Chemistry Ph. D. Blasini built fuel cell materials program at CHESS

E. Fontes (July 19, 2006)

Daniel R. Blasini was recently awarded his Ph. D. degree for his thesis entitled "Characterization of Thin Films and Thin Film Phenomena in Electrochemically Active Systems via X-Ray Methods." While studying with Héctor Abruña, professor of chemistry and chemical biology, Blasini spent almost five years using x-ray techniques applied to chemical systems at the G2 experimental station at CHESS, the Cornell High Energy Synchrotron Source. His work encompassed basic research into materials needed for advancing technologies in organic light-emitting diodes (OLED) and fuel cell energy sources.

Blasini was one of a dozen students who helped build the latest beamline sector at CHESS, called G-line, where he specialized in motorizing the x-ray front-end, optics and in-vacuum equipment. This sector has three experimental stations simultaneously fed by a high-intensity wiggler insertion device. Inside the G2 station, Daniel worked closely with fellow graduate student David Nowak (Baker group in Materials Science and Engineering) and CHESS staff scientist Detlef Smilgies to build an instrument for grazing incidence x-ray diffraction (GID). GID is especially sensitive to chemistry and chemical ordering at the surfaces of materials. More recently, he collaborated with graduate student Yi Liu (Abruña group) in the commissioning of an *in-situ* electrochemical specimen cell for the G2 station. Because high-energy x-ray beams penetrate the thin covering film and trapped liquid layer of the cell, measurements could be made on the actual catalytic surfaces. *In-situ* measurements with x-rays are one of the few ways scientists gather structural information on active, functioning chemical catalysts in working fuel cells.

Direct fuel cells (DFC) are making news headlines these days because of escalating concerns about the cost and long-term availability of fossil fuels. DFCs are attractive alternatives as a more efficient and less polluting means of generating electricity. A fuel cell converts chemical energy directly into electrical energy with minimal losses. Efficiencies well above 80% might be achieved, and a variety of different fuels might be employed. In a cell, the fuel (hydrogen or a small organic molecule such as methanol, ethanol, formic acid, or other) enters via an anode where it is oxidized at a catalyst site. Oxygen enters via an opposing cathode compartment and is reduced to water. Protons released in the reaction travel through an intervening polymer electrolyte membrane to the cathode, where they combine with electrons that have traveled outside the cell as electrical current. During recombination water is produced.

Blasini started his thesis studies on ordered intermetallic compounds such as PtBi and PtPb. Both materials are good electrocatalysts in oxidizing small organic molecules, with enhanced catalytic activity for methanol and formic acid and superb tolerances to carbon monoxide poisoning. Carbon monoxide poisoning causes catalysts to lose their ability to function due to preferential bonding and blocking of active sites. This poisoning is one

of the main hurdles to the widespread use of fuel cells as alternatives to fossil fuel consumption.

Even though fuel cells were invented in 1839, little has changed in the use of platinum as the catalyst material. Because platinum is susceptible to poisoning by very low levels of carbon monoxide or sulfur, better materials are needed to produce cells whose energy output can remain high over long periods of time. Platinum-based ordered intermetallic phases such as PtBi and PtPb have the potential to make significant breakthroughs, which was one of the reasons the U.S. Department of Energy began funding the Cornell Fuel Cell Institute (CFCI) in 2003. This grant represented an interdisciplinary effort of Cornell faculty to explore new materials and new approaches to fuel cell technologies. Abruña is one of the principal investigators on the grant. (CFCI was highlighted in the Cornell Chronicle here: http://www.news.cornell.edu/Chronicle/03/10.30.03/fuel_cell_institute.html.) Daniel's initial studies, in combination with Yi's recent results, had generated a great deal of interest and CFCI researchers will be making extensive use of the CHESS facilities in future *in-situ* investigations.

