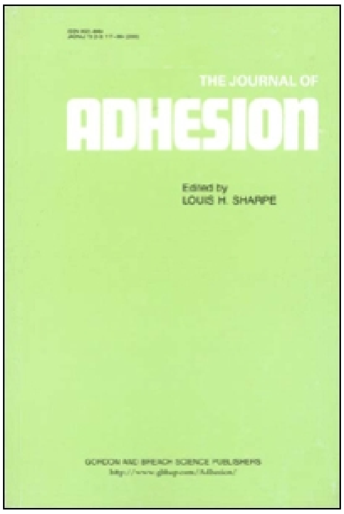
This article was downloaded by:
On: *22 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



The Journal of Adhesion

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713453635

Electrochemical Aspects of Adhesive Joint Failure

K. A. Klinedinst[a]; W. M. Vogel[a]
[a] Power Systems Division, United Technologies Corporation, Connecticut, U.S.A.

To cite this Article Klinedinst, K. A. and Vogel, W. M.(1978) 'Electrochemical Aspects of Adhesive Joint Failure', The Journal of Adhesion, 9: 2, 123 — 133
To link to this Article: DOI: 10.1080/00218467808075107
URL: http://dx.doi.org/10.1080/00218467808075107

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

J. Adhesion, 1978, Vol. 9, pp. 123–133

Printed in Scotland

Electrochemical Aspects of Adhesive Joint Failure

K. A. KLINEDINST and W. M. VOGEL
Power Systems Division, United Technologies Corporation,
South Windsor, Connecticut 06074 U.S.A.

(*Received December 10, 1976*)

The effect of varying potential upon the stability of a bond formed between an adhesive and an electronically conducting substrate has been examined both theoretically and experimentally. It has been found that, in the presence of a liquid which can wet the substrate and the adhesive, the possibility of adhesive/substrate separation exists, even though the bond might be very stable in the absence of such a liquid environment. Both the interfacial tension between the liquid and the substrate and specific adsorption at the substrate/liquid interface vary with potential, making the stability of the adhesive/substrate bond potential dependent. In the case of the PTFE/graphite bond in the presence of hot concentrated H_3PO_4, the measured variations in the rate of separation with potential can be rationalized on the basis of the probable changes in the free energy of the process with potential.

INTRODUCTION

Adhesive joints are sometimes assumed never to separate if they are proper, i.e. if there is true molecular contact between the phases and if no weak boundary layer exists.[1] This assumption is based on the argument that the change in free energy of the system which occurs during separation is positive and so large, even without chemical bonding, that unattainable stress would be required for separation at the actual interface. However, if a liquid is present which can wet both the adhesive and the substrate, separation can occur.[2, 3] It appears that the liquid diminishes the free energy of separation by altering the interfacial tensions of the freshly exposed surfaces. Since the interfacial tension between an electronic conductor and an electrolyte depends on the electrode potential it would seem reasonable to expect some correlation between the potential† and the separation tendency of a metal/adhesive

---

† The term potential used in this paper refers to the iR-free terminal voltage of the cell consisting of the electrode under study and a reference electrode [in this case a Pt/H_2 (1 atm total pressure) electrode in the same medium].

joint which forms a three-phase boundary line with an electrolyte, e.g., at a crack or other imperfection.

The results presented here pertain to the separation of joints between graphite and PTFE in hot concentrated H_3PO_4. This system was studied as a model for the adhesion of thin PTFE films on electrocatalysts in certain fuel cell electrolytes. It has been shown[4] that such structures contain very thin films of PTFE supported by the porous catalyst.

THERMODYNAMIC CONSIDERATIONS

The aforementioned argument of inseparable proper adhesive joints has to be modified if one deals with systems exhibiting three-phase boundary lines formed by the joint components and an electrolyte. An approximate expression relating the free energy of separation of such joints can be derived without much difficulty if the metal after separation forms a polarizable interface with the liquid, and if no specific adsorption occurs. Most practically interesting systems such as the present one do not conform to this ideal model and have to be dealt with more or less empirically. Nevertheless, it would appear useful to use the simpler model as a guide for understanding the more complex systems.

