Electrochimica Acta 53 (2008) 6513–6520

Contents lists available at ScienceDirect

Electrochimica Acta

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

The electroreduction kinetics of silver sulfite complexes

Gintaras Baltrūnas[a,*], Aušra Valiūnienė[a], Žana Margarian[a], Gintarė Viselgienė[a], George Popkirov[b,1]

[a] Department of Physical Chemistry, Vilnius University, Naugarduko 24, LT-2006 Vilnius, Lithuania
[b] Faculty of Engineering, University of Kiel, Kaiserstr. 2, D-24143 Kiel, Germany

ARTICLE INFO

Article history:
Received 7 February 2008
Received in revised form 10 April 2008
Accepted 14 April 2008
Available online 22 April 2008

Keywords:
Silver sulfite
Electrocrystallization
Charge transfer stage
Mechanism

ABSTRACT

The electroreduction kinetics of silver sulfite complexes was investigated by rotation disk electrode (RDE) voltammetry, chronopotentiometry (CP) and electrochemical impedance spectroscopy (EIS). The stability constants of the silver sulfite complexes, $p\beta_2 = 7.9$ and $p\beta_3 = 8.53$ were determined. For the series of isopotential solutions investigated, a reaction order of 0.67 was obtained, the diffusion coefficient of the silver complexes varies in the range of 3.36×10^{-6} to 5.54×10^{-6} cm^2 s^{-1} and the silver degree of complexation (2.31–2.67) were found. The analysis of the RDE, CP data and EIS spectra indicate the existence of a slow stage of the silver electrocrystallization in the region of the equilibrium potential and at stronger polarization of the electrode at initial time moments.

© 2008 Elsevier Ltd. All rights reserved.

1. Introduction

Silver electrodeposition from sulfite electrolytes is considered to be one of the most promising processes to replace the extremely toxic traditional cyanide-based silver plating solutions with the additional advantage, that sulfite electrolytes can be successfully applied for silver deposition for micro-electro-mechanical systems (MEMSs).

There are very few works dedicated to the chemistry and electrochemistry of silver sulfite complexes. Most publications related with this subject are concerned with the question of applicability. Silver sulfite complexes are stable in low alkaline solutions, thus the silver plating process based on electroreduction of these complexes is quite a prospective one [1,2]. The authors of [3] have used the rotating disk electrode (RDE) technique to measure the limiting current density of the electroreduction of sulfite complexes in solutions, prepared with 0.025 M free sulfite ions and 0.925 M $NaNO_3$. The complexes concentrations in the analyzed solutions were 10^{-4}; 2×10^{-4} and 5×10^{-4} M. Further, the limiting current density was found to depend linearly on the square root of the RDE rotation speed. The diffusion coefficient of $Ag(SO_3)_2{}^{3-}$ complexes calculated from the experimental data was reported to be 5.6×10^{-6} cm^2 s^{-1}, a value approximately three times less then the diffusion coefficient of free (hydrated) silver ions 1.55×10^{-5} cm^2 s^{-1} as determined in the same study.

X-ray photoelectron spectroscopy (XPS) investigation [4], has revealed that in the presence of sulfite ions, the silver dioxide adsorption on a silver monocrystalline (1 0 0) surface is accompanied by the build-up of a layer of chemisorbed sulfite. Surface-enhanced Raman scattering (SERS) spectra of electrochemically roughen silver surface [5], have shown that the adsorption behavior of the silver oxianion can be characterized by (i) weak electrostatic adsorption of sulfate and dithionate and (ii) by strong sulfite and tiosulfate chemisorption on the silver surface. The authors of [5] have, thus, assumed that a coating of Ag_2SO_3 builds up on silver surface.