Blasini and coworkers used a variety of x-ray techniques to try to understand compositional and structural changes taking place at catalyst surfaces as a function of applied voltage in an active electrochemical cell. Especially important was studying the pretreatment processing, or cleaning, that produced the most active and stable surfaces. X-ray photoelectron spectroscopy (XPS) measurements, done at the University of Puerto Rico at Rio Piedras with collaborators Dr. Carlos Cabrera and Dr. Esteban Fachini, were used to study the leaching of the less noble metal from the anode and electrocatalyst surfaces. In total, the combination of XPS and x-ray studies at CHESS helped to establish an efficient cleaning/activation procedure and helped identify the highest anode operation voltage under which these catalysts can be stable in fuel cells.

When asked how work at CHESS differed his previous experiences, Daniel recalls his prior history working in electrochemistry labs where all the instrumentation was commercially available. “We didn’t have to worry about data acquisition schemes or any instrument designing or machining.” He was quick to adopt a different mentality, learning to work with the scientific and technical staff at CHESS to design and build his own equipment and stay on the job until the x-ray instruments fully worked. He adds: “When someone asks me about G-line the first things that jumps into my head are cable making and motor testing. … it is amazing that something as simple as troubleshooting motors taught me a lot about how to approach and solve problems. I think in general all the logic behind the preparation, the performing, and the data analysis of the experiments that I performed at G2 made me a better problem solver.”

Blasini did his undergraduate studies in chemistry at the University of Puerto Rico (UPR), Rio Piedras, the same city where he was born and raised. While at UPR, Daniel received a NIH-MARC (Minority Accesses to Research Careers) Undergraduate Research Fellowship and worked as an analytical chemist research assistant under the supervision of Dr. Carlos R. Cabrera. In Cabrera’s group he was first introduced to work

on alternate forms of energy, particularly characterizing the surface of modified electrodes for various applications. In the summer of 1998 he participated in the NSF-REU (Research Experience for Undergraduates) program at Harvard University under Dr. Eric Mazur. There he designed and built an autocorrelator to measure femtosecond laser pulses, and was first introduced to motion control systems, machining, and the art of designing and building scientific instrumentation.

During the spring of 1997 he was granted the ACS Undergraduate Award in analytical chemistry. He earned the Undergraduate Excellence Award from the College of Chemists of Puerto Rico in both 1997 and 1998. He earned his Bachelor of Science degree in Chemistry on January 1999, that same year he joined the chemistry graduate program at UPR. A year and a half later he decided to join the Cornell graduate program in Chemistry and took on the challenge to build the x-ray instruments at CHESS. During his time at Cornell he also participated in activities to encourage the interest in science of Latino children and participated in numerous outreach activities throughout the Cornell Center for Materials Research.

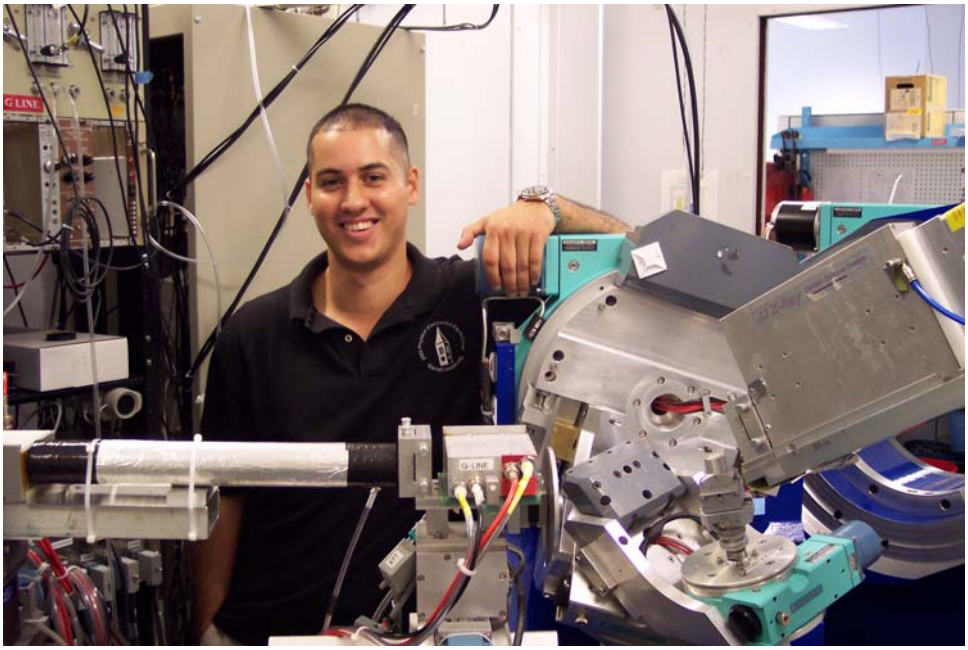
Blasini is now moving to Johns Manville in Littleton, CO, where he joins a group doing surface characterization analysis (AFM & XPS) of polymer binders on glass fibers for insulation applications. Abruña's group will continue using CHESS to further understand surface oxide structures and dynamic processes that produce the active catalytic surfaces. *In-situ* x-ray studies of functioning fuel cells are in the not-too-distant future.

