Title
VOLTAGE LOSSES IN FUEL CELL CATHODES

Permalink
https://escholarship.org/uc/item/46k2s2p6

Author
Ross, P.N.

Publication Date
1980-12-01
Voltage Losses in Fuel Cell Cathodes

Philip N. Ross, Jr.

December 1980

TWO-WEEK LOAN COPY

This is a Library Circulating Copy which may be borrowed for two weeks. For a personal retention copy, call Tech. Info. Division, Ext. 6782

Prepared for the U.S. Department of Energy under Contract W-7405-ENG-48
DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.
Voltage Losses in Fuel Cell Cathodes

R. P. Iczkowski and M. B. Cutlip

(pp. 1433-1440, Vol. 127, No. 7)
Voltage Losses in Fuel Cell Cathodes

R. P. Iczkowski and M. B. Cutlip (pp. 1433-1440, Vol. 127, No. 7)

Philip N. Ross, Jr.63 The authors are to be commended for the scope of the analysis of transport processes in polytetrafluoroethylene (PTFE)-bonded air cathodes, particularly the use of the Stefan-Maxwell equations for multicomponent gaseous diffusion. Their analysis is also the first to include the possible variation in Galvani potential within the electrolyte-filled agglomerates due to the effective resistivity of the electrolyte. As the authors show in Fig. 4, the resistive component is the largest component of voltage loss in a particular electrode to which they applied their analysis. They have, however, done very little to justify the physical model of the electrode structure to which their mathematical analysis was applied. The importance of establishing the physical validity of the model is appreciated by the authors who state: "This model is useful to evaluate how much voltage loss is caused by each of the basic transport processes ... identification of the most important sources of voltage loss allows research and development efforts to be directed towards the minimization of these voltage losses." The model will be useful in directing structure development only if the adjustable parameters of the model are truly related to real physical characteristics of the structure. Otherwise the model is just another example of parametric curve-fitting. The authors have done both themselves and electrochemical science an injustice by not properly exercising the model. Instead of applying the model to a single electrode (whose structural characteristics are not described), the model should have been applied to electrodes of variable structure and electrolytes of variable conductivity to determine whether the adjustable parameters relate to physical properties in a meaningful way. For example, Klinedinst et al.63 have shown that the structure of the PTFE-carbon black composite, i.e., the radius of flooded agglomerates, can be controlled by variation of the weight fraction of PTFE solids and the curing time and temperature. One would expect, for example, that as the weight fraction of PTFE solids varies, the effective agglomerate radius would change, and the voltage loss due to dissolved oxygen diffusion in the agglomerate should vary proportionately. Klinedinst et al.63 have also demonstrated analytical methods for independently measuring the effective agglomerate radius. In a Vulcan XC-72R/PTFE-30 composite containing 50 w/o PTFE solids cured at 610 K the independently measured63 agglomerate radius is ca. 10−6m. It would be of great interest to know whether the value of ra determined by application of the model to polarization curves from this type of electrode is of the correct magnitude. According to the model, changing the conductivity of the electrolyte should decrease the "ohmic" component of the voltage loss. Again, exercising the model with the same electrode in phosphoric acid of variable concentration, and therefore variable conductivity, would provide a more adequate test for validity of the analysis, particularly the suspect treatment of ionic conduction in the catalyst layer.

The treatment of ionic conduction within the agglomerate, and its effect on electrode polarization, is over-simplified and the conclusions related to it misleading. The authors simply write Ohm's law to relate the Galvani potential in solution (in their notation Ep) to the ionic current, and then assume the electrochemical reaction rate depends only on (Ep - Et), the catalyst-solution Galvani potential difference. This treatment is incorrect. Physically, the process they attempt to describe is actually an ionic diffusion polarization due to the absence of excess supporting electrolyte. Hydrogen ion is consumed at the catalyst surface via the reaction

\[ \text{O}_2 + 4	ext{H}^+ + 4e^- \rightarrow 2	ext{H}_2\text{O} \]

The appropriate diffusion equation is that for a binary electrolyte where one of the two ionic species is electroactive. For this case, it can be shown64 that the gradient in hydrogen ion concentration is related to the ionic current by

\[ -I_\text{i}(z) = n_+ \left( 1 + \frac{n_+}{|n_-|} \right) D_+ \frac{dC_+}{dz} \tag{1} \]

where z is the spatial variable in the author's Eq. [33] and [34], n+ and D+ are the hydrogen ion valence and diffusivity, respectively, n− is the anion valence, and C+ the hydrogen ion concentration. The ionic concentration at any point is related to the Galvani potential in solution from the equilibrium condition of the (inert) anions

\[ \frac{n_+ + C_+}{n_-} = \frac{|n_-| F E_i}{\text{constant}} \tag{2} \]

and the electroneutrality condition

\[ n_+ + C_+ = |n_-| (C_-) \tag{3} \]

