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Authors: Heineman, William R.; Seliskar, Carl J.; Bryan, Samuel A.; Hubler, Timothy L.

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Recipient/contractor point of contact: William R. Heineman, Distinguished Research Professor, William.Heineman@uc.edu, 513-556-9210; University of Cincinnati

Abstract

During the period of this grant several significant milestones have been passed pursuant to designing a fluorescence sensor for pertechnetate (TcO_4^-). They are as follows: Fluorescence spectroelectrochemistry and less than picomolar limit of detection for a model non-radioactive analyte have been demonstrated. The spectroelectrochemical sensor and associated instrumentation for fluorescence mode of operation have been made, are portable, and easily transported to and used at DOE sites. The sensor has sufficient selectivity for its application to complex samples, even including tank waste, that exist at DOE sites such as the Hanford Site. Pertechnetate has been preconcentrated in sensor films and electrochemically reduced. This is the first critical step in operation of a spectroelectrochemical sensor for TcO_4^- . New Tc complexes have been made that fluoresce and these complexes have been preconcentrated and electrochemically modulated in a sensor film leading to fluorescence modulation, which is the second critical step in operation of the spectroelectrochemical sensor for TcO_4^- . We have determined that fluorescence offers a means of dramatically improving the limit of detection. Based on measurements on our new fluorescent complexes of Tc, we estimate the limit of detection for the sensor to be $5 \times 10^{-12}\text{M}$. In related work, we have shown that the sensitivity of the spectroelectrochemical sensor for some metal cations can be improved by forming a metal complex with better optical and electrochemical properties. In addition, some heavy metals can be detected with the spectroelectrochemical sensor by depositing them directly as metals on the sensor surface.

Executive Summary

- Fluorescence spectroelectrochemistry and less than picomolar limit of detection for model analyte demonstrated.
- The spectroelectrochemical sensor and associated instrumentation for fluorescence mode of operation have been made, are portable, and easily transported to and used at DOE sites.
- The sensor has sufficient selectivity for its application to complex samples, even including tank waste, that exist at DOE sites such as the Hanford Site.
- TcO_4^- preconcentrated in sensor films and electrochemically reduced. This is the first step in operation of a spectroelectrochemical sensor for TcO_4^- .
- New Tc complexes made fluoresce and these complexes have been preconcentrated and electrochemically modulated in a sensor film leading to fluorescence modulation, which is the second step in operation of the spectroelectrochemical sensor for TcO_4^- .
- Fluorescence offers a means of dramatically improving the limit of detection. Based on measurements on fluorescent complexes of Tc, we estimate the limit of detection to be $5 \times 10^{-12}\text{M}$.
- Sensitivity of the spectroelectrochemical sensor for some metal ions can be improved by forming a metal complex with better optical and electrochemical properties.
- Some heavy metals can be detected with the spectroelectrochemical sensor by depositing them as metals on the sensor surface.

Final Technical Report (DOE grant DE-FG-02-03ER63655)

The general aim of our work funded by DOE is 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 sensor is based on a unique combination of electrochemistry, spectroscopy and selective partitioning into a film that collectively provide an extraordinary level of selectivity for the target analyte. Our goal is a reversible sensor in which the fluorescent Tc-complex formed in the film is re-oxidized to TcO_4^- and free ligand. TcO_4^- in the film would then re-equilibrate with the sample. The sensor would therefore satisfy requirements for both applications described above. Making significant progress towards this goal has required us to discover new chemistry and spectroscopy for technetium itself. Indeed, we needed to find the first technetium complexes which fluoresced in solution at room temperature – we have made that breakthrough discovery this last year. **We are now in the unique position of being able to reach our goal of a reversible sensor for Tc.**

The concept for this TcO_4^- sensor is innovative and represents a breakthrough in sensor technology. The sensor concept derives from several important factors:

- Our pioneering development of a sensor that provides three modes of selectivity by the judicious combination of electrochemistry, spectroscopy, and selective partitioning into a film
- Our prior experience with Tc chemistry that provides workable strategies with which to apply the unique characteristics of the sensor to TcO_4^-
- Our prior work on formulating and coupling new chemically selective optical materials to sensor surfaces as thin films
- Our recent success in fabrication and testing of a new miniature fluorescence spectroelectrochemical cell for measurements on very low concentrations of metal complexes

The relationship of our prior successes that were leveraged as contributions is illustrated in **Figure 1**.

Fig. 1: Relationship of the proposed research to successes under EMSP projects.

Development of Spectroelectrochemical Sensor Supported by DOE

Under DOE funding (this grant and our previous grant: Heineman, WR; Seliskar, CJ; Ridgway, TH. *Design and Development of a New Hybrid Spectroelectrochemical Sensor*). DOE-EMSP Grant # DE-FG07-96ER2311) we have developed sensors and associated portable instrumentation, demonstrated detection of several analytes, and analyzed one complex sample from a DOE site. Specifically, we have accomplished the following:

Demonstration of sensor concept on different analytes

- Sensor concept demonstrated for direct detection of analyte that exhibits a large absorbance change during electromodulation using ferrocyanide¹⁻⁸, Ru(bpy)₃²⁺, Re(DMPE)₃⁺^{4,5,9,11}, MnO₄⁻¹², and methyl viologen¹³ as model analytes
- Sensor concept demonstrated for detection of analyte that exhibits a negligible absorbance change during electromodulation by forming a strongly chromophoric metal complex within the sensing film using Fe²⁺ and Cu²⁺ as analytes^{14,15}
- Sensor concept demonstrated for detection of non-absorbing analyte indirectly via a strongly absorbing mediator for electron exchange using ascorbate as an analyte¹⁶

Sensor fabrication, selective materials development, and portable instrumentation development

