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An electrochemical tool for studying composite formation from PTFE and contacting porous materials

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An electrochemical method has been devised whereby the formation of PTFE–porous material composites (at temperatures in excess of the PTFE melting temperature) may be investigated. The electrochemical oxidation or reduction of a gaseous molecular species on a suitable catalytic material is used as a probe to monitor the degree of penetration of the PTFE into the contacting porous substance. Applied to the formation of PTFE–carbon black composites, this new technique has yielded results in substantial agreement with those previously obtained by electron microscopy. In addition, the electrochemical data can be interpreted to yield the diffusivity–solubility products for electro-active gases dissolved in the electrolytic solutions. Again, there is good agreement between the data obtained in this manner and those obtained using other techniques. Taken as a whole, the accumulated experimental results indicate the reliability of this new electrochemical method for the study of interesting PTFE–porous material composite systems.

1. Introduction

Composites of PTFE with porous materials are generally made by heating (above the melting point of the PTFE) mixtures or contacting layers of the two substances. It has recently been shown that, during the heating process, the PTFE penetrates into the contacting porous material, the penetration distance increasing linearly with the square root of the heating time [1, 2]. (Composites of PTFE with carbon black, gold or platinum black, and porous sintered gold or nickel have so far been examined.) The penetration of the PTFE into the contacting porous material is unexpectedly rapid and occurs by the spreading of a very thin film followed by a thickening of this film with increasing time at temperature until a limiting concentration is reached. The lower the average molecular weight of the PTFE or the higher the temperature, the more rapidly the polymer penetrates into the porous material. It has also been found that, presumably as a result of the penetration of the PTFE into the porous material, the polymer volatilizes many times faster than it does in the absence of a contacting porous substance.

Heretofore, it has been necessary to rely upon electron microscopy as the primary technique in the investigation of the interaction between PTFE and contacting porous materials. It appeared that a simpler method was needed in order to facilitate further study of these unexplored phenomena. Thus, an electrochemical method was devised whereby the formation of PTFE–porous material composites can be more readily investigated.

2. Experimental

The electrochemical oxidation or reduction of a gaseous molecular species on a suitable catalytic material is used as a probe to monitor the degree of penetration of the PTFE into the contacting porous material. The experimental sample (constructed of adjacent layers of contacting materials and illustrated below) serves as one electrode of an electrochemical cell (anode or cathode, depending upon whether the gas phase contains an oxidizable or reducible molecular species). Any electrolyte which wets the porous material but which does not wet the PTFE can be used.

Gas containing oxidizable or reducible molecules	PTFE (containing gas pores)	Porous material	Electrocatalyst	Electrolyte

Each sample is first thermally pretreated at a temperature above the melting temperature of the PTFE for a predetermined time. With increasing time and/or temperature, the extent of penetration of the PTFE into the contacting porous material increases. As the PTFE penetrates into the porous substance (forming a new composite material), the amount of electrolyte which this material can subsequently absorb decreases due to the non-wettability of the PTFE. PTFE-lined pores are formed through which the gas molecules can rapidly diffuse. As the advancing front of PTFE approaches the electrocatalyst layer, the measured mass transport-controlled limiting current (arising from the electro-oxidation or electro-reduction of the gas molecules in the layer of catalytic material) increases. When the duration of the thermal pretreatment (at a given temperature) has been sufficient to cause the PTFE to penetrate to the electrocatalytic layer, the measured current density will increase dramatically due to the formation of continuous gas-filled pores. The rate of penetration of the PTFE through the contacting porous material can then be determined, as a function of pretreatment temperature, from the known thickness of the layer of porous material.

