The synthesis of solid oxide fuel cell by electrolyte systems based Bi$_2$O$_3$ doped with Ho$_2$O$_3$, Dy$_2$O$_3$

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Abstract: In this study, Bi$_2$O$_3$ couple system sample materials were synthesized using solid state reaction method sintering each of them. Structural and electrical properties of these electrolyte samples for solid oxide fuel cells (SOFCs) have been evaluated by means of XRD, TG / DTA, SEM and four-probe method. In this work, (Bi$_2$O$_3$)$_{1-x-y}$(Dy$_2$O$_3$)$_x$(Ho$_2$O$_3$)$_y$ tenary systems have been investigated. As a result of XRD measurements, $\delta$ (cubic)-phase samples were obtained with a stable structure. As a result of electrical conductivity measurements, (Bi$_2$O$_3$)$_{1-x-y}$(Dy$_2$O$_3$)$_x$(Ho$_2$O$_3$)$_y$ tenary system, increase Dy$_2$O$_3$ molar ratio corresponds to a fixed molar ratio of Ho$_2$O$_3$ conductivity value falls was obtained.

Keywords: Fuel cell, Solid electrolyte, Solid state reaction, Electrical conductivity, Activation energy.

1. Introduction:

Energy demand increases rapidly due to population growth, industrialization and technological developments in the world. Fossil fuels are the biggest cause of natural disasters caused by global warming [1]. Environmental problems such as global warming, climate change and greenhouse effect occur due to the continuous secretion of gases such as carbon dioxide, carbon monoxide, nitrogen oxides, methane, sulfur dioxide, which are produced by burning fossil fuels [2]. In addition to increasing energy demand, the reserves of fossil energy sources are also decreasing rapidly.

Assuming the fact that these fuels will run out in the near future, the search for alternative energy has gained importance in scientific circles [3]. Fuel cells in alternative energy production have increased their research worldwide in recent years and the application range of fuel cells is among the most popular research topics. A fuel cell electrochemically converts chemical energy into electrical energy [4,5,6,7]. Such a system, which maintains electricity production when continuously fueled from outside, can be considered as a conventional power generation system. Fuel cell is a power generation element that converts the chemical energy of fuel (hydrogen) and oxidizer (air) into energy that can directly use it in the form of electricity and heat [8]. It is quite clear that it will constitute an alternative energy source. This allows it to be used as an environmentally friendly renewable energy source. It has many advantages over conventional power supplies [9]. Today, a wide variety of fuel cells are produced for different purposes. It is possible to classify the fuel cells according to the type of fuel and oxidizer component fed or the fuel fuel fed into a "useful fuel" other than the battery, or whether this process is inside the battery [10,11,12,13]. Apart from these, the operating temperatures or the difference of electrolytes used are also the variables used in making this distinction [14,15]. The most commonly used in the classification of fuel cells is the type of classification according to the difference of electrolyte used [16,17].
Finger 1.1: Advantages of fuel cells.

There are five different fuel cells depending on the difference of electrolyte used:
1. Phosphoric acid fuel cell, 2. Polymer electrolyte membrane fuel cell, 3. Alkaline fuel cell
4. Melt carbonate fuel cell, 5. Solid oxide fuel cell.

Fuel cells operate on the same electrochemical principles, but they operate at different temperature ranges using different components. Therefore, depending on the type of fuel cell, the power densities and fuel tolerances of these fuel cells differ. It is given together with fuel cell types and comparisons commonly known in Table 1.1.

Table 1.1. Fuel cell types and their comparative features [18].

