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Influence of the Carbon Backing Paper on Oxygen Reduction Parameters in Phosphoric Acid Fuel Cell Electrodes

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Significant diffusion overpotential losses are encountered due to the carbon backing paper alone in phosphoric acid fuel cell electrodes. Above that, the diffusion overpotentials in the electrocatalyst layer are also significant, so gains are still to be made by further reducing both of these diffusion overpotentials. Since the overpotential in the backing paper is proportional to the thickness of the paper, reduction of the thickness is very important for the improvement of the electrode performance.

Optimization of electrocatalyst layer structures in gas-diffusion electrodes for fuel cells, or mathematical simulation of electrode performances based on various structure models of electrocatalyst layers have been studied extensively, for examples, references 1-7 for the former and references 8-12 for the latter. Porous carbon paper is used as the electrode substrate for the catalyst layer of phosphoric acid fuel cell (PAFC) electrodes. However, the influence of such carbon paper substrate on the apparent performance of the porous fuel cell electrode has not been previously appreciated, especially when measurements are obtained on the electrode structures leading to diagnoses of the electrocatalyst operation. Only a few mathematical simulations for the backing paper effect were attempted on a typical electrode chosen for convenience,[10-12] but no experimental proof. It is the purpose of this paper to explore the influence of the carbon paper substrate experimentally, since there are significant diffusion effects that arise from gas-phase porosity constraints. This is particularly evident at high current density situations.

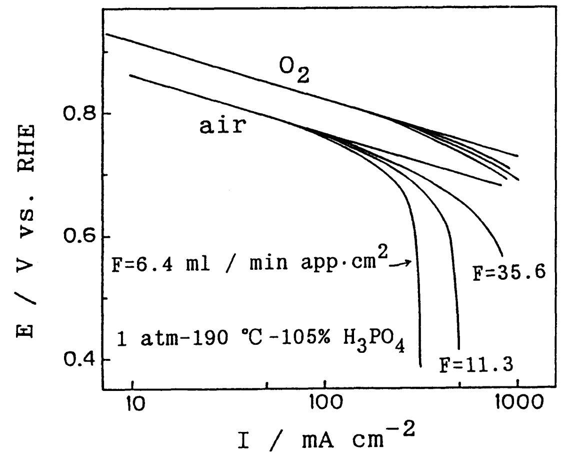

Fig.1. An example of iR free polarization curves for the reduction of oxygen and air with variations in the flow rates at 190 °C in 105% H_3PO_4. Electrode : platinum of 0.5 mg/cm^2 was catalyzed on a carbon paper substrate of 0.1 mm thickness.

Porous carbon papers in a series of thicknesses derived from PAN based carbon fiber were obtained from Toray Ind., Inc. The carbon papers were wet-proofed with FEP to a 30 wt% level and sintered. Carbon supported electrocatalysts were prepared with platinum dispersed by a colloid technique and fabricated into gas-diffusion electrodes with polytetrafluorethylene (PTFE) to 40 wt% PTFE in the electrode structure. The porous carbon paper had an average pore size of 44 μm in diameter and an average porosity of 75%. The electrocatalyst platinum loading on the carbon support was 10 wt% with a surface area of 125 m^2/g. The loading on the electrode was 0.5 mg Pt/cm^2. Electrodes were tested in 105% H_3PO_4 at 190 ℃. Performance curves were obtained under constant current conditions. Oxygen and air gas supplies were used under flow rate (F) control in an experimental cell operated in the half cell mode with a RHE in the same electrolyte.[6] Gas supply to the back of the electrode was directed through a series of machined channels in a non-porous carbon block supporting plate. The configuration of the circular electrode in relation to the gas channels on the carbon backing plate was such that the gas traversed the electrode backing paper by means of multiple channels of 1 mm x 1 mm with spacings of 1 mm between the channels.

