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- 1) Michael Stegemiller, Graduate Student, University of Cincinnati. April 2000, and March 2001.
- 2) David J. Monk, Graduate Student, University of Cincinnati. April–December 2001; June–December 2002.
- 3) Ana C. Ebeling, Post Masters, Washington State University, March 2002 – present.

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- 5) Colin Carver, undergraduate student, Columbia Basin College, January - August 2001.
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Progress Report

RESEARCH OBJECTIVE

The general aim of this project is to continue the design and implementation of a new sensor technology that offers the unprecedented levels of specificity needed for analysis of the complex chemical mixtures found at DOE sites nationwide. The new sensor concept combines the elements of electrochemistry, spectroscopy and selective partitioning into a single device that provides three levels of selectivity. The specific goal of this project is the development of a sensor for technetium (Tc) that is applicable to characterizing and monitoring the Vadose Zone and associated subsurface water at the Hanford site. The first goal is a sensor that determines technetium in the chemical form pertechnetate (TcO_4^-).

RESEARCH PROGRESS AND IMPLICATIONS

This report summarizes work during 6/16/01 - 6/15/02 of a three-year project that began on 9/15/99. During this period our efforts have focused on four areas that are discussed in the following sections.

- Electrochemistry of pertechnetate (TcO_4^-) at bare ITO and film-coated ITO electrodes
- Enhancing sensitivity by increasing analyte absorptivity
- Development and characterization of selective films
- Improved field portable spectroelectrochemical sensor

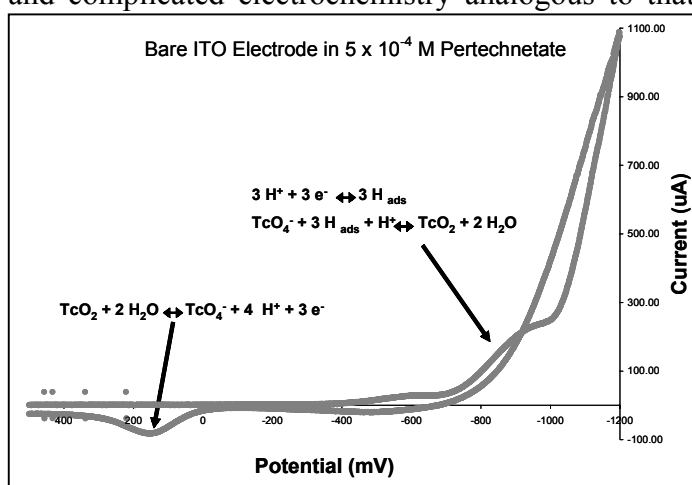
1. Electrochemistry of Pertechnetate (TcO_4^-) at Bare ITO and Film-coated ITO Electrodes.

We have performed experiments at PNNL with our collaborators there that demonstrate key features in the development of the proposed spectroelectrochemical sensor for TcO_4^- .

The electrochemistry of pertechnetate was investigated at ITO because this is the OTE that has worked so well for our spectroelectrochemical sensors. Voltammograms at bare ITO gave a poorly defined reduction wave for TcO_4^- and complicated electrochemistry analogous to that reported by Mazzocchin et al on platinum (1). A representative voltammogram is shown in **Fig. 1** with electrode reactions as assigned by Mazzocchin.

Fig. 1. Cyclic voltammogram of TcO_4^- on ITO. Scan rate 25 mV/s.

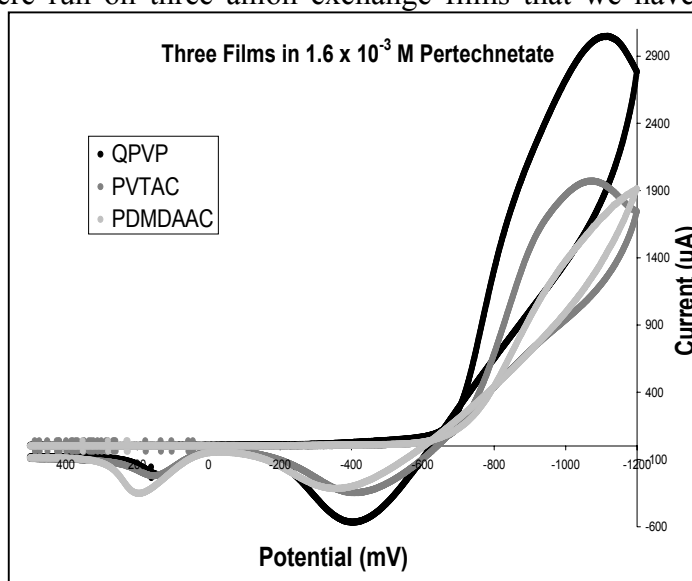
An important observation is that TcO_4^- is reducible to lower oxidation states on ITO, which is a key step in developing the spectroelectrochemical sensor for TcO_4^- .



The electrochemistry of pertechnetate was then investigated at ITO coated with anion exchange films to determine if TcO_4^- is preconcentrated from solution into the sensing film, which is another key step in the sensor concept. Since TcO_4^- is anionic, tests were run on three anion exchange films that we have developed and used successfully to preconcentrate other anions: PVA-PVTAC, PDMDAAC- SiO_2 , and QPVP- SiO_2 . Voltammograms of TcO_4^- (**Fig. 2**) showed a much more sharply defined reduction wave at all three films tested.

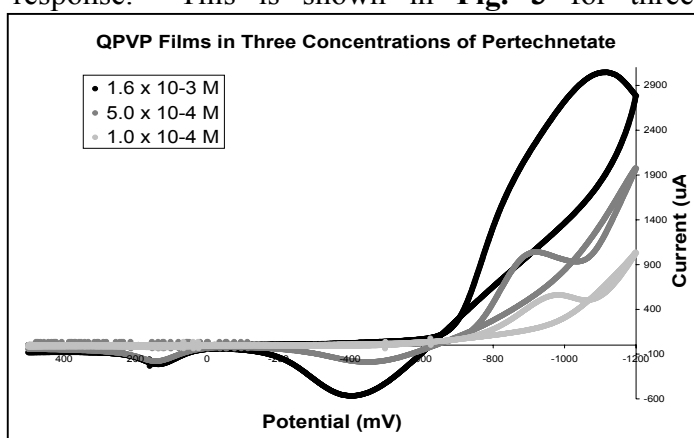
Fig. 2. Cyclic voltammogram of TcO_4^- on ITO coated with films with QPVP, PVTAC and PDMDAAC after 30 min of immersion in sample. Scan rate 25 mV/s.

