Journal of Applied Electrochemistry **33**: 161–169, 2003.
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Electrolytic reduction of trichloroethylene and chloroform at a Pt- or Pd-coated ceramic cathode

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Received 26 February 2002; accepted in revised form 10 December 2002

Key words: catalyst poisoning, chloroform, Ebonex, electrolytic dehalogenation, electrochemical reduction, palladium, platinum, trichloroethylene

Abstract

Trichloroethylene (TCE) and chloroform (CF) were electrolytically dechlorinated in a two-compartment cell in which the working electrode (cathode) consisted of an Ebonex ceramic sheet plated with platinum (Pt) or palladium (Pd). The halogenated targets were not reduced using a cathode of untreated Ebonex. Under typical experimental conditions (e.g., cathode potentials $E_C = -0.3$ V to -1.4 V vs SHE, pH 7.0), transformations were first order in TCE and CF. Reaction kinetics were mass transport limited at $E_C < -1.4$ V. Transport-limited rate constants were 0.45 cm min^{-1} for TCE reduction and 0.42 cm min^{-1} for CF. The primary products of CF reduction were methane and hydrochloric acid. For TCE reduction, major products were ethane, ethylene and hydrochloric acid. Carbon and chlorine mass balances were within 5–10%. Current efficiencies ranged from nearly 100% at $E_C = -0.5$ V (both reactants) to 24.4% for TCE and 16.6% for CF at $E_C = -1.4$ V. Rate constants for TCE and CF transformations were inversely related to pH in the range $2 < \text{pH} < 11$. Pt–Ebonex resisted sulfate and chloride poisoning. The Pd–Ebonex electrode quickly lost activity (50% loss in 5–10 min) in 0.1 M K_2SO_4 electrolyte (cathode potential, $E_C = -1.15$ to -1.4 V vs SHE).

1. Introduction

Chlorinated, volatile organics are the most frequently encountered organic contaminants at Superfund and other groundwater contaminated sites in the United States. Among these the chlorinated ethylenes and methanes, including trichloroethylene (TCE) and chloroform (CF) are suspected human carcinogens [1, 2]. The US Environmental Protection Agency has established maximum contaminant levels of 5 μg L^{-1} for both TCE and CF in drinking water [3]. Because of broad industrial use and widespread inappropriate disposal, both contaminants are commonplace in groundwater and soil. Decontamination of affected groundwater using established technologies is very time consuming and expensive [4, 5].

Previous work has shown that aqueous-phase TCE can be electrolytically oxidized to CO_2 and CO at an Ebonex ceramic anode [6–9]. CF resists electrolytic transformation under the same conditions. CF also reacts slowly with such strong oxidants as ozone, hydrogen peroxide, and hydroxyl radicals [10]. On the other hand, TCE and CF are susceptible to chemical transformation on appropriate catalytic surfaces in the presence of hydrogen peroxide. The process is enhanced by ultraviolet radiation. Previous studies have shown that electrolytic reduction of chlorinated hydrocarbons can be conducted in nonaqueous solutions using carbon or metal-modified carbon electrodes [11–14]. They can also be electrolytically reduced in aqueous solution using Ag, Zn, Cu, Pt and Pd foil cathodes [15–17].

In experiments described here, elemental Pt or Pd was electrolytically deposited onto the surface of a conductive ceramic, Ebonex. The advantages afforded by Ebonex as a catalyst support include corrosion resistance, ease of catalyst deposition, high electrical conductivity, strong adherence with cathodically deposited metals (i.e., Pt, Pd) and convenience in regeneration (by reversing the electrode polarity) [18, 19]. Ebonex based electrodes have been studied for a variety of applications including sulfur dioxide removal from waste gases [20], battery and fuel cell electrode manufacture [21], and oxidation of organic wastes in sewage and aqueous wastestreams [22, 23]. In this study, the applicability of Pt- and Pd-coated Ebonex cathodes for reductively dehalogenating toxic volatile organic contaminants (VOCs) is investigated. The ceramic electrode's behaviour in sulfate and chloride containing electrolytes was investigated, and the dependence of reduction rate on target concentration, cathode solution pH and cathode potential (E_C) was established. Reaction stoichiometry and efficiency were studied as a function of the same independent variables.

2. Experimental details

2.1. *Materials*

Electrochemical reduction experiments were performed in a commercial three-electrode, two-compartment glass reactor (Electrosynthesis, Inc.) in which the cathode and anode compartments were separated by a 15 cm^2 Nafion® cation-exchange membrane (Figure 1). The cathode compartment was filled to capacity (320 mL) with aqueous 0.1 M K_2SO_4 or 0.05 M KCl. A 100 mL syringe was connected to the top of the compartment to maintain atmospheric pressure (about 0.92 atm in Tucson, Arizona) in the headspace in the reactor despite considerable H_2 production. The cathode was a 1.9 cm × 12.7 cm × 0.3 cm Ebonex (Electrosynthesis, Inc., NY) ceramic sheet that was plated with Pt or Pd. Ebonex is a highly conductive ($6.3 \times 10^{-4}\ \Omega^{-1}\ \text{cm}^{-1}$) porous ceramic material comprised of Magneli phase titanium oxides with the general formula Ti_nO_{2n-1}. The Ti_4O_7 and Ti_5O_9 phases show particularly high electrical conductivity [19] and a commercially available sheet material of mixed Ti_4O_7 and Ti_5O_9 was used for this study. The 100 mL anode compartment contained 50 mL of the same electrolyte solution. The anode was an untreated Ebonex ceramic sheet (1.6 cm × 12.7 cm × 0.3 cm). The reference electrode was a saturated silver–silver chloride electrode (SSCE; Accumet). The chamber containing the reference electrode was separated from the cathode compartment by a glass frit. All potentials are reported against SHE.

