THE USE OF TETRAALKYLAMMONIUM SALTS AS ELECTROLYTES FOR REDUCTIONS AT METALLIC SOLID CATHODES. WHY TETRAMETHYLAMMONIUM SALTS BEHAVE SO DIFFERENTLY?

Jacques Simonet and Charles Cougnon
Laboratoire d'Electrochimie
Université de Rennes 1
Campus de Beaulieu
35042 Rennes Cedex (France)

Tetraalkylammonium salts R_4NX has been widely used in organic solvents to reach very negative potentials (up to –3 V vs SCE) at mercury cathodes. However, when such very cathodic potential ranges are attained, the formation of tetraalkylammonium amalgams was reported. Such amalgams were additionally used as reducing reagents in ex-cell processes or two-time electrolyses. A constant research for better environmental conditions aims to advise against the use of mercury. Platinum and palladium can be employed as a substitute but such metals exhibit very small hydrogen overvoltages and then force the electrochemist to carefully dry organic solutions in order to better explore very cathodic potential ranges. Unfortunately at very low levels of moisture (< 50 ppm), platinum and palladium cathodically react with the electrolyte. Thus, platinum generally intereacts with R_4NX to give a phase of the form:

$$[Pt_2^-, NR_4^+, NR_4X] \text{ with } X = \text{halides}$$

and $$[Pt_4^-, NR_4^+, NR_4X] \text{ with } X = ClO_4^- \text{ and } BF_4^-$$

We want to stress on the fact that tetramethylammonium salts (iodide, perchlorate and tetrafluoroborate behave very unexpectedly compared to other R_4NX's. As a matter of fact, they display a quasi reversible step in very dry dimethylformamide (see figure 1) with two anodic peaks both assigned to the reoxidation of platinum reduced layer. When very negative potentials behond –3V vs SCE are reached (or if long holds at the level of the peak are made), additional reoxidation steps account for hydrogen redox systems (around 0 V vs SCE). With thin deposits of platinum on conductive unreactive substrates (principally gold), it has been shown that a stoechiometry of one electron per Pt atom can be obtained. EQCM measurements revealed a large mass increase which fits roughly with such a stoichiometry. Several sweeps demonstrated that the charge/discharge processes were totally reversible (Fig. 2) with a total deinsertion of ions at each run. Moreover, at extremely low potentials one never notices a drop of the total mass.

On the contrary, the cathodic behaviour of other R_4NX's was found to be dramatically different. In particular, when R = n-Bu, n-Hex, n-Octyl (as displayed in Figure 3), a neat maximum was observed in massogrammes followed by a fast decay. Thus, at very negative potentials, the mass increase has more or less totally vanished. It is expected that the organometallic layer formed at the platinum surface at moderate potentials is suddenly destroyed under additional electron transfer leading then to the cleavage of R_4N^+.

$$[Pt_2^-, NR_4^+, NR_4X] \xrightarrow{e^-} 2\,Pt + X^- + 2R^- + 2NR_3$$

$$2R^- + 2NR_4^+ \xrightarrow[\text{degradation}]{\text{Hoffmann}} 2RH$$

In conclusion, the classical scheme of reduction of tetraalkylammonium cations, is not respected at least at metallic solid electrodes and a classical cleavage such as

$$NR_4^+ + e^- \longrightarrow R^\bullet + NR_3$$

$$R^\bullet + e^- \longrightarrow R^- \xrightarrow{\text{Hdonor}} RH$$

but should correspond to a kind of electrocatalytic process with a preliminary chemical modification of the metal surface.

