

Full Length Research Paper

The electrochemical formation of ternary compound NaCu_5S_3

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The electrochemical reactions of a copper electrode in Na_2S solution were studied using cyclic voltammetry, potentiostatic and galvanostatic measurements. In addition surface examination and morphological studies were applied using scanning electron microscopy (SEM), energy dispersive analysis of X-rays (EDAX), and X-ray powder diffraction. Three anodic peaks were found in the anodic branch of the voltammograms. These peaks correspond successively to the formation of Roxbyite (Cu_{2-x}S), Covellite (CuS) and possibly CuO . On the other hand, the cathodic branch contains four peaks. These peaks correspond mainly to the reduction of copper oxide and the copper sulfides formed on the anodic branch. The ternary compound NaCu_5S_3 is formed by a consecutive reaction of cuprous sulfide with sodium sulfide.

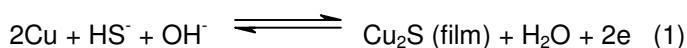
Key words: Copper, sodium sulfide, electrochemistry.

INTRODUCTION

The sulfidization of metals is a process of practical importance as well as of theoretical interest. From the theoretical point of view, sulfidization reactions afford important parallels and contrasts with the corresponding oxidation reactions. Investigations on the electrochemical behavior of copper in sulfide solutions and the formation of sulfide films on copper are relatively scarce despite their importance in many areas of applied chemistry and electrochemistry (De Chialvo and Arvia, 1985; Rand, 1977; Peter, 1978). Stoichiometric and non-stoichiometric copper sulfide films have been widely used in dielectric metallization (Stepanova et al., 2003), in solar cell technology (Schimmel et al., 1998) and as ion specific electrodes (Zirino et al., 2002). When soluble sulfides are present in potable water or seawater, a thick black, poorly adherent scale forms on a copper or brass surface (Jacobs and Edwards, 2000). This scale is composed mainly of Cu_2S although CuS , Cu_2O and non-

stoichiometric copper sulfide species such as $\text{Cu}_{1.8}\text{S}$ have also been reported (McNeil et al., 1993).

Cu_2S has been formed as an insoluble film on Cu electrode in aqueous sulfide solutions according to Velasquez et al. (2001):



The aim of the present work aims to give new lights on the characteristics of the electrochemical reaction and its products on a copper surface in sodium sulfide solution (mainly 0.8 M).

EXPERIMENTAL

Cyclic voltammograms (CVs), potentiostatic and galvanostatic polarization techniques were performed with the computer-controlled electrochemical measurement system Autolab (ECO Chemie) combined with the software package GPES (General Purpose Electrochemical System). A standard electrochemical cell with five holes - three holes for the electrodes and two for nitrogen inlet and outlet - was used.

A commercial Ag/AgCl electrode was used as reference electrode. The counter electrode was a platinum wire. The working copper electrode was prepared from a high purity (99.98%) copper

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Abbreviation: CVs, Cyclic voltammograms; SEM, scanning electron microscopy.