In the work reported here, O_2 was employed as the reducible gaseous species (as pure O_2, air, and 4% O_2 in N_2), Pt black was used as the electrocatalyst ($2\,mg\,cm^{-2}$), and the porous material was the same carbon black used in an earlier investigation [2]. It was determined by microscopic examination of cross-sectioned samples that the average thickness of the carbon black layer was $20\,\mu m\,cm^{-2}$. The PTFE material used had an average molecular weight of approximately 5×10^6 and contained 30 wt % carbon black as a pore former. (It was found that layers of the carbon-containing PTFE remain sufficiently porous so as not to significantly retard the transport of molecular oxygen under the range of experimental conditions employed in this work.) The electrolyte used was 96 wt % H_3PO_4. Unless otherwise noted, the thermal pretreatment temperature was 335 to 337° C, and the electrochemical measurements were made at 160° C. The design of the electrochemical cell (constructed from PTFE) has been reported previously [3]. Polarization (I–E) curves were measured and the limiting currents were obtained by extrapolation.

In cases when the porous material is electronically conducting (as is the carbon black used in this work), it is possible to vary the procedure by dispersing the electrocatalyst (in the form of small crystallites) within the porous material, rather than employing a separate layer of the electrocatalytic material. In the work reported here, the Pt black electrocatalyst layer was replaced by incorporating 10 wt % Pt into the carbon black layer in the form of small crystallites adhering to the carbon surface. The modified experimental sample is illustrated below.

Gas containing oxidizable or reducible molecules	PTFE (containing gas pores)	Porous material (containing dispersed electrocatalyst particles)	Electrolyte

Now, as the PTFE penetrates into the contacting porous material, the extrapolated limiting current will increase proportional to the distance of penetration. (The limiting current, being determined by reactant diffusion through the thin electrolyte films present in the PTFE-containing portion of the layer of porous material, will increase proportional to the thickness of this PTFE-containing region until the PTFE has penetrated entirely through the layer or until another process becomes current limiting [4–6]). Since the distance of penetration increases linearly with the square root of the duration of the thermal pretreatment, the experimental limiting currents will also exhibit this functional dependence upon the time of heating [1, 2].

3. Results and discussion

3.1. Experiments with adjacent layers of porous material and electrocatalyst

The extrapolated limiting currents measured with a $1\,mg\,cm^{-2}$ layer of carbon black are plotted versus the square root of the duration of the thermal pretreatment step in Fig. 1. (The data

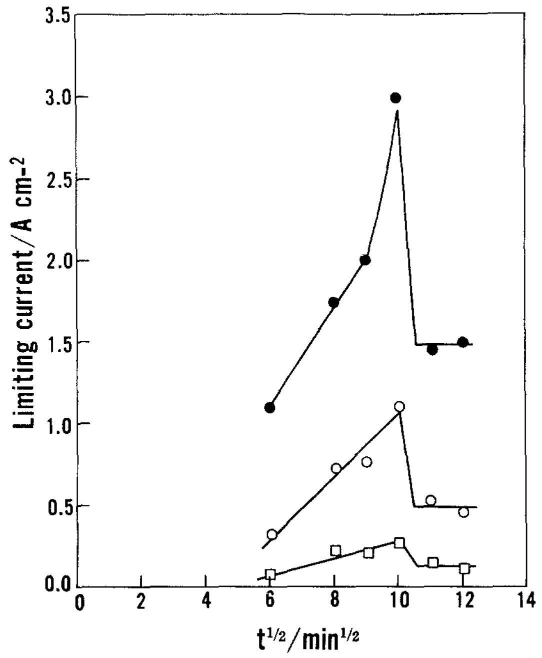

Figure 1 Extrapolated limiting current data reflecting PTFE penetration into carbon black (1 mg cm^{-2}) at 335 to 337° C (obtained with adjacent layers of carbon black and electrocatalyst). □, 4% O_2 in N_2; ○, air; ●, pure O_2.

