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Electrochemical silver microcoulometers with fluoroborate electrolyte

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The results of some electrochemical investigations on a silver microcoulometer with an electrolyte consisting of Ag^+ in concentrated fluoroboric acid are reported. The advantages of this system are confirmed as wide ranges of current and charge, low resistance and low influence of temperature. The investigated solution may also be used in other electrochemical investigations.

1. Introduction

Silver coulometers, known for a very long time, are now used not only in chemical laboratories, but also in many electronic circuits and automatic devices [1–4]. This became possible because of chronopotentiometric detection applied to the silver microcoulometer [1–5]. Microcoulometers (also called integrators) are characterized by low weight, small dimensions, permanent memory of charge and the possibility of multiple use.

Fig. 1 shows the principle of construction of a microcoulometer, e.g. as produced as an 'E-cell' by Plessey-Electroproducts Co., USA [5].

The silver microcoulometer works on the principle of quantitative transfer of Ag from an Ag-electrode onto the gold cathode

$$Ag^+ + e \rightarrow Ag(Au). \qquad (1)$$

Reversal of the polarity of the electrodes causes the dissolution of Ag (mass m_i) back into the solution.

$$Ag(Au) - e \rightarrow Ag^+. \qquad (2)$$

The electrical charge q_i passed during the deposition stage with current I_i in time t

$$q_i = \int_0^t I_i(t)\,dt \qquad (3)$$

is determined by measurement of the time, t_r, during which a constant current I_r is used to dissolve the silver

$$q_i = I_r t_r. \qquad (4)$$

The time t_r is indicated by a jump in the voltage of the cell occuring when the gold electrode has been stripped of all the silver. The jump is a substantial one (from several tens of millivolts to about 1·2 V) and thereafter the cell behaves as an electrochemical capacitor. The cycle has to be interrupted at about 0·6 V because the next reaction at the gold electrode is evolution of oxygen which may spoil

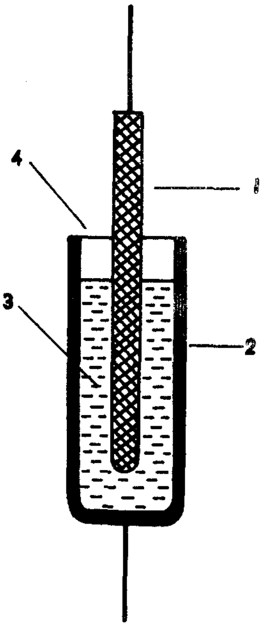

Fig. 1. Silver microcoulometer. 1, gold electrode; 2, silver electrode; 3, electrolyte; 4, plastic stopper.

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the system. The switching off of the current before O_2 formation is ensured by a parallel silicone diode or by a transistorized threshold system. The latter acts as a simultaneous electrical output for all practical applications of microcoulometers.

Silver microcoulometers similar to other electrochemical integrators with discrete readout, e.g. silver chloride [6, 7], may be applied mainly for integration of current, for counting impulses, for generation of very low frequencies, and for construction of time relays and voltage–frequency transducers [8, 9].

Commercially produced silver microcoulometers mainly contain solutions of Ag^+ ions in concentrated ortho-phosphoric acid [10]. The advantages of o-H_3PO_4 are unquestionable because of good electrical conductivity, low freezing temperature, low reactivity, and practically 100% efficiency of anodic dissolution as well as cathodic deposition of silver.

It is the aim of this paper to present the results of studies on aqueous solutions of silver ions in concentrated fluoroboric acid and their application in microcoulometers. Better diffusion of Ag^+ ions in these solutions [11] and easier preparation of pure HBF_4 were the main motivation for this investigation. Good conductivity and a wide temperature range are known advantages of HBF_4 [12] which until now has only been used for the deposition of metals, e.g. of cadmium and copper [13, 14]. Good results were achieved recently with HBF_4 mercury microcoulometers with visual readout [15]. The possibility of electrochemical application of Ag^+ solution in HBF_4 was mentioned in [13].

2. Experimental

2.1. *Measuring devices*

Fig. 2 shows the layout of a system for chronopotentiometric measurements.

A d.c. supply and resistor allowed the variation of current density between 0·01 to 1·0 mA. A polarity switch served to apply the charge manually or automatically and also makes possible the multiple readout of the dissolution charge. The voltage across the cell was read out onto a recording millivoltmeter and was used for the determination of current–voltage plots and for the estimation of internal resistivity. At transistorized threshold system switched off the current at 0·57 V. The accuracy of the integrator operation $\Delta = (t_r/t_i)\,100$ was determined for $I_i = I_r =$ constant. All measurements were made at room temperature, except the investigation of the influence of temperature which was performed between − 60° and + 75° C.