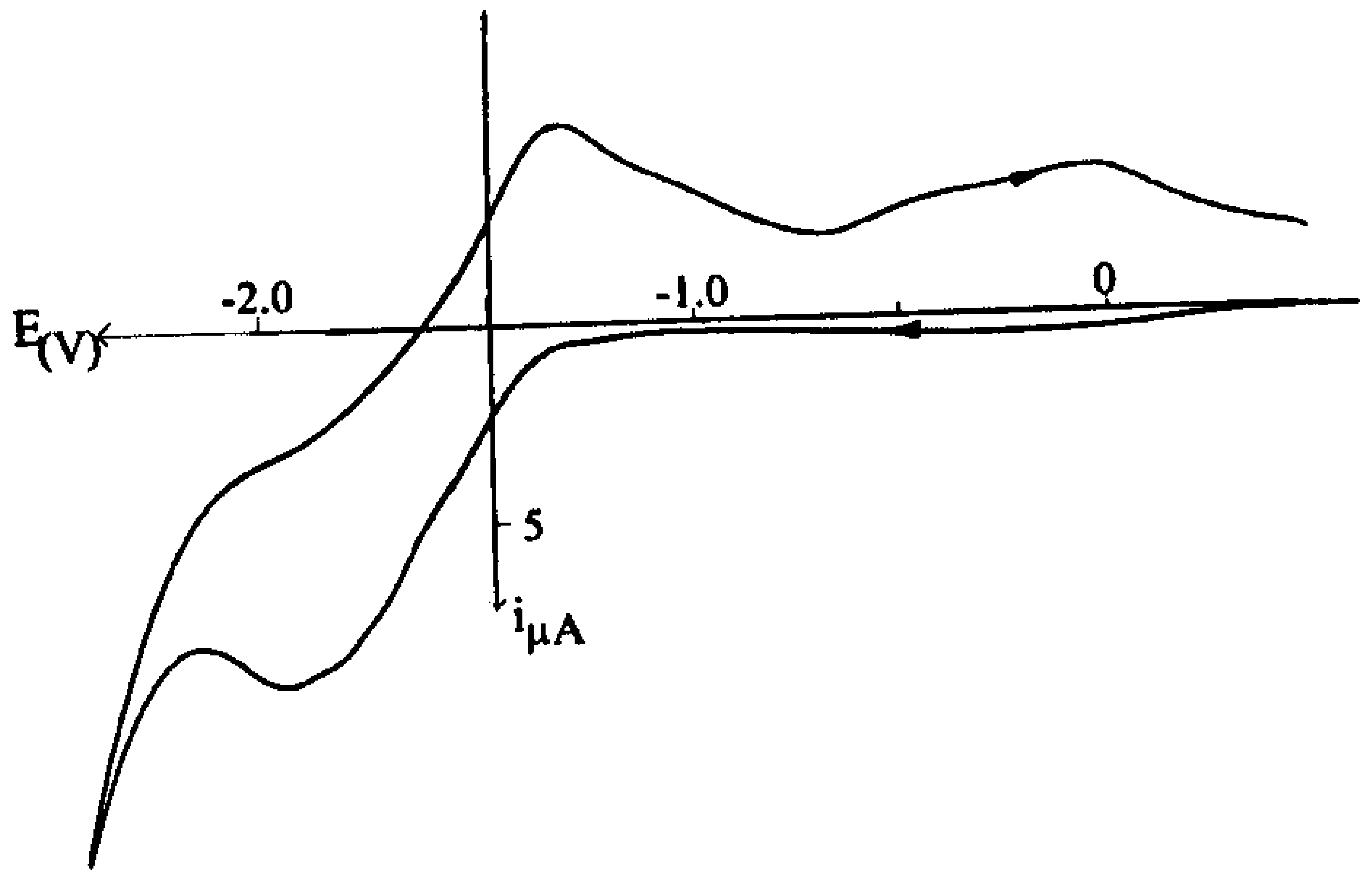

Figure 1 : Cyclic voltammetry of a solution of 0.1 M tetramethylammonium tetrafluoroborate at a stationary platinized platinum electrode. Sweep rate: 100 mVs^{-1}. Reference system: Ag/AgI/0.1M I$^-$.

