An electrosynthesis of tetrafluoroethylene in molten salts

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The electroreduction of difluorodichloromethane, CF_2Cl_2, has been studied at porous electrodes in LiCl-KCl eutectic. Tetrafluoroethylene is produced in high efficiency at low conversions; the reaction is believed to proceed via difluorocarbene. At high conversions carbon is a major product. In the presence of oxygen, trifluorochloromethane is also formed. Application of fuel cell electrodes to electrosynthesis of gaseous products from gaseous reagents is briefly discussed.

1. Introduction

1.1. Chemical considerations

We have investigated the two-electron electrolytic reduction of dichlorodifluoromethane to give difluorocarbene

$$CF_2Cl_2 + 2e \longrightarrow :CF_2 + 2Cl^- \qquad (1)$$

under conditions favouring subsequent dimerization to tetrafluoroethylene (TFE).

Reports have been made of small yields of adducts attributable to carbene intermediates when alkenes are added in the electrochemical reduction of gem-halides in organic solvents at room temperature [1]. The low efficiency of trapping is probably due to loss of carbene by reaction with the medium. We hoped to generate difluorocarbene in a medium with which it should not react. A metal chloride melt should be particularly suitable for this purpose since there are no bonds in the solvent in which the carbene can insert, and additionally the anode reaction is a simple fast discharge of chloride ions to give chlorine.

$$2Cl^- \longrightarrow Cl_2 + 2e \qquad (2)$$
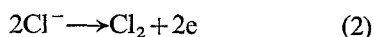
Chloride is liberated in reaction (1) and consumed in reaction (2) in equivalent quantities, so

that ideally there is no net change in melt composition. Precedents for the reactions of difluorocarbene under similar conditions are known from its generation in the gas phase and by pyrolysis [2].

Difluorocarbene is thought to be produced by pyrolysis of trifluoromethyl derivatives of arsenic, antimony, tin and phosphorus. At 180–220°C $(CF_3)_3MCH_3$ (where M = As or Sb) gave some TFE and hexafluoropropene (HFP) and $CF_3Sn(CH_3)_3$ gave HFP at 150°C. $(CF_3)_3$ PF_2 gave largely HFP at 120°C and TFE at 200°C; polytetrafluoroethylene (PTFE) (10%) was formed in both cases. Difluorocarbene is formed from fluorocarbons in the gas phase by radio frequency discharge or flash photolysis and simply dimerizes to TFE at 25°C; $:CF_2$ disappears in a second order process (not a wall reaction) [3].

Our method involves generation of $:CF_2$ at a conductor surface. Little is known of its reactions under these conditions. A patent claims that a friction-lowering film is formed on metals by the action of the decomposition products of $CClF_2$ CO_2Na, a known difluorocarbene precursor [4]. There are thus good grounds for supposing that $:CF_2$ generated in an inert medium would give TFE or perhaps PTFE. At the temperature of the chloride eutectic, PTFE would decompose [5] to oligomers of $:CF_2$. TFE and hexafluoropropene

may be reducible cathodically under our conditions; this was not checked.

The reaction medium must contain no readily reducible cations whose reduction might compete with that of CF_2Cl_2. Alkali metal, alkaline earth and quaternary ammonium cations are generally the most difficult to reduce and offer the best chance of discriminating between the reductions of the cation and CF_2Cl_2 by choice of cathode potential (or current density). Reduction of an alkali metal cation would lead to alkali metal deposition at the cathode; sodium and potassium are known to give carbon with CF_2Cl_2. Ternary mixtures of alkali metal chlorides melt little lower than the lithium-potassium chloride eutectic (350°C) and we chose the latter for most of the work. A few experiments were carried out with NBu_4 NO_3.

1.2. *Fuel cell technology applied to electrosynthesis*

We are dealing with a gaseous reagent whose solubility in molten LiCl/KCl is probably only of the order of that of a rare gas (10^{-7} mole ml^{-1}). A large gas, melt, electrode interface becomes of prime importance in the present application. Fuel cell porous electrodes were used and these must be prevented from flooding to achieve maximum current densities. This can be achieved in these ways:

(i) Applying pressure to the reactant gas so that the interface with the melt is kept within the pores of the electrode.