- Sensor miniaturized with waveguides as the optical element¹⁷⁻¹⁹
- Robust materials with required properties for sensing layer for detection of both cationic and anionic analytes developed^{9,11,20-26}
- Selectivity against direct interferences demonstrated^{5,7,27}
- Portable instrumentation for sensor operation in visible absorbance mode developed^{2,8}
- Cyclic, step, and sinusoidal electrochemical waveforms evaluated²⁸
- Signal averaging used to improve detection limit¹⁰

Application to Hanford tank waste

- Determination of ferrocyanide in Hanford U-Plant 2 simulant solution demonstrated^{6,27}
- Sensor system (microcell and instrumentation) developed for analysis of tank waste sample for ferrocyanide at Hanford^{2,6,8,29}
- Demonstration of sensor for determination of ferrocyanide in actual Hanford tank waste²

Sensors for TcO₄⁻ – results

- Fluorescence spectroelectrochemistry with less than picomolar limit of detection for model analyte demonstrated³⁰
- Portable spectroelectrochemical sensor and associated instrumentation for fluorescence mode for easy transportation to and use at DOE sites
- Sufficient selectivity for application to complex samples, even including tank waste, that exist at DOE sites such as the Hanford Site.
- First step in operation of a spectroelectrochemical sensor for TcO₄⁻ demonstrated: TcO₄⁻ preconcentrated in sensor films and electrochemically reduced
- Second step in operation of the spectroelectrochemical sensor for TcO₄⁻ demonstrated: new Tc complexes made that fluoresce and preconcentrate and electrochemically modulate in a sensor film leading to fluorescence modulation

Electrochemistry of TcO₄⁻ at Bare ITO and Film-coated ITO Electrodes

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 thin, uniform films
- Provide a level of selectivity for the analyte by excluding at least some potentially interfering substances
- Exhibit optical transparency at the wavelength used for optical detection
- Electrochemically inactive potential window
- Not interfere with electrochemistry at the underlying electrode
- Be sufficiently robust for the intended application
- Serve as host for ligands to form complexes that enhance sensitivity

Consequently, coincident with our work on sensor design, we have developed chemically-selective optical materials that satisfy these criteria.^{9,20-24,31,32} We have developed two classes of optical quality chemically-selective films based on two different host materials, namely, sol-gel processed silica (SiO₂) and cross-linked poly(vinyl alcohol) (PVA). We have made composites of these host materials with a variety of ionomers the structures of which are shown below. We have also made selective films of polymers by cross-linking precursor materials directly on sensor surfaces. Examples (see also structures below) include quaternized poly(vinyl pyridines)³² and most recently the SSEBS polymer system.³³ In turn, these composites of host material with ionomers and the neat polymer systems function well as either cation or anion preconcentration films.

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.

Key features in the development of the proposed spectroelectrochemical sensor for TcO₄⁻ have been demonstrated by electrochemistry on TcO₄⁻ performed at PNNL. The electrochemistry of TcO₄⁻ was investigated at ITO coated with anion exchange films to determine if TcO₄⁻ can be preconcentrated from solution into the sensing film, which is another key step in the sensor concept.³⁴ Since TcO₄⁻ is anionic, tests were run on anion exchange films that we have developed and used successfully to preconcentrate other anions (*vide supra*), namely, QPVP, PVTAC-PVA, PDMDAAC-SiO₂ and QPVP-SiO₂. The current for the reduction wave of TcO₄⁻ (at about -1100 mV) is considerably larger at all of the film-coated ITOs compared to bare ITO, which is indicative of a preconcentration of TcO₄⁻ into all of the films. The peak heights for the TcO₄⁻ reduction wave are proportional to TcO₄⁻ concentration, indicating a quantitative response.

Demonstration of Fluorescence Spectroelectrochemical Detection of Tc

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.^{35,36} Consequently, we have developed a fluorescence-based spectroelectrochemical sensor and have shown proof of concept using a model analyte. In turn, we extended the applicability of the sensor to significantly lower limits of detection. We have also built a small volume fluorescence spectroelectrochemical sensor with a fluid volume of about 4 microliters that could be operated either under flow or non-flow conditions. With this microvolume sensor we were able to reach a limit of detection of 10⁻¹² M with a ruthenium complex.³⁰

The fluorescence spectroelectrochemical sensor can reach limits of detection of at least 10⁻¹² M given even a low-to-moderate quantum yield fluorescent material.³⁰ As a result we find this result very exciting since the limit of detection for an analogous Tc-based fluorescent species would need to be about 10⁻¹⁰ M. Based on our recent work on the fluorescent complexes of technetium, we calculate the limit of detection for Tc to be 5 x 10⁻¹² M.

Electrochemical and Photophysical Characterization of [Tc(DMPE)₃]²⁺ in Solution

To demonstrate the basic functioning and selective sensing capability, we chose [Tc(DMPE)₃]⁺ as an example of an analyte (DMPE = 1,2-bis(dimethylphosphino)ethane) that

exhibits a fluorescence change with electrochemical modulation. $[\text{Tc}(\text{DMPE})_3]^+$ is part of a redox couple with well-defined, reversible electrochemistry that is accompanied by distinct fluorescence changes in the visible wavelength region.³⁷

Fig. 2. Cyclic voltammogram corresponding to $[\text{Tc}(\text{DMPE})_3]^+$ in aqueous solution is shown (center). Left and right of the voltammogram are the fluorescence spectra of fluorescent $[\text{Tc}(\text{DMPE})_3]^{2+}$ (left) and non-fluorescent $[\text{Tc}(\text{DMPE})_3]^+$ (right) at the extremes of the potential scan.

We have studied the properties of $[\text{Tc}(\text{DMPE})_3]^+$ in solution.³⁷ The electrochemical and spectroscopic characteristics of $[\text{Tc}(\text{DMPE})_3]^+ / [\text{Tc}(\text{DMPE})_3]^{2+}$ at ITO are shown by the cyclic voltammogram and spectra in **Figure 2**. Spectroelectrochemical modulation is accomplished by either scanning or stepping the potential from -300 mV, at which no fluorescence is observed to $+400$ mV at which excitation light is absorbed and fluorescence is observed.