Assume a proper joint between an adhesive (A) and a metallic substrate (S) which, in contact with the electrolyte (L), forms a polarizable interface without chemisorption. Upon separating 1 cm^2 of this joint under the influence of a mechanical stress 1 cm^2 of interface S/A is eliminated and 1 cm^2 each of S/L and A/L are created. The change in free energy is

$$\Delta G = \gamma_{SL} + \gamma_{AL} - \gamma_{SA} + \Delta G_p \tag{1}$$

where ΔG (<0) is due to the mechanical stress relaxation. We also have for the interfacial tension between a liquid (1) and a solid (2)

$$\gamma_{12} = \gamma_{2V} - \gamma_{1V} \cos \theta_{12}. \tag{2}$$

Treating the adhesive at S/A as the liquid we have

$$\Delta G = \gamma_{SL} - \gamma_{SV} + \gamma_{AV}(1 + \cos \theta_{SA}) - \gamma_{LV} \cos \theta_{AL} + \Delta G_p \tag{3}$$

The electrocapillary curve of electrodes of the assumed kind is described by the well known equation

$$\gamma_{SL} = (\gamma_{SL})_{max} - \tfrac{1}{2}C\,(\varepsilon - \varepsilon_{max})^2. \tag{4}$$

We now have

$$\Delta G = (\gamma_{SL})_{max} - \gamma_{SV} + \gamma_{AV}(1 + \cos \theta_{SA}) - \gamma_{LV} \cos \theta_{AL} + \Delta G_p - \\ - \tfrac{1}{2}C\,(\varepsilon - \varepsilon_{max})^2 \tag{5}$$

The index (max) refers to the electrocapillary maximum where the metal surface is charge free. C is the (differential) double layer capacitance of the interface S/L.

$(\gamma_{SL})_{max}$ can be assumed to have a value similar to that calculated by applying Eq. (2) to this interface. Thus, for a wettable metal γ_{SL} will be smaller than γ_{SV}. At potentials more positive (anodic) or more negative (cathodic) than the point of zero charge (pzc, ε_{max}), γ_{SL} will be smaller than $(\gamma_{SL})_{max}$. We see that separation at S/A is thermodynamically least favored at the pzc. At other potentials it is possible that the mechanical stress required to make ΔG negative is small enough to allow separation at the actual interface, i.e. that it is smaller than the cohesive strength of the adjoining phases, or of a weak boundary layer if present. Assume a typical double layer capacitance of $C \simeq 20\,\mu F/\text{cm}^2$. At a rational potential $(\varepsilon - \varepsilon_{max})$ of 1 volt (e.g. a basal plane graphite electrode with $\varepsilon_{max} \simeq 0$ volt[5] under air where the open circuit potential is in the vicinity of 1 volt) ΔG is reduced by 10^{-5} VA sec/cm^2 = 100 erg/cm^2 from its maximum value. This value corresponds to a reduction in the separation stress of the order 10^4 atm.

Unfortunately, few metal/electrolyte interfaces behave in the idealized manner considered so far. Even if a continuous charge transfer reaction such as corrosion does not occur, chemisorption is frequently present. Specific adsorption will distort the electrocapillary curve and Eq. (4) cannot be used under such conditions to describe the electrocapillary curve. However, the Lippmann equation, relating the slope of the electrocapillary curve to the metal charge,

$$\frac{d\gamma_{SL}}{d\varepsilon} = -Q \tag{6}$$

is still applicable. Equation (4) is derived from Eq. (6) using a constant capacitance C. It would appear reasonable, therefore, to use Eq. (5) with the empirically determined integral $\int Q\, d\varepsilon$ instead of the parabolic term. This is equivalent to using the pseudo-capacitance C^* instead of C. Pseudocapacitances are typically larger than double layer capacitances and their influence is restricted to certain potential regions. Thus, rather than vary linearly with potential as without chemisorption, the metal charge changes more abruptly in regions where specific adsorption occurs. As a result, the interfacial tension also changes more abruptly in such regions.[6]

For electrodes which cannot be polarized the slope of the electrocapillary curve is not equal to the metal charge.[7] We cannot change the potential by supplying an electrical charge to the electrode but only by varying the activity of the potential determining ions in solution. As a result the variation of γ_{SL} with potential cannot be estimated from charging curves but has to be measured directly.