A potentiostat (Amel 410, Electrosynthesis, Inc., NY) was used to fix E_C relative to the reference potential. The cathode solution pH was controlled by automatic addition of 0.1 M HCl using a pH-stat (Brinkman Metrohm 691 pH meter, 614 Impulsomat and 665 Dosimat). The cathode solution was stirred continuously with a 2.5 cm Teflon-coated magnetic stir bar at 600 rpm, which maintained a turbulent, well-mixed condition in the cathode chamber. TCE and CF stocks were reagent grade (Aldrich, 99%).

Before plating, the Ebonex sheet was soaked in a mixture of strong acid (3:1, HCl:HNO_3) for 2 h and then rinsed with deionized water. Two Ebonex electrodes were immersed in 300 mL of aqueous $PdCl_2$ solution (Aldrich, 99%, 0.05 g) and NH_4Cl (0.03 g) and stirred for 15 min. A d.c. potential was applied for 1 h between the electrodes so that Pd was plated on the cathode (pH $\sim$ 1.0, 5 mA cm^{-2}, 313–323 K) [24]. After electroplating with Pt or Pd, the surface was lightly scrubbed with a polymer sponge to remove any nonadherent deposits. Finally the plated electrode was rinsed thoroughly with deionized water. The cathode was stored under water until needed. The Pt coating procedure was similar: 0.1 g K_2PtCl_6 (Aldrich, 98%)/300 ml, pH 2 $\sim$ 3 adjusted with HCl, 2 $\sim$ 5 mA cm^{-2}, 303–313 K. The Pt-coated Ebonex appeared to be shiny and

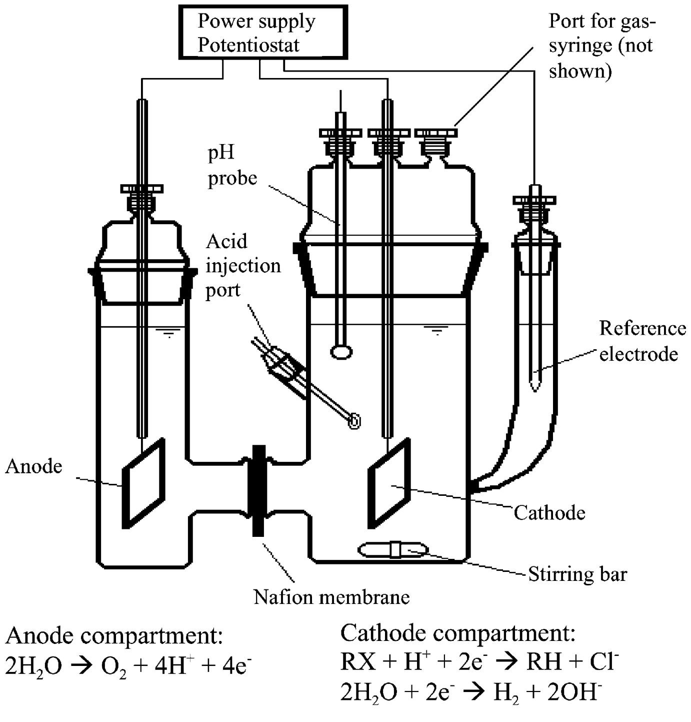

Fig. 1. Schematic representation of the two-compartment, three-electrode reactor including primary reactions at the anode and cathode. Gas syringe to maintain constant cathode pressure and the pH stat not shown.

metallic. Separate plating experiments not reported here showed that Pt and Pd plating efficiencies were $>80\%$ under these conditions. Because the focus of this study was to investigate the practical applicability of using Ebonex amended electrodes for destruction of halogenated contaminants in water, additional efforts were not undertaken to quantify or visualize the electroactive surface area of the plated electrode beyond verifying that a reproducible, durable metal surface could be simply applied to the ceramic material.

Previous work has shown the highly variable porosity of different Ebonex formulations can significantly affect their conductivity and electrochemical behaviour [25]. With this in mind, both porous and nonporous (fully hardened) grade sheets of Ti_4O_7/Ti_5O_9 were tested as cathode materials in preliminary work. No significant difference in electroreduction rates was found between the two grades, so subsequent work utilized only the porous material. It seems likely that the precious metal deposition process blocked most of the pore entrances when applied to the porous material, so that its subsequent behaviour mimicked the behaviour of the nonporous Ebonex.

2.2. *Methods*

Pure liquid TCE or CF (normally 20 μL) was injected into the cathode compartment and allowed to equilibrate for about 30 min. The desired cathode potential was applied to initiate the experiment. Liquid samples (20 μL) were withdrawn every 10 min to determine TCE or CF, and gas samples (50–100 μL) were withdrawn for measurement of TCE or CF and any volatile transformation products. Mass balances computed on carbon and chlorine included all identified liquid and gas-phase species.

The 20 μL liquid samples were extracted into 1 mL of pentane in a sealed vial. TCE or CF was determined by gas chromatography (Hewlett-Packard 5890 A, electron capture detector; DB-624 column; oven temperature 313 K, injector temperature 423 K, detector temperature 523 K; He carrier; flowrate 0.117 $cm^3\ s^{-1}$). Gas-phase species were also analysed by gas chromatography (Hewlett-Packard 5790, flame ionization detector).

