

**Project 90076**  
**Spectroelectrochemical Sensor for Pertechnetate Applicable**  
**to Hanford and Other DOE Sites**  
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**RESULTS TO DATE:**

**Task 1: Refinement of the chemically-selective film for pertechnetate**

**New film materials for pertechnetate:** A new film material comprised of quaternized poly(4-vinylpyridine) cross-linked with 1,10-diiododecane has been developed for use in the spectroelectrochemical sensor. Films were prepared in a one-pot synthesis by stirring poly(4-vinylpyridine), cross-linker and methyl iodide in 1-butanol for 1 h, after which the solution was spin-coating onto ITO-glass. Film thickness was varied either by changing the spin rate or by dilution of the original precursor solution. The thinnest film prepared was 30 nm; the thickest 930 nm. Spectroscopic ellipsometry was used to study the dynamics of film changes on soaking in aqueous salt solution and on preconcentrating model analyte ferrocyanide. The results document that, on hydration, films expanded by almost 90% in 0.1 M KNO<sub>3</sub>, then contracted slightly when ferrocyanide solution was introduced probably due to electrostatic cross-linking. IR spectroscopy was used to determine the extent of quaternization of the film. For a polymer solution stirred for 1 h, films were about 20% quaternized. This can be increased to ~30% by adding more solvent to the precursor solution and stirring for an additional hour. Solubility of the partially cross-linked material was a factor that limited the quaternization process. Use of a more appropriate solvent may enable greater quaternization. A more quaternized film should preconcentrate more pertechnetate by virtue of having a higher density of charged binding sites. Film ruggedness is critical. To investigate this, films on ITO-glass were soaked in methanol and butanol overnight, in 0.1M KNO<sub>3</sub>, and in 0.1M KNO<sub>3</sub> adjusted to pH 12 and pH 2 for 30 days. Each film was then tested as a spectroelectrochemical sensor for model analyte ferrocyanide. The results showed only the pH 2 conditioned sensor behaved abnormally. The film soaked in pH 2 electrolyte delaminated but did not dissolve. Delamination was most likely due to the acid digestion of the ITO layer of the sensor and not to any film-based process. We have also shown that it is possible to regenerate the film by flushing with 1M KNO<sub>3</sub> solution. Response curves were prepared from a single sensor by injecting different concentrations of ferrocyanide, monitoring the uptake, then regenerating the film and injecting the next concentration. To check reproducibility, a film was regenerated 10 times with almost no change in response. Film selectivity was demonstrated by adding a model cationic species, Ru(bipy)<sub>3</sub><sup>2+</sup> to the ferrocyanide sample. Even at 10 times the ferrocyanide concentration, only a very small electrochemical signal and no optical signal due to the cation were observed. Additionally a competitive anion Ru(CN)<sub>6</sub><sup>4-</sup> could be distinguished from Fe(CN)<sub>6</sub><sup>4-</sup> based on the redox potential and absorbance spectrum differences between the two anions. Both species were preconcentrated into the film, and both could be electrochemically modulated simultaneously or individually. The films exhibited a linear absorbance response to ferrocyanide over the range 0.008-0.2mM. From 0.1mM ferrocyanide solution, the analyte was concentrated in a 320 nm thick film by a factor of ~6,000. The films have recently been used at PNNL to repeat cyclic voltammetry experiments with pertechnetate (TcO<sub>4</sub>) as previously performed with other candidate films. The results showed that the new films performed very well and better than films previously used, and showed reversible waves in the voltammogram with the film present where none appeared when a bare ITO-glass substrate was used. Our results clearly show that cross-linked quaternized poly(4-vinylpyridine) films made this way are superior materials for preconcentrating pertechnetate.

**Fundamental film studies:** It is well known that internal reflection spectroscopy is affected not only by the extinction coefficient,  $k$ , of the sample, but by the real part of the refractive index,  $n$ , as well. This becomes especially important for sensor films that have dimensions comparable with the wavelength of the light. In order to understand the implications of this property on our sensor measurements thin highly-

absorbing Ru(bpy)<sub>3</sub><sup>2+</sup>-doped Nafion films on SF11 glass were studied by internal reflection spectroscopy. For this system, two modes of light interaction with the film are possible: attenuation due to evanescent wave penetration and light propagation within the absorbing film itself. Unlike evanescent wave spectroscopy, light propagation within the film can cause distortions in measured spectra due to leaky waveguide propagation modes. For example, light propagation in a film doped with Ru(bpy)<sub>3</sub><sup>2+</sup> can lead to spectral red shifts up to 50 nm and even additional absorbance peaks can appear in the spectrum. These film-based distortions depend on the complex refractive index, the thickness of the film and the angle of incidence. These effects become significant for an extinction coefficient, *k*, above 0.01 and a film thickness above 200 nm. The net result of our work has been that we must anticipate such spectral distortions in thick films that have high values of *k* and that these distortions could lead to complex dynamics in the internal reflection spectra upon analyte preconcentration in sensor films. From studying Ru(bpy)<sub>3</sub><sup>2+</sup> partitioning into Nafion films, we know that significant refractive index changes in the film in turn alter leaky waveguide mode conditions in the film and, can even lead to a reduction of measured absorbance or luminescence despite the increase in the extinction coefficient of the film. Our sensor designs for pertechnetate will recognize this property of the films used and adjust for it as needed.

