Experimental Requirements for Determination of SOFC Electrode Kinetics Mogens Mogensen and Peter Vang Hendriksen Materials Research Department, Risoe National Laboratory, DK-4000 Roskilde

There seems still to be a great need in the solid oxide fuel cell community for basic information about how to measure electrode potentials properly and how to find electrochemical reaction orders. The presentation gives a brief overview of these two important areas of electrochemistry.

The geometric requirements to the position of electrodes have been treated in details previously, see (1,2) and references therein. In spite of this some workers, who are indeed well established in the SOFC area, still claim that a reference electrode on an electrode supported cell can reveal the electrode polarization, as the following quote (3) reveals: "The overpotentials at the anode and the cathode, as well as the ohmic overpotential (IR drop) of the cells, were measured with a reference electrode located next to the cathode." The statement is made for an anode supported cell with an electrolyte thickness of ca. 10 µm. We think this is incorrect. A reference to the thorough analysis of ref. (1) was made in ref. (3). Our theoretical result is rejected based on "the experience in our laboratory". Such a rejection should be qualified better.

Obviously, the results of the theoretical analyses (1,2) have not been accepted. Therefore, key points are repeated here in graphical form (4). Figs. 1 and 2 illustrate the situation. Hopefully, it is clear that the "reference" electrode measures only the Emf of the cell with the



Fig. 1. a) A sketch of an electrode supported cell as often seen. Note that such a drawing necessarily must be totally out of scale. b) Blow-up of certain parts and the type of current distribution are indicated by schematic current lines. It should be noted that the current, apart from being approximately parallel to the electrolyte plan, is very small at the position of the "reference" electrode.



Fig. 2. The course of the electrical potential through the electrode supported cell with no current across the electrolyte at the "reference" electrode position (thick line) and through the cell part with the current load Thin line). It is seen that:

 $(V_{ref} - V_4)/i = R_{p,anode} + R_{p,cathode} + R_{elyt}$ = the total polarization of the cell apart from concentration polarization.

actual gas compositions at the "reference" and in the support at the lateral position opposite to the "reference" electrode while the current is running. Thus, no account for what happens on the individual electrodes can be derived from such measurements.

Another incorrect conclusion made in the SOFC electrode literature is that the reaction orders of the electrode processes may be derived from polarization resistances at open circuit voltage. This is in general not possible as will be explained in the paper. Also the requirements of a proper reference electrode will be discussed. For example, it should be noted that the electrode potential of an air electrode will change with temperature, while a pure oxygen electrode has a constant electrode potential for constant pressure.

REFERENCES

- J. Winkler, P.V. Hendriksen, N. Bonanos, M. Mogensen, J. Electrochem. Soc. 145 (1998) 1184
- G. Reinhardt and W. Göpel, in Proc. Third International Symp. on Ionic and Mixed Conducting Ceramics, T.A. Ramanarayanan, W.L. Worrell, H.L. Tuller, A.C. Khandkar, M. Mogensen, W. Göpel, Editors, PV 97-24, p.610, The Electrochemical Society Proceedings Series, Pennington, NJ (1998).
- T.J. Armstrong, A.V. Virkar, J. Electrochem. Soc., 149, A1565 (2002.
- M. Mogensen, P.V. Hendriksen, K. Kammer, in: 5th European SOFC Forum, Ed. J. Huijsmans, Vol. 2, p. 893, European Fuel Cell Forum, Oberrohrdorf, Switzerland (2002).