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The electrochemical behaviour of a molten CF_3COOK-CF_3COONa eutectic

R. DALLENBACH*, O. JOHN, P. TISSOT†

Département de Chimie Minérale, Analytique et Appliquée Sciences II, 30 quai E. Ansermet, 1221 Genève 4, Switzerland

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Electrolysis with platinum electrodes of a molten CF_3COOK–CF_3COONa mixture yields at the anode mainly CO_2 and C_2F_6; CF_4, C_3F_8 and C_2F_4 are also present in low quantities. At the cathode, only sodium is formed. The useful potential range of this molten electrolyte is 4·9 V at a current density of 1 mA cm^{-2}.

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1. Introduction

The binary system CF_3COOK–CF_3COONa has been studied previously [1]. The phase diagram shows an eutectic (62 wt% CF_3COOK, melting point 112·4° C) which is sufficiently stable in the molten state to allow its use as an electrolytic solvent [2]. We present here a preliminary study on the behaviour of this medium; these first results show interesting possibilities in the field of organic preparative electrolysis and kinetic studies of electrochemical reactions in the molten state at low temperature.

2. Experimental

2.1. *Preparation of salts*

Potassium and sodium trifluoroacetates were prepared as described previously [1]. The mixture used (wt% CF_3COOK/CF_3COONa = 65/35) has a melting point of 116° C. All the experiments were performed at 117° C; at this temperature the electrical specific conductivity is 0·006 Ω^{-1} cm^{-1}.

2.2. *Preparative electrolysis*

The U-shaped cell was made with Pyrex glass and was thermostated at 117° C in a silicone-oil bath. The two compartments had a volume of 19 cm^3 and were separated by means of a sintered-glass disc (porosity 2). 15 g of salt mixture were introduced in each compartment which was then flushed with a stream of helium (5 cm^3 min^{-1}) before melting and during the experiments Gaseous anodic products were analysed by gas chromatography, on a Porapak Q column at 80° C, and were identified by comparison of retention times with those of the pure fluorinated gases (Baker). All preparative electrolysis was performed at constant current density, on platinum electrodes (area, 2 cm^2). The current was controlled by means of a galvanostat (Wenking 68FR 0·5)

2.3. *Reference electrode*

A silver wire and 2·3 g of the mixture of trifluoroacetates containing 0·34 mM kg^{-1} of $AgNO_3$ was placed in a glass bulb with a thin wall ($\leqslant$ 0·2 mm). The molar ratio was 5 × 10^{-2} (MR = moles of $AgNO_3$/moles of CF_3COOMe). This Ag/Ag^+ reference electrode was stable for long periods and presented an overall resistance of about 5 MΩ at 117° C.

2.4. *Potentiostatic curves*

For these measurements a cylindrical Pyrex cell with three electrodes was used; the distance be-

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* Present address: Union Carbide, 43 rue L.J. Chevrolet 2301 La Chaux-de-Fonds, Switzerland.
† To whom correspondance should be addressed.

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Table 1. Faradaic yield of main anodic products. (anodic current density, 2·5 mA cm^{-2})

Products	*Faradaic yield (%)*
CO_2	100
C_2F_6	67·1
CF_4	7·8
C_3F_8	2·8

tween each electrode was 15 mm. The working electrode was a platinum wire (area, 2·8 mm^2) welded at the extremity of a glass tube. The counter electrode was a platinum foil (geometric area, 2 cm^3). Stirring of the electrolyte was ensured by bubbling pure nitrogen.

3. Results and discussion

3.1. *Preparative electrolysis*

The faradaic yields of the main anodic products are presented in Table 1. Yields are calculated with two electrons for the formation of C_2F_6, one for CF_4 and four for C_3F_8. Moreover, the presence of C_2F_4 and traces of other compounds not identified was noticed.

The main overall anodic reaction is therefore

$$2CF_3COO^- \rightarrow C_2F_6 + 2CO_2 + 2e.$$

This reaction has been extensively studied in other media and the mechanism proposed by Conway [3, 4] for the formation of C_2F_6 and CO_2 is generally accepted. All other minor products can be explained by radical reactions involving $CF_3^\bullet$ as the primary intermediate.

