

Full Paper

Silver Oxyfluoride Modified Silver Electrode: Application for Electrocatalytic Oxidation of Methanol

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Abstract- Silver oxyfluoride modified silver electrode was prepared and used to electrocatalytic oxidation of methanol. Fluoride can form a complex with silver ion, and thus be used to modify a silver electrode surface. The electrocatalytic activity of the modified electrode for the oxidation of methanol, in aqueous basic solution was studied by using cyclic voltammetry. Results showed that, silver oxyfluoride modified electrode can improve the activity of Ag towards the oxidation of this small organic molecule. The exchange current density (j_0) were 20.37, 10.38 and 1.61 folds higher than for that of bare silver electrode respectively for silver oxyfluoride, silver oxychloride and silver oxybromide modified silver electrodes. The modified electrode showed a stable and linear response in the concentration range of 5×10^{-3} to 5×10^{-2} mol L⁻¹ with a correlation coefficient of 0.9953. For silver oxyfluoride modified silver electrode, the transfer coefficient (α), the number of electrons involved in the rate-determining step (n_α) and the catalytic rate constant (k) for modified electrode were calculated as 0.45, 1 and 1.113×10^5 cm³ mol⁻¹ s⁻¹ respectively.

Keywords- Methanol, Oxyfluoride, Modified electrode, Electrocatalytic oxidation, Silver

1. INTRODUCTION

The use of bare electrodes for electrochemical detection have a number of limitations, such as low sensitivity and reproducibility, slow electron transfer reaction, low stability over a wide range of solution composition and high overpotential at which the electron transfer process occurs. The chemical modifications of inert substrate electrodes with redox active thin films offer significant advantages in the design and development of electrochemical sensors. In operation, the redox active sites shuttle electrons between the analyte and the electrodes with significant reduction in activation overpotential.

Surface modification is a very useful method in electrochemistry. The concept of modified electrodes is one of the exciting developments in the field of electroanalytical chemistry [1]. Chemically modified electrodes (CMEs) have played an important role in the studies of electrocatalysis [2–4], electron transfer kinetics [5], membrane barriers [6] and electroorganic synthesis [7]. To prepare the CME, most often a thin film of a selected chemical is either bound or coated on to the electrode surface to endow desirable properties of the film in rationally and chemically designed manners. Electrocatalytic property is one of the distinguishable features of CME to be utilized in electroanalytical chemistry.

Silver (Ag) has been extensively used in a variety of applications such as catalysis, electronics, photonics and photography due to its unique properties. For example, silver has the highest electrical conductivity, thermal conductivity and reflectivity of all metals and lower cost than gold [8,9]. Also, it is a metal of commercial importance for use in high strength and corrosion resistance alloys, and jewellery. Silver compounds and alloys have been widely used in dental and pharmaceutical preparations, and in implanted prosthesis [10–12]. Ag is one of important metals and can be used not only as modification metal but also as substrate metal in surface modification [13].

Ag electrode is attractive for its high catalytic activity toward the reduction of organic halides, for example, Ag electrode for reductive dehalogenation of polyhalogenated phenols and Ag nanoparticles and nanorods deposited on glassy carbon substrates for the reduction of benzyl chloride [14–17]. But Ag electrode shows low catalytic activity for the oxidation of alcohols such as methanol, ethylene glycol and glycerol [18,19].

It seems reasonable if a layer of silver oxyfluoride, silver oxychloride or silver oxybromide is formed on the surface of the Ag, it can be effectively enhances the electrochemical properties of it. The modified electrode was examined for electrocatalytic oxidation of methanol and very promising results were obtained.

The results of the present work showed that in comparison to bare silver electrode, electrochemical behavior of methanol have been greatly improved at silver oxyfluoride modified silver (SOFMS) electrode, indicating that the anodic oxidation of methanol could be catalyzed at silver oxyfluoride modified silver electrode.

2. EXPERIMENTAL

2.1. Reagents and instrumentation

All chemicals were of analytical grade supplied by Merck (Darmstadt, Germany) and were used without further purification. All solutions were prepared with doubly distilled water. All electrochemical measurements were carried out in a three-electrode cell using an Autolab electrochemical system (Eco Chemie, Utrecht, the Netherlands) equipped with PGSTAT-12 and GPES software. A bare or modified silver electrode, was used as a working electrode, Ag/AgCl/saturated KCl and a Pt wire were used as reference electrode and counter electrode, respectively. All experiments were carried out at room temperature.

2.2. Preparation of silver oxyfluoride/oxychloride/oxybromide modified silver electrodes

Prior to each experiment, the base silver electrode surface was polished with a slurry 0.05 μm alumina powder until a mirror-like surface was obtained. The electrode was then washed thoroughly with acetone and distilled water. The polished electrode was immersed in 0.1 mol L⁻¹ KX (X=F, Cl, Br) solution by applying one cycle potential scan between -1400 mV and 800 mV (*vs.* Ag/AgCl) at scan rate of 50 mV s⁻¹. In this step, halide can form a complex with silver ion. Then the electrode was inserted into an electrochemical cell containing 0.1 mol L⁻¹ NaOH, and cycled twenty times between 170 and 800 mV (*vs.* Ag/AgCl) at a scan rate of 50 mV s⁻¹, regime until a stable voltammogram was obtained. Based on the literatures silver oxyhalide has been formed at the surface of silver electrode [20-22]. The modified electrodes have been denoted as SOFMS (silver oxyfluoride modified silver electrode), SOCMS (silver oxychloride modified silver electrode) and SOBMS (silver oxybromide modified silver electrode) throughout the text.

