Nano/Microfluidic Electrocatalysis: Towards High Conversion, Continuous Reactions

Nicholas M. Contento[a] and Paul W. Bohn[a,b]
[a]Department of Chemical and Biomolecular Engineering,
[b]Department of Chemistry and Biochemistry
University of Notre Dame
Notre Dame, IN

Micro and nanofluidic devices provide kinetic advantages for heterogeneous chemical reactions[1]. These advantages arise from the relatively high rate of molecule-surface interactions in confined geometries like micro- and particularly nano-channels in which molecular surface collisions occur at ~10^5 s^{-1}[2],[3]. This enhanced transport of species provides benefits for a broad range of heterogeneous reactions, such as those encountered in electrochemistry, catalysis and electrocatalysis.

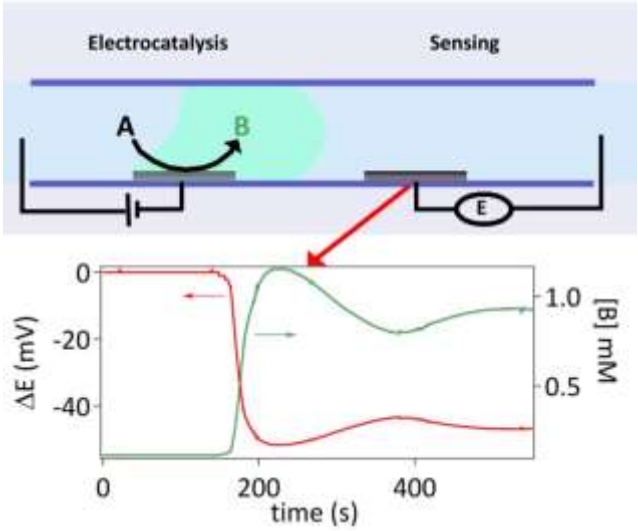

Figure 1: Depiction of microfluidic device used for electrocatalysis and downstream sensing of reaction products. Inset shows sensor response (ΔE and corresponding [B]) during application of an electrocatalytic potential. In this case B=Cl^- from the electrocatalytic reduction of ClO_4^-.

We have recently fabricated micro and nanofluidic devices capable of continuous electrocatalytic conversions of relatively refractory molecules under moderate reaction conditions (i.e. neutral pH and ambient temperature). The devices are fabricated in lab-on-chip (LOC) format, developed using standard microfabrication procedures including soft lithography for the formation of fluidic channels in polydimethylsiloxane (PDMS) and photolithography for the patterning of electrodes. Nanofluidic channels are formed in a more robust polymer composite of *hard*-PDMS/PDMS.

In an illustrative case the LOC structure allows for sequential arrangement of multiple operations needed to sense ClO_4^- and effect its catalytic reduction to Cl^- downstream. In this case reactive and sensing modalities are achieved in parallel allowing for an upstream reaction followed by downstream characterization of the reaction products. Micrometer-scale thermally deposited gold thin film electrodes are modified *in situ* to provide desirable catalytic and sensing properties via various metallic depositions and subsequent chemical modifications. For example, Pd thin films with nanoscale morphologies are electrochemically deposited to enhance electrocatalytic activity. Similarly, a Ag/AgCl layer is generated by sequential electrodeposition and chloridization of a Ag film and used for the potentiometric detection of chloride.

The improved conversions achieved via micro/nanofluidic electrocatalysis, the ability to operate the reactor continuously, and the ability to massively scale up micro/nanofluidic arrays suggest these devices as an effective alternative to typical reactors, particularly for refractory molecules for which confinement benefits are most evident.

Acknowledgements
The work described here was supported by the Department of Energy (DE FG02 ER0715851) and the National Science Foundation through the Center for Advanced Materials for Water Purification with Systems (CTS0120978).

References

[1] S. P. Branagan, N. M. Contento and P. W. Bohn, *J. Am. Chem. Soc.*, **134**, 8617 (2012)

[2] N. M. Contento, S. P. Branagan and P. W. Bohn, *Lab on a Chip*, **11**, 3634 (2011)

[3] W. Sparreboom, A. v. d. Berg and J. C. T. Eijkel, *Nat. Nanotechn.*, **4**, 713 (2009)