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Investigation of Novel Electrode Materials for Electro-chemically-Based Remediation of High- and Low-Level Mixed Wastes in the DOE Complex

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Research Objective

One of the key issues that must be solved to achieve a successful remediation of the high level liquid wastes (HLW) at the Hanford and at Savannah River sites is the removal of the significant quantities of nitrate and nitrite in the existing liquid waste streams that are presently on these sites in the DOE complex. One method of waste stream remediation is electrochemical oxidation, which is an in-situ method that has been well-documented to have significant advantages in many areas with respect to pump-and-treat approaches to waste remediation. There are, however, significant aspects of the electrochemical oxidation process that need to be addressed from a basic research viewpoint. The research to be performed under this proposal will investigate new materials, initially based on degenerately-doped titanias, for use in the electrochemical degradation of organics and nitrogen-containing compounds in sites of concern to the DOE remediation effort.

Research Progress and Implications

This report summarizes work after 1.5 years of a 3-year project. Progress has been made in two main areas of work. First, significant effort has been made in synthesis and characterization of new anode materials for electrochemical remediation purposes. Secondly, these materials have also been characterized as photoanodes for photoelectrochemical activity and remediation applications. Due to space limitations, only work in the former area is summarized here but information on the latter is of course available upon request from the PI's.

The primary focus of studies on electrochemical remediation is to develop titania-coated electrodes for use as improved anode materials for remediation purposes. Sol-gel processing methods were employed to prepare thin films (<1 μm thick) of titania on four metallic substrates: copper, aluminum, 304 stainless steel, and titanium. Stable electrodes were obtained by dip coating suspensions of titania on titanium supports. The resulting electrodes were tested in a batch reactor employing a three-electrode configuration for their ability to photodegrade formic acid (at 25 ppm as C) in 0.01 M NaCl. When these electrodes were fired at 300°C, they displayed reproducible performance when employed for three consecutive tests. The presence of dissolved salt did not inhibit the activity of the photoelectrodes at an applied potential of +0.5 V. When copper (at 25 ppm) was added to the test solution, removal of both copper and formic acid was observed, although the actual amounts removed depended on the type of cathode used (either platinum mesh or reticulated vitreous carbon) and the presence or absence of oxygen. An electrode that provided optimum performance in the batch reactor under an applied potential of +0.5 V is presently being tested in a recirculating system using a two-electrode configuration for possible treatment of mixed wastes.

For comparison, titania-coated titanium electrodes were also prepared by thermal oxidation in air. Electrodes prepared by heating at 300°C displayed almost no catalytic activity at an applied potential of +0.5 V. However, electrodes prepared at 500°C were both reasonably active (only some 25% less effective than the optimized electrode prepared by sol-gel processing) and stable for two tests at +0.5 V. Additional studies were conducted on the use of zirconia thin films, which are not photocatalytic, to passivate 304 stainless steel. Samples were tested using dynamic anodic polarization in a three-electrode cell with deoxygenated 0.05 M NaCl solution as solvent. Potentials were swept between -

1.0 and +1.0 V. Electrodes were analyzed by scanning electron microscopy before and after corrosion testing. An electrode coated with zirconia and then fired at 700°C in air formed particles of iron oxide on the surface and readily corroded in the tests. Both this electrode and a coated electrode that was fired at 500°C in air displayed much higher currents during testing than did an untreated, unfired stainless steel electrode. However, an electrode that was coated with an aqueous zirconia sol and fired at 300°C in air was more resistant to corrosion than an untreated electrode. It thus appears that thin film sol-gel coatings, when fired at relatively low temperatures, can provide some protection for metallic electrodes and that these materials appear promising for the remediation application envisioned in the initiation of the work Further investigation of materials properties and optimization of the electrodes under both lab and batch reactor conditions will be undertaken during the next project period.