In order to investigate the mechanism of electrochemical reaction, i.e. to identify the complex particle, which directly participates in the charge transfer stage we may apply the well known [6,7] equation which relates the exchange current density, j_0, to the free ligand concentration C_L:

$$\frac{\partial \ln j_0}{\partial \ln C_L} = R_L + \alpha \frac{zF}{RT} \frac{\partial E_{(0)}}{\partial \ln C_L} \qquad (1)$$

where R_L is the electrode reaction order depending on the ligand, α is the charge transfer coefficient, and $E_{(0)}$ is the equilibrium electrode potential. As follows from Eq. (1) in order to determine the reaction order, we need to know the value of the charge transfer coefficient. Fortunately, in the case of isopotential solutions Eq. (1) simplifies [7] to:

$$\left(\frac{\partial \ln j_0}{\partial \ln C_L}\right)_{E_{(0)}} = R_L \qquad (2)$$

Thus performing the measurements in a series of isopotential solutions we were able to determine the reaction order R_L

---

* Corresponding author. Tel.: +370 5 233 6419; fax: +370 5 233 0987.
E-mail address: gintaras.baltrunas@chf.vu.lt (G. Baltrūnas).

[1] On leave from Central Laboratory for Solar Energy and New Energy Sources, Bulgarian Academy of Sciences, Sofia, Bulgaria.

0013-4686/$ – see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.electacta.2008.04.038

by simple measurement of the exchange current density. Values of the current density measured upon equilibrium potential with the RDE were extrapolated to infinite rotation rate, this, it was possible 'to purify' the charge transfer overvoltage and to determine exchange current density by using the classic kinetic equation [8]:

$$j = j_0 \left[\exp\left(\frac{\alpha zF}{RT}\Delta E_{\mathrm{ct}}\right) - \exp\left(-\frac{\beta zF}{RT}\Delta E_{\mathrm{ct}}\right) \right] \tag{3}$$

where α and β are the charge transfer coefficients ($\alpha + \beta = 1$), and ΔE_{ct} is the charge transfer overvoltage. For higher values of the overvoltage, $|\Delta E_{\mathrm{ct}}| \gg RT/zF$, one of exponential terms of Eq. (3) becomes negligible and a linear dependence is obtained in the plot of $\ln(j)$ vs. ΔE_{ct}. An extrapolation towards $\Delta E_{\mathrm{ct}} = 0$, thus yields the value of $\ln j_0$. It should be possible to avoid the requirement $|\Delta E_{\mathrm{ct}}| \gg RT/zF$ by applying the coordinates of Allen–Hickling [9], when $\ln(Y)$ is plotted instead of $\ln(j)$, where

$$Y = \frac{j}{1 - \exp(\pm zF/RT\Delta E_{\mathrm{ct}})} \tag{4}$$

Here the sign '−' is for anodic currents, whereas '+' is for cathodic currents. Using these new coordinates one of the exponential terms in Eq. (3) will also be eliminated and for the case of a charge transfer controlled process rate the dependence $\ln(Y)$ vs. ΔE_{ct} must be linear even for low polarizations.

During the process of metal electrodeposition a new phase is formed, thus the total rate of the process should also depend on (possibly) slow crystallization phenomena. The deposition can be slowed down by: (i) slow formation of two- and/or three-dimensional crystallization centres and (ii) by slow surface diffusion of ad-atoms [7,10]. Obviously, these two stages are strongly related—the more crystallization centers are formed, the less is the distance, which ad-atoms have to diffuse on the surface. The concentration of crystallization centers very fast increases receding from equilibrium potential [10], i.e. the input of slow crystallization stage decreases. Therefore, the influence of the slow electrocrystallization can be easily avoided by performing measurements at a relatively high electrode polarization, i.e. at potentials rather far from the equilibrium potential. Conversely, in order to investigate the crystallization separately, the electrode potential should be chosen as close as possible to its equilibrium value. In the later case, the electrochemical impedance spectroscopy (EIS) represents the method of choice, because an impedance data can be obtained in a measurement with very low deviation from the equilibrium state. The formation of the crystallization centers, their growth, and the surface diffusion of ad-atoms will show up in the measured impedance spectra, however a good understanding of these processes and their effect on the obtained spectra is to be developed yet [11–13]. Probably the most successful model describing the surface diffusion impedance was proposed in [13]. The authors succeeded in modeling the surface diffusion impedance by parallel connected surface diffusion resistance and capacitance [13]. Unfortunately, these both parameters depend on the alternating current frequency as this is the case with the Warburg impedance. In our analysis we have chosen a simplified approach, taking into account that the non-dimensional alternating current frequency term of the mathematical expressions given in [13] becomes sufficiently large for higher frequencies. As a result, the surface diffusion impedance becomes qualitatively similar to the conventional Warburg impedance, with a constant B characterizing the surface diffusion of ad-atoms instead of the Warburg constant for the case of three-dimensional diffusion:

