Electrode Surfaces Probed by Direct Adhesive Force Measurements

Chi-Woo Lee and Allen J. Bard*

Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712

We describe a new electrical method of characterizing electrode surfaces and probing the surface characteristics of conductors by measuring the adhesive forces acting between two electrodes in an ultrathin layer cell (UTLC) apparatus (1). In addition to the classical electrochemical techniques for probing surface properties (2,3), other methods, for example, measurement of the dynamic coefficient of friction between an electrode surface and a quartz microslide (polaromicrotribometry) (4) can be used to detect surface changes. The surface forces apparatus, which has been highly developed for measurements with atomically smooth mica surfaces (5) has recently been adapted for measurements at Pt electrodes. We describe here measurements of the current flow between a pair of platinum on mica (Pt/mica) and unactivated and activated highly oriented pyrolytic graphite (HOPG) electrodes in air and aqueous electrolyte solution as the electrodes are moved together (to contact) and then separated. Measurements of the adhesive forces suggest that platinum and activated HOPG surfaces are hydrophilic, while unactivated HOPG is hydrophobic.

Platinum films (< 1000 Å) were prepared by RF sputtering on thin (< 5 μm) mica sheets. Thin layers (< 0.1 mm) of graphite were peeled off from a HOPG plate (Union Carbide, Cleveland, OH). The thin film electrodes were attached to the quartz lens substrate with optical glue (Epoxy-30, Transene Company, Rowley, MA) and the prepared electrodes were washed with Millipore water and dried during the alignment step with the apparatus in a clean hood (Contamination Control Inc., Lansdale, PA). The UTLC apparatus was identical with that described previously (1). The force constant of the leaf spring holding the lower electrode was determined by measuring the displacement under a known mass load to be about 300 N/m. The electrodes were brought to close proximity by a combination of coarse, medium and fine distance controllers. During the distance adjustments a constant potential of 10 mV was applied between the two electrodes, and the contact was noted by a sudden jump in current. Once the two electrodes contacted, the interelectrode separation was controlled only by driving the PZT pusher (PZ-30; Burleigh Instruments, Fishers, NY). In this way the electrodes could be moved together to contact and separated repeatedly at a rate of ca. Å/s. This same slow scan mode was used to calibrate the PZT by multiple-beam interferometry These measurements showed that hysteresis of the PZT pusher was negligibly small. Overall system drift was checked by scanning the PZT alone to the contact point and back to separation several times and the measurements were performed only when the drift was less than 10 A/min. With the pair of Pt/mica electrodes, distance displacements were monitored independently by observing changes in the Newton rings.

Figure 1 shows representative current vs. distance traces observed between a pair of Pt/mica on a quartz substrate in a crossed-cylindrical geometry in air and immersed in an aqueous electrolyte solution. Here the "interelectrode distance" is actually the displacement of the PZT pusher. The surface forces apparatus has been used extensively to determine the forces between two mica surfaces immersed in different solutions as they are moved toward one another (5,8). A schematic representation of a force-distance curve between electrodes based on these concepts is shown as an inset in Figure 1. The two surfaces jump into contact on approach when the attractive force exceeds that of the spring. In our measurements this contact is recognized by a jump in the current. The force necessary to pull the two surfaces apart is the adhesive force, which is estimated from the amount of displacement of the PZT after contact and the spring force constant. The actual contact area between the two curved (hemicylindrical) electrode surfaces is not known, but should be about the same for different atomically smooth electrodes (such as Pt/mica and HOPG), so that relative measurements of the adhesive forces under different conditions are informative.

Curves for Pt/mica electrodes in air and in an aqueous 0.5 M Na_2SO_4 solution are shown in Figure 1. The measured adhesive forces are 66 (air) and 21 (aq. soln.) μN. The smaller adhesive force observed in water suggests that repulsive hydration forces are operating between two Pt/mica in aqueous solution and that the Pt surfaces are hydrated or hydrophilic (9).