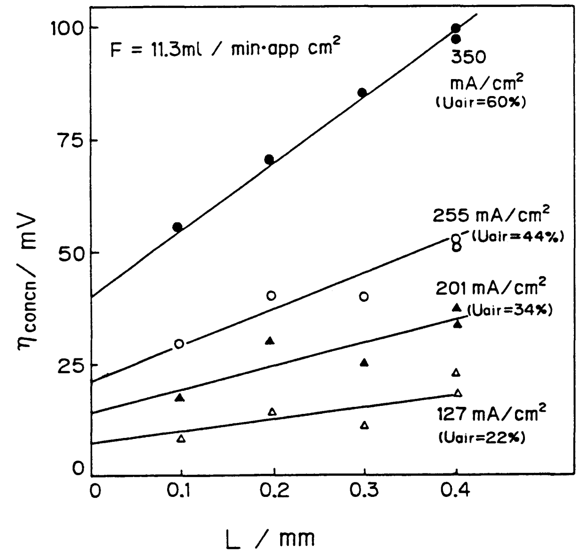

Fig.2a. An example of the relationship between the thickness of the electrode substrate and its influence on the concentration polarization in the cathodes at a series of current densities or air utilizations.

An example of an iR free cathode performance is shown in Fig.1, showing polarization curves on oxygen and air with variations in the gas flow rates. An overpotential appears at high current densities, which manifests itself as a deviation from a Tafel line. The point at which deviation occurs is at a lower current density under air than with oxygen. Since the Tafel line is expected under activation controlling conditions, this deviation by the cathode performance may be attributed to a gas diffusion overpotential (η_{concn}) and is produced from diffusion constraints within the electrode structure as well as the backing paper. The diffusion influence of the backing paper can be obtained from an examination of performance curves for electrodes under identical reaction conditions, but with variations in the backing paper thickness.

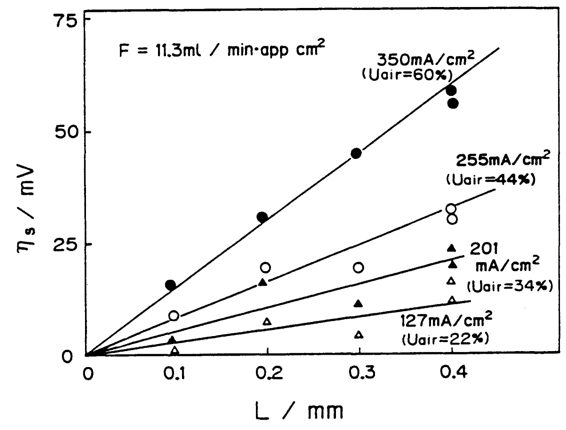

Fig.2b. The relationship between the thickness of the electrode substrate and the overpotential due to the carbon substrate in cathodes, which is obtained by separating the overpotential in the catalyst layer from the total overpotentials shown in Fig.2a.

Some examples of the relationship between the backing paper thickness and its influence on the concentration polarization (η_{concn}) are shown in Fig. 2. It is seen from Fig. 2a that η_{concn} increases linearly with increasing thickness of the electrode substrate, and the effect is amplified as the current density (or air utilization) is increased. On extrapolation of the concentration overpotential values to zero thickness for the backing paper (L=0), then the concentration polarization in the electrocatalyst layer (η_c) is obtained from the intercepts. Separation of the concentration overpotential in the electrocatalyst layer from the observed total diffusion polarization, results in Fig. 2b, showing that polarization due to the carbon substrate alone. The overpotential due to the carbon paper substrate (η_s) is then described by the equation, $\eta_s = \eta_{concn} - \eta_c$. Since the η_s is proportional to the thickness of the paper, it is possible to reduce the polarization more than 40 mV when the thickness is reduced from 0.4 mm to 0.1 mm, where the former is now widely adopted for PAFC uses. The thinner the substrate thickness, the smaller the η_s. However, the thickness reduction is limited by mechanical strength of substrates. A compromise thickness of the backing substrate satisfying the adverse requirements seems to be one third or a quarter to that of the present levels, i.e. about 0.1 - 0.2 mm.

Clearly, there are multiple families of overpotential values due to the carbon paper substrate for each current density as a function of electrode thickness and air utilization. Two such families are shown in Figs. 3a and 3b for 200 and 350 mA/cm^2, respectively, with variations in the carbon paper substrates from 0.1 mm to 0.4 mm. A simulated η_s at 200 mA/cm^2 in the porous backing layer was only 3.5 mV at about 60% air utilization for a typical electrode made in 1974 at a company of the United State.[10] However, it becomes clear from Fig. 2 that the practical η_s is higher compared to that of such estimated value not only at the similar thickness substrate of 0.4 mm but also at the other thin substrates.