were plotted in this fashion because, as previously determined, the distance of penetration of the PTFE into the contacting carbon black increases linearly with the square root of the time at temperature [1, 2].) As the figure shows, in every case a rapid increase in I_{lim} with increasing time at temperature was observed, followed by a sharp decrease to a much lower I_{lim} value with further heating. The increasing limiting current obviously corresponds to the penetration of the PTFE into the layer of carbon black, resulting in gas pore formation and reduced oxygen transport resistance. The sudden sharp decrease in performance corresponds to the arrival of the PTFE at the carbon black/platinum black interface. (It has previously been shown that the tendency of PTFE to penetrate into platinum black is slight compared with its tendency to penetrate into carbon black [1, 2]. It is most probable that the sharply reduced limiting current occurs when the PTFE, reaching the carbon black/platinum black interface, penetrates into the interfacial zone, partially separating the electrocatalyst from the porous carbon. This results in increased electronic and/or gas phase transport resistance and, hence, the lowered limiting currents.)

From the data in Fig. 1 and that obtained in similar experiments with varying carbon layer thicknesses, a value of 2.0 μm min$^{-1/2}$ is obtained for the rate of penetration of the PTFE into the porous carbon black at 335 to 337° C.

3.2. Experiments with the electrocatalyst dispersed in the layer of porous material

The extrapolated limiting currents measured with a 0.225 mg cm^{-2} layer of carbon black are plotted versus the square root of the duration of the thermal pretreatment step in Fig. 2. The expected linear increase in I_{lim} with $t^{1/2}$ is evident. The extrapolated limiting current ceases to increase with further heating when the PTFE has penetrated completely through the layer of porous carbon. (The subsequent decrease in I_{lim} with long periods of heating results from the fact that, as the PTFE penetrates more and more into the layer of carbon black, portions of the carbon layer are no longer wetted by the contacting electrolyte. Similarly, the electrolyte films in portions of the carbon layer may become so thin that resistance polarization effects begin to predominate.)

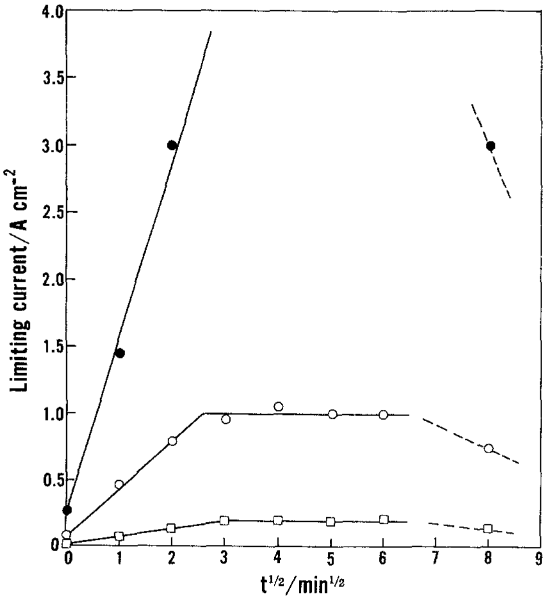

Figure 2 Extrapolated limiting current data reflecting PTFE penetration into carbon black (0.225 mg cm^{-2}) at 335 to 337° C (obtained with the electrocatalyst dispersed in the layer of carbon black). □, 4% O_2 in N_2; ○, air; ●, pure O_2.

Combining these data with the comparable results obtained with samples containing carbon black layers of varying thickness yields a calculated PTFE penetration rate of 1.8 μm min$^{-1/2}$, which is in good agreement with the value obtained above using the contacting layers of porous carbon and platinum black.

In addition to the limiting currents, the low current portions of the *I–E* curves (obtained with the electrocatalyst dispersed within the porous material) can also be analysed to obtain the rate of PTFE penetration into the contacting layer of porous material. Additionally, information can be extracted concerning the transport of the electro-active species through the electrolytic solution. It is first necessary to know the electrochemical response of samples containing varying amounts of the porous material when no thermal pretreatment is employed (i.e. when the PTFE has not ben allowed to penetrate into the porous material). In Fig. 3 the current density measured at 900 mV (R.H.E.) under these conditions, with pure O_2 as the reactive gas, is plotted as a function of the thickness of the carbon black layer. (The data were corrected for currents originating from the electro-oxidation of the carbon by subtracting the current density measured with the O_2 replaced by pure N_2.) As indicated in the figure, the measured current density increased linearly with the thickness of the layer of porous carbon until, for layers thicker than about 10 μm, a constant current density was obtained.

