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Direct Observation of Double Layer Interactions between the Potential-controlled Gold Electrode Surfaces Using the Electrochemical Surface Forces Apparatus

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(Received March 9, 2011; CL-110203; E-mail: kurihara@tagen.tohoku.ac.jp)

We have designed a new apparatus, an electrochemical SFA, for measuring the forces between symmetric gold electrode surfaces under electrochemical potential control. The surface separation was determined by two-beam (twin-path) interferometry. The potential was applied to the gold surfaces (working electrode) in 1 mM aqueous $KClO_4$ using Ag/AgCl as the reference and Pt as the counter electrode. We observed the van der Waals attraction and the double layer repulsion which decreased with the increasing potential from -0.1 to 0.2 V (vs. Ag/AgCl).

The electric double layer at the electrode–electrolyte interface plays an important role in electrochemical processes.[1] Surface forces measurements have been regarded as a promising tool for understanding the double layer phenomena.[2–4] Toward this aim, attempts have been made for preparing metal electrode surfaces, i.e., platinum[5] and gold[6] on mica, for the forces measurements. Some groups[2,3,7] had developed an electrochemical surface forces apparatus (EC-SFA) to study the potential dependence of the electric double layer. Their systems employed nonidentical surfaces such as mica/mercury electrodes[2] and mica/gold electrodes.[3,7] Therefore, quantitative analysis of any interactions is more difficult compared to the symmetric cases. This limitation comes from the multiple beam interferometry of white light employing fringes of equal chromatic order (FECO) used for the distance determination. For FECO, one of the substrates needs to be transparent.

Recently, we designed a new surface forces apparatus using two-beam (twin-path) interferometry, i.e., twin-path SFA, for measuring the interactions between nontransparent substrates.[8] In this study, we developed a new EC-SFA which enabled us to perform the forces measurements on symmetric gold electrode surfaces as a function of the surface separation under potential control.

A schematic illustration of the measurement system is shown in Figure 1a. The gold electrode surface was prepared by the template stripping method[9] on cylindrical silica disks (curvature radius, $R = 20$ mm). The gold (99.99% pure, Tanaka Kikinzoku Kougyo) was vapor-deposited on a mica template, which was glued on the disk with the gold side down and subsequently removed just prior to use. These prepared gold surfaces were molecularly smooth. Their RMS roughness evaluated by atomic force microscopy (AFM, Seiko II, SPI3800-SPA400) was 0.19 nm for a 1 μm × 1 μm area, and 0.22 nm for a 10 μm × 10 μm area. A wire was connected to the gold surfaces using conductive epoxy (ITW Chemicals, CW2400), then the connected area was covered with epoxy resin (Shell, Epikote1004). This gold electrode was used as the
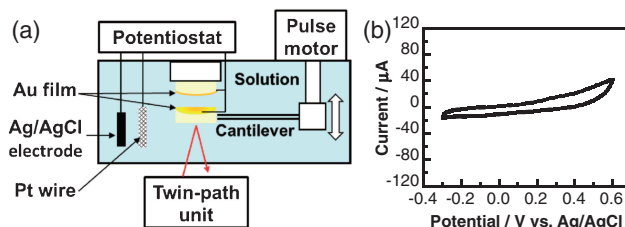
Figure 1. Schematic drawing of the EC-SFA (a). A cyclic voltammogram obtained for gold working electrodes in 1 mM aqueous $KClO_4$ in the EC-SFA, at the scan rate of 0.1 V s^{-1} (b).

working electrode (WE) along with a potentiostat (BAS, ALS/CH Instruments electrochemical analyzer model 600C) for controlling the WE potential. The counter electrode (CE) was a Pt wire (99.9999%, Tanaka Kikinzoku Kougyo, 0.2ϕ, 200 cm), and the reference electrode (RE) was a Ag/AgCl (saturated KCl) electrode (BAS). A salt bridge made of agar gel was used for connecting the twin-path SFA and the RE. This arrangement allowed us to run electrochemical measurements in the three-electrode cell arrangement inside the twin-path SFA.

The $KClO_4$ solution was prepared from $KClO_4$ of the highest available purity (99.99%, Aldrich, Miliwaukee, WI) which was used without further purification and dissolved in pure water (NANOpureII, Barnstead, 18 MΩ cm^{-1} resistance). Before all the measurements, argon (99.9999%) was bubbled through the solution for more than 1 h for deaeration, and the experiment was done under an argon atmosphere.

The interaction force (F) between the gold electrode surfaces was measured as a function of the surface separation (D) in a 1 mM $KClO_4$ solution (unbuffered, pH 5.6) following a previously reported procedure.[8] We continuously changed the surface separation between gold surfaces at a constant approaching rate (25 nm s^{-1}) when we obtained force curves. The obtained force was normalized by the radius R of the surface curvature using the Derjaguin approximation,[10]

$$F/R = 2\pi G_f \tag{1}$$

where G_f is the interaction free energy per unit area between two flat surfaces. We used 20 ± 2 mm for R which is a typical value when we measured R of surfaces using the FECO SFA in our laboratory.