(ii) Stabilizing the interface within the electrode by dual porosity. If the pores on the electrolyte side are fine and those on the gas side coarse, keeping the interface at the pore discontinuity by applying pressure to the gas is a simple matter.

(iii) Making a composite electrode of a conducting material that is wetted by electrolyte and a second, non-wetted material which need not be conducting. The non-wetted material may either form a layer on the gas side of the electrode or be mixed with the wetted conductor.

(iv) Using a non-wetted conductor as the electrode.

In fuel cell and battery applications the reagent is generally passed over the rear of the electrode ('flow-by mode'), and not allowed to bubble through the electrolyte ('flow-through mode'). Higher current densities are known to be achieved when this flow-through occurs, but the attendant problems of reagent recovery and recycling make the mode unattractive in energy conversion. In electrosynthesis recovery and recycling are more acceptable.

Fuel cell development has floundered largely because the electrodes need to be catalytic (i.e. to break bonds in the reagent before electron transfer can occur) and electrodes lose their activity with prolonged use. In the electrochemical reduction of organic halides bond fission is not a prerequisite of electron transfer and this difficulty should not arise. We have tried to avoid electrode flooding by the approaches (i), (iii) and (iv), with gas flowing both over and through the electrode. Dual porosity electrodes are obsolete in fuel cells and were not thought worth making for this work.

Models of fuel cell electrodes guided our electrode designs and choice of materials. At a non-wetted electrode the reaction takes place at the interface between the mouths of the pores and the electrolyte. In this case using the flow-by mode, the maximum current density is proportional to $P_r\phi_r/r$, where P_r is the partial pressure of reagent gas at the electrode/electrolyte interface and ϕ_r is the volume fraction of pores of radius r in the electrode. P_r is increased by high gas feed pressures, but decreased by the resistance to flow in the pores and the build up of impurity gases at the interface. A thin high porosity electrode and a high gas feed pressure maximize the current [6].

At a partially wetted electrode the reaction takes place at areas of electrode covered by thin films of electrolyte. A high reactant gas partial pressure above these films is desirable, but too thin an electrode reduces the area covered by electrolyte films. There is generally an optimum thickness [7].

Fuel cell and battery reactions are different from ours in the important respect that the products are ions or molecules soluble in the electrolyte. A gaseous product would decrease the partial pressure of the reactant gas within

the electrode, and could lead to a reduction in current.

2. Experimental and results for reduction of CF$_2$Cl$_2$

2.1. Melt composition and purification

Lithium chloride (BDH anhydrous) and potassium chloride (BDH AR) were ground together (41·5 mole % KCl) and dried for 10 h at 0·05 mm and 150°C. In some early experiments no further purification was given to the melt. Two alternative treatments were given later. The first consisted of bubbling a stream of hydrogen chloride through the melt for 1 h, followed by a stream of argon. The hydrogen chloride removed hydroxide ion (Equation 3) which is formed on heating wet lithium chloride. Argon removes the excess of HCl [8].

$$OH^- + HCl \longrightarrow Cl^- + H_2O \qquad (3)$$
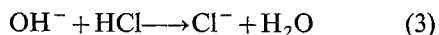
The second treatment removes hydroxide ions with chlorine, which is claimed to be more efficient than HCl [9]. Excess of chlorine was removed by argon. This treatment was followed by electrolysis at a nickel tube cathode at a potential some 0·5 V more cathodic than that to be used in the reduction of CF$_2$Cl$_2$. Background currents were reduced from 100 mA cm^{-2} to 15 mA cm^{-2}. Tetra-n-butyl ammonium nitrate was prepared by neutralization and crystallized twice from benzene.

2.2. Apparatus

The experimental set-up is shown schematically in Fig. 1. Various electrode designs were used and are described in detail later. Either a Chemical Electronics potentiostat capable of a 50 ampere output at 10 V was used or simple d.c. power sources with an auxiliary ammeter and a voltmeter to measure the potential between the cathode and the reference electrode, a carbon rod. The reference electrode used with the potentiostat was a graphite rod in a compartment of melt containing dissolved chlorine. A low inertia d.c. motor (Ether Corp.) served as a coulometer.

