We describe an electrochemical cell containing a single faradaic electrode (a Pt ultramicroelectrode) and a blocked (polarized) electrode (Si with an insulating SiO₂ film) that served as a capacitive counter electrode. When a bias was applied between the two electrodes, a current was observed from a faradic process at Pt and a capacitive current at the blocking electrode. A steady charging current was obtained when the solution was moved along the insulator to continuously contact fresh surface (emerging a layer of charged ions and electronic countercharge into the gas phase). Electrogenerated chemiluminescence was clearly observed from a system containing Ru(bpy)₃²⁺ in this kind of cell under pulsed excitation, demonstrating that faradaic reactions can be carried out in an electrochemical cell without generation of any products at a counter electrode. The use of such a system for coulometric addition of desired species in nanosystems and in synthesis is suggested.

Electrodes in electrochemical cells are typically classified as either faradaic or capacitive (blocking). With faradaic electrodes, charge can cross the electrode/solution interface and produce chemical changes in the vicinity of the electrode. With blocking electrodes (sometimes called ideally polarized electrodes), charge does not cross the interface and any current that passes results in charging the metal electrode, with compensating ionic charge from solution, to form a so-called double layer, and with no redox chemical changes in the solution. The usual electrochemical cells employ two faradaic electrodes, an anode (where oxidations occur) and a cathode (where reductions occur) to carry out desired chemical reactions. Since two separate half-reactions occur at these electrodes, two products are formed and the solution as a whole maintains charge (ionic) neutrality at all times (since equal anionic and cationic charge is generated). For most electrochemical systems, e.g., for synthesis, only the reaction or product at one of these electrodes, the indicator or working electrode, is of interest and the other electrode, the counter electrode, is often placed in a different compartment separated by an ionically conducting separator to prevent mixing of the products. The amount of product generated at the working electrode is precisely controlled by the charge (number of electrons passed) as governed by Faraday’s law, so electrochemical generation has been a useful and absolute way of introducing exactly known amounts of chemical species to a solution via a faradaic electrode reaction (coulometric methods). Such coulometric methods have been suggested as ideal ways of adding a small quantity of a species in a nanosystem via an ultramicroelectrode (UME), where the current and time can be controlled very precisely (e.g., 1 pA applied for 1 s produces ~10⁻¹⁷ equiv or ~6 million molecules for a one-electron reaction). However, because of the small size of these systems, the usual cell separators cannot be employed, so undesired products generated at the counter electrode would also be introduced. This can be avoided, however, if the counter electrode is a capacitive one, where the charge stored compensates the faradaic charge from the injecting electrode. In this paper, we examine the behavior of such cells. Cells of this type have been used, for example, to inject charge into thin layers and observe spectroscopic changes, where one electrode contacts the layer and the other is a small tip separated from it by a ~10-nm insulating layer of impurities or air. We also examine the possibility of using this type of configuration in larger cells where the capacitive counter electrode is continuously renewed to provide a greater amount of capacitive charge (and hence faradaic coulombs) and address the question of charging with electrode emersion (removal of the electrode from the solution phase). Finally, we should note that configurations involving a capacitive electrode and a faradaic one have been classically used to examine double layer effects. However, in these studies, attention has been paid only to the polarized electrode where the faradaic effects at the counter electrode, typically a reference electrode like Ag/AgCl, are not of interest and are neglected.

**EXPERIMENTAL SECTION**

**Single Faradaic Electrode Cell.** A 25-μm-diameter Pt wire sealed in a glass UME tip served as the faradaic electrode and contacted a few millimeter diameter drop of deionized (MilliQ) water placed on the SiO₂ film (500 nm thick) on a single-crystal

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*To whom correspondence should be addressed. E-mail: ajbard@mail.utexas.edu.

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Si wafer with a thin insulating film of SiO₂ functioning as the capacitive electrode that blocks charge transfer into the solution. Samples of SiO₂/Si were prepared at Sematech (Austin, TX) by chemical vapor deposition without further treatment. In experiments where a water drop was moved along the SiO₂ surface under a bias as shown schematically in Figure 1, a 2-mm-diameter glass tube was attached to the 25-μm Pt tip with Parafilm to avoid water leakage. The tube was slightly overfilled so that a water drop was formed at its top to contact the SiO₂ surface and the drop could be moved horizontally to continuously make contact with a fresh part of the oxide surface.

ECL Experiments. A 250-μm Pt wire was bent at a right angle, coated with epoxy cement, and then polished to expose an area of ~0.02 mm² facing a photomultiplier tube (R4220p, Hamamatsu, Bridgewater, NJ). A Si/SiO₂ (film ~50 nm thick) with an area of ~40 cm² was the counter electrode in an aqueous solution containing 0.5 mM tris(2,2′-bipyridine)ruthenium(II) (Ru(bpy)₃²⁺) in 0.10 M tri-n-propylamine (TprA) with 0.10 M Tris/0.10 M LiClO₄ buffer (pH 8). An Autolab potentiostat (model PGSTAT100, EcoChemie, Utrecht, The Netherlands) was used to control the applied potential with Pt as the working electrode and the Si back contact as counter/reference electrode. The ECL emission and the current were recorded simultaneously during the measurement. Potential pulses from 1.4 (30 s) to −0.5 V (20 s) were applied to the system Pt/solution/SiO₂/Si. In a separate measurement to obtain an ECL image, a 25-μm Pt UME tip was used with the same solution over a 9-cm² Si/SiO₂ surface mounted on the stage of an inverted microscope (Nikon, model TE300, Melville, NY).