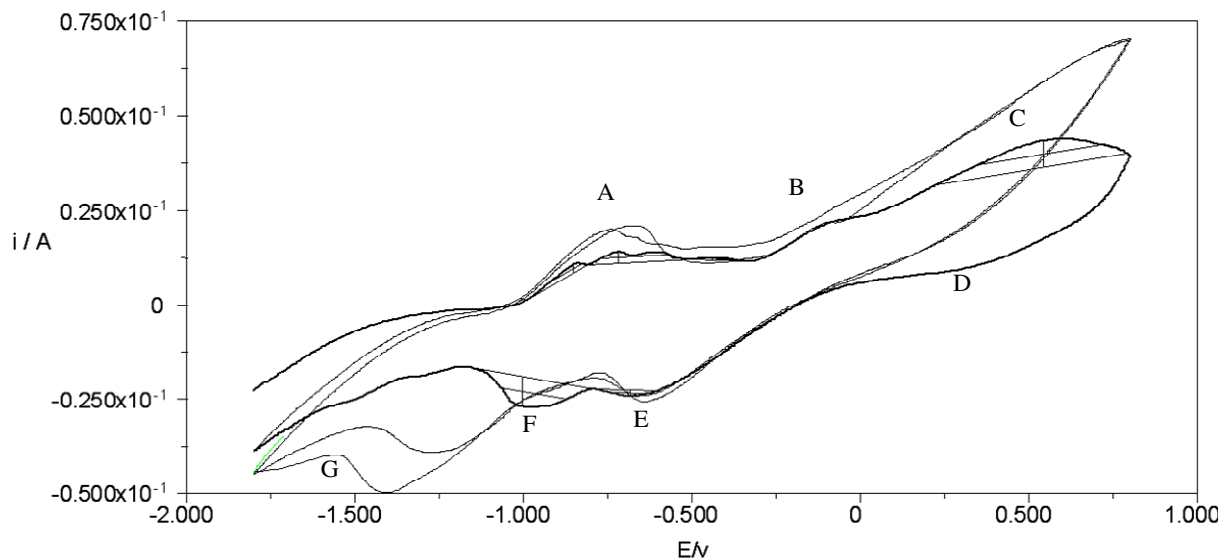


Figure 1. Cyclic voltammogram of copper in 0.8 M Na₂S at sweep rate 50 mV/s.

rod. A small piece of copper rod - diameter 6 mm, length 6 mm was placed in a "Kel-F" shield, secured by epoxy resin. The bottom electrode was screwed onto a polyethylene holder with a contact wire in order to obtain good electrical contact. The electrodes were successively abraded with finest grade emery paper and degreased with acetone. Complete wetting of the surface was taken as indication of its cleanliness when rinsed with bi-distilled water. All chemicals used were of A.R. quality. The solutions were prepared using bi-distilled water; no attempts were made to de-aerate them.

Cyclic voltammetric sweeping was generally between -1.8 V (hydrogen evolution) to +0.8 V (oxygen evolution). All measurements were taken at $25 \pm 1^\circ\text{C}$.

The surface of the electrode and the scales formed at the electrode were investigated by scanning electron microscopy (SEM) and energy dispersive X-ray elemental analysis (EDAX). Guinier powder photographs were used for the crystallographic phase analysis of the products.

RESULTS AND DISCUSSION

Cyclic voltammetry

Figure 1 represented the CV'S of a Cu electrode in 0.8 M Na₂S recorded in three successive sweeps at 25°C and at a voltage sweep rate of 50 mV/sec. The observed difference in the curves could be attributed to different initial states of the electrode surface and can be recognized along both the anodic and cathodic branches of the cyclic voltammograms. It is of interest to remark that the second and third sweeps gave essentially similar voltammograms which differ from that of the first sweep in some significant characteristics. Obviously the initial state of the electrode surface determines the shape of the resulted cyclic voltammograms to an important extent. There were three peaks (A, B and C) in the anodic branch of the voltammograms and four peaks in

the cathodic branch [D, E, F and G]. No passivation is observed, the current rises steadily.

Peak A is composite, as can be seen from the fine structure in the first sweep and the three reduction peaks E, F, and G. The X-ray analysis of the black scales formed at sweeps in the range -1.8 to +0.2 V, as well as potentiostatic experiments at -0.7 and -0.8 V indicated Roxbyite Cu_{2-x}S. Other possible reactions that belonged to peak A were the formation of Cu (I) oxide or hydroxide and the oxidation of HS⁻ to elemental sulfur. There is an interesting interplay between the reduction peaks F and G: Peak F only appeared at the first cycle and disappeared in the following cycles while the new peak G is appearing. Peak F may be associated with an oxide reduction and peak G to sulfide reduction to metallic copper.

The black layers formed by cycling between -0.8 to +0.8 V and by potentiostatic treatment at +0.1 V were Covellite (CuS). SEM micrographs revealed also some small patches of sulfur. Thus peak B corresponded to Covellite formation and peak C is probably due to some oxidation of Covellite to CuO + S₈.

Guinier powder photographs were used for the crystallographic phase analysis of the products (Tables 1-3).

