

Electrochemical Behaviour of Zinc on Copper and on Vitreous Carbon Electrodes. The Influence of Gluconate

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Abstract

The zinc electrochemical behaviour from sulphate and sulphate-gluconate baths was studied both on a vitreous carbon and a copper electrode. The voltammetric response depends on the complexing agent concentration, the electrode material, the pH and the cathodic potential limit. The reduction of zinc ions proceeds with hydrogen evolution, and at less negative potentials on the copper electrode than on the vitreous carbon electrode, specially in absence of gluconate. Gluconate decreases the efficiency of the process. On the other hand, gluconate favours zinc electrodeposition on vitreous carbon but retards it on copper.

Keywords: zinc, vitreous carbon, copper electrode, gluconate, sulphate baths.

Introduction

Zinc is widely used in electrometallurgy. Zinc electrodeposition has usually been studied using a vitreous carbon electrode in highly acidic baths of both chloride and sulphate. Other electrodes as zinc or platinum have also been used. Few studies have reported the influence of complexing agents and of slightly acidic pH on the electrodeposition process of zinc.

The electrodeposition of zinc from sulphate baths was studied by Lamping and Keefe [1], and by Despic and Pavlovic [2] on platinum, gold and graphite

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electrodes from buffered solutions at $\text{pH} = 3.55$, and by Beshore et al. [3] on a vitreous carbon electrode in a high acidic bath. Cachet and Wiart [4] studied zinc electrodeposition on a zinc electrode from highly acidic sulphate electrolytes, Muñoz et al. [5] studied zinc electrodeposition on a vitreous carbon electrode from chloride or sulphate baths at pH close to 3, and Teixeira et al. [6] on platinum. Other reported media for zinc electrodeposition are solutions of chloride [7, 8], zincate [9], an organic bath [10], or commercial accumulator solutions [11].

Underpotential deposition of zinc on Pt(111) in alkaline solution was studied by Igarashi et al. [12]. Formation of zinc films using electro-plating versus electroless-plating was described by Maeda and Nishio [13].

Gluconate is a complexing agent that has been used in electrodeposition studies of other metals such as Sn [14]. Zinc ions are also complexed by gluconate and this complexing action can influence the zinc electrodeposition. The gluconate ions compete with the sulphate ions for complexing the zinc ions.

In this study the electrochemical behaviour of zinc in the presence of gluconate from several slightly acidic sulphate baths is presented, in order to determine the influence of this complexing agent on the electrochemical behaviour of zinc. The influence of the substrate is tested using a vitreous carbon and a copper electrode, and no references have been found in the literature about the use of a copper electrode. The zinc electrochemical behaviour is also compared with that of zinc from other baths, as well as with that of other metals from sulphate/gluconate baths.

Experimental

The electrochemical measurements were performed in a three-electrode cell using a rod of vitreous carbon or copper as the working electrode (area = 0.031 cm^2), a platinum wire as the counter electrode and Ag/AgCl/NaCl (1 M) as the reference electrode, inserted in a Luggin capillary. All potentials reported in the text are referred to this electrode. A microcomputer-controlled AUTOLAB PSTAT20 was used as potentiostat. Different sets of cyclic voltammetric

experiments were performed running only one cycle in each experiment and scanning at first towards negative potentials, until a cathodic limit potential E_1 . Anodic stripping voltammetric experiments were performed immediately after potentiostatic deposition without removing the electrode from the cell. The anodic stripping voltammetry was always carried out starting at an initial potential at which deposition did not occur and scanning to an anodic potential limit where the zinc is totally dissolved. The working temperature was of 25 °C. The chemicals used were $ZnSO_4 \cdot 7H_2O$, sodium gluconate ($NaC_6H_{11}O_7$) and Na_2SO_4 (analytical grade). All solutions were freshly prepared with water, first distilled and then treated with a Millipore Milli Q system. The sulphate bath contained 0.01 M $ZnSO_4$ and 1 M Na_2SO_4 as supporting electrolyte (pH of the bath 5.1). The gluconate/sulphate bath contained 0.01 M $ZnSO_4$, 1 M Na_2SO_4 as supporting electrolyte and 0.2 M sodium gluconate as the complexing agent (pH of the bath 5.7). The working pH in the experiments was that of the bath or was adjusted to 4 using 1 M H_2SO_4 . Before and during each experiment the solution was deaerated with argon. The working electrode was polished mechanically before each run with 3.75 and 1.87 μm alumina powder, cleaned ultrasonically and followed by a short electrochemical conditioning applying a potential of -200 mV during 20 s.