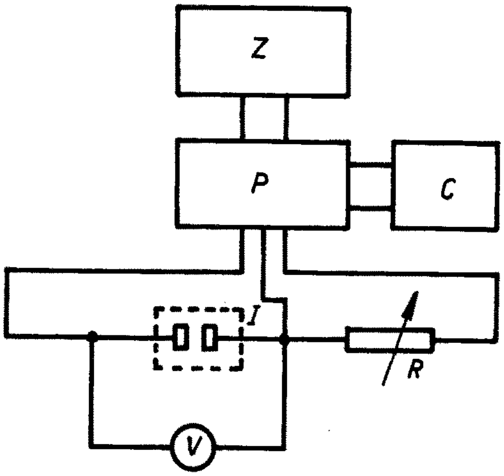

Fig. 2. Layout of chronopotentiometric arrangement. Z, d.c. power supply; P, polarity switch with threshold arrangement; C, digital clock; R, resistor for adjustment of current intensity; V, recording voltmeter; I, investigated microcoulometer.

2.2. *Preparation of cell and materials*

2.2.1. Indicator electrodes. The silver was deposited onto electrodes made of gold (99·99%) wire, 1 mm diameter. The end of the wire was rounded by melting in an oxygen–natural gas flame. The wire was dipped 7 mm into the solution. The surface of the metal was polished electrochemically in a cyanide bath at 60° C and 1·5 A cm^{-2} for 1·5–2 min [16]. Before electrolytic polishing the electrodes were degreased in benzene and ethyl alcohol and rinsed in triply distilled water. Electrolytic polishing produced better smoother surfaces; all scratches deeper than about 0·5 μm were removed. Fig. 3 shows the increase in accuracy after electrolytic polishing. It is evident that polishing makes the system independent of Ag^+ concentration. The surface treatment also improved the reproducibility, the ranges of charges quantitatively reproduced and the permanence of

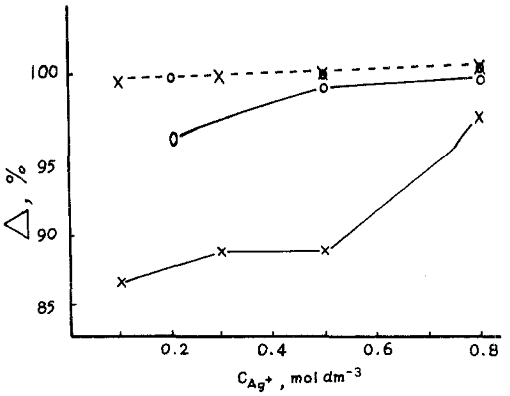

Fig. 3. Accuracy, Δ, as a function of Ag^+ concentration. —— Au electrode before polishing; - - - Au electrode after polishing; × in phosphoric electrolyte; ○ in fluoroboric electrolyte.

the memory of charge. All the measurements reported were carried out on electropolished electrodes additionally cleaned in a hot mixture of concentrated $H_2SO_4 + HNO_3 + H_2O$ (1 : 1 : 10) for 2 min. After rinsing with distilled water, electrodes were dipped in fresh chromic–sulphuric mixture and rinsed several times with triply distilled water.

2.2.2. Silver electrodes. The majority of experiments on microcoulometers were carried out on silver electrodes which also served as the container. They were extruded from silver rod, forming a cylindrical vessel, 4·2 mm in internal diameter (Fig. 1). The inside walls constituted the electrode, which was carefully cleaned with water containing detergents and rinsed with triply distilled water.

2.2.3. Reagents and solutions. The following reagents were used: fluoroboric acid (pure, POCh Gliwice), orthophosphoric acid (p.a., POCh Gliwice, and analar by BDH) and silver tetrafluoroborate, $AgBF_4$, (Schuchardt, West Germany). Silver phosphate, Ag_3PO_4, was prepared from Ag_2O (p.a., POCh Gliwice) and orthophosphoric acid.

Solutions of Ag^+ (0·1–0·8 M) in phosphoric acid (5–9 M) and (0·1–1·5 M) in fluoroboric acid (3–5 M) were prepared. These concentrations were determined by the need for good conductivity and low temperature of solidification of the solutions. According to [17], phosphoric acid solution shows the maximum of conductivity at 47% (~ 6·25 M). In the case of fluoroboric acid a high concentration prevents its hydrolysis, securing durability and limiting the chemical aggresiveness of its solutions [18].

