JOURNAL OF APPLIED ELECTROCHEMISTRY **10** (1980) 593–596

Electrochemical studies in a molten CF_3COOK-CF_3COONa eutectic at platinum, gold and pyrolytic graphite electrodes

O. JOHN, P. TISSOT

Département de Chimie Minérale, Analytique et Appliquée, Sciences II, 30, quai Ernest Ansermet, 1211 Genève 4, Switzerland

Received 17 December 1979

Electrolysis at platinum, gold and pyrolytic graphite anodes of a molten mixture of CF_3COOK–CF_3COONa leads to mainly C_2F_6 and CO_2. Smaller quantities of CF_4, C_3F_8 and C_2F_4 are also observed particularly at gold and pyrolytic graphite. Voltammetric studies of some oxidation and reduction reactions in this medium are presented.

1. Introduction

In a previous paper [1] we described the general electrochemical behaviour of the molten salt eutectic CF_3COOK–CF_3COONa (65/35 wt %, m.p. = 116° C [2]) at a platinum electrode. We have carried out further work at gold and pyrolytic graphite electrodes and describe a voltammetric study of the oxidation of acetate ions in this medium and the behaviour of three metallic ions.

2. Experimental

The preparation of the salts, the experimental device for the preparative electrolysis and the recording of potentiostatic curves were described previously [1]. In this work, we used stationary or rotating (469 r.p.m.) cylinder electrodes with the following areas: Pt, stationary 3.8 mm^2, rotating 15.1 mm^2; Au, stationary 2.8 mm^2, rotating 19.7 mm^2; pyrolytic graphite, stationary 7.5 mm^2, rotating 9.5 mm^2.

3. Results and discussion

3.1. *Preparative electrolysis*

Table 1 presents results of the quantitative analysis of the products. In addition to the products listed, we observe the presence of C_2F_4 at all three electrodes: tetrafluoroethylene has not been determined quantitatively but its yield is 5–10% in each case. The yield of each product is quasi-independent of current density (on platinum the decrease is probably due to the configuration of the cell used) and this behaviour is particular to this molten salt eutectic. In fact, in aqueous media, in anhydrous acetic acid [3–5] or in fused salts [6], we generally observe an increase in yield with increasing current density.

The influence of the anode material on the pro-

Table 1. Faradaic yields (%) of main anodic products

Anodic current density (mA cm^{-2})	C_2F_6			CF_4			C_3F_8		
	Pt	*Au*	*P.G.*	*Pt*	*Au*	*P.G.*	*Pt*	*Au*	*P.G.*
2.5	67	23	93	8	7	~ 0	3	2	0.6
5.0	62	24	85	7	12	~ 0	3	2	0.9
7.5	50	26	89	5	12	~ 0	2	2	1.0
10.0	47	28	92	5	11	~ 0	2	3	0.9

0021–891X/80/050593–04$02.40/0

ducts formed is similar to that in non-aqueous media; in aqueous media the Kolbe dimer is not observed at gold [3, 7]. At all anodes, the C_2F_6 and CO_2 are probably formed by the same mechanism [3, 8]. For the other products, a mechanism involving radicals is consistent with the results on gold and platinum. On the other hand, the low yield of CF_4 and C_3F_8 and the presence of C_2F_4 on pyrolytic graphite may imply the intermediate formation of the perfluoromethylperfluoroacetate. The ester is the main product obtained for the Kolbe reaction of the acetate at graphite anodes in non-aqueous solvents [9, 10]. This ester [11], formed by the intermediate CF_3^+, decomposes at the working temperature according to the reaction:

$$2CF_3COOCF_3 \rightarrow 3C_2F_4 + 2O_2.$$

3.2. *Electroactivity range of the bath*

Fig. 1 presents voltammetric curves obtained on platinum, gold and pyrolytic graphite. The electroactivity ranges obtained are 5.3, 5.2 and > 8 V respectively, at 10 mA cm^{-2}. The cathodic limiting reaction on all electrodes is the reduction of sodium ions and on the reverse scan, the reoxidation of deposited sodium can be observed. On pyrolytic graphite, there is no peak before the cathodic limit. On platinum, the reduction peak at -2.6 V is the reduction of CF_3COF [1]. On gold this peak is also seen as well as another at -2.3 V and on the reverse scan there is an oxidation wave at -2.2 V; we assign these peaks to the reduction of CF_3COOH and to the oxidation of CF_3CHO respectively, products due to traces of water in the bath. This interpretation is supported by the presence for the gold electrode of a cathodic peak at 0.2 V corresponding to the reduction of gold oxide.

The anodic limiting reaction on platinum and gold is the oxidation of trifluoroacetate anion

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

On pyrolytic graphite, it is possible to polarize the anode up to + 5 V although two or three ill-defined peaks between + 1 and + 3.5 V are seen. With this anode, the situation is more complicated because carbocations like CF_3COO^+ and CF_3^+ could be formed.