Results and Discussion

The voltammetric response depends on the presence or not of the complexing agent, on the electrode material and on the pH. The anodic scan also depends on the cathodic potential limit.

Blank solutions

Previously to the zinc studies, voltammetric experiments were done in blank solutions of sulphate, either in the absence or in the presence of gluconate. Fig. 1 shows the results of these experiments on the copper electrode. It is seen that hydrogen evolution is favoured at lower pH, as is usual, and in the presence of

gluconate. The hydrogen formation is also more favoured on the copper than on the vitreous carbon electrode.

Absence of gluconate

Fig. 2 shows the voltammetric responses, at a scan rate of 50 mV s^{-1} , of a sulphate bath containing zinc ions at pH 4, using both a copper or a vitreous carbon electrode. It is seen that zinc deposition shifts to more positive potentials for the copper electrode, as well as hydrogen formation. Then, while the electrodeposition process occurs with a significant overpotential on the vitreous carbon electrode, it occurs with no or a small overpotential on copper. The cathodic scan also shows, for the copper electrode, a significant capacitive current at potentials where, neither deposition nor hydrogen formation, occurs (see Figs. 1 and 2).

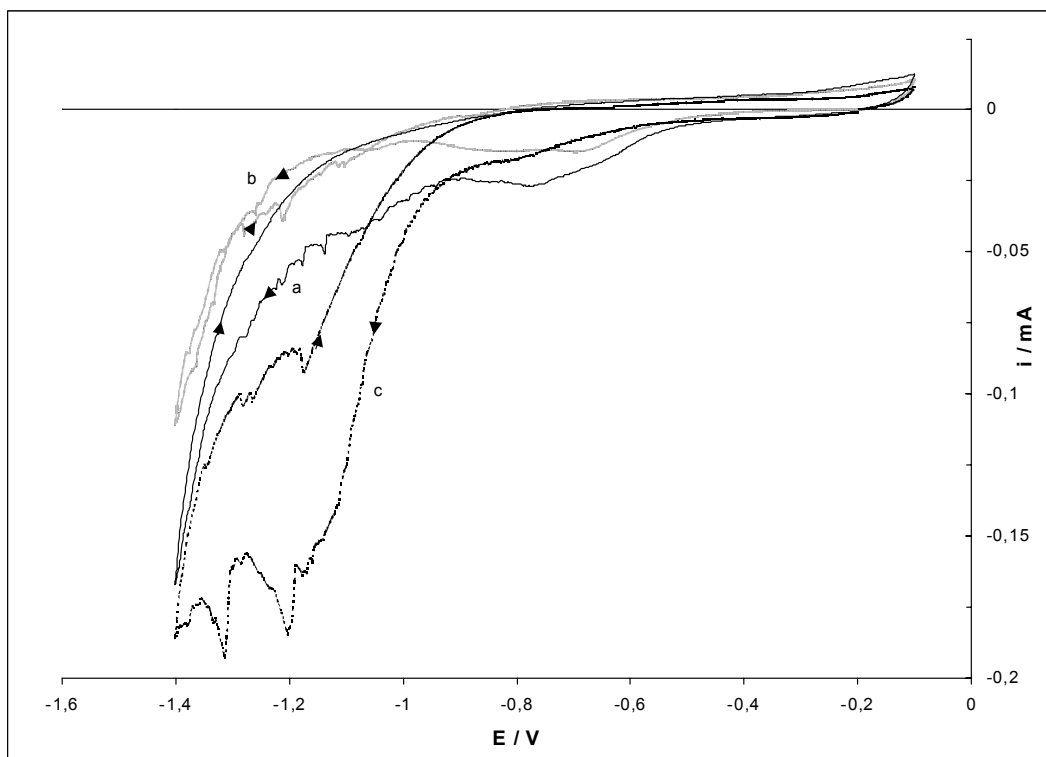


Figure 1. Cyclic voltammograms on a copper electrode, at 50 mV s^{-1} and $E_1 = -1\ 400 \text{ mV}$, for blank solutions with $1 \text{ M Na}_2\text{SO}_4$, and: a) pH = 4, b) pH = 5.1, c) pH = 4 and 0.2 M in sodium gluconate. Arrows indicate scan direction.

The cathodic scan at 50 mV s^{-1} shows a reduction peak at around $-1\,460 \text{ mV}$ for the vitreous carbon electrode, but a principal reduction peak (IIr) at around $-1\,300 \text{ mV}$, preceded by a smaller one (Ir), for the copper electrode. In the later, the zinc reduction is followed by massive hydrogen formation.

At lower scan rates (Fig. 3, curve d), the peak labelled as Ir appears well defined. Since hydrogen evolution is important on copper, noise peaks due to gas bubbles also appear in the voltammetric curve (see peak H in curve d of Fig. 3) and superimpose with zinc reduction peaks.

The anodic scan at 50 mV s^{-1} shows a principal peak at around $-1\,050 \text{ mV}$ for the vitreous carbon, and around $-1\,035 \text{ mV}$ for the copper electrode (peak Io). This principal peak is followed by other peaks which shape depends on the cathodic limit reached, E_1 , and on the electrode material. On the vitreous carbon electrode several secondary oxidation peaks at more positive potentials are present, when $E_1 = -1\,400 \text{ mV}$ (see curve a in Fig. 3), which shift towards the principal oxidation peak or practically disappear when $E_1 = -1\,600 \text{ mV}$ (Fig. 2, curve a). On the copper electrode a secondary oxidation peak (IIo), as a prolongation of the principal peak, is always present, which becomes more important for more negative values of E_1 .

