Anodic Oxidation of Sulphite on Graphite Electrode in Alkaline Media

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This paper presents studies of anodic oxidation of sulfite ions on a graphite electrode in aqueous alkaline solutions. Over the past few years, extensive research has been focused on the use of graphite as electrode material because of its availability, physico-chemical properties, processability and relatively low cost. Grahite electrodes are thermally and mechanically stable, chemically resistant in different solutions (from strongly acidic to strongly basic) and chemically inert [1, 2].

Electrochemical oxidation of graphite during operation of fuel cells has been widely studied [3-6], because electrochemical behavior of graphite has relevant influence on detrimental to the performance and life of fuel cells.

Carbon is oxidised to carbon dioxide at higher potential than $E° = + 0.207$ V (vs. NHE) in accordance with reaction (1). Even if this value means that carbon is unstable to the electrochemical corrosion, slow kinetics of the oxidation reaction ensures good stability of carbon in solid fuel cells [6].

$$C + 2H_2O = CO_2 + 4H^+ + 4e^- \qquad E^o = 0.207 \text{ V (vs NHE)} \qquad (1)$$

The reaction of sulphite at room temperature has been examined by cyclic and linear voltammetric methods on a graphite electrode. Polarization curves have been plotted in 1M NaOH support electrolyte solution in which have been added different amounts of Na_2SO_3 in order to obtain concentrations of 10^{-1}M, 10^{-2}M, respectively 10^{-3}M. The mechanism of the oxidation reaction was studied by varying the scan rate and the concentration of sulphite in electrolyte solutions.

The sulphite oxidation on graphite electrode occurs in two steps. In the first one, a radical anion $SO_3^{•-}$ is formed by losing one electron. Further more oxygen transfer undergoes by losing the second electron. Two sulphite radical can combine and form dithionate, which can then disproportionate into sulphite and sulphate, but the formation of dithionate on the graphite electrode (Equation 4) can be neglected in accordance with the literature [7].

Therefore, anodic oxidation of sulphite ions in alkaline solution on graphite electrode can be expressed by the following equations:

$$SO_3^{2-} = SO_3^{•-} + e^- \qquad (2)$$

$$SO_3^{•-} + 2OH^- = SO_4^{2-} + H_2O + e^- \qquad (3)$$

$$2SO_3^{•-} = S_2O_6^{2-} + 2e^- \qquad (4)$$

From figure 1, at a potential value of $+ 0.3$ V vs. Ag/AgCl, the beginning of the anodic oxidation of sulphite ions can be observed. Due to the evolution of oxygen and possible the oxidation of graphite, gas bubbles are formed on the electrode surface and consequently the oxygen evolution diminished the oxidation of sulphite. Finally the current increased with increasing potential exhibiting the abundantly evolution of oxygen.
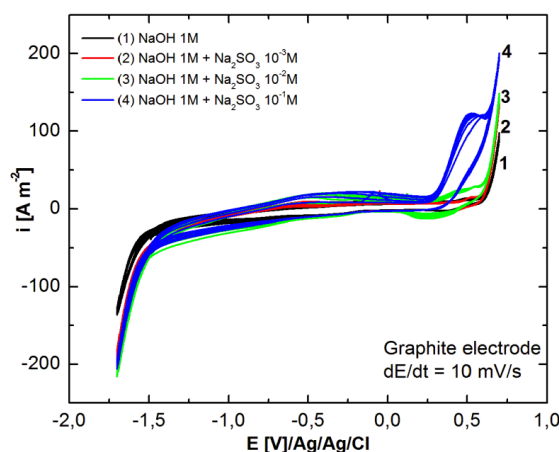
Fig. 1. Cyclic voltammograms (5 cycles) on the graphite electrode dE/dt = 10 mV/s in the alkaline electrolyte with different concentrations of sodium sulfite.

Based on polarization curves resulting from linear voltammetry kinetic parameters (*1-α* and i_o) for electrochemical oxidation of sulphite to sulphate have been calculated for each electrolyte solution using Tafel method.

Acknowledgement

References

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