

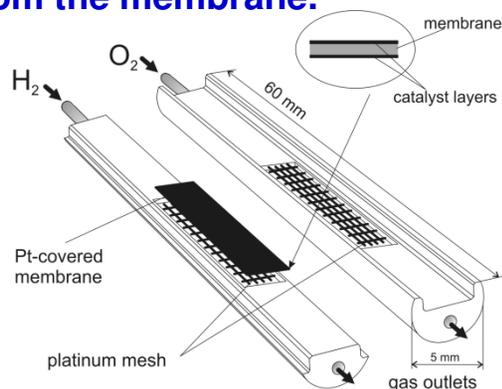
# Morphological and Spatial Aspects in Polymer Degradation: From Heterophasic Polymers to Proton Exchange Membranes Used in Fuel Cells

Shulamith Schlick

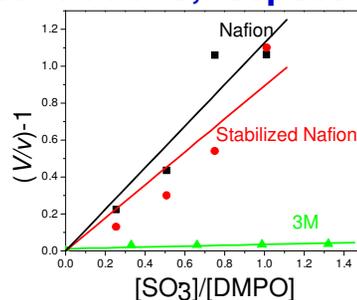
University of Detroit Mercy

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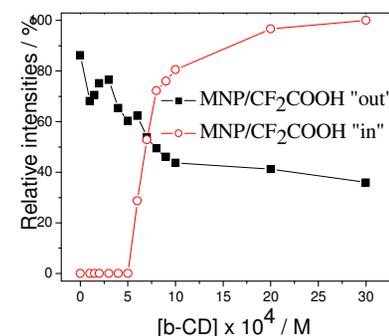
(A) The first In Situ study of a fuel cell (FC) inserted in the resonator of an ESR spectrometer has been published.<sup>1</sup> The FC can detect separately processes at the anode and the cathodes sides, and visualize early events: The chemistry leading to formation of oxygen radicals, hydrogen atoms, and fragments derived from the membrane.



(B) The mitigating effect of Ce(III) on membrane degradation was quantified for perfluorinated membranes.<sup>2</sup> The competitive kinetics approach allowed ranking of membrane stability to attack by hydroxyl radicals: In the graph below  $V$  and  $v$  are initial reaction rates of DMPO/OH adduct formation in the absence and presence of competitor (membrane or Ce(III)), and  $[SO_3^-]$  and  $[DMPO]$  are the membrane and DMPO concentrations, respectively.



(C) Free radicals and their spin adducts are short-lived. In order to increase their longevity, we have initiated a study of spin adduct complexation by cyclodextrins (CDs), which have the potential to form complexes with hydrophobic guests. Below we observe the increase of % "in" with  $\beta$ -CD content. Moreover,  $\beta$ -CD has also demonstrated selectivity: To preferentially enclose hydrophobic fluorinated spin adducts.<sup>3</sup>



1. Danilczuk, M.; Coms, F.D.; Schlick, S. *J. Phys. Chem. B* 2009, 113, 8031-8042.

2. Schlick, S.; Perkowski, A.J.; Lin, Lu.; Mao, Q.; Danilczuk, M. *Polym. Prepr.* 2009, 50(2), 158-159.

3. Spulber, M.; Schlick, S., poster at ACS Meeting, Washington DC, 2009. Full manuscript is in preparation.

# Broader Impact Activities

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- PI Schlick is part of DOE7, a group of scientists and engineers at 3M Company in St. Paul, MN, and five professors at US universities. In annual meetings, teleconferences, and quarterly reports, the PI's fundamental research on the degradation of fuel cell membranes has contributed to the recent "go" DOE decision (funding until 2011).
- The collaboration with scientists at the GM Fuel Cell Activity Center continues, and we are planning together the In Situ FC for ESR Imaging experiments.

- **The Group:** Undergraduate A. J. Perkowski, graduate students Lu Lin, Peng Cong, and Dong Shihang, visiting graduate students M. Spulber ("Petru Poni" Institute, Yassy, Romania) and L. Lancucki (University of Krakow, Poland), postdoctoral M. Danilczuk, and visiting scientists M. Pinteala ("Petru Poni") and K. Kruczala (Krakow, Poland).

- **Translational Research.** Our collaboration with scientists and engineers from 3M, Ford Laboratories, and the Fuel Cell Activities Center of General Motors on the degradation and stabilization of membranes used in fuel cells is an example of the connectivity between fundamental research and applications: Understanding the mechanism of membrane degradation enables work on better membranes.

- **International Collaborations.** PI Schlick has continued the collaboration with former postdoc Yohei Miwa (now at Mitsubishi, Japan), with K. Kruczala (who just defended in Krakow his Habilitation based on work in the PI's group over a period of  $\approx 10$  years as visiting student, postdoc, and visiting scientist) and with the group of Bogdan Simionescu at the Petru Poni Institute, Yassy, Romania.