Two gas-liquid chromatographs and three sets of column conditions were used for analysis. A Perkin-Elmer Model 452 was fitted with a 2 m × 6 mm Poropak Q column at 80°. Helium (40 ml min^{-1}) was the carrier gas and the output from the thermistor detector was fed to a Kent Chromalog integrator. This was used for qualitative confirmation of product identifications. Large (2 ml) samples were injected and the material corresponding to a particular detector signal collected in an infrared cell (minimum volume type); the spectrum was compared with that of an authentic sample. For quantitative analyses, samples of 0·5 ml or less were injected

The Perkin-Eloer FII chromatograph was. used with a flame ionization detector. A 4 m × 3 mm Poropak Q column with a nitrogen flow rate of 16 ml min^{-1} served to analyse those
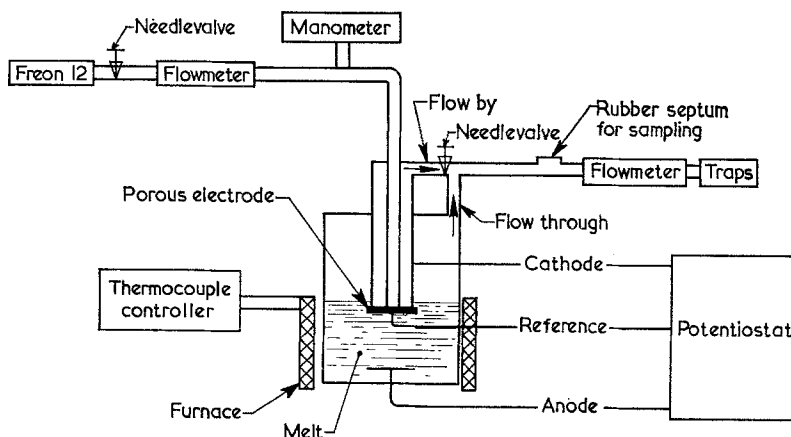

Fig. 1. Schematic layout of the apparatus for study of reduction of CF$_2$Cl$_2$ in molten salts.

components with shorter retention times than
CF_2Cl_2 and to confirm the results of the 452
separation. A 2 m × 3 mm polypropylene glycol
on Chromosorb W column with a nitrogen flow
rate of 10 ml min^{-1} was used to separate those
components with longer retention times than
CF_2Cl_2.

Authentic samples (TFE, hexafluoropropene
and octafluorocyclobutane) were supplied by Dr
J. Edwards of ICI Plastics Division, Welwyn
Garden City and those of CF_3Cl and CF_4 were
Matheson samples, supplied by Cambrian
Chemical Co. CF_2Cl_2 was from Air Products.

2.3. Results

2.3.1. *Poco graphite cathodes.* Poco AX
graphite, supplied by Poco Graphite Inc.,
Decatur, Texas, was available in experimental
quantities and was known not to be wetted by
molten LiCl. The porosity is high (57%), the
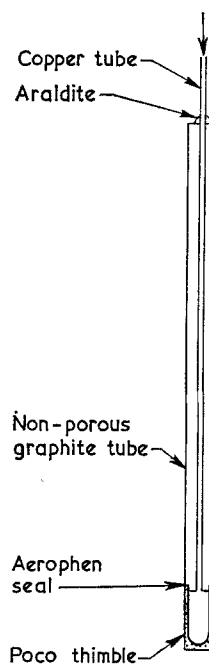pores small (median diameter 1·4 μm) and the