It seems clear that the argument of inseparable proper adhesive joints cannot be applied generally to joints between a conductor and an adhesive if three-phase boundary lines are formed with an electrolyte. The potential at this boundary line can be enforced and controlled with an external voltage source or, at open circuit, it will be determined by the electrically neutral sum of all possible electrochemical reactions. Examples of the latter are the cathodic O_2 or H_2O reduction, the anodic adsorption of oxygen containing groups, anodic metal corrosion, etc. Such open circuit potentials are usually difficult to predict and they can vary, sometimes very substantially, from experiment to experiment for reasons hard to identify. For this reason, and because of the possible magnitude of the effect of potential on the free energy of separation, the present experiments were done at controlled potentials.

EXPERIMENTAL

1. Materials

The carbon substrate material was as deposited pyrolytic graphite, provided by the Union Carbide Corp. The graphite was sectioned parallel to the principal axis of symmetry so as to expose an edge plane oriented surface. (The resulting graphite substrate had dimensions 1 cm × 1 cm × 2 mm, with two parallel 1 cm^2 edge plane oriented surfaces exposed.) The sample was polished with Linde Al_2O_3 powders down to 0.05 μm particle size. SEM photomicrographs indicated that the polished surfaces did not contain pores with diameters greater than 0.1 μm, with most pores considerably smaller than this.

The PTFE material used had an average molecular weight of about 5×10^6. It was obtained in the form of a water suspension of submicron-sized particles with no added surface active agents.

The porous gold foil substrates employed were prepared by the high temperature sintering of pressed layers of Englehard 100 mesh (nominal) gold powder. The flexible gold foil prepared in this manner was about 1 mil thick and contained pores ranging up to several micrometers in diameter.

2. Preparation of samples for testing in room temperature air environment

Layers of the PTFE material about 20 μm thick and about 7 mm in diameter were prepared by filtration upon the porous sintered gold substrates. These layers were dried and heated in the air for 1 hour at 350°C, conditions chosen to allow the PTFE to flow into the porous gold substrate, thereby effectively anchoring it by means of mechanical interlocking effects.[4] The 350°C thermal processing operation also served to consolidate the PTFE, creating a smooth surface for subsequent bonding to the polished carbon surface. The PTFE–carbon bond was subsequently formed by heating the contacting materials for 1 hour at 350°C.

3. Preparation of samples for testing in hot, concentrated electrolytic environment

The sample preparation technique finally adopted was the result of much trial and error experimentation. The major difference between this technique and that used to prepare the samples for testing in the room temperature air environment is the use of a layer of FEP between the porous gold substrate and the layer of PTFE. The FEP bonds very well to the PTFE (presumably by chain entanglement during the thermal processing operation). Further, due to its lower melt viscosity and melting temperature, it flows much more rapidly into the porous gold substrate than does the PTFE. Thus, the PTFE film is more strongly bonded (primarily by mechanical interlocking effects) to the porous gold by virtue of the intermediate layer of FEP. (This stronger adhesion is required because of the much longer duration of the tests performed in the hot, concentrated electrolytic environment.)

The PTFE on gold foil sample was bonded onto the polished edge plane oriented pyrolytic graphite surface using the same procedure employed to prepare the samples for testing in the room temperature air environment, except that the PTFE on gold foil was positioned so as to extend out over the edges of the polished carbon surface on three sides. Following this, a single-edged razor blade was used to trim the PTFE on gold substrate as close as possible to the two parallel edges of the carbon substrate, leaving the PTFE on gold foil extending out over the edge of the carbon sample on one side only. An aluminum mold was used to bend the PTFE on gold foil "tab" up from the edge of the piece of pyrolytic graphite so that the "tab" (except for the portion in the bend) was now perpendicular to the carbon surface.

4. Testing procedure—room temperature air environment

The procedure used was basically that described in the ASTM "Standard Method of Test for Tensile Properties of Adhesive Bonds".[8] A fast setting epoxy resin was used to bond the exposed sides of the gold substrate and the piece of pyrolytic graphite to the flat surface of two stainless steel lugs. Each lug was threaded on the end opposite to the bonded sample so that it could be attached to an Instron screw-type tensile testing machine equipped with an X–Y recorder. An aluminum guide was used to ensure good linear alignment of all bonded parts, two set screws being used to immobilize the stainless steel lugs during the setting of the epoxy resin.

The entire assembly (with the stainless steel lugs attached to the aluminum guide by the two set screws) was then attached to the tensile testing machine, one set screw was loosened, and the room temperature stress–strain curve was recorded using a 0.005 in./hr rate of elongation. The tensile strength of the adhesive bond between the PTFE and the carbon is calculated from the force required to break the experimental piece.

