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A new look at oxygen pumping characteristics of BICUVOX.1 solid electrolyte

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The operational characteristics of an oxygen pump using Cu substituted bismuth vanadate, BICUVOX.1, solid electrolyte for an open system was investigated in detail. The major objectives were to show a correlation between oxygen pumping current and cell voltage, Faradic efficiency, oxygen production rate, and to investigate structural stability of the solid electrolyte under current flow. The dc polarization diagram showed four different, well defined regions. They correspond to the electron transfer reaction and Ohm'ic resistance of the electrode and electrolyte respectively. The last two regions at high current densities showed a progressive deviation from the Ohm'ic behavior and finally voltage instability. These were considered to be the result of current induced structural modification, which was detected by X-ray analysis of cathode and anode side separately. The oxygen production rate was examined for different temperatures (450 to 550°C). It increased by increasing the current density up to 800 mA/cm^2, where instability in cell potential was observed, and the Faradic efficiency was declining slightly from100 to 95%.

1. Introduction

$Bi_2V_{1-x}Me_xO_{5.5-3x/2}$ family of solid electrolytes, based on iso- and aliovalent substitutions of the parent phase $Bi_4V_2O_{11}$, has been known as fast oxide ion conductors [1, 2], which shows the highest ion conductivity at moderate temperature [3].

The crystal structure and ionic conductivity characteristics of the BIMEVOX materials have been the subject of great attention of researches in recent years and as a result, copper [4], titanium [5] and zinc [6] or their combinations [7–9] have been found to be the best substitution elements for vanadium. However, just a few reports [10, 11] concern electrochemical oxygen pumping characteristics, the most promising application of this family of solid electrolytes. The present work concerns detailed studies on operational characteristics of the most famous member of the mentioned solid electrolytes family, BICUVOX.1, as a separator membrane of an oxygen pump system.

2. Experimental procedure

Polycrystalline BICUVOX.1 powders with nominal composition of $Bi_2V_{0.9}Cu_{0.1}O_{5.35}$ were prepared by solid sate reaction from stoichiometric amounts of analytical grade oxides (Bi_2O_3, V_2O_5, and CuO; Aldrich, 99.99% purity), using the same procedure described in detail previously [11].

X-ray diffraction data, using CuKα source were collected at room temperature and used for identification of the crystal structure of the synthesized compound as well as detecting any probable structural modification, during its usage as a solid electrolyte in an electrochemical oxygen separator set up.

The BICUVOX.1 powder was co-pressed with two gold meshes as electrodes to a disc shape specimen, 15 mm in diameter and 3.5 mm thick, under hydrostatic pressure at 350 MPa. The green pellet-gold meshes system was sintered at 730°C for 5 h, which was reported

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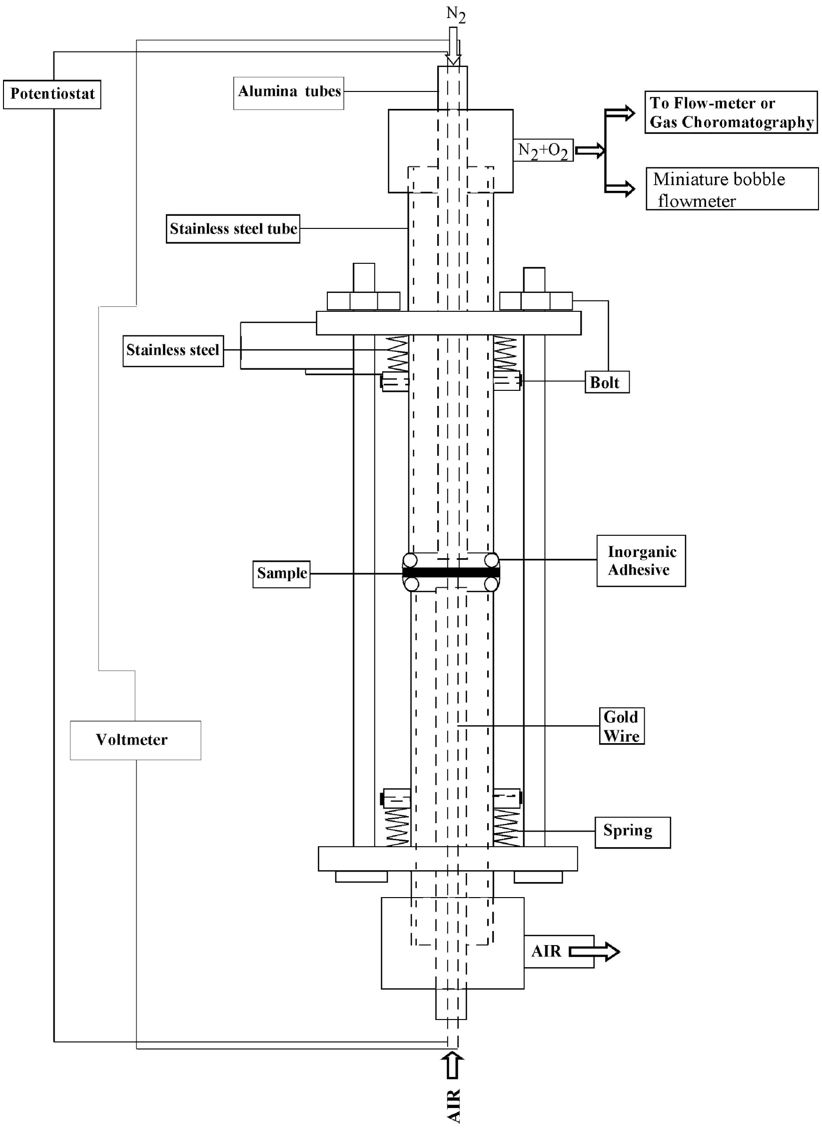