Relevant publications:

Volpe, D.; Casado-Rivera, E.; Alden, L.; Lind, C.; Hagerdon, K.; Downie, C.; Korzeniewski, C.; DiSalvo, F. J.; Abruna, H. D. *Journal of the Electrochemical Society* **2004**, *151*, A971.

Blasini, D.R.; Rochefort, D.; Fachini, E.; Alden, L.R.; DiSalvo, F.J.; Cabrera C.R.; Abruña H.D. *Surface Science* **2006**, *600*, 2670.

Smilgies, D.M.; Blasini, D.R.; Hotta S.; Yanagi H. *J. Synchrotron Rad.* **2005**, *12*, 807.



Daniel Blasini with the grazing-incidence x-ray diffractometer inside the CHESS G2 experimental station.

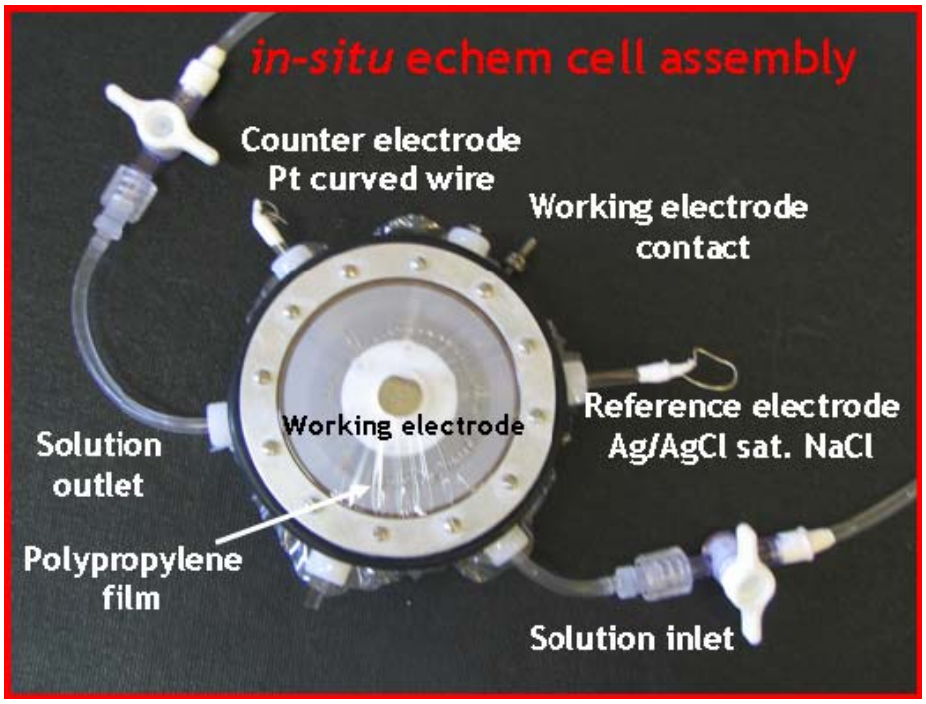


Photo of the electrochemical cell used to collect *in-situ* x-ray diffraction data from an electrode surface (disk at center) while immersed in solution contained by the polypropylene film.

Blasini (center) helps the CHESS technical crew install a 2-meter long in-vacuum optics translation stage. Tom Krawczyk is left, Chris Conolly right, and Dana Richter controlling the hand lift in rear.