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Electrochemical Reduction of CO_2 in a Mixed Supercritical Fluid

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A mixture of 1,1,1,2-tetrafluoroethane (HFC 134a) and carbon dioxide is used as a medium for electrochemical study. The reduction of CO_2 in the liquid and supercritical states was investigated on both Pt and Pb electrode surfaces. It was shown that there is a decrease in the reduction potential on both electrode materials in the supercritical state compared to the liquid. The reduction of CO_2 on a Pt electrode is shown to have a high faradaic efficiency for oxalate production. This is discussed in terms of the adsorption of the $CO_2^{\bullet-}$ anion radical on the electrode surface.

Introduction

Following the work of Royer in 1870,[1] the electroreduction of carbon dioxide has been studied at a variety of cathode materials in both aqueous and nonaqueous electrolyte solutions.[2−5] A variety of organic compounds have been produced accordingly. The most abundant reactions, however, are

$$CO_2 + H^+ + 2e^- \rightarrow HCOO^- \qquad (1)$$

$$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O \qquad (2)$$

$$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O \qquad (3)$$

$$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O \qquad (4)$$

$$2CO_2 + 2e^- \rightarrow (COO^-)_2 \qquad (5)$$

$$2CO_2 + e^- \rightarrow CO + CO_3^- \qquad (6)$$

Electroreduction of CO_2, therefore, commonly produces a mixture of organic compounds. Large overpotentials are required to activate the CO_2 molecule because of its stability.[6] Thus, in aqueous solutions hydrogen evolution always accompanies the reduction of CO_2.[7,8] The faradaic yield of each product is therefore a critical parameter used to assess the reaction selectivity.

In aqueous solutions, the majority of organic compounds formed possess a single carbon atom.[2,9] The nature of the cathode and electrolyte solution largely determines the faradaic yields and composition of the electroreduction products. The metallic cathodes can be generally grouped in accordance with the primary reaction products.[2] Of all the organic products listed above, formic acid is the least desirable. It is difficult to separate from solution, and on oxidation to carbon dioxide its energy content is extremely low.

Many studies in aqueous solutions have focused on metal electrodes that require high overpotentials for the cathodic evolution of hydrogen. By employing cathode materials such as lead, mercury, tin, and indium,[7,9−12] hydrogen evolution can be minimized at low overpotentials. Teeter and van Rysselberghe, for example, observed faradaic yields close to 100% for formate production at a mercury electrode in aqueous solution, but this is of limited value.[12,13]

More recent investigations have concentrated on the electroreduction of CO_2 in aqueous solutions at a variety of nonmetallic cathodes, such as oxide and semiconductor electrodes.[14−19] Bandi demonstrated the electrosynthesis of methanol with a faradaic efficiency of 50−70% by employing an electrode prepared from mixed oxides of ruthenium and titanium.[15] Taniguchi and co-workers also produced methanol with reasonable faradaic efficiency (44%) on a p-type GaP cathode in the presence of a crown ether.[17] A number of studies have also investigated the electroreduction of CO_2 in aqueous media containing complex catalysts.[20−22]

The problems associated with hydrogen evolution in the electrochemical reduction of CO_2 can be completely irradicated by using aprotic solvents. Reactions 1−4 can then be neglected. Hence, the electroreduction of CO_2 in nonaqueous media promises high yields of oxalate anions. In the first such study in 1967, Haynes and Sawyer investigated CO_2 reduction in dimethyl sulfoxide at gold and silver electrodes via a variety of electroanalytical techniques.[23] On both metals, somewhat unexpectedly, CO and formate were the main reaction products. The electrosynthesis of formate ions on gold, however, was shown to be strongly dependent on the water content of the solvent.

Any adventitious water present in the system acts a proton donor, facilitating reaction 1 and thus increasing the faradaic efficiency of formate production at the expense of that of oxalate and CO.[9] Subsequent studies in nonaqueous solvents have shown that high yields of oxalate ions can be obtained if the water content of the system is minimized and an appropriate electrode material employed.[9,24−26] In 1972, for example, Baizer et al. employed a mercury electrode in dimethylformamide and acquired a faradaic efficiency of approximately 90% for oxalate production in the absence of water.[26] The variation in product selectivity achieved with metallic cathodes in aprotic solutions prompted Ito and co-workers to introduce a scheme of electrode classification.[9]