Figure 1b is a cyclic voltammogram obtained in the EC-SFA. No specific redox peak appeared during the potential sweep between -0.3 to $+0.6$ V vs. Ag/AgCl. This result indicates that there was only a slight faradic current, and this potential region is called the potential window, where no redox reaction occurs. The current was also monitored throughout the
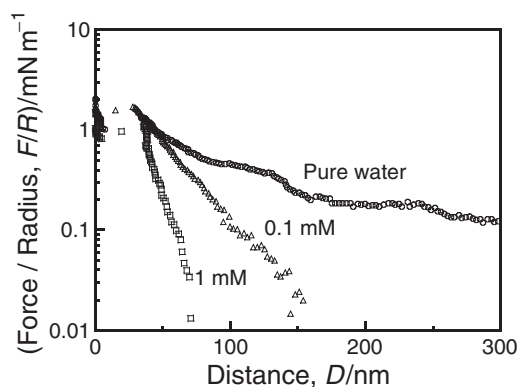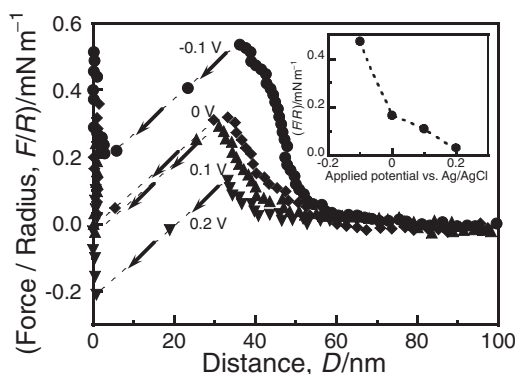
Figure 2. Surface forces between gold electrode surfaces in pure water and 0.1 and 1 mM aqueous $KClO_4$.

Figure 3. Surface forces between gold electrode surfaces at various potential, at −0.1 (●), 0 (◆), 0.1 (▲), and 0.2 (▼) V vs. Ag/AgCl. The allows indicate the jump-in movements of the surfaces. The insert plots the force at $D = 40$ nm vs. the applied potential.

forces measurements to ensure that there was little or no faradic current.

Shown in Figure 2 are the measured force curves between the gold surfaces in pure water and in aqueous $KClO_4$ (0.1 and 1 mM). All distances are relative to the contact position (after jump-in) of the surfaces. Force profiles were similar under all conditions and consisted of a longer-range repulsion and a shorter-range attraction. This behavior was basically similar to that observed for gold–gold interactions in water.[6] The longer-range repulsion was well described by an exponential function with a decay length of 137 nm for pure water, 29.7 ± 1.5 nm for 0.1 mM $KClO_4$, and 9.2 ± 0.2 nm for 1 mM $KClO_4$. These decay lengths well agreed with the reported value for water (129 nm)[8] and theoretical values of the double layer force for the corresponding salt concentrations, 30.4 nm for 0.1 mM and 9.6 nm for 1 mM.[10] This indicated that the electric double layer force between the gold surfaces has been properly measured in this setup. The shorter-range attraction appearing at ca. 40 nm was the van der Waals attraction. The distance where jump-in occurred was longer than the distance observed between the gold surfaces deposited on silica.[6] The longer jump-in distances observed by the twin-path method was attributed to the deformation of the epoxy layer used as glue,[11] which was not the case in ref 6 in which the gold layers were directly deposited on solid silica.

Figure 3 shows the force curves between the gold electrode surfaces at different potentials applied within the potential window. The forces consisted of a long-range repulsion, which followed the exponential function, and the shorter-range attraction. The decay lengths of the repulsion under all applied potentials, 9.6 ± 0.8 nm, were in good agreement with the theoretical Debye length (9.6 nm) of the double layer repulsion.[10] This repulsion decreased with the increasing applied potentials from −0.1 to 0.2 V vs. Ag/AgCl. A plot of the force at a distance of 40 nm vs. the applied potential showed a greater decrease from $F/R = 0.48$ mN m^{-1} at −0.1 V to 0.16 mN m^{-1} at 0 V and then a gradual decrease to 0.11 mN m^{-1} at 0.1 V (vs. Ag/AgCl) (Figure 3). The force nearly disappeared at 0.2 V vs. Ag/AgCl, which was in good accord with the potential of zero charge (PZC), 0.2–0.25 V vs. Ag/AgCl, reported for a gold electrode in aqueous $KClO_4$.[7] We did not perform the surface forces measurement at applied voltages higher than 0.3 V because the current did not become zero in the high voltages.

The distance at which the shorter-ranged attraction appeared slightly decreased from ca. 40 nm at −0.1 V to ca. 30 nm at 2.0 V vs. Ag/AgCl.

In conclusion, the interactions between the gold electrode surfaces at various applied potentials were directly measured using the electrochemical surface forces apparatus, EC-SFA. The interactions changed depending on the applied electrode potential. The results demonstrated that this technique could be used for studying a wide variety of potential-controlled surface phenomena. In this study, the gold electrode was used as the working electrode of a three-electrode cell arrangement inside the twin-path SFA. The method is not restricted to gold but also applicable to inert metals such as platinum. This technique should be effective for obtaining fundamental knowledge about electrochemical devices such as a battery.

References and Notes
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11 The longer jump-in by the twin-path SFA was observed for mica–mica at ca. 10 nm, compared to the distance of 2–3 nm measured by FECO SFA.[8] This difference was explained by the influence of deformation of the epoxy layer on the measured distance by the former.