The PTFE and carbon surfaces were examined after the tensile testing. Water wettability was used to test for the presence of a thin PTFE film that might still be adhering to the carbon surface. Additionally, these surfaces were examined microscopically by the use of a Leitz Optholux microscope with a double beam interferrometer attachment.

5. Testing procedure—hot, concentrated electrolytic environment

In order to measure the rate of debonding of the PTFE from the smooth carbon surface, a device was constructed capable of detecting submicron-sized changes in the extent of the PTFE–carbon bond. The heart of this device is a Hewlett-Packard linear displacement transducer, model 24DCDT-050. The PTFE–carbon sample is attached to hardware constructed entirely of tantalum so that it may be totally immersed in the electrolyte (104 w/o H_3PO_4 at 160°C) under conditions of controlled electrochemical potential. The piece of carbon is firmly attached to the immovable base of the testing apparatus (by means of a set screw), while the gold foil "tab" is attached to the movable tantalum rod (by means of another set screw). The rod is connected to the transducer core whose position is detected as it moves through an electromagnetic field. A pulley assembly enables the application of a small, constant load to the PTFE film in order to provide a way of lifting the unbonded portion of the PTFE film (attached to the gold foil "tab") so as to assure the maintenance of the three phase interface (PTFE–carbon–electrolyte). (A 6 gm weight was used in these experiments, equivalent to 6×10^{-4} gm per micrometer of PTFE/carbon interface.)

The sample (attached to the adhesion testing device) is then lowered into the electrolyte solution, becoming the working electrode of an electrochemical cell, with a platinum foil counter electrode and a 1 atm H_2/Pt black reference electrode also immersed in the electrolytic solution. All of the other cell parts were constructed from molded PTFE. A potentiostat and function generator were employed in order to measure the stability of the PTFE/carbon bond as a function of electrochemical potential. The entire adhesion testing device, including the transducer and the electrochemical cell, was contained within a thermally insulated box so as to avoid problems arising from air temperature variations. The temperature within the insulated box remained at about 31°C throughout the experiment. The insulated box rested upon vibration damping cushions which themselves rested upon a heavy marble table. The output of the linear displacement transducer was calibrated and fed into a strip chart time base recorder so that a record of the movement of the gold foil "tab" (and, therefore, a record of the separation of the PTFE film from the carbon surface) was obtained.

6. Procedure for determining the reactivity of the polished carbon surface as a function of electrochemical potential

A gold wire contact was pressed into a hole drilled into one of the basal plane edges of a piece of the edge plane oriented pyrolytic graphite. The carbon was then coated with FEP by repeated dipping in an FEP dispersion and heating at 335°C. One of the edge plane surfaces (1 × 1 cm) was then polished, cleaned, and dried. It was heated in the air at 350°C for $1\frac{1}{2}$ hours (to at least partially simulate the process of bonding the PTFE to the carbon surface). It was then attached to the potentiostat-function generator combination and immersed in N_2-saturated 104 w/o H_3PO_4 at 160°C. The potential was increased from the open circuit potential (about 750 mV) up to 900 mV, and then repeatedly cycled (7 sec/V) between 900 and 50 mV. The I–E data were recorded.

RESULTS

1. Room temperature air environment

An applied stress of about 1200 psi was required to separate the experimental sample, and the manner in which the sample separated was most significant. The PTFE simultaneously tore away from both the porous gold substrate and the smooth edge plane oriented pyrolytic graphite. The tests were quickly terminated, leaving one end of the stretched PTFE film still attached to the carbon surface while the other end of the film was still attached to the porous gold foil.

The portions of the carbon surface and the porous gold substrate to which the layer of PTFE had previously been attached were both water nonwettable, indicating that a film of PTFE still adhered to both of these surfaces (since both surfaces were water wettable before being bonded to the separated film of PTFE.) It was shown by interferrometry that the thin PTFE film that still adhered to the carbon surface was very nonuniform, with a mean thickness of about 0.1 μm.

2. Hot, concentrated electrolytic environment

The rates of separation of the PTFE from the smooth edge plane carbon surface in the potential range from 20 to 980 mV are plotted in Figure 1. The data showed good reproducibility at a given potential, both with the same sample and with different samples. Thus, in a given experiment the rates could be changed from one value on the curve to another one by changing the potential.

