Cyclic voltammetric behavior of copper electrode in sodium sulfide solutions

I. ZAAFARANY¹ and H. BOLLER²

¹Chemistry Department Faculty of Applied Science, Umm Al-Qura University, Makkah Al Mukarama, P.O.Box:118 (Saudi Arabia).
²Institute of Inorganic Chemistry, Johannes-Kepler-Universität Linz, A-4040 Linz (Austria).

(Received: July 30, 2009; Accepted: October 01, 2009)

ABSTRACT

The cyclic voltammograms of the copper electrode in Na₂S solution was studied using cyclic voltammogram’s technique. Three anodic peaks were observed in the anodic branch of the voltammogram’s. The peaks may be attributed successively to the formation of Cu₂S, CuS and Cu₂O. On the other hand, the cathodic branch shows four peaks. These peaks correspond to the reduction of copper oxide and copper sulfide formed in the anodic branch.

Key words: Copper electrode, sodium sulfide, cyclic voltammetry.

INTRODUCTION

The sulfidation of metals is a process of practical importance as well as of theoretical interest as oxidation. From the theoretical point of view, sulfidation reactions afford important parallels and contrasts with the corresponding oxidation reactions. On reaction films of solid were formed on metals and alloys consist in general, field of study of great importance in electrochemistry, which is still open for 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. Stoichiometric and non-stoichiometric copper sulfide films have been widely used in dielectric metallization, in solar cell technology and as ion specific electrode, when soluble sulfides are present in potable water or seawater, a thick black, poorly adherent scale forms on copper or brass surface. This scale is composed mainly of Cu₂S although CuS, Cu₂O and non-stoichiometric copper sulfide species such as Cu₁.₈S have also been reported.

Cu₂S has been formed as an insoluble film on Cu electrode in aqueous sulfide solutions according to the equations:

\[2Cu + HS^- + OH^- \rightarrow Cu_2S \text{(film)} + H_2O + 2e^-\]  \hspace{1cm} (1)

The aim of the present work aims to give new lights on the characteristics of the reaction products performed on the copper surface in sodium sulfide solution using cyclic voltammogram technique.

EXPERIMENTAL

The working copper electrode was prepared from high purity (99.98 %) copper rod. A small piece of copper rod, diameter 6 mm, length...
6 mm was placed in a “Kel-F” shield. This was fixed to a borosilicate glass tube with epoxy resin. Electrical contact was achieved through a copper wire soldered to the end of the electrode, not exposed to the solution. Before being used, the electrode surface was polished with different grade emery papers until it appeared free of scratches and other defects. Then, it was rinsed with acetone and finally washed twice with distilled water. All chemical used were of A.R. quality. The electrolytic cell was made up of pyrex glass and is described elsewhere.

Cyclic voltammetry curves (CV’s) were performed using autolab [ECO Chemie] combined with the software package GPES (General Purpose Electrochemical System) was used. This is a computer-controlled electrochemical measurements system. It consists of data-acquisition system and a potentiostat/galvanostat. CV was used to study the corrosion of copper in sodium sulfide solutions (Na$_2$S) sweeping from -1.25V to 0.025 V. All measurements were taken at 25 ± 1°C.

RESULTS AND DISCUSSION

Cyclic Voltammetry

Fig. 1 represents the CV’s of a copper electrode in 0.8 M Na$_2$S recorded in three successive sweeps at 25 ºC and at a voltage sweep rate of 50mV/sec. The observed difference in the curves can 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 give 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 resulting cyclic voltammograms to an important extent. There are 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 as the current flows 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. Other possible reactions belonging to peak A are 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 while Peak F only appears at the first cycle and disappears in the following cycles while the new peak G is appearing. Peak F may be attributed to an oxide reduction while peak G to sulfide, reduction to metallic copper.
Fig. 2: Effect of sweep rate on the anodic charge capacity for copper electrode in 0.8M-sodium sulfide from –1.2 to 0.1V

Fig. 3: Effect of sweep rate on the cathodic charge capacity for copper electrode in 0.8M-sodium sulfide from –1.2 to 0.1V

Fig. 4: Effect of multicycles on the anodic charge capacity for copper electrode in 0.8M-sodium sulfide from –1 to 0.25V, scan rate 50mv/s
Fig. 5: Effect of multicycles on the cathodic charge capacity for copper electrode in 0.8M-sodium sulfide from -1 to 0.25V, scan rate 50mv/s

Fig. 6: Effect of multicycles on the anodic charge capacity for copper electrode in 0.8 M-sodium sulfide from -1.8 to 0.8V, scan rate 200mv/s

Fig. 7: Effect of multicycles on the cathodic charge capacity for copper electrode in 0.8M-sodium sulfide from -1.8 to 0.8V, scan rate 200mv/s
Influence of sweep rate and concentration

It was demonstrated previously¹¹ that two of the most important factors influencing the development of charge storage capacity in the case of copper electrodes were, the values for the upper and lower limit of the potential sweep. The observed optimum values 1.8V for the lower limit and +0.8V for the upper limit, were adopted throughout the present investigation. A relatively small number of sulphide growth cycles were used in most experiments in order to maintain reasonably small current values (and hence, minimize potential errors associated with iR drop) and to ensure a high level of reactivity throughout the surface layer. Figs. 2 – 7 show the influences of the sweep rate on the CVs. The CV for sweep rate 1mv/s shows rather complicated features that are beginning to be smeared out at 10mv/s. This shows that the kinetics of the electrode processes are rather slow. At lower sweep rates the layers formed are thicker than at higher sweep rates. In Figs. 8 – 11 the influence of the concentration on the CV is shown.

Development of charge capacity

A marked dependence of charge capacity development on the sulphide growth sweep rate was calculated from Figs. 2 to 3. The nature of this dependence is influenced by the layer thickness, which is usually decreasing with higher sweep rates.

Fig. 8 shows that QA decreases with the increase of the sweep rate and finally is attaining a constant value and show that QC is rising with increasing sweep-rate however, QC stays always smaller than QA within the range of the experiments.
The variation of charge capacity development with increasing number of sulphide growth cycles are outlined in Figs. 4-7.

The anodic charge, QA, consumed in the potential range $1.8V \leq E \leq 0.8V$, and the cathodic charge, QC, recovered during the stripping of the deposited sulphur layer change not very much as a function of multicycling. QC is always smaller than QA, indicating incomplete reduction of the anodically formed layer. QA and QC increase almost linearly with sulfide concentration and pH (Figs. 8-11).

Fig. 10: Effect of pH on the anodic charge capacity for copper electrode in sodium sulfide solution from −1.8 to 0.8V, scan rate 50mv/s

Fig. 11: Effect of pH on the cathodic charge capacity for copper electrode in sodium sulfide solution from −1.8 to 0.8V, scan rate 50mv/s

REFERENCES