RESULTS AND DISCUSSION

Transients. Figure 2 shows the current as a function of time with a bias of 1 V applied between Pt and Si in the two-electrode system: Pt/water/SiO₂/Si. The current consisted largely of a faradaic current at Pt, e.g., hydrogen generation, and only a capacitive current at the Si/SiO₂. [More precisely, the current at the Pt electrode did include some charging current to charge the Pt interface double layer and move the potential to a value where a faradaic reaction can occur while the Si/SiO₂ probably can pass a small amount of faradaic (leakage) current. However, both of these contributions are negligible in the system described.] The current decreased with time with a response governed by both the reaction at the tip and the charging. The apparent time constant is largely governed by the resistance between the electrodes and the capacitance of the Si/SiO₂ electrode. The total faradaic charge injected at the Pt is given by

$$Q_f = \int i \, dt - Q_{c,Pt} = C_{dl,Pt}A_{Pt}\Delta E = C_{dl,Si}A_{Si}\Delta E - C_{dl,Pt}A_{Pt}\Delta E \quad (1)$$

where $Q_f$ is the total faradaic charge injected, $i$, the total current, $Q_{c,Pt}$ the capacitive charge at the Pt, $C_{dl,Pt}$ the integral capacitance of the Pt, and $C_{dl,Si}$ the integral capacitance of the Si; $A_{Pt}$ and $A_{Si}$ are the areas of Pt and Si, respectively, and $\Delta E$ is the applied bias.

Once the current became negligibly small, the external circuit was disconnected for ~8 s. When it was reconnected at the same bias, the charging current was significantly smaller as shown in Figure 2, (inset) in which the initial sharp spike was an electronic artifact resulting from capacitive coupling. When the circuit was opened for a longer time, such as 15–20 s, the charging current

![Figure 1. Schematic diagram showing the system Pt/water/SiO₂/Si with the possibility of lateral tip movement to generate fresh contact surface. The tip was attached to a translation stage that could be moved with an inchworm motor, with a micrometer, or by hand.](image)

![Figure 2. Charging current as a function of time in a system of Pt/water/SiO₂/Si under a bias of 1 V applied between Pt and Si. After the charging current reached baseline, the circuit was disconnected for ~8 s and reconnected again still under the same bias; only a very small charging current was seen as shown in the inset.](image)
after reconnection did not appear very different than that in the inset in Figure 2. This demonstrates that the electronic and ionic charges brought to the SiO₂ interface by the external potential changed only slightly at open circuit.

**Moving Tip at Constant Bias.** A typical steady charging current was seen when the tip was stationary and the potential was scanned at a rate of 100 mV/s as shown in the inset of Figure 3. The calculated capacitance \( C = \epsilon / d \), where \( \epsilon \) is the relative permittivity of the dielectric material, 3.9 for SiO₂, \( \epsilon_0 \) the permittivity of space, \( A \) the area, and \( d \) is 500 nm, the thickness of SiO₂ with a diameter of 3.2 mm, which closely matched the actual area contacted by the drop.

Next, the water drop and associated Pt UME were moved across the SiO₂ surface under a constant bias. Before movement, a bias of −1 V was applied to the tip and the surface became fully charged. Then the tip was moved laterally by pushing the translation stage manually at a rate of roughly 1 cm/s over a distance of about 0.5−4 cm without disconnecting the bias and the current increased as shown in Figure 3. The current reached a steady state at the nanoampere level, which was maintained by continuous exposure to fresh surface. The current did not drop until the movement ended and the charging at this location approached saturation (Figure 3). The contact area of the SiO₂ and the water drop remained virtually constant during the lateral tip movement. The steady-state current depended on how fast the fresh surface was contacted. The faster the drop was moved, the higher was the current produced. For example, at a tip movement rate of 25 μm/s controlled with an inchworm motor, the steady-state current was only ~3 pA (the leakage current was not detectable at subpicoampere-level sensitivity with such a thick oxide layer). The 25-μm movement of the water drop in 1 s generated a new contact area corresponding to a capacitance of ~5 pF, assuming a parallel capacitor with SiO₂ as the dielectric material. In other words, under a bias of 1 V neglecting potential drops at the Pt electrode and the solution resistance, a maximum current of ~5 pA should be obtained compared to the actual current of 3 pA observed. At such a low rate of tip displacement, it took several minutes for the water drop to completely move away from its previous spot. We interpret this to mean the stored charge on both interfaces of SiO₂ (ions in solution and electronic charge in the Si) either did not move at all or moved far too slowly to follow the water drop. Note that the observed behavior did not depend on the polarity of the bias applied to the system. When a supporting electrolyte, such as 0.1 M Na₂SO₄, was introduced, the system charged more quickly because of the decrease of solution resistance. However, the basic features, as discussed above, were the same.