Aqueous-phase chlorine-containing ions were analysed by ion chromatography (IC) using a Dionex analyser (Ion-Pac AG4A guard column, HPIC-APIC-AS4A analytical column, ASRS-1 self-regenerating anion suppressor). The eluent consisted of 0.85 mM sodium bicarbonate ($NaHCO_3$)/0.9 mM sodium carbonate (Na_2CO_3) (flowrate 0.033 $cm^3\ s^{-1}$). Sample injections (25 μL sample loop) were made through pre-rinsed 0.45 μm PTFE membrane filters (Gelman).

3. Mechanism and kinetic model

The basic mechanistic steps for reductive dehalogenation are common to chlorinated VOCs and are discussed in the context of the TCE and CF targets used in this study. In aqueous solution, protons (H_3O^+) accumulate around the negatively polarized chlorine atoms [26] of TCE and CF due to electrostatic attraction yielding a positively charged ion pair ($C_nHCl_3{\cdot}n_oH_3O^+$, where $n=1$ for CF or $n=2$ for TCE and n_o is the number of protons).

$$C_nHCl_3 + n_oH_3O^+ \longleftrightarrow C_nHCl_3 \cdot n_oH_3O^+ \tag{1}$$

This positively charged ion pair migrates through the boundary layer to the cathode surface. The mass transfer rate can be expressed as

$$-\frac{dm}{dt} = Ak'_m(C_l - C_s) \tag{2}$$

where k'_m is the mass transfer coefficient (cm min^{-1}) which depends on the diffusion coefficient (D), ionic strength, pH, and fluid type. A (cm^2) is the cathode surface area, and $m\,(\text{mmol}) = V_lC_l + V_gC_g$. V (cm^3) is the volume and C (M, or mmol cm^{-3}) is the concentration. Subscripts 'l' and 'g' represent the properties of the liquid phase and surface, respectively.

On the cathode surface, the ion pair captures n_o electrons from the electrode and is dissociated into

$$\begin{aligned} &C_nHCl_3 \cdot n_oH_3O^+ + n_oe^- \\ &\quad \rightarrow (C_nHCl_3^*) + n_oH^* + n_oH_2O \end{aligned} \tag{3}$$

where superscript '*' represents the dissociated state. This dissociation has been reported previously for the Pd catalyst surface reaction [27, 28] and a similar reaction is assumed for the Pt catalyst. This is the rate controlling kinetic step and can be described using the Butler–Volmer equation [29, 30].

$$-\frac{dm_s}{dt} = Ak'_cC_s\exp\left(-\frac{n_o\alpha_cFE_c}{RT}\right) \tag{4}$$

where m_s is the mass (mmol) of the ion pair ($C_nHCl_3 \cdot n_oH_3O^+$) on the electrode surface and k'_c (cm s^{-1}) is a rate constant for electron transfer (cathode to target compound) that depends on material and reactor-dependent parameters such as the equilibrium potential and exchange current density for the reaction of interest. In the form given, k'_c is not an intrinsic constant (for a given E_C value), but depends on the reference potential selected (here SHE). E_C is the cathode potential (V), F (96 500 C mol^{-1}) is the faradaic constant, R (8.314 J mol^{-1} K^{-1}) is the gas constant, T is the absolute temperature (K), α_c is the cathode transfer coefficient (the efficiency with which electrode potential is applied to overcome the energy barrier to electron transfer), and n_o is the number of electrons transferred in the rate-limiting electrode reaction.

The dissociated chlorinated compounds are very reactive [27, 28] and react with atomic hydrogen (H*) (in a fast reaction) to form hydrocarbon compounds and chloride ions which are released from the surface. Using a steady-state assumption

$$\frac{\mathrm{d}m}{\mathrm{d}t}=\frac{\mathrm{d}m_\mathrm{s}}{\mathrm{d}t} \tag{5}$$

and combining Equations 2 and 4, the modified Butler–Volmer equation can be derived which accounts for the limit of mass transfer at the cathode surface [6, 20, 21].

$$-\frac{\mathrm{d}m}{\mathrm{d}t}=AC_\mathrm{l}\left[\frac{1}{k_\mathrm{m}}+\frac{1}{k_\mathrm{c}}\exp\left(\frac{n_\mathrm{o}\alpha_\mathrm{c}FE_\mathrm{c}}{RT}\right)\right]^{-1} \tag{6}$$

Integration of Equation 6 with $t=0$, $m=m_\mathrm{o}$; and $t=t$, $m=m$, results in

$$m_\mathrm{o}-m=\left[\frac{1}{k_\mathrm{m}}+\frac{1}{k_\mathrm{c}}\exp\left(\frac{n_\mathrm{o}\alpha_\mathrm{c}FE_\mathrm{c}}{RT}\right)\right]^{-1}A\int_0^t C_\mathrm{l}\,\mathrm{d}t \tag{7}$$