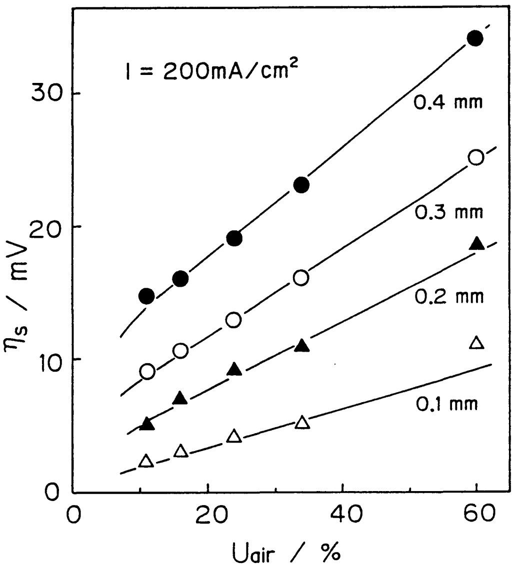

Fig.3a. The effect of the air utilization on the cathode concentration overpotential at 200 mA/cm^2 in the carbon paper substrates of a series of thicknesses.

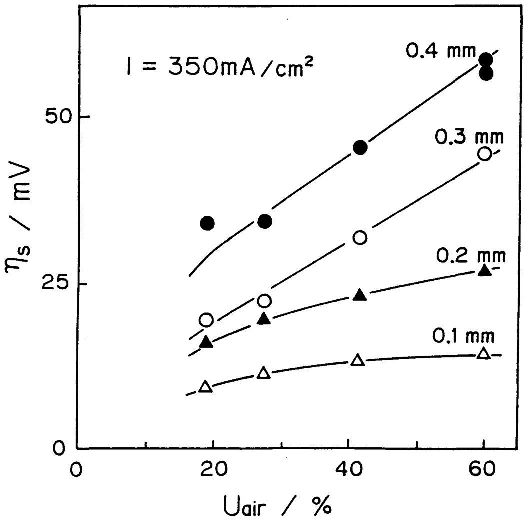

Fig.3b. The effect of the air utilization on the cathode concentration overpotential at 350 mA/cm^2 in the carbon paper substrates of a series of thicknesses.

The concentration overpotential in the electrocatalyst layer, described as the residual concentration overpotential after extraction of the carbon backing paper overpotential is shown in Fig. 4 for three gas flow rates, F= 6.4, 11.3, and 35.6 ml/min electrode cm^2. As the current densities of the electrodes increase, the air utilizations also increase, so a cross plot would be required to show the concentration overpotentials at constant air utilizations.

The thickness effects of electrode substrates on the concentration polarizations mentioned above may have been enhanced a little due to the adoption of circular active area of the test electrodes, namely the polarization of the electrode in the area of maximum diameter is higher compared to that of the electrode at the edge, due to higher air utilization. It is still surprising that such significant average diffusion losses as mentioned above are encountered due to the backing paper alone. Above that, the diffusion overpotentials in the electrocatalyst layer are also significant, so gains are still to be made by reducing both of these diffusion overpotentials further.

Improved experimental results using test electrodes having an active area of square shape will be reported elsewhere.

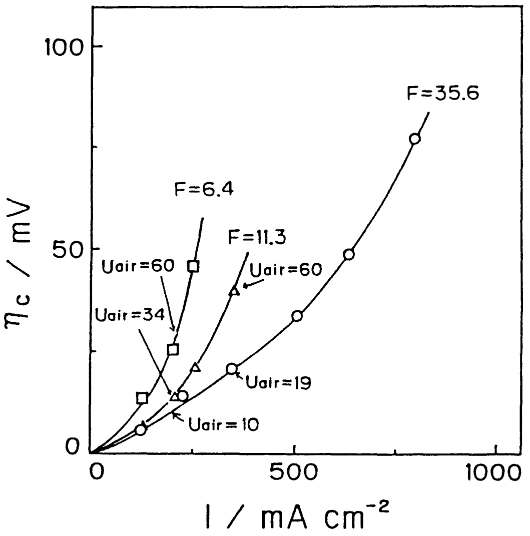

Fig.4. The concentration overpotential in the catalyst layer as the function of current density for three gas low rates.

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