

Photoelectric Effect of Sulphur Deposited from a Thiocyanate Melt onto a Platinum Electrode

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Summary A layer of sulphur produced on a platinum electrode by anodic electrodeposition from an alkali thiocyanate melt gives a marked photoeffect with visible light in solution or in melts containing S^{2-} ions.

A PLATINUM electrode, electrodeposited with a layer of sulphur from a melt of alkali (Na, K) thiocyanates at 180 °C, shows a pronounced photoeffect in the presence of sulphide ions in the melt or in aqueous solution. However, when the sulphur layer is deposited from an aqueous sulphide solution at ordinary temperatures, no photoeffect is observed even in the thiocyanate melt. Attempts to produce a photosensitive sulphur layer on platinum by electrolysis of aqueous solutions of thiocyanates were

equally unsuccessful. The light used in the irradiation of the electrode (λ ca. 350—650 nm) was not absorbed by the solution or the melt.

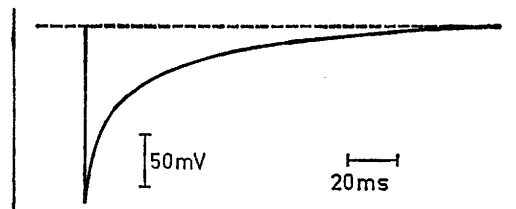


FIGURE 1. Time course of potential of a Pt electrode coated by sulphur in a thiocyanate melt after irradiation.

When the electrode is exposed to light its potential drops in a fraction of a second from a stationary value to a value 100–150 mV more negative and remains constant under

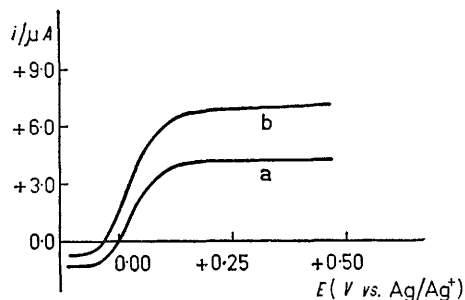


FIGURE 2. Voltammetric curves of the oxidation of S^{2-} (10^{-3} m) in a (K, Na)SCN melt at 160°C . Pt vertical alternating movement electrode¹ coated by sulphur, a; in the dark, b; under irradiation.

steady irradiation; in the dark it returns to its original value (see Figure 1). The change of potential on irradiation increases with increasing coverage of the electrode by sulphur to a maximum value corresponding to a thin and

¹ L. Busulini and P. Cescon, *Ann. Chim. (Italy)*, **1966**, **56**, 852.

complete coating; with prolonged deposition of sulphur it decreases. A linear relationship holds between the potential change on irradiation and the logarithm of the light intensity. When followed voltammetrically, the effect of light consists in generation of an anodic photocurrent in the potential region of the deposition of sulphur, as shown in Figure 2.

The photoelectric activity of the sulphur layer is probably due to the presence of a small amount of thiocyanate ions, either adsorbed at the electrode surface between sulphur atoms or occluded in the bulk of the sulphur phase. The mechanism of the photoeffect presumably proceeds as follows: the electrons set free by light as charge carriers in the sulphur layer move away from the sulphur-solution interface towards the metal, and, at the same time, more sulphide ions from the solution are discharged at the electrode. In consequence, the electrode changes its potential to a more negative value or the anodic current of sulphur deposition increases.

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