

## LETTERS TO THE EDITOR

### COMMENT ON “CURRENT–VOLTAGE CURVES FROM A $\text{Bi}_2\text{O}_3\text{--Y}_2\text{O}_3$ OXYGEN CONDUCTOR”

**B.A. Boukamp, I.C. Vinke and A.J. Burggraaf**

*Faculty of Chemical Technology, University of Twente, Laboratory of Inorganic Chemistry, Materials Science and Catalysis,  
P.O. Box 217, 7500 AE Enschede, The Netherlands*

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In this article [1] the authors present three-electrode current-voltage ( $I$ - $V$ ) measurements on  $(\text{Bi}_2\text{O}_3)_{0.75}(\text{Y}_2\text{O}_3)_{0.25}$  (abbreviated BY25) provided with painted and subsequently sintered gold electrodes. In order to explain their measured  $I$ - $V$  curves they use the theory developed by Mizusaki [2]. With respect to the data analysis and interpretation a number of comments can be made as there are some inconsistencies and errors present in this paper.

(1) The first inconsistency is that the authors compare their  $I$ - $V$  curves measured at *high temperature* (973 K) with Butler–Volmer curves simulated for *room temperature* (298 K). This misconception explains in part the large differences between the measured and simulated curves presented in fig. 2 of ref. [1].

(2) The authors do not correct their  $I$ - $V$  measurements for the ohmic polarization between the work and reference electrode. With this correction the measured data would most likely follow a Butler–Volmer type curve. In fact we analyzed the published data including the estimation of this polarization resistance, following the procedure outlined in [3], and obtained a very reasonable fit to a Butler–Volmer type equation. These NLLSF data analysis results will be part of a forthcoming paper.

(3) The Mizusaki model was developed for the dissociative adsorption of oxygen on platinum, assuming that surface diffusion of oxygen towards the three phase boundary would be the rate limiting step. An important factor was that the surface coverage of

oxygen on Pt is rather high even at high temperatures. In contrast the surface coverage of oxygen on gold is very small and dissociative adsorption is rather unlikely [4]. This difference in behaviour is clearly demonstrated by the large difference in electrode resistance for Au and Pt on cubic yttria stabilized zirconia (YSZ,  $R_{\text{Au}} \gg R_{\text{Pt}}$ ) as observed by Badwall et al. [5]. With respect to this application of the Mizusaki model does not seem appropriate.

(4) The comparison of their measured  $I$ - $V$  curve with the simulation based on the Mizusaki model is in error as the horizontal (voltage/polarization) axis have different scales. The scale of the upper (= measurement) axis is 2.39 times the scale of the lower (= theoretical) axis if the correct temperature is inserted in the dimension of the lower scale, see fig. 14 of ref. [1].

(5) If the authors would have calculated the exchange current densities, using a Butler–Volmer model while correcting for the ohmic polarization, they would have seen that these values are even higher than generally found for Pt on YSZ. Taking into account the fact that Au is much less active than Pt for the dissociative adsorption of oxygen, then this must be a strong indication that here the *electrolyte surface* is the important factor in the electrode behaviour. A similar effect has been observed by us for  $(\text{Bi}_2\text{O}_3)_{0.75}(\text{Er}_2\text{O}_3)_{0.25}$  (BE25) with either gold or platinum electrodes [6]. Supporting evidence for the notion that the, Bi containing, electrolyte surface enhances the (surface) oxygen exchange reaction can

also be found from oxygen isotope exchange measurements [7,8].

(6) The so called *zero-current potential* of 0.01722 V must be due to an instrumental offset voltage (i.e. an incorrect calibration of the 1286 Solartron ECI) as it is constant at all temperatures. If it were a fundamental property of the material it would most likely depend on temperature and oxygen partial pressure. If all three electrodes are identical and at the same temperature and oxygen partial pressure such an offset voltage cannot exist.

In conclusion, the proposed "Mizusaki" mechanism for the observed  $I-V$  characteristics of gold electrodes on BY25 is highly improbable. Preliminary analysis of the published data by us indicate similar behaviour as found for BE25 [6]. Hence it is more realistic to assume that the properties of the electrolyte surface are essential in the electrode behaviour of BY25 and that the oxygen transfer mechanism is identical to that of BE25. The description of these rate determining step(s) at the electrode/elec-

trolyte boundary for BE25 is currently under investigation and will be published in a future issue.

## References

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## REPLY TO THE LETTER TO THE EDITOR

J.A. Aceves Hernández, L. Cabrera Castillo and A. Padilla Ibarra

*Departamento de Química, Centro de Investigación y de Estudios Avanzados del Instituto Politécnico Nacional, Apdo. Postal 14-740, 07000 México, D.F.*

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The authors of the comment have done a thorough analysis of our paper; however, we feel that their reasoning is too biased by previous results from their own work in this field. Indeed, we hope to make evident several errors and inconsistencies present in the comment:

(1) On page 233 of the abovementioned article we state: "For comparison purposes both types of curves were plotted in fig. 2"; while the calculation of the Butler-Volmer equation was carried out at 973 K, we noticed that the difference between the curve at 298 K and the experimental one is more relevant. Nevertheless, there are obvious differences in trends for one of the branches of the curves even at 973 K.

(2) It is worth noting that making a constant polarization resistance in reference to the applied potential does not modify the tendency of the Butler-Volmer equation in our paper as can be observed in fig. 1. Thus, the application of a correlation constant could be artificial due to the fact that a good correlation coefficient can be obtained between any experimental curve and the fitting curve with statistical weights conveniently selected (taking more points in one side of the curve). Therefore, we believe the information on the fitting method suggested is insufficient.

(3) As to the statement: "The Mizusaki model was developed for the dissociative adsorption of oxygen in