Four features of the voltammograms are important. First, the current for the reduction wave of TcO_4^- is considerably larger at all of the film-coated ITOs



compared to bare ITO, which is indicative of a preconcentration of TcO_4^- into all of the films. Second, there are different levels of enhancement of the TcO_4^- reduction wave by the three films, even though they are all nominally attracting TcO_4^- electrostatically by interaction with a quaternary ammonium group. These differences indicate the importance of film choice. Third, the voltammogram has now taken on the look of a quasi-reversible couple for the reduction wave of TcO_4^- by the appearance of a new anodic wave on the reverse scan. The appearance of this new anodic wave is accompanied by a proportionate disappearance of the anodic wave attributed to TcO_2 . This behavior is even more marked in repetitive voltammograms (not shown). Thus, the presence of the film has caused a change in mechanism of the reduction of TcO_4^- that is consistent with the formation of a soluble, relatively stable lower oxidation state of Tc, other than the insoluble TcO_2 observed on bare ITO. This change in mechanism is important to our strategy of converting TcO_4^- into a complex for spectroelectrochemical detection. Fourth, the peak heights for both the TcO_4^- reduction wave and this anodic peak are proportional to TcO_4^- concentration, indicating a quantitative response. This is shown in **Fig. 3** for three concentrations of TcO_4^- at a QVP coated electrode. Similar behavior is observed with films containing PDMDAAC and PVTAC.

Fig 3. Cyclic voltammograms of three concentrations of TcO_4^- on ITO coated with film of QPVP after 30 min of immersion in sample. Scan rate 25 mV/s.



Interestingly, the fraction of reduced Tc that forms TcO_2 as a precipitate on the electrode scatters light and this by itself could be the basis for a spectroelectrochemical sensor. At high concentrations this can be visualized (**Fig. 4 left**). Measurement of the absorbance (scattering) of the precipitate by passing light perpendicularly through the film and the substrate ITO showed a linear relationship between concentration of TcO_4^- in the solution to which the electrode was exposed and absorbance and radioactivity from ^{99}Tc by beta counting (**Fig. 4 right**).

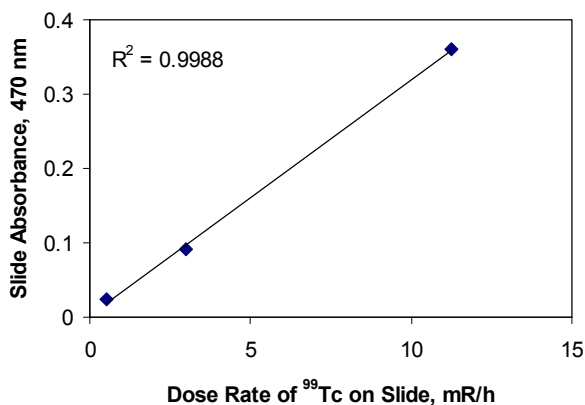
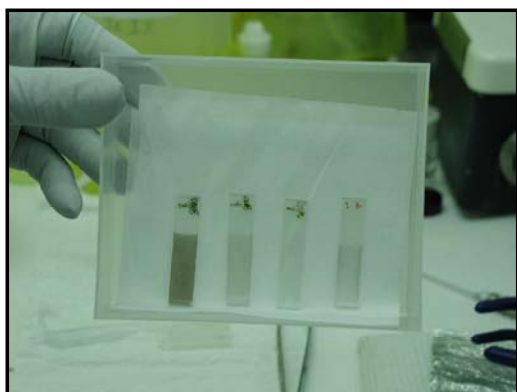


Fig. 4. (left) Photograph showing TcO_2 deposited in the film on ITO from different concentrations of TcO_4^- . **(right)** Plot of absorbance versus ^{99}Tc dose rate for three concentrations of TcO_4^- .

2. Enhancing Sensitivity by Increasing Analyte Absorptivity. The spectroelectrochemical sensor is most directly applicable to analytes that have two oxidation states with sufficiently different spectra to give a large change in ΔA upon electrochemical modulation. However, many analytes of importance do not exhibit this property, and the applicability of the sensor would be severely restricted if these were the only analytes that could be detected with reasonable sensitivity. Therefore, a major focus of this project is to expand the applicability of the spectroelectrochemical sensor to analytes with vanishing or only weak spectral changes in the visible range for electromodulation such as pertechnetate. Our approach is to form a metal complex in the sensing film by immobilizing a complexing ligand that serves as a chromophore in the film. When the metal ion partitions into the film, it reacts with the ligand in the film to form a complex that gives a much larger optical change when it is electrochemically modulated. Basically, the strategy is to enhance $\Delta\varepsilon$ (where ε = molar absorptivity) between the two oxidation states of the metal ion.

We have recently demonstrated this strategy with two examples: a sensor for Fe^{2+} using the ligand 2,2'-bipyridyl (bpy) and for Cu^{2+} using neocuproine as the ligand. This general strategy is shown for Fe^{2+} in **Fig. 5**.