Electrodeposition of zinc takes place together with evolution of hydrogen. From the calculation of the Q_+/Q_- ratio (voltammetric efficiency), where Q_+ and Q_- are, respectively, the oxidation and the reduction charges involved in the voltammetric scans, it is observed that hydrogen evolves in an important way, and is more important on the copper electrode (see Table 1). At low overpotentials the hydrogen formation is even more important than the zinc reduction.

It has been reported in the bibliography [7] that zinc electrodeposition proceeds via metastable phases which can present different hydrogen content. The presence of secondary oxidation peaks in the voltammetric response can be attributed to this fact. The position and the importance of these peaks depend on several factors, basically the cathodic limit reached, but also the presence of gluconate (see next section) and the electrode material. Table 1 shows that

hydrogen evolution is significant even at low cathodic limits, but at these potentials, hydrogen can remain adsorbed [11] on the electrode surface and trapped in the zinc deposit, forming metastable hydrogenated phases. At higher cathodic limits, hydrogen formation is so important that evolves far from the electrode and the metastable phases practically disappear. When the voltammetric scan rate is reduced to 10 mV s^{-1} (Fig. 3, curves b and d), the zinc reduction peak shifts to positive potentials, as is usual, while the principal oxidation peak practically does not change. On the other hand, in the anodic scan at 10 mV s^{-1} , secondary oxidation peaks shift towards the principal oxidation peak for the vitreous carbon electrode, but no visible changes are seen in their position for the copper electrode. This behaviour may be due to the evolution of the metastable phases, specially on the vitreous carbon electrode, because the voltammetric experiment then lasts more time. A similar behaviour is observed when anodic stripping experiments are performed immediately after potentiostatic electrodeposition with stirring. Stirring favours hydrogen release far from the electrode, hindering the formation of the hydrogenated phases, and the secondary oxidation peaks shift towards the principal peak or disappear.

