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ARTICLE

Polysulfide Poisoning of Ag Electrocatalyst during L-Ascorbate Ion Electro-oxidation in Alkaline Solution

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Abstract: L-ascorbate anion electro-oxidation on a silver electrode in hydroxide solution in the absence and presence of sodium polysulfide of concentrations from 1×10^{-5} to 4.5×10^{-4} mol/L was studied using cyclic voltammetry and electrochemical impedance spectroscopy. Both hydroxide and polysulfide ions inhibited L-ascorbate ion oxidation, with the poisoning effect of polysulfide ion being more pronounced in the potential range of –0.3 to –0.2 V/SCE. The time constants for L-ascorbate ion oxidation in the absence and presence of polysulfide were, 10^{-3} to 1×10^{-2} s and 1×10^{-4} to 1×10^{-2} s, respectively depending on the potential used for the impedance analysis. Based on the cyclic voltammetry findings, a mechanism for L-ascorbate oxidation in the presence of polysulfide ions was proposed. Impedance calculations based on the kinetic analysis can account for the occurrence of a negative impedance in a potential region around –0.2 V/SCE in the Nyquist polts.

Key words: L-ascorbic acid; polysulfide; electrode poisoning; silver; electro-oxidation

L-Ascorbic acid (L-AA) is a vital substance in the metabolism of living organisms and the determination of its concentration in aqueous solution is very important. Traditional procedures for this determination use enzymatic methods, titration with oxidizing agents, or HPLC analysis [1]. Recently, sensors have been developed for the electrochemical detection of L-AA [2,3]. L-AA has also been proposed as a potential environmentally friendly fuel for fuel cells [4]. The electro-catalytic activity of a number of transition metals [4,5] for L-AA electro-oxidation has been investigated, and silver was suggested as the best candidate in alkaline solutions [6]. In a cyclic voltammetry (CV) study, the oxidation of 0.25 mol/L L-AA in alkaline solution on polycrystalline Ag started at –0.5 V/SCE [6], which is 0.5 V more negative than in the reaction carried out in acidic media on electrodes of glassy carbon, Au, Pt-group metals or their alloys [4,5,7–9]

The electrochemistry of the sulfide anion on Ag has been studied in alkaline solution [10–17] but no definitive conclusion on the nature of the electrode processes was reached. The only electrochemical study on the polysulfide anion on Ag was carried out in a Ag/HS_4^- system in the potential range of –1.5 to 0.6 V/SSCE (sodium saturated calomel electrode) [10]. This voltammetric study reported that the cathodic decomposition of HS_4^- to HS^-, which occurred in the vicinity of –1.3 V/SSCE, was the source of sulfide for silver sulfide formation that occurred at –0.6 V/SSCE. HS_4^- decomposition to the sulfide anion was confirmed by holding the potential at –1.3 V/SSCE for 10 s before scanning anodically, which gave a dramatic increase in the peak height at –0.6 V/SSCE [10] that indicated that the Ag/HS_4^- system was transformed to a Ag/HS^- system.

The Ag_2S film formation reaction was [14]

$$2Ag + HS^- + OH^- \leftrightarrow Ag_2S + H_2O + 2e \quad (1)$$

This reaction occurred at the reversible potential, E_r (V/NHE) [14] of

$$E_r = -0.684 - 0.0296\log\left(HS^-\right) - 0.0296\log\left(OH^-\right) \quad (2)$$

In this study, HS^- was produced by polysulfide decomposition in a reaction similar to that of tetra-sulfide decomposition in vicinity of –1.3 V/SCE [10]:

$$HS_4^- + 6e + 3H_2O \leftrightarrow 4HS^- + 3OH^- \quad (3)$$

In this study, the OH^- and polysulfide concentrations were about 1×10^{-2} and 1×10^{-5} mol/L, respectively, and a very small fraction of polysulfide was transformed to HS^- during one anodic potential sweep in a cyclic voltammetry experi-

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ment. Assuming a HS^- concentration of 1×10^{-6} mol/L, E_r would be –0.69 V/SCE. This potential is much more positive than the potential of the redox peaks that we witnessed at –0.8 and –1 V/SCE. So, the redox peaks were not due to silver sulfide formation but instead were due to the sulfide/sulfur redox pair, which has been reported (–0.8 and –1.1 V/SCE) for the Au/sulfide system [18]. Also, contrary to the case of Ag_2S film formation [11], no dark (black) layer was witnessed during anodic polarization even after many hours of cycling.

The purpose of the present work was to investigate the kinetics of L-ascorbate ion oxidation on Ag in more detail and to study the poisoning effect of polysulfide ions on this reaction. Based on literature results [10], the potential range used in this study guarantees the presence of polysulfide and not sulfide anions in the solution.

