduced particle size compared to conventional sintering. HR-SEM surface micrograph reveals that the microwave sintered samples possess homogeneous particle size distribution with less degree of porosity. TEM analysis confirms uniform distribution of particles with an average particle size of 20 nm for the microwave sintered sample. SAED pattern

reveals that the microwave sintered samples possess improved crystallnity compared to conventional sintered samples. The apparent porosity and density of ZTA nanocomposites measured for different zirconia contents show that the densification of 97% could be achieved for the microwave sintered samples with higher content of zirconium.

Barium titanate ($BaTiO_3$) nanoparticles were prepared by high energy ball milling and subjected to conventional and microwave post sintering at 1000^oC. The synthesized material exhibits strong tetragonality with large c/a ratio. SEM results show the formation of tetragonal shaped $BaTiO_3$ crystals in the nanometer scale and a significant reduction in the particle size for the microwave sintered sample. The microwave sintered sample possesses an average particle size of about 85 nm with high crystallinity as revealed by TEM analysis. UV-VIS spectroscopy studies confirm the higher optical band gap (E_g) of 4.157 eV for the microwave sintered sample. Microwave sintered sample shows higher dielectric constant of ε_r = 4445 with a low dielectric loss of tanδ = 0.0961. Microwave sintered sample exhibits a high polarization maximum of about 73 $\mu C/mm^2$ with reduced coercivity to be 0.293 kV/mm.