The low solubility of CO_2 in both protic and aprotic liquid media commonly limits the rate of the reduction process. The concentration of CO_2 in solution can be raised by increasing the CO_2 pressure. At 25 °C, for example, CO_2 has a solubility in water of only 0.033 mol dm^{-3}, a concentration that increases

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to 1.17 mol dm^{-3} at a CO_2 pressure of 60 atm.[27] Ito and co-workers investigated the effects of increasing pressure on the electroreduction of CO_2 in aqueous solution at Zn, Pb, In, and Sn electrodes.[11,28] Increasing the CO_2 pressure to approximately 20 atm led to a gain in both the faradaic efficiency and current density of the reductive process. Further investigations have shown that CO_2 can be reduced with relatively high faradaic efficiencies (16−62%) under high CO_2 pressures (50−60 atm) on Co, Fe, Pt, Pd, and Ni electrodes.[29] The electroreduction of CO_2 was negligible, however, when employing the same electrode materials and a CO_2 pressure of 1 atm.

Bandi and co-workers suggested that liquid CO_2, containing a tetraalkylammonium electrolyte, could be employed as the electrochemical solvent in the reduction of CO_2.[30,31] The problems associated with CO_2 solubility and hydrogen evolution would, therefore, be irradicated. Although CO_2 can be made conducting through the introduction of bulky hydrophobic electrolytes,[32] the resistivity of the medium is still too high as to make the reduction reaction impractical.

Supercritical media are miscible with gases in all proportions, which facilitates very high CO_2 concentrations. Mass transport of an electroactive species to or from the electrode surface is also rapid in such low-viscosity media. Furthermore, CO_2 itself has conveniently low critical constants ($T_c = 31.4$ °C; $p_c = 72.3$ bar). As a result, supercritical CO_2 has been reduced under nonelectrochemical conditions using catalysts such as ruthenium(II) complexes.[33]

Abbott and Harper were the first to investigate the electrochemical reduction of CO_2 in the supercritical state.[34] The reductive process was studied at platinum and lead electrodes in a supercritical CO_2/H_2O solvent mixture. The aqueous component of the mixture acts as a polar modifier, permitting the dissolution of a $TBABF_4$ electrolyte and hence substantially increasing the conductivity of the medium. At platinum electrodes formate was the only significant product detected, with faradaic efficiencies below 30%. Oxalate was shown to be the major organic product formed at a lead electrode with a faradaic efficiency of approximately 16%. The low faradaic efficiencies of the organic products were attributed to competition from the hydrogen evolution process

$$H_2O + e^- \rightarrow {}^1/_2H_2 + OH^- \tag{7}$$

In this work, 1,1,1,2-tetrafluoroethane (HFC 134a) rather than water will be employed as a polar modifier in the supercritical mixtures. Mixtures of CO_2 and HFC 134a were recently shown to be useful fluids because of their low critical constant, lack of toxicity, and relatively high polarizability per unit volume.[35] Significant solubility of quaternary ammonium electrolytes can be obtained, which permits electrochemical processes to be studied. Reactions 7 and 1−4 can then be completely neglected at negative overpotentials because HFC 134a is aprotic. As a result, the electroreduction of CO_2 should be more efficient and the formate anion should not form. HFC 134a also has a considerably lower critical temperature than water, leading to relatively mild critical conditions for the solvent mixture.[36] The current work reports the product distributions and efficiencies associated with the electroreduction of CO_2 at Pt and Pb electrodes in supercritical CO_2/HFC 134a solvent mixtures.

Experimental Section

A schematic of the high-pressure apparatus is shown in Figure 1. Prior to each experiment the reaction vessel was purged with the HFC 134a/CO_2 gas mixture. Pressure was then applied using a model 10-600 pump (Hydraulic Engineering Corp., Los Angeles, CA), driven by compressed air. The temperature of the high-pressure cell was measured using an iron/constantan thermocouple, the tip of which was in contact with the solvent close to the cell center, and retained at a given value (±0.5 K) using a CAL 9900-controlled heater. The pressure was monitored (±0.2 MPa) using a UCC type PGE 1001.600 manometer.