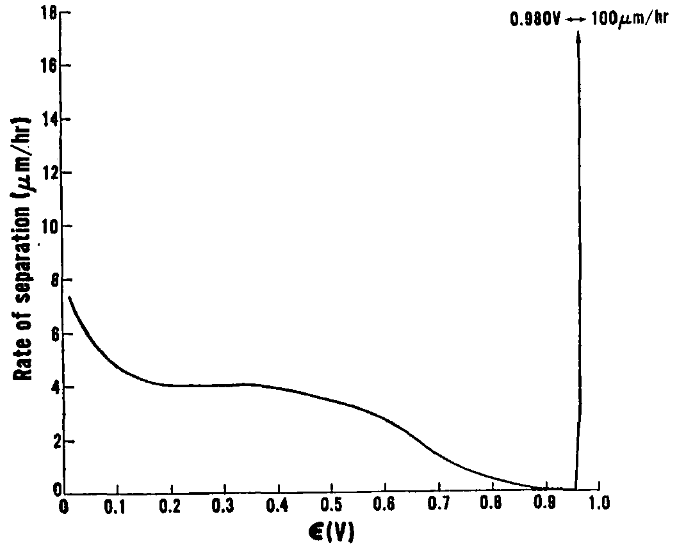


FIGURE 1 Rate of separation vs potential (in electrolytic environment).

At potentials between 900 and 955 mV, the joints were found to be completely stable, i.e. no separation was found for up to 90 hours (the longest experimental time). At potentials above 955 mV the rate of separation (r) increased approximately exponentially with increasing potential. Thus

$$r \propto \exp(\alpha\varepsilon), \qquad \alpha \approx 0.2\ \mathrm{mV}^{-1}. \tag{7}$$

When the potential was cycled rapidly between 20 and 920 mV using a square wave function generator with the pulses at both ends being of equal duration, a separation rate of 3.3 μm/hr was observed. This value is almost exactly the average of the separation rates at 20 mV (7.0 μm/hr) and 920 mV (0.0 μm/hr). This result also indicates how reproducible and specific the potential effect is.

For a given sample, the total amount of separation over the duration of an experiment should, of course, equal the time integral of the separation rate. The former was determined in two tests by post test microscopic examination. Good agreement (±10%) was found, thus confirming the rate measurements.

Important is the observation that the graphite surface exposed during separation was always found to be water wettable, and that no traces of graphite could be detected on the PTFE surface. Thus, separation occurred at the actual graphite/PTFE interface.

DISCUSSION

These results indicate that the strength of the PTFE/edge plane pyrolytic graphite bond is greater than the cohesive strength of the PTFE. This conclusion is confirmed by a comparison of the stress required to separate the experimental sample (about 1200 psi) with the room temperature yield strength of PTFE according to the manufacturer (1300 psi).[9]

Our results also demonstrate the absence of a weak boundary layer that might be formed at the interface during the process of bond formation at 350°C.

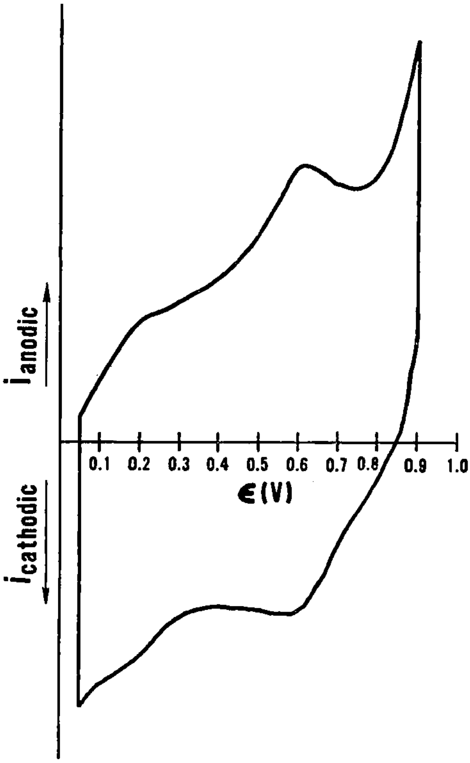


FIGURE 2 Measured voltammogram for the carbon substrate in the electrolyte.

