Electrochemistry Communications 61 (2015) 125–128

Contents lists available at ScienceDirect

Electrochemistry Communications

journal homepage: www.elsevier.com/locate/elecom

Short communication

Electrochemical behaviour of tin in alkaline electrolyte

D. Kwaśniewski, M. Grdeń [1]

Faculty of Chemistry, Biological and Chemical Research Centre, University of Warsaw, Żwirki i Wigury 101, 02-089 Warsaw, Poland

ARTICLE INFO

Article history:
Received 18 September 2015
Received in revised form 27 October 2015
Accepted 28 October 2015
Available online 5 November 2015

Keywords:
Tin
Anodic dissolution
RRDE
Impedance

ABSTRACT

The electrochemical behaviour of two types of tin electrodes, Sn rod and electrodeposited Sn is investigated in 0.1 M KOH_{aq} in order to evaluate processes related to anodic Sn dissolution. Potential regions of formation of soluble Sn(II) and Sn(IV) are identified by means of a rotating ring disk electrode. An anodic reactivation peak observed for cathodic potential scans for partially passivated electrodes is accompanied by formation of soluble Sn(II) species and a minimum in the imaginary part of the impedance. This confirms that the reactivation peak is due to active dissolution of metallic Sn exposed to the electrolyte during rupture of the oxidised layer.

1. Introduction

Tin is one of non-noble elements of special interest in electrochemistry with a special attention paid in studies on corrosion processes. Although many papers deal with studies on Sn electrochemical behaviour in alkaline solutions [1–18] several questions related to Sn behaviour in an alkaline environment require unequivocal explanation. This includes potential ranges of formation of Sn species with a certain oxidation state as well as to formation of an unusual anodic current peak during cathodic potential scan for incomplete passivated electrode [15,17,18]. This "reactivation" peak is observed also for Sn in neutral and acidic electrolytes [19–21] and is attributed to a reactivation process due to exposition of metallic electrode surface to the electrolyte accompanied by further passivation [19] or active dissolution [15,17,18,22]. The dissolution products, which formation was confirmed by means of rotating disk experiments [17,18], have not been identified, however. A similar feature is observed also for other electrodes, such as e.g. Pb [23–25], steel [26,27], Ti [28] or Ag [29] with proposed various explanations. Evaluation of formation of soluble species may help understanding the process.

This paper presents results of studies on electrochemical behaviour of tin in 0.1 M KOH. Two types of electrodes were used: polycrystalline Sn rod and Sn electrodeposits, the latter were used in rotating ring-disk electrode (RRDE) experiments. The electrochemical behaviour is discussed on the basis of RRDE and impedance measurements results.

2. Experimental

Two types of Sn electrodes were investigated: polycrystalline Sn rods (99.9%) and Sn deposits. The Sn rods were cleaned with a diamond polishing compound (Metadi, Buehler, 1 μm). The electrodeposits (Sn/RRDE) were prepared by a constant potential ($E = -1.2$ V vs. Ag|AgCl) electrodeposition on a Pt disk of RRDE from a bath containing 7.5 mM $SnSO_4$ in 0.5 M H_2SO_4. The electrodeposition was carried out at room temperature with a Sn rod serving as a counter electrode. A scanning electron microscope (LEO 435 VP) and EDX (Röntec EDR286) analysis showed that obtained deposits were thin and tightly covered the substrate, loose parts of the deposit, such as needle like features, were mechanically removed from the deposit.

All the electrolytes and solutions were prepared with water purified in a Millipore system (18.2 MΩ cm) and analytical grade reagents. The electrochemical examination of Sn rod and deposits was carried out in a three electrode system with an Au foil (99.9%, Mint of Poland) and Hg|HgO|0.1MKOH_{aq} (0.169 V vs. NHE) as a counter and as a reference electrode, respectively. AFMT28T (Pine Instruments) Pt–Pt ring-disk electrode controlled by an AFMSRX modulated speed rotator (Pine Instruments) and a CHI 700C (CHInstruments) bipotentiostat were used in RRDE experiments. During Sn deposition the RRDE was rotated (usually 1000 rpm) while the ring was kept at open circuit potential. This preserved a Sn-free surface of the ring. The disk currents are expressed in respect to the geometrical area. The impedance measurements were carried out with a single frequency of 2930 Hz and 5 mV amplitude for anodic and cathodic potential changes with 20 mV steps (CHInstruments CHI660D).