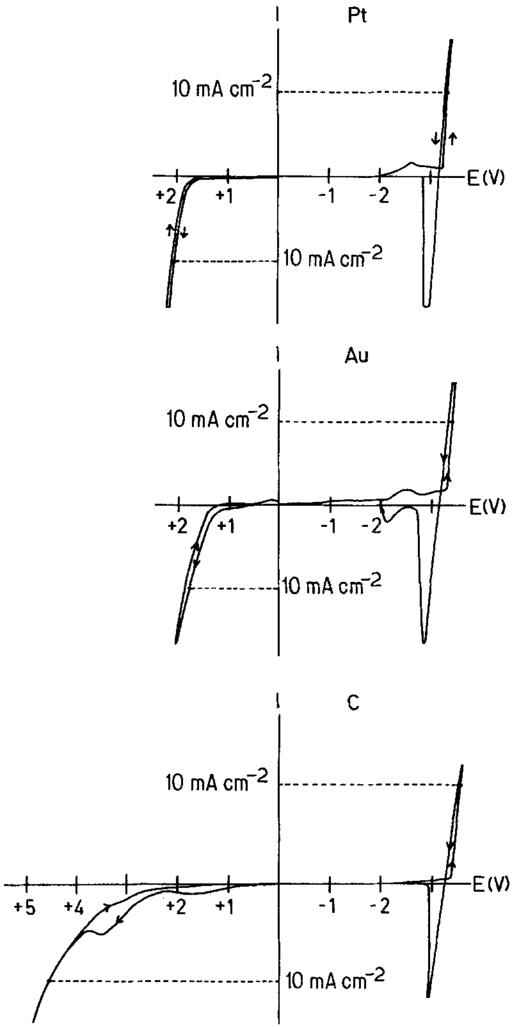

Fig. 1. Voltammetric curves at 100 mV s^{-1} for three electrodes in CF_3COOK–CF_3COONa (65/35%).

3.3. *Oxidation of sodium acetate*

Voltammetric and potentiostatic curves in the presence of sodium acetate in the molten eutectic were recorded for a platinum electrode. The oxidation of CH_3COO^- is observed at 1.2 V, 0.5 V less positive than that for the oxidation of CF_3COO^-. The interpretation of these voltammetric curves is difficult because these peaks are badly defined at every scan rate. We have, however, determined that $\alpha n_a = 0.27$, a value in good agreement with that obtained by Weafler in acetonitrile [12]. Tafel slopes determined by potentiostatic experiments are 0.19 and 0.32 V for the oxidation of CF_3COO^- and CH_3COO^-, respec-

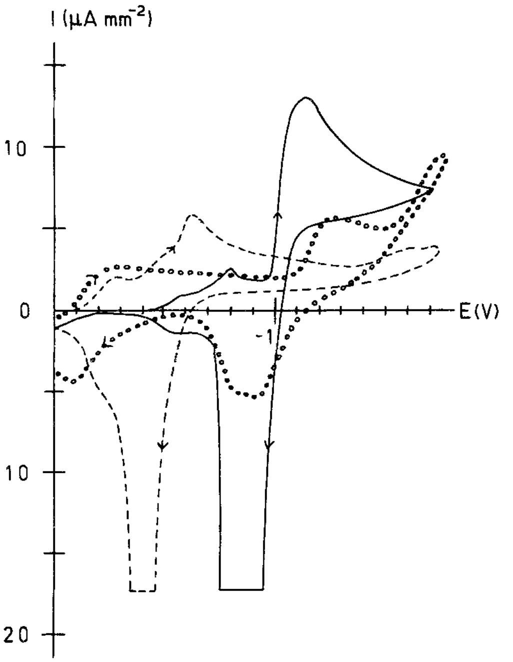

Fig. 2. Voltammetric curves at 100 mV s^{-1} on gold. $CF_3COOK–CF_3COONa$ (65/35%). (— 540 mg $Pb(CH_3COO)_2$, - - - 540 mg $Cu(CH_3COO)_2CuO$, ooo 540 mg $FeCl_3 \cdot 6H_2O$).

tively. These high values are explained by a model involving a dipole layer of adsorbed radicals [3]. The oxidation potentials of CF_2ClOO^- and CF_2BrCOO^- are situated between the values of CH_3COO^- and CF_3COO^-.

3.4. *Behaviour of some metallic cations*

Fig. 2 shows voltammetric curves on gold after addition of lead, copper and iron salts to the molten salt eutectic. Assuming the salts are totally dissociated, the concentrations of Pb^{2+}, Cu^{2+} and Fe^{3+} are 4.9×10^{-2}, 2.3×10^{-2} and 1.9×10^{-2} M, respectively. Lead and iron behave similarly: we observe one reduction step with a coupled peak on the reverse scan, corresponding to the oxidation of the metal deposited on the electrode. No alloy has been observed. The E_p shift with scan rates and high values of $E_{p_c} - E_{p_a}$ indicate an irreversible reaction and an important crystallisation overpotential. Several authors note a certain degree of irreversibility of Pb/Pb^{2+} in molten (Li, Na, K) acetate mixtures [13, 14]. Before the reduction, peaks attributable to chemisorption are observed, and these are particularly well defined for lead. Fig. 3 shows such peaks obtained on gold, which are in good agreement with Conway's work [15].

