# 192b Pore Accessibility and Ion Transport in Ordered Mesoporous Silica Thin Films Determined by Electrochemical Methods

*Ta-Chen Wei and Hugh W. Hillhouse*

Ordered mesoporous silica films synthesized by self-assembly have attracted great interest for templates for electrodeposition of nanowires for thermoelectric devices [1] and use in electrochemical sensors [2]. However, for these applications it is crucial to develop films with good accessibility and transport while minimizing defects. In order to evaluate these parameters we have conducted electrochemical experiments and compared them to models of the films structure. The pinhole model proposed by Matsuda [3] can be used to simulate the diffusion current for partially covered electrodes; however it is only applicable for pinholes having a diameter on the order of the film thickness. The membrane model proposed by Bard [4] is more suitable for our system, but it does not consider the current coming from the cracks. Here we proposed a strategy to obtain the area of film defects, total exposed electrode area, and diffusion coefficient within the film by using impedance spectroscopy, cyclic voltammetry and chronoamperometry. First, mesoporous silica films were formed on Au substrate by dip-coating under controlled RH [5]. The films were then calcined at 400 degree C for 4 hour at a heating rate of 1 degree C per min. Grazing-angle of incidence small-angle X-ray scattering (GISAXS) has been used to characterize the structure and orientation of the films. The Faradaic impedance of a Au electrode covered by R3m and c2mm silica films was studied over a wide frequency range in acidic KCl solutions in the presence of 5mM Fe(CN)63-. At high frequency, we observed a semicircle which represents the charge transfer resistance and double layer capacitance in Argand diagram. The exposed area can be calculated from the charge transfer resistance because the standard rate constant and concentration of redox couple were already known. However, it is difficult to study the ion transport in the nanopores because the current is also contributed from the presence of cracks. In order to quantify the crack area, we used cyclic voltammetry to observe the transition from 3D diffusion to 1D diffusion with increasing scan rates. The crack area was then estimated from the change of slopes in the plot of current versus square roots of scan rate. We were able to extract the diffusion coefficient and partition coefficient within the film by using the modified membrane model to fit the corrected chronoamperometric data. We found that the diffusion coefficient within the c2mm silica film is about two orders of magnitude smaller than that in bulk.

References:

1. Hillhouse, H. W., Tuominen, M. T. Microporous and Mesoporous Mater. 2001, 47, 39-50.]

2. Innocenzi, P., Martucci, A., Guglielmi, A., Bearzotti, A., Traversa, A., Pivin, J. C. J. Eur. Cer Soc. 21, 1985 (2001).

3. Gueshi, T., Tokuda, K., Matsuda, H. J. Electroana. Chem., 89, 247-260, 1978.

4. Peerce, P. J., Bard, A. J. J. Electroana. Chem., 112, 97-115, 1980.

5. Tate, M. P., Eggiman, B. W., Kowalski, J. D., Hillhouse, H. W. Langmuir in progress.