The mass of TCE or CF in the reactor is obtained from measurements of gas- and liquid-phase concentrations. It is evident that the area-specific rate of TCE or CF conversion should be first order in concentration of the target compound with a conditional first-order rate constant that is defined by

$$k=\left[\frac{1}{k_\mathrm{m}}+\frac{1}{k_\mathrm{c}}\exp\left(\frac{n_\mathrm{o}\alpha_\mathrm{c}FE_\mathrm{c}}{RT}\right)\right]^{-1} \tag{8}$$

where $k_\mathrm{m}=K_1k'_\mathrm{m}[\mathrm{H_3O^+}]^{n_\mathrm{o}}$ and $k_\mathrm{c}=K_1k'_\mathrm{c}[\mathrm{H_3O^+}]^{n_\mathrm{o}}$. K_1 is the equilibrium constant of Reaction 1. A plot of $m_\mathrm{o}-m$ against $A\int C_\mathrm{l}\,\mathrm{d}t$, obtained using data collected at a single cathode potential and pH should yield a straight line with slope equal to k (cm min^{-1}). Parameters k_m, k_c, and $n_\mathrm{o}\alpha_\mathrm{c}$ can be determined from the dependence of k and E_C using nonlinear regression methods. For investigating pH effect on the reaction rate, Equation 8 can be expressed as

$$k=[\mathrm{H_3O^+}]^{n_\mathrm{o}}\left[\frac{1}{k_\mathrm{m}}+\frac{1}{k_\mathrm{c}}\exp\left(\frac{n_\mathrm{o}\alpha_\mathrm{c}FE_\mathrm{c}}{RT}\right)\right]^{-1} \tag{9}$$

Thus, a plot of $-\log k$ against pH will form a straight line with slope equal to n_o.

4. Results and discussion

4.1. *Stoichiometry*

At pH 7.0 and an initial liquid-phase concentration of 1.0 mM ($-1.4 \leqslant E_\mathrm{C} \leqslant -0.3$ V), methane was the primary carbon-containing product of CF reduction, and ethane/ethylene were the principal carbon-containing products of TCE reduction. At less negative potentials ($E_\mathrm{C} > -1.0$ V), traces of dichloromethane (CF reduction experiments) and dichloroethene/*n*-butane (TCE reductions) were usually observed. Vinyl chloride or other volatile toxic products were not detected under any conditions. Carbon mass balances during CF and TCE reductions were acceptable (Figures 2 and 3) indicating that, at least at the end of each experiment, no major carbon-containing products were undetected. Notice that in each curve 5–10% of the carbon-containing target/product compounds were unaccounted for 30–40 min into the experiment. Near-complete recovery of carbon is apparent, however, after about 60 min. These results suggest that there is one or more metastable intermediates that are subsequently converted to stable end products. A reasonable, although experimentally unverified, hypothesis is that the metastable intermediates are adsorbed on the electrode surface and hence are not detected in the bulk liquid or gas head space. Alternatively, the analytical technique for intermediates may have been too insensitive to detect their presence, although this seems unlikely since

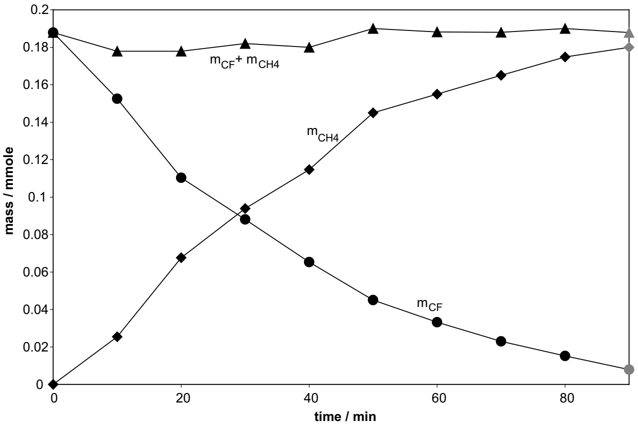

Fig. 2. Carbon mass balance for CF reduction in 0.05 M KCl electrolyte (pH 7.0) using a Pd–Ebonex cathode at −1.4 V. Methane production accounts for virtually all CF lost.

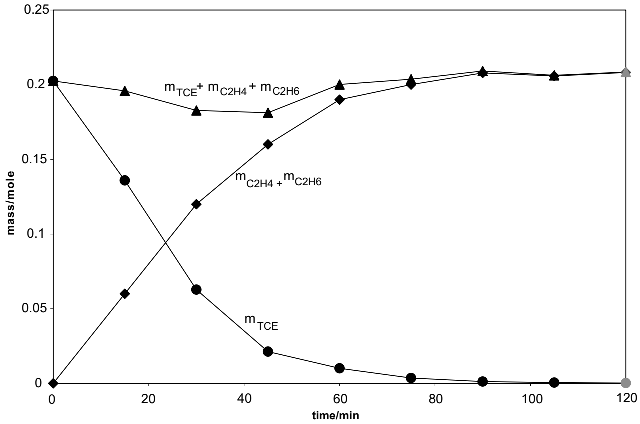

Fig. 3. Carbon mass balance for TCE reduction in 0.1 M K_2SO_4 electrolyte (pH 7.0) on Pt–Ebonex cathode at −1.4 V. Ethane and ethene accounted for all of the TCE transformed. Chlorinated intermediates not observed.

samples were analyzed using both ECD and FID techniques. A chlorine mass balance in a TCE reduction experiment was equally good (Figure 4). There is no evidence of chlorine-containing metastable intermediates in these data, however. Virtually all of the chlorine originally present as TCE was recovered as chloride ion at the end of the experiment. Thus, it would seem likely that any metastable intermediates retained on the cathode surface are completely dehalogenated.

