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Comparison of Silver(II), Cobalt(III), and Cerium(IV) as Electron Transfer Mediators in the MEO Mixed Waste Treatment Process

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INTRODUCTION

Mediated electrochemical oxidation (MEO) has been developed by a number of researchers over the past decade as a method to treat mixed hazardous waste.[1-7] The technology has for the most part been targeted toward wastes generated by the nuclear industry, consisting of a hazardous or non-hazardous organic material contaminated by a radioactive substance. The MEO process consists of the electrochemical generation of a powerful oxidizing agent, which serves as an electron transfer mediator to bring about the oxidation of the organic component. Numerous studies on a variety of organic substrates have demonstrated complete oxidation to carbon dioxide can be realized under the proper reaction conditions, with water serving as the source of oxygen.. The radioactive component, usually an actinide element or heavy metal isotope, can then be recovered from the resulting organic free aqueous solution by standard methods such as ion exchange or solvent extraction.

In addition to the variety of organic compounds tested, investigators have also looked at a number of process parameters including choice of mediator, temperature, concentration of mediator, current density, anode material, acid concentration, and cell separator material. From these studies it would appear that for a given organic substrate, the two most important process parameters are choice of mediator and temperature. The purpose of this work is to evaluate these two parameters for a given organic material, holding all other parameters constant.

The organic material chosen for this study is the industry standard sulfonated styrene-divinyl benzene based cation exchange resin. This material is ubiquitous throughout the nuclear complex as a process residue, and is very resistant to chemical attack making it an ideal substrate to evaluate MEO capability. A high acid concentration is necessary to solubilize the mediator in its higher oxidation state, 6 M nitric acid was chosen since it is compatible with existing subsequent actinide element recovery processes.

EXPERIMENTAL

All electrochemical measurements were carried out in a standard H-cell fitted with a medium porosity glass frit to separate the anolyte and catholyte compartments. Each compartment held approximately 80 mL total volume. A 0.3 cm^2 surface area glassy carbon working electrode (BAS) was used to record cyclic voltammograms. This electrode was polished with alumina polishing suspension prior to each scan. A 31 cm^2 platinum foil electrode was used to carry out controlled current bulk electrolysis experiments. All potentials were measured using a double junction silver/silver chloride reference electrode. The internal filling solution was saturated potassium chloride, while the outer filling was composed of 10% sodium nitrate. This electrode was placed in the anolyte compartment in close proximity to the working electrode for voltammometric measurements. During bulk electrolysis experiments this electrode was also used to track the rest potential of the working electrode. However, the powerfully oxidizing media slowly

attacked the plastic body of the electrode, especially at elevated temperatures. To prevent destruction of the electrode, the reference was placed in the catholyte compartment during bulk electrolysis.

Ion exchange resin (Dowex 50W-8X)was dried in a vacuum oven at 110 °C prior to use to obtain an accurate dry weight. Before and after weight comparisons gave an as received water content of approximately 41%. Titration of the resin with standardized base solution yielded 5.33 milli-equivalents per gram of dry resin. Assuming sulfonated vinyl benzene with a molecular weight of 185 grams as the standard polymer unit in the resin results in a calculation of the maximum capacity of 5.41 milli-equivalents per gram. Thus for all practical purposes the resin can be considered as consisting exclusively of sulfonated vinyl benzene groups.

All electrochemical measurements were made using a PAR model 273 potentiostat controlled by Corrware software. Solution concentrations of the mediators were measured spectrophotometrically using a Perkin-Elmer model 8452 A UV-visible spectrometer fitted with either a 1.0 or 0.1 mm path length flow cell. Silver(II), cobalt(III) and cerium(IV) concentrations were measured at 392, 610, and 370 nm wavelengths respectively.

The electrochemical cell was placed in a water bath on a Whatman Dataplate 430 stirrer/hot plate, using thermocouple feedback to maintain the temperature to within ± 1 °C of the preset value. Both compartments of the cell was filled with 6 M nitric acid, the reduced form of the mediator was added to the anolyte compartment and the system was allowed to come to thermal equilibrium. A measured quantity of previously dried cation exchange resin was added and a current of 1 ampere was passed through the cell for a period of three hours. At the completion of the electrolysis, the reaction was immediately quenched by placing the cell in a chilled water bath. The anolyte solution was then filtered through a fine porosity glass filter crucible. The residue was washed twice with 30 mL portions of 6 M nitric acid to remove any residual mediator from the resin, and with three 30 mL portions of deionized water to remove the excess nitric acid. The crucible and its contents were then vacuum dried in an oven at 110 °C.

