

ELECTROCHEMICAL OXIDATION OF SULPHIDE AND THIOSULPHATE IONS ON THE TITANIUM-MANGANESE DIOXIDE ANODE

Tamila PETROVSKAYA, Guido RAJALO, and Maya GLUSHKO

Eesti Teaduste Akadeemia Keemia Instituut (Institute of Chemistry, Estonian Academy of Sciences), Akadeemia tee 15, EE-0026 Tallinn, Eesti (Estonia)

Presented by J. Kann

Received January 20, 1994; accepted April 21, 1994

Abstract. The simultaneous soft electrochemical oxidation of sulphide and thiosulphate ions was carried out in a nondiaphragm electrolytic cell using an insoluble titanium-manganese dioxide anode. The transformation of sulphide ions into thiosulphate and further into sulphate depending on time and current density was investigated.

Key words: electrochemical oxidation, sulphide oxidation, titanium-manganese dioxide anode.

INTRODUCTION

Waste waters coming from various chemical, oil-shale processing and tannery works contain sulphide and thiosulphate ions. The toxic sulphide ion can be converted into less harmful compounds using electrochemical oxidation. For the sulphide oxidation platinum, ruthenium-titanium oxide a.o. anodes have been used. The titanium-manganese dioxide anode (TMDA) has been used for the electrolysis of weak hydrochloric acid and sodium chloride solutions [1] as well as for electrochemical destruction of organic compounds in waste water [2]. It also seems to be a promising anode for the sulphide oxidation, mostly on account of its lower cost.

In our previous work [3], we have demonstrated the possibility of selective electrochemical oxidation of sulphides in tannery waste water using insoluble anodes, including TMDA, the process being carried out in soft conditions (at low current density). Nevertheless, the detailed investigation of the kinetics of the simultaneous electrochemical oxidation of sulphur-containing ions seems to be necessary.

EXPERIMENTAL

The studies were carried out in a laboratory rectangular nondiaphragm electrolytic cell 155×110×18 mm. The cell had two cathodes, the anode was placed between them. The surface area of the anode was 300 cm², the liquid volume was 240 cm³. The scheme of the apparatus used was presented in our previous report [3]. The experiments were performed in the periodic mode of operation, the process time varying from 5 to 30 min. The current density ranged from 0.24 to 0.67 A/dm².

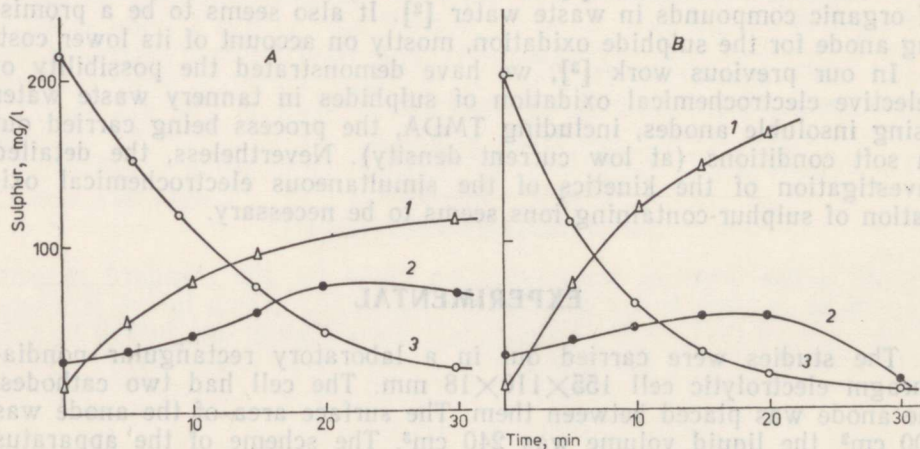
The average temperature was $18 \pm 1^\circ\text{C}$. As electrolyte, aqueous solutions of sodium sulphide, sodium thiosulphate and sodium sulphate, $\text{pH} = 13-14$, were used.

