Electrochemical reduction of CCl_2F_2 on Nafion solid polymer electrolyte composite electrodes

E. Delli, S. Kouloumtzoglou, G. Kyriacou*† and C. Lambrou

Department of Chemical Engineering, Aristotle University of Thessaloniki, Thessaloniki 54006, Greece

The electrochemical reduction of CCl_2F_2 (CFC-12) was carried out at Pd, Au, Cu and Ag cathodes, which were chemically deposited on Nafion 117 (H^+ form) membrane; the main electrolysis product at −1.0 V *vs.* Ag/AgCl at Au, Pd and Cu was CH_4, with current efficiencies (CE) of 14, 15 and 47% respectively, while at Ag cathode, in addition to CH_4, a considerable quantity of CH_2F_2 (CE 60%) was also detected, which might be used as a new technology refrigerant.

The production of chlorofluorocarbons (CFCs) has been stopped since 1996, in line with the Montreal Protocol, because of their ability to react in ways that destroy tropospheric ozone.[1] At present, almost 2×10^6 tonnes of these compounds are stored in various freezing devices, the bigger percentage of which is CFC-12.[2] These large quantities must be destroyed or preferentially converted to other useful products. Recently Cabot and co-workers[3,4] achieved the electrosynthesis of trifluoroethene and difluoroethene from 1,1,2-trichloro-1,2,2-trifluoroethane (CFC-113) in organic solvents.

This work deals with the possible conversion of CFC-12 to non-polluting substances *via* electrochemical reduction at metallic electrodes which are deposited on Nafion 117 (H^+ form) membrane. These electrodes enable us to perform electrochemical reactions with reactants that are insoluble in water, without employing organic solvents.

For the metal deposition, aqueous 0.1 M solutions of $AgNO_3$, $HAuCl_4$, $Pd(OAc)_2$ and $CuSO_4$ were used, combined with 10% aqueous $NaBH_4$ solution, using the method previously described for copper.[5] The charged side of the metal surface of the membrane, having an apparent effective area of 2.35 cm^2 was in contact with CFC-12, while the other side was in contact with 2 M aqueous NaOH solution (10 cm^3), as shown in Fig. 1. As a reference, an Ag/AgCl electrode was used. The analysis of the products was performed by gas chromatography using a flame ionization detector and a Porapak QS 1/8 in, 4 m column at 120 °C.

The voltammogram at the Ag electrode, between −0.7 and −1.6 V *vs.* Ag/AgCl (Fig. 2), showed that the reduction of CCl_2F_2 was taking place at potentials more negative than −0. 8 V, while hydrogen was produced at cathodic potentials more negative than −1.3 V. This value is in accordance with hydrogen evolution at Ag wire at the same pH value.[6]

Based on the voltammetry results, constant potential electrolysis was performed in the region −0.8 to −1.6 V *vs.* Ag/AgCl. The main products of the electrolysis were CH_2F_2 and CH_4 at all potentials examined. CH_2F_2 is a compound of great practical importance, due to its application as a new technology refrigerant which does not cause ozone depletion.[7] Small amounts of $CHClF_2$, CH_3F and HCF_2CF_2H were also detected in the reaction products.

Fig. 3 illustrates the rate of CF_2H_2 production *vs.* cathodic potential where a sharp maximum was observed at about −1.4 V. The rate of CH_4 production was slightly increased at potentials more negative than −1.4 V. The CEs of CF_2H_2 and CH_4 formation at −1.4 V were 60 and 30%, respectively. Repeated experiments showed that the distribution of products was as shown by the curves of Fig. 3, with a reproducibility of about 15%. The form of these curves can be explained by a consecutive reaction mechanism corresponding to $CCl_2F_2 \rightarrow CH_2F_2 \rightarrow CH_4$.