Within the ranges indicated above the influence of changes in concentration was small and therefore model solutions were chosen and used throughout the investigation:

fluoroboric solution: HBF_4 4·3 M, $AgBF_4$ 1 M
phosphoric solution: H_3PO_4 6·2 M, Ag_3PO_4 0·8 M.

High concentrations of Ag^+ were chosen to allow measurement of comparatively high currents and charges.

The results with both solutions were very similar and therefore mainly results with fluoroborate electrolyte are given below. The phosphoric acid solution is quoted only for comparison.

3. Results and discussion

Fig. 4 presents typical chronopotentiometric characteristics of charging and discharging of a gold electrode in a microcoulometer with fluoroborate electrolyte. At low currents there is an error Δt_r due to the charge q_c, caused by the electrical capacitance of the gold electrode; Δt_r may be determined from the dependence of the excess of the deposition time on the reciprocal of the intensity of current when $I = I_r = I_i$:

$$\Delta t_r = t_r - t_i = q_c I^{-1}. \qquad (5)$$

The equation holds if side reactions, e.g. adsorption and oxide formation, may be neglected.

The good reproducibility of q_c makes it possible to introduce a correction when small charges are measured without a change of the threshold voltage. Fig. 5 illustrates the dependence of the error on the integrator operation, Δ, versus the logarithm of current density with the normal threshold voltage of 0·57 V (curve 1). Curve 3 shows the influence of the correction for q_c calculated from Equation 5 on the value of Δ. Curves 2 and 4 were measured for the same microcoulometers with the threshold limited to 0·12 V.

Fig. 6 shows plots of Δt_r as a function of the reciprocal current at different temperatures. Fig. 7 illustrates the dependence of q_c and the capacitance of the gold electrode on the temperature. The capacitances were calculated from q_c values and the threshold voltage. They agree to within a

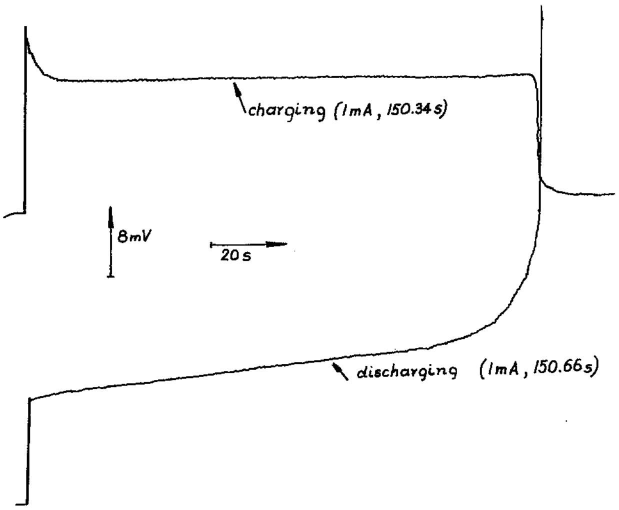

Fig. 4. Typical chronopotentiometric characteristics of charging and discharging of silver microcoulometer.

few per cent of the values determined by the a.c. bridge at 10 kHz.

This unwanted charge q_c may be lowered considerably by the addition of surface active substances such as gelatine, tylose, tartaric acid, etc. But the presence of these substances diminishes the useful ranges of current and charge which can be measured with the coulometer. Changes in the concentration of Ag^+ ions in the range of 0·1–1·5 M do not influence the value of q_c.

Fig. 8 shows typical current–voltage characteristics of silver microcoulometers with fluoroboric acid solutions. The curves show a non-linear dependence of internal resistance on the current intensity. A considerable increase of internal resistance at lower current densities results from concentration polarization which is larger for the cathodic process than for the anodic one. At sufficiently high currents, securing rapid levelling of the concentration between the layer at the electrode and the bulk of the solution, the internal resistance of microcoulometers approaches the resistance of the solution.