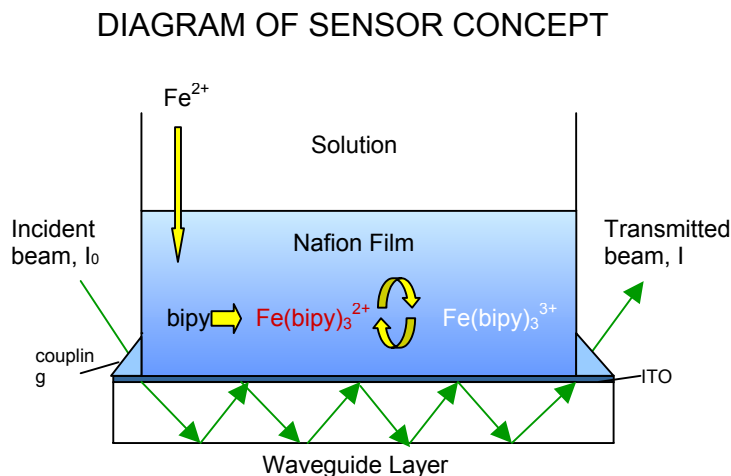


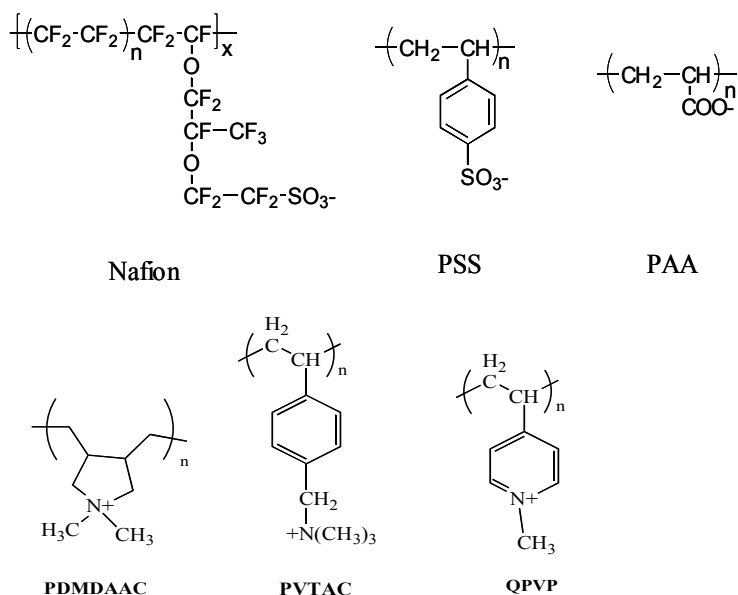
Fig. 5. Schematic diagram of spectroelectrochemical sensor for Fe^{2+} .

The novelty of this sensor stems from its ability to uptake colorless iron ion (Fe^{2+}) from solution and complex it with an organic ligand, 2,2'-bipyridine (bipy), which has been previously loaded in the optically transparent charge-selective Nafion film coating the electrode. The resulting complex ion, tris-(2,2'-bipyridyl)iron(II), $Fe(bipy)_3^{2+}$, absorbs strongly, thus making it easily detectable via optical spectroscopy. $Fe(bipy)_3^{2+}$ loaded into the selective film is oxidized to colorless $Fe(bipy)_3^{3+}$, which gives rise to an absorbance change for quantifying iron.

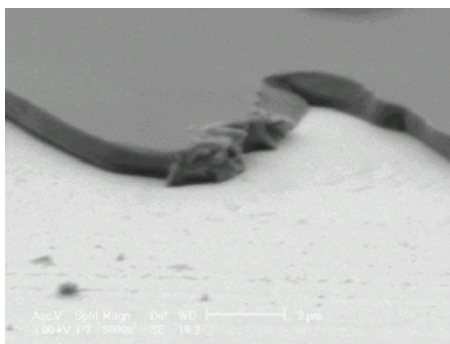
3. Development and Characterization of Materials for Selective Films. A critical component of the sensor is the selective film into which the analyte partitions for detection by spectroelectrochemical modulation. Required characteristics of the film are:

- Preconcentrate the analyte into the film
- Provide a level of selectivity by excluding at least some potentially interfering substances
- Exhibit optical transparency at the wavelength used for detection
- Electrochemically inactive potential window
- Not interfere with electrochemistry at the underlying electrode
- Form thin, uniform films by spin-coating
- Be sufficiently robust for the intended application
- Reasonable cost

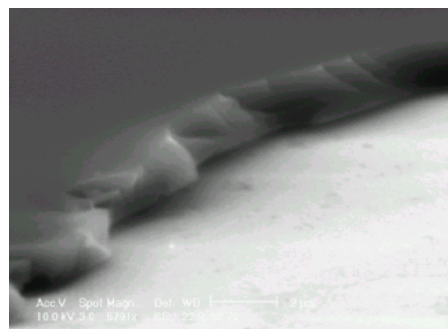
Consequently, coincident with our work on sensor design, we have developed chemically-selective optical materials that satisfy these criteria. We have developed two classes of optical quality chemically-selective films based on the two different host materials, namely, sol-gel processed silica and cross-linked poly(vinyl alcohol). These hosts can be bonded to oxide surfaces, for example, glass or indium tin oxide yielding sufficiently robust films on sensor surfaces.



In turn, these composites of host material and the ionomers shown above function well as either cation or anion preconcentration films. These films are amazingly uniform as shown in the scanning electron micrographs (**Fig. 6**).



QPVP-SiO₂



PVTAC-PVA

Fig 6. Scanning electron micrographs of two types of films on ITO. Thicknesses are ca. 500 nm.

Evaluation of the optical constants for these films over a wide wavelength range and, recently, the dynamics of the uptake of various analytes has been achieved using spectroscopic ellipsometry. Our experience with these films has shown that they preconcentrate analytes from very dilute solutions up to film concentrations approaching *one molar*, which leads to an enormous enhancement in sensitivity of the sensor. Adapting these films to fluorescence spectroelectrochemical sensing will involve combining selective fluorophores and other reagents into the films.

New Ellipsometry Cell for Selective Film Dynamics. A new liquid cell design for in situ ellipsometric measurements on transparent multilayer samples using variable angle spectroscopic ellipsometry has been designed and tested. In this cell, films made on transparent sensor substrates are in direct contact with liquid solution. Ellipsometry measurements are made through the transparent substrate, that is, from the back-side relative to the incident light so that films are in continuous contact with the liquid. This cell is not limited to just one angle of incidence of light, allowing the films to be characterized at several angles before, during, and after liquid contact. The spectral range of measurements is limited only by absorption of light in the underlying transparent substrate and not by the liquid solution that the film is in contact with. As a demonstration, we have measured and analyzed the dynamics of an ITO film on glass undergoing acid etching (such as might be used for patterning of ITO for sensor arrays); see **Fig 7**. Data from this in situ experiment were successfully modeled and the ITO layer thickness decreased uniformly during the etching process with an average etch rate of 0.23 nm/min (see **Fig 8**).

