Project 1 Chem E 530

Electrochemical Tomography

Introduction

It is common in electrochemical microfabrication[1,2] and combinatorial electrochemistry[3] to have multiple electrochemically-active sites on a single conductive substrate. A schematic of this situation is shown on the next page. Here the substrate is a thin conductive film grown on an insulator. The schematic shows 17 small electrochemically-active sites. Nowhere else on the substrate is electrochemically-active.

For the case of electrochemical microfabrication (e.g., the technique used to make HD write heads), the active sites are microcomponents being electrodeposited through a photolithographically-defined polymeric mask. Ideally, the total deposition current is evenly divided among each microcomponent on the wafer, so they all grow at the same rate. Unfortunately, some fraction of the sites are often defective, and thus do not growth at the average rate. We would like to be able to detect faulty sites in a simple manner using only the electrochemical response we measure at the edge of the wafer where we have electrical contact. Electrochemical Tomography will permit us to do that.

In combinatorial electrochemistry, the electrochemically-active sites are normally dots of catalysts of different composition. If we are doing things right, some dots will have significantly more electrocatalytic activity than other dots. The very active dots of catalyst are the ones we wish to study further in our effort to discover better materials. The difficult part of combinatorial electrochemistry on a single conductive substrate is screening each catalyst for its activity. Currently, there is no direct way to measure the individual electrochemical activity of many dots on a single substrate, so indirect (optical) methods have been developed. We seek to develop Electrochemical Tomogaphy as a way to determine electrochemical kinetic parameters for individual dots using only the electrochemical response we can measure at the edge of the wafer where we have electrical contact.

1. S.D. Leith and D.T. Schwartz, Through mold electrodeposition using the uniform injection cell: Workpiece and pattern scale uniformity, *Electrochim. Acta*, **44**, 4017-27 (1999).
2. S.D. Leith and D.T. Schwartz, High throughput electrodeposition of uniform NiFe micromachined components through thick molds, *J. MEMS* **8**, 384-92 (1999).
3. Reddington E, Sapienza A, Gurau B, et al., Combinatorial electrochemistry: A highly parallel, optical screening method for discovery of better electrocatalysts, *Science*, **280** 1735-1737 (1998).

Broad Objectives

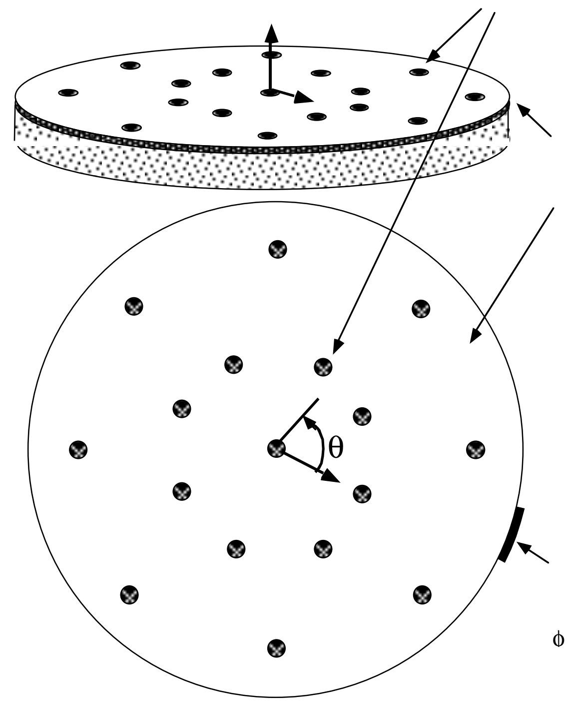
(1) Derive a nondimensional 2-D governing equation and boundary conditions that account for the very thin nature of the conductive film (in heat transfer, this is called the “thin fin” approximation).

(2) Establish the feasibility of using electrochemical tomography to discern spatially localized events using only measurements from the wafer edge.

(3) Explore the role of geometric, physical, and electrochemical properties on the sensitivity of Electrochemical Tomography.

(4) Recommend an optimized system for Electrochemical Tomography (*i.e.*, what combination of geometric, physical, and electrochemical parameters are optimal for high resolution operation).

(5) Provide evidence for the trustworthiness of your computations (comparison to analytical results and/or evidence of solution convergence).



Physical Description

The substrate to be considered is a conductive thin film grown on an insulator. The thin film has a thickness H (cm) and electrical conductivity of κ (ohm^{-1} cm^{-1}). The substrate has between 16 and 25 electrochemically-active sites arranged in a pattern on the surface. The best pattern for laying out the sites is one of the geometric properties you seek to optimize. Each electroactive site is circular with 0.01 cm diameter. All other portions of the substrate are inactive. The radius of the substrate is ρ (cm), with $\rho \leq 1$ cm. Ideally, you will pack many active sites on a small subsrate. This substrate is immersed in an electrolyte (either for electrodeposition or electrocatalysis), hooked to a power supply, and a current is passed to a counter electrode also immersed in the electrolyte..