Figure 1 Schematic of the cell were used for electrochemical separation of oxygen form air.

previously to be the optimum sintering condition [12, 13]. The specimen was polished with a coarse grain abrasive paper (grade 300) in order to expose the gold mesh on the surface. Oxygen permeability of the samples was evaluated using a cell shown in Fig. 1. The cell constituted by two stainless tubes, where the sample was sealed between them with an inorganic insulating ceramic adhesive and the help of a spring loaded system. On both sides of the sample, the electrical connections were obtained using two thin alumina tubes, which each of them carried two separated gold wires and pressed against the pellet, so that the current and voltage could be applied and measured separately. The current was applied using a potentiostat device (Solartron 1287), and the corresponding cell voltage was recorded using a precise voltmeter.

Anode and cathode side of the specimen were flashed with pure nitrogen ($O_2 < 10^{-5}$ ppm) as the carrier gas and artificial air as oxygen supplier respectively. Oxygen production rate was measured directly by using a miniature bubble flow meter and also by gas chromatography, which was also used for checking the quality of sealing at high temperature.

The total dc polarization diagrams were obtained in the range of 450 to 550°C and for 0.1 to 1000 mA/cm^2 current density. The Faradic efficiency of the oxygen separation process was determined by calculating the ratio of the theoretical and experimental oxygen production rates.

3. Results and discussion

The dc polarization diagrams obtained at different temperatures are given in Fig. 2. By increasing the current density, four distinct regions of different behavior were recorded. At low current density (0.1 to 1 mA/cm^2), electron transfer processes dominated. At very low currents a linear part, followed by an almost exponential relation between current and voltage, was observed. The measured behavior can be related to the sum of the charge transfer polarization of anode and cathode following the Butler/Volmer relationship. More increase in current density transfers the first linear behavior to another one, which

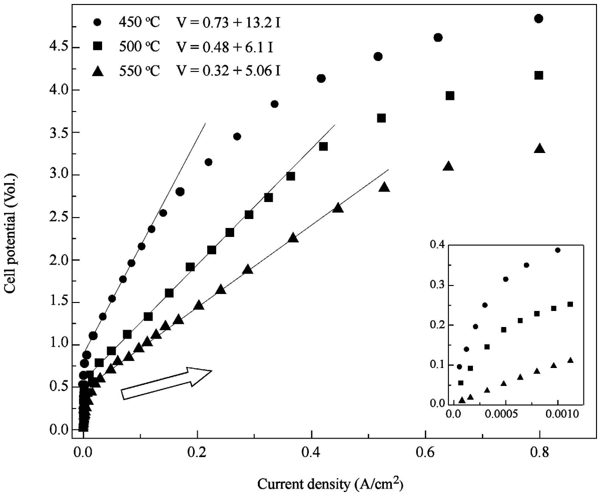

Figure 2 Dc polarization diagrams obtained for BICUVOX.1 material at three different temperatures.