Fig. 3. Electromodulation in solution from newly observed luminescent $\text{Tc}(\text{DMPE})_3^{2+}$ complex. Consecutive fluorescence spectra (left) during solution bulk electrolysis: initial solution at time = 0 contained only $\text{Tc}(\text{DMPE})_3^+$ followed by oxidation (time 0 to 20 min); immediately followed by reduction time (time 20 min to 80 min); (right) photograph of luminescent $\text{Tc}(\text{DMPE})_3^{2+}$ in solution excited by laser light emanating from an optical fiber.

The luminescence of $[\text{Tc}(\text{DMPE})_3]^{2+}$ in aqueous solution was observed by excitation at 404 nm. The one electron $\text{Tc(I)}/\text{Tc(II)}$ couple is reversible. Concurrent with potential step oxidation (at 0.4 V) and reduction (at -0.3 V) the fluorescence first increased and then decreased (**Figure 3**). The fluorescence increased during the oxidation of the Tc(I) complex forming the Tc(II) complex, and diminished on reversing the electrode potential.

Preconcentration of $[\text{Tc}(\text{DMPE})_3]^+$ by SSEBS Films from Aqueous Solution

The rapid uptake of $[\text{Tc}(\text{DMPE})_3]^+$ by a SSEBS polymer-coated ITO OTE is shown by the cyclic voltammograms in **Figure 4**. The increasing current in the repeated voltammograms on the right shows the continuous uptake into the film over an 18 min period. The three voltammograms on the left compare the response of a bare ITO OTE with the initial (<1 min) and final (40 min) responses at the SSEBS coated ITO electrode. A significant enhancement in current is obtained at the SSEBS polymer-coated ITO OTE compared to the bare ITO OTE.

Fig. 4. Preconcentration of $[\text{Tc}(\text{DMPE})_3]^{+/2+}$ into SSEBS film. Left, Cyclic voltammogram (50 mV/s) for film after soaking in $[\text{Tc}(\text{DMPE})_3]^+$ solution (2.2×10^{-4} M in 0.1 M KNO_3 (aq.)) for 40 min. The CV for bare OTE is shown for comparison. Right, Repeat cyclic voltammograms performed using a SSEBS coated ITO electrode.

Electromodulation of $[\text{Tc}(\text{DMPE})_3]^+$ in SSEBS Film

The fluorescence response to electrochemically cycling $[\text{Tc}(\text{DMPE})_3]^+$, which is loaded into the SSEBS film on the ITO OTE, between Tc(I) and Tc(II) is shown in **Figure 5**. Electrochemical cycling was accomplished by stepping the potential between -300 mV (Tc(I) , nonfluorescent) and 700 mV (Tc(II) , fluorescent) using the waveform shown at the top of the figure. For this experiment the film was first loaded with $[\text{Tc}(\text{DMPE})_3]^+$ by soaking in an aqueous solution of $[\text{Tc}(\text{DMPE})_3]^+$ (4.3×10^{-4} M) for 30 min. The OTE was removed from the solution, rinsed with distilled water, and placed in a cuvette containing clean electrolyte solution (0.1 M KNO_3 (aq.)) for the electromodulation experiment. During electrochemical modulation of the Tc(I/II) couple, the transparent SSEBS/OTE was illuminated at 488 nm and fluorescence of the film was measured. It is clear that the fluorescence is turned on and off as the trapped complex is cycled between its two oxidation states. Modulation of the fluorescence signal is the critical procedure in the spectroelectrochemical sensor concept, which relies on measurement of this change in fluorescence, ΔF , to measure concentration and to distinguish the target species from others that might be in the sample.

Fig. 5. Fluorescence response to potential-step modulation of $[Tc(DMPE)_3]^+/ [Tc(DMPE)_3]^{2+}$ within SSEBS polymer on ITO electrode. Potential was held for 90 s at each step and was continuously switched between +700 mV and -300 mV vs. Ag/AgCl.

Demonstration of Fluorescence from Other Tc-complexes: *trans*-dioxotechnetium(V) complexes, *trans*- $[TcO_2(L)_4]^+$ (L = py or pic) and *trans*- $[TcO_2(CN)_4]^{3-}$

Key to our ability to detect Tc at very low environmental contamination concentrations, we have begun preparing new luminescent materials containing technetium. Up to this point, there had been no known examples of fluorescent technetium complexes reported. We demonstrated³⁸ the first examples of luminescence for Tc complexes. The discovery of luminescence from *trans*-dioxotechnetium(V) complexes provided the first opportunity to directly compare fundamental luminescence properties of second- and third-row d^2 metal-oxo congeners. It is significant that despite well established studies of the reactivity and spectroscopy of Tc complexes in several oxidation states, luminescence had yet to be reported for a Tc complex until now.

A New Collaboration: PNNL/EMSL-UWY-UC

To broaden our expertise and efforts in discovering new luminescent complexes of technetium, we have formed a new collaboration which consists of the Co-PIs from PNNL/EMSL (Andrew Del Negro, Samuel A. Bryan) and UC (Professors Carl J. Seliskar and William R. Heineman) and a new collaborator from the University of Wyoming (Prof. B. Patrick Sullivan). It is important to note that before we began working to find luminescent technetium complexes no such complexes had been reported in the literature. It was, in part, through this new collaboration that we have made groundbreaking progress in identifying new luminescent complexes of technetium. This collaboration has already produced one *Journal of the American Chemical Society* Communication and another is about to be submitted for review. These two Communications summarize some of our very recent progress.