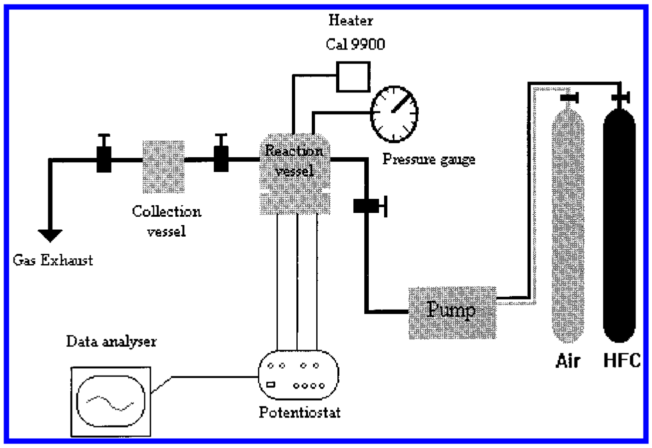

Figure 1. Schematic of the high-pressure apparatus.

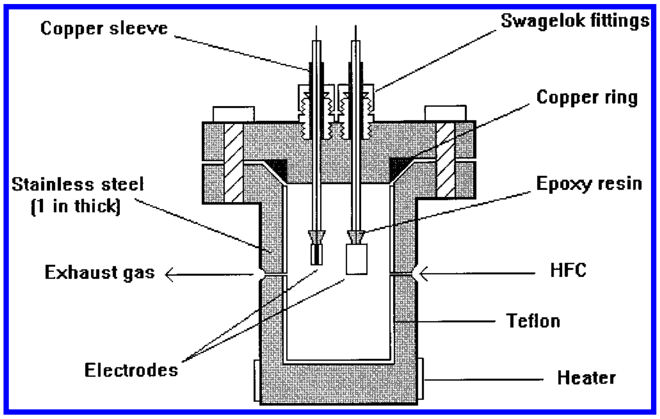

Figure 2. High-pressure cell.

Figure 2 shows the cell used in the high-pressure experiments. The cell was constructed from 316 stainless steel and was rated to 1.5 kbar. The cell, lined with a layer of Teflon 1 mm thick, had a volume of approximately 15 cm^3. A copper ring was used to provide a high-pressure seal between the head and base of the cell. The electrical feedthroughs consisted of microwave cable (RS Components Ltd.) sealed by Swagelok fittings. Voltammetric studies were carried out on a 10 μm diameter electrode using a Ag/Ag$^+$ pseudoreference electrode. A PGSTAT 20 potentiostat (Ecochemie, Utrecht, Holland), computer controlled via GPES software was used to collect the voltammetric data.

A concentric cylindrical two-electrode configuration, with an electrode separation of 2 mm, was used in all bulk electrolyses. The outer stainless steel cylinder formed the anode and was platinized by the standard technique.[37] The inner cathodic cylinder was formed from either platinum black on stainless steel or lead. The electrode areas of the anode and cathode were 45.4 and 38.6 cm^2, respectively. Each electrolysis was performed under potentiometric control, employing an EG&G Princeton Applied Research potentiostat.

The 30.6 mol % 1,1,1,2-tetrafluoroethane (HFC 134a) in CO_2 mixture (ICI Klea group, 99.99%) and the electrolyte, tetrabutylammonium tetrafluoroborate (Fluka, electrochemical grade), were used as received.

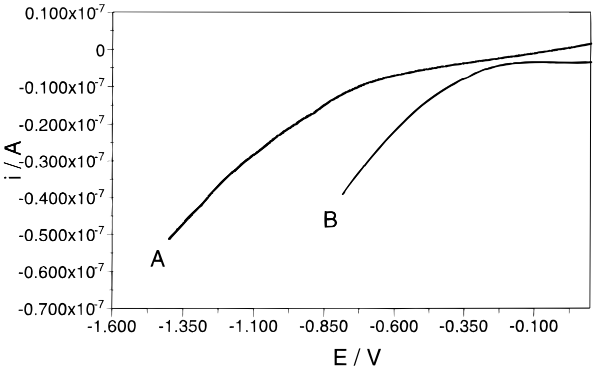

Figure 3. Voltammograms recorded at a 10 μm diameter Pt disk microelectrode in CO_2/HFC 134a ($x_{\mathrm{HFC\ 134a}} = 0.304$) with 20 mM $TBABF_4$; A = 30 °C and 150 bar (liquid), B = 60 °C and 150 bar (supercritical). Scan rate = 20 mV s^{-1}.