4.2. *Kinetics: effects of target concentration and cathode potential*

TCE reduction experiments were conducted using the Ebonex-Pt electrode at potentials from −0.1 to −1.4 V. CF reductions were performed using the Ebonex-Pd electrode at $-1.4\ \mathrm{V} \leqslant E_{\mathrm{C}} \leqslant -0.3\ \mathrm{V}$. In each case, pH was maintained at 7.0, and initial concentrations of TCE or CF were near 1.0 mM. Normalized, time-dependent masses of TCE and CF are shown in Figures 5 and 6. As expected (Equation 6), kinetics were first order in the target compound (Figures 7 and 8). Figures 7 and 8 data are reported in mass rather than the more conventional concentration units since headspace volume varied during these experiments. From plots of conditional first-order rate constants (k; cm min^{-1}) against E_{C} at pH 7.0 (Figure 9), parameters k_{c}, k_{m} and α_{c} (Equation 8) were estimated using nonlinear regression analysis (Sigma Plot, Chicago). The mass transfer coefficient, k_{m}, for TCE and CF reduction was 0.45 and 0.42 cm min^{-1}, respectively. From Figure 9, it is evident that k_{m} values could be higher than estimates reported here, but not lower. The k_{m} value obtained here was about three times larger than the k_{m} reported in previous work (for TCE

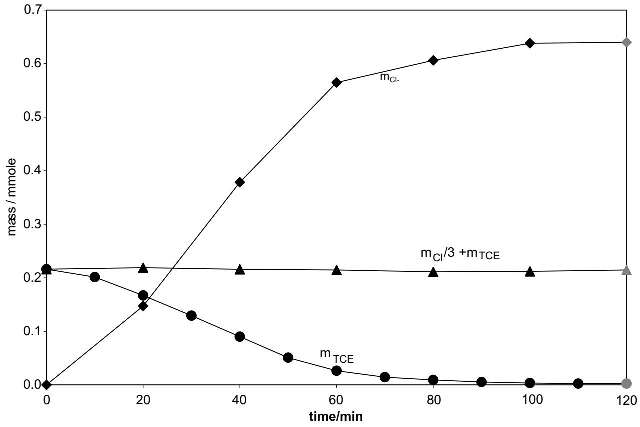

Fig. 4. Chlorine mass balance for TCE reduction in 0.1 M K_2SO_4 electrolyte (pH 7.0) on Pt–Ebonex cathode at −1.13 V. Chloride ion accounted for all chlorine lost due to TCE transformation. Chlorinated intermediates not observed.

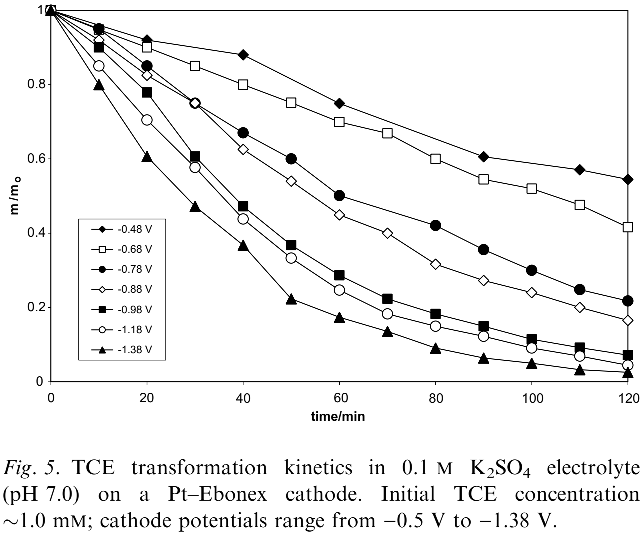

Fig. 5. TCE transformation kinetics in 0.1 M K_2SO_4 electrolyte (pH 7.0) on a Pt–Ebonex cathode. Initial TCE concentration ~1.0 mM; cathode potentials range from −0.5 V to −1.38 V.

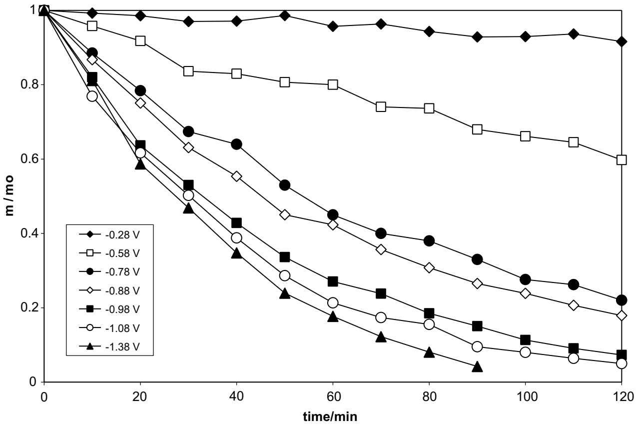

Fig. 6. CF reduction kinetics in 0.05 M KCl electrolyte (pH 7.0) on a Pd-Ebonex cathode. Initial CF concentration ~1.0 mM; cathode potentials range from −0.3 V to −1.4 V.

