Electrochemical dissolution of tin in methanesulphonic acid solutions

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Abstract

High-rate electroplating of tin on a moving steel strip is generally carried out in cells with dimensionally stable anodes. To obtain a matt tin deposit a concentrated acidic tin methanesulphonate solution containing a small concentration of sulphuric acid is used. The concentrated tin methanesulphonate solution is prepared by dissolution of tin particles with oxygen in a special column. To describe this dissolution process electrode reactions (namely, reduction of oxygen, hydrogen peroxide and hydrogen ions on a tin electrode and oxidation of tin) were studied using electrochemical techniques. It was concluded that on tin, oxygen is almost entirely reduced to water and that H₂O₂ cannot corrode tin directly, but its decomposition products, for instance oxygen, can. The exchange current density and the charge transfer coefficient for the investigated electrode reactions are estimated. The dissolution of tin by oxygen is determined by the kinetic parameters of the oxygen reduction reaction and by the mass transfer of (i) dissolved oxygen to and (ii) Sn²⁺ ions from the tin electrode surface. Hydrogen evolution can be neglected during the dissolution of tin in the presence of oxygen. Moreover, it was found that the rate of tin corrosion increases with (i) increasing H⁺ concentration, (ii) oxygen concentration, (iii) convection intensity and (iv) temperature. It is likely that the tin surface is not covered with oxygen during corrosion in pure methanesulphonic acid solutions; but an oxide layer may be present on the tin surface during oxygen corrosion in pure sulphuric acid solutions. This oxide layer may hinder the oxygen corrosion of tin.

List of symbols

- \( A_e \) electrode surface area (m²)
- \( b \) Tafel slope based on \( E/\log i \) curve (V)
- \( b^0 \) modified Tafel slope (V) based on \( E/\ln i \) curve; \( b^0 = 0.435 \ b \)
- \( c \) concentration (mol m⁻³)
- \( cO_2 \) oxygen solubility in a solution at an oxygen pressure of 1 bar
- \( D \) diffusion coefficient (m² s⁻¹)
- \( d_e \) diameter of disc electrode (m)
- \( E \) electrode potential (V)
- \( E_r \) reversible electrode potential (V)
- \( E_{act} \) activation energy (J mol⁻¹)
- \( E_{cor} \) corrosion potential (V)
- \( F \) faradaic constant (96 487 C mol⁻¹)
- \( f \) rotation rate of electrode (s⁻¹)
- \( h \) slope of \( \log i - T^{-1} \) curve (K)
- \( I \) current (A)
- \( i \) current density (A m⁻²)
- \( i_0 \) exchange current density (A m⁻²)
- \( i_0^s \) standard exchange current density (A m⁻²)
- \( i_l \) limiting current density (A m⁻²)
- \( i_{gd} \) limiting diffusion current density (A m⁻²)

- \( i_{cor} \) corrosion current density (A m⁻²)
- \( K_a \) ionization constant of an acid (mol dm⁻³)
- \( k_t \) mass transfer coefficient (s⁻¹)
- \( n \) number of electrons involved in electrode reaction (mol⁻¹)
- \( R \) gas constant (8.3144 J mol⁻¹K⁻¹)
- \( R_{cor} \) corrosion resistance (Ω m²)
- \( R_\Omega \) ohmic resistance between working electrode and tip of Luggin capillary
- \( T \) temperature (K)
- \( t \) time (s)

Greek symbols

- \( \alpha \) charge transfer coefficient of reaction (-)
- \( \alpha_{cor} \) corrosion charge transfer coefficient (-)
- \( \delta_N \) thickness of Nernst layer (m)
- \( \eta \) overpotential (V)
- \( \eta \) dynamic viscosity (kg m⁻¹ s⁻¹)
- \( \eta_\Omega \) Ohmic overpotential (Ω)
- \( \kappa \) conductivity (Ω⁻¹ m⁻¹)
- \( \lambda \) equivalent conductivity (Ω⁻¹ m⁻¹ mol⁻¹ kg)
- \( \nu \) kinematic viscosity (m² s⁻¹)
- \( \rho \) density (kg m⁻³)
- \( \omega \) angle rotation rate (s⁻¹)
Subscripts/superscripts

a anodic reaction  
b bulk of solution  
c cathodic reaction  
e electrode surface  
H$_2$ hydrogen formation or H$_2$ ↔ 2H$^+$ redox couple  
H$_2$O$_2$ hydrogen peroxide reduction  
HSA sulfuric acid  
HMSA methanesulfonic acid  
n potential scan in the negative potential  
O$_2$ oxygen reduction or O$_2$ + 4H$^+$ ↔ 2H$_2$O redox couple  
ox oxidizing agent  
p potential scan in the positive direction  
r reversible  
red reducing agent  
ref reference condition  
Sn tin  
T temperature  
w water  
η fixed overpotential