Development and Characterization of New Materials for Preconcentrating Films

As pointed out above, the film on the spectroelectrochemical sensor serves the very important role of preconcentrating the target analyte in the sensor's detection zone while also providing partial selectivity. We have continued to investigate new materials in a search for improved film characteristics. Two materials were investigated during this period: quaternized poly(4-vinylpyridine) (QPVP) in its pure form³² and immobilized in porous silica,³⁹ and partially sulfonated polystyrene-block-poly(ethylene-ran-butylene)-block-polystyrene (SSEBS).³³

Quaternized poly(4-vinylpyridine) (QPVP). QPVP has been used as an anion exchanger alone³² as well as incorporated into sol-gel derived silica films (QPVP-silica)³⁹ for the spectroelectrochemical sensor. The preparation, characteristics and performance of these films were determined. The films, which are spin-coated onto the surface of ITO, are optically

transparent and uniform. Scanning electron microscopy and spectroscopic ellipsometry were used to examine film structure, thickness and optical properties. These films have been shown to preconcentrate ferrocyanide, a model analyte for the sensor. They can be regenerated for multiple measurements by exposure to 1 M KNO_3 . Their overall response is comparable to the poly(dimethyldiallylammonium chloride)-silica films previously developed for this sensor.¹

Partially sulfonated polystyrene-block-poly(ethylene-ran-butylene)-block-polystyrene (SSEBS).³³ The potential of partially sulfonated polystyrene-block-poly(ethylene-ran-butylene)-block-polystyrene (SSEBS) thin polymer films for chemical sensing was explored. Spectroscopic ellipsometry was used to measure optical and surface properties of air-dried and hydrated material. SSEBS incorporates a relatively small amount of water (overall change of 25%) mainly determined by the complex dynamics of the film. The decrease in the refractive index after complete hydration of the film can be predicted based on the magnitude of swelling using effective medium approximation models. Films adhered tightly on various surfaces (glass, indium tin oxide, gold) as evaluated with the tape peel-off method. The voltammogram in **Figure 6a** shows a wide potential window for electrochemistry. The ability of the SSEBS material to preconcentrate cations was evaluated by cyclic voltammetry, absorbance, and luminescence measurements using the following model analytes: $\text{Ru}(\text{bpy})_3^{2+}$, phenosafranin (PSF), and rhodamine 6G (R6G)). **Figures 6 and 7** show cyclic voltammograms and the absorbance responses, both of which increase showing uptake of the probes. The detection limits of the sensor for $\text{Ru}(\text{bpy})_3^{2+}$ under unoptimized conditions can be significantly improved if luminescence is used as the detection modality ($\text{DL} = 5 \times 10^{-10}$ M) instead of absorbance ($\text{DL} = 5 \times 10^{-7}$ M). Overall, the results demonstrate the effectiveness of the SSEBS material for spectroelectrochemical sensing. Consequently, SSEBS was evaluated for preconcentrating $[\text{Tc}(\text{DMPE})_3]^{2+}$ as described above.

Fig. 6. a) Cyclic voltammograms of 0.1 M KNO_3 at bare ITO (—), ITO coated with a 24 nm thick SSEBS film (.....), and ITO coated with a 340 nm thick SSEBS film (- - -). The potential was scanned at 25 mV/s for 3 cycles. The last cycle for each electrode is shown. b-e) Cyclic voltammograms of the uptake of $\text{Ru}(\text{bpy})_3^{2+}$ and PSF into SSEBS films of different thicknesses: b) $\text{Ru}(\text{bpy})_3^{2+}$ / 24 nm; c) PSF/ 24 nm; d) $\text{Ru}(\text{bpy})_3^{2+}$ / 340 nm; and e) PSF/ 340 nm. Analyte solution concentration was 10^{-5} M, which was prepared in a 0.1 M KNO_3 supporting electrolyte solution. Voltammograms were obtained by scanning at 5 mV/s with a 20 s delay between each scan.

Fig. 7. Normalized absorbance for the uptake of 10^{-5} M or each analyte in 0.1 M KNO_3 . The absorbance of each analyte was monitored at the following wavelengths: $\text{Ru}(\text{bpy})_3^{2+}$ at 450 nm; PSF at 520 nm; R6G at 526 nm. A 340 nm thick SSEBS film was used for all measurements.

Characterization of Films by Spectroscopic Ellipsometry

An interesting, but complicating, aspect of the films is that they are dynamic systems and solution components partition into them by electrostatic interactions (i.e., ion-exchange).⁴⁰⁻⁴³

Once this process begins, the optical and physical properties of the film can change dramatically. For example, exposing a Nafion film to water increases the formerly dry film thickness by 31%. When exposed to an analyte like $\text{Ru}(\text{bpy})_3^{2+}$, the change in thickness is more complicated. At first, the film contracts, but as equilibrium is approached with the bulk solution, the film re-expands. Similar results were observed with other film materials.

Improvement of Detection Limits

Four strategies for improving limits of detection and response time have been explored: in situ formation of metal complexes, in situ ligand exchange, improved mass transport and thinner film thickness.⁴⁴

In Situ Formation of Metal Complexes. Some metal ions such as TcO_4^- do not have ideal electrochemical and/or spectroscopic properties for sensitive detection by spectro-electrochemistry. This situation can be addressed by In situ formation of a metal complex with improved properties.^{14,44,45} Aqueous iron(II) serves as a simple model system for this situation. Both forms of the redox couple $\text{Fe}(\text{II})/\text{Fe}(\text{III})$ absorb light weakly in the visible region and, therefore, do not give a strong electromodulation signal. A strategy used to detect this type of analyte is to enhance the absorptivity of one oxidation state by forming a complex with a chromophoric ligand present in the selective film.¹⁴ In addition to enhancing the absorptivity difference between different oxidation states, the ligand must be able to partition into the selective film and form a stable complex with the metal ion in the film. The resulting complex would ideally have reversible electrochemistry within the coated ITO OTE potential window.

This strategy was demonstrated using Fe^{2+} and the ligand 2,2'-bipyridine, bpy. $\text{Fe}(\text{bpy})_3^{2+}$ strongly absorbs at 520 nm (molar absorptivity = $86,500 \text{ M}^{-1} \text{ cm}^{-1}$); $\text{Fe}(\text{bpy})_3^{3+}$, the oxidized form, does not absorb.