Galvanostatic measurements

The diagram at zero current (Figure 2) is most interesting. After switching off the current, the potential rapidly increases towards more negative values, as a consequence of active Cu dissolution. The first potential arrest, which is believed to correspond solely to the monolayer of Cu(I) sulfide is denoted as the nucleation

Table 1. Crystallographic data and Guinier diagram of Roxbyite, Syn Cu_7S_4 .

h	k	l	d_{obs}	i_{obs}	h	k	l	d_{obs}	i_{obs}
4	4	0	6.720	vw				1.500	mw
12	2	0	4.250	mw				1.463	vw
10	0	2	4.240	mw					
3	7	2	3.600	mw					
16	0	0	3.350	mst					
8	0	4	3.000	m					
18	2	1	2.864	st					
20	0	1	2.630	st					
20	4	0	2.537	m					
1	5	5	2.452	mw					
			2.374	vst					
0	16	0	1.938	vst					
8	8	6	1.861	vst					
			1.679	m					
			1.628	mw					

Table 2. Crystallographic data and Guinier diagram of Covellite, Syn CuS .

h	K	l	d_{obs}	i_{obs}	h	k	l	d_{obs}	i_{obs}
0	0	2	8.180	vw	2	1	3	1.210	vw
1	0	0	3.285	vw	3	0	0	1.094	vw
1	0	1	3.220	mw	2	1	8	1.060	vw
1	0	2	3.048	st	3	0	6	1.015	vw
1	0	3	2.813	vst					
0	0	6	2.724	mst					
1	0	5	2.317	vw					
0	0	8	2.040	vw					
1	0	7	1.902	mw					
1	1	0	1.896	st					
1	0	8	1.735	m					
2	0	3	1.572	vw					
1	1	6	1.556	m					
1	1	8	1.390	vw					
2	0	8	1.820	vw					

potential (E_0). The potential plateau reaches thereafter approximately -0.7, corresponded to peak A in the cyclovoltogram. This potential is denoted as the formation potential E_f . The period of time corresponding to the potential plateau are denoted as transition time (Southampton Electrochemical Group, 1990).

After the plateau is completed, the potential begins to increase again with time, indicating the further growth of another sulfide layer. The second step is phenomenolo-

Table 3. Crystallographic data and Guinier diagram of Sodium Copper Sulfide NaCu_5S_3 .

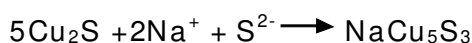
h	K	l	d_{obs}	i_{obs}	h	k	l	d_{obs}	i_{obs}
1	0	0	6.043	st	2	1	5	1.219	w
1	0	1	4.631	vst	5	0	0	1.208	vw
1	1	0	3.489	st	3	2	3	1.200	w
1	1	1	3.140	m					
2	0	0	3.021	m					
1	0	3	2.232	mst					
3	0	1	1.940	m					
2	1	2	1.929	st					
3	0	2	1.758	st					
3	1	1	1.632	m					
2	2	2	1.570	mw					
2	2	3	1.411	w					
4	0	2	1.393	mw					
4	1	1	1.297	mw					
4	1	2	1.238	w					

gical similar to the first one. Thus the formation of two well defined layers is indicated.

Surface analysis

Layers formed by CV and potentiostatic experiments at different potentials were investigated by SEM, EDAX (Figures 3 to 8) and powder diffractometry (Tables 1,2 and 3). Thus peak A in the cyclovoltogram (Figure 1) could be associated with mainly Roxbyite (Cu_{2-x}S) formation and peak B with Covellite (CuS) formation. The microstructure of the scales was inhomogeneous and porous (Figures 3 and 4). Scale growth obviously occurred by the reaction of Cu^+ ions formed at the metal surface with the sulfide by direct contact or after moving through the Roxbyite bulk to the layer surface.

In CV sweeps -1.8 to -0.2 V the formation of the ternary compound NaCu_5S_3 (Effenberger and Pertlik, 1985) as small rod-like crystals was observed (Figure 5). Potentiostatic experiments gave reproducible results with more concentrated 3 M Na_2S solutions at potentials between -0.8 and +0.4 V. Obviously the ternary compound is formed by a secondary reaction:



Conclusions

This study has corroborated the complex character of the electrochemical sulfidization of copper in 0.8 M Na_2S