Similar experiments were carried out with HOPG electrodes with fresh surfaces, formed by peeling off a layer, to investigate the effect of electrochemical activation on the behavior (Figure 2). Cyclic voltammograms with an aqueous solution of 1 mM potassium ferricyanide and 0.5 M sodium sulfate at HOPG electrodes differ before and after electrochemical activation (Fig. 2 inset) (10). The graphite electrode was activated in the test

solution by applying +1.5 V and −1.5 V (20 s each). The method was the same as that used for Pt/mica to measure the adhesive forces between a pair of HOPG electrodes before and after activation. In general, the contact current fluctuated during the measurements because of the change in contact area. The electrode resistance was ca. 10 ohm/□ for both activated and unactivated HOPG. The results for HOPG are as follows: unactivated-air, 53 μN; unactivated-solution, 51 μN; activated-solution, 2 μN. The measured adhesive forces for unactivated HOPG are about the same in both air and aqueous solution, which probably reflects little hydration of the fresh graphite surface. The hydrophobic character of the surface can account for the less reversible couple at the unactivated HOPG (10b). With the activated HOPG, the adhesive force measured in aqueous solution is at least one order of magnitude smaller than that of unactivated HOPG, indicating that strong repulsive hydration forces are operating at activated HOPG surfaces, suggesting that HOPG surfaces become hydrophilic after electrochemical activation. Improved electrochemical behavior of some redox couples at graphite electrodes with electrochemical treatment has been attributed to changes in the state of the electrode surface to a more hydrophilic one (10 b,c). Our results here provide direct experimental evidence for such surface changes.

In summary, we have described a new method of measuring adhesive forces for two conducting surfaces and showed that Pt and activated graphite electrode surfaces are hydrophilic, while unactivated graphite surfaces are hydrophobic. This method may be useful for investigating surface characteristics of other bare and modified electrodes commonly used in electrochemical studies.

ACKNOWLEDGMENT

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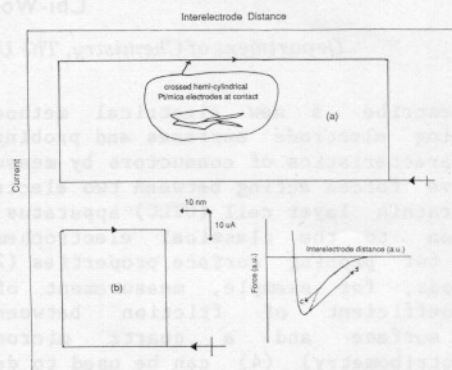
Fig. 1. Representative current vs. distance traces for a pair of Pt/mica electrodes in (a) air and (b) 0.5M Na_2SO_4. Applied potential, 10 mV; scan rate, 2 Å/s. Inset shows schematic of the force acting between two electrodes as a function of interelectrode separation. Dotted portions represent the instability region and the arrows indicate the jumps to contact (c) or separation (s) when the force gradient equals the spring force constant.
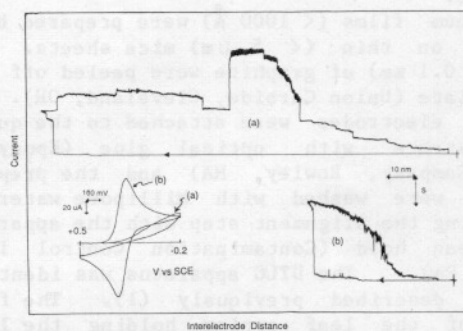

Fig. 2. Representative current vs.distance traces for a pair of HOPG electrodes in 0.5M Na_2SO_4 and 1 mM $K_3Fe(CN)$ under the same conditions as Fig. 1. (a) Unactivated S=1 μA; (b) activated S=5 μA. Inset shows cyclic voltammogram at HOPG for the test solution before (a) and after (b) activation. Electrode area, 0.4 cm^2; scan rate, 0.1 V/s.