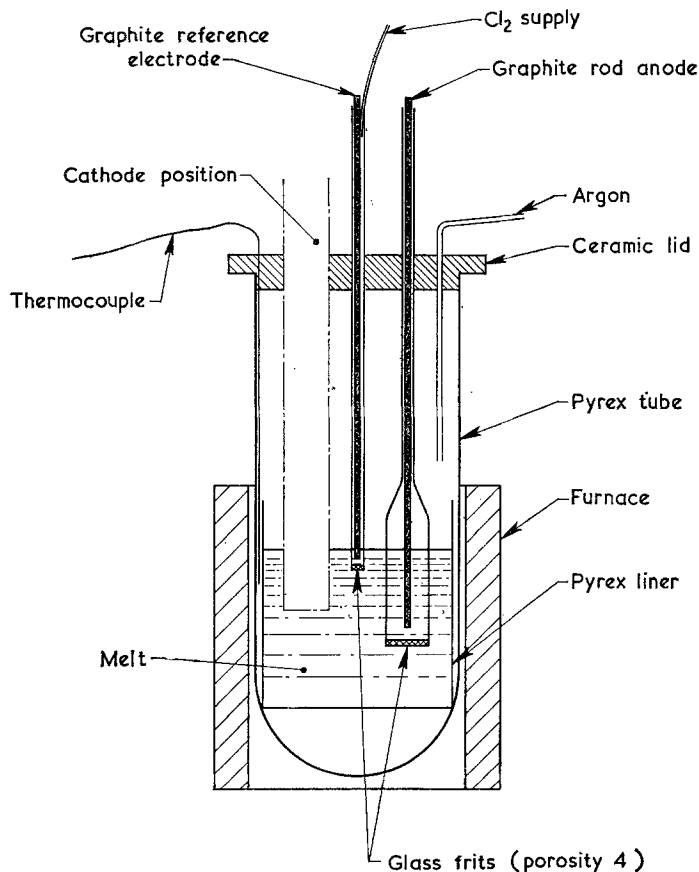Fig. 2. The 'Poco' porous carbon thimble electrode.

Fig. 3. The electrolysis cell.

pore size distribution narrow. Excellent performance as a chlorine electrode in molten salts is claimed [6]. At 1 atm a current of 5 A cm^{-2} is sustained at a 1·5 mm thick electrode and at 5 atm a current of 15 A cm^{-2}, for chlorine reaction in the flow-by mode. For a current efficiency of 100% the former figure would correspond to a rate of TFE production of 17 ml min^{-1} cm^{-2} in the reduction of CF_2Cl_2.

Thimble electrodes, Fig. 2, were constructed by machining Poco block and stuck with Aerophen glue to the end of a non-porous graphite tube which served both as gas feed and electrical connection. The electrodes were used in the electrochemical cell shown in Fig. 3.

The electrochemical evidence for reduction of CF_2Cl_2 came from current-voltage curves. Large currents flowed with helium present at high cathodic potentials and were presumably due to deposition of alkali metal. An increase in current at less cathodic potentials occurs with CF_2Cl_2 and is due to its reduction.

Using a redox reference electrode, a carbon rod in a sintered compartment in which the melt contained chlorine, reduction of CF_2Cl_2 took place at potentials more cathodic than $-1·8$ V versus Cl/Cl_2 and preparative reduction at a controlled potential of $-2·4$ V gave largely TFE as judged by the g.l.c. trace. Quantitative estimation was made difficult by the failure of the Aerophen after 1–2 h in the melt. Reduction currents were in the region 32–106 mA cm^{-2} and a limiting plateau region extended for about 0·5 V.

2.3.2. Nickel sheet cathodes.

Porous nickel sheet was supplied by Energy Conversion Ltd. Thicknesses of 0·02 and 0·01 cm were found to be suitable for this application. The porosity and pore size distribution in these samples was unknown but scanning electron microscopy suggested that they had been produced by sintering powder of diameter ~ 2 μm. Use of cathodes made from the sheets in lithium-potassium chloride eutectic for a few hours caused crystallization of the nickel. However, the electrodes remained porous. Electrodes were made by welding, with a spot- or microplasma-welder, a disc pressed from one of the sheets to a lip spun at the end of a nickel tube. Cathodes

were contained in pyrex sleeves so that gas flowing through the porous material left the cell via the sleeve. A small hole in the sleeve avoided screening the reference electrode from the working electrode (Fig. 4). The nickel disc
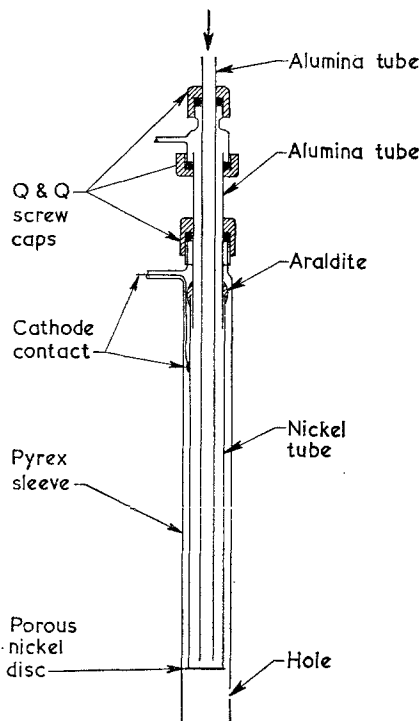

