**APPLICATION FORM, 2003-2004**
**PART A: Student Application**
SCHOLARLY AND CREATIVE ACTIVITY GRANTS FOR UNDERGRADUATES

Instructions: Please complete all sections of Part A (in projects with multiple students, each student in a project must complete his or her own Part A Form). The faculty and student(s) application must be submitted as one package. Complete applications must be typed and are due Wednesday, November 26, 2003, by 5:00 p.m. in the Office of Curriculum and Undergraduate Studies, Cramer Hall 345. Please submit the original and 3 copies by the due date. Late applications will not be accepted.

Student Name: **David L. Rogow**

Student ID Number: [redacted]

Address: [redacted]

Major: **Chemistry**

E-mail address: [redacted]

Academic Standing: (circle one)

Freshman/ Sophomore/ Junior/ **Senior**

Faculty Sponsor for Project:

**Dr. George M. Coia**

Title of Project: **Vinyl-Bipyridine Based Polymer-Film Electrocatalysts for $O_2$ Reduction**

(If you wish to receive academic credit for your involvement in this project, you must arrange with your faculty mentor to register for the appropriate course, either 401, 402, or 406.)

Have you been the recipient of this award before? YES /**NO**

If yes, when?_____

(If yes, total award cannot exceed $1000. Only $750 +OPE can be allocated to student wages)

# Vinyl-Bipyridine Based Polymer-Film Electrocatalysts for $O_2$ Reduction

## Objectives

The polymer electrolyte membrane (PEM) fuel cell is a promising new technology,[1,2] it produces electrical energy from oxygen and hydrogen,

$$2\,H_2 + O_2 \rightarrow 2\,H_2O.$$

Catalysts are needed at the cathode where oxygen is reduced and at the anode where hydrogen is oxidized. At the present time, the best catalyst for the cathode is platinum, which is expensive and inefficient at ambient temperatures.[3] Our goal is to study $O_2$ reducing catalysts which are less expensive and more efficient at ambient temperatures. Because the reduction of $O_2$ is limited by slow reaction kinetics,[4] the cathode is our major focus.

Potential new catalysts for the fuel cell cathode are similar to naturally occurring $O_2$ reducing enzymes such as cytochrome *c* oxidase in that they contain iron in their active sites.[5] We propose to study novel catalysts based on simple iron complexes. These catalysts will be immobilized on fuel cell electrodes as insoluble metallopolymer films.[6] Catalyst-coated electrodes will be characterized electrochemically to see how efficiently they catalyze $O_2$ reduction. If an electrode proves to be effective, it will be incorporated into a fuel cell and tested further.

## Methodology

To make the desired catalyst, iron(II) chloride is reacted with two equivalents of 4-vinyl-4'-methyl-2,2'-dipyridyl (vbpy) in acetone. This forms the neutral complex $Fe(vbpy)_2Cl_2$. One equivalent of 2,2'-dipyridyl (bpy) is then added to form $[Fe(vbpy)_2(bpy)]^{2+}$. This complex will be polymerized electrochemically to form a thin metallopolymer film (Figure 1a). Once the film has been formed, it will be manipulated chemically, to give the desired catalyst. Film-coated electrodes will be placed in a solution containing metal ions that will displace the bpy ligand, exposing two binding sites where water will coordinate (Figure 1b). After the film is modified in this way, it will be characterized by cyclic voltammetry to measure catalytic activity, and by atomic-force microscopy to determine film thickness and morphology.

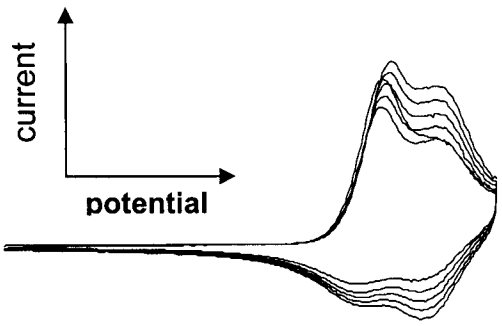
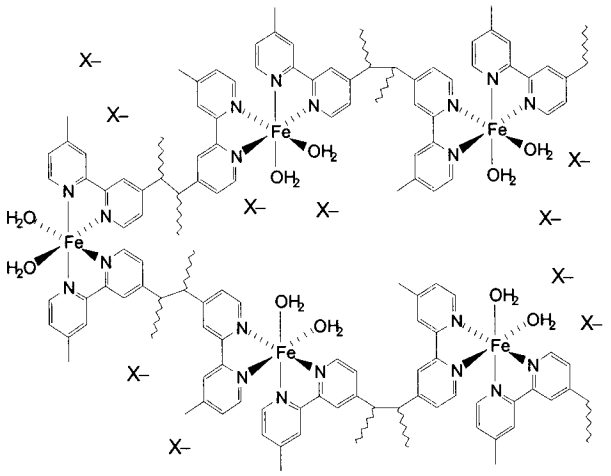