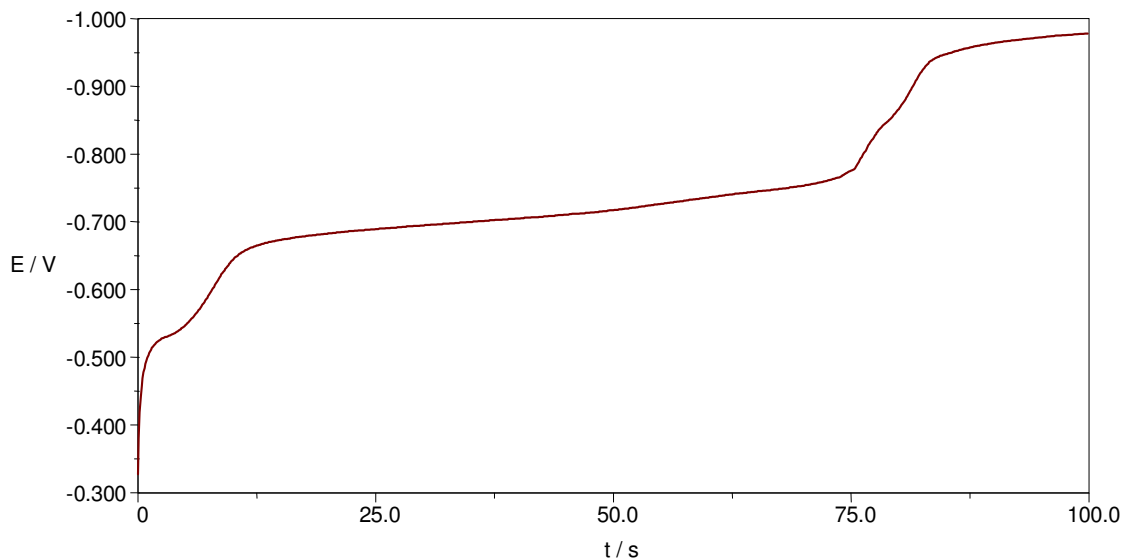


Figure 2. Galvanostatic curve recorded for copper electrode in 0.8 M Na_2S current = 0.

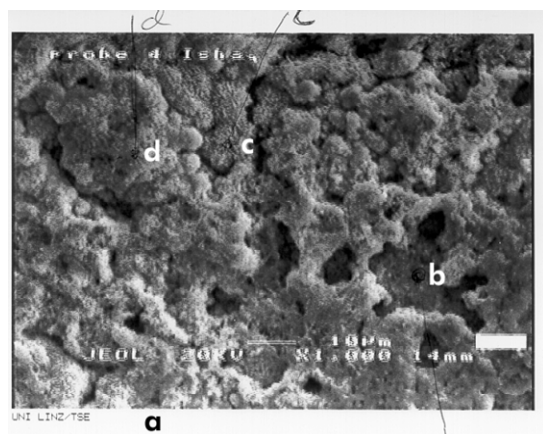


Figure 3. Scanning electron micrographs of Cu in 0.8M Na_2S , CV -1.8 to +0.2V, Roxbyite (Cu_{2-x}S).

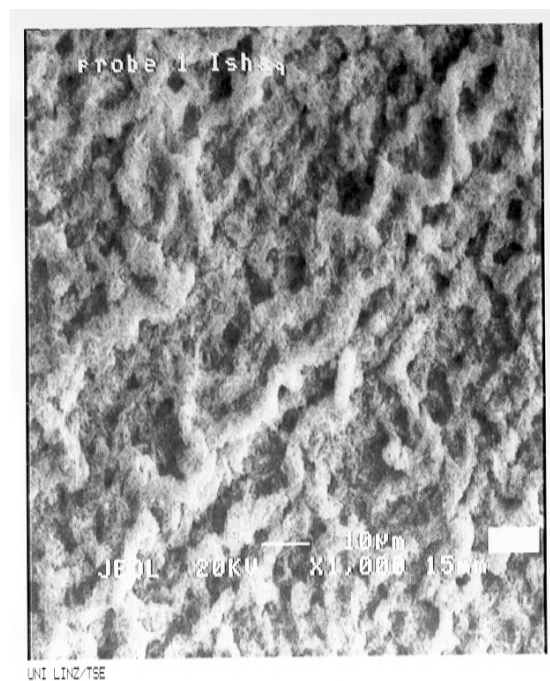


Figure 5. Scanning electron micrographs of Cu in 0.8 M Na_2S , CV -1.8 to -0.2 V, (NaCu_5S_3).