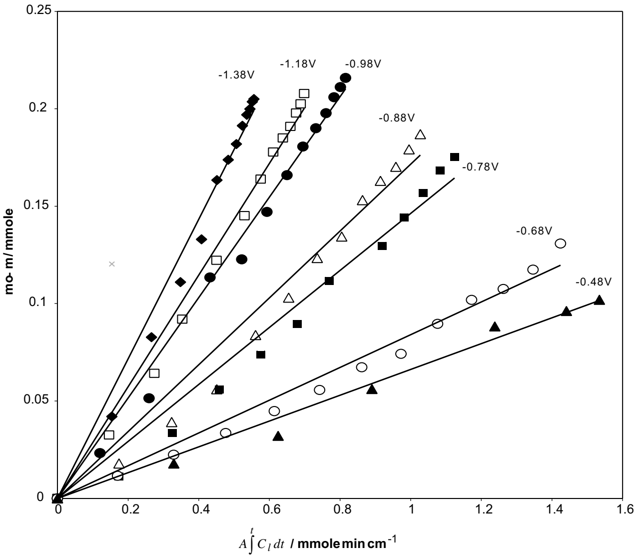

Fig. 7. Mass of TCE reduced as a function of cathode potential and time-integrated liquid-phase TCE concentration ($A\int C_{\ell}\mathrm{d}t$). Slopes of linear regression lines shown for each cathode potential data set represent conditional first-order rate constants for TCE reduction (k). Reactor conditions: 0.1 M K_2SO_4 catholyte; pH 7.0; Pt-Ebonex cathode; initial TCE concentration 1.0 mM; and $E_{\mathrm{c}} = -0.5$ V to −1.38 V.

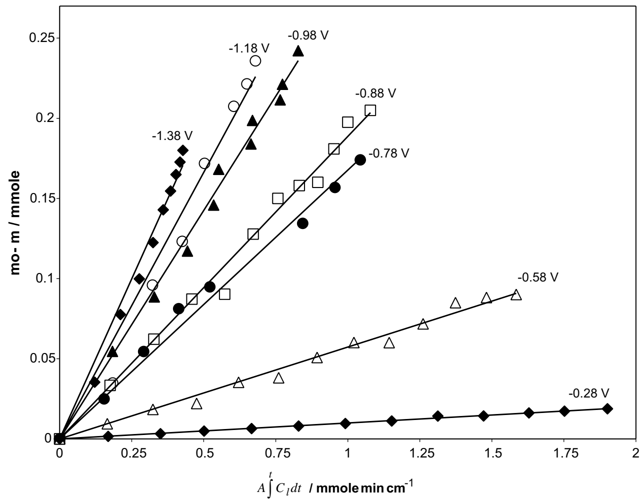

Fig. 8. Mass of CF reduced as a function of cathode potential and time-integrated liquid-phase CF concentration ($A \int C_\ell \mathrm{d}t$). Slopes of linear regression lines shown for each cathode potential data set represent conditional first-order rate constants for CF reduction reactions (k). Reactor conditions: were 0.05 M K_2SO_4 catholyte; pH 7.0; Pd–Ebonex cathode; initial CF concentration 1.0 mM; and $E_c = -0.3$ V to -1.4 V.

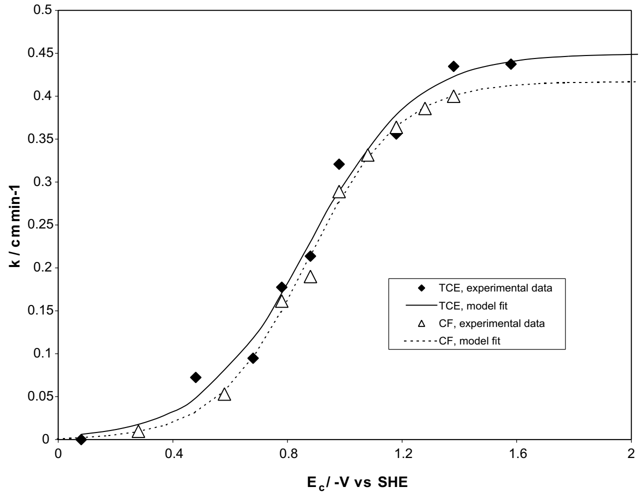

Fig. 9. Rate constants for TCE reduction on Pt-Ebonex cathode and for CF reduction on Pd-Ebonex cathode. Constants derived from the slopes of lines in Figures 7 and 8. Lines of best fit obtained using Equation 2 and nonlinear regression analysis. Fitted parameters provided in the text.

oxidation) in the same reactor with the same reactor stirring rate [6]. The apparent discrepancy may be due to differences in the mobilities of weak complexes formed by the chlorinated targets and hydronium ions in the anode and cathode boundary layers. That is, the weakly associated (positively charged) pairs may find it easier to approach the cathode surface in these experiments than the anode surface as required in the previous oxidative experiments [6]. The product of the cathode transfer coefficient and the number of electrons transferred in the rate limiting step ($\alpha_c n_0$) for TCE and CF reduction was 0.14 and 0.16, respectively.

Additional experiments were run at micromolar levels of TCE (0.1 M K_2SO_4 electrolyte, Pt-Ebonex electrode, $E_C = -0.9$ V, pH 7.0) and CF (0.05 M KCl, pH 7.0, Pd-Ebonex cathode, $E_C = -1.3$ V) to show that kinetic relationships derived at millimolar concentrations could be used to predict contaminant transformation rates in lower concentration regimes. Plots of m/m_o against time proved to be independent of initial concentration (data not shown) indicating that kinetic relationships derived here are valid over a broad range of contaminant concentrations.

4.3. *pH dependence and current efficiency*

The pH dependence of TCE reduction rate was investigated from $2 \leqslant \mathrm{pH} \leqslant 11$ and cathode potentials of -0.45 V and -0.9 V. As predicted by theory (Equation 9), area-specific rate constants ($-\log k$) were inversely and linearly dependent on pH (Figure 10). Because a pH shift accompanies hydrogen generation during these trials, a pH controller was used to automatically stat the pH by appropriate acid/base addition as required. The rate of reduction of halogenated targets, the hydrogen formation rate and the current density all decreased as pH increased. The observed dependence of k on hydronium ion concentration does not support selection of a mechanism for pH effects, however. Complexation with hydronium ion as a condition for transport to the cathode surface has already been mentioned. Alternatively, hydrogen produced at the cathode could participate in dehalogenation reactions in the acid pH range or acid catalysis may play a role.

