Electrochemical characterization of nano structured silver oxide film modified polycrystalline silver electrode

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Abstract

Electrochemical characterization of nano structured silver oxide film modified polycrystalline silver electrode in 1M NaOH + 5 x 10^-5 M Na2HPO4 solution is carried out by sweep rate variation studies. Two specific anodic current peaks at 0.25V and 0.32V were observed in current-potential curves. It was concluded that 0.32V was due to the incomplete oxidation of Ag2O to AgO under the anodic sweep or due to the partial decomposition of AgO layer, and 0.25V was due to the catalytic reaction of AgO followed by the electrochemical oxidation of Ag2O to AgO. Studies of various scan rates from 10-100 mV/s were carried out. By comparing, 0.25 Ip vs ν gives better linearity than Ip vs ν^0.5 indicating the surface adsorption controlled process are operative. But at 0.32V Ip vs ν^0.5 gives better linearity when compared to Ip vs ν indicating diffusion controlled process are operative.

1. Introduction

Nanoparticle research has become an immense developing field due to its wide range of applications in different areas of science and technology. Nanomaterials are gaining interest and prominence due to their many new-fangled properties in contrast to that in traditional bulk materials. Among the metal nanoparticles (NPs), transition metal NPs, in particular the nanoparticles of cobalt (Farhadi et al., 2013), nickel (Abdelhalim et al., 2012; Huang et al., 2007; Nejati and Zabibi 2012), palladium (Xiong et al., 2005), platinum(Cuenya et al., 2011; Zhang et al., 2008), gold (Merza et al., 2012), and titanium (Misra et al., 2013), have attracted much attention of the researchers for a long time due to their size-induced properties and application-oriented importance in many industries as well as in advanced technologies. Among these transition metal nanoparticles, silver nanoparticles (Ag NPs) have been extensively studied due to their surface enhanced properties with fascinating structures and unique electrical, chemical, optical and antimicrobial properties. Several synthesis aspects have been reported for formation of silver oxide on to silver metal Murray et al., (2005) have reported the synthesis of Ag2O with diameters ranging from 0.7 to 1.1 µm by electrochemical step edge decoration on highly oriented pyrolytic graphite electrode surface. Wei et al., (2011) have synthesized...
oriented silver oxide nanostructures through a template free electrochemical route. De Mott et al employed dual pulse programmed electro deposition of silver oxide on silver disc electrode in the flow system from sodium hydroxide or sodium hydroxide with traces of sodium phosphate for the amperometric detection of carbohydrates, aminoacids (De-Mott et al., 2005), and related compounds (De-Mott et al., 1998).

Electrochemical characterization of nano structured silver oxide film modified polycrystalline silver electrode in 1M NaOH + 5 x 10^{-5} Na_2HPO_4 solution is carried out (Subha et al., 2013).

2. Materials & Methods

2.1 Instruments and reagents

Electrochemical experiments were performed at room temperature in a three electrode cell using a potentiostat/galvanostat-Autolab system (Ecochemie, The Netherlands). The system was run on a PC using GPES 4.9 software. Working electrode was polycrystalline Ag disc of surface area of 0.0314cm^2. Reference electrode and counter electrode [Elico Ltd] were Ag/AgCl (in saturated KCl solution) and platinum sheet respectively.

Analytical reagent grade chemicals were used throughout the experiments. NaOH, Na_2HPO_4 chemicals were of analytical reagent grade (Merck, Mumbai, India). Working solutions were prepared using double distilled water.

3. Results and Discussion

Electrochemical characterization of nano structured silver oxide film modified polycrystalline silver electrode in 1M NaOH + 5 x 10^{-5}M Na_2HPO_4 solution is carried out. Figure 1 shows the cyclic voltammetric curves of nano structured silver oxide film formation on polycrystalline silver electrode in 1M NaOH + 5 x 10^{-5} Na_2HPO_4 solution (pH 11.8). Studies of various scan rates from 10-100 mV/s were also carried out.