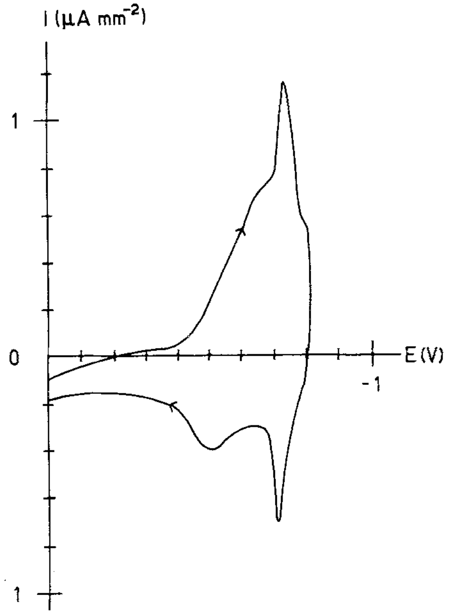

Fig. 3. Voltammetric curves at 100 mV s^{-1}. $Pb(CH_3COO)_2$ in $CF_3COOK–CF_3COONa$ (65/35%). Au electrode.

In the case of iron, the reduction occurs in two irreversible steps, corresponding to the successive formation of Fe^{2+} and Fe^0. On the reverse scan, the oxidation current is about the same as that for the reduction, probably because Fe^{2+} is formed on the electrode by the reduction of Fe^{3+}.

It is not easy to compare the measured potentials with those in other solvents. Assuming a shift of 0.8 V between our reference (Ag/Ag^+) and the NHE reference in aqueous solution, the values of the couples are compared in Table 2.

Table 2. Comparison between E^0 and our measurements for the couples studied

	E^0(V)*	Our value (V)†
Fe^{2+}/Fe^{3+}	0.77	0.63
Cu/Cu^{2+}	0.34	0.29
Pb/Pb^{2+}	−0.13	−0.19
Fe/Fe^{2+}	−0.44	−0.22

* Normal potential at 25° C.

† $(E_{p_c} + E_{p_a})/2 + 0.8$ at 20 mV s^{-1}, 117° C, conc. $\sim 3 \times 10^{-2}$ M.

4. Conclusion

Several authors [16–18], have mentioned the possibility of using molten acetates as the solvent for electrochemical studies. This work shows that the trifluoroacetates have properties which make them suitable as interesting molten salt media. The thermal stability of the eutectic (65/35 wt% CF_3COOK/Na) is sufficient even 10° C above the melting point at 116° C. At this temperature, the electrical specific conductivity is $6\,m\Omega^{-1}\,cm^{-1}$.

Finally, the potential range is broad and it allows the study of both oxidation and reduction reactions.

References

[1] R. Dallenbach, O. John and P. Tissot, *J. Appl. Electrochem.* **9** (1979) 643.
[2] R. Dallenbach and P. Tissot, *J. Thermal Analysis* **1** (1977) 61.
[3] B. E. Conway and M. Dziecivch, *Can. J. Chem.* **41** (1963) 38.
[4] S. N. Shukla and O. J. Walker, *Trans. Farad. Soc.* **27** (1931) 35.
[5] J. Robertson, *Trans. Farad. Soc.* **30** (1934) 1007.
[6] R. Lautié, *Bull. Soc. Chim. Fr.* **63** (1948).
[7] T. Dickinson and W. F. K. Wynne-Jones, *Trans. Farad. Soc.* **58** (1962) 382.
[8] A. K. Vijh and B. E. Conway, *Chem. Rev.* **67** (1967) 623.
[9] N. Sato, T. Sekine and K. Sugino, *J. Electrochem. Soc.* **115** (1968) 242.
[10] W. J. Koehl, *J. Amer. Chem. Soc.* **86** (1964) 4686.
[11] E. L. Varetti and P. J. Aymonino, *An. Asoc. Quim. Argentina* **59** (1971) 435.
[12] J. P. Waefler, Thèse No. 1802 Université de Genève (1977).
[13] H. Giess, M. Francini and S. Martini, *Electrochim. Metal* **4** (1969) 17.
[14] R. Marassi, V. Bartocci and M. Fiorani, *Chim. Ind.* **52** (1970) 365.
[15] B. E. Conway, in 'Electrochemistry' (edited by H. Bloom and F. Gutmann) New York, Plenum Press (1977) p. 189.
[16] G. G. Bombi, M. Fiorani and C. Maccà, *Chem. Commun.* **14** (1966) 455.
[17] R. Marassi, V. Bartocci, P. Cescon and M. Fiorani, *J. Electroanal. Chem.* **22** (1969) 215.
[18] R. Marassi, V. Bartocci and F. Pucciarelli, *Talanta* **19** (1972) 203.