Properties of Anodic Deposits in Molten Thiocyanates

By Filippo Pucciarelli and Paolo Cescon*
(*Istituto Chimico dell'Università di Camerino,* 62032 *Camerino, Italy, and Istituto di Chimica Generale dell'Università di Genova,* 16132 *Genova, Italy*)
and Michael Heyrovský
(*The J. Heyrovský Institute of Physical Chemistry and Electrochemistry, Czechoslovak Academy of Sciences,* 11840 *Prague, Czechoslovakia*)

Summary The anodic deposit on platinum electrodes in thiocyanate melts is a complex mixture of species which, depending on experimental conditions, undergoes various chemical reactions terminated by complete polymerisation.

Platinum electrodes polarized anodically in KSCN or (K,Na)SCN melts become coated by an orange–yellow layer which some authors[1,2] supposed to consist of sulphur while others[3] thought to be essentially parathiocyanogen, $(SCN)_x$. We found[2] that a platinum electrode with the anodic deposit is photoelectrically active.

Further results show that the deposit is a chemically unstable system. We prepared the deposit, galvanostatically at a current density of *ca.* 100 μA cm^{-2}, with a thickness of *ca.* 100 Å. When freshly formed, its weight is in good agreement with that expected from Faraday's laws for the formula $(CNS)_x$. However, when the coated electrode is maintained under an inert atmosphere at the temperature at which it was formed (160—180 °C), its weight gradually decreases, falling to *ca.* 70% after 120 h. Elemental analysis of the deposit after several days shows that it contains *ca.* 96% S and 1·6% N.

Similarly, the electrode with the deposit changes its potential in the negative direction when dipped in the thiocyanate melt in which it was coated (see Figure, curve a). The potential change is faster at higher temperatures, and is particularly affected on exposure to light from a xenon lamp (Figure, curve b).

The photoelectric effect, *i.e.* the previously reported[2] fast and reversible response of the electrode potential to light, was found not to be specifically related to the presence of sulphide ions in the medium, but to be of a more general nature. The electroreduction of cadmium ions, for example, on the photoactive electrode, is accelerated by light to the same extent as the reported[2] oxidation of sulphide ions. The magnitude of the photoeffect depends on the condition of the deposit and decreases with its ageing. Electrodes prepared in the usual way and exposed to air at room temperature maintain their photoelectric activity for several days, but they lose the activity completely when kept in distilled water. When alternating voltage is applied between the coated and reference electrodes in the melt, the colour of the deposit darkens and the photoactivity of the electrode decreases. With an a.c. frequency of 50 Hz the photoeffect falls to zero in 1·5—2 min; with frequencies of

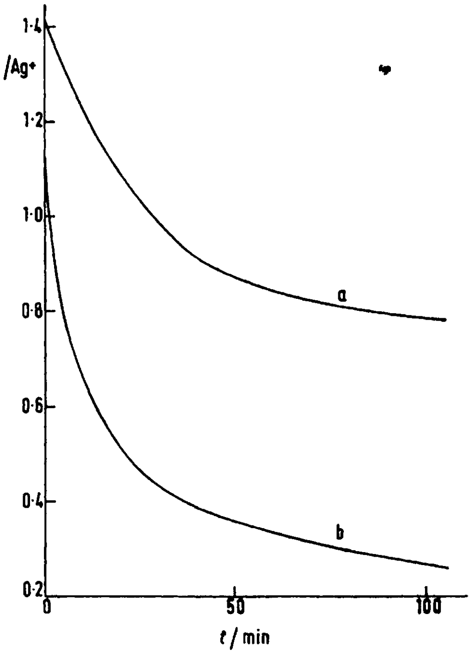

Figure. Change of potential of platinum electrode with a deposit from thiocyanate melt in molten (K,Na)SCN at 160 °C: (a) electrode in the dark, (b) electrode irradiated by xenon lamp.

the order of kHz the photoeffect decreases more slowly, the course of its decrease depending on the temperature of the melt.

The slow changes observed in the anodic deposit are obviously due to the polymerisation process. The reaction is initiated by production of [SCN]· free radicals at the electrode and ends with the free-radical species bound up in a polymeric form. Comparison of the present results with previous reports indicates that the course of the reaction after the free radical has been primarily formed depends on the experimental conditions. It seems probable that isomerisation of the radical, analogous to the well known thermal isomerisation of organic thiocyanates into isothiocyanates[4] may play a role in the initial stage.

While the isomeric structure could undergo direct polymerisation, only the thiocyanate structure would be able to split off the ·CN group. The experimental conditions further decide whether the cyanogen escapes from the melt as a gas or undergoes self-polymerisation to paracyanogen.[5] The formation of both paracyanogen[6] and parathiocyanogen[7] is known to be accelerated by light.

The effect of light is twofold: it produces an electrical photoeffect in the layer of deposit which behaves as a semiconductor when freshly prepared, and also speeds up the chemical process of polymerisation.

We thank the Italian National Research Council (C.N.R.) for support, and Professor M. Fiorani for his interest.

(*Received*, 23*rd August* 1974; *Com.* 1088.)

---

[1] G. Metzger, Report CEA-R-2566 Commissariat à l'Energie Atomique, Centres d'Etudes Nucleaires, Saclay, France; (*Nuclear Sci. Abs.* 1965, **19**, 1333); A. Eluard and B. Tremillon, *J. Electroanalyt. Chem.*, 1967, **13**, 208.

[2] F. Pucciarelli, P. Cescon, F. Diomedi-Camassei, and M. Heyrovský, *J.S.C. Chem. Comm.*, 1973, 154.

[3] R. E. Panzer and M. J. Schaer, *J. Electrochem. Soc.*, 1965, **112**, 1136; A. J. Calandra, M. E. Martins, and A. J. Arvia, *Electrochim. Acta*, 1971, **16**, 2057; B. Cleaver, A. J. Davies, and D. J. Schiffrin, *ibid.*, 1973, **18**, 747.

[4] I. T. Millar and H. D. Springall, 'A Shorter Sidgwick's Organic Chemistry of Nitrogen,' Clarendon Press, Oxford, 1969, p. 363.

[5] C. F. Cullis and J. G. Yates, *J. Chem. Soc.*, 1964, 2833.

[6] D. Berthelot and H. Gaudechon, *Compt. rend.*, 1912, **155**, 207.

[7] H. P. Kaufmann and J. Liepe, *Chem. Ber.*, 1923, **56**, 2515; G. Cauquis and G. Pierre, *Compt. rend.*, 1968, **266**, 883.