The results shown in Figure 3 could be reproduced many times at different locations and also as the tip traveled in a stepwise, repeated stop-and-go mode as shown in Figure 4. Each time, the charging current increased as the water drop started to move and a steady-state charging current was seen and decreased when the water drop stopped. Note that the SiO₂ surface in this sample was hydrophobic (contact angle with pure water ~87°) and no visible trace of water was left after the drop moved away from a spot. In some cases, the water drop was moved in a predesigned pattern so that the locations of each stop could be revisited later. When the water drop was moved back to those spots, previously fully charged after a period of 10−20 min, no appreciable amount of charge could be observed under the same charging conditions (the charging current was comparable to the one shown in the inset of Figure 1), confirming that the charges remained at their original spot and did not move anywhere else. Moreover, stored charges were not discharged at a neighboring spot that was ~7.5 mm away, indicating that there were no communication among stored charges at different locations. Independent of the charging history, all of the spots could be restored to their initial state by discharging the Si under short circuit conditions. These findings are in agreement with earlier studies of the emersion of a metal

**Figure 3.** Charging current recorded during the relative movement under a bias of −1 V applied between Pt and Si in a system of Pt/water/SiO₂/Si. Lateral scan rate, ~1 cm/s. Inset: charging current as a function of bias with stationary tip at a scan rate of 100 mV/s.
electrode from solution into high vacuum that indicated that the solution-formed double layer still existed in the high-vacuum chamber after charging of the metal electrode in solution and then transfer to vacuum under a bias.5

**Electrogenerated Chemiluminescence (ECL).** The realization of a sustainable steady-state charging current offers some interesting opportunities for carrying out a faradaic process at an electrode with the countercharge at a blocked (capacitive) one. Such a faradaic process was demonstrated by an ECL experiment employing the well-known Ru(bpy)32+/TPrA system, which produces emission upon oxidation.6,7 As described in the Experimental Section, ECL was generated by potential steps applied between a 0.02-mm2 Pt electrode and Si/SiO2 (40 cm2). As shown in Figure 5, ECL was detected immediately following the application of a potential pulse of 1.4 V to the Pt electrode, triggering a negative charging process at the SiO2 interface. As the charging current decreased, the ECL emission intensity simultaneously decreased. The decreasing current in this case represented charging of the counter electrode rather than the usual reactant depletion at the Pt. As expected, no ECL was seen under a negative bias of −0.5 V, which served, however, to discharge the interface at the Si/SiO2 electrode (with a corresponding faradaic reaction at the Pt electrode). This cycle could be repeated many times, and the ECL intensity decreased just slightly each time due to the depletion of active species near the Pt electrode surface. Note that ECL was not detected at the blocked electrode whose leakage current was therefore negligible. In a different measurement with a 25-μm Pt tip over a 9-cm2 Si/SiO2 with the same Ru(bpy)32+/TPrA solution under a constant bias of 1.4 V, an ECL image of the Pt tip was clearly seen with an inverting microscope as shown in the inset in Figure 5. The production of ECL provides clear evidence for a faradaic process in the single electrode electrochemical system and offers an interesting way to generate ECL in a microcell without interference from counter electrode reactions.

**Additional Considerations.** While the work described here was mainly focused on quantitative faradaic electrochemistry in microsystems, the same approach might be used for macroscale electrolysis where an undivided cell is desired. In this application, the blocking counter electrode must be continuously passed into the solution to expose fresh area, analogous to the moving tip on the Si/SiO2 shown above. For example, one could pass a roll of conductive wire or film coated with a thin insulating layer through a solution containing a salt under a fixed bias as shown in Figure 6; anions would be removed from the solution when a negative bias is applied to the metal electrode and excess cations would be left in the solution to provide electroneutrality for the cathodic faradaic reaction. Similarly, cations would be removed at the blocking counter electrode when the working electrode is an anode. Another possibility (although much less practical) would be a streaming mercury electrode, whose surface is continuously renewed, operated in the potential region where it behaves as an ideally polarized electrode.8 The arrangement where the counter electrode is blocking would have the advantage of not requiring a separator and, in a preparative cell, would not involve products of a counter electrode reaction. This arrangement might also be interesting because the blocking counter electrode would remove ions of a single sign (i.e., without a counterion) where the ionic charge is compensated by electronic charge.

One could also carry out similar experiments in a three-electrode configuration, where the reference and counter electrode functions are separated. In such a configuration, the observed

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Figure 4. Charging current, as in Figure 3 during repeated steps, i.e., a stop-and-go lateral movement, under a constant bias of −1 V between Pt and Si. The current increased as the water drop movement started and decreased when the movement stopped, with a brief steady-state charging current during the movement.

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current would be controlled by the faradaic process (as in the usual electrochemical cell) with continued charging of the blocking electrode until the voltage compliance limit of the potentiostat was attained or dielectric breakdown occurred at the blocking counter electrode, which then started to pass charge to the solution.

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