The mediators were added to the solution as nitrate salts, $AgNO_3$ (J. T. Baker), $Co(NO_3)_2.6H_2O$ (Fisher), and $Ce(NH_4)_2(NO_3)_6$ (Fisher). Cerium(IV) was pre-reduced to Ce(III) at an applied potential of 0.75 volts prior to addition of the ion exchange resin. All experiments were run using a mediator concentration of 0.1 M.

RESULTS

Mediator Properties

Platinum is the usual choice of electrode material for determining the electron transfer characteristics of redox couples in aqueous acidic media in the anodic region. However, previously published results on the electrochemical behavior of cerium indicates the formation of an oxide layer on the surface of the platinum electrode that complicates the evaluation of the heterogeneous electron transfer reaction. Those complications do not seem to exist on freshly polished glassy carbon electrodes. Thus all of the cyclic voltammetric measurements were carried out on this electrode material.

The cyclic voltammograms for cobalt, cerium and silver in 6M nitric acid are presented in figure 1. The oxidation of cobalt(II) to cobalt(III) does not appear within the solvent limit. However, it must lie just positive of the solvent limit since it can be generated electrochemically in high yield by constant current bulk electrolysis. The silver(I) to silver (II) oxidation occurs at a potential of 1.61 volts vs. a standard silver/silver chloride reference electrode or upon conversion, approximately 1.81 volts vs. the normal hydrogen electrode. Since the cobalt oxidation occurs beyond the solvent limit commencing at approximately 1.9 volts, cobalt(III) is at least a 0.3 volts more powerful oxidizing agent than silver(II) in this media. This is in contradiction to the standard redox potential values of 1.98 volts for the silver(I)/(II) couple and 1.83 volts for the cobalt(II)/(III) couple.

The discrepancy in relative order of oxidizing power is due to complexation phenomena. The accepted value for the silver potential, 1.98 V, was obtained in perchloric acid where minimal complexation from the perchlorate ion is expected. When nitrate is added to this media, the silver redox potential shifts in the negative direction indicating complexation by nitrate. In 6 M nitric acid the net shift due to complexation is approximately 0.17 volts. The accepted value for the cobalt oxidation, 1.83 V, was obtained in 2 M sulfuric acid where apparently complexation by sulfate had shifted the redox potential negative from its true uncomplexed value. In nitric acid which forms a weaker complex with cobalt than sulfate, the potential is shifted back more towards its true value which lies beyond the anodic solvent limit. In nitric acid, and more than likely in perchloric acid as well, cobalt(III) is a more powerful oxidizing agent than silver(II).

An additional complication arises from the silver oxidation in this media. As observed in the cyclic voltammogram, the solvent oxidation also appears to have shifted as indicated by the sharp rise in current just beyond the silver oxidation wave. This is due to the catalytic oxidation of water by electrochemically generated silver(II). This reaction is quite facile and significantly impacts the stability of silver(II) in this media, especially at elevated temperatures.

Cerium displays a reversible electron transfer reaction with a standard potential of 1.25 volts vs. the standard silver/silver chloride reference electrode. Once again this potential is shifted in the negative direction from the standard literature value indicative of nitrate complexation. Unlike silver, there is no catalytic solvent oxidation wave associated with the oxidation of cerium(III) to cerium(IV). In fact cerium(IV)/nitric acid solutions are quite stable even at elevated temperatures.

In summary, cyclic voltammetric results indicate the oxidizing power of the three electron transfer mediators under investigation lie in the order: Co(III)>Ag(II)>Ce(IV), with potentials of approximately 0.3-0.4 volts separating the redox couples respectively.

Bulk Electrolysis

It was discovered that large area glassy carbon electrodes were not a good choice for large scale bulk electrolysis experiments, especially at elevated temperatures. They had a tendency to fall apart, leaving a fine powder graphite residue. Therefore all of the bulk electrolysis experiments were carried out using a smooth platinum foil anode.

The reaction for complete oxidation of the resin to carbon dioxide is given in equation 1, with 41 equivalents of electrons necessary for each resin unit reacted.

$$C_8H_8SO_3H - 41\ e^- + 17\ H_2O \rightarrow 8\ CO_2 + SO_4^{2-} + 43\ H^+ \qquad (1)$$

Alternatively, this corresponds to 21,084 coulombs or 5.86 amp-hours per gram of dry resin. Each of the resin destruction experiments was run at 1 ampere for three hours, which was theoretically sufficient to destroy just over half a gram of resin. Results of the resin destruction studies are summarized in figure 2. Each data point is the average of a minimum of two experiments at each temperature for each mediator.