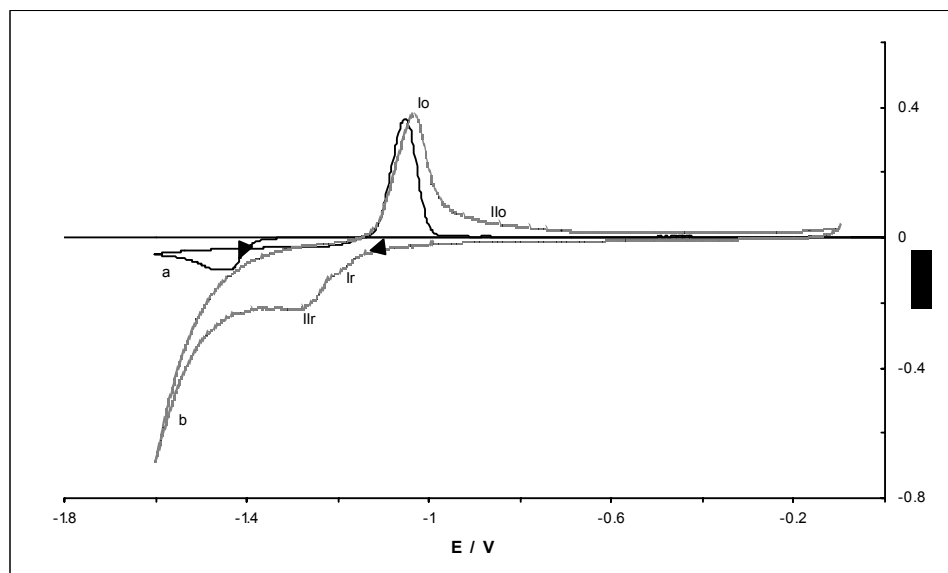


Figure 2. Cyclic voltammograms at 50 mV s^{-1} for solution 0.01 M ZnSO_4 , $1 \text{ M Na}_2\text{SO}_4$ at $\text{pH} = 4$ and $E_i = -1.600 \text{ mV}$: a) vitreous carbon, b) copper. Arrows indicate scan direction.

Table 1. Q_+/Q_- ratios from the voltammetric responses on vitreous carbon and on copper electrodes, at different cathodic limit potentials, E_l , and for different bath conditions.

	$[Zn^{2+}] = 0.01\text{ M}$ Vitreous carbon				$[Zn^{2+}] = 0.01\text{ M}$ Copper	
	[Glu]=0		[Glu]=0.2		[Glu]=0	[Glu]=0.2
	pH=4	pH=5.1	pH=4	pH=5.7	pH=4	pH=4
$-E_l$	Q_+/Q_-	Q_+/Q_-	Q_+/Q_-	Q_+/Q_-	Q_+/Q_-	Q_+/Q_-
1200					0.22	
1300	0.49	0.91			0.54	0.37
1400	0.81	0.93	0.74	0.85	0.60	0.35
1600	0.86	0.89	0.44	0.87	0.30	0.27
1800	0.73	0.75	0.34	0.78		