Fig. 7. Measured (circles) and calculated (solid lines) data from model with fitted thickness for etching of ITO on Corning 1737F glass. For simplicity, data at only four wavelengths (in nm: 400, 500, 600 and 700) are presented which cover different parts of the spectrum. For fitting, the complete data set was used. Experimental and calculated values at other wavelengths matched comparably well to data presented. Depolarization was also measured and included in fitting process but data are not presented. It too matched calculated data. Arrows point to data series in increasing wavelength direction. In the Δ graph, the discontinuity from low delta values to high is artificial. Δ is continuous 360° function and only for graphing purposes it is discontinued at -90° and continues at 270° (these two points are one and same point in polar coordinates).

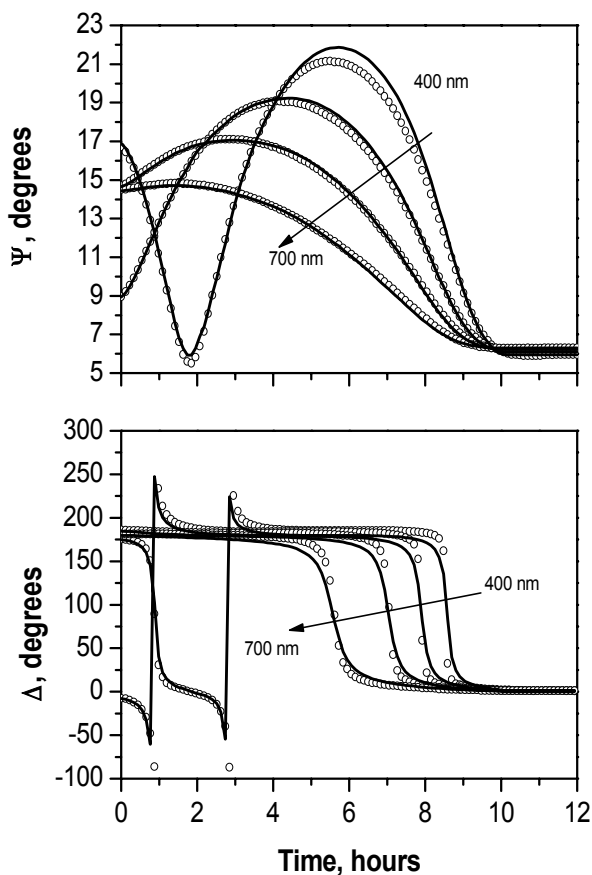
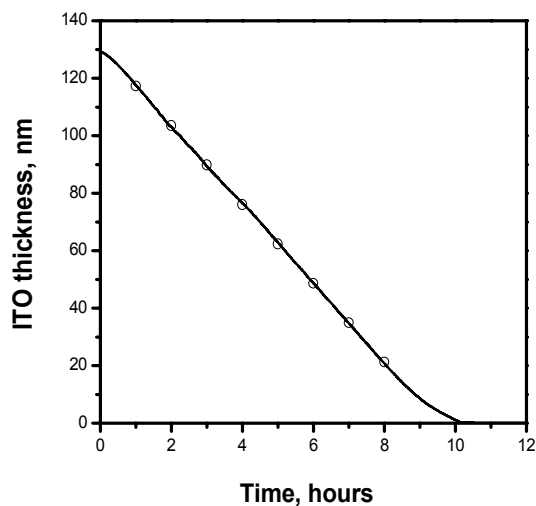


Fig. 8. Fitted ITO layer thickness during the course of the dynamic experiment (see also Fig. 8 above). Solid line represents determined thickness at each time slice of the data set. Circles mark linear fit region for etching.

In proof-of-principle studies we have shown that it is possible to measure the uptake of analytes in the spectroelectrochemical sensor selective film *in situ*, that is, during actual sensor operation. We made this breakthrough using the new ellipsometer cell described above. Studies of dynamics of chemically-selective films for pertechnetate on transparent ITO sensor substrates are underway.

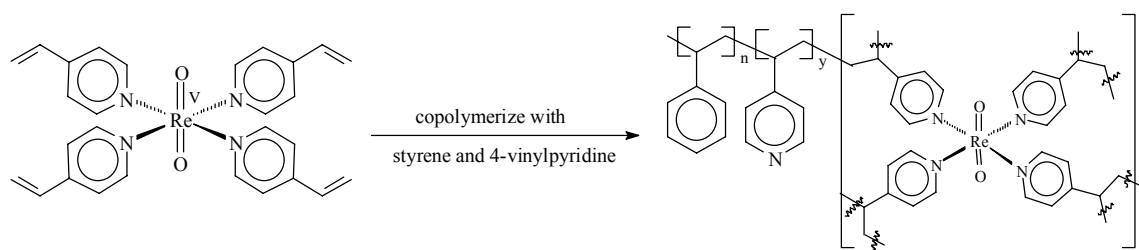


Pertechnetate Selective Film Studies. Of the three selective films for pertechnetate discussed previously, the PVTAC-PVA film shows very promising behavior. As a result, we have further studied the physical chemical and optical properties of this interesting film material. We have determined the optical constants of this material by spectroscopic ellipsometry under various conditions of hydration and ion exchange. Quantitative studies of the robustness of this material

(dimensional and chemical stability, optical constants) under typical sensor aqueous environments and we find that it is a very stable film material. In a comparative series of studies with other pertechnetate film candidates (QPVP-SiO₂, PDMDAAC-SiO₂), we have found that PVTAC-SiO₂ films have the best overall properties for pertechnetate sorption. Thus, knowing the optical constants and physical properties of this material we are now in the position of being able to design spectroelectrochemical sensors with this as the selective film.