The blank experiment consisted of adding the resin to a solution containing 6 M nitric acid with no mediator present and passing a current of 1 ampere for three hours. The average loss in weight of the resin was approximately 2-3 percent, verifying the chemically inert nature of this material even at elevated temperatures in nitric acid solution.

At room temperature, 20 °C, with addition of silver or cobalt as mediator at 0.1 M concentration, the reaction proceeds smoothly with the amount of resin destroyed exceeding the theoretical amount possible based solely on the number of coulombs of electricity passed. Two possible explanations exist for this behavior. First, the resin may not react completely to produce carbon dioxide, resulting instead in a water soluble intermediate. Second, it is possible that while the resin itself is resistant to chemical attack by the nitric acid media, the intermediate products generated are not. Once the benzene ring has been opened by attack from the mediator, the solvent can participate in the oxidation reaction. When a deficiency of resin is used instead of an excess, a total organic carbon analysis of the resulting solution typically gives a result of in the order of 100 ppm. Thus the reaction will proceed to completion. During the electrolysis the characteristic green color of cobalt(III) or brown color of silver(II) is always present indicating a build up of mediator and slow reaction with the resin.

A room temperature reaction of the resin with cerium(IV) does not occur. The weight loss is no greater than the weight loss associated with the reaction of nitric acid alone. The characteristic orange color of cerium(IV) appears at the onset of electrolysis but the presence of cerium(IV) has no effect on the resin.

When the temperature is raised to 50 °C, the resin destruction rate using silver and cobalt as mediators is slightly greater than at room temperature, but the solution never develops the characteristic colors associated with the ions in their higher oxidation states. Two reactions are occurring simultaneously, reaction of the mediator with the resin and reaction of the mediator with solvent, as given in equation 2.

$$2\,H_2O + 4\,Co^{3+} \rightarrow O_2 + 4\,Co^{2+} + 4\,H^+ \qquad (2)$$

The former reaction is expected to proceed at a faster rate at elevated temperatures, but the latter reaction, which also proceeds at a faster rate, lowers the effective mediator concentration. Thus raising the temperature appears to have little effect on the resin destruction rate. If the temperature is raised still further, to 70 °C, the resin destruction rate with silver and cobalt actually decreases. The deleterious solvent/mediator reaction rate begins to exceed that of the mediator/resin reaction.

The rate of resin destruction using cerium as mediator increases dramatically as the temperature is raised. From essentially an immeasurably slow reaction at room temperature it increases to greater than 100% destruction efficiency at 50 °C, comparable to the rate observed with silver(II). At 70 °C, the rate approaches a phenomenal 400%, far exceeding either cobalt or silver. As expected there is an exponential increase in the reaction rate between cerium and the resin with increasing temperature, denoting then absence of a deleterious side reaction. At 90 °C, the reaction rate ceases to increase indicating the onset of the solvent reaction.

DISCUSSION

For the electrochemical destruction of ion exchange resin, cobalt and silver mediators are the clear choice at room temperature, where greater than 100% destruction efficiency can be realized. With these mediators, there is no advantage to running the reaction at elevated temperature since the rate will not increase significantly at moderate temperature and will actually decrease at high temperature. Of these two mediators, cobalt would be a better choice due to its lower cost, insensitivity to reaction with halides and ease of disposal. If a greater reaction rate is desired, the use of cerium at 70 °C is the best choice, producing a reaction rate 3-4 times that obtainable with either silver or cobalt at any temperature. Interestingly, it is probably cerium's low oxidizing power that makes it a better mediator at elevated temperatures, since the kinetics of the side reaction with solvent are greatly diminished relative to cobalt or silver.

As a final note it should be mentioned that the results of this study pertain only to the destruction of ion exchange resin. Each organic substance will have its own unique set of parameters for optimum reaction efficiency.