Figure 2 reproduces a typical voltammogram for polished edge plane pyrolytic graphite in the same electrolyte that was employed in the adhesion testing, and at the same temperature. The nearly reversible current maxima appear at around 620 mV which presumably correspond to the reduction/oxidation of surface groups, such as a quinone–hydroquinone couple.[10–13] At potentials $\geq$ 0.8 volt the irreversible oxidation of carbon to CO_2 commences.[14, 15]

In attempting to correlate the observed separation rates with the thermodynamics of the process much depends on whether the apparent stability of the joint at 0.9 to 0.955 volt is of thermodynamic or kinetic origin. We cannot answer this question conclusively but can merely state that no separation was observed for up to 90 hours. However, it is tempting to assume that in this potential region thermodynamic stability is reached, i.e. that ε_{max} lies somewhere in this region. [The data of Morcos[5] refer to basal plane graphite at 25°C in salt solutions and are thus not applicable to the present system.] Even with this assumption it seems apparent that kinetic phenomena must be involved because the voltammogram (Figure 2) indicates that graphite in this region is not essentially polarizable. The surface reaction at the three-phase boundary line graphite/PTFE/acid must be blocked somehow. If it were otherwise we should expect to observe the steep rise in the separation rate to commence at $\approx$0.8 volt rather than at $>$ 0.955 volt.

The observed separation at $\varepsilon \leq 0.9$ volt indicates that, whatever the value of ΔG is at 0.9 to 0.955 volt, it is negative at $\varepsilon \leq 0.9$ volt. The voltammogram indicates that at potentials below about 0.85 V the carbon undergoes reactions which appear to be restricted to the surface. As a result we expect γ_{SL} to decrease at such lower values for ε, and separation to become thermodynamically more favored. The observed rates do not contradict this simple explanation based on the probable changes in the free energy of the process with potential.

CONCLUSIONS

In general, in the presence of a liquid which can wet the substrate and the adhesive the possibility of adhesive/substrate separation exists, even though the bond might be very stable in the absence of such a liquid environment. In addition, if the substrate is an electronic conductor, the interfacial tension between liquid and substrate will vary with the potential. In this way, the relative stability of the adhesive/substrate joint (in the presence of such a liquid environment) becomes a function of the potential, as well. If, in addition, the possibility for specific adsorption at the substrate/liquid interface exists, then additional bond destabilizing forces are similarly introduced. It is unnecessary that the liquid wets the adhesive for separation to occur.

In the case of graphite/PTFE, forming three-phase boundary lines with hot concentrated H_3PO_4, the variations in the rate of separation with potential can be rationalized on the basis of the probable changes with potential in the free energy of the process.

References

1. J. J. Bikerman, *The Science of Adhesive Joints* (Academic Press, N.Y., 1968), p. 139.
2. D. K. Owens, *J. Applied Polymer Science* **14,** 1725 (1970).
3. R. A. Gledhill and A. J. Kinloch, *J. Adhesion* **6,** 315 (1974).
4. K. A. Klinedinst, W. M. Vogel and P. Stonehart, *J. Mat. Sci.* **11,** 209 (1976).
5. I. Morcos, *J. Phys. Chem.* **76,** 2750 (1972).
6. K. J. Vetter, *Electrochemical Kinetics* (Academic Press, NY, 1967), p. 81.
7. G. Kortüm, *Lehrbuch der Elektrochemie* (Verlag Chemie, Weinheim, 1966), p. 371.
8. *Standard Method of Test for Tensile Properties of Adhesive Bonds,* ASTM No. D 897–72 (Approved July 10, 1973).
9. *Teflon Fluorocarbon Resins Mechanical Design Data,* Sect. 3, p. 4, E. I. du Pont de Nemours and Co. Publication E-05561.
10. B. D. Epstein, E. Dalle-Molle and J. S. Matson, *Carbon* **9,** 609 (1971).
11. J. V. Hallum and H. V. Drushel, *J. Phys. Chem.* **62,** 1502 (1958).
12. I. F. Jones and R. C. Kaye, *J. Electroanal. Chem.* **20,** 213 (1969).
13. G. Mamanov, *et al., J. Electroanal. Chem.* **9,** 305 (1965).
14. K. Kinoshita and J. Bett, *Carbon* **11,** 237 (1973).
15. K. Kinoshita and J. Bett, *Carbon* **12,** 525 (1974).