Aqueous Fe^{2+} , impossible to detect spectroelectrochemically without a strategy for enhancement of ΔA , was successfully detected by the ATR absorbance sensor when bpy was pre-loaded into the Nafion film prior to exposure to an aqueous solution of Fe^{2+} . Free Fe^{2+} partitioned into the film, forming the $\text{Fe}(\text{bpy})_3^{2+}$ complex.

Iron in the Fe^{3+} form can also be determined by this strategy.⁴⁵ Here Fe^{3+} partitions into the film and forms the colorless $\text{Fe}(\text{bpy})_3^{3+}$ complex, which is then electrochemically reduced to the red complex $\text{Fe}(\text{bpy})_3^{2+}$ for detection. Mixtures of aqueous $\text{Fe}^{2+}/\text{Fe}^{3+}$ can also be determined by judicious use of potential control. In this case, both Fe^{2+} and Fe^{3+} are simultaneously loaded into the film under open circuit conditions so that the concentrations of $\text{Fe}(\text{bpy})_3^{3+}$ and $\text{Fe}(\text{bpy})_3^{2+}$ in the film reflect the ratio of concentrations of Fe^{2+} and Fe^{3+} in solution. The red $\text{Fe}(\text{bpy})_3^{2+}$ in the film is first measured directly from the absorbance. Colorless $\text{Fe}(\text{bpy})_3^{3+}$ is then reduced to red $\text{Fe}(\text{bpy})_3^{2+}$ and its concentration determined from the increase in absorbance that accompanies its electrochemical reduction.

The chemical reaction between Fe^{2+} and bpy in the thin Nafion film was examined by spectroscopic ellipsometry.⁴⁶ Changes in the optical constants and the thickness of the film upon exposure to various solutions allowed diffusion in the film and the chemical reactions that are important in the sensing of Fe^{2+} to be studied.

In Situ Ligand Exchange. Another strategy for enhancing sensitivity of metal complex ions is by ligand exchange in the selective film of the spectroelectrochemical sensor.¹⁵ This approach would be useful for the determination of a metal that is already coordinated with an organic ligand, but the redox couple for electrochemical modulation gives only a small change in molar absorptivity. This concept has been demonstrated using $\text{Cu}(\text{en})_2^{2+}$ (en = ethylenediamine) as a model analyte. Electrochemical modulation of this analyte would be between $\text{Cu}(\text{en})_2^{2+}$ and the 1-e⁻ reduction product $\text{Cu}(\text{en})_2^{1+}$ whose small molar absorptivities of $75 \text{ M}^{-1}\text{cm}^{-1}$ and $39 \text{ M}^{-1}\text{cm}^{-1}$, respectively, at 547 nm would give a very weak electromodulated absorbance signal. In this case neocuproine (nc) can be used as an exchange ligand that is preloaded in the sensing film. Reduction of $\text{Cu}(\text{en})_2^{2+}$ to the less stable $\text{Cu}(\text{en})_2^{1+}$ in the presence of nc results in ligand substitution to give very stable $\text{Cu}(\text{nc})_2^{1+}$, which absorbs at 545 nm with a molar absorptivity of $7950 \text{ M}^{-1}\text{cm}^{-1}$. Oxidation of $\text{Cu}(\text{nc})_2^{1+}$ to $\text{Cu}(\text{nc})_2^{2+}$ results in ligand exchange to reform $\text{Cu}(\text{en})_2^{2+}$ with little absorbance at 545 nm. This is the basis of the ligand exchange spectroelectrochemical sensor as depicted in **Figure 8**.

Fig. 8. Sensing $\text{Cu}(\text{en})_2^{2+}$ with enhancement of sensitivity by ligand exchange with nc within the film.

Effects of Mass Transport and Film Thickness on Limits of Detection. Another important factor in sensitivity is the extent to which analyte is extracted from the sample and preconcentrated into the sensing film. Perhaps the most important consideration here is choice of film material to maximize the film-sample partition coefficient for maximum sensitivity.

However, other factors such as cell design and mass transport to the film can also affect sensitivity. In our earlier work we employed relatively large-volume cells without stirring during the preconcentration step and the films were relatively thick, typically 500 – 2000 nm. Because mass transport to the film was by diffusion only and the films were thick, loading of the film from the sample was slow and detection limits for analytes such as ferricyanide and $\text{Ru}(\text{bpy})_3^{2+}$ were typically in the range of 10^{-5} to 10^{-6} M using the sensor in absorbance mode.

In efforts to miniaturize the ATR cell design and the volume of sample required, we moved to smaller cells² and then to thin-layer cells.¹⁸ Because of the large partition coefficients for analyte into the film that can be achieved, substantial depletion of the analyte from the sample is possible when the sample volume becomes sufficiently small. This affects the concentration detection limit because the film ultimately equilibrates with a sample that is lower in concentration of analyte than the original sample. This problem can be overcome by circulating a larger volume of sample through the cell so the amount that partitions into the film is only a small portion of that in the sample. Not only does the constant circulation of sample provide rapid mass transport of the analyte to the film surface, but it also continuously replenishes the analyte in the cell. During this time of cell design evolution, we also improved our ability to make thinner films. Combining a continuous flow cell with thinner films (50 nm and less) resulted in a faster response and a 100-500 fold enhancement in the detection limit.⁴⁷ For example, a detection limit of 10 nM was achieved for $\text{Ru}(\text{bpy})_3^{2+}$ in such an absorbance-based spectroelectrochemical sensor with a 24-nm thick film of Nafion .

