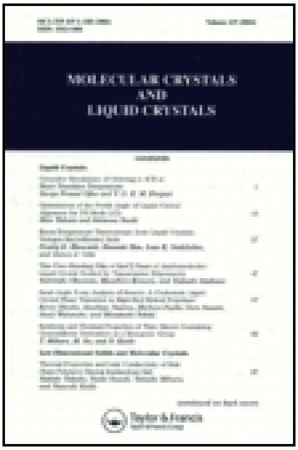

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Elkctrodeposition and Photoelectrochemical Properties of Dithiooxamido Copper (II) Films Onto Copper Electrodes

Gianni Zotti [a] , Giuliano Mengoli [a] & Franco Decker [a]
[a] 1st. Polarografia C.N.R., 35100, Padova, (Italy)

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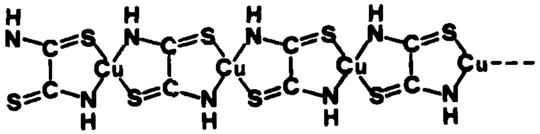
ELECTRODEPOSITION AND PHOTOELECTROCHEMICAL PROPERTIES OF DITHIOOXAMIDO COPPER (II) FILMS ONTO COPPER ELECTRODES

GIANNI ZOTTI, GIULIANO MENGOLI and FRANCO DECKER
Ist.Polarografia C.N.R.,35100 Padova (Italy)

Abstract Dithiooxamido copper (II)(copper rubeanate), a very insoluble and intractable coordination polymer, was successfully produced in the form of adherent films of controlled thickness (40-200 nm) by anodization of copper electrodes in aqueous solution of rubeanic acid. Under illumination the filmed electrodes show a p-type semiconducting behaviour. Though the material suffers from a short-wavelength absorption domain and possible photodecomposition processes, high quantum yields (ca.10%) were achieved.

INTRODUCTION

Investigations on the electric properties of 1D organometallic materials have mainly been focused on planar transition-metal chelated complexes arranged in molecular stacks. Scarce attention has been paid to coordination polymers in which bis-chelating ligands bridge the metal ions in a linear sequence of square planar moieties, such as those formed from dithiooxamide(rubeanic acid) and bivalent transition metal ions (e.g. Co^{2+}, Ni^{2+}, Cu^{2+})$^{1-5}$.



In order to check the photoconverting ability of these compounds, we electrodeposited thin films (20-400 nm) of dithiooxamido copper (II)(copper rubeanate, CuRA) onto copper electrodes and examined their photoactivity in a liquid-junction device.

FILM DEPOSITION AND CHARACTERIZATION

CuRA films onto copper electrodes were obtained by controlled electrodissolution of copper in hydroalcoholic solution of rubeanic acid:

$$Cu^{2+} + NH_2-\underset{S}{\overset{}{C}}-\underset{S}{\overset{}{C}}-NH_2 \longrightarrow 1/n\left[Cu(NH-\underset{S}{C}-\underset{S}{C}-NH)\right]_n + 2H^+$$

By cyclically driving the electrode potential in the range -0.9 ÷ ÷ 0.0 V vs.SCE the electrode passivates, with the formation of a thin film. Alkaline conditions favouring deprotonation of rubeanic acid produce thicker films but cause a slow decomposition of the ligand. Good results were obtained in O_2 saturated 0.1M LiCl solution by cycling between -0.9 and -0.5 V. The cyclic voltammogram (fig.1) shows an anodic peak at ca.-0.7 V attributable to copper oxidation in the presence of rubeanate anions, while the reverse cathodic process is due to oxygen reduction. The in-situ increase