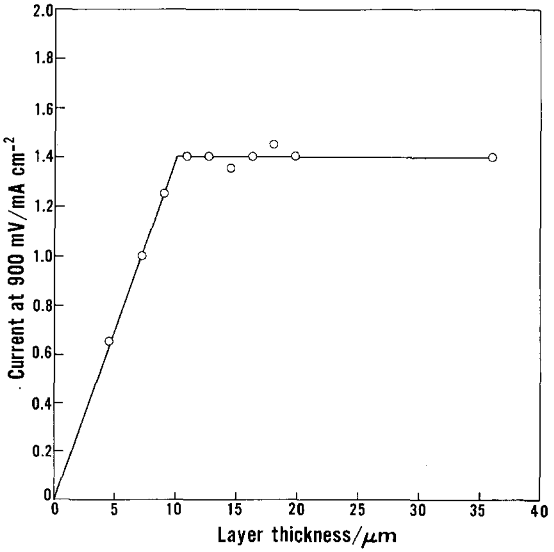

Figure 3 Current density measured at 900 mV with pure O_2 versus carbon black layer thickness, no thermal pretreatment (obtained with the electrocatalyst dispersed in the layer of carbon black).

In general, for a completely liquid-filled porous layer of catalytically active material, the current density at which the transition from the Tafel to the double-Tafel slope occurs (from activation to diffusion control) is a function of the thickness of the layer. If the liquid-filled layer were to operate under pure activation control independent of layer thickness, then the measured constant potential current density would simply increase proportional to the layer thickness. However, upon the onset of diffusion control, the measured current density will become independent of the layer thickness. The layer thickness at which diffusion control begins, δ_{tr}, is related to the transition current, I_{tr}, by the equation,

$$I_{tr}\delta_{tr} = nFD_{eff}C_0 \qquad (1)$$

where D_{eff} is the effective diffusivity of the electro-active species in the liquid-filled layer of porous material, and C_0 is the solubility of the electro-active species in the electrolyte [7].

From the data in Fig. 3, a value of 3.6×10^{-12} (mol sec^{-1} cm^{-1}) is calculated for the product, $D_{eff}C_0$ for O_2 in 96 wt% H_3PO_4 at 160° C ($n = 4$). The DC_0 product obtained previously by extrapolation of values obtained by an entirely independent procedure was 4.4×10^{-12} (mol sec^{-1} cm^{-1}) [8]. Since $D_{eff} = D\,\theta/\tau$ (where θ and τ are the porosity and tortuosity, respectively, of the liquid-filled porous material), this gives $\theta/\tau \approx 0.80$. The good agreement between the diffusivity–solubility product obtained from the current densities measured here as a function of layer thickness and the diffusivity–solubility product obtained earlier by an entirely independent technique substantiates the validity of our experimental procedure and results.

The experimental results plotted in Fig. 3 can now be used to extract the rate of PTFE penetration into the porous material from the current densities measured at constant potential (in this case, 900 mV) with samples of constant thickness subjected to thermal pretreatments of varying duration. In Fig. 4 are plotted the current densities measured at 900 mV (R.H.E.) with pure O_2 (corrected for carbon electro-oxidation as before) as a function of the square root of the time at temperature. The data are shown for a thin layer containing 0.225 mg of the carbon black per cm^2 (the horizontal line) and for a thick layer

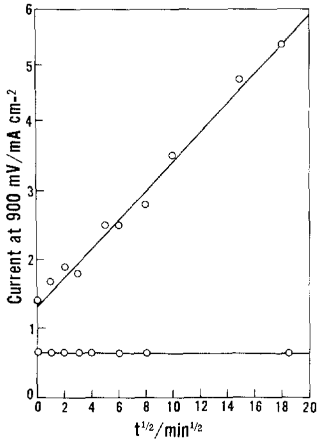

Figure 4 Current density measured at 900 mV with pure O_2 reflecting PTFE penetration into carbon black at 335 to 337° C (obtained with the electrocatalyst dispersed in the layer of carbon black). Horizontal line, 0.225 mg cm^{-2}; diagonal line, 1.8 mg cm^{-2}.

containing 1.8 mg of the porous carbon per cm^2 (the diagonal line).