4. Re Complexes

A rhenium complex has now been copolymerized within a polymer matrix, specifically 79.5% styrene and 20.0% 4-vinylpyridine, using AIBN as radical initiator (Scheme 1). The bright yellow polymer obtained is reasonably soluble in THF and CH₂Cl₂ with $\overline{M}_w = 500,000$. The rhenium complex monomer (**Fig. 9**) and the complex-containing polymer (**Fig. 10**) exhibit emission spectra in dichloromethane that are similar: ReO₂(4-vpy)₄I, 630 nm (excitation at 388 nm); ReO₂(4-vpy)₄I/styrene/4-vinylpyridine polymer, 640 nm (excitation at 362 nm). Our approach to covalently bind the rhenium complex within the polymer matrix works as predicted. Over the course of several weeks, a large sample of the polymer was suspended in CH₃CN; the polymer itself softened but there was no evidence of the rhenium complex leaching from the polymer itself (the monomer is very soluble in CH₃CN).



Scheme 1. Copolymerization of Re(V) complex with styrene and 4-vinylpyridine.

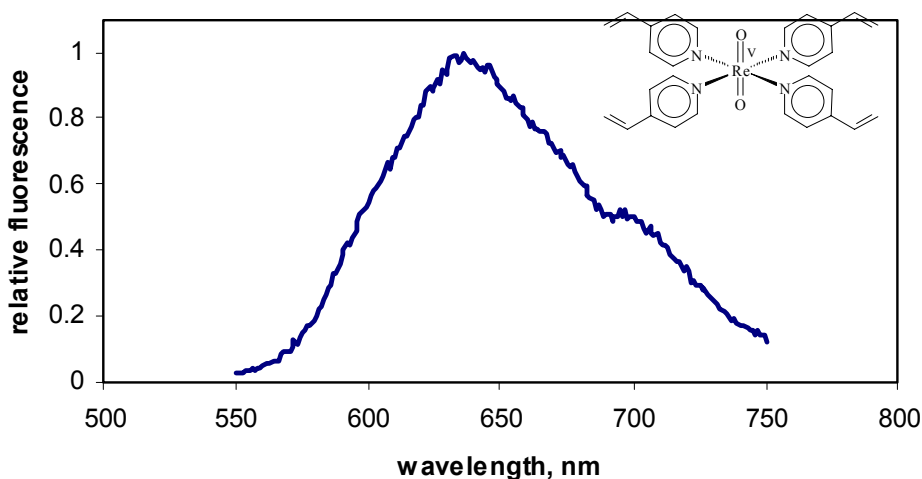


Fig 9. Fluorescence spectrum of ReO₂(4-vpy)₄I monomer in CH₂Cl₂. Excitation for fluorescence spectrum was 380nm.

We have also recently prepared a porphyrin molecule with a pendant vinyl group, and have copolymerized the porphyrin into the same styrene/4-vinylpyridine mixture to obtain a deep red polymer that is soluble in THF and CH₂Cl₂. The porphyrin-containing polymer and the

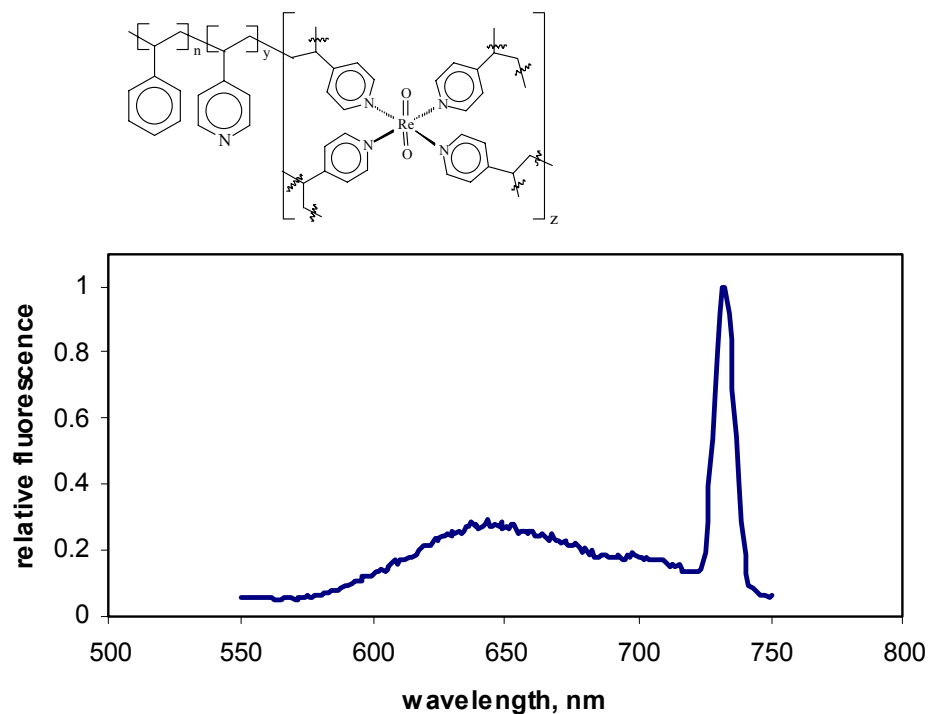


Fig 10. Fluorescence spectra of polymer 0.5% ReO₂(4-vpy)₄I / 20% 4-vpy / 79.5% styrene (neat sample). The band with maximum at 735 nm is due to scattering.

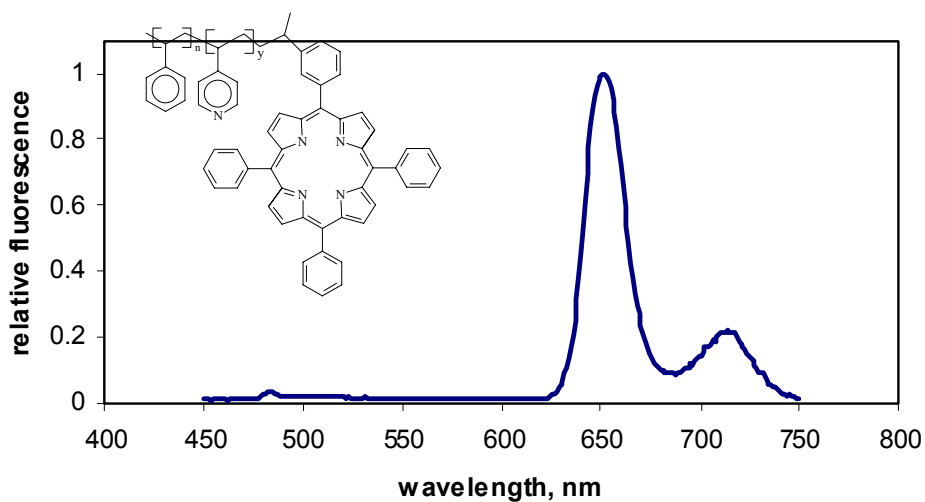


Fig 11. Emission spectrum of tetraphenylporphyrin copolymerized with styrene and 4-vinylpyridine.