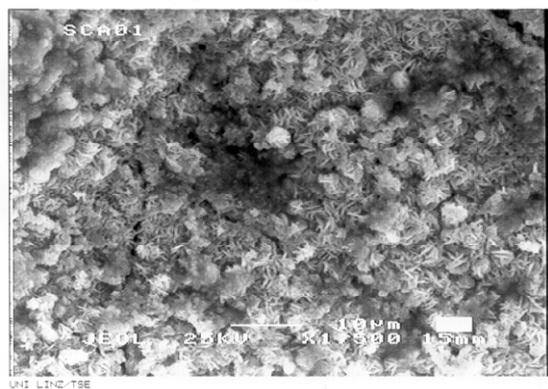


Figure 4. Scanning electron micrographs of Cu in 0.8 M Na_2S , CA 0.1V, Covellite (CuS).

solutions. The most important oxidation peaks in the cyclic voltammograms could be assigned to the formation of Roxbyite (Cu_{2-x}S) and Covellite (CuS). SEM micrographs revealed the heterogeneous and porous character of the scales. The formation of NaCu_5S_3 by a secondary reaction of cuprous sulfide with sodium sulfide was observed.

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Version: 3.1 deu                Eo:20.0 keV (AW:35.0 KW: 0.0)
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*** PUzaf Ergebnisse ***

Elem/Linie	P/U	R	F	c	c(Atom)	Vertr.	h
Cu K-alpha	@410.8	1.05432	1.04239	73.54	65.74	+ - 5.66	-
S K-ser	@133.9	1.02392	1.01208	19.34	34.26	+ - 2.71	-
standardfrei				92.88	100.00	[2s]	

