

Poly(dimethylsiloxane) as a material for oxygen delivery in electrochemical devices

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Final Seminar

August 13, 2012

The electrochemically catalyzed oxygen reduction reaction (ORR) is essential to operation of most fuel cells and many types of batteries; oxygen, being prevalent in air, provides a costless, ambient, high-energy (1.23 V vs. normal hydrogen electrode (NHE)) hole source to complete the electrochemical redox circuit.¹ Cathodic (ORR side) overpotentials however represent the largest efficiency losses in conventional polymer electrolyte membrane (PEM) fuel cells.^{1b, 2} Oxygen mass transport is limited by the inherent low permeability of O₂ in water.^{1b, 3} This low solubility and diffusivity can be overcome through reduction of electrolyte thickness, and by utilizing a thin cell wall of highly permeable material, such as poly(dimethylsiloxane) (PDMS), a material with a permeability coefficient of O₂ ~6 times larger than in H₂O (Fig. 1A).^{1b, 3-4} Besides its highly permeable nature, PDMS proves an excellent electrochemical cell material also due to its ubiquitous use in microfluidics and stability in aqueous electrolytes.^{3, 5} The results presented herein utilize PDMS microfluidics to reduce the electrolyte thickness (and therefore the thickness of the diffuse layer), and control the thickness of the PDMS layer (Fig. 1A).^{4a} This in turn provides large, highly controllable and stable ORR currents for a direct formic acid fuel cell (DFAFC) in a fully passive, planar form-factor (Fig. 1B).^{4a}

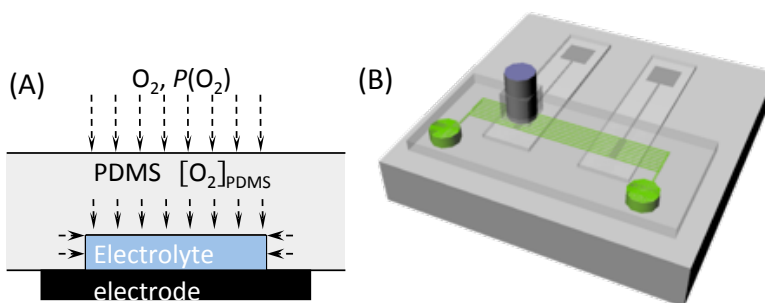


Figure 1: (A) A microfluidic network molded from PDMS can reduce the electrolyte diffuse layer to the thickness of the microfluidic channel height, and due to the high O₂ permeability in PDMS, large steady state O₂ fluxes to the embedded electrode (black) may be achieved. (B) A depiction of our fully passive, planar microfluidic fuel cell. A fuel reservoir, placed over the anode, sufficiently supplies formic acid in a passive manner by passive permeation through the PDMS to the anode below. Reprinted with permission from Wiley.^{4a}

Lessons learnt from this DFAFC study enabled us to design an in-situ electrochemical X-ray Absorption Spectroscopy (XAS) cell for the study of mechanistic details of ORR electrocatalysis on platinum, the most commonly utilized ORR cathode material.⁶ The large ORR overpotential on Pt (~0.33 V loss at onset potential) accounts for the majority of polymer electrolyte membrane (PEM) fuel cell efficiency losses, as well as a huge cost that prevents fuel cell economic viability.^{2, 7} Maximum ORR activity is correlated to related properties such as d-band center, and metal-oxide binding energy and bond distances.⁸ These properties are observable through XAS.⁹ XAS at lower energies, X-ray absorption near edge structure (XANES) can define d-band occupancy changes, related to oxidation states of the metal.⁹⁻¹⁰ XAS at higher

energies, extended X-ray absorption fine structure (EXAFS) can derive bond distances through X-ray interaction with backscattered electrons.^{9,11} From these bond distances, bond types may be inferred, as well as coordination numbers and degree of bond disorder.^{9,11} The experiments described herein exploit the high oxygen permeability through PDMS in the design of an in-situ electrochemical XAS cell to study the evolution of the Pt electrocatalyst during ORR electrocatalysis.⁶ A depiction of this cell, which provided highly controllable, large steady-state oxygen flux to the working electrode, is shown in Fig. 2.⁶ These XAS results found that oxygen adsorbs to platinum over a wide potential range (e.g. 1.2 to 0.4 V vs. NHE), causing an ORR current-dependent Pt-Pt bond expansion.⁶

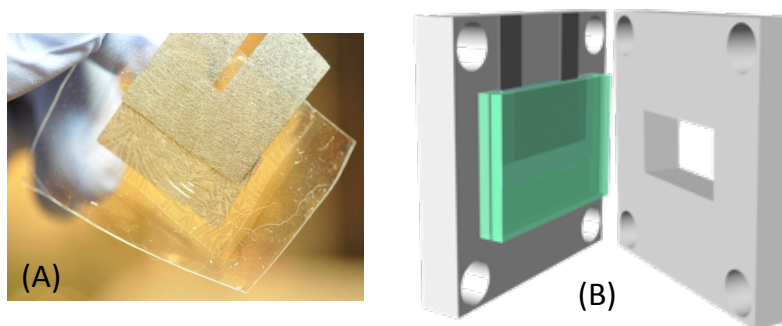


Figure 2: (A) The thin PDMS pouch used to house the electrolyte and electrodes, shown with two C-paper electrodes placed inside. (B) A 3-D computer generated depiction of the cell pouch between two Teflon compression plates that hold the cell in place. Reprinted with permission from Erickson, E. M.; Thorum, M. S.; Vasić, R.; Marinković, N. S.; Frenkel, A. I.; Gewirth, A. A.; Nuzzo, R. G., In Situ Electrochemical X-ray Absorption Spectroscopy of Oxygen Reduction Electrocatalysis with High Oxygen Flux. *J. Am. Chem. Soc.* **2012**, *134*, 197-200. Copyright 2012 American Chemical Society.

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