Research Paper Nano Science

Merits and Demerits of Ceria Based Electrolytes

P Koteswara Rao	Nano Science and Technogy Centre, Jawaharlal Nehru Technological University, Hyderabad
B N Wani	Chemistry Division, Bhabha Atomic Research Centre, Trombay Mumbai
P V Bhaskara Rao	Department of physics, ST.MaryEngineering Science and Technology, Nalgonda.

ABSTRACT

Ceria-based electrolytes for solid oxide fuel cells (SOFCs) offer many advantages over traditional zirconia-based YSZ electrolytes, notably higher Conductivities at lower operating temperatures and low activation energy. Pure ceria has both electronic and ionic conductivity nature. Pure ceria shows high electronic conductivity than ionic conductivity at high temperature. Rare-earth doped ceria solid solutions have more oxygen conductivity than conventional YSZ because Ce^{+4} radius (0.97Å) is greater than Zr^{+4} (0.72Å) as a result oxygen ions easily migrate through Ce^{+4} sub lattice at operating temperature range of ~ 700°C.

Alivolant cations doped ceria shows high ionic conductivity at relatively low temperature below 800°C which also include less thermal mismatch between its cell components, rapid startup time with less energy consumption. Among those doped with rare-earth oxides, gadolinium and samarium doped ceria shows high ionic conductivity, low activation energy as well as highest stability against reduction at lower temperature than conventional YSZ. Fuel Cell Materials offers a full line of ceria-based electrolyte materials for solid oxide fuel cell and ceramic oxygen Generators. But main limitation is conversion of Ce4+ to Ce3+ in reducing atmosphere at high temperature which converts them from pure oxide ion conducting material to mixed conducting electrolyte material. Various advantages and problems faced for commercialization of ceria based electrolyte will be presented.

KEYWORDS

Ceria has fluorite type crystal structure with space group Fm3m over whole Temperature range(RT to 2750K). The structure can be viewed as an FCC array of Ce ions with the oxygen ions residing in the tetrahedral holes. The 1:2 statiometric is maintained. Single unit cell contains 4 Ce, 8 oxygen ions. Ceria has both electronic and ionic conductivity nature. Pure ceria it shows high electronic conductivity than ionic conductivity. The electrical conductivity of various types of fluorite oxides order

$Bi_2o_3 >$ $Ceo_2 > ZrO_2 > ThO_2 > Hf0_2$.

GENARALLY, YSZ is best electrolyte for SOFC due to its pure ionic conductivity, heat resistance, thermal and mechanical stability(strength and tough ness 1000MPa,7-10Mpam,at room temperature) at high temperature SOFC (900-1000K)

Main drawback of YSZ is ionic conductivity decreases when temperature of solid oxide fuel cell reduces to below 1000K due to increasing resistance of the cell.EX: YSZ of its ionic conductivity at 1273K is 0.1S/cm, when temperature reduced up to 1000K its ionic conductivity is 0.02S/ cm. However, the ionic conductivity of ceria based electrolytes Can be improved by introducing aliovalent cations to doped ceria eg: Gd^{+3} or Sm3+to create the oxygen vacancies to increase the ionic Conductivity.Cation doped Zirconia, Thoria, ceria, with a fluorite structure have been known as Ionic conductors. They contain number of vacancies in crystal lattice which are produced by partial replacement of host cations by Aliovalent solutions (alkaline earth oxides and rare earth oxides). It is used as an electrolyte for electrochemical devices fuel cells, gas sensors, because it has more ionic conductivity than YSZ.

According Kim's Expression r_c =0.1106nm for Divalent ions (alkaline earth oxides) and 0.1038nm for trivalent ions (Rarearth oxides) to get maximum electrical conductivity due to similar ionic radius as the host ion as a result to Minimize the enthalpy between them.(Reduce activation energy)

Addition of aliovalant cation to ceria or Zr oxygen ion conduction mechanism depends on 1) Due to random vacancies inside the material,, which allows conducting anions. 2) Aliovalant cation addition appears to defined relationship between the ionic radii of additive to parent lattice.(1)

Ionic conductivity maximum in fluorites when cation radius matches with critical radius of parent atom.

Ex: In case of Zr^{+4} (0.84A) system the Sc+3(0.87A) cation is most effective do pant where Mg+2 (0.89A) least effective do pant open path way for the conducting anions.

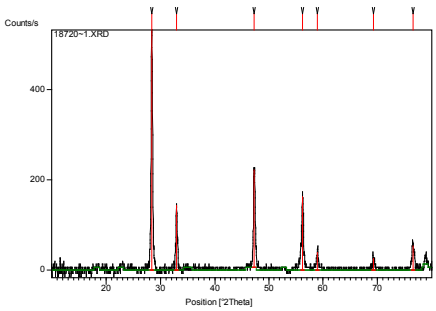
Ceria doped with cations, the host lattices of ceria are compatible with trivalent cations, stable structure is formed when ratio of cations &anions close to 0.70.

According to DFT, Anderson et al., have concluded that the material corresponds to highest ionic conductivity and minimum activation energy if the atomic number lies between 61 (Pm) and 62 (Sm).

Finally, they noticed that if the average atomic number of trivalent dopants lies between 61 and 62 that could be the right choice. Rare-earth doped ceria solid solutions has more oxygen conductivity than conventional YSZ because Ce^{+4} radius (0.97A) greater than Ze+4 (0.72A) as a result oxygen ions easily migrate through ce+4 in operation temperature range 500-700c.(2,3)

Alkaline earth oxides(CaO,SrO,MgO,BaO) doped ceria enhances the electrical conductivity of ceria and minimize the activation energy. MgO and BaO Doped Ceria Shows Less Electrical Conductivity Comparing with SrO and CaO Due to Ionic Mismatch Between Host and Dopant Ions.

