ENVIRONMENTAL AND WASTE MANAGEMENT: ADVANCEMENTS THROUGH THE ENVIRONMENTAL MANAGEMENT SCIENCE PROGRAM

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MATERIALS FOR ELECTROACTIVE ION-EXCHANGE (EAIX) SEPARATIONS OF PERTECHNETATE ION

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INTRODUCTION/BACKGROUND

The cost for treatment and disposal of approximately 90 million gallons of high-level waste (HLW) at the U.S. DOE's Savannah River Site (SRS), Idaho National Engineering and Environmental Laboratory (INEEL) and Hanford Site is neither cost effective nor practical. Processes to separate the HLW constituents from the low-level waste (LLW) fraction are required to reduce the volume and achieve an acceptable cost for disposal. Utilization of EaIX materials can help meet these critical goals because this technique can significantly reduce or eliminate secondary wastes associated with more traditional ion-exchange or solvent extraction technologies.

An ion exchange process using electroactive materials sorbs contaminants selectively and then expels (elutes) them electrochemically by changing the charge balance through redox reactions in the sorbent as opposed to requiring the addition of a chemical eluant. Such processes can theoretically remove anions (*e.g.*, pertechnetate, chromate and perchlorate) and concentrate them in a separate product stream while excluding additional process chemicals. Our work focuses on manipulating specific properties of redox polymers to control the hydrophobicity and ion-pair properties pertinent to the reversibility, selectivity, stability, intercalation/de-intercalation rates and capacity of the polymers.

Initially, our work examined use of the redox polymer polyvinyl-ferrocene (PVF). This polymer appeared to be selective for perrhenate ion, ReO_4^-, (a non-radioactive surrogate for the pertechnetate ion, TcO_4^-) in the presence of nitrate ion. Two important issues surfaced regarding the use of this particular polymer: 1) the pH instability of the oxidized form (ferrocenium) in alkaline solutions precludes use of PVF itself for the highly alkaline wastes present at the Hanford Site and 2) enhancement of selectivity of the polymers for TcO_4^- will be needed for reasonable efficiency of the separation process. Regarding pH stability of PVF, we found that functionalization of the Cp rings with *tert*-butyl groups did enhance alkaline stability of the polymer during redox cycling, but preparation of uniform polymers of reasonable molecular weight becomes much more problematic. The selectivity of the PVF polymers for ReO_4^- or TcO_4^- in competition with NO_3^- is primarily due to the differing hydration energies of the two ions, concluded in part on EXAFS studies that were completed for both ions with PVF.[1,2]

CURRENT WORK

We have developed a synthetic strategy to prepare vinyl-bipyridyl and -terpyridyl ligands which allow incorporation of ion-selective architectures with a polymerizable handle. Fe complexes formed with these ligands should provide the working core of the electroactive polymers. Vinyl substituted bipyridyl ligands have been synthesized *via* palladium catalyzed cross coupling reactions[3] as shown in Figure 1.

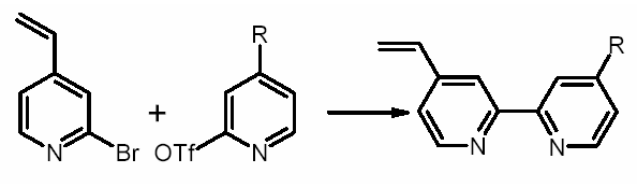

Figure 1. Negishi Cross Coupling

Instead of adding the vinyl group to the bipyridyl ligand as described by Abruña[4] the vinyl function is prepared on a mono-pyridyl unit first and then coupled with another pyridyl unit. This led to higher yield than the conventional method but more importantly allows by variation of the group R to tailor the selectivity of the final material. A method for preparing such terpy analogs is shown in Figure 2.[5]

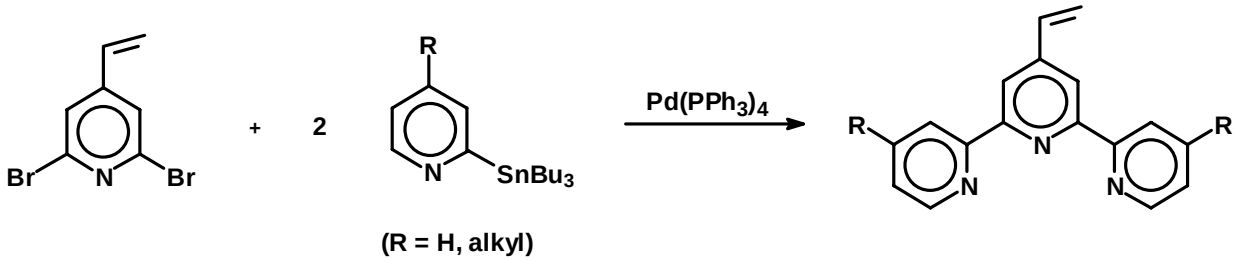

Figure 2. Stille coupling procedure for terpy ligands.

Using a combination of the above ligands with other pyridyl and monodentate ligands, several Fe complexes have been prepared; many of these show enhanced stability in alkaline solution. In turn, these complexes have been copolymerized into polymer matrices to form the EaIX polymers themselves and characterization of these materials will be presented.

To increase the kinetics and capacity of the EaIX materials, we have been able to prepare the polymers as porous composites. Figure 3 shows a SEM image one of the composites prepared using a PNNL prepared electroactive polymer.

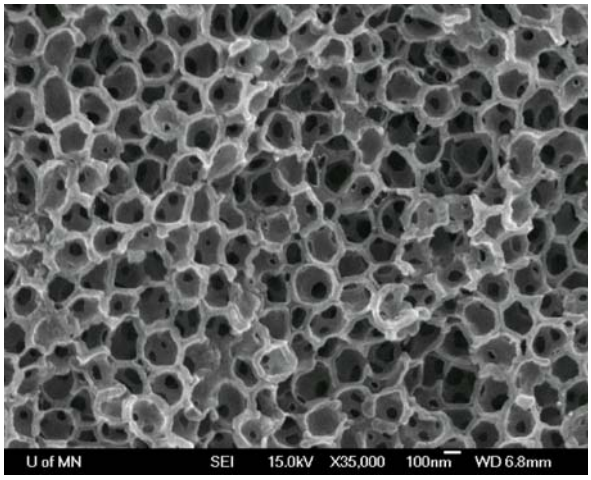

Figure 3. SEM image of porous composite prepared using electroactive polymer.

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