As the figure shows, the current density measured with the thin carbon layer is independent of the time of heating (i.e. independent of the extent of PTFE penetration into the carbon layer). This is to be expected since, as shown in Fig. 3, completely electrolyte-filled layers thinner than about 10 μm operate on the Tafel slope at 900 mV and so are not affected by mass transport limitations. On the other hand, the current density measured with the thick carbon layer increases linearly with the square root of the time of heating, again in agreement with the data in Fig. 3 and the fact that, as the PTFE penetrates into the carbon layer (with penetration distance proportional to $t^{1/2}$), the resulting PTFE-containing region of the layer will operate on the Tafel slope.

From the variation of the measured current density with sintering time for the samples containing 1.8 mg of the porous carbon per cm^2, a value of 1.6 μm min$^{-1/2}$ is calculated for the PTFE penetration rate at 335 to 337° C, in good agreement with the 1.8 μm min$^{-1/2}$ value calculated from the variation of the extrapolated limiting current with time of heating.

The purposes of comparison, similar data were obtained for samples containing 1.8 mg cm^{-2} carbon black layers with a thermal pretreatment temperature of 327 to 329 °C. By combining these data with those plotted in Fig. 3, a PTFE penetration rate of 1.0 μm min$^{-1/2}$ was calculated corresponding to this lower temperature. This finding is in agreement with the earlier observation that the rate of penetration of the high molecular weight PTFE into the contacting carbon black increases with increasing temperature [2].

Since the distance of PTFE penetration increases linearly with the square root of the heating time, the Washburn equation for capillary flow (Equation 2) can be applied to obtain at least an order of magnitude estimate of the apparent viscosity of the high molecular weight PTFE.

$$x^2 = \frac{\gamma \cos\theta \, rt}{2\eta} \tag{2}$$

where x is the distance of penetration in time, t, γ is the PTFE surface tension (taken to be 20 dyn cm^{-1}), η is the viscosity, r the pore radius (0.01 to 1.0 μm, and θ the contact angle (assumed to be 0°). Using these values, the determined rate of penetration at 335 to 337° C leads to a calculated viscosity of between 2×10^4 and 2×10^6 P. These values are several orders of magnitude smaller than the commonly accepted range of viscosity for high molecular weight PTFE, but are in substantial agreement with previously reported values obtained from other experimental data for various PTFE–porous material systems. In particular, an electron microprobe investigation of the same PTFE/porous carbon system examined here resulted in a calculated viscosity range of 10^4 to 10^6 P at the same temperature [2]. This good agreement again points to the validity of our experimental approach and the reliability of the data.

4. Conclusions

An electrochemical method has been devised whereby the formation of composites from PTFE and contacting porous materials (at temperatures in excess of the PTFE melting temperature) may be investigated. By the use of this technique, an average value of 1.8 μm min$^{-1/2}$ has been determined for the rate of penetration of high molecular wieght PTFE into a contacting layer of porous carbon at 335 to 337° C. A value of 1.0 μm min$^{-1/2}$ was determined corresponding to a temperature of 327 to 329° C. These results are in substantial agreement with those previously obtained by electron microscopy for the system examined here. In addition, the electrochemical data can be interpreted to yield values of diffusivity–solubility products for electro-active gases dissolved in the electrolytic solutions. Such derived values have been found to be in good agreement with those obtained by other techniques. Taken as a whole, the experimental results obtained so far indicate the reliability of this novel electrochemical approach to the study of interesting PTFE–porous material systems.

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