The problem mainly addresses the potential and current distribution in the thin conductive film. Potential in the film is denoted $\phi(r,\theta,z)$ (units of V) and current density is given by $\mathbf{i} = -\kappa\boldsymbol{\nabla}\phi$ (A/cm^2). Note that current density is a vector quantity. Conservation of charge demands that LaPlace's equation

$$\nabla^2\phi = 0$$

be satisfied within the conductive thin film.

Electrical contact to the substrate is made along the edge over some small edge segment (see top view). The length of the edge contact will influence the tomographic resolution. The potential on the contact is set by the power supply to be ϕ_c (V). The potential can be positive or negative. The tomographic method you will develop involves moving the contact segment to various locations on the edge and measuring the resulting current flow from the substrate. The more different places you make contact, the better the resolution, though ideally, you will seek to maximize the information for the fewest number of measurements.

All other boundaries of the thin conductive film have no normal current flow, that is,

$$\mathbf{n}\bullet\boldsymbol{\nabla}\phi = 0 \ ,$$

except at the electrochemically-active sites, where

$$-\kappa(\mathbf{n}\bullet\boldsymbol{\nabla}\phi) = i_o nF/RT\{\phi - \phi^{sol}\} \ .$$

This equation is a linearized Butler-Volmer kinetic expression that connects the current density at an active site to the potential difference between the substrate and the solution (ϕ^{sol}) at the active site. There is little loss of generality if we set $\phi^{sol} = 0$. The other parameters are as follows: i_o (A/cm^2) is an electrochemical kinetic parameter called the exchange current density, n is the number of electrons transferred in the reaction (normally between 1 and 4), F is Faraday's Constant (96,486 C/mole e$^-$), R is the universal gas constant (8.314 J/K-mole), and T is absolute temperature (K).

In either combinatorial electrochemistry or electrochemical microfabrication, i_o can vary among the electroactive sites. At the most basic level, Electrochemical Tomography seeks to determine i_o for each active site.

You will want to non-dimensionalize your equations using ρ as the characteristic length and ϕ_c as the characteristic potential. It is also advisable to spatially average the z-dependence of potential in the film to reduce the problem from a 3-D to a 2-D problem (the "thin fin" approximation in heat transfer).

Crude Tomography: Reconstruction via linear back projection.

Using the proposed characteristic length and potential will lead to a single nondimensional electrochemical parameter called the Wagner number ($Wa = HRT\kappa/\{\rho^2 i_o nF\}$), a ratio of kinetic-to-ohmic resistances. For a reconstruction, you will need M contact segments around the edge; label each contact segment m=1, 2, ... M. You will also have J different active sites; label each site j=1, 2, ... J.

Step (1): Establish reference weightings for uniform Wa.

Give each active site the same Wagner number, and determine the current at each site j for contact m=1. This will give $I_{1,j}$ and I_1 = **sum**($I_{1,j}$). Repeat for each contact to find all the $I_{m,j}$ and I_m. I_m is the total current we measure at the contact segment m. Note that current $I_{m,j}$ (amps) is the area integral of active site j's current density when contact m is used.

The reference weighting for each site j, using contact m, is $\omega_{m,j} = I_{m,j}/I_m$.

We also need to calculate the average current, I = **sum**(I_m/M). The portion of this average current generated by site j is I_j = **sum**($I_{m,j}/M$).

Change Wa and repeat process to find weightings as a function of Wa. You will want to plot I vs. Wa as a way to estimate the mean Wa for a surface with variable Wa.

Step (2): Measurements at surface with variability in Wa among sites.

Measure each I_m. Calculate I = **sum**(I_m/M) and find average Wa from plot of I vs. Wa. Now, we use the reference weightings appropriate for the average Wa, and estimate $I_{m,j}$ (I'll call the estimate $<I_{m,j}>$) according to $<I_{m,j}> = \omega_{m,j} * I_m$. Our estimate of the average current generated by site j is $<I_j>$ = **sum**($<I_{m,j}>/M$). If you plot $<I_j>/I_j$ vs j, some sites will be more active (>1) than the average surface, and some will be less active (<1). See how well this maps back to the Wa numbers you set for each of the active sites.

The quality of the reconstruction will depend on Wa. It will also depend on the number, size and location of edge contacts, as well as the number, size, and spacing of active sites. Experimentally, you want to pack a high density of active sites on a surface, use the fewest edge measurements, and get perfect reconstructions. This is impossible, so you'll need to work on compromise solutions. You should make sure to discuss these compromises and the rationale for your "optimized" design.