| Electrolyte       | PEMFC          | AFB            | FAFC            | MCFB             | SOFF               |
|-------------------|----------------|----------------|-----------------|------------------|--------------------|
| Work temperature  | 80°C           | 65°C-220°C     | 150°C-220°C     | 650°C            | 600°C – 1000°C     |
| Catalyze          | Platinum       | Platinum       | Platinum        | Nickel           | Perovskite         |
| Transferred Ion   | H⁺             | OH⁻            | H⁺              | CO₃²⁻            | O²⁻                |
| Fuel Treatment    | Battery Out    | Battery Out    | Battery Out     | Inside the battery | Inside the battery |
| Anode Gas         | Hydrogen       | Hydrogen       | Hydrogen        | Hydrogen, Methane | Hydrogen, Methane  |
| Cathode Gas       | Pure oxygen or air | Pure Oxygen   | Oxygen from air | Oxygen from air | Oxygen from air    |
| Heat Management   | Cooler         | Cooler-Generates | Cogeneration   | Cogeneration     | Cogeneration       |
| Yields            | %35-60         | %50-70         | %35-50          | %40-55           | %45-60             |
| Other Features    | Electrolyte solids being brought advantages it has. Low the temperature Other work is an advantage. | Hydrogen and Good with oxygen performance Shows. Space Like research closed For applications Suitable. | Performance AFC Den is low. | Electrolyte corrosive And movement We could. Battery For structural stainless steel must. Expensive No metals needed. | Materials heat between expansion disproportion it may occur. |
The atomic number of bismuth, which is a 5A group, is 83 and its mass number is 208.980 units. It is found in the 6th period. Its electronic configuration is [Xe] 4f^145d^106s^26p^3. It is found in the bismuth compounds in the oxidation steps +3 ve +5. Metallic bismuth forms rhombohedral crystals. This metal is light gray, hard and brittle, and it conducts heat very little. Its melting point is 544.5°C, its boiling point is 1560 °C and its density at 20 °C is 9.80 g/cm³. [19] Crystal structure of pure Bi₂O₃ at room temperature is as seen in Figure 1.2.

![Crystal structure of pure Bi₂O₃](image)

Figure 1.2. Crystal structure of pure Bi₂O₃

2. Computational Method:

Solid state reactions were carried out in ash furnaces and alumina crucibles working in an open atmosphere. Alumina crucibles were heat treated at 48 h and 700 °C before the reaction processes were started. Empty masses were measured before and after this heat treatment. This process was repeated until the masses of the crucibles were the same before and after heat treatment. The aim is to bring the crucibles to constant weighing. Thanks to this method, the weighing to be made during the heat treatments applied to the samples and the expected mass changes will only belong to the samples. The masses of the samples to be used were determined with 10-5 g precision scales while the samples were in the crucible. Mass changes were continuously monitored by weighing the samples before and after heat treatment. Color changes of the samples were also monitored depending on the reaction temperature. In the heat treatment step, a certain amount of powder sample was taken to make XRD measurements, to understand whether any phase was formed and to measure the electrical conductivity of the phases formed. Subsequently, the powder samples taken to the measurement were pressed and made into tablets and prepared for measurement. Pressing was done with a Specac brand press machine. The samples placed in the 13 mm diameter mold were pressed under 5 tons of pressure. Again care was taken to ensure that all the tablets formed were at least 1 mm thick. Then the conductivity measurements of the tablets were started. Phase conversion temperatures, thermal stability and other relevant thermal properties of materials synthesized as single phase were tried to be determined by making measurements in DTA / TG system. In these measurements, Perkin Elmer brand DTA / TG system, which can work simultaneously, was used. Analyzes, with a heating rate of 10 °C / min, from room temperature to temperatures of 800-900 °C, in a dynamic inert gas atmosphere, in platinum sample containers, α-Al₂O₃ inert reference and approx. Made with sample amounts of 11-12 mg. Several other methods have been used [20-27].

Electrical conductivity measurements of the pallets produced during this thesis study, four point d.c. made with the system. Measuring system; It consists of PC, IEEE-488.2 Bus, Interface card, scanner card
multimeter (Keithley brand 2700 model), programmable current source (Keithley brand 2400 model) and specially prepared package programs for this purpose. All measurements were made with DAQ (Data Acquisition) control system. The electrical conductivity (dust and thin layer) conductivity measurements of solid electrolytes were made under computer control depending on temperature and doping concentration. In order to determine the actual temperature of the sample whose conductivity is measured, the thermal pair was placed at a distance of 2-3 mm from the sample. The average of 10 data at each measurement temperature was determined by determining the conductivity value of the sample at that temperature. Ceramic conductivity measurement kit, Specially designed and produced by our research group, was used for conductivity measurements. During conductivity measurements, platinum wires with a diameter of approximately 0.5 mm were placed on the pallets by direct contact with four different points, with a distance of 2 mm between the wires. provided. In the measurements, it is preferred to provide direct contact without using binding paste (Ag paste or Pt paste) in order to minimize contact resistance. Also, the sample with the highest conductivity was tried to be determined. Activation energies were calculated by determining the electrical conductivity values, one of the material characterizations, which have the highest conductivity. In the conductivity mechanism of ionic conductors, the ions in the braid migrate from their braiding points to other vacant positions, creating conductivity. In this case, the activation energy defined here is the threshold energy that ions need in this ionic conductivity mechanism formed by the movement of ions to separate from their position in the lattice and move to another empty state. Activation energy can be determined from the conductivity equation.