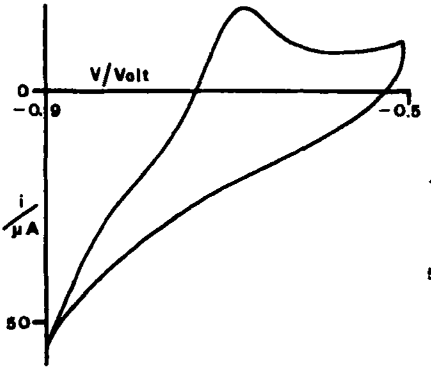


FIGURE 1

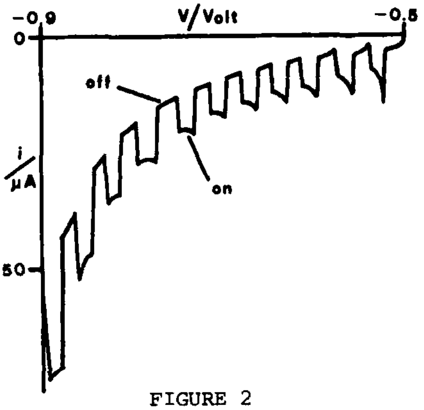


FIGURE 2

of pH accompanying O_2 reduction appears to favour CuRA formation without the complication of the long-term instability of RA in alkaline medium.

IR reflectance spectra of the deposited films agree with data in the literature for CuRA[4] and the intensity of the signals is proportional to the number of cycles employed for filming. The integrated charge required to reduce the CuRA films in acetonitrile (at ca.-1.8 V vs.SCE) was found to relate analogously to the number of cycles and allowed an indirect determination of thickness. The films are uniform and possess good adhesion to the substrate up to a thickness of 300-400 nm.

PHOTOELECTROCHEMISTRY

CuRA filmed electrodes, immersed in 0.1M LiCl degassed solution, do not show appreciable photocurrents before an underlying layer of copper oxide is fully reduced. Afterwards, cathodic photocurrents (ca.60 μAcm^{-2} at -0.9 V) under ca.100 $mWcm^{-2}$ white light are

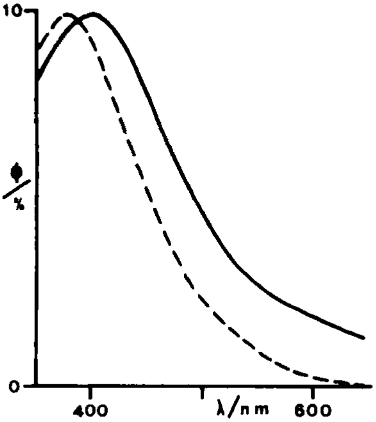


FIGURE 3

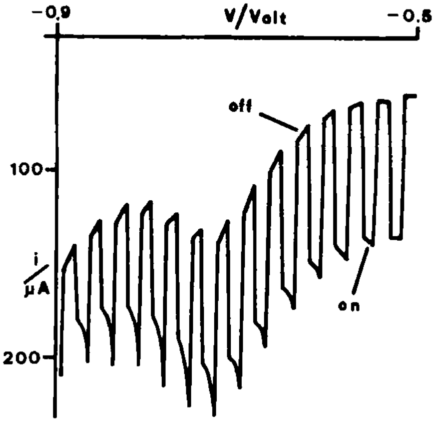


FIGURE 4

developed in the potential range -0.9 ÷ -0.5 V (fig.2). From the action spectrum, which satisfactorily follows the absorption spectrum (dashed curve in fig.3), a maximum monochromatic quantum yield of ca. 10% is obtained for a 200 nm film at -0.9 V (yields are lower for films thinner than 100 nm).However, the photocurrent decays slowly depending on incident light power. Maximum positive photovoltages of only 20-30 mV are obtained. The presence of oxygen increases both photocurrents (ca.25 $mAcm^{-2}$ at -0.5 V, fig.4) and photovoltages (30-50 mV). This phenomenon appears to be associated with the formation of interstitial copper oxide in this medium.

REFERENCES

1. R.N.Hurd, G.DeLaMater, G.C.MacElheny and L.V.Peiffer, J.Amer. Chem.Soc., 82, 4454 (1960).
2. S.Kanda and S.Kawaguchi, J.Chem.Phys., 34, 1070 (1961).
3. V.M.Vozzhennikov, Z.V.Zvonkova, E.G.Rukhadze, G.S.Zhdanov and V.P.Glushkova, Dokl.Akad.Nauk.SSSR, 143, 1131 (1962).
4. S.Kanda, A.Suzuki and K.Ohkawa, Ind.Eng.Chem.Prod.Res.Develop., 12, 88 (1973).
5. S.Son, S.Ueda, F.Kanamaru and M.Koizumi, J.Phys.Chem., 80, 1780 (1976).