monomer have virtually identical fluorescence spectra with emission observed at 650 and 714 nm (excitation at 418 nm) (See **Fig. 11**). The porphyrin materials provide the basis for complexation and detection of first-row transition metals for the spectroelectrochemical sensor; of particular interest are Cr and Cu. Further studies are under way to prepare porphyrin-type macrocycles that exhibit the desired optical properties for Re/Tc complexes (Re complexes to a single face of standard porphyrin molecules).

We have completed preparation 2-methyl-2'-vinyldipyridyl (vbpy, a bidentate ligand) and the $\text{ReO}_2(\text{vbpy})_2\text{I}$ complex. The $\text{ReO}_2(\text{vbpy})_2\text{I}$ complex is a fluorescent indigo blue-colored complex. Copolymerization of the templated rhenium complex will give the proper ligand set for coordination of Tc for the sensor.

5. Improved Field Portable Spectroelectrochemical Sensor.

Second generation instrumentation consisting of control electronics for the electrochemistry, electronics for the optical components, and a “virtual instrument” (**Fig. 12**) for the field portable spectroelectrochemical sensor has been developed and tested.

Improvements over the first generation instrument include: The design and development of a custom external data acquisition system that performs the same function as the previous National Instruments Data Acquisition Card and allows for a laptop computer to control experiments. Custom electronics, which have decreased the size of the rest of the instrumentation to roughly the dimensions of a paperback book. New software that facilitates the real time display of experimental data, which was not possible on previous systems, and allows for the generation of complex waveforms for electrochemical modulation. When this function is employed with battery control, it allows for remote operation over extended periods of time for analytical flexibility. Other improvements include reconfigurable, customized gain settings for use of large surface area electrodes and flexible optical system allowing the use of various LED's for selective wavelength analysis. Laser diodes may also be employed.

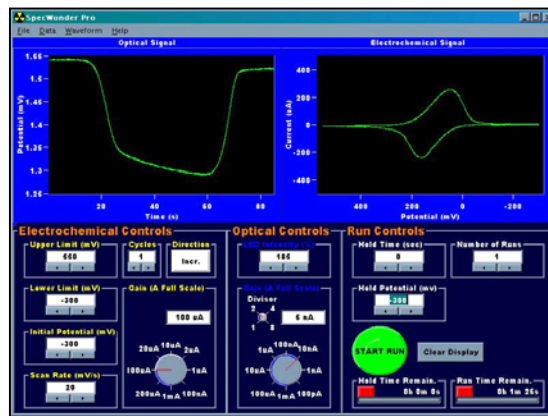


Fig. 12. Virtual instrument for spectroelectrochemical sensor. Displays show an absorbance plot on the left and the associated cyclic voltammogram on the right.

6. Demonstration of Fluorescence Spectroelectrochemical Detection. The excellent detection limits of fluorescence spectroscopy are well known, and fluorescence is often the method of choice when achieving a low detection limit is important. Consequently, we are

beginning to develop a fluorescence-based spectroelectrochemical sensor, which will enable us to extend the sensor to lower limits of detection. We have reported the electrochemistry and absorption spectroscopy of $\text{Ru}(\text{bpy})_3^{2+}$ in the Nafion- SiO_2 and other coated sensors. We have now done “proof of principle” measurements of the fluorescence of a model analyte ($\text{Ru}(\text{bpy})_3^{2+}$) entrapped in a chemically selective film (Nafion) on an ITO glass multiple internal reflection (MIR) optic. To excite the fluorescence we used the evanescent wave mode excitation. Using a HeCd blue laser line, the fluorescence of $\text{Ru}(\text{bpy})_3^{2+}$ can be easily evanescently excited and measured by collecting fluorescence from a single fluorescent spot on the top side of the MIR optic (**Fig. 13**). For fluorescence data acquisition, the end of a fiber optic bundle was butted up against a single (red) spot and the fluorescence collected by the bundle was dispersed by a monochromator and detected with a cooled CCD camera. When a potential was applied to the ITO, the fluorescence decreased as $\text{Ru}(\text{bpy})_3^{3+}$ was formed. This decrease, and the recovery of $\text{Ru}(\text{bpy})_3^{2+}$ with reversing the potential, was associated with concentration and potential. With these measurements, we have demonstrated that the limit of detection based on fluorescence changes of just one fluorescing $\text{Ru}(\text{bpy})_3^{2+}$ spot is $\approx 10^{-10}$ M and that is four orders of magnitude lower than we have reported with absorbance mode and the same sensor. In turn, this means that the fluorescence spectroelectrochemical sensor can also be miniaturized and yield extremely low limits of detection.

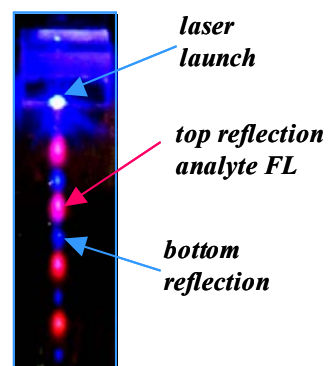


Fig. 13. Photograph of a top view of a spectroelectrochemical sensor with $\text{Ru}(\text{bpy})_3^{2+}$ preconcentrated in the selective film. HeCd laser 441.6 nm excitation of fluorescence launched by prism occurs with each reflection at the ITO/selective film interface as shown by red fluorescence of $\text{Ru}(\text{bpy})_3^{2+}$. Reflections at the air-glass interface (blue spots on bottom side) alternate with the red spots in a top side view of the sensor.