$$Z' = -Z'' = B\omega^{-1/2} \tag{5}$$

The specific objectives of this study was to investigate the kinetics of silver sulfite complexes electroreduction, i.e. to determine the limiting stages of the electrochemical reaction; to determine the dependences of the exchange current density on the free sulfite ions concentration in a series of isopotential solutions; to make clear the mechanism of electrochemical reaction (to identify the particle participating in the charge transfer reaction).

2. Experimental

The solutions prepared were based on distilled water and p.a. quality Na_2SO_3 and Ag_2SO_4. The electrolytes were prepared freshly before every new experimental series, in order to avoid the sulfite ion oxidation by air oxygen. All experiments were performed at 20 °C temperature.

The electroreduction of silver sulfite complexes was investigated using a rotating disk electrode of 0.2 cm^2 surface area made of a silver rod embedded in Teflon to isolate its side surface. An Ag disk of 25-mm diameter was fitted in parallel to the working area of the working electrode and served as counter electrode.

The silver electrode potential was measured potentiometrically using a saturated Ag/AgCl, KCl electrode as the reference electrode ($E_{\mathrm{H}} = 0.2$ V). In this work, all potentials are referred to the scale of the standard hydrogen electrode: $E_{(0)} = E_{\mathrm{Ag/AgCl}} + 0.2$ V.

Chronopotentiometry and EIS measurements were performed using an ordinary three-electrode cell. The working electrode was a platinum wire of 0.5 mm in diameter and 1.08 cm in length, which was coated (10 μm) with silver galvanostatically (3 $\mathrm{mA\,cm^{-2}}$) in a sulfite-based electrolyte (2 M Na_2SO_3 and 0.3 M $AgNO_3$) before each measurement. The surface area of the working electrode was 0.17 cm^2. The counter electrode was made of an Ag spiral of 40 cm^2. The reference electrode was a saturated Ag/AgCl, KCl electrode, placed as close as possible to the working electrode by means of a Lugin capillary.

The EIS measurements were performed galvanostatically at controlled zero current using a fast Fourier transform (FFT) impedance spectrometer as described in [14,15]. Chronopotentiometry measurements were performed using μAUTOLAB (Type III) measurement system.

3. Results and discussion

3.1. Stability of complexes

It was determined experimentally that anodic and cathodic yields of the electroreduction of silver sulfite complexes are practically equal to 100%. This shows that electrochemical reaction $Ag(SO_3)_x^{1-2x} + e \rightleftarrows Ag^0 + xSO_3^{2-}$ could be treated as equilibrium.

Since literary data concerning stability of silver sulfite complexes are rather contradictionary [16,17], we attempted to determine the dissociation constants of complexes experimentally. We have measured the silver electrode potential as a function of Na_2SO_3 concentration for different concentrations of Ag(I) in the solution. At higher concentration of the sulfite (>0.3 M), the slopes ($\partial E_{(0)}/\partial \log[SO_3{}^{2-}]$) of all curves become −150 to −160 mV. Such values can be related to the dominating role of the complex $Ag(SO_3)_3{}^{5-}$ in the solutions. For lower concentrations of the sulfite ions, the potential dependence on the sulfite concentration becomes more complicated. This may be explained either by the possible coexistence of two kinds of complexes $Ag(SO_3)_2{}^{3-}$ and $Ag(SO_3)_3{}^{5-}$ or by the suggestion that part of the sulfite ions are bounded into complexes, i.e. $[SO_3{}^{2-}] \neq [Na_2SO_3]$. The less the total concentration of sulfite is, the more these both factors influence the value of the equilibrium potential. In order to describe

Download English Version:

https://daneshyari.com/en/article/195288

Download Persian Version:

https://daneshyari.com/article/195288

Daneshyari.com