The samples for analysis were taken from the electrolyte at the beginning and at the end of the process. The sulphide ions were precipitated from the solution as CdS, dissolved in a hydrochloric acid solution and titrated iodometrically. In the filtrate both the thiosulphate and sulphite ions were titrated iodometrically separating the sulphite ions by formaldehyde [4]. The sulphite ions were practically non-existing in our electrolytic solutions. The sum of polysulphide and colloidal sulphur was determined from the difference between the iodide and bromide oxidation of sulphur containing ions [5]. The concentration of the sulphate ion was determined by means of an ion chromatograph (anion exchange column 4×150 mm with sorbent RM, $25-40 \mu\text{m}$ particle size, Institute of Chemistry of the Estonian Academy of Sciences), eluent — phthalic acid, $\text{pH} = 4.36$, detector — Knauer spectrophotometer, $\lambda = 260$ nm.

The TMDA was prepared by repeated thermal combustion of manganese nitrate on the titanium plate treated previously with hydrofluoric acid solution [6].

RESULTS

The figure shows the contents of sulphide, thiosulphate and sulphate sulphur in the electrolyte vs. time at the current densities of 0.24 and 0.67 A/dm^2 . In both cases, the concentration of the sulphide sulphur is continuously decreasing and that of the sulphate sulphur is continuously increasing in time. The concentration curve of thiosulphate as an intermediate product has a maximum which is higher for the lower current density. The oxidation rate increases remarkably with increasing current density. In case of sufficiently long electrolysis time and high current density, the sulphide sulphur will be mainly oxidized to sulphate as the end product. The conversion of sulphide to polysulphides and elementary sulphur is less than 5% at the current density of 0.67 A/dm^2 and it is less than 12% at 0.24 A/dm^2 .



Dependence of sulphate (1), thiosulphate (2), and sulphide (3) sulphur concentration on time. Current density 0.24 (A) and 0.67 A/dm^2 (B).

ACKNOWLEDGEMENT

The authors wish to thank E. Urbas from the Institute of Chemistry of the Estonian Academy of Sciences for her help in the analytical determination of sulphate.

REFERENCES

1. Калиновский Е. А., Шембель Е. М., Стендер В. В. Анодный процесс на титано-двуокисномарганцевом электроде при электролизе растворов соляной кислоты. — Ж. прикл. хим., 1972, **14**, 4, 810—815.
2. Краснобородько И. Г. Деструктивная очистка сточных вод от красителей. Химид, Ленинград, 1988.
3. Petrovskaya, T., Rajalo, G. Electrochemical oxidation of sulphides in tannery waste water. — Proc. Estonian Acad. Sci. Chem., 1992, **41**, 4, 194—199.
4. Лурье Ю. Ю. Аналитическая химия промышленных сточных вод. Химия, Москва, 1984, 207—210.
5. Szekeres, L. Eine Schnellmethode zur Bestimmung der Sulfid-, Polysulfid- und Thio-sulfationen nebeneinander. — Z. anal. Chem., 1960, **B178**, 2, 81—84.
6. Слесаренко О. А., Жарский И. М., Лецко В. В., Воробаев Л. Е. Изобретение SU 1546516 AI, 1990 (к авт. свид. № 289823, 1971).

SULFIID- JA TIOSULFAATIOONIDE ELEKTROKEEMILINE OKSÜDATSIOON TITAAN-MANGAANDIOKSIIDANOODIL

Tamila PETROVSKAJA, Guido RAJALO, Maia GLUSKO

On uuritud sulfiid- ja tiosulfaatioonide üheaegset oksüdatsiooni titaan-mangaandioksiidanoodil diafragmata elektrolüüseris madala voolutiheduse korral ning määratud alg-, lõpp- ja vaheproduktide sisaldus elektrolüüdis olenevalt ajast ja voolutihedusest. Peamiseks lõpp-produktiks osutus sulfaatioon.

ЭЛЕКТРОХИМИЧЕСКОЕ ОКИСЛЕНИЕ СУЛЬФИД- И ТИОСУЛЬФАТ-ИОНОВ НА ТИТАНДИОКСИДНОМАНГАНЦЕВОМ АНОДЕ

Тамила ПЕТРОВСКАЯ, Гуйдо РАЯЛО, Майя ГЛУШКО

Изучено совместное окисление сульфид- и тиосульфат-ионов на титандиоксидномарганцевом аноде в бездиафрагмовом электролизере при низких плотностях тока. Определено содержание исходных, промежуточных и конечных продуктов в зависимости от времени и плотности тока. Установлено, что главным продуктом окисления является сульфат-ион.