The temperature dependence of the current–

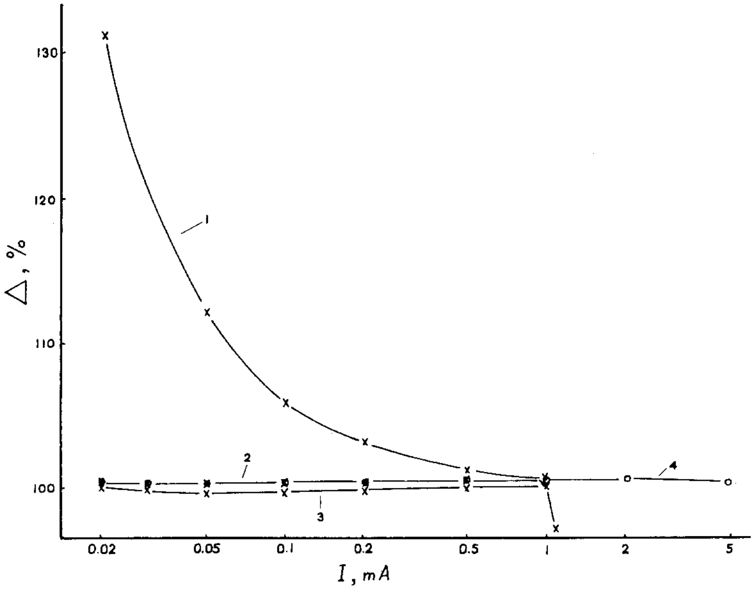

Fig. 5. Typical dependence of recovery of charge on the current density. × for phosphoric electrolyte; ○ for fluoroboric electrolyte.

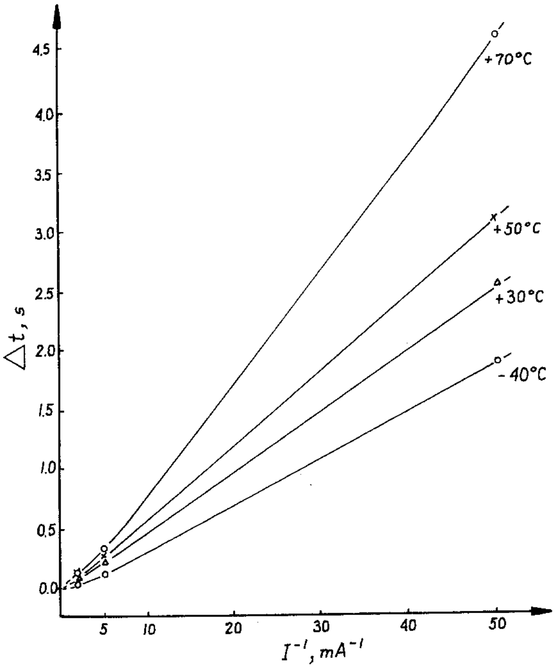

Fig. 6. Influence of temperature on the dependence of transition time on the reciprocal of current.

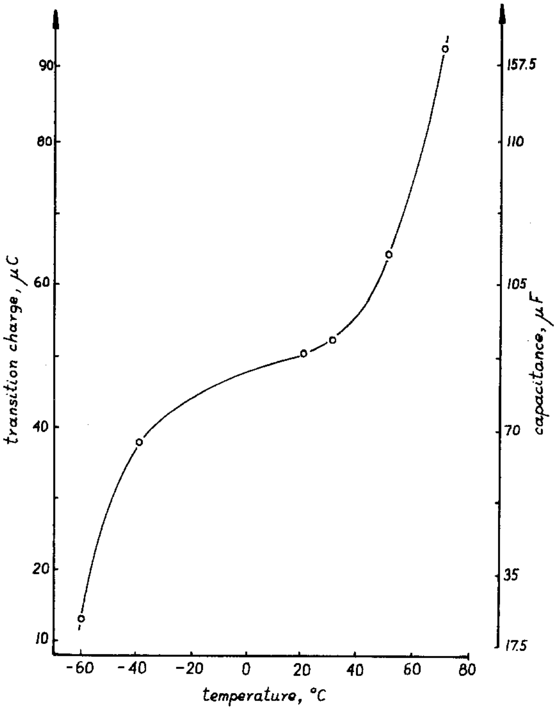

Fig. 7. Influence of temperature on the transition charge and the capacitance of the gold read-out electrode.

