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CHEMICALLY MODIFIED ELECTRODES AND RELATED SOLUTION STUDIES

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Abstract

During the period covered by this report studies have been conducted in the following areas:

1. Mechanistic studies of polymerization reactions of vinyl containing metal complexes.
2. Theoretical considerations of the mechanisms of charge transport in redox and electronic conductors.
3. Spectroscopic studies of the modes of interactions of pyridine containing ligands with metal surfaces.
4. Spectroscopic and quartz crystal micro-balance studies of ion transport in electroactive polymer films.
5. Development of new composite conducting polymers for use as electrode materials.
6. Attempted synthesis of gem-dihalide containing polymers for attachment of Mo_2S_4 clusters.
7. Synthesis of oxo-ruthenium dimer complexes as catalysts for H_2O oxidation.
8. Studies of porphyrin based polymers which catalyze the oxidation (oxygenation) of olefins and benzylic carbons.

The work listed in the abstract in points 1, 2, 3, and 5 has largely appeared in print. Reprints of the relevant articles are included, thus no additional discussion of these areas will be given here. The other four areas will be discussed briefly. Much of this work is still in progress.

Item IV In our continuing efforts to better understand the mechanisms of electron and ion conduction in conducting polymers and the mechanisms of polymer "failure" we have conducted a series of spectroelectrochemical studies on electroactive polymer films (see also VIII below). We have designed cells to carry out spectroelectrochemical studies of polymer films in the visible, ultraviolet, and infra red regions of the spectrum. These experiments are proving most useful in understanding changes in polymer films under electrochemical conditions,

In addition to the spectral studies we have embarked on a collaborative study with Professor D. A. Buttery at the University of Wyoming to study these film using a quartz crystal micro-balance (QCM). From this technique we have been able to obtain much important information about ion and solvent content of our various polymers under electrochemical cycling.

Item VI During the last funding period we have been involved in an effort to develop polymers and monomers containing gem-dihalide groups ($R-CH_2X_2$) that could be used in attachment reaction with Mo_2S_4 in an attempt to form electrode bound films. In brief, this effort has met with very limited success. In instances where we succeeded in

cluster. In other instances where more reactive dihalides were prepared on preformed polymers the polymers tended to crosslink sufficiently to render the polymer insoluble prior to reactions with the molybdenum sulfur cluster. We are thus changing our strategy in this regard.

Item VII Meyer and others have reported that μ -oxo-(bis(bipyridine)aqueoruthenium) is an effective catalyst for the oxidation of water to oxygen. We have synthesized several analogous complexes that differ in the fact that one of the bipyridines on each ruthenium is linked via an alkyl chain. This has been done for two reasons: to increase the stability (which will be necessary for inclusion into polymer films if a practical catalyst is to be produced) and to force differences in the orientation of the bound water ligands which are ostensibly the source of the oxygen atoms in the dioxygen molecule produced. These molecules are presently under study to evaluate their stability and catalytic activity.

Item VIII We have continued our studies of polymer films formed by the polymerization of the following molecule.

This molecule, both in solution and incorporated into a polymer film has the ability to oxidize olefins and benzylic carbons in a fashion similar the peroxidase enzymes. We have largely completed our study of this material and will be preparing a report of our findings shortly.

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