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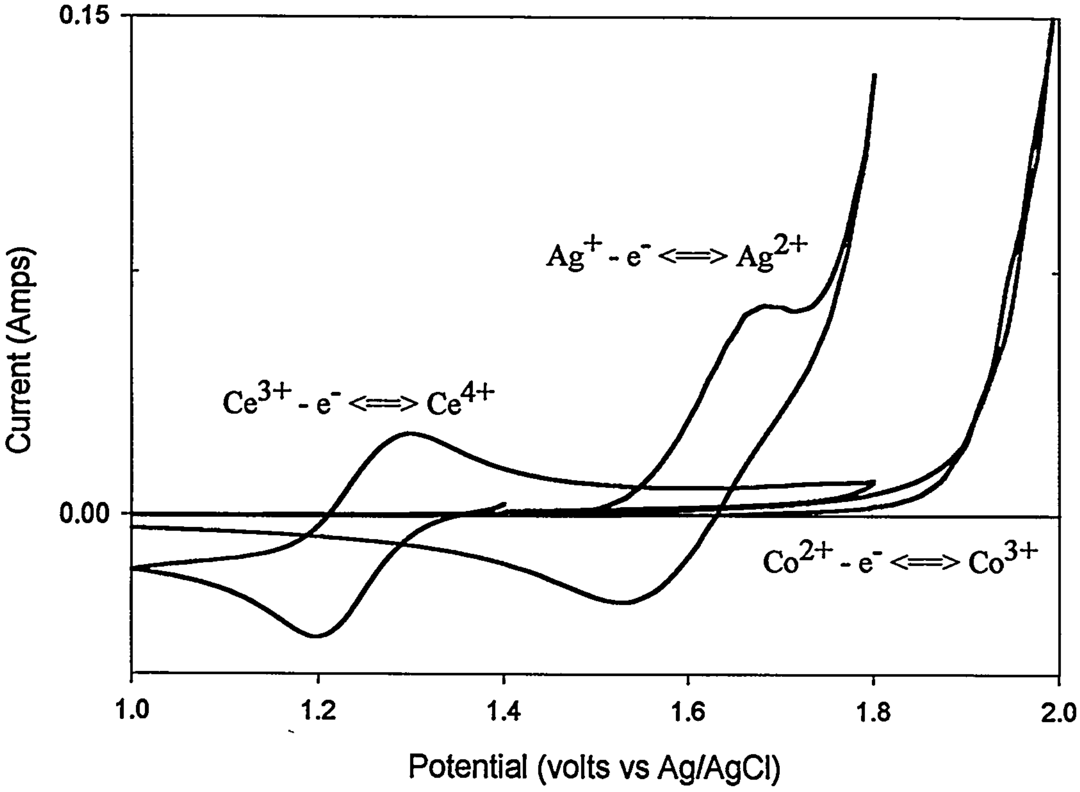

Figure 1. Cyclic voltammometric behavior of cobalt, silver and cerium in 6 M nitric acid on a glassy carbon electrode. Concentration 0.10 M, sweep rate 0.20 V/s.

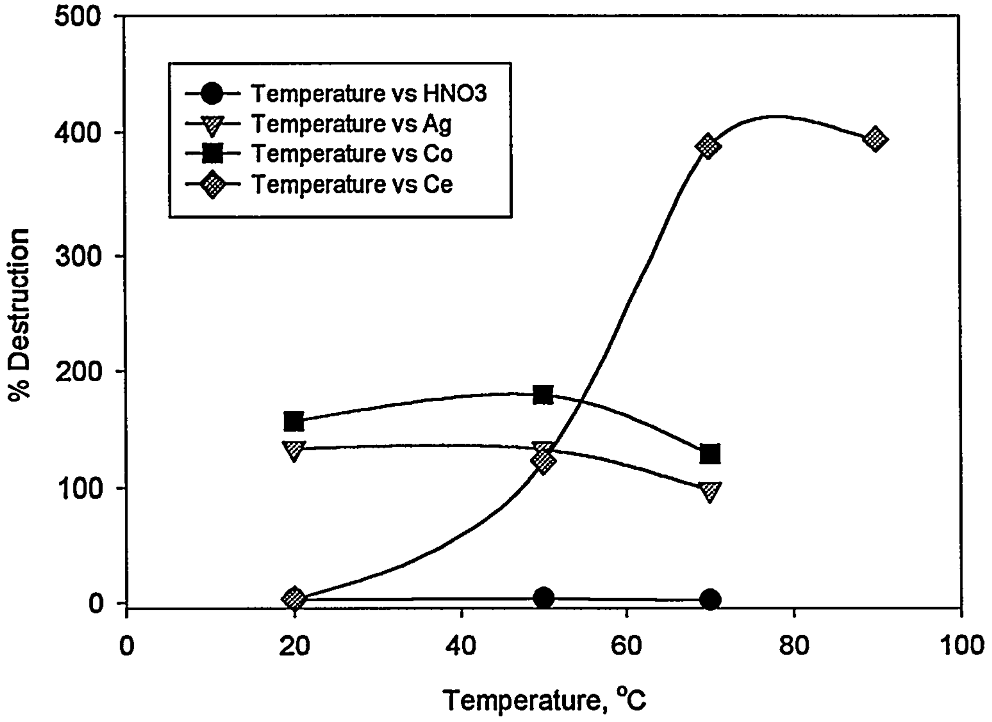

Figure 2. Percent destruction efficiency of cation exchange resin as a function of mediator and temperature.