Spectroelectrochemical Sensor for Heavy Metals

We have explored the possibility of extending the spectroelectrochemical sensor concept to the detection of heavy metals such as mercury, lead zinc, copper, and cadmium.⁴⁸⁻⁵⁰ Changes in attenuation of light passing through an ITO-OTE accompany the electrodeposition and stripping of the metal ions as metal atoms on the electrode surface. The change in absorbance during stripping of electrodeposited metal constitutes the analytical response that enables detection over the following ranges for each metal: mercury - 2.5×10^{-7} to 5×10^{-5} M; lead - 5×10^{-8} to 5×10^{-5} M; cadmium - 1×10^{-9} to 5×10^{-7} M ; and copper - 5×10^{-7} to 5×10^{-5} M. The spectroelectrochemical responses were characterized and optimized with respect to solution conditions, the potential excitation signals used for deposition and stripping, and wavelength for detection. The deposited metals were examined by ESEM and the electrodeposition patterns were found to influence the optical response.

Conclusions from this work

- Fluorescence spectroelectrochemistry and less than picomolar limit of detection for a model analyte has been demonstrated.
- The spectroelectrochemical sensor and associated instrumentation for fluorescence mode of operation have been made, are portable, and easily transported to and used at DOE sites.
- The sensor has sufficient selectivity for its application to complex samples, even including tank waste, that exist at DOE sites such as the Hanford Site.
- TcO_4^- has been preconcentrated in sensor films and electrochemically reduced. This is the first step in operation of a spectroelectrochemical sensor for TcO_4^- .

- New Tc complexes made fluoresce and these complexes have been preconcentrated and electrochemically modulated in a sensor film leading to fluorescence modulation, which is the second step in operation of the spectroelectrochemical sensor for TcO_4^- .
- Fluorescence offers a means of dramatically improving the limit of detection. Based on measurements on fluorescent complexes of Tc, we estimate the limit of detection to be $5 \times 10^{-12}\text{M}$.
- Sensitivity of the spectroelectrochemical sensor for some metal ions can be improved by forming a metal complex with better optical and electrochemical properties.
- Some heavy metals can be detected with the spectroelectrochemical sensor by depositing them as metals on the sensor surface

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Students supported

Sara Andria - University of Cincinnati, doctoral student
 Laura Morris - University of Cincinnati, doctoral student
 Nebojsa Pantelic – University of Cincinnati, doctoral student
 Derek Julian – University of Cincinnati, doctoral student

Dr. Andy Del Negro – PNNL, postdoctoral fellow
 Dr. Sean Hightower - PNNL, postdoctoral fellow

PhDs granted

Trace Metal Detecting Sensors for Environmental and Biomedical Applications, Anne T. Maghasi, 2003, University of Cincinnati.

Development of Optical and Spectroelectrochemical Sensors for Copper and Cadmium, Tanya Shtoyko, 2003, University of Cincinnati.

In situ Studies of Sensor Film Dynamics by Spectroscopic Ellipsometry, Imants Zudans, 2003, University of Cincinnati, University of Cincinnati.

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Presentations (2003-2006)

University of Cincinnati

1. Characterization of Poly(vinyl alcohol)-Poly(vinylbenzyltrimethylammonium chloride) Blend Films and Their Use in the Spectroelectrochemical Sensor, J. R. Paddock*, C. J. Seliskar, W. R. Heineman, Pittcon 2003, Orlando, FL, March 9-14, 2003.
2. Development of Spectroelectrochemical Sensors for Monitoring Mercury and Lead, A. T. Maghasi*, C. J. Seliskar, W. R. Heineman, Pittcon 2003, Orlando, FL, March 9-14, 2003.
3. Ligands and Their Polymerizeable Analogs as Analog Tools for Spectroelectrochemical Sensing, D. J. Monk*, T. H. Ridgway, W. R. Heineman, C. J. Seliskar, Pittcon 2003, Orlando, FL, March 9-14, 2003.
4. Modeling of Spectroelectrochemical Sensor, A. Piruska*, C. J. Seliskar, W. R. Heineman, Pittcon 2003, Orlando, FL, March 9-14, 2003. (Poster session)
5. Spectroelectrochemical Sensor for the Determination of Concentration of Aqueous Iron, C. M. Wansapura*, W. R. Heineman, C. J. Seliskar, Pittcon 2003, Orlando, FL, March 9-14, 2003. (Poster session)
6. Spectroelectrochemical Sensor for Technetium: Preconcentration and Quantification of Technetium in Polymer-modified Electrodes in the symposium on Environmental Management Science Program Symposium Environmental Sensing and Monitoring: Effects of Radiation Exposure on Humans and Biota, D. J. Monk, M. L. Stegemiller, S. Conklin, J. R. Paddock, W. R. Heineman*, C. J. Seliskar, T. H. Ridgway, S. A. Bryan, T. L. Hubler, 225th ACS National Meeting, New Orleans, LA, March 23-27, 2003. (Invited Lecture)
7. An Attenuated Total Reflectance Sensor for Copper: An Experiment for Analytical or Physical Chemistry, T. Shtoyko*, I. Zudans, J. N. Richardson, C. J. Seliskar, W. R. Heineman, 225th ACS National Meeting, New Orleans, LA, March 23-27, 2003. (Poster session)

