Direct Measurement of *iR*-free Individual-Electrode Overpotentials in PEFC

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The possibility of reliable measurement of individual fuel cell electrode overpotentials under load is of utmost importance to the fuel cell community. In order to successfully measure an electrode overpotential one needs two things: (i) a reference electrode of fixed potential placed in contact with the same electrolyte as the electrode of interest and (ii) knowledge of the *iR* drop between the reference electrode and the electrode of interest. A stable potential of the reference electrode is achieved by providing it with a fast redox couple and/or making sure that the current drawn through the reference electrode is close to zero. In classical electrochemistry, the knowledge of the *iR* drop is acquired either by driving it down almost to zero with the use of a Luggin capillary and/or excess of supporting electrolyte, or by calculating it from known local i and R. In order to learn about the *iR* drop in the case of fuel cells possessing thin-slab geometry, one would have to precisely place a reference electrode within the thin electrolyte in the main fuel cell current path (adding excess of supporting electrolyte is not an option). This, however, is impractical given the very thin electrolyte layers used. Moreover, it has been shown [1-4] that the electrical potential in the electrolyte layer protruding from the electrolyte-electrode assembly is a strong function of the fine details of the electrode edge geometry and the fuel cell current density/electrode overpotentials. Therefore, when a reference electrode is placed in contact with the protruding part of the electrolyte layer, the necessary effective *iR* drop has to be obtained by 2-D modeling of electrical potential distribution in the electrolyte layer. Modeling of fuel cells, however, is always based on many assumptions. Hence, it would be desired to measure the overpotentials directly.

In this contribution we will evaluate a method for direct measurement of *iR*-free, individual-electrode overpotentials in fuel cells of the thin-slab geometry. Although we will focus on the polymer electrolyte fuel cells (PEFCs) working either in H_2-air or direct methanol-air modes, the method should be applicable to any type of fuel cell. The overpotential measurement can be accomplished by placing a reference electrode in direct ionic contact with the catalyst layer of the fuel cell electrode of interest, away from the main fuel cell current path. This helps to eliminate problems associated with nonlinear electrical potential distribution in the electrolyte layer. The proposed reference electrode arrangement is shown in **Figure 1**.

For the setup shown in Figure 1, one reference electrode is sufficient to obtain *iR*-free overpotentials of both fuel cell electrodes, provided that the internal resistance of the fuel cell is simultaneously measured. Nevertheless, using two reference electrodes, one for each fuel cell electrode, is also useful. **Figure 2** presents the results of an experiment on an H_2-air fuel cell equipped with two reference electrodes of the proposed configuration, each sensing the potential of one of the fuel cell electrodes.

The reference electrodes were dynamic hydrogen electrodes operating at a small current density. From the comparison of the recorded *iR*-free polarization curve (squares) with the polarization curve calculated from anode and cathode overpotentials measured versus their respective reference electrodes (diamonds), it can be seen that both reference electrodes allowed for a relatively correct measurement of *iR*-free overpotentials of their respective fuel cell electrodes under all actual fuel cell current densities.

We have found that in order for the proposed reference electrode setup to work, the half-cell fuel cell reaction cannot be disturbed in the part of the catalyst layer that remains in ionic contact with the reference electrode. In other words, current collection by means of the conductive gas-diffusion backing as well as reactant access and product removal all have to be preserved for the section of the catalyst layer underneath the reference electrode. This conclusion is supported by the results of 2-D modeling of electrical potential distribution in membrane, catalyst layers, and the ionic conduits from the catalyst layers to the reference electrodes.
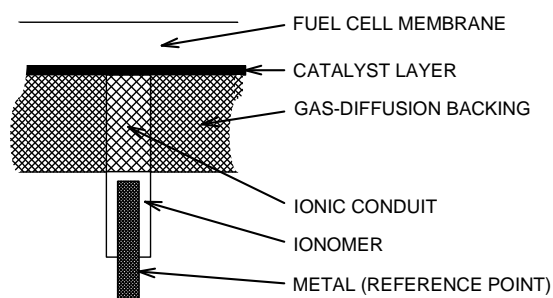

Figure 1. Reference electrode configuration for direct measurement of *iR*-free overpotential of a fuel cell electrode under load.
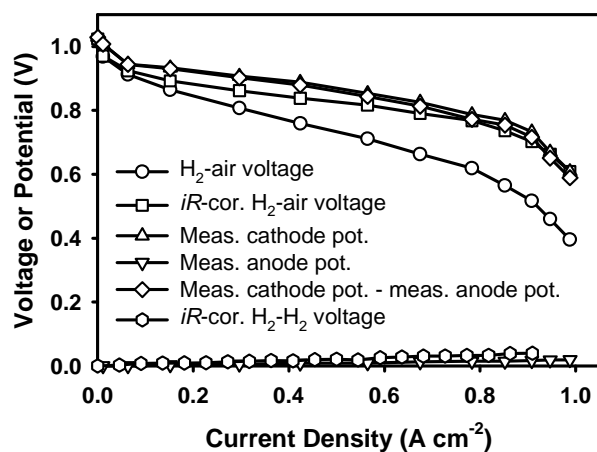

Figure 2. Cell and individual-electrode polarizations for H_2-air PEFC.

References

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