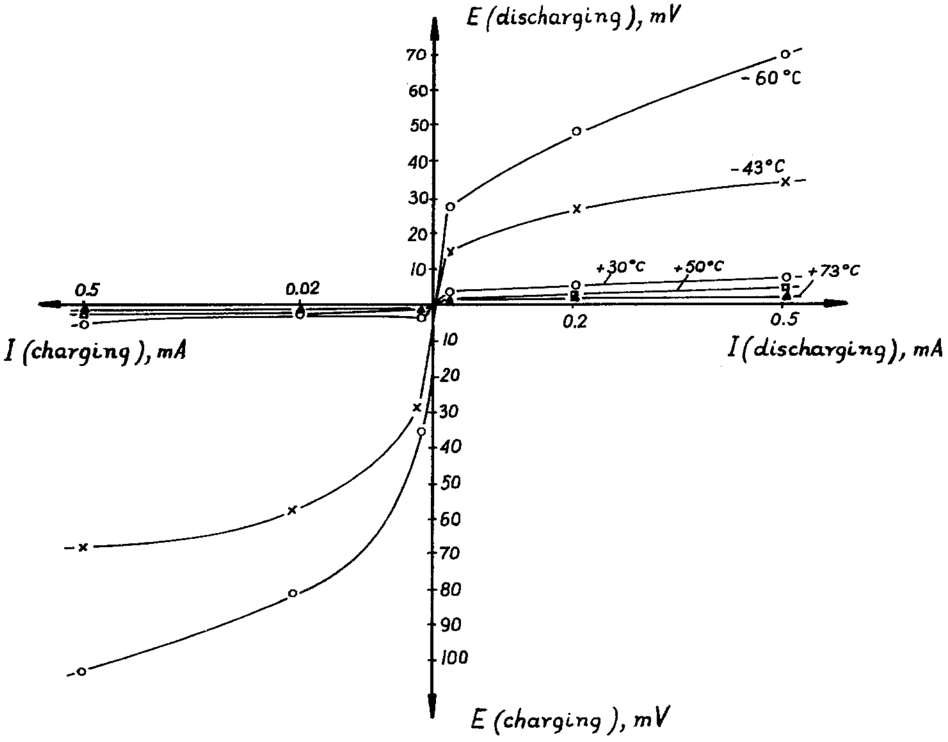

Fig. 8. Influence of temperature on the current–voltage characteristics.

voltage characteristics of the silver microcoulometer explains why the upper limits of current and charge (defined by the accuracy) are reduced at lower temperatures.

The characteristics shown in Figs. 5–8 and referring to fluoroborate electrolytes are very similar to those with *o*-phosphorate electrolytes. Differences appear at higher current intensities only (Fig. 5), at charges greater than 2 C and with long periods (above one week) between charging and reading out. In these conditions better behaviour was observed with fluoroborate electrolyte. The wider range of current is due to the lower viscosity and greater diffusion coefficients of Ag^+ ions in HBF_4 in comparison to H_3PO_4 solutions [11].

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References

[1] H. Feitler, *Electronics* 16 November (1974) 67
[2] *Idem, Electronic Design* **11** (1967) 122.
[3] A. P. Shorygin, *Entsiklopediya Izmerenii, Kontrolya, Avtomatizatsii, Energiya, Moskow* 8 (1967) V.20008-1.
[4] A. F. Bogenschütz and W. Krusemark, 'Elektrochemische Bauelemente', Verlag Chemi, Weinheim (1976).
[5] E-Cell Device, Appl. Note, Bull. 500, Plessey-Electroproducts, USA.
[6] W. E. Dmitrenko, W. W. Sobol and E. A. Maznichenko, *Pribory i Systemy Upravleniya* 8 (1972) 17.
[7] Z. Koczorowskii, *Symposium IUREMA XIX,* Vol. 3 (1974) p. 55.
[8] E-Cell Device, Appl. Note, Bull. 2100, 3200, 5300, 5301, Plessey-Electroproducts, USA.
[9] Z. Koczorowski and W. Wilczyński, Patent PRL 84 654 (1972).
[10] R. J. Roethlein, *J. Electrochem. Soc.* **120** (1973) 730.
[11] Z. Koczorowski, to be published.
[12] A. B. Garret, S. A. Woodrruff, *J. Phys. Colloid Chem.* 55 (1951) 477.
[13] H. Narcus, *Metal Finishing* 43 (145) 188, 199, 242.
[14] L. J. Kadaner, 'Galvanostegia', Tiekhnika, Kiev (1964).
[15] J. Kotowski and Z. Koczorowski, *J. Appl. Electro-Chem.* 7 (1977) 511.
[16] W. I. Teggart, 'The Electrolytic and Chemical Polishing of Metals in Research and Industry', Butterworths, London (1959).
[17] Ch. M. Mason and J. B. Culver, *J. Amer. Chem. Soc.* 71 (1949) 2387.
[18] 'Advances in Fluorine Chemistry', edited by M. Stacey, Vol. 1, Butterworths, London (1960).