EXPERIMENTAL REQUIREMENTS IN DETERMINATION OF SOFC ELECTRODE KINETICS

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ABSTRACT

The problem of using potential probes as reference electrodes in electrode supported thin film electrolyte cells is illustrated. In fact, in such a case little, if any, information is gained compared to a simple measurement of cell voltage as a function of the current density. Other mechanistic information, which in principle may be derived from electrochemical kinetic measurements, is the reaction orders and the activation energy. In the case of SOFC it is, however, often very difficult to reveal these numbers, and much of what is in the literature is incorrect.

INTRODUCTION

There seems still to be a great need in the solid oxide fuel cell (SOFC) community for basic information about how to measure electrode potentials properly and how to find correct electrochemical reaction orders and activation energies for the electrochemical processes. This paper addresses these important areas of electrochemistry.

POTENTIAL PROBES MAY BE FALSE REFERENCE ELECTRODES

The geometric requirements to the position of electrodes have been treated in details previously, see (1,2,3,4) 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 (5) 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 statement is incorrect. A reference to the analysis of reference (3) was made in reference (5). Our theoretical result is rejected based on “the experience in our laboratory”. Such a rejection should be qualified better, especially because our finding has later been confirmed by others (6).

Obviously, the results of the theoretical analyses (3,4) have not been accepted. Therefore, key points were repeated in graphical form in reference (7) and again here. Figures 1 and 2 illustrate the situation. An electrode-supported cell with a "reference" electrode is often sketched as shown in Figure 1a. However, such a sketch is very
deceiving when it is used for an assessment of the current distribution. For this purpose the sketch should be drawn to scale, i.e. the electrolyte thickness is the relevant unit of distance. On such a Figure (1b) it is evident that the displacement of the edge of the upper electrode is huge. This means that the current distribution around the edge of this electrode on the "reference" electrode side becomes very different from the even current distribution of the main part of the cell. Furthermore, the current in the vicinity of the "reference" electrode will be close to parallel to the electrolyte plane, i.e. there is no significant change in the potential across the electrolyte inside the electrolyte.

Figure 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 density, apart from being approximately parallel to the electrolyte plane is very small at the position of the "reference" electrode, at least 50 (500 μm / 10 μm) times smaller than the current density of the cell.

Figure 2a illustrates the course of the electrical potential across a cell in the open circuit voltage (OCV) condition. Note, that for a good electrolyte, which for practical purposes may be regarded as an electronic insulator (and a good ionic conductor), there will be no potential gradient inside the electrolyte in case of zero current. The whole potential change across the cell is localized at the interfaces between the electrolyte and the electrodes. These regions are the so-called electrochemical double layers with thickness in the nanometer range and with high space charge concentrations as a result of the very high potential gradients. Figure 2b gives the course of the potential across a cell when it is loaded, i.e. when a current flows through it. Note that there is a potential loss across
Figure 2. a) The course of the electrical potential through the electrode supported cell with no current, and b) Through a cell with a current load. c) Illustrates the potential course 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: \[(V_{\text{ref}} - V_4)/i = R_{p,\text{anode}} + R_{p,\text{cathode}} + R_{\text{lyt}}\] the total polarization of the cell apart from concentration polarization.
the electrolyte due to the electrolyte resistance. The potential steps at the interfaces are now smaller compared to the OCV condition due to the losses originating from the polarization resistance of the electrode processes. Figure 2c illustrates the case of an anode-supported cell. The course of the potential is given for both the position of the "reference" electrode where no current flows across the electrolyte (i.e. the electrical potential is constant across the electrolyte), and for a position far away from the electrode edges as in Figure 2b.

As the potential along the anode, which is a very good electronic conductor, is the same everywhere (the anode constitutes an isopotential plane), the potential of the anode at the "reference" electrode must be equal to the potential in the middle of the current bearing part of the anode. Thus the two potential curves in Figure 2c must start in the same point. Therefore, as it is seen in Figure 2c, the potential difference between the "reference" electrode and the upper electrode in Figure 1 is simply the total polarization of the full cell.

Hopefully, it is clear that the "reference" electrode measures only the emf of the cell with the actual gas compositions at the "reference" and in the support at the lateral position opposite to the reference while the current is running. Thus, no account for what happens on the single electrode can be derived from such measurements. If the concentrations of the reactants and products at the lateral position of the reference electrode were the same as in the active electrode/electrolyte interfaces, then it would be possible to deduce the total concentration potential. This is, however, in general not the case, and this means that in general the difference between the working "reference" electrode voltage and the cell voltage cannot be assigned any clear meaning. Clearly, it does not tell anything about the charge transfer overpotential of the single electrodes.