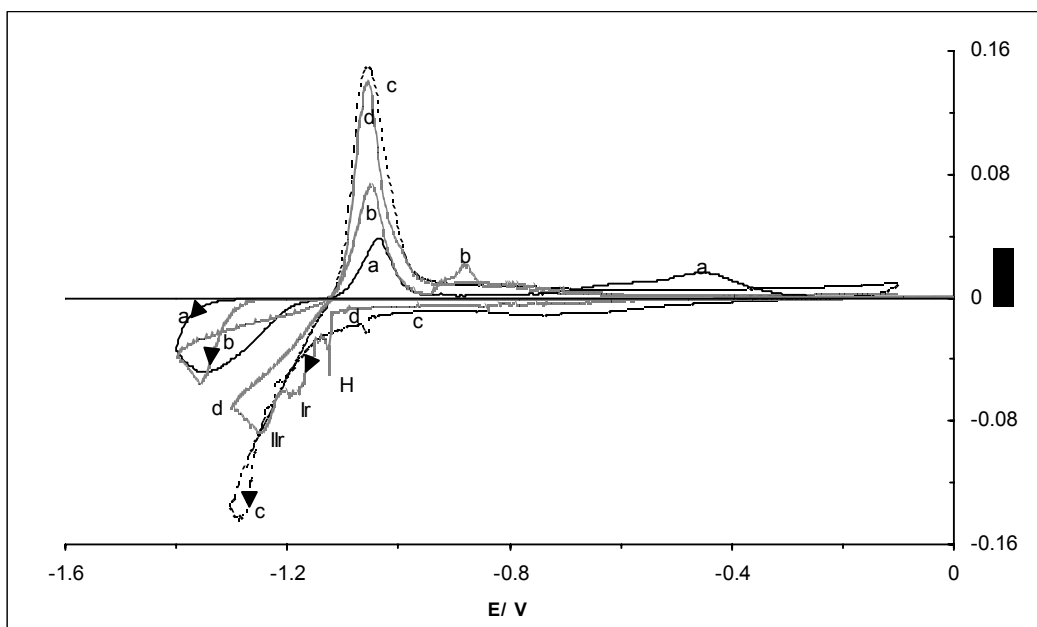


Figure 3. Cyclic voltammograms for solution 0.01 M $ZnSO_4$, 1 M Na_2SO_4 at pH = 4 and: a) vitreous carbon, $E_l = -1\ 400\text{ mV}$, $v = 50\text{ mV s}^{-1}$ b) vitreous carbon, $E_l = -1\ 400\text{ mV}$, $v = 10\text{ mV s}^{-1}$, c) copper, $E_l = -1\ 300\text{ mV}$, $v = 50\text{ mV s}^{-1}$, d) copper, $E_l = -1\ 300\text{ mV}$, $v = 10\text{ mV s}^{-1}$. Arrows indicate scan direction.

Presence of gluconate

Figs. 4 and 5 present the influence of gluconate on the zinc voltammetric response. Fig. 4, when compared with Fig. 2, shows that on vitreous carbon

(curve a), gluconate shifts slightly the zinc reduction to positive potentials and that the reduction peak appears as a not well defined double peak, instead of a single peak. This behaviour is due to the complexing action of gluconate anions that compete with the complexing action of sulphate anions. Since the formation constant of the zinc ion/gluconate complex ($\log K_1 = 1.70$ [15]) is lower than that of the zinc ion/sulphate complex ($\log K_1 = 2.30$ [15] or 2.08 [16]), the first reduction peak, Ir, can be assigned to the gluconate-Zn species, and the second peak, Iir, to the sulphate-Zn species. In the anodic scan, the principal oxidation peak also appears as a double peak. As the first oxidation peak, Io, is situated at a potential value similar to that in absence of gluconate, this peak can be assigned to oxidation via sulphate anion complexation, and the second peak, Ilo, to the oxidation via gluconate anion complexation. In the presence of gluconate, the secondary oxidation peaks at more positive potentials tend to disappear. When the voltammetric scan rate is reduced to 10 mV s^{-1} (Fig. 4, curve c), the zinc reduction peak observed on the vitreous carbon electrode at 50 mV s^{-1} (Fig. 4, curve a), shifts to positive potentials but doesn't changing the shape. But on the oxidation scan, the peak Io, assigned to oxidation via sulphate anion complexation, is enhanced. This behaviour may be due to a kinetic factor, that is, to a higher rate of complexation by sulphate anions of the zinc ions formed in the oxidation. At lower scan rates, sulphate is not so depleted in the interface close to the electrode and can complex most of the zinc ions formed in the oxidation process.