1. Introduction

Matt tin deposits are generally formed from acidic Sn(II) baths. Modern electroplating lines use alkyl sulphonates. Methanesulphonic acid (HMSA) is gaining favour and is an attractive alternative to tetrafluoboric acid [1]. Most insoluble anodes are based on titanium coated with noble metals, in particular IrO$_2$/Ta$_2$O$_5$/Ti anodes operate satisfactorily in alkyl solutions containing Sn(II) alkysulphonate and sulphonic acids [1]. Sn(II) loss is replenished externally. In practice the tin(II) solution is pumped from the plating bath to a dissolution reactor filled with tin particles and fed with oxygen gas, and thereafter the more concentrated tin(II) solution is pumped back to the plating bath.

From the Pourbaix diagram for the tin–water system [2] it can be deduced that in an acidic solution containing dissolved oxygen the dissolution of tin can take place by two different corrosion processes, viz. the hydrogen corrosion and the oxygen corrosion. No results about both corrosion types for tin in HMSA have been previously reported. In contrast, extensive information on the corrosion and its subprocesses (oxidation of Sn to Sn(II), hydrogen evolution and the reduction of oxygen) in inorganic acids, like sulphuric acid, is available [3].

Since the earlier studies gave conflicting results, Quintin and Hagymas [4] have reinvestigated hydrogen evolution on tin in H$_2$SO$_4$ solutions. They found that the cathodic charge transfer coefficient is $\gamma_{H_2} = 0.5$ and the exchange current density is about $i_0 = 10^{-5} \text{ A m}^{-2}$. The corrosion of tin in acid solutions is quite fast if oxygen is present in the corroding medium [5]. Delahay [6] studied the reduction of oxygen on a Sn-plate electrode in a phosphate buffer of pH 6.9. He found that oxygen is practically completely reduced to water at potentials more negative than $−0.30$ V vs SHE.

The kinetics of the electron transfer in the Sn$^{2+}$/Sn system were studied extensively [5, 7]. Based on the critical evaluation of the results [5], it was concluded that for Sn oxidation in HCl and H$_2$SO$_4$ solutions at 293 K the apparent anodic charge transfer coefficient $\gamma_a$ and the standard exchange current density $i_0^*$ are about 2 and 0.8 A cm$^{-2}$, respectively. The activation polarisation for Sn deposition on polycrystalline and single crystal tin is so low that the concentration polarization is usually predominant in steady-state polarization measurements [7].

The aim of this research is to determine the electrochemical parameters of the various electrode reactions for corrosion of tin in HMSA solutions with and without the presence of oxygen.

2. Experimental details

The experiments were performed in a thermostatic electrochemical cell using a rotating disc electrode as working electrode, a 5 cm$^2$ platinum counter electrode placed at a distance of about 10 cm from the working electrode, and a saturated calomel reference electrode. The latter was connected to the cell via a Luggin capillary, which was filled with a salt bridge (Agar Agar/ H$_2$SO$_4$ or HMSA). The working electrode was a tin disc with a geometric surface area of 28.4 mm$^2$ and surrounded by a Perspex cylinder with a wall thickness of 1.0 mm. The tin disc electrode was polished mechanically with 0.3 µm alumina. After polishing alumina was removed by rinsing and placing the electrode in an ultrasonic water bath. After a series of experiments and, in some cases, after each experiment in a series, the tin electrode was repolished to improve the reproducibility of experimental results.

The hydrogen evolution was also investigated on a stationary upwards facing Sn electrode with a geometric surface area of 11.3 cm$^2$. This electrode was located at the bottom of one branch of a thermostatic H-shaped electrolysis cell. In this case the potential was scanned between $−0.6$ and $−1.0$ or $−1.2$ V and the stand-by potential was $−0.6$ V to prevent Sn corrosion.

The working electrode compartment of the cell was air-tight. After adding the ‘air-free’ solution into the cell, a flow of nitrogen gas saturated with water vapour was passed through the solution for about 30 min until just before the measurement started. During the measurement under ‘oxygen-free’ conditions the electrolyte was kept under a blanket of water-saturated N$_2$. To saturate