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Fabrication, characterisation and conductivity measurement of a perovskite-type proton conductor

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Abstract

Ceramic based materials from the ABO_3 perovskite family, show both proton and oxide ion conductivity at intermediate temperatures depending on the gaseous environment. Due to these multi-species transport features of them and their potential to be utilised as an electrolyte in solid oxide fuel cells operating at intermediate temperature, there has been lot of research focused on them and their properties. In this study, a perovskite type proton conductor was synthesised by using solid state reaction method. X-ray diffraction (XRD) and Energy dispersive X-ray spectroscopy (EDXS) characterisation techniques were utilised to determine crystal structure, phase purity and the elemental materials composition in powder form. The results were compared with International Centre for Diffraction Data (ICDD) database and displayed excellent match with standard perovskite structure. Also, the surface area measurement was performed via utilising the Brunauer-Emmett-Teller (BET) method. The conductivity measurement was carried out at the intermediate temperature (500-800°C) using AC impedance at different atmospheres.

Keywords: *Perovskite materials, AC impedance, intermediate temperatures.*

Perovskit tipi proton ileten bir malzemenin sentezi, karakterizasyonu ve iletkenlik ölçümü

Özet

ABO_3 perovskite ailesinden olan seramik esaslı malzemeler, gaz ortamına bağlı olarak orta sıcaklıklarda (500-800°C) hem proton hem de oksijen iyonu iletkenliğini göstermektedir. Bu tür malzemeler çok yönlü taşıma özelliklerinden ve bunların orta sıcaklık katı oksit yakıt pillerinde elektrolit olarak kullanılma potansiyellerinden dolayı ilgi çekmiştir. Bu çalışmada, katıhal reaksiyon yöntemi kullanılarak bir perovskit tip proton iletken malzeme sentezlenmiştir. X-ışını difraksiyonu (XRD) ve X-ışını enerji dağılımı spektrometresi (EDXS) karakterizasyon teknikleri kullanılarak toz formundaki malzemenin kristalografik yapısı, faz saflığı ve element bileşimi belirlenmiştir. Sonuçlar Uluslararası Kırınım Merkezi Verileri (ICDD) veri tabanı ile karşılaştırılmış olup, standart perovskite yapısı ile mükemmel uyum göstermiştir. Yüzey alanı ölçümü Brunauer-Emmett-Teller (BET) yöntemi kullanılarak gerçekleştirildi. İletkenlik ölçümü, farklı gaz ortamlarında AC empedansı kullanılarak orta sıcaklık aralığında gerçekleştirildi.

AnahtarKelimeler: *Perovskit malzemeler, AC empedansı, ortasıcaklık.*

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1. Introduction

The world is facing growing energy demands and carbon footprint which results in depletion of limited world energy sources and high pollutant emissions. This requires immediate action by shifting from current energy producing technologies to much efficient and greener technology. From this point of view, hydrogen energy and fuel cells can offer to the world the prospect of reducing pollutant emissions and increasing energy efficiency [1-3] . Fuel cells have the ability of converting chemical energy of a fuel into electrical energy with high efficiency and low, even no emissions of harmful substances to the environment. Between the different types of fuel cells, solid oxide fuel cell (SOFC) is one of the most strongest candidate in fuel cell technology owing to its high efficiency and fuel flexibility [4] .

A typical SOFC uses an oxide ion conducting electrolyte such as yttria-stabilised zirconia (YSZ) which usually operates between 750 and 1000°C [5]. Operation of an SOFC at high temperature decreases its applicability to real life owing to the problems such as long start up time, expensive interconnect materials, thermal stress etc. [6] . Therefore, protons conducting ceramic electrolytes have gained a lot of interest recently. They have the ability to reduce operating temperature down to 500-800 °C and increase the open circuit potential so as the whole efficiency of the SOFC. Proton conductivity in ABO_3 perovskite family was first shown by Iwahara *et el.* [7] in 1981. Further studies have been carried out on $SrCeO_3$, $BaCeO_3$, $BaZrO_3$ by doping a trivalent cation M(M = Y, Nd, Sm, Gd and Yb) into B sites ($AB_{1-x}M_xO_{3-\delta}$) which creates oxygen vacancy in the crystal [8] . The interaction of oxygen vacancies with water or hydrogen creates protonic defects [9, 10] and thus, oxygen ion and proton (mixed ionic) conductivity [11, 12] .

