



## The Application of Scanning Tunneling Microscopy to *In Situ* Studies of Nickel Electrodes under Potential Control

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Scanning tunneling microscopy (STM) [1] has been finding growing application to studies of surface topography at Å-level resolution, mainly in ultra high vacuum (UHV) environments. However, the use of STM for surfaces immersed in aqueous media is also possible [2,3] with the possibility of obtaining surface structure information unattainable by any other *in situ* technique. While STM has been used to look at electrode surfaces [4,5], in these studies the electrode was either removed from the solution and examined in UHV or air or the electrode was not under potential control during the STM scan. A difficulty with studying the surfaces of operating electrodes by STM is the presence of faradaic current across the substrate/solution interface that is often large compared to the tunneling current between the substrate and the scanning tip that perturbs the STM measurement. We demonstrate here that STM can be used to study the surface of an operating (externally polarized) electrode by presenting results on a nickel electrode polarized in the active dissolution region and at rest. These results show that STM can be employed for *in situ* investigations of potential-driven phase transitions, e.g., in the area of passivation and corrosion of metals.

The anodic dissolution of nickel in sulfuric acid solution has been studied extensively and the general features of the *i*-*V* curve (Figure 2a) are well established [6]. At low potentials active dissolution of nickel takes place, followed at higher potentials by passivation, presumably due to formation of a semiconductive oxide layer that blocks ionic migration from the metal to the liquid interface [7]. The physical and chemical nature of the passivating oxide are still obscure. Reported film thicknesses, based mainly on ellipsometric studies, range from 60 Å [8] to 9-12 Å [9]. Similarly, electronic resistivity of the oxide is not clear [7-11]. According to a theory initiated by Vetter [12] and commonly employed for nickel passivation in acidic media, the lower resistance of the oxide prevents the buildup of a high electric field across the film, thus decreasing the driving force for the transport of Ni ions through the film and passivating the electrode.

A block diagram of STM configuration is depicted in Figure 1. In addition to the conventional STM control, we added a battery power supply to maintain a constant voltage between the nickel sample and a counter platinum flag electrode, situated parallel to it. The tip was

constructed of 25 μm platinum wire (Alfa Products) etched electrochemically [3,13] to a sharp needle. The tip was sealed in glass up to its very end, exposing less than 50 μm<sup>2</sup> of bare metal. The sample was nickel foil 0.2 x 0.3 mm 99% purity (Alfa Products). Sulfuric acid (0.5 M) prepared from reagent grade H<sub>2</sub>SO<sub>4</sub> and millipore water were used throughout. The potential of the working electrode was measured vs. a saturated calomel electrode (SCE), and the steady-state current was recorded prior to the STM scan. During the STM scan the Ni substrate was connected through the battery power supply to the counter electrode, but the ammeter was shorted and the circuit to the SCE opened to decrease electrical pickup.

Figure 2 depicts typical surface images of rough nickel obtained at its rest potential (b) and at -0.1 V vs. SCE (c). The tip to sample voltage was 10 mV (tip positive) and the tunneling current set point was 6 nA. The steady-state faradaic current from the tip when the counter electrode/substrate circuit was connected was less than 0.2 nA, as determined with the tip moved to a distance several hundred Å from the Ni substrate. It was only slightly affected by the applied potential between sample and counter electrode and not at all by the tip to sample distance.

When applying STM to an electrode at its rest potential, the tip and sample potentials adjust to such positions on their *i*-*V* curves so that the current emanating from one electrode equals the current to the other electrode. A positive polarization is then recommended to avoid etching of the sample. Incorporating a counter electrode fixes the potential ( $\phi$ ) of the sample electrode and thereby the potential of the tip. Both positive and negative polarization of the tip relative to the substrate is then permitted, as long as  $\phi_{tip}$  remains in the potential window between hydrogen and oxygen evolution.