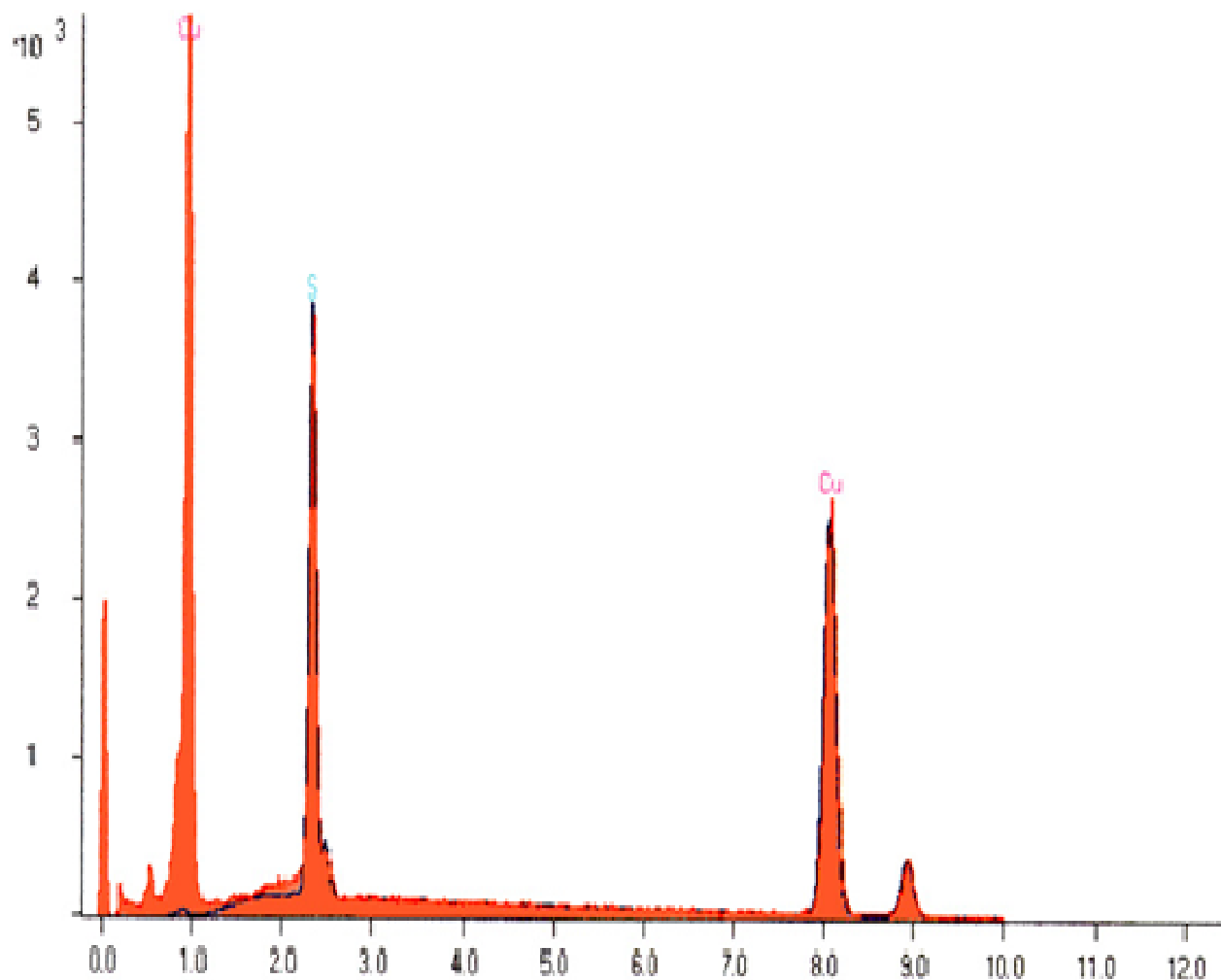


Figure 6. SEM pattern and Edax profile of the layer form by CV from -1.8 to $+0.2$ V at sweep rate 50 mv/s in Na_2S 0.8 M.

RÖNTEC EDWIN WinTools		NCA02_1 19.01.2000 (15:43)					
Version: 3.1 deu		E ₀ :20.0 keV (AW:35.0 KW:90.0)					
*** PUzaf Ergebnisse ***							
Elem/Linie	P/U	R	F	c	c(Atom)	Vertr.	h
S K-ser	@194.1	1.02257	1.00986	26.81	53.73	+/- 1.78	
Cu K-alpha	@272.7	1.05126	1.04657	45.77	46.27	+/- 2.54	
standardfrei				72.58	100.00	[1s]	