Fig. 4. Construction of the porous nickel electrode in its sleeve.

electrodes generally remained leak-tight during reductions and a more complete investigation of the electrochemical reaction was then possible. Our initial experiments aimed at establishing conditions under which high reduction currents could be obtained and gave results consistent with the behaviour in fuel cells described above. The electrode was sited in the electrolyte surface and a current-voltage curve over the potential range $-1·5$ to $-3·0$ V versus Cl_2/Cl^- was recorded first with helium and then CF_2Cl_2 supplied to the electrode. A small (10–15%) increase of current was obtained with CF_2Cl_2 at atmospheric pressure. With the gas pressure increased (to 25 cm Hg) so that flow through the electrode occurred, the current rose from less than 15 mA cm^{-2} to 300–350 mA cm^{-2} at $-2·7$ V. The total cell voltage was 5 V. The

Table 1. Effluent gas composition after reduction of CF_2Cl_2 at nickel electrodes in LiCl-KCl eutectic

$T^{\circ}C$	Cathode Potential versus Cl_2/Cl^-	CF_2Cl_2 inlet pressure cm Hg	CF_2Cl_2 flow rate at 1 atm ml min^{-1}	Current less background mA	Effluent composition in the steady state			% TFE in effluent calculated for 100% current efficiency	Current efficiency % for TFE
					TFE	CF_3Cl	CF_2Cl_2		
520	−2·7	38	12	75	3	0·2	93	3	100
	−2·7	25	8	92	3·9	1·3	90	4	98
460	−2·40	51	14·5	40	0·9	0·1		1	90
	−2·55	51	14·5	70	1·0	0·05		2	50
440	−2·55	0	1·4	50	2·0	0·05	88	13	14
400	−2.40	31	7	450	3	0		29	10
450	−2·55	49	1·7	200	3·5	0	94	33	11
450	−2·10	50	1·2	100	2·3	0·04	90	39	6
440	−2·25	50	3·9	180–380	4	0	95	18–40	10–22
440	−1·95	40	2·3	265	1·1	0·2	89	62	2
		39	2·1	285	0·7	0·05	91	81	1

current was sustained over only a small range of pressure which was difficult to maintain; at pressures outside that range currents hovered around 200 mA cm^{-2}. At low pressures the electrode is flooded and the efficiency low; at high pressures the interface is pushed beyond the critical position. During the first 15 min. of electrolysis an increasing pressure was needed to cause the gas to flow through the electrode. The flow-through then stopped and could not be re-established. The current fell to 100–150 mA cm^{-2} above background levels but could be maintained there for a few hours. TFE was the major volatile product in the gas flowing through and over the electrode. g.l.c. samples were removed for product analysis when the cell had been operating at one set of conditions for one h. The results are collected in Table 1 and can be summarized as follows.

2.3.3. *Tetrafluoroethylene.*
TFE was the major volatile product in the gas flowing through and over the electrode, except when air was admitted. TFE was shown to be a product of electro-chemical reduction and not of a thermal reaction by experiments in which the effluent was analysed with no potential applied, and in which the cathode potential was made more positive until no current flowed. Only residual TFE was present.