Spectroscopic ellipsometry is a nondestructive quantitative optical technique routinely used in our labs in measurements of the optical constants *n* and *k* (*n*, refractive index and *k*, extinction coefficient) and thickness of thin films. Previously we reported dynamic in situ measurements on the partitioning of the model chromophore Ru(bpy)<sub>3</sub><sup>2+</sup> into a Nafion thin film by using spectroscopic ellipsometry. We have also documented the failure of ferrocyanide sensing films in time using similar optical techniques. Taken as a whole, we have demonstrated how dynamic spectroscopic ellipsometry can be used to quantitatively track both chemical and physical changes in thin sensing films on the spectroelectrochemical sensor. Continuing fundamental work also demonstrated the detection of ferrous ions by spectroelectrochemical sensing where 2,2'-bipyridine (bpy) was first preconcentrated in the sensing layer (Nafion), and then ferrous ions, during partitioning, formed stable colored complexes enabling efficient sensing. This model system mimics another important feature of our pertechnetate sensor, namely, conversion of an analyte into a more easily sensed chemical specie. Three important factors that strongly affected the sensing have been studied: (1) optimization of the incorporation of the bpy ligand into the Nafion film, (2) retention of the iron-bpy complex within the sensing layer upon exposure to aqueous ferrous ion solution, and (3) retention of the charged iron-bpy complex over the time frame of the sensor measurement. A principal goal was to study the details of metal complexation within a thin solid sensing film. To focus on sensing film changes we used a simple prototype system composed of a thin Nafion film on a glass substrate. The film was interrogated using a "back-side configuration" that enabled measurement of film properties only. The influence of the different chemical species on the film properties was extracted by a stepwise experimental approach that consisted of examining the component parts of the system (film soaking in sodium chloride, bpy, and ferrous ion solutions one after another, respectively). Collected experimental data were then modeled using appropriate optics software. In related studies, detection of ferrous, ferric iron and the speciation of iron using a spectroelectrochemical sensor was also demonstrated. The optical response at 520 nm due to the electrochemical modulation of the Fe(bipy)<sub>3</sub><sup>2+/3+</sup> complex formed in the film was measured. The corresponding change in sensor absorbance (*A*) was proportional to the concentration of ferrous or ferric ions in the film, which in turn was proportional to the bulk concentration of each iron specie in the sample. Optimizing film thickness and ligand concentration with respect to the sensor response yielded a detection limit of 5 × 10<sup>-6</sup> M for each iron redox species and a sensor response time of 6 min. Sensor selectivity in the presence of potential interfering metal ions was also examined. Two important general conclusions were drawn from our results: (1) the ligand complexation of an electrochemically generated specie within the thin chemically-selective film can be efficiently accomplished, (2) long term sensor deployment may require covalently-bound ligand to avoid leaching of the ligand from the film.

**New Ligand and Tc-complex Syntheses:** New ligands for Tc are being developed primarily from the pyridyl group of nitrogen ligands. We wish to incorporate three characteristics into the ligands for optimal performance of the sensor: 1) the ligands should be bidentate or multidentate as this helps to maintain the preorganized cavity for coordination of the metal within the polymer film; 2) the ligands should have a polymerizable group such that they can be covalently attached into the polymer film; and 3) the ligands

should incorporate any structure which may be likely to aid optical detection (e.g., multicyclic aromatic compounds). We have prepared several ligands which incorporate these characteristics; specifically 4-vinylbipyridine, 4-vinyl-4'-methylbipyridyl, 6-vinylisoquinoline, 2,2'-diisoquinoline, and 4-vinylterpyridyl. We are trying to prepare complexes which are iso-structural with the tetrakis-4-vinylpyridinedioxotechnetium ion and its isoquinoline analog which have been previously prepared and studied electrochemically and with fluorescence spectroscopy. We have now arrived at some useful methods for making the vinyl-derivatives of the ligands in reasonable yield, and the syntheses that are being used allows the best opportunity to functionize the ligands with other groups in addition to vinyl groups. Several polymers have been made with vinyl ligands and complexes of rhenium prepared with the vinyl-functionalized ligands. Additionally, we have done some preliminary studies on incorporating a trimethoxyvinylsilane group into the polymers so that we can covalently attach these polymers to the ITO surface of the sensor.

