ELECTROCHEMICAL PROPERTIES OF STABILIZED δ - Bi_2O_3 . OXYGEN PUMP PROPERTIES OF Bi_2O_3 - Er_2O_3 SOLID SOLUTIONS

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Received 7 July 1988; accepted for publication 2 March 1989

The oxygen pumping characteristics of the solid electrolyte material $(\text{Bi}_{0.75}\text{Er}_{0.25})_2\text{O}_3$ with gold and platinum electrodes have been studied by three-electrode I - V measurements. These experiments show only little influence of the electrode material used on the electrode behavior. Exchange current density values are high and are confirmed by $^{18}\text{O}_2$ exchange data on the bare electrolyte. This leads to the conclusion that $(\text{Bi}_{0.75}\text{Er}_{0.25})_2\text{O}_3$ has good properties for oxygen pumping applications and is an electrochemically active material in oxygen transfer processes.

1. Introduction

In recent years, solid state electrochemical devices such as oxygen pumps and solid state fuel cells, have received increasing attention. Optimization of the performance of these devices, requires combinations of electrolyte and electrode materials with improved oxygen exchange and oxygen as well as electronic (mixed) transport properties. New material systems showing interesting properties are frequently based on the high temperature fluorite phase of Bi_2O_3 (δ - Bi_2O_3) [1]. From previous studies by Verkerk et al. [2] it is known that the erbia stabilized bismuth oxides are among the best solid oxide oxygen ion conductors. Experiments by Winnubst et al. [3] who substituted bismuth (III) oxide in yttria-stabilized zirconia showed a decrease of the electrode polarization for these substituted samples. Preliminary two electrode I - V measurements by Verkerk et al. [4] also showed evidence for a high oxygen exchange rate of the stabilized bismuth oxide surface. Steele et al. [5] have determined the $^{18}\text{O}_2$ exchange rate of a bare ceramic sample of erbia stabilized δ -bismuth oxide. The exchange rate was much higher for the erbia stabilized bismuth oxide than for yttria-stabilized zirconia. In numerous research results the stabilization of the δ - Bi_2O_3 phase down to room temperature by doping with 20 to 50 at.% lanthanide ions was re-

ported [6–8]. Studies of Watanabe et al. [9] on yttria stabilized Bi_2O_3 however showed the development of a second phase under certain conditions. Verkerk et al. [10] did not observe phase changes on erbia stabilized Bi_2O_3 although short range ordering was reported. Careful phase studies by Kruidhof et al. [11] on the erbia stabilized bismuth oxide showed phenomena comparable to those observed by Watanabe et al. [12]. In spite of this phase change the mechanical stability of the material surprisingly is preserved.

The aims of this paper are to study (i) the oxygen ion pumping rates of ceramic erbia-stabilized bismuth oxide systems as a function of temperature and (ii) the effect of the noble metal electrode material on the electrochemical oxygen transfer rate. The results are compared with those of related materials e.g. yttria stabilized zirconia and bismuth lead oxide.

The materials system mainly studied in this paper is the ceramic solid solution system $(1-x)\text{Bi}_2\text{O}_3$ - $x\text{Er}_2\text{O}_3$ with $x=0.25$ (BE25) as the ionic conductivity of this composition was found to be the highest [13] in the range of compositions, given a required phase stability.

An alternative method for establishing the oxygen pumping rates was used. The oxygen pumping rates are calculated from standard three electrode I - V measurements and the results are compared with

oxygen pumping curves directly measured by two electrode I - V measurements. This method was chosen because the three-electrode measurements allow for a separation of the anodic and cathodic electrode contributions to the overall polarization. This method also allows a study of the kinetics of the electrode reactions:

(Kröger-Vink notation). The reaction equation reflects that the electrode, the electrolyte and the gas phase take part in the oxygen electrode reaction of the system:

as was shown by van Dijk et al. [14]. Mechanistic aspects of these kinetic studies will be published at a later time because the interpretation of the electrode mechanism has not yet been completed. Gold and platinum are studied as electrode materials because of the difference in electrochemical activity and catalytic oxygen adsorption on these materials which may play an important role in the overall electrode process (eq. (1)). In the literature platinum is considered as being catalytically active in oxygen adsorption whereas pure gold is considered relatively inactive [14].

