

## Steady-State Behavior at Finite Conical Microelectrodes

Single microelectrodes of a variety of geometries including inlaid disks, inlaid rings, and micro-hemispheres have revolutionized electroanalytical chemistry since the early 1980's. The behavior of these electrodes is now thoroughly documented theoretically and well understood under transient and steady-state conditions. With the advent of scanning probe techniques, particularly scanning tunneling microscopy (STM), atomic force microscopy (AFM), and more recently, scanning electrochemical microscopy (SECM), conically-shaped microelectrodes have moved to the forefront. However, their quantitative use has been limited due to the absence of a theory to explain their behavior under even the simplest electrochemical conditions.

In this work, the behavior of finite conical microelectrodes is established by solving the relevant diffusion and kinetic equations using a commercially available, finite element solver software package which creates a triangular adaptive grid that allows difficult problems involving singularities to be solved with high accuracy and computational efficiency. The behavior of conical electrodes is characterized by three geometric parameters: a basal radius,  $a$ , a height,  $h$ , and an insulation thickness,  $RG$ . The effects of these parameters on the ability of a conical electrode to reach a steady-state is discussed. An approximate-analytical expression for the diffusion-limited steady-state current is derived for a range of  $h$  and  $RG$  values. The effect of heterogeneous kinetics on the shape of steady-state waves at conical electrodes is demonstrated and quantified. Finally, a comparison of the behavior of a steady-state conical electrode with the similar microdisk and microhemispherical geometries is made in terms of interpreting experimental data.