Results in Table 1 also show that the Q_+/Q_- ratio decreases when gluconate is present in the bath. It seems that gluconate favours hydrogen evolution and then, as can be seen by voltammetry, the secondary peaks decrease and consequently hydrogenated metastable phases are formed with more difficulty.

On the other hand, Fig. 4 shows that on copper, the reduction peak disappears as a consequence of an inhibitory effect of gluconate. Though zinc electrodeposition superimpose at an important hydrogen reduction, it is seen that on reversing the scan the voltammetric response presents a loop, with a higher reduction current, indicating clearly that zinc deposition occurs. In the anodic scan a broader double

peak is formed, and at high E_1 an oxidation peak is formed at around -300 mV. This peak can be assigned to hydrogen since its formation is then noticeable (see Table 1) and its potential corresponds to the zone of hydrogen oxidation. Comparing the voltammograms of Fig. 5 (copper electrode, gluconate bath) with that of the corresponding blank solution (Fig. 1, curve c), it is seen that in presence of zinc ions the hydrogen formation is retarded, but calculation of the cathodic and anodic charges indicates that the efficiencies are low (Table 1), due to the important hydrogen formation. Also in the presence of gluconate, hydrogen evolves easier on copper than on vitreous carbon. At low cathodic limits hydrogen formation on copper is more important than zinc deposition, and the voltammetric curve doesn't show the characteristic loop of a deposition process (curve c in Fig. 5). Also, and due to this fact, in the oxidation scan a small hydrogen peak at around -300 mV is formed.

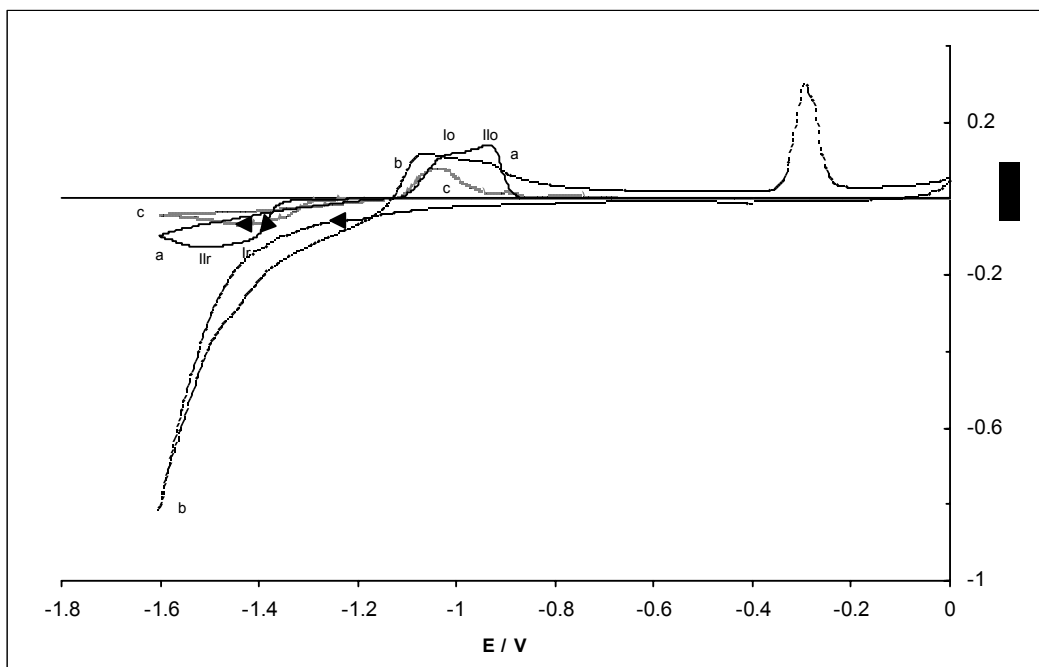


Figure 4. Cyclic voltammograms for solutions 0.01 M $ZnSO_4$, 1 M Na_2SO_4 , $pH = 4$ and 0.2 M sodium gluconate: a) vitreous carbon, at 50 $mV s^{-1}$, b) copper, at 50 $mV s^{-1}$, c) vitreous carbon, at 10 $mV s^{-1}$. $E_1 = -1.600$ V. Arrows indicate scan direction.