2. Experimental

Solid solutions of bismuth oxide and erbium oxide were prepared by the coprecipitation method used by Kruidhof et al. [11] in which stoichiometric amounts of the oxides were dissolved in nitric acid and precipitated simultaneously in ammonia. The obtained powder was calcined at 933 K, milled in acetone, pressed into boules and sintered to a density of >98% at a temperature of 1023 K. From these boules samples of 12 mm diameter and a thickness of 1 to 1.5 mm were cut. These samples were polished with 1 μ m diamond paste. On both sides of the polished samples a 300 nm thick annular ring of either gold or platinum was sputtered (fig. 1). These rings had an inner diameter of 6 mm and an outer diameter of 10 mm. Afterwards the samples were annealed at 1023 K for two hours, in order to obtain an open electrode structure.

Fig. 1. Electrode configuration used in three-electrode current-voltage measurements.

The sample holders used for both the two electrode and the three electrode measurements consisted of two annular electrical contacts of the same size and material as the sputtered electrodes. For the three-electrode I - V measurements a point electrode was placed as reference electrode at the center of one of the annular electrodes (functioning as working electrode). The shape of the electrodes was chosen following Boukamp et al. [15] who found this electrode configuration to have the lowest potential drop correction $R_{u(\text{known})}$ between reference and working electrode. The electrochemical measurements were performed as a function of temperature with the samples surrounded by a controlled homogeneous gas atmosphere. A Solartron 1286 ECI was used as potentiostat. For two electrode I - V (pumping) experiments the reference electrode connector of the potentiostat was detached from the reference electrode of the cell and also connected to the counter electrode leaving the reference electrode of the cell disengaged. For frequency dispersion measurements a Solartron 1174 FRA was connected to the potentiostat (fig. 2).

The frequency response measurements were used to determine the ohmic potential drop ($I \cdot R_u$) between the working and the reference electrode. Analysis of these measurements with the Equivalent Circuit program package running on an IBM compatible personal computer [16] gives information about the

Fig. 2. Schematic representation of the experimental setup used for the electrochemical experiments.

contribution of ($I \cdot R_u$) to the polarization effects measured during three-electrode I - V experiments. These $I \cdot R_u$ values were used to calculate the current overpotential (I - η) data from the current voltage (I - V) data according to eq. (2):

$$\eta_i = V_i - I \cdot R_u. \quad (2)$$

During the two and the three-electrode current-voltage measurements the potential was changed stepwise. The current measurement was performed after sufficient time to allow the system to come to steady state conditions. The current-voltage data from the three-electrode measurements were analyzed in terms of the Butler-Volmer equation using a non linear least square fit program running on an Apple II micro computer [15] in order to extract the electrochemical parameters for the electrode reaction.

The two electrode experiments were used to check the stability in time of the samples and to check the validity of the two electrode data obtained by calculation from the three-electrode experiments using the procedure described below.

The experimentally determined polarization under steady state conditions in two electrode I - V measurements consists of the linear sum of the anodic electrode polarization (η_a), the ohmic polarization of the bulk ($I \cdot R_{b(ulk)}$) and the cathodic electrode polarization (η_c) (eq. (3)):

Fig. 3. Principle of the calculation of a two-electrode current overvoltage curve from three-electrode current-overvoltage data.

$$V_{\text{pump}, I} = \eta_{a, I} + R_b \cdot I - \eta_{c, I}. \quad (3)$$

For a study of the electrode characteristics the contribution of the bulk resistance is of no interest. In our experiments the contribution of $I \cdot R_b$ to the polarization is only about 10% of the total polarization at low overpotentials [15]. Therefore it can be subtracted from V_{pump} without effect on the precision of the η values. This results in eq. (4):

$$V_{\text{pump}, I} = \eta_{a, I} - \eta_{c, I}. \quad (4)$$

It is also possible to calculate the difference between the electrode polarizations at any current value from three-electrode I - V measurements. In a two electrode cell the anodic and the cathodic currents are equal. Taking both the anodic and the cathodic polarization from three-electrode I - η plot at equal currents (see fig. 3, e.g. the line at $I = 0.05$ mA and $I = -0.05$ mA, yielding η_{ai} and η_{ci} as indicated by the arrows) and taking the sum of these polarizations as the polarization of a two electrode experiment with the chosen current, (V_{pump}) can be calculated. By plotting the current values versus the calculated V_{pump} values, a two electrode pumping curve for a symmetric cell can be generated.