8. Characterization of Cross-linked Polymer Films for Incorporation into Spectroelectrochemical Sensors, L. E. Faulkner*, S. Conklin, W. R. Heineman, 225th ACS National Meeting, New Orleans, LA, March 23-27, 2003. (Poster session)
9. In situ Measurement of Sensor Film Dynamics, I. Zudans*, W. R. Heineman, C. J. Seliskar, ICSE-3, Vienna, Austria, July 6-11, 2003. (Poster session)
10. Studies of the Influence of Optical Effects on Spectroelectrochemical Sensor's Performance, A. Piruska*, I. Zudans, C. J. Seliskar, and W. R. Heineman, 226th ACS National Meeting, New York, NY, Sept. 7-11, 2003. (Poster session)
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12. Absorbance and Fluorescence Spectroscopy of Rhenium-dioxo Compounds for the Development of a Spectroelectrochemical Sensor for Analogous Technetium Complexes, J. S. Kegerreis*, D. J. Monk, W. R. Heineman, C. J. Seliskar, J. R. Paddock, Pittcon 2004, Chicago, IL, March 7-12, 2004. (Poster session)
13. Evaluation of the Detection Limits of $\text{Ru}(\text{bpy})_3^{2+}$ with an Attenuated Total Reflectance Spectroelectrochemical Sensor, S. A. Andria*, J. N. Richardson, N. Kaval, I. Zudans, C. J. Seliskar, W. R. Heineman, Pittcon 2004, Chicago, IL, March 7-12, 2004. (Poster session)
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17. Optimization of the Detection Limits of $\text{Ru}(\text{bpy})_3^{2+}$ using an Attenuated Total Reflectance Spectroelectrochemical Sensor, S. E. Andria*, J. N. Richardson, N. Kaval, I. Zudans, C. J. Seliskar, W. R. Heineman, 227th ACS National Meeting, Anaheim, CA, March 28-April 1, 2004. (Poster session)
18. Absorbance and Fluorescence Spectroscopy of Rhenium-dioxo Compounds for the Development of a Spectroelectrochemical Sensor for Analogous Technetium Complexes, J. S. Kegerreis*, J. R. Paddock, D. Monk, W. R. Heineman, C. J. Seliskar, 227th ACS National Meeting, Anaheim, CA, March 28-April 1, 2004. (Poster Session)
19. Spectroelectrochemical Sensors based on Multimode Selectivity Simultaneously Achievable in a Single Device, in the symposium on Analytical Chemistry in Nuclear Technology Developments in Sensor Technology, C. J. Seliskar*, W. R. Heineman, S. A. Bryan, T. L.

Hubler, N. Kaval, 227th ACS National Meeting, Anaheim, CA, March 28-April 1, 2004. (Invited Lecture)

20. Toward a Spectroelectrochemical Sensor for Pertechneate, in the symposium on Analytical Chemistry in Nuclear Technology Developments in Sensor Technology, S. D. Conklin*, D. J. Monk, J. R. Paddock, N. Kaval, W. R. Heineman, C. J. Seliskar, 227th ACS National Meeting, Anaheim, CA, March 28-April 1, 2004.

21. Spectroelectrochemical Sensors Based on Multimode Selectivity Simultaneously Achievable in a Single Device, C. J. Seliskar*, W. R. Heineman, ACS Prospectives Conference on Emerging Opportunities in Chemical and Biosensing, Santa Fe, NM, May 16-19, 2004.

22. In Situ Studies of the Complexation of Ferrous Ion with 2,2-Bipyridine in a Thin Nafion Film by Spectroscopic Ellipsometry, C. Wansapura*, N. Pantelic, C. J. Seliskar, W. R. Heineman, 36th Central Regional ACS Meeting, Indianapolis, IN, June 2-4, 2004. (Poster session)

23. Poly(4-vinylpyridine-co-styrene) Selective Films that Preconcentrate Anions for Spectroelectrochemical Detection, L. K. Morris*, W. R. Heineman, C. J. Seliskar, 230th ACS National Meeting, Washington, DC, Aug. 28-Sept. 1, 2005. (Poster)

24. Sensors Based on Spectroelectrochemistry: Detection of Metal Ions in the Symposium on Electrochemical Science for Sensing and Energy Conversion, W. R. Heineman*, C. J. Seliskar, 2005 Center for Integrated Molecular Systems (CIMS), Pohang University of Science & Technology, Pohang, Korea, Sept. 22-23, 2005. (Invited lecture)

25. Sensors based on Spectroelectrochemistry: A Strategy for Improved Selectivity in the Symposium on Analytical Electrochemistry, W. R. Heineman*, C. J. Seliskar, 56th Annual Meeting of the International Society of Electrochemistry, Busan, Korea, Sept. 25-30, 2005. (Invited lecture)

26. Electrochemical Sensors, W. R. Heineman, 56th Annual Meeting of the International Society of Electrochemistry, Busan, Korea, Sept. 25-30, 2005. (Invited tutorial course)

27. Sensors Based on Spectroelectrochemistry: Detection of Metal Ions, W. R. Heineman*, C. J. Seliskar, Matrafured 05, International Conference on Electrochemical Sensors, Matrafured, Hungary, Nov. 13-18, 2005. (Invited lecture)

28. Characterization of Polystyrene-block-poly(ethylene-ran-butylene)-block-polystyrene Thin Films for Sensing Purposes, S. Andria*, W. R. Heineman, 2006 UC Graduate Poster Forum, March 3, 2006. (Poster)

29. Towards Development of Spectroelectrochemical Sensor for Detection of 1-Hydroxypyrene in Complex Liquid Sample Media, T. Sakova*, W. R. Heineman, C. J. Seliskar, 2006 UC Graduate Poster Forum, March 3, 2006. (Poster)

30. Sensors Based on Spectroelectrochemistry: Strategies for Improved Selectivity in the Symposium on New Trends in Spectroelectrochemical Methods for Chemical Analysis, W. R. Heineman*, C. J. Seliskar, T. Battaglia, N. Pantelic, C. Wansapura, L. Morris, S. Andria, T. Sakova, A. Doepke, T. Clinton, Pittcon 2006, Orlando, FL, March 12-17, 2006. (Invited lecture)