Since the product of interest was TFE, we

have tabulated the results to show the efficiency of its production directly (Table 1). From the controlled flow rate and measured current we have calculated the percentage of TFE in the effluent gas, assuming the current efficiency for TFE production to be 100% and that no other reaction occurs. This is then compared with the percentage of TFE found in the effluent by g.l.c. analysis. Note that at low calculated conversions the fraction of TFE found in the effluent approaches the theoretical value closely but falls far short at higher calculated conversions (Table 1 and Fig. 5). In no case were hexafluoropropene and octafluorocyclobutane found, both products of pyrolysis of PTFE. The pro-
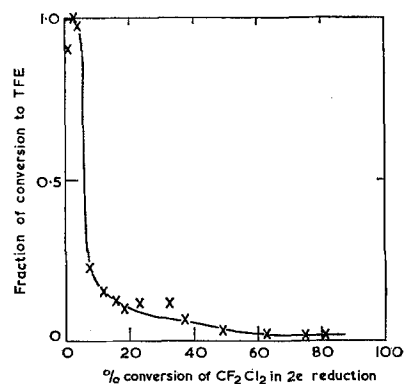

Fig. 5. Yield of TFE as a function of conversion of CF_2Cl_2 on reduction at a nickel electrode in LiCl-KCl eutectic.

duct identified as TFE by g.l.c. was confirmed by IR spectroscopy of a sample collected from preparative g.l.c.

2.3.4. *Trifluorochloromethane*. CF_3Cl was detectable in the cylinder of CF_2Cl_2 used in this work at an original level of 0·2%. Its concentration in the effluent was in several cases significantly greater than this, up to 24% of the total effluent. Its production could always be associated with accidental admission of air due to either insufficient purging with inert gas at the start of an experiment, or later failure.

CF_2Cl_2 is known to give CF_3Cl with chromic oxide at 700°C [10] and reactions similar to those suggested are possible with NiO.

$$NiO + CF_2Cl_2 \longrightarrow NiF_2 + COCl_2$$
$$NiF_2 + 2CF_2Cl_2 \longrightarrow 2CF_3Cl + NiCl_2$$
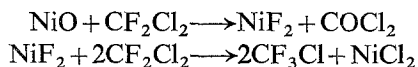
These workers have shown that NiF_2 is converted quantitatively to $NiCl_2$ by CF_2Cl_2. We had no authentic phosgene to test formation of phosgene by this mechanism. In any case it is a simple matter to keep oxygen levels low enough to make the reaction unimportant.

2.3.5. *Carbon*. At the end of reductions (~ 5–6 h) the electrode tube was removed and washed with water. A black solid could be collected from the inside. Most came from immediately behind the electrode, but a little was on the nickel and alumina tubes. Quantitative collection of these solids was difficult, but in two cases they were weighed and analysed for carbon. One of the samples was analysed for fluoride and 16% fluoride was found.

2.3.6. *Unidentified products*. In all cases products with longer g.l.c. retention times than CF_2Cl_2 under our conditions were formed. We failed to separate these from CF_2Cl_2 by fractionation and have no way of identifying or estimating them.

In each run a small peak was found with a retention time close to that of CF_4 under the FII/poropak gas chromatograph conditions (flame ionization detector). No peak corresponding to CF_4 was found under the 452/poropak conditions, however, and the amount of

CF_4 required to produce the observed flame ionization signal was greater than the sample injected.

2.3.7. *Variation with electrode potential*. The general pattern of behaviour of these nickel sheet electrodes seemed insensitive to electrode potential within the range $-1·95$ to $-2·70$ V versus Cl_2/Cl^-, although it was difficult to reproduce and maintain conditions of flow and pressure so that a reliable comparison could be made. The carbon-containing solid was found after runs at potentials throughout that range. In most experiments the reduction current was larger the more cathodic the electrode potential.

3. Discussion

TFE is produced by cathodic reduction of CF_2Cl_2 in a molten chloride eutectic with a very high electrochemical efficiency at low conversions (Fig. 5). Analogy with the reactions summarized in the Introduction suggests that difluorocarbene is an intermediate (Equation 1). The electrochemical evidence shows that CF_2Cl_2 is reduced directly and not via formation of alkali metal.