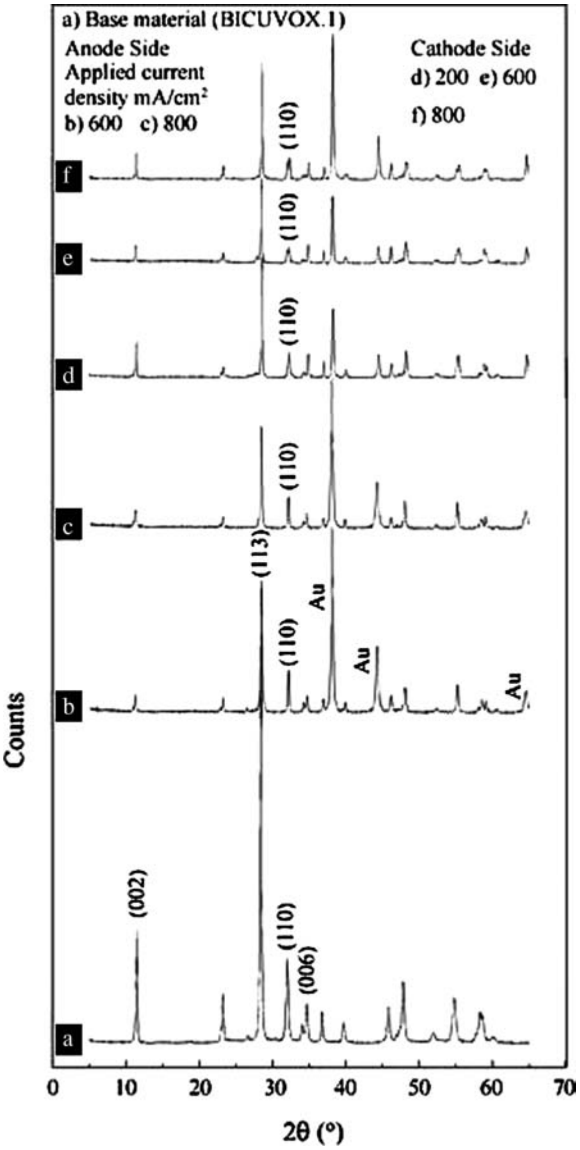

Figure 3 X-ray patterns of the cathode and anode side of the BICUVOX.1 used as an oxygen separator membrane at different current densities.

has lower slope and corresponds to the total Ohm'ic resistance (grain and grain boundary) of the electrolyte. It can be used for estimation of the total electrical conductivity of the samples at different temperatures. The total electrical conductivities, which were obtained by impedance spectroscopy and dc polarization at different temperature, are compared in Table I. As it can be seen there is a good agreement between these two methods.

For a pure ionic conductor such as ZrO_2, the Ohm'ic behavior remain stable until a high current density where the electrode process is dominating and causes a large positive deviation from the Ohm'ic behavior. In the case of BIMEVOX family of solid electrolytes a different behavior was observed. As Boivin *et al.* [10] also has reported, by increasing the current density above a limit, voltage-current relationship deviates negatively from the linear Ohm'ic behavior. The deviation increases with increase of the current density and becomes more pronounced at low temperature. In other words the cell showed a lower cell voltage than what the Ohm'ic law expects. This phenomena has been reasoned [10, 11] to be due to the partly reduction of the electrolyte and its change to a mixed conductor, which acts as an electrode. In this way the thickness of the electrolyte decreases and that for the electrode increases with increasing current density. Therefore the total cell resistance decreases as a function of current density and causes deviation from the Ohm'ic law. Ultimately, at high current density, the thickness of the electrolyte becomes too small and electrons percolate through the remained electrolyte thickness. As the result of that the cell potential shows an unstable behavior. This process seems to be reversible, and as Boivin *et al.* also mentioned [10], by returning back to a lower current density the cell potential became stable. In contrast with their results, in the present work the initial cell potential value was not recovered completely, so that it showed a lower value in the reverse path. In other words it seems that the created electrode was not fully transformed to the initial electrolyte (from crystal structure point of view). In order to investigate the structural modification, diffraction patterns of the anode and cathode side of the electrolytes were analyzed separately. Fig. 3 illustrates X-ray diffraction patterns of the cathode and anode side of the BICUVOX.1 electrolytes, which had been used as a membrane in the oxygen separator cell, at different current densities. As the figure shows, it is definitely clear that no permanent structural modification occurs for the cathode side after current load less than 200 mA/cm^2

TABLE I Total ionic conductivity obtained by Impedance Spectroscopy and dc polarization methods

Temperature (°C)	450	500	550
Total ionic conductivity ($\Omega^{-1}\cdot$cm^{-1}) by:			
1-Impedance spectroscopy	0.047	0.07435	0.108
2-Dc polarization	0.04	0.064	0.095

current density, while at the anode side no significant stable structure modifications were observed up to 800 mA/cm^2. The structural alteration showed a clear progressive splitting in the tetragonal 110 peak which is an evidence of the orthorhombic β type structure and resembles the $\gamma \rightarrow \beta$ well defined phase transformation of the bismuth vanadate, $Bi_4V_2O_{11}$, parent compound. As the other researcher [10] also mentioned, the transformation of the structure must be due to the partly reduction of the V^V to V^{IV}, which should be completely reversible. In contrast with their results, the X-ray diffraction pattern of the electrolytes after current load showed that the transformation is not completely reversible and the initial electrolyte crystal structure was not recovered, at least for the cathode side.

This result indicates that the structural modification at the anode and cathode side is not completely the same and the reducing condition at the cathode side is more effective in modifying the crystal structure. It is worth to note that the results presented in [10] were obtained at low temperature (330°C) and under a flow of hydrogen gas, which probably differ too much with the present practical condition.