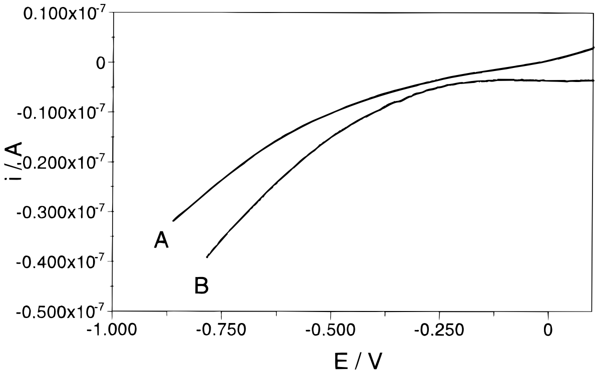

Figure 4. Voltammograms recorded at a 10 μm diameter Pt disk microelectrode in supercritical CO_2/HFC 134a ($x_{\mathrm{HFC\ 134a}} = 0.304$) at 60 °C with 20 mM $TBABF_4$; A = 200 bar, B = 150 bar. Scan rate = 20 mV s^{-1}.

Following electrolysis, all gaseous samples were transferred from the electrochemical cell into a high-pressure sample vessel. The stainless steel collection vessel had a volume of 250 cm^3 and a maximum working pressure of 30 bar. A measured volume of the gas sample was then introduced into a Tedlar bag with an internal volume of 1 dm^3. A Chrompack CP9000 with flame ionization detection was used to analyze the sample, where the Poropack Q-packed column was 2 m long and had an internal diameter of 4 mm. The oven temperature was held at 30 °C, while nitrogen was employed as the carrier gas.

The formate and oxalate content of the bulk electrolysis product was analyzed by high-performance liquid chromatography. The recovered electrolyte was first dissolved in 0.1 M H_2SO_4(aq) to ensure protonation of any formate and oxalate anions. Following filtration through a 20 μm glass sinter, the solutions were analyzed via a Hewlett-Packard 164 high-performance liquid chromatograph. A Whatman Partisphere C18 reversed phase column was used to detect both formic and oxalic acids. The mobile phase consisted of 10 mM H_3PO_4(aq), where the flow rate was maintained at 1 mL min^{-1} and the sample injection volume was 20 μL. The products were detected by UV absorbance, employing a fixed wavelength of 210 nm. Although analysis for carbonate was not carried out, it can be assumed that the faradaic efficiency was the same as that for CO.

Results and Discussion

A CO_2/HFC 134a mixture with a HFC 134a mole fraction, $x_{\mathrm{HFC\ 134a}}$, of 0.306 was employed as the solvent in all of the voltammetric experiments presented in the current work. This composition exhibits relatively mild critical constants ($T_c = 57$ °C; $p_c = 72$ bar),[36] while simultaneously facilitating the dissolution of a sufficient amount of $TBABF_4$ electrolyte to support electrochemistry without significant ohmic distortion. All of the CO_2/HFC 134a/$TBABF_4$ systems employed in the current work were present as a single phase, as confirmed by visual observation using an optical cell.

Figure 3 shows cathodic voltammograms recorded at a platinum microelectrode in both liquid and supercritical CO_2/HFC 134a mixtures with $TBABF_4$ concentrations of 20 mM. The cathodic current can be assigned to the reduction of CO_2 because both HFC 134a and $TBABF_4$ are electroinactive over the potential range investigated. In the liquid phase at 30 °C and 150 bar, CO_2 is electroreduced at potentials negative of approximately −0.6 V vs Ag/Ag^+. On increasing the temperature to 60 °C the reduction wave is shifted to more positive potentials. Under these supercritical conditions, the potential corresponding to the onset of CO_2 reduction is approximately −0.19 V. Negative shifts in the onset potential of CO_2 reduction are commonly ascribed to the adsorption of intermediates, such as CO, on the electrode surface.[38−41] It is, therefore, implied that adsorbed species such as CO exhibit a lower surface coverage on the platinum electrode under the supercritical conditions studied. Note that the observed positive shift in potential cannot be attributed to an increase in CO_2 concentration, as described by Ito and co-workers,[28] because the density of the specified supercritical mixture is lower than that of the liquid mixture studied.

Figure 3 also shows that the cathodic current associated with CO_2 reduction at a platinum electrode is higher under supercritical conditions. This result implies that the rate of CO_2 reduction is limited by mass transport in the liquid phase at 30 °C and 150 bar. The lower viscosity of supercritical CO_2/HFC 134a will allow any species involved in the electroreduction of CO_2 to diffuse to and from the electrode surface at higher rates than in the liquid.