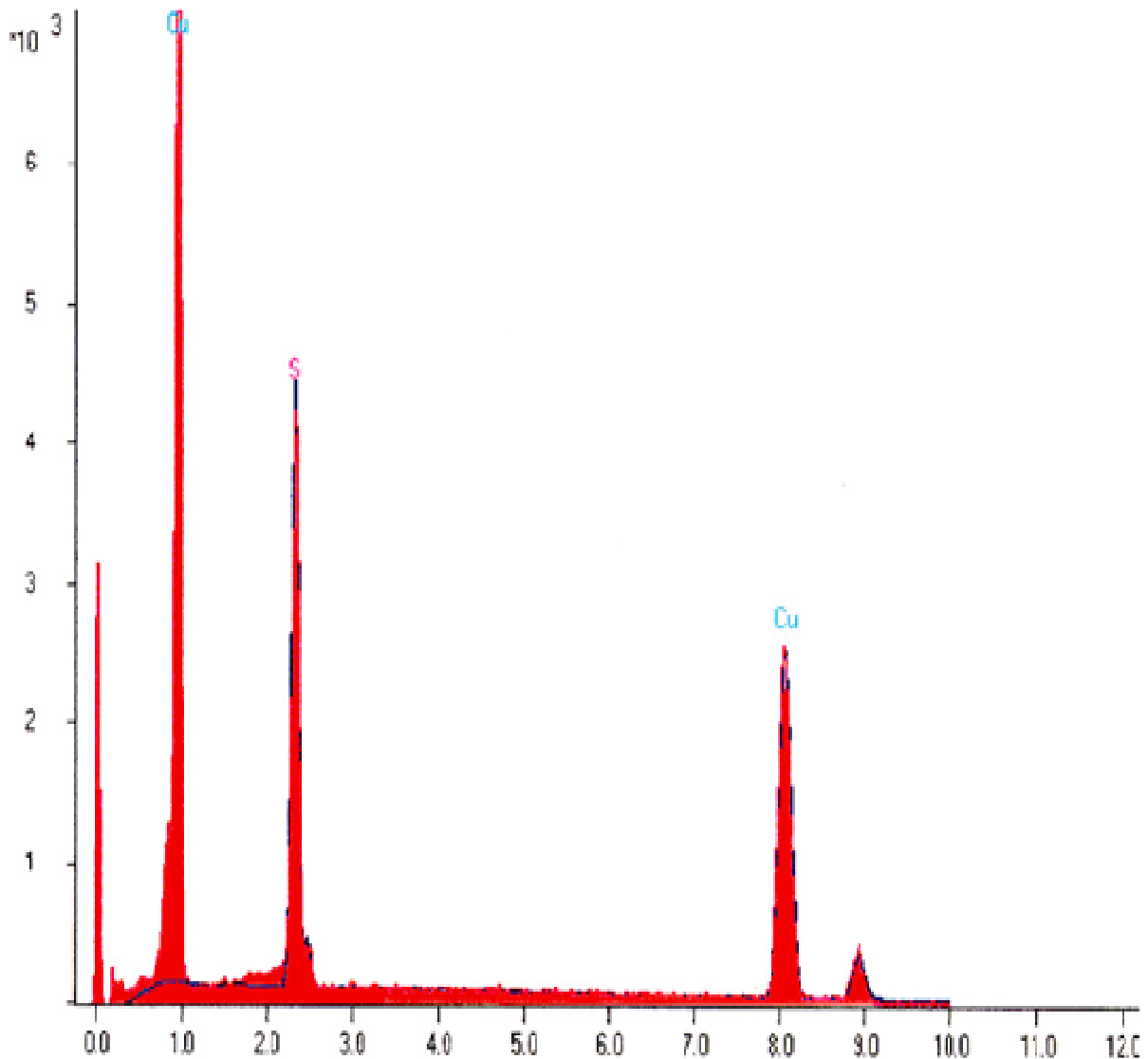


Figure 7. SEM pattern and Edax profile of the layer form at potential +0.1 V during 1 h in Na₂S 0.8 M.

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Version: 3.1 deu                Eo:25.0 keV (AW:35.0 KW:80.0)
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*** PUzaf Ergebnisse ***

Elem/Linie	P/U	R	F	c	c(Atom)	Vertr.	h
Cu K-alpha	@582.2	1.04826	1.04267	81.37	61.40	+ - 2.48	
Na K-ser	@ 21.4	0.99911	1.00170	5.29	11.03	+ - 0.76	
S K-ser	@135.9	1.01825	1.01365	18.43	27.57	+ - 0.86	
standardfrei				105.10	100.00	[1s]	