Equations [1]-[3] must be solved simultaneously with the diffusion equations for the dissolved neutral species and the kinetic rate equation. It is also important to note the coupling between hydrogen ion concentration and reaction rate was neglected. In fact, the rate of oxygen consumption at any point z in the agglomerate is given by65

\[ N_1(z) = \left( \frac{K}{4 F} \right) (C_+) \exp \left[-(E_0 - E_1)/T_s \right] \tag{4} \]

where C+, E0, and E1 are functions of z, and not by the simpler expression used by the authors

\[ N_1(z) = \left( \frac{K'}{4 F} \right) \exp \left[-(E_0 - E_1)/T_s \right] \tag{5} \]

The stronger coupling of ionic conductivity with the oxygen consumption rate implied in Eq. [4] vs. Eq. [5] would mean, in principal, an even larger effect of internal resistance on the total polarization for an electrode than would be computed in the model presented.

63 Lawrence Berkeley Laboratory, Materials and Molecular Research Division, Berkeley, California 94720.
In our laboratory, we have used the current ratios for varying oxygen partial pressure to separate ionic diffusion losses from molecular diffusion losses in air cathodes. We have found that ionic diffusion losses of 5-10 mV per 100 mA/cm² current density are observed only when the acid concentration exceeds 98 w/o, e.g., 99 w/o acid shows a 7.5 mV resistance polarization at 200 mV/cm² but only ca. 2 mV is observed in 95 w/o acid. We postulate that the dramatic appearance of this internal resistance polarization is due to a change in the majority proton species from \( \text{H}_2\text{O}_2^+ \) to \( \text{H}_3\text{PO}_4^+ \) in this region of concentration.

In their discussion on optimum electrode thickness, the authors express a very interesting rationale for the variations in voltage loss with PTFE content (at fixed Pt loading). In their model increasing PTFE content results in large diffusion losses and too much PTFE results in excessive "ohmic" loss, the optimum PTFE probably occurring at the crossover point for these competing effects. The conventional wisdom concerning the increase of voltage loss with PTFE content above the optimum has been that the structure has "dry" catalyst above a certain PTFE level. The authors present a new and more compelling explanation.

Finally, two assumptions were made in applying the model to phosphoric acid fuel cell cathodes that appear questionable, and further affect the general applicability of the breakdown of the losses shown in Fig. 4. Inside the gas pore, water vapor is assumed to be in equilibrium with the electrolyte at every point z. If this were always the case, the polarization curve at zero oxygen utilization would not depend on the partial pressure of water in the bulk air stream (in back of the substrate). This is in fact not the case, as we have observed that polarization curves for purely dry oxygen and for oxygen presaturated to the water vapor pressure of the bulk electrolyte are significantly different, e.g., the dry gas curve shows lower polarization. The magnitude of the diffusion losses determined by application of this model to polarization curves will depend critically on the kinetic parameters for oxygen reduction that are used, particularly the Tafel slope. The breakdown of voltage losses shown in Fig. 4 were produced by use of a 90 mV/decade Tafel slope, referring to the work of Kunz and Gruver as having determined this parameter independently. Careful reading of the cited article reveals a circular argument, since PTFE-bonded electrodes were used in the cited work to arrive at the 90 mV/decade Tafel slope with transport modeling employed to "deduce" this kinetic parameter. The definitive determination of the kinetic parameters for smooth platinum in concentrated \( \text{H}_3\text{PO}_4 \) appears to be the recent work by Yeager and co-workers, and shows that the Tafel slope is 120 mV/decade. For platinum clusters dispersed on carbon black, we have found that the true Tafel slope depends on the microstructure of the clusters (105-115 mV/decade), but for a catalyst like that used by Kunz and Gruver the true Tafel slope is 105 ± 5 mV/decade, instead of 90 mV/decade. It would be of interest to know how the analysis of losses in real fuel cell electrodes changes in light of these new kinetic parameters.

Erratum

In the paper "The Solubilities of \( \text{NiO} \), \( \text{Co}_9\text{S}_8 \), and Ternary Oxides in Fused \( \text{Na}_2\text{SO}_4 \) at 1200°K" by Dilip K. Gupta and Robert A. Rapp which appeared on pp.

2184-2202 in the October 1980 JOURNAL, Vol. 127, No. 10, Fig. 1 and 2 should be as follows:

---

P. Ross, Lawrence Berkeley Laboratory Report, Materials and Molecular Research Division, LBL-10799 (May 1980).

66 P. Ross, Lawrence Berkeley Laboratory Report, Materials and Molecular Research Division, LBL-10799 (May 1980).

67 H. Kunz and G. Gruver, This Journal, 122, 1279 (1975).

68 J. Huang, R. Sen, and E. Yeager, ibid., 126, 786 (1979).

This report was done with support from the Department of Energy. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the Department of Energy.

Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U.S. Department of Energy to the exclusion of others that may be suitable.