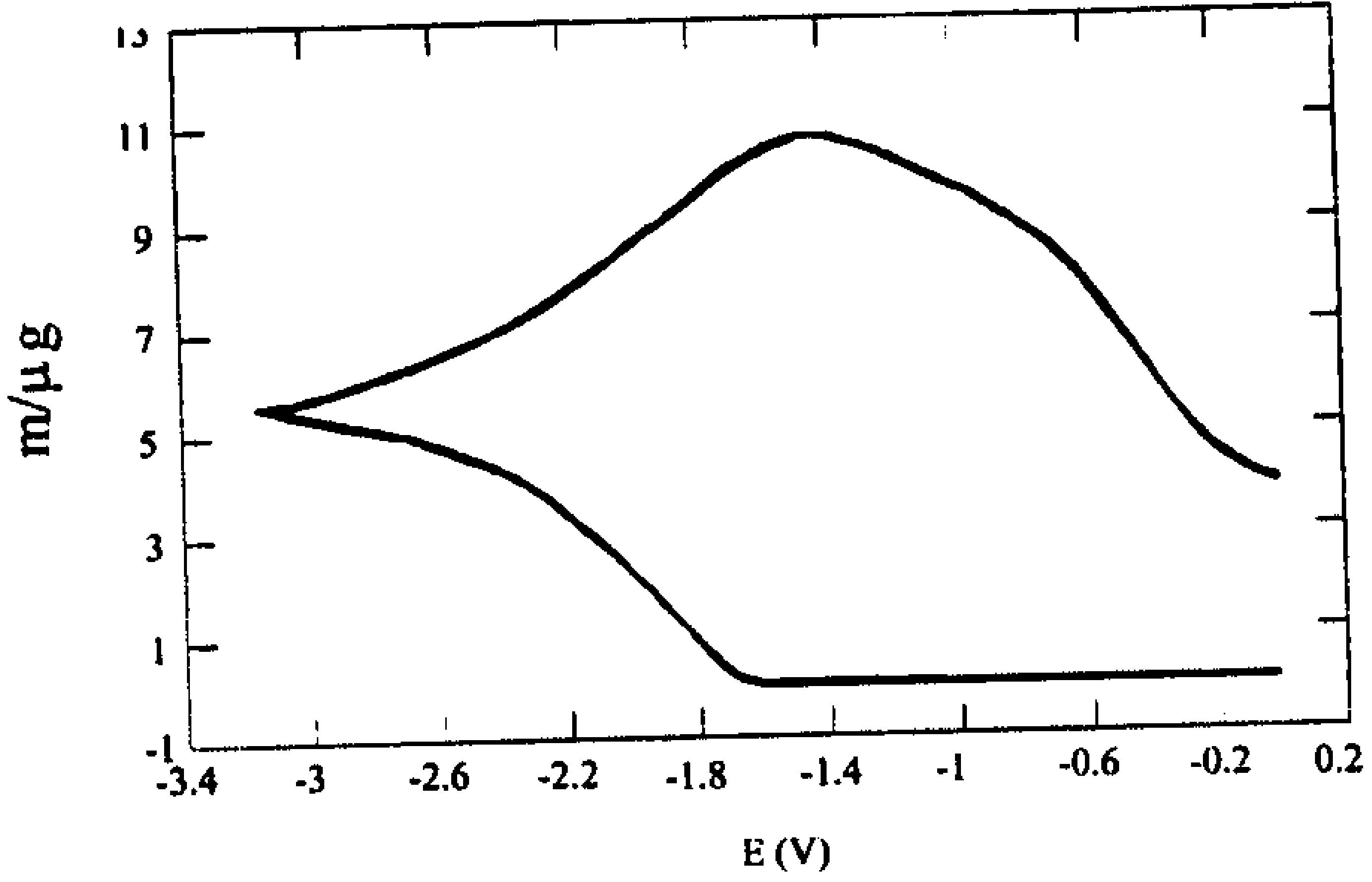

Figure 2 : Solution 0.1 M Me_4NBF_4 in DMF. Massogramme of a deposit of 17 mg of Pt onto gold substrate. Sweep rate: 10 mVs^{-1}.