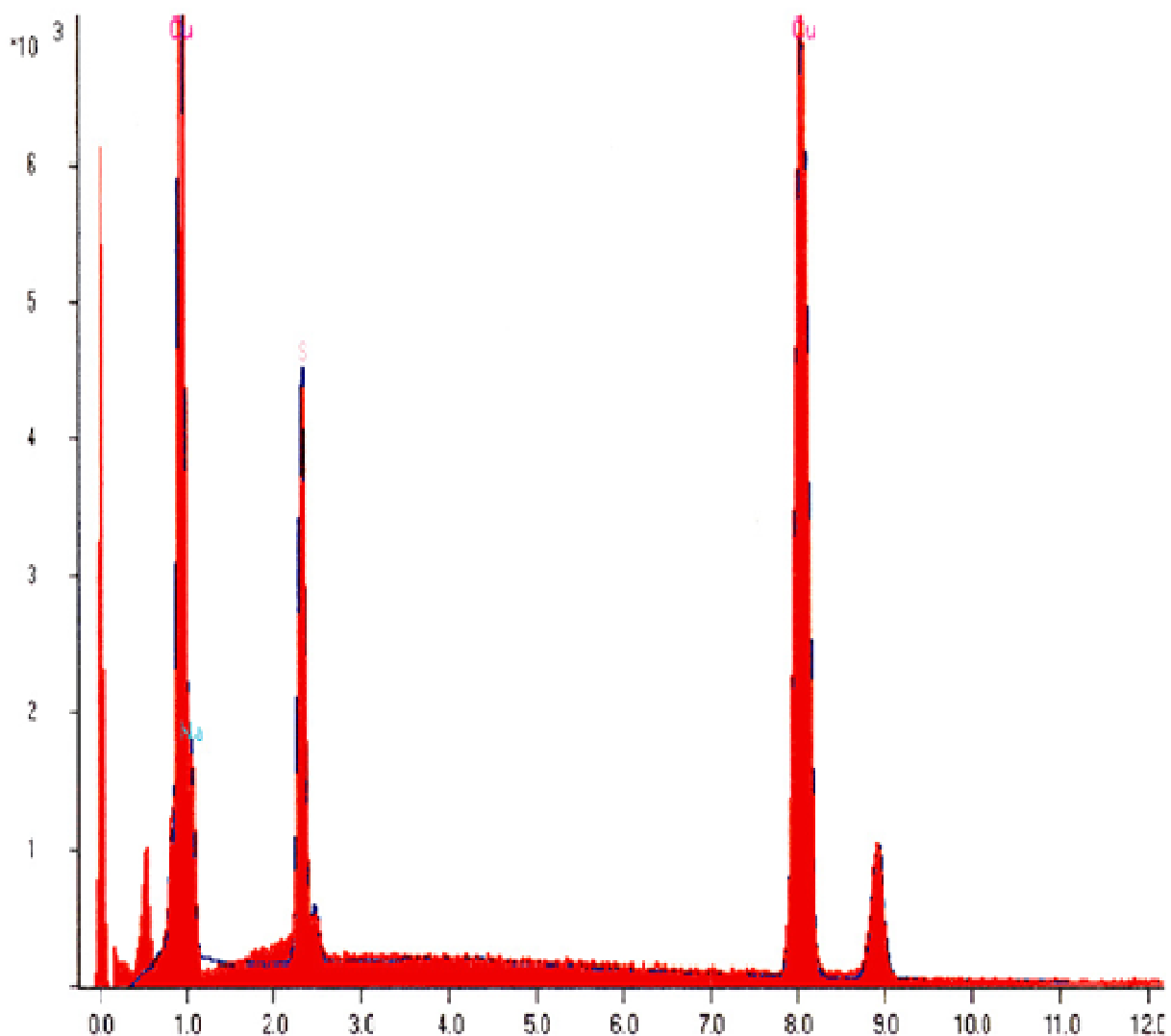


Figure 8. SEM pattern and Edax profile of the layer form by CV from -1.8 to -0.2 V at sweep rate 50 mv/s in Na_2S 0.8 M.

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NaCu₅S₃

COL:	ICSD Collection Code 61514
Date:	Recorded Dec 3, 1986
Name:	Sodium pentacopper trisulfide
Form:	Na Cu ₅ S ₃ = Cu ₅ Na S ₃
Title:	Crystal Structure of Na Cu ₅ S ₃
Reference:	Monatshefte fuer Chemie und verwandte Teile anderer Wissenschaften (109, 1978-) MOCMB 116 (1985) 921-926
AUT:	Effenberger H, PertlikyF
CELL:	A=6.978 (5) b=6.978 (5) c=7.209 (6) a=90.0 a=90.0 c=120.0 v=304.0 z=2
SGR:	P 63 2 2 (182) - hexagonal
CLAS:	622 (Hermann-Mauguin) - D6 (Schoenflies)
PRS:	hP18
ANX:	AB5X3
Comments:	<p>Space group P 6₃ 22-D₆⁶, Z=2> was synthesized under hydrothermal conditions. The crystal structure was solved direct methods from 140 single cerystal X-ray data. The refinement yiekded an R value of 2.3%. The Na atom has an octahedral coordination of S atoms < Na – S=2.89 A^o,6x>.</p> <p>The atom Cu(1) is bound to two S atoms at 2.19 A^o and the atom Cu(2) to three atoms at 2.36 A^o. In addition Cu(1) atom is coordinated to four Cu(2) atoms, and the Cu(2) atom to six Cu(1) atoms with Cu-Cu distance of 2.70 A^o and 2.72 A^o. The S atom has an irregular coordination figure built up by two Na and four Cu atom neighbours. The connection of the different coordination polyhedra results in a framework structure.</p>