The potential for the onset of CO_2 reduction is shown in Figure 4 to undergo a slight negative shift to approximately −0.25 V as the pressure of the supercritical fluid is increased from 150 to 200 bar at 60 °C. The density of the fluid increases with increasing pressure, suggesting that the negative potential shift is caused by an increase in intermediate adsorption on the electrode surface and not a CO_2 concentration decrease. At the lower pressure of 150 bar, there is also an increase in the cathodic current. This increase can be assigned to the drop in fluid viscosity and consequent increase in the diffusivity of any species involved in the reductive process.

Figure 5 shows voltammograms recorded in liquid and supercritical CO_2/HFC 134a at a lead microelectrode. At 30 °C and 165 bar the reduction of CO_2 only occurs at potentials negative of −2.15 V. This value is considerably more negative than the corresponding reduction potential on platinum. Vassiliev and co-workers also reported that the overpotential of CO_2 reduction in liquid aprotic solvents is more negative on lead than on platinum.[42] The large difference in onset potentials reported in this work suggests that there is a change in the major reaction mechanism of CO_2 reduction on replacement of the platinum electrode with lead.

In supercritical solutions at 60 °C and 240 bar the reduction wave reported in the liquid phase shifts to more positive potentials by approximately 1.2 V. This shift is larger than that observed on platinum and suggests that intermediates such as CO are adsorbed to a greater extent on lead under the liquid-phase conditions specified. The overpotential of CO_2 reduction

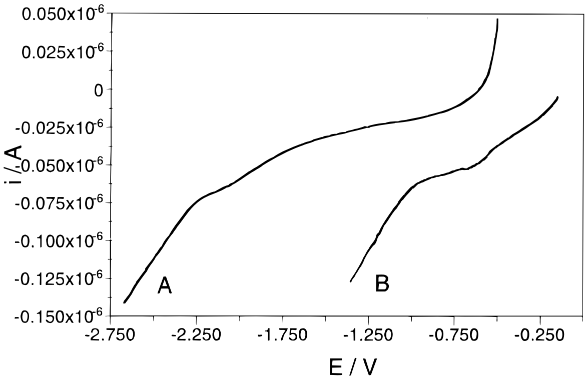

Figure 5. Voltammograms recorded at a 25 μm diameter Pb disk microelectrode in CO_2/HFC 134a ($x_{HFC\ 134a} = 0.304$) with 20 mM $TBABF_4$; A = 30 °C and 165 bar (liquid), B = 60 °C and 240 bar (supercritical). Scan rate = 20 mV s^{-1}.

TABLE 1: Electrochemical Reduction Products of CO_2 at Platinum and Lead Electrodes in CO_2/HFC 134a ($x_{HFC\ 134A} = 0.304$) with 0.1 M $TBABF_4$ (Charge Passed = 100 C)

			faradaic efficiency/%		
electrode	*T*/°C	*p*/bar	$(COOH)_2$	CO	HCOOH
Pt	60	260	41.6	14.6	0
	80	260	37.3	16.4	0
Pb	60	260	17.5	42.0	0
	80	260	13.7	42.9	0

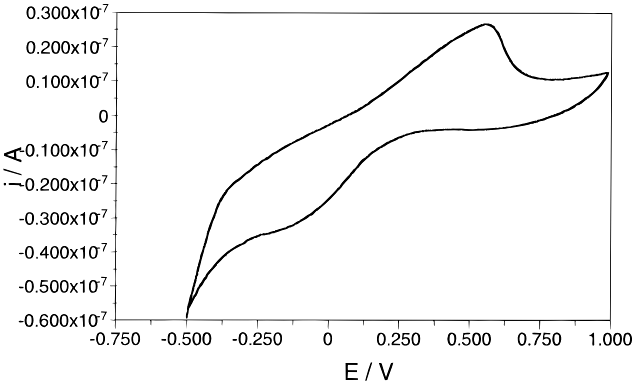

Figure 6. Cyclic voltammogram recorded at a 10 μm diameter platinum disk microelectrode in CO_2/HFC 134a ($x_{HFC\ 134a} = 0.304$) at 60 °C and 260 bar following the completion of a bulk electrolysis experiment. Scan rate = 20 mV s^{-1}.

is, however, still significantly more negative than that on platinum. Electroreduction of CO_2 on platinum is, therefore, a more attractive proposition because it is a more energy efficient process.