\[
\ln (\sigma_T) = - \frac{(E_a)}{k} \left( \frac{1}{T} \right) + \ln (\sigma_0)
\]

3. Result and Discussion:

XRD Measurements: In this term study (Bi₂O₃)₁₋ₓ₋ₚ (Ho₂O₃)ₓ (Dy₂O₃)ₚ triple system was studied. The mole ratios prepared of the triple system are shown in Table 1.2. Sample samples were prepared by solid state reaction by heat treatment at 750°C for 48 hours.

Table 1.2. Ho₂O₃, Dy₂O₃ additives and Bi₂O₃ base material in moles percentages.

| Sample | Ho₂O₃ | Dy₂O₃ | Bi₂O₃ |
|--------|-------|-------|-------|
| A1     | % 11  | % 4   | % 85  |
| A2     | % 12  | % 3   | % 85  |
| A3     | % 13  | % 2   | % 85  |
| A4     | % 14  | % 1   | % 85  |
| A5     | % 15  | % 1   | % 84  |
| A6     | % 15  | % 5   | % 80  |
| A7     | % 20  | % 1   | % 79  |
| A8     | % 20  | % 5   | % 75  |
| A9     | % 25  | % 5   | % 70  |
| A10    | % 30  | % 5   | % 65  |
Figure 1.3. XRD belonging to A1 sample heat treated at 750 °C for 48 hours comparison of spectra; (a) Without taking electrical conductivity measurement of A1 sample previous XRD spectrum, (b) 3 times consecutive electrical conductivity measurement of A1 sample XRD spectrum after receipt.

Figure 1.4. XRD belonging to A4 sample heat treated at 750 °C for 48 hours comparison of spectra; (a) Without taking electrical conductivity measurement of A4 sample previous XRD spectrum, (b) 3 times consecutive electrical conductivity measurement of A4 sample XRD spectrum after receipt.
Figure 1.5. XRD of A6 sample heat treated at 750 °C for 48 hours comparison of spectra; (a) Without taking electrical conductivity measurement of A6 sample previous XRD spectrum, (b) 3 times consecutive electrical conductivity measurement of A6 sample XRD spectrum after receipt.

Consequently, while the same heat treated samples A1, A2, A3, A4, A5, A6, A7, A8, A9, A10 were initially stable phase, Bi₂O₃ has a high conductivity range as a result of electrical conductivity measurements 3 times in a row. Bi₂O₃ stable phase has been determined.

**Electrical Conductivity Measurements**

![Graph](image_url)
Figure 1.6. Electrical belonging to A1 sample which is heat treated at 750 °C for 100 hours conductivity measurement results;
(a) 1. Electrical conductivity chart for heating and cooling,
(b) 2. Electrical conductivity chart for heating and cooling,
(c) 3. Electrical conductivity chart for heating and cooling.
Figure 1.7. Electrical of A4 sample which has been heat treated for 48 hours at 750 °C conductivity measurement results:

(a) 1st heating electrical conductivity chart,
(b) 2. Electrical conductivity chart for heating and cooling,
(c) 3. Electrical conductivity chart for heating and cooling.
Figure 1.8. Electrical belonging to A6 sample heat treated at 750 °C for 48 hours conductivity measurement results;
(a) 1. electrical conductivity chart for heating and cooling,
(b) 2. Electrical conductivity chart for heating and cooling,
(c) 3. Electrical conductivity chart for heating and cooling

The electrical conductivity graphs of samples A7, A8, A9, A10 were similarly obtained. According to the electrical conductivity results, the conductivity values of the phase of the phase of δ-Bi₂O₃, which is the stable phase, were found.