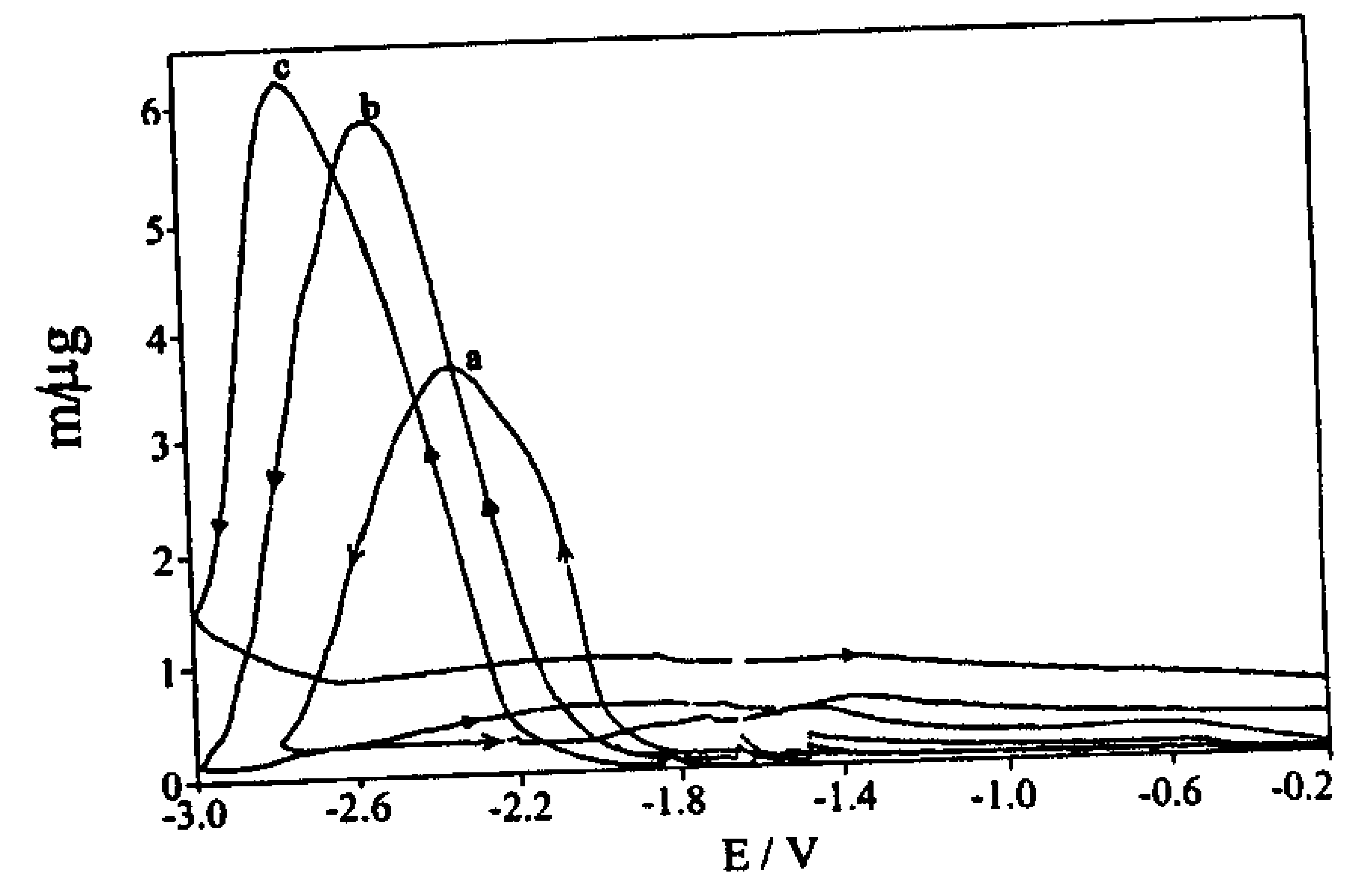

Figure 3 : Massogrammes for solutions of tetrabutyl (a) tetrahexyl (b) and tetraoctyl (c) chlorides 0.1 M in DMF. Response of a Pt film (15 μg) deposited onto gold. Sweep rate: 10 mVs^{-1}.