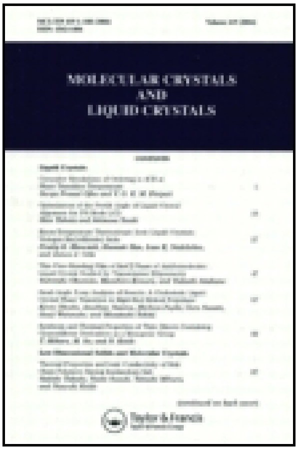

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Electrolytic Oxidation of Thiocyanate and Selenocyanate Salts and the Photoelectrochemical Effect.

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ELECTROLYTIC OXIDATION OF THIOCYANATE AND SELENOCYANATE SALTS AND THE PHOTOELECTROCHEMICAL EFFECT.

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Abstract. New photosensitive materials can be obtained by electrochemical oxidation of thiocyanate and selenocyanate salts. Using (K,Na)SCN eutectic melt, the formation of an electrodic deposit, with photoelectrochemical properties, has already been reported by us. To improve the photoelectrochemical characteristics of the deposit, futher investigations were carried out in the following sistems: selenocyanate ammoniate, KSCN-Acetamide eutectic mixture and KSCN ethylene carbonate solution. Attempts to obtain a massive deposit in the ammoniate solution were unsuccessful due to ammonia oxidation. Measurements performed on the other KSCN systems show that temperature is a parameter of remarkable importance. In fact, lowering the temperature one obtains a decrease on formation of parathiocyanogen on behalf of the polytrithiocyanogen, the species that gives rise to the photoeffect.

Anodic deposits obtained from electrolytic oxidation of both SCN^- in (K,Na)SCN eutectic melt, and $SeCN^-$ in ammoniate solution of KSeCN, show photoelectrochemical properties[1-4] .

In molten thiocyanate salts, it was observed that a remarkable increase in the photoeffect occured with decreasing temperature and this was ascribed to increase in formation of $[(SCN)_3]_x$, i.e. the semiconductor material, with respect to $(SCN)_x$, i.e. the insulating material. Accordingly, new experiments were performed in acetamide and ethylene carbonate solvents, in which both low temperature conditions and high salt concentrations are allowed. Conductivity measurements made on deposits obtained from electrolytic oxidation of SCN^- in these solvents, show linear dependencies of ln R on 1/T, as expected for a semiconductor material (Fig. 1). A gap energy of

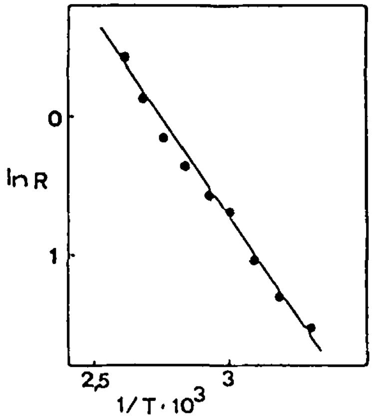

FIGURE 1. Graphic rappresentation of ln R vs. 1/T for the deposit obtained by electrolytic oxidation of KSCN in acetamide or ethylene carbonate, R in Ω cm.

about 0.13 eV can be computed from the slope of the line. Note that deposits previously obtained from molten salts showed an opposite dependence on temperature[1]. This behaviour suggests that formation of semiconductor-like species $[(SCN)_3]_x$ should predominate in the electrolytic oxidation of SCN^- under the present experimental conditions. Photopotentials of about 300-400 mV and photocurrents of about 10 μA, were obtained with materials prepared in such a way.

In selenocvanate ammoniate solution[2,4], the formation of both anodic deposit, possibly $(SeCN)_x$ matrix with trapped $(SeCN)_3^-$, and a soluble specie, $(SeCN)_3^-$, was observed at current densities below 0.3 mA/cm^2. At higher current densities only deposit formation was observed. However, massive growth of deposit could never be observed due to ammonia oxidation. Nevertheless the thin layer of deposit obtained exibits photoeffect[2] (Fig. 2). Cathodic stripping of the deposit was studied in the dark and under irradiation with visible light (Fig. 3). A positive shift of peak potential can be observed in the latter condition. This effect of light was observed also if the covered electrode was exposed to light before potetial scanning. Therefore the effect cannot be ascribed to deposit thinning with light. Moreover the potential shift is actually higher than that directly observed, owing to the negative photopotential arising under light irradiation. By contrary, the reduction peak of the $(SeCN)_3^-$ species in solution (when produced from low current density electrolyses) is not light sensitive. Experiment of Fig. 3 shows further evidence for the increasing conductivity of deposit under irradiation.

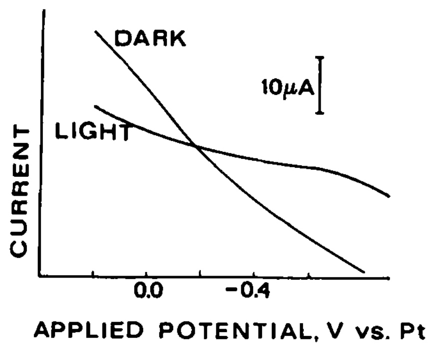

FIGURE 2. Current change of the coated platinum electrode in the dark and under irradiation.

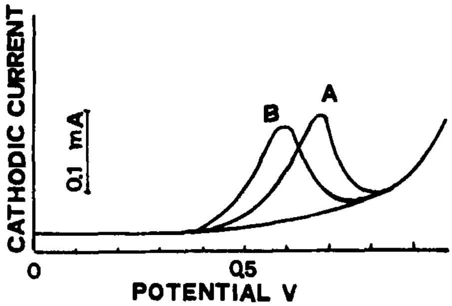

FIGURE 3. Catodic stripping of deposit (A) at dark (B) under light irradiation.

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