It seems that in gluconate baths the zinc reduction on copper proceeds slower than in non gluconate baths, and that the current values are also lower. This

behaviour is opposite to that observed on vitreous carbon, and also different to that observed for tin on vitreous carbon. The differences between the zinc behaviour and that of tin [14] are due to the very different values of the reduction potential, and to the different values of gluconate and sulphate complexation constants.

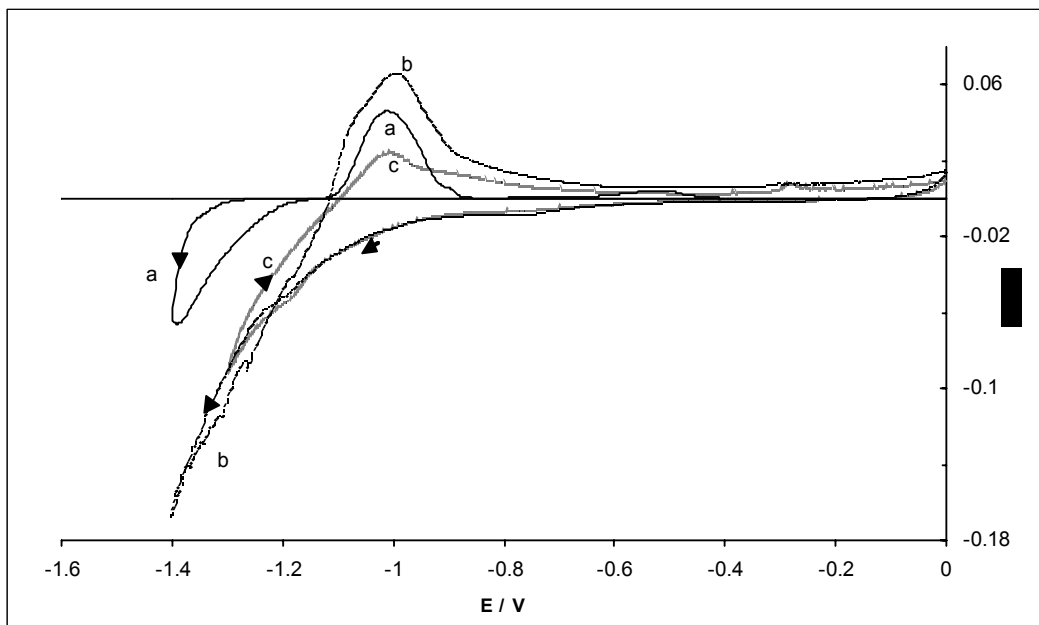


Figure 5. Cyclic voltammograms at 50 mV s^{-1} for solution 0.01 M ZnSO_4 , $1 \text{ M Na}_2\text{SO}_4$, $\text{pH} = 4$ and 0.2 M sodium gluconate: a) vitreous carbon, $E_1 = -1.400 \text{ mV}$, b) copper, $E_1 = -1.400 \text{ mV}$, c) copper, $E_1 = -1.300 \text{ mV}$. Arrows indicate scan direction.

Conclusions

The electrochemical behaviour of zinc from sulphate-gluconate baths is depending on the gluconate, the potential and the electrode material. Hydrogen evolution also proceeds with zinc electrodeposition, being the efficiency of the process higher on vitreous carbon than on copper. The efficiency decreases at more negative potentials and in the presence of gluconate, but it is also low at low overpotentials, where hydrogen formation is easier than zinc reduction.

The zinc reduction takes place at less negative potentials on the copper electrode than on the vitreous carbon electrode, specially in absence of gluconate. On the other hand, gluconate favours zinc electrodeposition on vitreous carbon but retards it on copper.

Acknowledgements

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