1 Experimental

L-AA, $NaNO_3$, and NaOH used were analytical grade from Merck. The sodium polysulfide was a general purpose reagent. The water used was first de-ionized. $NaNO_3$ was added as the supporting electrolyte to the solution. Experiments were conducted in conventional three electrode cells with a Ag ribbon (99.99% pure) with a geometric surface of 0.75 cm^{-2} as the working electrode. Its potential was measured against a commercial SCE (saturated calomel electrode). A Pt plate was the counter electrode. Electrochemical measurements, cyclic voltammetry, and impedance spectroscopy were performed using a Voltalab Model PGZ100 potentiostat/galvanostat. Impedance spectra were recorded in the frequency range of 25 kHz to 100 mHz and were fitted to the electric circuits by the Zview software.

2 Results and discussion

2.1 L-ascorbate ion/NaOH solution

The electrochemical oxidation of L-ascorbate ion at various excess (compared to stoichiometry) concentrations of NaOH in the range of 0.01 to 0.6 mol/L and in 0.5 mol/L $NaNO_3$ supporting electrolyte was studied. The cyclic voltammograms (CV's) are presented in Fig. 1.

The onset of reaction was shifted cathodically and the peak current increased asymptotically as the concentration of the excess alkali was increased. The onset potential shift was around –0.06 V and the current increase was less than 2-fold when the alkali concentration was increased 60-fold. From the asymptotic dependence of the anodic peak current on hydroxide concentration, it is probable that OH^- adsorption occurred and had a detrimental effect on the rate of oxidation at potentials more positive than –0.2 V/SCE. The broad oxidation peak in the reverse scan at –0.1 V/SCE indicated that the hydroxide species adsorbed in the forward cycle desorbed in this potential region.

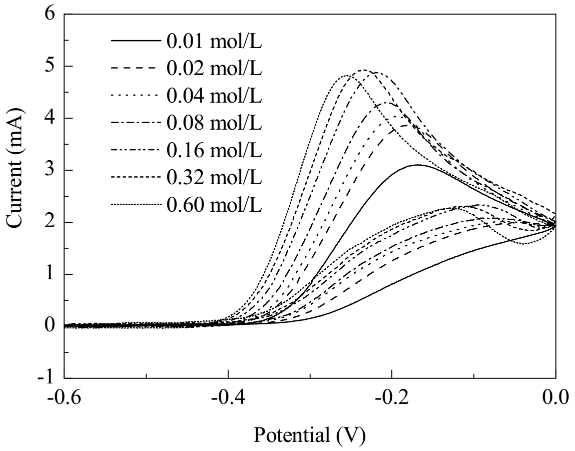

Fig. 1. Cyclic voltammograms recorded in solutions containing 0.5 mol/L $NaNO_3$ + 0.02 mol/L Na_2A + NaOH with different concentrations v = 0.05 V/s.

Figure 2 shows the dependence of the CV curves on the concentration of the L-ascorbate ion. An increase of peak current and its dramatic shift to higher potentials were observed.

From the hydroxide and L-ascorbate concentration dependences of the CV curves, the mechanism below can be put forward. This mechanism is in agreement with the L-ascorbic acid oxidation mechanism at pH of 8 and less [19–21].

$$OH^-_{aq} \leftrightarrow OH^-_{ads} \tag{4}$$

$$AH^-_{aq} + OH^-_{ads} \rightarrow D^- + H_2O + e \qquad \text{slow} \tag{5}$$

$$D^- \rightarrow D + e \qquad \text{fast} \tag{6}$$

D^- and D are the intermediate and final products of the oxidation, respectively. D is accepted to be dehydroascorbic acid [20,21]. The pH range of this study, 12 to 13.8, pK_{a1} and pK_{a2} for L-AA are 4.10 and 11.79, respectively [22]. So, at pH = 12, the ratio of the L-ascorbate di-anion to L-ascorbate anion species in the solution was 60/40. At pH values higher than 13.5, less than 2% of L-AA was in the form of the L-ascorbate

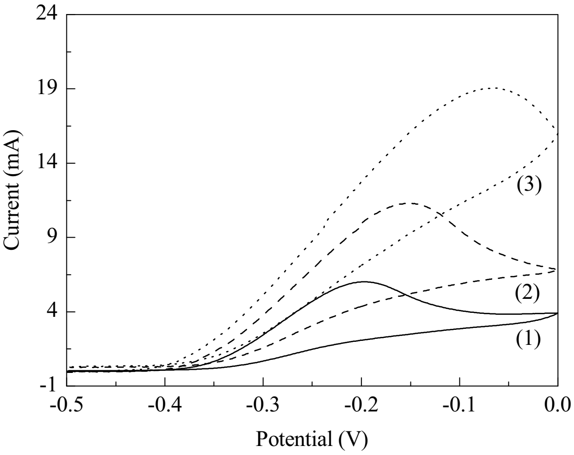

Fig. 2. Cyclic voltammograms recorded in solutions containing 0.5 mol/L $NaNO_3$ + 0.06 mol/L NaOH + Na_2A of concentrations of 0.02 mol/L (1), 0.04 mol/L (2), and 0.06 mol/L (3). v = 0.05 V/s.

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