3. Results and discussion

3.1. Voltammetry and RRDE experiments

Fig. 1 presents a comparison of cyclic voltammetry curves of Sn rod and non-rotating Sn/RRDE. The general shape of the curves is the same for both electrodes; hence Sn/RRDE electrodeposits do not exhibit

---

E-mail address: mgrden@chem.uw.edu.pl (M. Grdeń).

[1] Fax: +48 22 8225996.

http://dx.doi.org/10.1016/j.elecom.2015.10.019
1388-2481/

significant departures from electrochemical behaviour typical for a solid tin. Anodic currents A contain overlapped peaks due to formation of soluble and insoluble Sn species. The species formed on the electrode surface include SnO and SnO_2, depending on the applied potential [1,2,12]. The electrode surface becomes fully passivated at potentials positive to ca. -0.1 V as indicated by the current plateau A2.

The value of the anodic vertex potential, E_a, has a pronounced effect on the shape of the currents recorded during negative potential scan. When E_a is more cathodic than the beginning of the plateau region the currents on the respective cathodic curve are still anodic but decrease when the potential becomes more negative. An unusual feature of these cathodic scans is formation of an anodic reactivation peak A3 at ca. -0.9 to -1.0 V. A similar type of anodic peaks is observed for Sn at different pH [19–21]. This peak is absent when E_a is located deep in the region of current plateau A2, i.e. for a certain extent of the electrode surface passivation. Finally, a cathodic peak, C1, attributed to reduction of Sn oxide layer and/or Sn soluble species is observed at potentials more cathodic than the A3 peak.

Fig. 2 presents disk and ring currents vs. disk potential profiles for rotating Sn/RRDE with the ring polarised at E_{ring} of -1.2 (Sn^{2+} and Sn^{4+} reduction) and 0 or -0.2 (Sn^{2+} oxidation) V for detection and identification of soluble tin species, respectively. The standard potential of the Sn^{2+}/Sn red-ox couple is more negative than the onset of hydrogen evolution, HER; therefore, Sn reduction requires polarisation of the ring at potentials where HER strongly contributes to the overall ring current. The changes in the ring current for $E_{ring} = -1.2$ V are then interpreted in terms of reduction and deposition of Sn ions. Tin deposition on the ring was confirmed by an analysis of cyclic voltammetry curves recorded for the ring after completing the experiments. When the disk is polarised in HER region the ring currents may be affected by pH changes due to hydrogen evolution on the disk.

An analysis of RRDE ring currents indicates that anodic currents A1 are accompanied by formation of soluble Sn species, in agreement with [1,2,8,9,15,16,18,19,30]. Formation of Sn(II) species, which are oxidised at $E_{ring} = 0$ V, takes place in a narrow range of disk potentials $-1.06 \le E_{disk} \le -0.84$ V (Fig. 2A). For $E_{disk} > -0.84$ V the Sn(II) species are not detected on the ring indicating that at such positive potentials the final product of Sn oxidation are Sn(IV) species. A narrow potential window of Sn^{2+} formation of ca. 0.22 V corresponds well to the difference of standard potentials of Sn^{2+}/Sn and Sn^{4+}/Sn^{2+} red-ox couples of ca. 0.29 V [31]. A similar potential window of Sn^{2+} formation was reported for weakly acidic electrolytes [19]. It should be noted that strong solubility of tin in 0.1 M KOH is observed not only for Sn deposits, experiments with a massive Sn rod reveal an influence of solution stirring on Sn oxidation currents (results not shown). A similar influence of the solution stirring on Sn oxidation currents was reported for pH up to 11.6 [20,32].

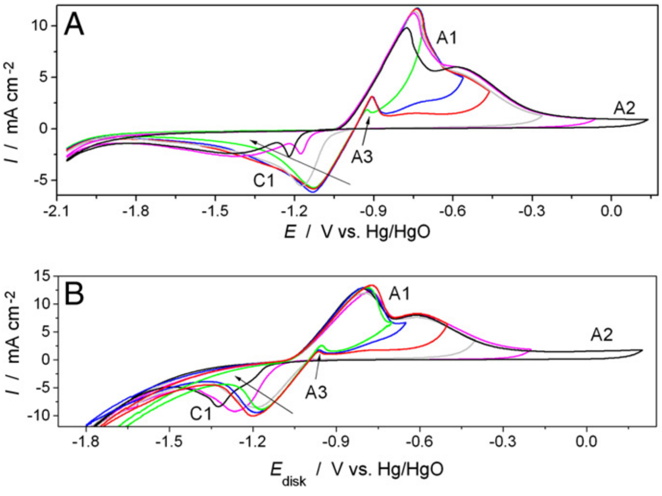

Fig. 1. Cyclic voltammetry curves in 0.1 M KOH (0.1 V s^{-1}) for: Sn rod with various anodic vertex potentials, E_a (1A); and for Sn/RRDE; 0 rpm (1B). Letters denote peaks described in the text, evolution of peak C1 with increasing E_a indicated by arrows.