Two new Tc(V) complexes containing pyridyl group nitrogen ligands were prepared within the Radiochemistry Processing Laboratory at PNNL. Starting with 300 mg of  $\text{NH}_4\text{TcO}_4$ , the precursor to the new pyridyl ligand complexes that are fluorescent was prepared by reducing the pertechnetate to the  $\text{N}(\text{Bu})_4[\text{Tc}(\text{O})\text{Cl}_4]$  complex using  $\text{H}_3\text{PO}_3$  as the reductant in the presence of  $\text{HCl}$ . The product was then divided and the exchange reaction with isoquinoline or 4-vinylpyridine gave the desired Tc(V) complexes,  $[\text{TcO}_2(\text{isoquinoline})_4]\text{Cl}$  and  $[\text{TcO}_2(4\text{-vinylpyridine})_4]\text{Cl}$  respectively. The absorption spectrum for each complex has a low energy absorption band at approximately 480 nm. The fluorescence spectra were recorded using a 488 nm excitation from an  $\text{Ar}^+$  laser source. The emission maximum for  $[\text{TcO}_2(\text{isoquinoline})_4]\text{Cl}$  is approximately 580 nm while  $[\text{TcO}_2(4\text{-vinylpyridine})_4]\text{Cl}$  complex shows emission maxima at approximately 540 and 570 nm.

To explore the electrolytic preparation and trapping of lower oxidation state Tc complexes using pyridyl group ligands, cyclic voltammetry experiments using pertechnetate in the presence of isoquinoline have been performed at PNNL. In argon purged acetonitrile, the reduction of  $\text{N}(\text{Bu})_4\text{TcO}_4$  at ITO is indistinguishable from the solvent limit. Cycling pertechnetate in the presence of excess isoquinoline, results in the reduction potential shifted more positive, with an increase in the cathodic current (ca. 1700 mV vs. SCE), and a new anodic feature is apparent upon the reverse scan (ca. 800 mV vs. SCE). These electrochemical features are not present with either pertechnetate or free ligand alone. This data indicates that  $\text{TcO}_4^-$  reduction is facilitated by the excess ligand and results in a lower oxidation state Tc-isoquinoline complex that is stable within the timeframe of the reverse potentiometric scan.

## **Task 2: Continued development of sensor prototype and associated portable instrumentation**

We have developed a first prototype luminescence-based portable spectroelectrochemical sensor instrument. The instrument is composed of the sensor, a small imaging spectrograph fitted with a Peltier-cooled CCD camera, a small diode laser as the excitation source and a potentiostat. Solutions to be interrogated can be introduced into the sensor using a simple syringe or a syringe pump. The sensor was fabricated from a modified BAS electrochemical flow cell (CC-44) by incorporation of specially designed electrode contacts and laser excitation and fluorescence collection optics. An assembly of two half-ball lenses has been used for coupling the laser excitation into the sensor and simultaneous gathering of luminescence. The instrument can be easily reconfigured by connecting the optic fibers to a portable standard cuvette holder if needed for making conventional luminescence and absorption measurements. Unlike many of our previous sensors based on absorbance, this sensor is light tight and, therefore, can be operated under ambient illumination. Use of optic fibers to carry the excitation and emission light to and from the sensor allows the sensor itself to be placed at a remote location. The sensor itself has a small footprint (ca. 5" by 3" including an enclosure for the sensor). The sensor uses 40 mm by 10 mm ITO-glass substrates. Only a 20 mm by 10 mm portion of this optical substrate is coated with the selective film. We have just transported and tested this instrument at PNNL for its detection capability and adaptability to a radioactive lab environment. We continue to optimize this instrument for eventual testing with pertechnetate at the Hanford Site.

Detection of pertechnetate ion ( $\text{TcO}_4^-$ ) at the Hanford Site requires detection limits as low as  $10^{-10}$  M. Thus, we are pursuing luminescence as a mode of detection to achieve the detection limit required. Due to restriction of the use of radioactive  $\text{TcO}_4^-$  to PNNL, at UC we have investigated the luminescence of  $\text{Ru}(\text{bpy})_3^{2+}$  cation as a model analyte coupled with its selective preconcentration into thin Nafion films. In these studies, we have already demonstrated extremely low limits of detection. We are able to measure  $\text{Ru}(\text{bpy})_3^{2+}$  concentrations as low as  $1 \times 10^{-13}$  M and the calculated limit of detection from our data indicated a value of  $5 \times 10^{-14}$  M. Furthermore, we have recently discovered that high sensitivity can be coupled with ultra-thin sensor films as selective preconcentration media. Currently we are able to make films as thin as ca. 6-7 nm which is a thickness very close to the average surface roughness of the ITO coating on the optical substrate. Besides providing much faster response times, ultra-thin films are superior in surface adhesion and mechanical properties. Due to its small volume, the sensor designed for luminescence measurements requires a flow of a very small amount of liquid sample in order to preconcentrate a measurable amount of analyte. We continue to improve this instrument.

### **Task 3: Demonstration of sensor performance on $\text{TcO}_4^-$ standards and samples from the vadose zone and subsurface water at Hanford Site**

We have evaluated new pertechnetate preconcentration materials at PNNL (see Task 1).

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**Presentations (11) were given at the following meetings:**

Pittcon 2004, Chicago, IL. 227th ACS National Meeting, Anaheim, CA. ACS Prospectives Conference on Emerging Opportunities in Chemical and Biosensing, Santa Fe, NM, May 2004. 36th Regional ACS Meeting, Indianapolis, IN.