At some potentials, the reduction of water to hydrogen was a major contributor to the overall electrolytic current, as evidenced by gas evolution. $H_2(g)$ production lowers current efficiency and may block catalytic sites on the cathode. Hydrogen production was assumed to be the only major parasitic reaction in these experiments. Thus, average current efficiency ($\bar{\eta}$) up to time t may be defined as

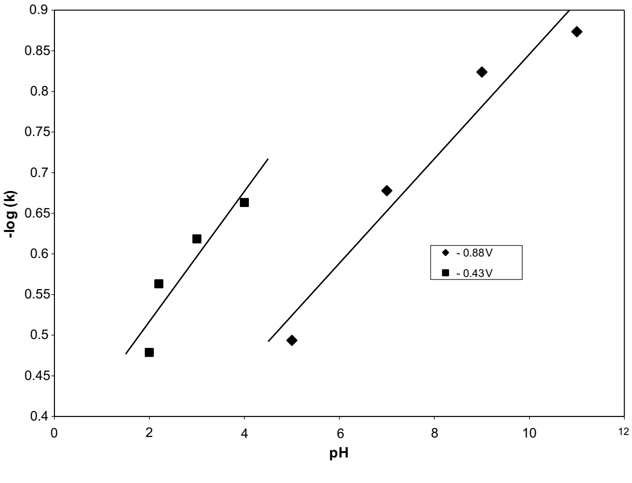

Fig. 10. TCE reduction rate constants as a function of pH (aqueous 0.1 M K_2SO_4; Pt–Ebonex cathode; and E_c – 0.43 V and −0.88 V).

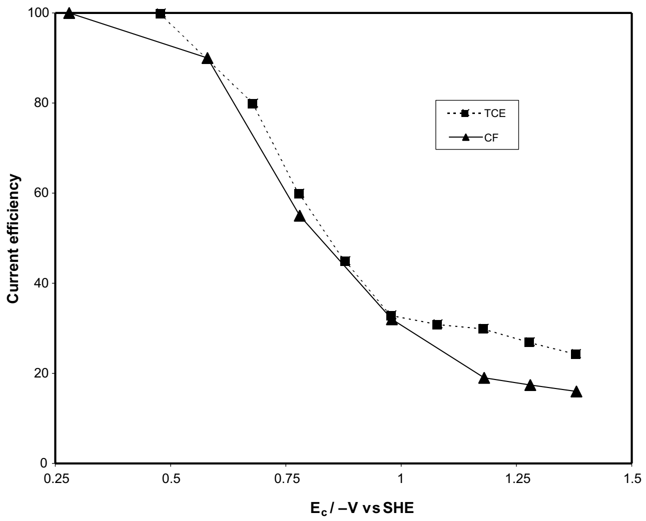

Fig. 11. Current efficiencies as a function of cathode potential for TCE and CF reductions. Experimental conditions as described in Figures 5 and 6.

$$\bar{\eta} = 1 - \frac{2Fm_{H_2}}{\int_0^t i_c \, dt} \qquad (10)$$

where i_c, m_{H_2}, and F represent the instantaneous cathodic current, the moles of hydrogen generated in time t, and faradaic constant, respectively. Average current efficiencies for TCE and CF reductions are shown as functions of E_C in Figure 11. Efficiencies approached 100% at −0.3 V for CF and −0.5 V for TCE. The lowest efficiencies were 16.6% for CF and 24.4% for TCE ($E_C = -1.4$ V). Although our results substantiate the suggestion [31, 32] that water decomposition consumes a significant portion of the current applied, the current efficiencies for TCE and CF dehalogenation were much greater than reported by Tsyganok and Otsuka [32] for 2,4-dichlorophenoxyacetic acid (2,4-D) dehalogenation. Loss of current efficiency should coincide with increased depletion of the target compounds. That is, there should have been less residual target material in experiments run at very low (highly negative) cathode potentials. Efficiency should also decrease when mass transfer limits the rate of reduction of the chlorinated targets since the reduction of water is not similarly limited. Loss of cathode active surface areas due to gas blocking could have been a factor, although probably not an important one since departures from Butler–Volmer kinetic predictions (which are based on a constant area assumption) appear to be minor.

4.4. *Electrocatalytic poisoning*

Both SO_4^{2-} and Cl^- can poison palladium catalysts [33–35]. To examine their effects on Pd- and Pt-coated Ebonex electrodes, a cathode was first soaked overnight in aqua regia (HCl:HNO_3, 3:1 v/v) to remove all Pd or Pt from the surface. After rinsing with deionized water, Pt or Pd was again electrochemically deposited. TCE was the target compound for all Cl^- poisoning studies. In the poisoning trials the freshly coated cathode was exposed to the catholyte (containing ~0.22 mmole TCE) and TCE reduction was monitored with time. The second trial was initiated by replacing the TCE depleted catholyte with fresh catholyte (again containing ~0.22 mmole TCE) and monitoring TCE reduction with time with the previously used cathode. The sequence was repeated up to five times. Since chloride ion is produced via electrolytic reduction of TCE, the effect of Cl^- on electrode performance was examined first. The electrolyte for these experiments consisted of 0.05 M NaCl and the solution pH was maintained by injecting HCl. Thus, the chloride ion concentration increased continuously during the course of each experiment. However, the catalytic activity over several repeat, 2 h experiments was essentially unaffected, indicating that the chloride ion did not poison the Pd- or Pt-coated Ebonex (data not shown).