Fig. 2B indicates that the Sn dissolution is significantly inhibited in passive region for $E_{disk} > -0.5$ V [8] as follows from very low reduction currents recorded on RRDE ring for $E_{ring} = -1.2$ V. During the cathodic potential scan an abrupt increase in Sn dissolution takes place at potentials of A3 peak, as follows from respective ring currents for $E_{ring} = -1.2$ V. Such a current response indicates that the Sn species reduced on the ring and formed at disk potentials of A3 peak originate from the electrode oxidation rather than oxidation of other species already present in the electrolyte. Formation of soluble species accompanying reactivation peak is in line with reports for Sn in NaOH and Na_3PO_4 solutions [15,17,18] but in contrast to citrate buffers for which formation of surface Sn(IV) compounds was assumed [19]. However, the soluble species formed in NaOH and Na_3PO_4 solutions were not identified. The ring currents recorded for $E_{ring} = 0$ V (inset in Fig. 2B) indicate that the soluble species contain Sn(II). Thus, A3 peak is due to Sn → $Sn(II)_{aq}$ reaction.

3.2. Impedance measurements

The impedance measurements allow collecting additional data related to the interface changes accompanying processes studied. Fig. 3 shows the real and imaginary part of the impedance for anodic and cathodic potential scans. Apart from the potential influence on the charge transfer processes the Z' and Z'' are affected also by changes in the surface coverage with the oxide layer and thickening of the latter. For $E_a = -0.562$ V the potential influence is more pronounced for Z'' than for Z'. For the frequency as high as 2930 Hz and sufficiently high impedance of parallel resistances (Z' for few Hz is several tens of Ω greater than Z' for 2930 Hz) the Z'' is less affected by parallel elements, such as faradaic resistance, and Z'' evolution mirrors changes in the interfacial capacitance. On the other hand, the Z' is determined by the ohmic resistance and varies by only ca. 9% in potential range of -2.06–0.038 V.

The anodic Z'' vs. E curve exhibits a minimum at -1.07 - -0.86 V, which roughly corresponds to the potential range of formation of Sn(II) species (Fig. 2A) and current peak A3 (Fig. 1). An initial decrease in Z'' at ca. -1.04 V can be related to strong solubility of Sn. The dissolution may lead to an increase in the surface roughness due to formation of pits or nuclei of surface Sn(II) compounds via a dissolution–redeposition mechanism [18]. The ascending section of the Z'' minimum (ca. -0.87 V) corresponds to the onset of formation of Sn(IV) (Fig. 2B). One may link this Z'' increase with a transition of Sn(II) surface compounds into Sn(IV) species. Respective Sn(II) and Sn(IV) compounds differ in respect to chemical composition and/or physical properties, such as crystallographic structure [14,33] and these differences may affect the interfacial capacitance of the electrode. At potentials higher than -0.86 V an inflection point and a further Z'' increase are observed, most likely related to increasing surface coverage with the oxide layer.

Similarly to the voltammetric curves (Fig. 1A), the shape of Z'' vs. E curves depends on E_a. For E_a low enough as to develop A3 peak the cathodic Z'' vs. E curve also exhibits a minimum at roughly the same potentials as A3 peak and Z'' minimum seen on the anodic Z'' vs. E curve. One may suggest that processes the same as those responsible for the formation of the Z'' minimum for anodic scan, but with reversed order, accompany formation of current peak A3 and the Z'' minimum for the cathodic scan. Hence, Sn(IV) compounds, probably SnO_2, may undergo a partial reduction to SnO which remains on the surface. This process may lead to formation of cracks in the oxide layer due to a difference in crystallographic structures of SnO and SnO_2 [33–35] leading to development of the minimum on Z'' vs. E curve (Fig. 3). The surface of metallic Sn exposed due to cracks formation may undergo anodic dissolution to Sn(II) species identified using the RRDE ring. The currents due to anodic dissolution (A3) may overlap currents due to Sn(IV) reduction leading to a net anodic current. A relation between A3 peak and formation of