7. Conclusions

- TcO_4^- preconcentrates in films containing anion exchange polymers and can be electrochemically reduced. This is the first step in developing a spectroelectrochemical sensor for TcO_4^- .
- Ellipsometry is an effective technique for evaluating sensor films.
- The sensor is most directly applicable for the detection of ionic species that are electroactive and that exhibit an optical change upon electrolysis. However, species not meeting this requirement can be sensed after being converted into a strong chromophore by forming a metal complex within the sensing film.
- A templated rhenium complex can be copolymerized to form a film that should give the proper ligand set for coordination of Tc for the spectroelectrochemical sensor.
- The spectroelectrochemical sensor and associated instrumentation are portable and easily transported to and used at DOE sites.
- Fluorescence offers a means of dramatically increasing the sensitivity of the spectroelectrochemical sensor.

8. List of Collaborations

- *June to December 2001* – UC Student David Monk performs extended research visit at PNNL and obtains Rad Worker II certification.
- *August 2001* – All collaborators attend and present at the ACS National Conference in Chicago.
- *February 2002* – William Heineman, Carl Seliskar, Sam Bryan, and Tim Hubler meet at PNNL to discuss research progress and future aims.
- *March 2002* – William Heineman, Carl Seliskar, Sam Bryan, and Tim Hubler meet at PNNL to discuss research progress and future aims.
- *May to December 2002* – David Monk performs second extended research visit to PNNL.
- *Summer 2002* – Imants Zudans travels to PNNL initiating experiments on new hybrid electrode materials.

9. Literature Cited

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PLANNED ACTIVITIES

Given the encouraging results that were obtained for TcO_4^- at PNNL, a graduate student from UC (David Monk) is spending June – December at PNNL doing more experiments with TcO_4^- . He will mainly focus on the synthesis and testing of ligands for complex formation with electrochemically reduced TcO_4^- for the TcO_4^- sensor. Another student is spending about one month at PNNL making new types of electrodes for the sensor such as gold coated ITO. We shall continue our work of developing and characterizing new films to improve sensor performance

INFORMATION ACCESS

Publications:

◆ Novel Spectroelectrochemical Sensor for Ferrocyanide in Hanford Waste Simulant in *Nuclear Site Remediation: First Accomplishments of the Environmental Management Science Program*, ACS Symposium Series 778 (P. G. Eller and W. R. Heineman, Eds.), 364-378, ACS, New Orleans, LA, 2001. M. Maizels, M. Stegemiller, S. Ross, A. Slaterbeck, Y. Shi, T. H. Ridgway, W. R. Heineman, C. J. Seliskar, S. A. Bryan.

◆ Spectroelectrochemical Sensing Based on Multimode Selectivity Simultaneously Achievable in a Single Device. 8. Selectivity at Poly(vinyl alcohol)-Polyelectrolyte Blend Modified Optically Transparent Electrodes, *Electroanalysis*, 13, 613-620 (2001). L. Gao, C. J. Seliskar, W. R. Heineman.

◆ Spectroelectrochemical Sensing Based on Multimode Selectivity Simultaneously Achievable in a Single Device. 12. Characterization of a Channel Waveguide Sensor, S. E. Ross, C. J. Seliskar, W. R. Heineman, S. Aryol, J. H. Nevin in *Chemical and Biological Sensors and*

Analytical Methods II, (eds. M. Butler, P. Vanysek, N. Yamazoe). Proceedings Volume 2001-18, The Electrochemical Society, Pennington, NJ, pp. 499-510.

◆ Spectroelectrochemical Sensing Based on Multimode Selectivity Simultaneously Achievable in a Single Device. 13. Detection of Aqueous Iron by In Situ Complexation with 2,2'-Bipyridine, J. N. Richardson, A. L. Dyer, M. L. Stegemiller, I. Zudans, C. J. Seliskar, W. R. Heineman, *Anal. Chem.* 000, 0000-0000, 2002. (In press)

◆ Spectroelectrochemical Sensing Based on Multimode Selectivity Simultaneously Achievable in a Single Device. 15. Development of Portable Spectroelectrochemical Instrumentation, D. J. Monk, T. H. Ridgway, C. J. Seliskar, W. R. Heineman, accepted, *Electroanalysis*, 2002.

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◆ Spectroelectrochemical Sensing Based on Multimode Selectivity Simultaneously Achievable in a Single Device. 11. Design and Evaluation of a Small Portable Sensor for the Determination of Ferrocyanide in Hanford Waste Samples, M.L. Stegemiller, W. R. Heineman, C. J. Seliskar, T. H. Ridgway, S. A. Bryan, T. Hubler, R. L. Sell, submitted, *Environmental Science & Technology*, 2002.

Book

Nuclear Site Remediation: First Accomplishments of the Environmental Management Science Program, P. G. Eller, W. R. Heineman, Eds., ACS Symposium Series **778**, ACS, New Orleans, LA, 2001.

Presentations:

Talks at Conferences (*presenter)

◆ Chemical Sensors: Why They are Important to You, W. R. Heineman*, Southern Illinois University at Edwardsville, February 18, 2002, William J. Probst Memorial Lecture. (Invited lecture)

◆ Sensors: Significant Developments in Selectivity, W. R. Heineman, ACS 222nd National Meeting, Chicago, IL, Aug. 26-30, 2001. (Invited lecture)

◆ Evaluation of a Novel Silica Composite Containing Quaternized poly(4-vinylpyridine) as an Anion Exchanger for use in a Chemical Sensor for Technetium, S. D. Conklin*, W. R. Heineman, C. J. Seliskar, ACS 222nd National Meeting, Chicago, IL, Aug. 26-30, 2001.