**Figure 1**. (a) Cyclic voltammogram of reductive electropolymerization of $[Fe(vbpy)_3]^{2+}$. The growing cathodic wave illustrates the growth of the film.



(b) Representation of the desired metallopolymer film. The water groups become displaced by $O_2$ to facilitate reduction catalysis.

Synthesis of a mixed-chelate iron complex, $[Fe(vbpy)_2(bpy)]^{2+}$ is the first step toward successful completion of this research project. In order to establish proof of concept, I have attempted the synthesis of $[Fe(bpy)_2(dmb)]^{2+}$, ( dmb = 4,4'-methyl-2,2'-dipyridyl), a mixed chelate iron complex with similar ligands. The electrochemical and spectroscopic characterization of this product has been encouraging and

confirms that we are able to make such compounds. I expect to complete this research before spring of 2005.

**Expected Outcome**

Research on new catalysts of this type will contribute to the chemical literature in the area of catalytic $O_2$ reduction on iron. Demonstrating the ability to make mixed-chelate complexes of iron is publishable in itself, as similar complexes have been considered unstable and difficult to isolate. Obtaining preliminary results will facilitate the grant writing process so that other sources of funding can be secured. I intend to present the results of this research at a national conference of the American Chemical Society in April of 2004. This research project will also serve as my undergraduate honors thesis, which will be presented in the spring of 2005.

**Significance**

New technologies stem from basic science. We must recognize that the transition to alternative sources of energy depends on the cost of the new technology *versus* the conventional technology. The development of new catalysts which are more efficient and less expensive could significantly reduce the cost of implementation of fuel cell technology. Reduction in cost is what is needed to speed the transition to a hydrogen economy and thereby reduce the level of harm being done to the environment by humans.

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[1] Tullo, A. H. "A Fuel Cell in Every Car" Chemical & Engineering News **2001**, 79, 19-22.

[2] Koppel, T. *Powering the Future: The Ballard Fuel Cell and the Race to Change the World;* Wiley: New York; **2001**.

[3] Wilson, M. S., Gottesfeld, S. "High Performance Catalyzed Membranes of ultra-low Pt Loadings for Polymer Electrolyte Fuel Cells" *J. Electrochem. Soc.* **1992**, 139, No. 2, L28-L30.

[4] Boring, E., Geletii, Y. V., and Hill, C. L. "A Homogeneous Catalyst for Selective $O_2$ Oxidation at Ambient Temperature. Diversity-Based Discovery and Mechanistic Investigation of Thioether Oxidation by the Au(III)$Cl_2NO_3$(thioether)/$O_2$ System" *J. Am. Chem. Soc.* **2001**, 123, 1625-1635.

[5] Palmer, G. "Current Issues in the Chemistry of Cytochrome *c* Oxidase" *Bioenerg. Biomembr.* **1993**, 25, 145.

[6] Denisevich, P., Abruna, H. D., Leidner, C. R., Meyer, T. J., and Murray, R. W. "Electropolymerization of Vinylpyridine and Vinylbipyridine Complexes of Iron and Ruthenium: Homopolymers, Copolymers, Reactive Polymers" *J. Inorg. Chem.* **1982**, 21, 2153-2161.


Student Signature _____ 11.26.03

Faculty Signature _____ 11/26/03

**APPLICATION FORM, 2003-2004**
**PART B: Faculty Application**
SCHOLARLY AND CREATIVE ACTIVITY GRANTS FOR UNDERGRADUATES

Instructions: Please complete parts B and C. Have student complete Part A. All parts must be submitted as one package.