Table 1.3. Electrical conductivity data of Ho₂O₃ - Dy₂O₃ - Bi₂O₃ triple system Comparing.

| Sample | Ho₂O₃ | Dy₂O₃ | Bi₂O₃ | σ (ohm.cm)⁻¹ (conductivity) | Log σ (ohm.cm)⁻¹ | Temperature (°C) |
|--------|-------|-------|-------|-----------------------------|------------------|-----------------|
| A1     | % 11  | % 4   | % 85  | 3.84E-01                   | -0.41            | ~820            |
| A2     | % 12  | % 3   | % 85  | 3.13E-01                   | -0.50            | ~820            |
| A3     | % 13  | % 2   | % 85  | 3.16E-01                   | -0.49            | ~820            |
| A4     | % 14  | % 1   | % 85  | 2.93E-01                   | -0.53            | ~820            |
| A5     | % 15  | % 1   | % 84  | 1.35E-01                   | -0.86            | ~820            |
| A6     | % 15  | % 5   | % 80  | 1.32E-01                   | -0.87            | ~820            |
| A7     | % 20  | % 1   | % 79  | 1.71E-01                   | -0.76            | ~820            |
| A8     | % 20  | % 5   | % 75  | 1.53E-01                   | -0.81            | ~820            |
| A9     | % 25  | % 5   | % 70  | 7.36E-02                   | -1.13            | ~820            |
| A10    | % 30  | % 5   | % 65  | 4.10E-02                   | -1.38            | ~820            |
Activation energy

Table 1.4. When examined, it varies within the range of $0.52 \leq E_a \leq 0.71$ eV. The lowest activation energies in the studied f2z-phase triple systems are δ-phase Bi$_2$O$_3$ compounds with 14,13,11 mol% Ho$_2$O$_3$ and 1,2,4 mol% Dy$_2$O$_3$. Figure 1.14. The graphs indicate the change in the activation energies of the compounds with-phase. Graphic; In Dy$_2$O$_3$ - Ho$_2$O$_3$ additive system, when the Dy$_2$O$_3$ additive amount is kept constant and examined according to the increase of the Ho$_2$O$_3$ additive level, the activation energies decreased. In addition, the activation energies have the same mold lowest activation energies in δ-phase Bi$_2$O$_3$ compounds with 14,13,11 mol Ho$_2$O$_3$ 1,2,4 mol Dy$_2$O$_3$ doped, where the total contribution remains the same in other compounds.
Figure 1.14. Change of activation energies according to the amount of additives

Table 1.4. Activation energies of binary compounds with Dy₂O₃ and Ho₂O₃ additives.

| Synthesis Temperature (°C) | Ho₂O₃ Contribution Rate (% mol) | Dy₂O₃ Contribution Rate (% mol) | Eₐ (eV) |
|---------------------------|---------------------------------|---------------------------------|---------|
| 750                       |                                  |                                 |         |
| 11                        | 4                               | 0.52                            |         |
| 12                        | 3                               | 0.64                            |         |
| 13                        | 2                               | 0.52                            |         |
| 14                        | 1                               | 0.52                            |         |
| 15                        | 1                               | 0.58                            |         |
| 20                        | 1                               | 0.64                            |         |
| 25                        | 5                               | 0.57                            |         |
| 30                        | 5                               | 0.71                            |         |

TG / DTA Measurements

Figure 1.15. A5 sample heat treated at 750 °C for 48 hours is electrica TG / DTA plot before conductivity measurement.

Figure 1.16. A5 sample, which was heat treated at 48 °C for 48 hours, 3 times TG / DTA plot after electrical conductivity measurement is taken.

SEM Measurements: SEM images were taken to examine the superficial structures of the (Bi₂O₃)₁₋ₓ₋ₐ (Ho₂O₃)ₓ (Dy₂O₃)ᵧ triple-system samples and SEM images of some of these triple-system are given below.
4. Conclusion:

The overall concept is very useful for new researchers as indicated in the results. Activation energy was found that having the values varying from 0.48 eV to 1.27 eV. The end study, \((\text{Bi}_2\text{O}_3)_{1-x-y}(\text{Dy}_2\text{O}_3)x(\text{Ho}_2\text{O}_3)y\) ternary system, activation energy was found that having the values varying from 0.52 eV to 0.71 eV. The solid electrolytes we have synthesized in this study can be used in diverse industrial applications such as solid oxide fuel cells (SOFC).

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