OXYGEN TRANSPORT AND TRANSFER PROPERTIES OF ERBIA-STABILIZED BISMUTH OXIDE

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The electrode resistances of solid solutions of 75 mol% Bi_2O_3 –25 mol% Er_2O_3 with sputtered and with copressed gold gauze electrodes were compared. In contrast with literature no enhancement of the electrode process could be observed for the copressed electrodes. The measurements show an oxygen partial pressure dependence of power -0.5 for the electrode resistance. Additionally $^{18}\text{O}_2$ exchange results also point to a low oxygen coverage and dissociative adsorption of oxygen. The electrode surface contributes significantly to the electrode process.

1. Introduction

For electrochemical applications minimization of energy losses is of great importance. The choice of a highly conducting electrolyte is as important as the choice of a good electrode material and the choice of an optimal electrode configuration. It was shown previously that the solid solution 75 mol% Bi_2O_3 –25 mol% Er_2O_3 (BE25) is an excellent electrolyte material [1]. In a more recent paper [2] it was shown that, for this material, the electrode material is of minor importance as only little difference in pumping rates and oxygen exchange currents were observed for sputtered and annealed gold or platinum electrodes.

In this paper we focus on the third of the optimization parameters i.e. the electrode configuration. Dumélié et al. [3] showed a remarkable improvement of the electrode performance of $\text{Bi}_{0.571}\text{Pb}_{0.428}\text{O}_{1.285}$ using copressed gold gauze electrodes instead of vacuum deposited gold electrodes. As the structure of sputtered and of vacuum-deposited electrodes are similar after annealing it is of interest to study the influence of using copressed gold gauze electrodes on BE25.

2. Experimental procedures

BE25 powder was prepared by coprecipitation as described by Kruidhof et al. [4]. For the experiments with sputtered electrodes, boules were pressed and sintered. From these boules disks were cut. Before applying sputtered electrodes on both faces of the disk these disks were polished with $0.5\ \mu\text{m}$ Al_2O_3 . The sputtered electrodes had an annular shape with an outer diameter of 10 mm, and inner diameter of 5 mm and a thickness of approximately 300 nm. For the experiments with the copressed gold gauze electrodes a piece of gold gauze of 1024 mazes per cm^2 and a wire thickness of 0.06 mm, was cut to the same shape as the sputtered electrodes. The gauze electrode was placed at the bottom of an uniaxial die which was filled with enough BE25 powder to produce a disk of approximately 1.5 mm thickness. After uniaxially and subsequently isostatically pressing the disk was sintered at 1125 K for eight hours to a relative density higher than 99%. The disk was then cut to a diameter of 12 mm and carefully polished as to bring the gold gauze to the surface of the disk. On the opposite face of the disk a counter electrode was sputtered of the same dimensions as mentioned above. After sputtering the electrodes were annealed for one hour at 1123 K.

The current–voltage measurements were performed potentiostatically in a three electrode cell [5]

using a computer controlled Wenking Pos 85W potentiostat. The voltage was changed stepwise. Measurements were performed after the system had reached a steady state. The current–voltage curves were analyzed in terms of a Butler–Volmer relation by a NLLS-fit procedure. This procedure incorporates the $R_{u(\text{known})}$ (i.e. the contribution to the potential due to non Faradaic processes) as a fit parameter [6]. Frequency dispersion measurements were performed to independently establish the magnitude of R_u . The impedance data were analyzed using the EQUIVALENT CIRCUIT software package [7]. Measurements were carried out in a temperature range of 650 to 1000 K and a P_{O_2} range of 1.10^{-3} to 1.0 atm.

3. Results and discussion

Fig. 1 shows an example of an uncorrected I – V curve for the sputtered gold electrode and for the gold gauze electrode, both at 994 K and 1 atm P_{O_2} . The results of the NLLS fit, represented by the continuous lines, show good agreement with the measured data. The difference in the values for R_u established from the I – V curve fit and from the impedance analysis was typically around 10%.

Fig. 1. Examples of the current–voltage curves as measured for sputtered gold electrodes ($\square$) and copressed gold gauze electrodes ($\diamond$) at 994 K in oxygen. The solid lines represent the NLLS-fit result.

The similarity between the shape of the I – V curves in fig. 1 indicates that the electrode resistances, R_{el} , are of the same order of magnitude. The difference between the curves are attributable to the R_u . In this paper we will only discuss the influence of the electrode geometry on R_{el} , a more elaborate analysis of the Butler–Volmer parameters, I_0 , α_a and α_c , will be presented in a future paper. The Arrhenius plot of fig. 2 shows the temperature dependence of $1/R_{\text{el}}$ at several P_{O_2} values. From this figure it is obvious that although difference exists between the R_{el} values for sputtered and gauze electrodes, they are much smaller than expected, and in contrast with the findings of Dumélié et al. [3] for bismuth lead oxide. It is important to note that the length per unit area of the three phase boundary line is about a factor 100 larger for the sputtered electrode than for the gauze electrode. This indicates that the electrode geometry has only a minor influence on the rate of oxygen transfer on BE25. Earlier it was also observed that the electrode material (e.g. Pt and Au) had only little effect on the electrode resistance [5].

On the other hand recent ^{18}O exchange experiments [8] on (bare) BE25 revealed very high surface oxygen exchange rates (K_s exhibiting a power 0.5 dependence on the P_{O_2}). Exchange current density values (i_0) calculated from these K_s values were

Fig. 2. Arrhenius plot of R_{el} for BE25 with copressed electrodes (open symbols) and sputtered electrodes (closed symbols) at several P_{O_2} values: ($\circ$) 1.0 atm, ($\square$) 0.21 atm, ($\triangle$) 0.05 atm, and (∇) 0.001 atm.

found to be very close to values obtained from I - V measurements [9]. Careful analysis of the ^{18}O exchange data further suggested dissociative oxygen adsorption as the rate limiting step [8]. The same $(P_{\text{O}_2})^{0.5}$ dependence was observed for $1/R_{\text{el}}$ obtained from measurements on gauze electrodes, (see fig. 3). From literature [2] it is known that this dependency indicates a fractional oxygen coverage (θ) well below 0.5. Combination of these electrochemically obtained results with those from isotope exchange experiments strongly suggests that the oxygen transfer reaction is *not* limited to a small "three phase boundary region" but rather involves a much larger part of the BE25 surface. From the above it becomes obvious that the oxygen transfer reaction for BE25 cannot be described in terms of existing reaction models. In a forthcoming paper this subject will be treated in relation with the other electrochemical parameters obtained from the analysis of the current-voltage curves.

Fig. 3. Electrode resistances of BE25 with copressed gauze electrodes as function of P_{O_2} at several temperatures. (993 K, 923 K, 859 K, 804 K, 756 K and 673 K).

4. Conclusions

(i) A substantial decrease in the electrode resistance by using copressed gold gauze electrodes, as observed for $\text{Bi}_{0.571}\text{Pb}_{0.428}\text{O}_{1.285}$ by Dumélié et al. [3], is not observed for BE25.

(ii) The electrode reaction is not restricted to a three phase line. It is most likely that a large part of the electrolyte surface is active, while the electrode only functions as a current collector.

(iii) The oxygen adsorption on BE25 is dissociative and fractional oxygen coverage of BE25 is lower than 0.5.

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