31. Attenuated Total Reflection Spectroscopy and Spectroscopic Ellipsometry of Thin Ion Exchange Films, N. Pantelic*, W.R. Heineman, C.J. Seliskar. 231st ACS National Meeting, Atlanta, March 26-30, 2006. (Oral)
32. Sensors Based on Spectroelectrochemistry: A Strategy for Improved Selectivity, W. R. Heineman*, Spring 2006 Ernest B. Yeager Symposium of the Cleveland Section ECS, Cleveland, OH, June 16, 2006. (Invited lecture)
33. Characterization of Trans-dioxotechnetium(V) and Technetium(II)phosphine Excited States and Spectroelectrochemical Detection of Pertechnetate, S. Bryan*, A.S. Del Negro, Z. Wang, T.L. Hubler, W.R. Heineman, C.J. Seliskar, P.B. Sullivan. 61st Northwest Regional Meeting of the ACS, Reno, NV, June 25-28, 2006.
34. Sensors Based on Spectroelectrochemistry: Detection of Metal Ions in the Symposium on Electrochemical Sensors, W. R. Heineman*, C. J. Seliskar, 210th ECS Meeting, Cancun Mexico, Oct. 29-Nov. 3, 2006. (Sensors Award lecture).
35. New Strategies for Chemical Sensors, W.R. Heineman, invited seminar for Department of Chemistry, University of California, Riverside, January 29, 2003.
36. Sensors Based on Spectroelectrochemistry. W.R. Heineman, invited seminar for Department of Chemistry, Case Western Reserve University, February 13, 2003.
37. Sensors Based on Spectroelectrochemistry. W.R. Heineman, invited seminar for Department of Chemistry, Michigan State University, April 24, 2003.
38. Sensors Based on Spectroelectrochemistry. W.R. Heineman, invited seminar for Department of Chemistry, University of Maryland, Baltimore County, February 10, 2004.
39. Sensors Based on Spectroelectrochemistry. W.R. Heineman, invited seminar for Department of Chemistry, Procter & Gamble, June 22, 2004.
40. Sensors Based on Spectroelectrochemistry. W.R. Heineman, invited seminar for Department of Chemistry, Hope College, March 4, 2005.
41. Sensors Based on Spectroelectrochemistry. W.R. Heineman, invited seminar for Department of Chemistry, Kalamazoo College, March 7, 2005.
42. Sensors Based on Spectroelectrochemistry. W.R. Heineman, invited seminar for Department of Chemistry, Kent State University, March 17, 2005.
43. Sensors Based on Spectroelectrochemistry. W.R. Heineman, invited seminar for Department of Chemistry, Lund University, Lund, Sweden, December 8, 2006.
44. Fluorescence-based sensor for pertechnetate, C. J. Seliskar*, W. R. Heineman, S. A. Bryan, and A. S. Del Negro, Invited talk, National ACS Meeting, Boston, MA August 22, 2007.
45. Spectroelectrochemical Sensors Based on Multimode Selectivity Simultaneously Achievable in a Single Device, C. J. Seliskar*, W. R. Heineman, Invited talk, ACS Prospectives Conference on Emerging Opportunities in Chemical and Biosensing, Santa Fe, NM, May 16-19, 2004.

46. Spectroelectrochemical Sensors based on Multimode Selectivity Simultaneously Achievable in a Single Device, in the symposium on Analytical Chemistry in Nuclear Technology Developments in Sensor Technology, C. J. Seliskar*, W. R. Heineman, S. A. Bryan, T. L. Hubler, N. Kaval, Invited talk, 227th ACS National Meeting, Anaheim, CA, March 28-April 1, 2004.

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2. Bryan, Samuel A; Del Negro, Andy; Wang, Zheming; Hubler, Timothy L; Heineman, William R; Seliskar, C "Characterization of trans-dioxotechnetium(V) and technetium(II)phosphine excited states and spectroelectrochemical detection of pertechnetate." Presented at the Actinide Separations Conference, Richland, WA, May 22-25th, 2006.
3. Andrew S. Del Negro, Zheming Wang, Timothy L. Hubler, and Samuel A. Bryan, "Luminescent trans-Dioxotechnetium (V) Excited States and Spectroelectrochemical Detection of Pertechnetate" Fairbanks, AK June 17, 2005.
4. Monk, David J.; Stegemiller, Michael L.; Conklin, Sean; Paddock, Jean R.; Heineman, William R.; Seliskar, Carl J.; Ridgway, Thomas H.; Bryan, Samuel A.; Hubler, Timothy L. Spectroelectrochemical sensor for technetium: Preconcentration and quantification of technetium in polymer-modified electrodes. Abstracts of Papers, 225th ACS National Meeting, New Orleans, LA, United States, March 23-27, 2003 (2003), ENVR-251.
5. Monk, David J.; Stegemiller, Michael L.; Conklin, Sean; Paddock, Jean R.; Heineman, William R.; Seliskar, Carl J.; Ridgway, Thomas H.; Bryan, Samuel A.; Hubler, Timothy L. Spectroelectrochemical sensor for technetium: Preconcentration and quantification of technetium in polymer-modified electrodes. Abstracts of Papers, 225th ACS National Meeting, New Orleans, LA, United States, March 23-27, 2003 (2003), ENVR-251.

Inventions disclosures/patents

Invention Title: Technetium Sensor based on Luminescence from a Technetium Chromophore. IDR/IPID #: 14893; S#: 107,362. Inventor(s) Name(s): Samuel A Bryan (PNNL), Timothy Hubler (PNNL), Andy Del Negro (PNNL), Carl Seliskar (University of Cincinnati), William Heineman (University of Cincinnati). Invention disclosure date Submitted: 7/28/2005 at PNNL

Provisional Patent: UC case # 106-105; Provisional Patent # 60/801,696, "System and Method for Imaging of Tissue" Inventor(s) Name(s): Samuel A Bryan (PNNL), Timothy Hubler (PNNL), Andy Del Negro (PNNL), Carl Seliskar (University of Cincinnati), William Heineman (University of Cincinnati). Application filed May 19, 2006 at University of Cincinnati.

Invention Title: Highly Oxidizing Ligand-to-Metal Charge Transfer Excited States for Solar Energy Conversion. IDR/IPID #: 15430; S#: 111,672. Inventor(s) Name(s): Bryan, Samuel A (PNNL), Del Negro, Andy (PNNL), Carl Seliskar (University of Cincinnati), William Heineman

(University of Cincinnati), Brian Sullivan (University of Wyoming). Invention disclosure date Submitted: 6/1/2006 at PNNL.

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