The fraction of CF_2Cl_2 reduced electrochemically to TFE falls dramatically when the conversion exceeds 5% (Fig. 5) and carbon becomes a major product. Evidence for the mode of formation of the carbon is conflicting. There is evidence that the carbon is produced in a gas-phase reaction since although most of the carbon-containing solid was found behind the electrode a little appeared on the walls of the nickel and alumina gas feed tubes. The mass balance obtained in one case, Experiment 3, Table 2, shows that the electrochemical reactions leading to products other than TFE also involve an average of two electrons per molecule. Formation of carbon from $:CF_2$ in a non-electrochemical reaction must involve elimination of fluorine. Our only evidence for fluorine comes from observation of etching on the glass outlet tubes. Against this must be set results of experiments in which the carbonaceous material formed was collected and analysed, Experiments 1 and 2, Table 2. In these cases sufficient

Table 2. Carbon formation in reductions at nickel cathodes

Experiment No.	Carbon collected g atom	Coulombs needed to produce C with 4 electrons	Coulombs passed	
			background	reduction to non-volatiles
1	8.3×10^{-3}	3300	600	3000
2	3.3×10^{-3}	1300	300	1500
3	$8 \times 10^{-3*}$	3000	140	1400

* Gram equivalents CF_2Cl_2 converted to non-volatiles from mass balance.

current was passed to account for formation of the carbon in a four electron process

$$CF_2Cl_2 + 4e \longrightarrow C + 2F^- + 2Cl^- \qquad (4)$$
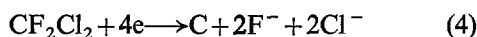
in addition to the current consumed in TFE production, and fluoride ion was found in the melt. However, carbon collection was certainly incomplete. The rapid onset of the reactions leading to products other than TFE at a conversion of 5% at 20 cm Hg pressure suggest a branched radical-chain mechanism if in the gas phase, or a critical dependence on partial pressure for adsorption of $:CF_2$ if an electrochemical process. Attempts were made to influence the degree of adsorption by change of electrode material from nickel to carbon or steel and by variation of electrode potential. No significant changes were produced. Some attempts were made to carry out the reduction in a lower temperature melt, NBu_4NO_3; though TFE was produced, lack of thermal stability of this melt made it unsuitable. Branched chain processes are often very sensitive to temperature and it may well be that carbon formation could be suppressed in a more suitable lower melting salt. The insensitivity of the reaction to electrode potential shows that the reaction could be regulated adequately by control of current density.

The current densities achieved ranged up to about 500 mA cm^{-2} at porous nickel electrodes, depending on pressure and electrode fabrication. The largest current density attained on reduction of CF_2Cl_2 at a Poco porous graphite cathode was about 200 mA cm^{-2}; under similar conditions chlorine reduction would support a current of about 3 A cm^{-2} [6]. These authors

[6] predict that the current is proportional to the solubility of the gas, and if CF_2Cl_2 is similar to a rare gas in this respect, the current should be of an order of magnitude less than that with chlorine, which can form Cl_3^- (10^{-6} moles cm^{-3} atm^{-1}). The observed current density is therefore similar to that expected. Thus for a practical system porous nickel electrodes are preferable and current densities could be increased to 1 A cm^{-2} by better electrode design.

An analysis of cell design requirements for a commercial process is illuminating. A rate of production of TFE of 1000 tons per year requires a 138 000 amp installation assuming 90% current efficiency and operation for 24 h over 300 days. Despite the use of a gaseous reagent the cell could be made very compact. Sandwich cell design, with each cell width 2 cm leads to a total cell volume of 0.3 m^3 for a current density of 1 Acm^{-2} or of 0.6 m^3 for 0.5 Acm^{-2}. Fabrication of 1 ft^2 porous electrodes in sandwich cells is standard in fuel cell technology and porous steel sheet capable of supporting at least 2 ft^2 is available. Thus with stacking a very compact electrolysis assembly could be made at 1 Acm^{-2}, i.e. 2 ft^2 by 5 ft, 0.18 m^3 by 1.67 m, or multiples of this length depending on the current density achieved. Indeed heat dissipation and current feed may be a problem in such a compact assembly and it may have to be split into smaller units. Rates of gas flow for 5% conversion at the cathodes would need to be 2.24 1 s^{-1} over 1 ft^2 or 25 1 s^{-1} over 1 m^2 of electrode for 1 Acm^{-2}. Rate of chlorine evolution at the anodes at this current density is 56 ml s^{-1} over 1 ft^2; production would be 1400 tons per year.

Acknowledgements

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