GDC XRD pattern:



Ceria based electrolytes conductivity depends on dopant concentration:

Conductivity decreases in heavily doped ceria was due to the clustering of dopant cations and their associated oxygen vacancies

If the doping concentration is less, the majority of clusters involve only one cation bounded to the only one single oxygen vacancy.

if the doping concentration is more then density of clusters consists two or more do pant cations increases , as a result stronger traps for associated oxygen vacancies. It is very difficult to diffusion of oxygen vacancies as result conductivity decreases.

Due to high concentration doping lattice distortion takes place as a result conductivity decreases Ionic conductivity increases by reduced its grainsize boundary at nano ceria based electrolyte:

Impurities such as Si and Ca segregate at grain boundaries and form thin blocking layers within the grain boundary which affect the grain boundary conductivity. One way of reducing the larger Contribution of segregated impurities is to reduce the grain size, so that the grain Boundary per unit volume is increased and the total amount of impurities can be spread over a large interfacial areas a result, in the nanostructured materials, grain boundary may provide fast diffusion pathway for ionic defects resulting enhanced ionic conductivity in the finely grained materials. (4,5)

So, the nanocrystalline materials with improved electrochemical properties are expected to overcome some ofthe drawbacks associated with microcrystalline ceria based electrolyte, opening widerange of applications in the intermediate temperature range.

Therefore, in recent days, the nanostructured ceria based electrolyte materials doped with different do pants and dopant-concentrations have attracted a great Interest for their development as electrolyte materials for SOFCs.Currently enormous efforts are being made to understand the electrolytic properties of nanoscale ceria based materials for application purpose.

Ionic conductivity increases by reducing Thickness of electrolyte layer by using thin layer technology (Nano size) or Co-doping on ceria:

Due Co-doping on ceria shows high mechanical stability, enhancement of electrical conductivity than single doped ceria based electrolytes due to Dopant ion, dopant concentration, oxygen vacancy concentration, defect association energy and local defect structure are the factors, which can influence the total ionic conductivity in ceria .

ex:
Ce0.8(CaGdSm)0.2O2 , Ce0.8Gd0.2–xPrxO1.9 ,Ce0.8Gd0.2–xSmxO1.9 , Ce1.9Gd0.1O1.95 adding 2 wt.%Co , Ce0.85Gd0.1Mg0.05O1.9 , Ce1–aGda–ySmyO2–0.5.

Deposition methods to prepare thin films:(6,7,8)
1. Chemical methods: 1.CVD 2. EVD 3.sol-Gel
2. Liquid precursor route: Spray paralysis
3. Physical methods: Thermal spray technique, laser deposition, PLD, Laser spraying
4. PVD technique: R.F Sputtering Technique.
5. Ceramic powder processing methods:
1. Screen printing,
2. Slurry coating
3. Tape casting
4. Slip casting
5. Filter pressing.

Applications of ceria:
1. Catalysis
2. Chemicals
3. Glass
4. Ceramics
5. Metallurgy

Advantages of ceria based electrolytes:
1. SOFC electrolytes (up to 700°C)
2. Electrolyte for oxygen generation systems
3. Additives for anodes and cathodes
4. Interlayer's for high performance SOFCs
5. Higher ionic conductivity than YSZ for better results at lowerOperating temperature
6. Chemical inertness and thermal expansion match with high Performance cathode materials such as LSCF and SSC
7. Enhanced performance when used in composite electrodes
8. High crystalline-phase and chemical purity

Drawbacks of ceria based electrolytes:
1. Ceria-based electrolyte, under. Reducing conditions on the anode side, some of the ions Ce4+ reduce to Ce3+ (.unprotected against reduction on the anode side) these results in mixed ionic/electronic conductivity, a decreased open-circuit voltage and internal short circuiting.
2. A disadvantage Of CeO2 electrolytes is their tendency to undergo reduction at high temperatures (above 700 oC) and low oxygen partial pressures (P02), with the consequent introduction of electronic defects
3. Pure ceria has a serious problem in degradation in performance with time at elevated temperature.

REFERENCES

1) Inaba H, Tagawa H (1996) Solid State Ionics 83:1 | 2. Kharton V, Figueiredo F, Navarro L, Naumovich E, Kovalevsky | A, Yaremchenko A, Viskup A, Carneiro A, Margues M, Frade J(2001) J Mater Sci 36:1105 | 3)Chourasia , J Y Patil, S H Pawar, L D Jadhav, Studies on Structural, morphological | and Electrical properties of Ce1-x GdxO2-x/2 . Mat Chem and Phy. 109 (2008), 39-44 | 4)Herle J V, Horita T, Kawada T, Sakai N, Yokakawa H andDokiya M 1996 Solid State Ionics 86–88 1255 | 5)Herle J V, Horita T, Kawada T, Sakai N, Yokakawa H andDokiya M 1997 J. Am. Ceram. Soc.80 933 | 6)Hirano M and Kato E 1996 Commun. Am. Ceram. Soc. 79 777 | 7)Mogensen M, Sammes N M and Tompett G A 2000 Solid Statelonics 129 63 | 8)Park I S, Kim S J, Lee B H and Park S 1997 Jpn. J. Appl. Phys. |