Bulk electrolysis experiments were performed in supercritical CO_2/HFC 134a mixtures at both platinum and lead electrodes. In each case, a constant potential of −4 V was applied to the working electrode until 100 C of charge were passed. The faradaic efficiencies of the detected products are given in Table 1.

The faradaic efficiency of oxalate formation is reasonably high at a platinum electrode at the supercritical conditions listed. In comparison, previous studies in liquid aprotic media have reported faradaic efficiencies no higher than 5%.[9] In these liquid media CO was the main product with faradaic efficiencies higher than 60%. It was thus suggested that the $CO_2^{\bullet-}$ radical anions easily desorb from the Pt surface and are then attacked by CO_2 molecules in the bulk to form CO. In the supercritical CO_2/HFC 134a mixture, however, the CO_2 concentration will be much higher at the electrode surface than in the aforementioned liquid bulk electrolysis experiments. There will, therefore, be a higher surface coverage of $CO_2^{\bullet-}$ radical anions, facilitating dimerization to the oxalate anion, as shown in eq 5. Consequently, a lower percentage of $CO_2^{\bullet-}$ radical anions will desorb from the electrode surface to form CO, as exemplified by the lower faradaic efficiencies of CO formation in Table 1. These results, therefore, show that when very high concentrations of CO_2 are employed, the efficiency of oxalate formation is less dependent on the energetics of CO_2 adsorption at the electrode surface.

Table 1 also shows that the faradaic efficiency of oxalate formation undergoes a slight decrease when the temperature of the supercritical system is raised from 60 to 80 °C. There is also a slight concurrent increase in the faradaic efficiency of CO formation. These changes could result from the lower density of the solvent at 80 °C and the consequent decrease in CO_2 concentration at the electrode surface or the increased desorption of the $CO_2^{\bullet-}$ anions at higher temperature. At 80 °C there will, therefore, be a lower surface coverage of $CO_2^{\bullet-}$ radical anions on the electrode surface and a reduced tendency to form oxalate ions.

It is evident from the results in Table 1 that the combined faradaic efficiencies of oxalate and CO formation fall some way short of 100%. This deficit can probably be attributed to design of the electrochemical cell, where the anode and cathode are not separated. Voltammetry was performed at a platinum microelectrode in the electrochemical cell after the bulk electrolysis of CO_2 at 60 °C and 260 bar, as shown in Figure 6. An anodic peak was observed at approximately +0.55 V, which can probably be ascribed to the oxidation of dissolved oxalate.

In an attempt to prove this idea the cathode and anode were separated using a medium porosity glass frit. The 3 mm thick frit was placed centrally between two rectangular platinum electrodes (26 × 10 × 0.5 mm), separated by a distance of 8 mm. The anode was then enclosed in Teflon so that the anodic compartment was only separated from solution by the glass frit. A bulk electrolysis experiment was then performed at 80 °C and 260 bar in supercritical CO_2/HFC 134a with 0.1 M $TBABF_4$ at −4 V. After the passage of 50 C of charge, the faradaic efficiency of oxalate production was 43.0%. This value is higher than that of 37.3% observed in the nonseparated electochemical cell, which tends to confirm the idea that the faradaic efficiencies listed in Table 1 are affected by the reoxidation of the oxalate ions at the anode. The oxidation of oxalate may be inhibited more efficiently by the employment of an ion exchange membrane. Considering that the experimental conditions in the present study were not optimized, supercritical CO_2/HFC mixtures appear to be extremely promising media for the efficient electrosynthesis of oxalate.

Conclusion

It has been demonstrated for the first time that CO_2 can be reduced electrochemically in aprotic mixtures in the supercritical phase. Voltammetry has shown that at a platinum electrode in a CO_2/HFC 134a mixture the reduction of CO_2 is under mass transport control. The kinetics of reduction are, therefore, enhanced by employing a supercritical CO_2/HFC 134a mixture.

The nature of the electrode material has been shown to affect both the kinetics and products of CO_2 electroreduction in supercritical CO_2/HFC 134a. Platinum has been shown to be far superior than lead as a cathode material on which to reduce CO_2 in supercritical CO_2/HFC 134a mixtures by both voltammetric and bulk electrolysis experiments. Employing a supercritical CO_2/HFC 134a mixture rather than an aprotic liquid as the electrochemical solvent dramatically improves the faradaic efficiency of oxalate formation at a platinum electrode. This increase in efficiency can be mainly attributed to the high concentration of CO_2 at the electrode surface in supercritical CO_2/HFC 134a mixtures.

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