3. Results and discussion

Examples of measured two and three-electrode I - V curves are presented in fig. 4a and 4b. In both graphs also the actual polarization curve, corrected

Fig. 4. (a) Directly measured two-electrode I - V curve of BE25 with Pt electrodes at a temperature of 982 K and a $P_{O_2}=0.21$ atm. showing the effect of R_b . The drawn line represents the corrected curve. The dotted line represents the curve as measured. The dashed line represents the correction due to $I \cdot R_b$. (b) Three-electrode I - V curve measured on BE25 with Pt electrodes at a temperature of 982 K and a $P_{O_2}=0.21$ atm. showing the effect of R_u . The drawn line represents the corrected curve. The dotted line represents the curve as measured. The dashed line represents the correction due to $I \cdot R_u$.

for the $I \cdot R$ drop, and the $I \cdot R$ drop itself are presented. Neither $I \cdot R_b$ nor $I \cdot R_u$ are constant factors, i.e. potential corrections which are less than 10% at low potentials will increase up to 15% at higher potentials. Because of the accuracy with which the val-

ues for R_b and R_u are determined the error introduced in the correction is limited. The anodic polarizations are much lower than the cathodic ones as appears from fig. 4b. This in combination with the similarity of the negative (cathodic) branches (figs. 4a and 4b), indicates that, the total electrode polarization for BE25 will be dominated by the cathodic electrode reaction.

Fig. 5 shows that there is a very good agreement between the I - η curves, calculated from three-electrode measurements, and the measured two-electrode curves. The small difference observed in the curves can be ascribed to the fact that when performing a two-electrode I - V measurement the morphology and/or geometry of the anode and cathode may be different. This will result in a slightly different current distribution and consequently a deviation of the polarization found in the three-electrode I - η curves as for these the electrode structure of the anode and the cathode are the same.

Fig. 6 presents a number of pumping curves calculated from three-electrode i - η data for BE25 ceramics as a function of temperature and for gold and platinum electrodes. This figure clearly shows that the pumping rates are almost independent of the noble metal electrode used. To study the electrode process in more detail an analysis of the three-electrode

Fig. 5. Comparison of a directly measured two-electrode I - η curve (+) and a calculated two-electrode i - η curve (O) both on BE25 with Pt electrodes at a temperature of 982 K and a $P_{O_2}=0.21$ atm.

Fig. 6. Calculated two-electrode i - η curves for BE25 with Au (open symbols) and Pt (closed symbols) electrodes at several temperatures at a $P_{O_2} = 0.21$ atm.

i - η measurements is made in terms of a Butler-Volmer equation (eq. 5.). In this equation the α 's include the number of transferred electrons:

$$I = I_0 [\exp(\alpha'_a \eta F / RT) - \exp(-\alpha'_c \eta F / RT)] \quad (5)$$

where I is the electrical current, T is the temperature, I_0 the apparent exchange current, α'_a the apparent anodic transfer coefficient, F , the Faraday constant, α'_c the apparent cathodic transfer coefficient, R , the gas constant and η is the overpotential.

As fig. 7 shows, an analysis in these terms is justified. The fit parameters must be considered as apparent values of i_0 and α in the Butler-Volmer equation as the sum of the α_a and α_c is not equal to 2. This should be the case for a charge transfer controlled reaction. An extensive discussion on these results lays however outside the scope of this paper. The obvious quality of the fit is supported by the good matching of the values for the ohmic resistance between the working and the reference electrode (R_u), obtained from the fit procedure and those directly obtained by the analysis of the complex impedance measurements. The values for the exchange current densities (I_0) estimated from Tafel plots of the three-

Fig. 7. Experimental three-electrode i - η data, measured on BE25 with Pt electrodes at a temperature of 997 K and a $P_{O_2} = 0.21$ atm., combined with a Butler-Volmer curve calculated from results of a non linear least square fit procedure on these data.

electrode i - η curves and refined by the non-linear least square fit procedure mentioned above are plotted in fig. 8. This figure presents the i_0 values as a function of temperature and the electrode materials used. Also data calculated from $^{18}O_2$ exchange experiments on bare BE25 [17] are added for comparison. This figure shows that all the i_0 values are represented by one single Arrhenius equation, con-

Fig. 8. Oxygen exchange current densities obtained from electrochemical and gas exchange measurements as a function of temperature for BE25 with different electrode materials: ($\square$) Au electrodes, ($\circ$) Pt electrodes, ($\times$) gas exchange data.

Table 1

Activation enthalpies of the exchange current densities calculated from electrochemical and ¹⁸O₂ exchange experiments on BE25 ($P_{O_2}=0.21$ atm.)