◆ Computer-controlled, Remote Spectroelectrochemical Sensor System, D. J. Monk*, T. H. Ridgway, C. J. Seliskar, W. R. Heineman, ACS 222nd National Meeting, Chicago, IL, Aug. 26-30, 2001. (Poster session)

◆ Development of a Spectroelectrochemical Sensor for Pertechnetate, M. L. Stegemiller*, W. R. Heineman, C. J. Seliskar, T. H. Ridgway, S. A. Bryan, T. L. Hubler, ACS 222nd National Meeting, Chicago, IL, Aug. 26-30, 2001. (Poster session)

◆ Development of New Ion-Exchange Polymers for Technetium Sensors Applicable to the Vadose Zone, T. L. Hubler*, S. A. Bryan, C. T. Carver, M. E. Thornton, K. L. Hammack, C. J. Seliskar, W. R. Heineman, ACS 222nd National Meeting, Chicago, IL, Aug. 26-30, 2001. (Poster session)

◆ PVTAC and Spectroelectrochemical Sensing, J. R. Paddock*, C. J. Seliskar, W. R. Heineman, ACS 222nd National Meeting, Chicago, IL, Aug. 26-30, 2001. (Poster session)

- ◆ Spectroelectrochemical Sensor for Ferrocyanide and Technetium, W. R. Heineman*, M. Maizels, M. Stegemiller, J. DiVirgilio Thomas, S. Ross, T. Rarog, S. Conklin, J. Wherley, I. Zudans, D. Monk, T. H. Ridgway, C. J. Seliskar, S. A. Bryan, T. L. Hubler, ACS 222nd National Meeting, Chicago, IL, Aug. 26-30, 2001. (Invited lecture)
- ◆ Spectroelectrochemical Sensing Based on Multimode Selectivity Simultaneously Achievable in a Single Device. 12. Characterization of a Channel Waveguide, S. Ross, C. Seliskar, W. Heineman*, S. Aryol, J. Nevin, 2001 Joint International Meeting of the Electrochemical Society and the International Society of Electrochemistry, San Francisco, CA, Sept. 2-7, 2001. (Invited lecture)
- ◆ Spectroelectrochemical Sensors, W. R. Heineman, 40th Eastern Analytical Symposium & Exposition, Atlantic City, NJ, Oct. 1-4, 2001. (Invited lecture)
- ◆ Spectroelectrochemical Sensor for Ferrocyanide and Technetium, W. R. Heineman*, M. Maizels, M. Stegemiller, D. Monk, T. Rarog, S. Conklin, J. Wherley, I. Zudans, T. H. Ridgway, C. J. Seliskar, S. A. Bryan, T. L. Hubler, Twelfth Symposium on Separation Science & Technology for Energy Applications, Gatlinburg, TN, Oct. 15-18, 2001.
- ◆ Dynamics of Chemically Selective Films and Their Thickness Optimization for Sensor Applications, I. Zudans*, C. J. Seliskar, W. R. Heineman, Pittcon 2002, New Orleans, LA, March 17-22, 2002.
- ◆ A Spectroelectrochemical Sensor for Pertechetate Based on a Quaternized Poly(4-vinylpyridine)-SiO₂ Film, S. D. Conklin*, W. R. Heineman, C. J. Seliskar, Pittcon 2002, New Orleans, LA, March 17-22, 2002.
- ◆ Computer-Controlled Remote Spectroelectrochemical Instrument, D. J. Monk*, T. H. Ridgway, W. R. Heineman, C. J. Seliskar, T. L. Hubler, S. A. Bryan, Pittcon 2002, New Orleans, LA, March 17-22, 2002.
- ◆ Design and Development of a New Hybrid Spectroelectrochemical Sensor, W. R. Heineman*, Pittcon 2002, New Orleans, LA, March 17-22, 2002. (Invited lecture)
- ◆ Characterization of a Cation Radical at a Polymer-Modified Electrode, J. H. Thomas*, J. M. Drake, J. Johnson, C. J. Seliskar, H. B. Halsall, W. R. Heineman, Pittcon 2002, New Orleans, LA, March 17-22, 2002. (Poster session)
- ◆ Poly(vinylbenzyltrimethylammonium chloride) Spectroelectrochemical Sensing, J. R. Paddock*, C. J. Seliskar, W. R. Heineman, Pittcon 2002, New Orleans, LA, March 17-22, 2002. (Poster session)
- ◆ Comparisons of the Uptakes of ABTS into Three Cationic Polymer Films, J. M. Drake*, J. H. Thomas, J. R. Paddock, M. Stegemiller, I. Zudans, S. Conklin, J. Johnson, W. R. Heineman, C. J. Seliskar, H. B. Halsall, 223rd ACS Meeting, Orlando, FL, April 7-11, 2002. (Poster session)
- ◆ Electrochemical and Spectroelectrochemical Evaluation of tris-(2,2'-bipyridyl)iron(II) at Bare and Nafion-coated ITO Electrodes: Toward a Spectroelectrochemical Sensor for Aqueous Iron, J. N. Richardson*, A. L. Dyer, M. L. Stegemiller, I. Zudans, C. J. Seliskar, W. R. Heineman, 223rd ACS Meeting, Orlando, FL, April 7-11, 2002. (Poster session)
- ◆ Development and Evaluation of a Multimode Spectroelectrochemical Sensor for Detection of Aqueous Iron, A. Dyer*, J. N. Richardson, M. Stegemiller, I. Zudans, C. J. Seliskar, W. R. Heineman, 223rd ACS Meeting, Orlando, FL, April 7-11, 2002. (Poster session)
- ◆ Sensors Based on Spectroelectrochemistry, W. R. Heineman*, M. Stegemiller, M. Maizels, J. DiVirgilio-Thomas, T. Rarog, S. Conklin, J. Paddock, I. Zudans, D. Monk, T. Ridgway, C. Seliskar, S. Bryan, T. Hubler, in the Symposium on Progress in Methods Used to Solve

Electrochemical Problems: Part 3-New Developments in Optical Methods, 201st ECS Meeting, Philadelphia, PA, May 12-17, 2002. (Invited lecture)

◆ Development of a New Hybrid Spectroelectrochemical Sensor, W. R. Heineman*, T. Rarog, S. D. Conklin, J. R. Paddock, I. Zudans, D. J. Monk, T. H. Ridgway, C. J. Seliskar, in the Symposium on Microbiosensors and Microarrays, Fifth Workshop on Biosensors and Biological Techniques in Environmental Analysis, Cornell University, Ithaca, NY, May 31-June 4, 2002. (Invited lecture)