Various data on conductivity was presented by the researchers for barium zirconates ranging from 10^{-6} S/cm to 10^{-2} S/cm at 600°C [13] . Especially, doped-$SrCeO_3$ and $BaCeO_3$ materials displayed high proton conductivity. The proton conductivities of them were given in the order of 10^{-3} to 10^{-2} S/cm in hydrogen containing atmosphere [8]. Barium cerates were reported as mainly ionic conductor under low oxygen partial pressure and mixed ionic–electronic conductor under high oxygen partial pressure [14] . The impact of doping level on the conductivity of the material was also investigated by Takeuchi *et al* [15] and Tauer *et al* [16] . Takeuchi *et al* varied yttrium concentration $0 \leq x \leq 0.3$ for $BaCe_{1-x}Y_xO_{3-\delta}$ and obtained higher total conductivity in the range of $0.15 \leq x \leq 0.25$. Taue r*et al* reported that hydration expansion of yttrium doped barium cerate increases with increasing dopant concentration. Another important parameter that can affect the proton conductivity of these kinds of ceramic materials is synthesis method. Many synthesis methods have been investigated in order to produce dense ceramics [17-20] . Solid state reaction and sol-gel method are the most common methods that have been utilised so far. It is possible to produce dense ceramics with high density values as high as ~97% with these methods. In this study, 20% yttrium doped barium cerate, which is the most promising proton conductor among others, is studied in terms of preparation, characterisation and conductivity. The conductivity measurements are carried out at different atmospheres in the intermediate temperature range (500-800°C).

2. Experimental

Solid state method was chosen to obtain ceramic powder. The row materials used in the preparation procedure were; $BaCO_3$ (99%, Aldrich), CeO_2 (99%, Aldrich), and Y_2O_3 (99%, Aldrich).The suitable amounts of beginning materials were grounded in ethanol. Ball mill was used to blend the mixture for 4 hrs. Then the mixture was calcined at 1300°C for 10 hrs. A 20 mm diameter die was used to apply 3 tons of pressure to press approximately 2.2 g of powder to pellet form. Then the following procedure was applied to sinter the pellet under ambient conditions; temperature was increased to 1450°C at a rate of 1°C/min, kept at1450°C for 12 hrs and decreased to room temperature at a rate of 1°C/min. The pellets were about 1.4-1.6 mm thick after sintering. The volume and mass of the pellet was used to calculate the density of pellet. The obtained density was higher than the 95% of the theoretical density of the pellet (6.154 g/cm^3[20]).The crystal structures of the pellets were confirmed by XRD (X-Ray Diffraction) and morphology of them was analysed by SEM (Scanning Electron Microscopy).A three electrode set up shown in Figure 1 was used to do AC impedance measurements. The three electrode set up was consisting of a working, a counter and a reference electrode. Pt (platinum) was applied on one side of the pellet as a working electrode with an area of 0.5 cm^2 whereas Au (gold) was applied on the counter side of the pellets as a counter electrode with the same area. Au was also applied as a reference electrode on the same surface of the pellet with an area of of 0.05 cm^2. The electrode connections were ensured by using gold wires. The conductivity measurements were carried out in single chamber reactor between 500-800ºC under a single gas environment. The feed gases were used with a 100 ml/STP flow rate. The humidification of feed gas was ensured by using a water bath. The conductivity data was obtained in the frequency range of 500 KHz to 50 MHz at an AC voltage of 100 mV for several times.

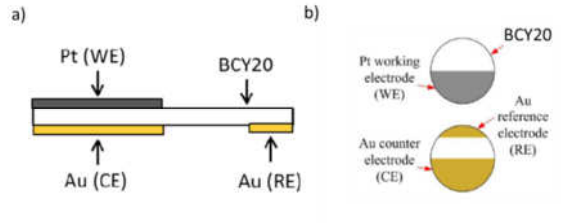

Figure 1.3-electrode set up used for AC impedance measurements.

3. Results and discussion

The crystal structure of BCY20 membrane in pellet form (after sintered at 1450ºC for 12 hrs) was identified by using X-ray diffraction (CuK_{α}, 1.5406 A^0) is depicted in Figure 2.The BCY20 pellets display an excellent match with the standard BCY20 rhombohedral structure(ICDD-01-070-6750)**[20-22]** . The data does not demonstrate any new phases and impurities. The low intensity peaks at 2θ values: 24 and 27 may be attributed to $BaCO_3$ according to crystallographic database.