The very few papers describing the electrolysis of fused carboxylates are only concerned with acetates and propionates [5–10]; in all cases the dimer yield is much smaller than the one obtained in this work with trifluoroacetates. Moreover, reaction between the alkali metal deposited at the cathode and the carboxylate was also found to occur. In our case, this reaction between sodium and the electrolyte was not observed, owing to the stability of trifluoroacetates. At higher current densities a decrease in the yield of fluorinated products at the anode was observed but the yield of CO_2 remained constant. This may be due to the formation of a gaseous film at the anode surface at high current densities. The film hinders the formation of the usual products and favours the formation of higher molecular weight molecules. The brown colour which appears near the anode, especially at high current densities, is probably due to the accumulation of these species. The same phenomenon has been observed by Moorhouse [8] in the case of the acetates, and Obstowski [11] has shown that an efficient stirring was necessary at high current density to eliminate the film present at the electrode during the preparation of fluorinated paraffin in fused salts. Waefler [12] did not notice a diminution of C_2F_6 yield with increasing

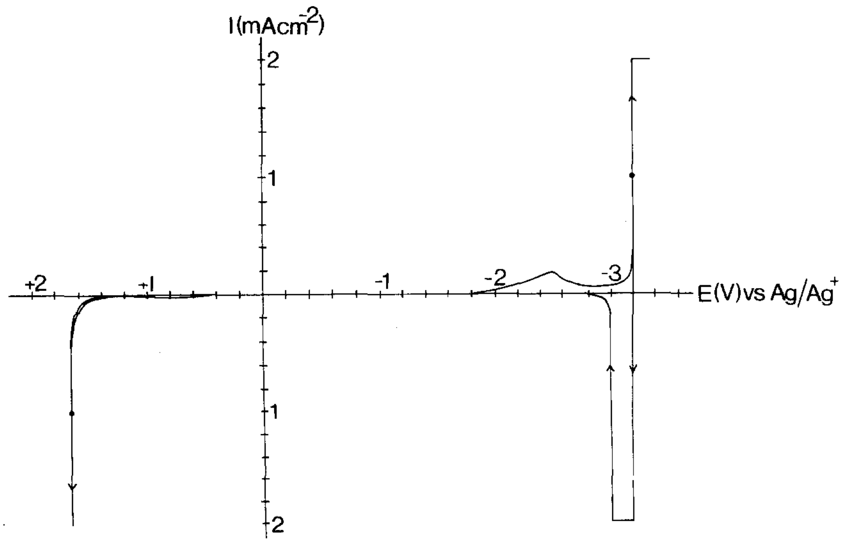

Fig. 1. Potentiostatic curve in trifluoroacetate eutectic (117° C). (Scan rate, 2 mV s^{-1}; platinum electrodes).

current density when electrolysing a solution of CF_3COONa in acetonitrile, probably because of the low viscosity of the medium. In aqueous solution, a critical anodic current density has been observed, below which the Kolbe coupling reaction is not possible [13]; with our fused salts system, we did not observed such a critical current density.

3.2. *Potentiostatic curves*

A quasi-potentiostatic curve (scan rate, $2\,mV\,s^{-1}$) is shown in Fig. 1. On the scan to positive potentials, there is a very small wave near 0·8 V, due to the formation of platinum oxide; as a matter of fact, it is impossible to avoid some trace of water in the bath. The reduction of this oxide film is not visible on the cathodic scan because the sweep has been stopped at 0 V. Otherwise, this reduction is noticed at − 0·2 V. On the cathodic part, near 2·5 V, a small current is always present. Several voltammetric studies suggest that this current is due to the reduction of CF_3COF. In fact, Dallenbach [14] has shown, by mass spectrometry analysis of anodic gases, that it is impossible to avoid a slow decomposition of the bath (about $10\,mg\,h^{-1}$) according to the reaction

$$2CF_3COOMe \rightarrow CF_3COF + CO + CO_2 + 2MeF$$
$$(Me = Na, K)$$

We estimate the steady state quantity of CF_3COF in the bath at 117° C to be 10^{-8} mole.

The velocity of the reduction being higher than the rate of formation of CF_3COF, no limiting current is reached and a peak appears even in quasi-potentiostatic conditions. The peak current is equal to $0{\cdot}2\,mA\,cm^{-2}$. The limiting anodic reaction is the irreversible oxidation of the trifluoroacetate ion

$$CF_3COO^- \rightarrow CF_3^{\cdot} + CO_2 + e$$

and the cathodic one is the reduction of Na^+

$$Na^+ + e = Na$$

For a current density of $1\,mA\,cm^{-2}$, the potential of the anodic reaction is + 1·7 V (versus Ag/Ag^+) and that of the cathodic reaction − 3·2 V (versus Ag/Ag^+). The potential range of the electrolyte at this current density is therefore 4·9 V.

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