Theoretical analysis of consecutive electrochemical reactions showed that the effect of potential on the selectivity and yield of the intermediate compound could be considered analogous to that of temperature in the conventional chemical reactions. In this case the selectivity of the intermediate product *vs.* potential

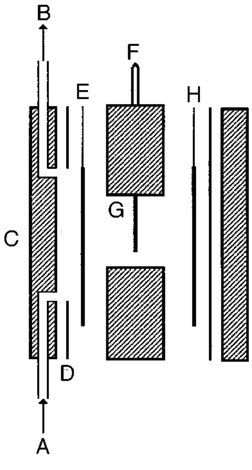

Fig. 1 Exploded view of the electrolysis cell: (A) gas inlet, (B) gas outlet, (C) PTFE gasket, (D) silicone screen spacer, (E) Nafion SPE electrode, (F) reference electrode, (G) electrolyte chamber and (H) Pt anode

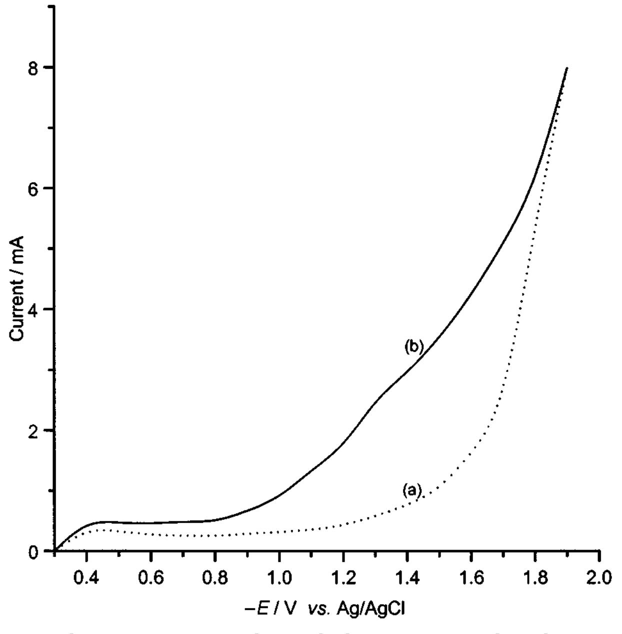

Fig. 2 Polarization curves at silver cathode, in 2 M KOH electrolyte at 10 mV s^{-1} (a) with N_2 and (b) with CFC-12

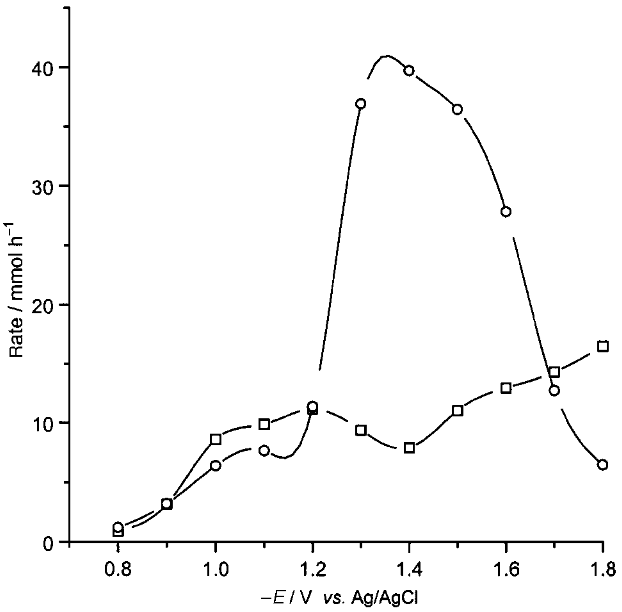

Fig. 3 Rate of (○) CH_2F_2 and (□) CH_4 production *vs.* cathodic potential at a silver electrode in 2 M KOH electrolyte

could show one or more maxima.[8] A similar consecutive reaction mechanism scheme was proposed for the hydrogenolysis of CCl_2F_2 in the gas phase.[9]

The electroreduction of CCl_2F_2 was also studied at −1.0 V *vs.* Ag/AgCl using Pd, Au and Cu electrodes. In all cases, the main product of the reduction was CH_4, with mean CEs of 14, 15 and 47%, respectively. The current density and time function shows that the current density stabilises after 30 min and remains stable for a long period of time. This implies that the electrode is not deactivated and the membrane is not destroyed. The current density at Ag, Cu and Pd was about 5 mA cm^{-2}, whereas at Au it is four times smaller.

Note and References

† E-mail: kyriakou@vergina.eng.auth.gr

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