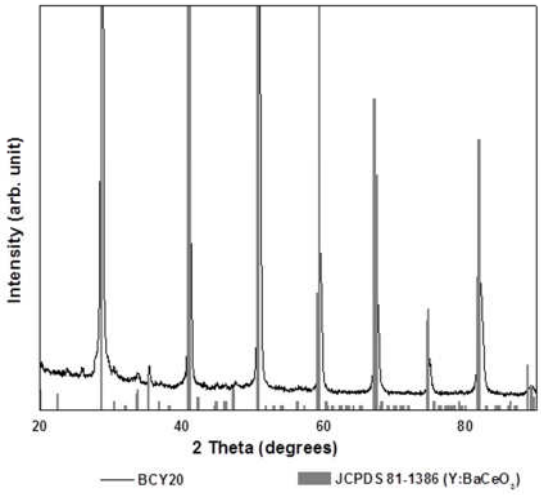

Figure 2.X-ray diffraction pattern of BCY20 pellets.

The EDXS (Energy Dispersive X-Ray Spectroscopy) result is given in Figure 3. This semi quantitative technique is applied to determine the stoichiometry of BCY20 pellet before conducting the AC impedance measurements. Table 1 presents the calculated stoichiometric rates for each element from the EDXS scans. The calculation was done by computing moles of each element and taking one of the elements' moles as a base. Barium is taken as a base element in the current calculation. Then the moles of other elements are divided by the moles of barium. As Table I shows, 20% yttrium was successfully doped.

Table 1. Calculated stoichiometric ratios for BCY20 from the EDXS results.

Membrane	Condition	Approximate atom (%)			
		Ba	**Ce**	**Y**	**O**
BCY20	bare	14.9 ± 1.8	11.7 ± 1.7	3.2 ± 0.9	70.2 ± 13.9
		Stoichiometric ratio			
BCY20	bare	**Ba**	**Ce**	**Y**	
		1	0.78	0.21	

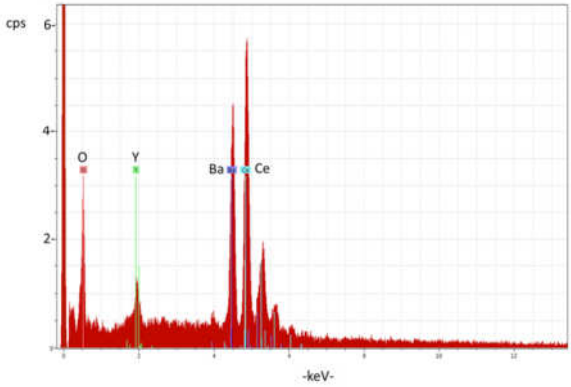

Figure 3.The EDX scan for BCY20 surface.

Further characterization of BCY20 pellets are done by using SEM regarding microstructure, pore sizes, density, morphology etc. The surface and cross section image of BCY20 pellet is displayed in Figure 4a and Figure 4b after application of sintering process. It can be clearly seen from Figure 4 that microstructure of the pellet is dense. No cracks are observed. The grain sizes vary from approximately 1 µm to 2 µm. Also, 6.154 m^2/g surface area is obtained from BET measurements.

The conductivity measurements are performed using a potentiostat. Figure 5 shows the conductivity results for different temperatures and atmospheres. In the AC impedance data, first intercept on the real axis at high frequencies is taken to obtain total resistance [23] and hence it can be regarded as bulk conductivity.

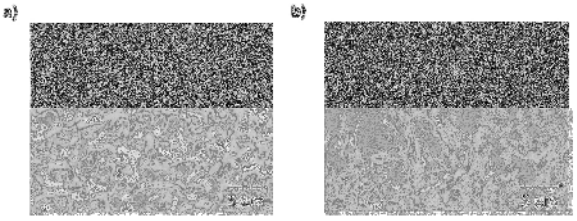

Figure 4. a) Surface SEM image and b) cross section image of BCY20 pellet.

The electrical conductivity of BCY20 pellet was obtained using the following equation;

$$\sigma = \frac{l}{A \times R} \quad (1)$$

Where Rpresents bulk resistance, lpresents the distance between working and counter electrodes (pellet thickness), Apresentsworking electrode surface area. In oxygen atmosphere, the total conductivity is due to holes and oxygen vacancies whereas in moist atmosphere, it is owing to oxygen vacancies and protonic defects. However, at moderate oxygen partial pressure the electronic conductivity can be neglected [24] and thus hole conductivity is neglected in this work.