Electrode material	ΔH (kJ/mol)	
Pt	-150 ± 22	from electrochemical experiments
Au	-145 ± 7	from electrochemical experiments
	134 ± 2	from ¹⁸ O ₂ exchange experiments [17]

sequently the activity for the oxygen exchange is largely independent of the metal used. This implies that the activity is mainly caused by the electrolyte surface and not by the electrode material applied. Further support is given by the activation enthalpies of the electrochemically established curves in fig. 8 as presented in table 1. The small differences between the exchange data and the electrochemical data can be attributed to the absence of electrode materials in the case of the exchange data. These observations are in contrast with values found in literature for other electrolyte materials [18] where differences of up to three orders of magnitude can be found between i_0 values measured for gold and platinum electrodes.

These results suggest that BE25 ceramics have catalytically a very active surface for oxygen exchange reactions.

A material used in electrochemical devices must be stable over a longer period of time. Kruidhof et al. [12] observed a slow reversible phase transformation for BE25 at temperatures around 950 K. A pumping experiment was therefore conducted over 600 h. A sample of BE30 showing no phase transformation (XRD) was used as reference. The results of this long term experiment are presented in fig. 9. The slow decrease in current observed for BE25 cannot however be attributed directly to this phase transformation. The impedance measurements conducted at regular intervals during the 600 h of measurement, show no change in the bulk conductivity of the sample. Moreover heating of the sample to a temperature of 1050 K should rapidly reverse the phase change restoring the original current density. As this was not observed, it is most likely an aging effect of the electrodes.

Fig. 9. Long term oxygen pumping characteristics of BE25 and BE30 with Au electrodes at a temperature of 903 K and a $P_{O_2}=1.0$ atm. Sample thickness was 1.5 mm and total cell polarization was 0.3 V.

In fig. 10 the oxygen pumping currents are given for BE25 as a function of the electrolyte thickness. The literature values for yttria-stabilized zirconia (ZY17) [2] are shown for comparison. The values for transported oxygen volumes presented in this figure are calculated under the assumption of total charge to mass conversion at the electrodes. The striking result from this figure is the difference between BE25 and the traditional material for oxygen transport applications, ZY17. Especially at higher overpotentials the pumping rate of the BE25 electrolyte is much larger than that of ZY17. This effect will become even larger when the thickness of the sample is increased because of the higher specific conductivity of BE25 in comparison to ZY17 (see table 2). In fig. 10 the influence of the thickness was calculated with conductivities as given in table 2. These results suggest a change of an electrode polarization controlled regime to a bulk conductivity controlled regime at an electrolyte thickness of approximately 200 μ m.

An attempt has been made to compare the results

Table 2

Bulk conductivities of some electrolyte materials at 900 K.

Electrolyte material	σ_{900} (Ω m) ⁻¹	Ref.
ZY17	0.778	[2]
BE25	6.25	[20]

Fig. 10. Oxygen pumping curves for BE25 (open symbols) and ZY17 (closed symbols) as a function of sample thickness. (●) 10 μm , (■) 100 μm , (▲) 1 mm.

on BE25 with those obtained on the high conducting phase of bismuth lead oxide. The data available in literature [19] however allow only a superficial comparison because of the lack of sufficient I - V data and geometrical data of the samples used. An estimate of the geometrical parameters shows that the pumping capacity of fresh BE25 is of the same order of magnitude (1000 A/m² at a cell voltage of 0.8 V and a temperature of 900 K) as of fresh bismuth lead oxide (1000 A/m² at a cell voltage of 1.5 V and a temperature of 872 K) with comparable electrodes in spite of the lower bulk conductivity of BE25. This leads to the conclusion that the electrode properties of BE25 are superior to those of bismuth lead oxide.

4. Conclusions

The oxygen pumping rates of BE25 and of bismuth lead oxide are of the same order of magnitude and are much higher than the oxygen pumping rates of ZY17.

Pumping rates of 180 ml/s·m² are obtained.

The oxygen pumping rate on BE25 is limited by the cathodic polarization.

The oxygen pumping rate of BE25 is independent of the electrode material used.

The oxygen pumping rate of BE25 is determined by the ionic electrolyte conductivity above an electrolyte thickness of 200 μm .

Oxygen exchange rates determined from the electrochemical data are in good agreement with the oxygen exchange rates calculated from ¹⁸O₂ exchange experiments.

Oxygen pumping curves can be calculated from three-electrode I - η measurements.

Acknowledgement

The authors wish to thank H. Kruidhof for preparing the samples. This investigation was supported by the Dutch Foundation for Chemical Research (SON) with the financial aid from the Dutch Organization for Scientific Research (NWO).

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