The variation of the cell voltage with time at 500°C versus the step-by-step increase in current density is shown in Fig. 4. As it shows for low current density, where the electron transfer is predominate, a longer time is needed for the stabilization of the cell potential, while for higher current density, where the Ohm'ic resistance of the electrolyte and the transformation of the electrolyte to electrode material is dominating, the required time for the cell potential adjustment's is just a few minutes. At high current density ($J \geq 300$ mA/cm^2), a peak in cell potential was observed before it became stable, which is due to the change of a part of the electrolyte to electrode material. On the other hand gradual change of the current density cause a gradual transformation of the electrolyte to electrode so that the decrease in cell potential dose not show any noticeable peak. For a sudden increase in current density, like a current step, in the first moment the cell voltage also increase step like, according to Ohm's law. But then, the electrolyte starts to transform into electrode material, decreasing the electrolyte thickness, therefore the total resistance and finally the cell voltage, which can be seen as a pronounced peak. A reverse phenomenon happens when the current density decreases.

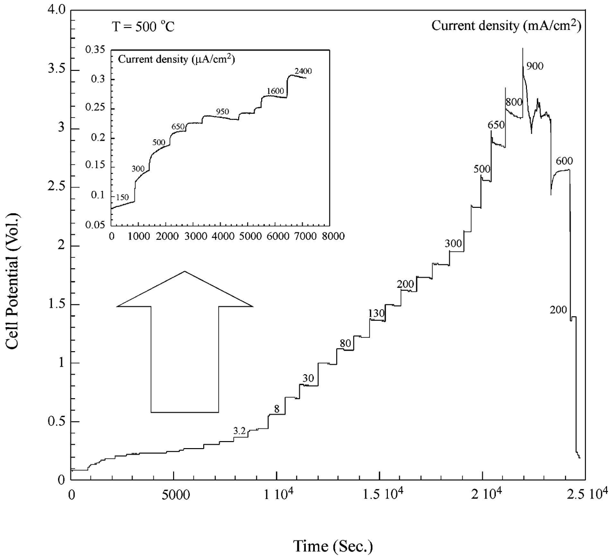

Figure 4 Cell voltage versus time at different imposed current density.

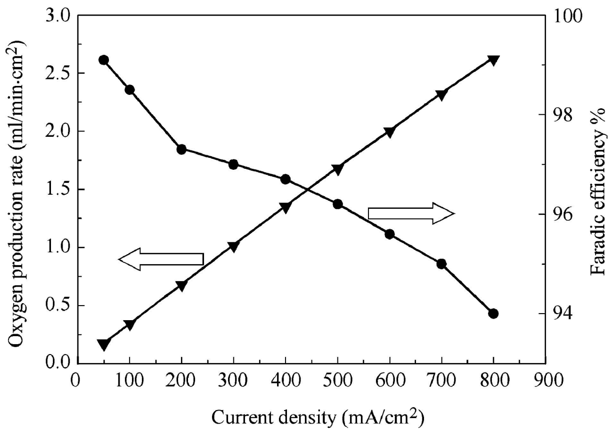

Figure 5 Oxygen production rate and Faradic efficiency of the BICUVOX.1 membrane versus current density at 500°C.

As Fig. 4 shows, at high current density ($J > 800$ mA/cm^2) the cell potential is unstable, which is due to the electrons percolating through the thin remained electrolyte. Anyway by decreasing the current density the cell potential became stable again and nearly the initial cell voltage value recovered.

The oxygen production rate and its corresponding Faradic efficiency of the BICUVOX.1 membrane are shown in Fig. 5. The oxygen volume produced depends on the current density. Below 800 mA/cm^2, a nearly linear relationship was observed. The Faradic efficiency of the oxygen production weakly depends on the current density and as Iharada *et al.* [14] also mentioned, it decreased slightly by increasing the current density. It remained larger than 94% for all the current densities before the cell voltage instability starts. Above that limit, the Faradic efficiency decreased largely.

4. Conclusion

The dc polarization diagram for BICUVOX.1 at different temperatures showed four definitely various regions. With increasing current density, electron transfer, Ohm'ic resistance of the electrolyte, electrolyte-electrode transformation and finally electron percolating through the remained thin electrolyte layer were the dominating processes respectively. The electrolyte-electrode transformation at the anode and cathode side was not the same so that the structural change at the cathode side was determined to be different from what happens reversibly at the anode side. The oxygen production rate of the BICUVOX.1

solid electrolyte was linearly dependent on the current density. About 2.6 ml/min·cm^2 was obtained in the temperature range of 450 to 550°C. Faradic efficiency of the oxygen production process using BICUVOX.1 membrane was nearly 100% and decreased slightly by increasing the current density, before the cell potential instability happens.

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