When the nickel surface was scanned with the nickel electrode polarized in the passivating region (0.7 V vs. SCE), under the same tunneling conditions as those in the active region, erratic motion of the tip was observed (Figure 2d). Moreover, the small fluctuations in tunneling current that arise from vibrations of the tip and were usually noted when the tip was held over a given position of the surface were much smaller in the passivating region. This suggests that the tip was resting on the surface. When the potential of the electrode was moved to one in the active region, the previous scanning tunneling behavior was regained.

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The difference in the surface properties of the nickel electrode in the different regions was probed by disconnecting the feedback circuitry that maintains the tunneling current ( $i_t$ ) constant and ramping the voltage applied to the  $z$ -piezoelectric element to move the tip towards the surface and then back from it, and recording  $i_t$  as a function of displacement. The results are shown in Figure 3. The current response in the rest (a) and active (b) regions are clearly symmetric, with an exponential rise and fall representing the expected tunneling response. The deviation from exponential behavior at high current is probably due to measuring circuit input impedance and mechanical vibrations. The features of the current response in the passivating region (c) is clearly very different; the response is asymmetric, drags over a large distance, and does not show a form typical of tunneling. The same asymmetric long distance response was observed when  $\Delta V_{tip}$  was held anywhere in the range  $\pm 100$  mV.

The results suggest that STM can be applied to the study of externally polarized electrodes. Application of STM to nickel passivation indicates qualitatively that the passive film constitutes an electronically, as well as ionically, resistive layer. The characteristics of the tip current that were observed in the passive region probably can be attributed to mechanical fractures in the oxide caused by the tip or to diffusion of holes through a thick oxide as a rate-determining step. A more quantitative measure of the energy levels of the oxide can probably be achieved by scanning the voltage of the approaching tip, as employed by Binnig [14], to study nickel oxide in air.

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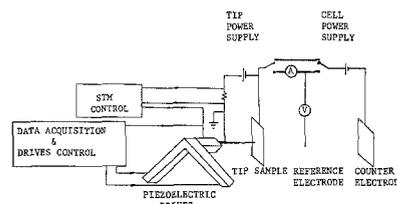


Fig. 1. Block diagram of STM combined with an electrochemical cell.

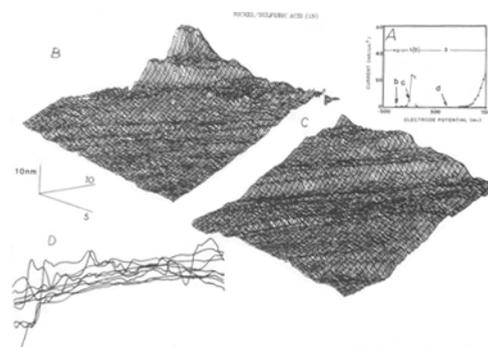


Fig. 2. STM image of nickel foil at 0.5M sulfuric acid (10 mV, 6.0 nA). (A) Typical steady-state  $i$ - $V$  curve of nickel in 0.5M sulfuric acid. Arrows mark the potential of scans shown in B-D. (B) At the rest potential. (C) Dissolution region (-0.1V vs. SCE). (D) Passive region (0.7V vs. SCE).

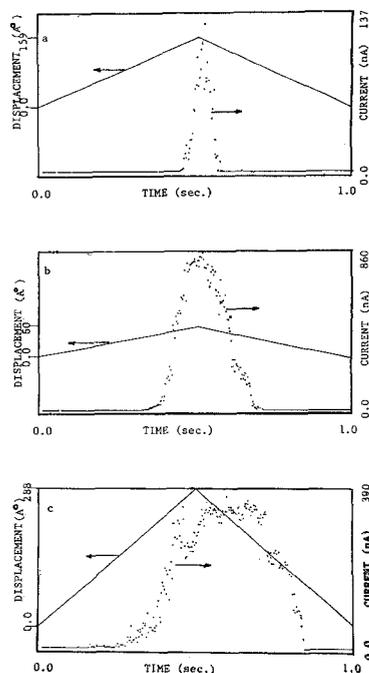


Fig. 3. Current response to change of distance between sample and tip (solid line represents tip movement). (a) Rest potential; (b) active dissolution region (-0.1V vs. SCE); (c) passive region (0.7V vs. SCE).