**REACTION ORDERS**

Another incorrect conclusion, which is often 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 explained below.

The total current density, \( i \), is given as the sum of the anodic current density, \( i_+ \), and the cathodic current density, \( i_- \), as shown by equation

\[
i = i_+ + i_-
\]

[1]

Thus, it is not meaningful to talk about a reaction order at zero net current, because two opposite directed reactions take place.

The reaction orders at a given temperature, \( p_r \) and \( p_o \), for given gaseous component are defined by eq. [2] for an anode reactant (subscript \( r \) for reduced species) and by eq. [3] for a cathode reactant (subscript \( o \) for oxidized species) under the condition that the partial pressure, \( P_j \), of component \( j \) is equal to the activity or in other words: equal to
the fugacity (8, 9). This condition is believed to be fulfilled with good approximation for species like H₂, H₂O and O₂ at temperatures above 500°C. It is seen from eqs. [2] and [3] that in order to derive the reaction order we must measure the current densities far away from the open circuit potential of the electrode. Also note, that everything apart from the partial pressure of the species in question must be constant including the electrode potential, e, measured against a well defined reference electrode.

\[
\left( \frac{\partial \log i_+}{\partial \log P_h} \right)_j = p_{r,h} \quad \text{if} \quad i_+ \gg |i_-| \quad [2]
\]

\[
\left( \frac{\partial \log |i_-|}{\partial \log P_k} \right)_j = p_{o,k} \quad \text{if} \quad |i_-| \gg i_+ \quad [3]
\]

When all relevant reaction orders are determined then the anodic and cathodic current densities can be described by eqs. [4] and [5].

\[
i_+ = k_+ \prod P_j^{p_{r,j}} f(e) \quad [4]
\]

\[
i_- = k_- \prod P_j^{p_{o,j}} g(e) \quad [5]
\]

where \(f(e)\) and \(g(e)\) are functions of the electrode potential. \(k_+\) and \(k_-\) are constants. These functions also have to be determined experimentally. We do not have any general physical law from which we can derive \(f(e)\) and \(g(e)\).

In practice it is usually troublesome to determine the reaction orders correctly, and in the case of SOFC electrode kinetics no publication, which reports proper reaction orders for SOFC electrode reactions, is known to us. One of many problems is to fulfill the demand of being far away from the open circuit potential, because this will usually result in high current densities, which in turn will cause a temperature increase. The temperature may of course be adjusted continuously during the measurements, but as steady state is required for each measurement of the current density, this may prolong the measurements considerably. Another difficulty is that simple interpretable reaction orders are only obtained in case the current density is limited by only one rate determining reaction step, and this reaction step must be the same over the range of conditions studied. This usually means that impedance spectroscopy must be performed for many points of the parameter space under investigation.

THE PROPER REFERENCE ELECTRODE

In order to determine the reaction order of an electrochemical process the requirement is that the electrode potential, not the overpotential (8,9), is constant as well as everything else apart from the varied partial pressure and the resulting current density, which is the measure of the reaction rate. This raises a need of a proper reference
The natural reference potential is the oxygen electrode with 1 bar pure oxygen. For example, it should be noted that the free energy of oxygen in air, and thus also the real electrode potential of an air electrode versus a proper reference will change with temperature (due to the RTln(P₂O₂)-term in the Nernst equation for a single electrode), while the free energy of oxygen at the standard pressure is zero by definition (the choice of standard condition), and thus a pure oxygen electrode (1 bar) is the natural choice of reference irrespective of the temperature. If an air electrode or a hydrogen/water electrode is used for practical reasons, the measured potentials can easily be converted to the 1 bar O₂ by calculation using relevant thermodynamic values.

The point of a constant reference potential should also be considered in determining the activation energy of an electrochemical reaction. All driving forces, i.e. the electrode potential and the partial pressures of the reactants should also be kept constant when the temperature is varied. The problem of the proper reference electrode for gaseous reactions at varying high temperatures is unfortunately more complicated. The internationally agreed standard reference electrode is the normal hydrogen electrode (1 bar H₂, aqueous solution with pH = 0 at 25°C). Now, the 1 bar oxygen potential at 25°C towards the normal hydrogen electrode is well known, and the potential of the 1 bar O₂ at any other temperature can then be worked out or measured against this 1 bar O₂ and 25°C. Most often only apparent activation energies are determined anyway, because more than one process is of importance in the over all process studied.

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