Sulfate effects on Pd-coated Ebonex were examined for CF and TCE reduction ($E_C = -1.13$ V and −1.38 V, resp.; pH 7.0; and 0.1 M K_2SO_4 electrolyte). Progressively lower rates of reaction were observed as the Pd–Ebonex cathode was used in sequential reduction experiments involving either CF or TCE. Results clearly reflect sulfate poisoning (Figure 12). On the newly prepared cathode, the CF half-life was 20 min. In a second experiment, the half-life increased to 80 minutes. After five repeat experiments, Pd–Ebonex activity for CF reduction was completely lost. Results were similar in a TCE reduction experiment at $E_C = -1.38$ V. On the other hand, SO_4^{2-} did not poison Pt-coated Ebonex (data not shown). The resistance of platinum cathodes to sulfur poisoning has been observed previously [36].

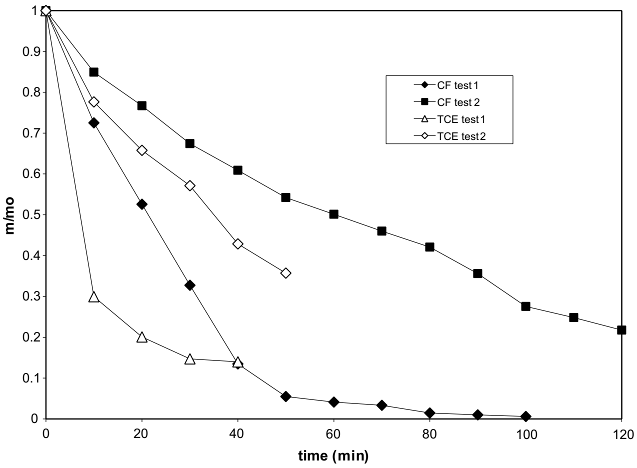

Fig. 12. Poisoning of Pd-Ebonex cathode in 0.1 M K_2SO_4 solution (pH 7.0) when used in sequential trials without cleaning. CF and TCE trials used constant cathode potentials of −1.13 and −1.38 V, respectively. In test one a new Pd plated cathode was exposed to the test solution, while in test two the cathode previously used in test one was exposed to a new, full strength target solution.

4.5. *Ebonex performance*

The Ebonex substrate for Pd and Pt proved to be a robust platform for development of a supported catalyst. Electrolytic deposition of both elemental palladium and platinum from salt-containing solutions was convenient and, although microscale measurements were not undertaken, produced a surface that was macroscopically uniform. There was no evidence of deterioration of performance by the platinum catalyst suggesting that corrosion will not interfere with the Pt–Ebonex interface. No attempt was made to optimize the mass of platinum deposited on the porous Ebonex support or its presentation in solution. Consequently, an operating reactor for reductive treatment of halogenated solvents may be capable of much better kinetic performance than was observed here. Issues associated with reactor design merit additional attention. Ebonex is less fragile than the carbon materials commonly used for reactor electrodes and its costs are not prohibitive. Thus, at this stage of development, Ebonex is an operationally and economically attractive material for the electrolytic treatment of halogenated solvents.

5. Summary

Ebonex ceramic was plated with Pt or Pd for the electrolytic dechlorination of TCE and CF to hydrocarbons and chloride ion. Without the Pt or Pd catalyst, no dechlorination occurred on Ebonex ceramic cathodes. The transformations of TCE and CF were pseudo first-order in target concentration at constant pH and cathode potential ($-0.3\ \mathrm{V} \leqslant E_C \leqslant -1.4\ \mathrm{V}$). Area-specific, first-order rate constants were the same at initial target concentrations of 1.0 μM and 1.0 mM. TCE and CF reduction kinetics were limited by mass transport to the electrode surface at $E_C \leqslant -1.4$ V. Maximum surface area-normalized rate constants for reduction reactions were 0.45 cm min^{-1} for TCE and 0.42 cm min^{-1} for CF. The current efficiency for TCE and CF reductions decreased as the cathode potential became more negative, probably because mass transfer limits restricted reductions of the targets, but not the reduction of water. Reduction rates were increased with hydrogen ion concentration in the range $2 \leqslant \mathrm{pH} \leqslant 11$. Sulfate poisoning of Pd plated cathodes was observed for both CF and TCE targets, but a similar effect was not observed for Pt plated cathodes.

The two most commonly applied technologies for treating VOCs, granular activated carbon adsorption and air stripping, do not destroy the target compound, but merely transfer it to another phase from which it is more easily disposed. The method of electrocatalytic reduction of VOCs investigated in this work suggests an attractive alternative treatment method, which could be easily adapted to treat a wide range of contaminant concentrations and VOC species on-site and destroy the target species without generation of toxic byproducts. Use of Pt-amended Ebonex electrodes in a reductive dehalogenation mode provides treatment of compounds such as chloroform, which are not easily dehalogenated oxidatively and provides a high resistance to sulfate and nitrate, common groundwater ions, which may poison electrodes. In addition, the Pt/Ebonex current can be reversed to remove scale deposits that would progressively inhibit performance.

Acknowledgements

This publication was made possible by grant number P42 ES004940 from the National Institute of Environmental Health Sciences, NIH. Ms C. Flowers prepared the manuscript.

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