Line Imaging Raman Spectroscopy of Heterogeneous Reaction Species Controlled using Hydrodynamic Boundaries

B.R. Lutz and D.T. Schwartz

Department of Chemical Engineering
University of Washington, Seattle, WA

The effectiveness of isolating heterogeneous reaction species using hydrodynamic boundaries was investigated using line imaging Raman spectroscopy and limiting current measurements. Linear oscillation of a fluid normal to a stationary cylinder produces a steady-state recirculating flow in each of four quadrants about the cylinder. Each region is bounded on one side by the electro-active cylinder and elsewhere by streamlines across which species move only by diffusion. Thus each region represents a 'container-less vessel' within which reaction products are concentrated and reactants are depleted. The great utility of this approach is the ability to control the size of the isolated region and the degree of mixing within it through control of the oscillation amplitude and frequency.

An optically transparent electrochemical flow cell and a custom-built Raman spectroscopy system with a 5-cm working distance allowed in-situ imaging of species during heterogeneous electrochemical reaction and acoustically-driven flow. A spectrograph designed to maintain the spatial integrity of the entrance slit was used to spatially map the Raman signal of species throughout the isolated region.

An equimolar aqueous solution of $Fe(CN)_6^{-3}$ and $Fe(CN)_6^{-4}$ was oxidized or reduced on a 500μm platinum wire at the limiting current for a range of oscillation amplitudes and frequencies. The distinct spectral difference between ferricyanide and ferrocyanide allowed determination of the steady state concentration of reactants and products along a line near the electrode. The results were compared to boundary layer thickness and limiting current measurements used previously to describe this flow [1-3]. The measured boundary layer thickness was found to decrease with frequency, and the limiting current was found to increase with amplitude and frequency. In addition a 2-dimensional map of the concentration field was demonstrated for a small set of parameters by rastering the line in one dimension.

[1] W.P. Raney, J.C. Corelli,, and P.J. Westerfelt, *J. Acoust. Soc. Am.* **26** (6), 1006-1014 (1954).
[2] C.V.R Raju, G.J.V.J. Raju, and C.V. Rao, *I. J. Tech.* **5**, 305-309 (1967).
[3] J.A. Bowman and D.T. Schwartz, *Int. J. Heat Mass Transfer*, **41** (8-9), 1065-1074 (1998).