![Cyclic voltammetric curves of nano structured silver oxide film modified polycrystalline silver electrode in 1M NaOH + 5 x 10^{-5} Na_2HPO_4 solution (pH 11.8). Potential sweep rates from 10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 mVs^{-1}.](image)
On the basis of the slopes of the linear dependence of the anodic peak currents with the potential sweep rates, by the equation,

$$I_p = \frac{n^2F^2\Gamma A\nu}{4RT}$$

where $I_p$ is the peak current, $A$ is the electrode surface area, $\Gamma$ is surface coverage.

On the basis of the slopes of the linear dependence of the anodic peak currents on the square root of the potential sweep rates, by Randel-Sevcik equation,

$$I_p = (2.99 \times 10^5) a^{1/2} n^{3/2} A C D^{1/2} \nu^{1/2}$$

where $I_p$ is the peak current, $A$ is the electrode surface area, $D$ is the diffusion co-efficient and $C$ is the bulk concentration.

Studies of various scan rates from 10-100 mV/s were carried out. During silver oxide film formation two anodic peaks were obtained i.e., at 0.25V and 0.32V and one reduction peak at 0.02V. By comparing Figure 2 (I) & 2 (II) at 0.25 $I_p$ vs $\nu$ gives better linearity compared to $I_p$ vs $\nu^{0.5}$ indicating surface adsorption controlled process are operative. But in Figure 3 (I) & 3(II) at 0.32V $I_p$ vs $\nu^{0.5}$ gives better linearity compared to $I_p$ vs $\nu$ indicating diffusion controlled process are operative.

![Fig. 2 (I): Plot of $I_p$ vs $\nu$ for nano structured silver oxide film modified polycrystalline silver electrode at 0.25V.](image)

![Fig. 2 (II): Plot of $I_p$ vs $\nu^{0.5}$ for nano structured silver oxide film modified polycrystalline silver electrode at 0.25V.](image)
Fig. 3 (I): Plot of $I_p$ vs $ν$ for nano structured silver oxide film modified polycrystalline silver electrode at 0.32V.

Fig. 3 (II): Plot of $I_p$ vs $ν^{0.5}$ for nano structured silver oxide film modified polycrystalline silver electrode at 0.32V.

**Tafel plot**

In order to obtain information about the rate determining step, the Tafel plot (b) was drawn using the following equation, for a diffusion controlled process,

$$E_p = \frac{b}{2} \log ν + \text{constant}$$

Based on the above equation, from the Tafel plot (Fig.4) the slope of $E_p$ vs. $\log ν$ is $b/2$ where $b$ indicates the Tafel slope. The slope of $E_p$ vs. $\log ν$ for nano structured silver oxide film modified polycrystalline silver electrode at 0.32V was found to be 0.044. In this work, thus $b = 0.044 \times 2 = 0.088$. This slope indicates an electron transfer co-efficient of $\alpha = 0.6715$ for a one electron transfer process, which is the rate determining step. Figure 4 shows the slope of $E_p$ vs. $\log ν$ for nano structured silver oxide film modified polycrystalline silver electrode at 0.02 V was found to be 0.0107 in this work, thus $b = 0.0107 \times 2 = 0.0214$. 

124
4. Conclusion

Electrochemical characterization of nanostructured silver oxide film modified polycrystalline silver electrode in 1M NaOH + 5 x 10^{-5}M Na2HPO4 solution is carried by sweep rate variation studies. Two specific anodic current peaks at 0.25V and 0.32V were observed in current-potential curves. It was concluded that 0.32V was due to the incomplete oxidation of Ag2O to AgO under the anodic sweep or due to the partial decomposition of AgO layer, and 0.25V was due to the catalytic reaction of AgO followed by the electrochemical oxidation of Ag2O to AgO. Studies of various scan rates from 10-100 mV/s were carried out. On comparison, 0.25 Ip vs v gives better linearity than Ip vs v^{0.5} indicating surface adsorption controlled process are operative. But at 0.32V Ip vs v^{0.5} gives better linearity as compared to Ip vs v indicating diffusion controlled process are operative. Nano structured silver oxide film modified polycrystalline silver electrode is first of its kind with superior electrochemical performance, characteristics towards sub-picomolar level sensing of endosulphan.

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6. References