In hydrogen atmosphere, the conductivity of BCY20 is given between 0.001 and 0.01 S/cm in literature[8] . At 700°C, a conductivity of approximately 5×10^{-2} S/cm was reported for BCY20 in hydrogen [25] . As seen from Figure 5 that the conductivity of about 0.049 S/cm is obtained at 700°C in 2.3% H_2O-5% H_2atmosphere similar to those reported values [25, 26] .All the conductivities rise as the temperature increases showing that migration of ions within the pellet is thermally activated. By comparing the data in Figure 5 at 700ºC for all atmospheres, it can be said that BCY20 is mostly a proton conductor at intermediate temperature range while oxygen ion conduction seems to be dominant at high temperatures.

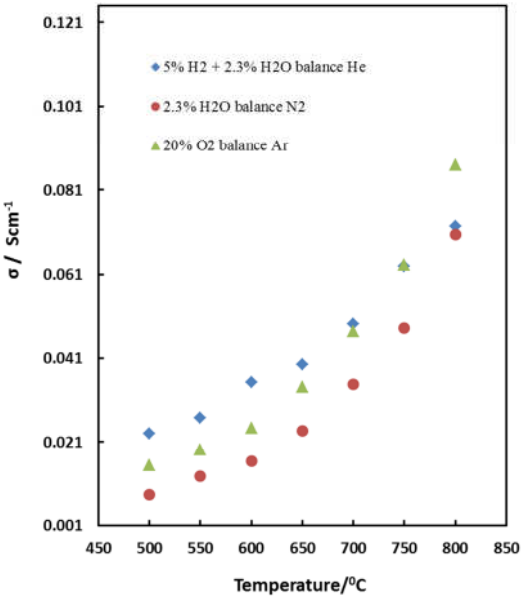

Figure 5. The AC conductivity results of BCY20 pellet as a function of temperature. (▲) 20% O_2 balance Ar, (●) 2.3% H_2O balance N_2, (♦) 5% H_2 + 2.3% H_2O balance He.

The proton conductivity activation energy for different temperatures is computed using the Arrhenius plot (Figure 6) and the equations below;

$$k = A\, e^{\frac{-E_a}{RT}} \quad (2)$$

$$\ln(k) = \frac{-E_a}{R}\left(\frac{1}{T}\right) + \ln(A) \quad (3)$$

Where k is rate constant, A is pre-exponential factor, R universal gas constant, T is temperature in Kelvin, E_a is activation energy.

The value that obtained for proton conduction at 700ºC is ~0.35 eV in in 5% H_2 + 2.3% H_2O environment. This data is line with the data presented in literature [20, 27, 28] .

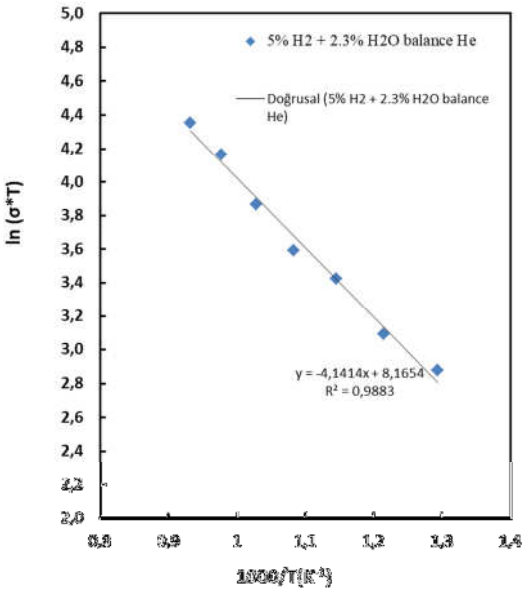

Figure 6.The Arrhenius plot of bulk conductivity of BCY20.

4. Conclusion

The perovskite ceramic pellets of BCY20 were successfully prepared using solid state reaction method from raw materials. The pellet's density was about ~95% of the theoretical density with grain sizes vary from approximately 1 µm to 2 µm. The XRD result depicted a rhombohedral phase with no impurities. The conductivity of approximately 5×10^{-2} S/cm and 0.35 eV activation energy was obtained at 700°C under 5% H_2 + 2.3% H_2O atmosphere which is well agree with the typical BCY conductivity data in literature under similar conditions.

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