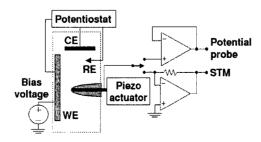
Probing Electrified Interface with a Potential Nano-probe

When an electrode is charged in an electrolyte solution, an electrical double (ED) layer is formed at the interface between the electrode and the solution. An ED layer is believed to be very thin (< 10⁻⁷ m), and the electric field inside this region can be extremely strong (> 10⁷ V/m). The potential profile of a diffuse ED layer was theoretically modeled by Gouy and Chapman (GC model) as early as 1910, which has provided a basic frame for understanding the electrochemical interface ever since. Experimental study of an ED layer, however, has been very scarce. ED capacitance measurement has provided convoluted information of the ED thickness, the surface charge, and the dielectric constant of the medium. Real-space measurement of the potential profile has never been done.

In this work, I introduce a novel potential probe designed to monitor the electrical potential inside an ED layer. An electrochemical scanning tunneling microscope (STM) was modified to the potential probe with subnanometer spatial resolution, in which the distance between a tip and an electrode surface is controlled by the STM feedback mechanism. Electrochemical potential is monitored at the apex of a tip using a voltage follower circuit. Various interfaces were tested for the potential measurement, including the ones involving Au(111) and alkanethiol-covered Au electrodes and KNO₃, NaBF₄, and NaClO₄ electrolyte solutions.



Schematic presentation of the apparatus. In an electrochemical cell depicted by the broken-lined box, a potential probe approaches toward the WE to read the local potential of the electrochemical interface. The probe is coated with an insulator material except its apex. Switching to a voltage follower reads the potential without passing the tunneling current.

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