Complete applications must be typed and are due Wednesday, November 26, 2003, by 5:00 p.m. in the Office of Curriculum and Undergraduate Studies, Cramer Hall Room 345. Please submit the original and 3 copies by the due date. Late applications will not be accepted.

Name: **George M. Coia**

Rank: **Assistant Professor**

Department: **Chemistry**

College/School: **CLAS**

Title of Project: **Vinyl-Bipyridine Based Polymer-Film Electrocatalysts for $O_2$ Reduction**

1. Will this project use: (circle all that apply):

Animal Subjects

Biohazards/Human Blood

Human Subjects

Recombinant DNA

Radiation/Isotopes/Lasers Hazardous Material

For projects requiring review for one of the above reasons, approval must be obtained prior to dispersal of award funds.

2. State the time period involved in this project:

   Start Date: **6/03** End Date: **8/04**

3. Describe in specific detail how you plan to mentor and support the student(s) involved in this project and the significance of the project for the student.

**David Rogow has been doing research in my laboratory since spring of 2003. He received undergraduate research (CH 401) credit during the normal academic terms and was compensated during the summer term. Rogow is an important member of my research team, and his project is a critical component of our program. The mentoring process is facilitated by the fact that Rogow has a desk in the laboratory, meets with me on a daily**

**basis, and reports on his progress at regular group meetings. The work has been supported through start-up funds and a small grant from the American Chemical Society. These sources of funding are sufficient for the materials costs of the project, but ensuring compensation for Rogow in his final summer at PSU will require additional support. Rogow plans to graduate in spring of 2005; his ability to present an honors thesis in Chemistry depends critically on his progress *this* summer, which will be greatly diminished if he finds it necessary to seek other employment. In addition, I intend for Rogow to present his findings in April of this year at a national meeting of the American Chemical Society. If he receives this award, the amount not spent on his wages will be used to offset travel, registration, and presentation costs. Finally, I should point out that Rogow intends to apply next year to a Ph.D. program in chemistry. He should have no difficulty being accepted into a top-ten program. I expect that his undergraduate research experience at PSU will be a valuable primer for graduate study.**

4. List or briefly describe any of your past or current collaborative research or creative activities that have involved undergraduates.

**Since the beginning of my appointment at PSU in the fall of 2000, I have mentored six undergraduate students. At the present time, four undergraduate students are doing research in my laboratory.**

**APPLICATION FORM, 2003-2004**
**PART C: Budget Narrative**
**SCHOLARLY AND CREATIVE ACTIVITY GRANTS FOR UNDERGRADUATES**

(NOTE: submit only 1 budget page for each proposed project)

Explain how ALL of the funds requested for this project will be expended. Monies may be used for items such as student wages (see limits), purchases of software and equipment, student (but not faculty) travel related to the project; funds are not available for faculty compensation or for projects involving course modification or classroom teaching or food purchases. For each category of items listed, provide a very brief justification or explanation, and the specific amount requested.

Category or Description & Explanation

**STUDENT WAGES: At a rate of $10/hour, it costs about $2000 to support an undergraduate researcher over the summer. This award would pay half of that; the remaining will be drawn from other research funding.**

**COSTS ASSOCIATED WITH AMERICAN CHEMICAL SOCIETY MEETING**

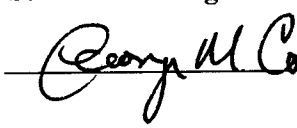
| | |
|---|---|
| **travel to Anaheim, CA:** | **$250** |
| **lodging (3 nights):** | **$150** |
| **registration:** | **$50** |
| **presentation costs:** | **$50** |

**This award would pay most of the costs associated with sending Rogow to the meeting to present; the remaining would be drawn from other research funding.**

(Student wages + OPE may not exceed $1000 for first year recipient or $750 for continuing recipient)

Do you have any extramural funding for this project?: YES /NO If yes, please describe what funding you have and explain the extent to which it supports undergraduates.

**I have a two-year, $35,000 research grant from the American Chemical Society for projects related to $O_2$ reduction in fuel cells. I am free to use these funds to support undergraduate students if I wish, but most of the grant is needed to cover materials costs.**

Faculty Signature:  Date: 11/26/03