3. RESULTS AND DISCUSSION

Electrochemical properties of the prepared SOFMS electrode were investigated. For the activation of this electrode, the electrode was placed in 0.1 mol L⁻¹ NaOH and the electrode potential was cycled between 170 and 800 mV (*vs.* Ag/AgCl) at a scan rate of 50 mV s⁻¹ for 20 cycles in a cyclic voltammetry regime until a stable voltammogram was obtained (Figure 1). After 20 runs, the SOFMS electrode shows reproducible cyclic voltammograms. In the anodic potential sweep, the SOFMS electrode showed three anodic peaks (A₁, A₂ and A₃) appearing at 0.260, 0.399, and 0.698 V, respectively (Fig. 1). During a reverse scan, one cathodic peak (C₁) appeared at 0.388 V. It seems that the first anodic peak (A₁) is due to the electroformation of the monolayer of Ag₄OF₂. The second anodic peak (A₂) is due to the formation of the multilayer of Ag₄OF₂. The third peak (A₃) is due to the oxidation of Ag₄OF₂ to Ag₂OF₂ or direct oxidation of Ag to Ag₂OF₂. When the nuclei of Ag₂OF₂ formed at the Ag₄OF₂ surface during the anodic scan, further formation of Ag₂OF₂ became easy, and

occurred at a lower potential than the initial formation of Ag_2OF_2 nuclei. The cathodic current peak C_1 is due to the reduction of Ag_2OF_2 to Ag_4OF_2 .

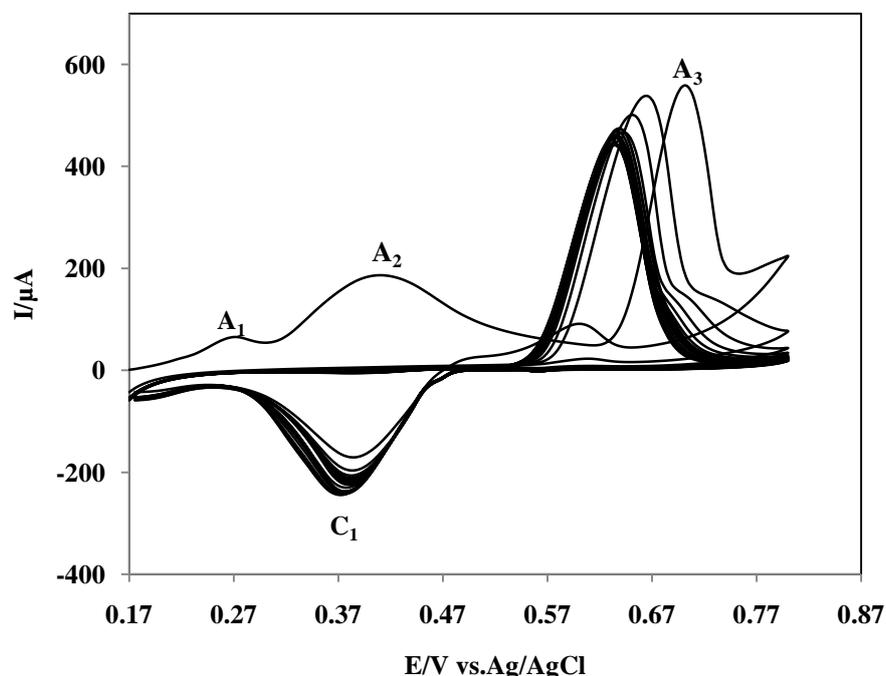


Fig. 1. Repetitive cyclic voltammograms of SOFMS electrode in 0.1 mol L^{-1} NaOH in the potential range of 170–800 mV. Potential sweep rate is 50 mV s^{-1}

Cyclic voltammetry was used to examine the electro-catalytic efficiency of the modified silver electrodes for the oxidation of methanol. Fig. 2 illustrates the CVs of methanol at the bare silver and SOFMS/ SOCMS/ SOBMS electrodes in 0.1 mol L^{-1} NaOH solution at 50 mV s^{-1} . From Fig. 2, it can be seen that at the SOFMS/ SOCMS/ SOBMS electrodes, the anodic currents of methanol oxidation have been greatly enhanced indicating that the anodic oxidation of methanol could be catalyzed at silver oxyhalide modified silver electrodes. This proves that the silver oxyhalide layer formed on the surface of the silver electrode bears the main role in the electrocatalytic oxidation of methanol. In comparison with the data at the bare silver electrode, an increase of 2.4, 2 and 2.07 folds in peak currents (at E_p) of methanol were observed at the SOFMS/ SOCMS/ SOBMS electrodes respectively. It can be seen that the electro-catalytic efficiency of SOFMS electrode is higher than the SOCMS/ SOBMS electrode.

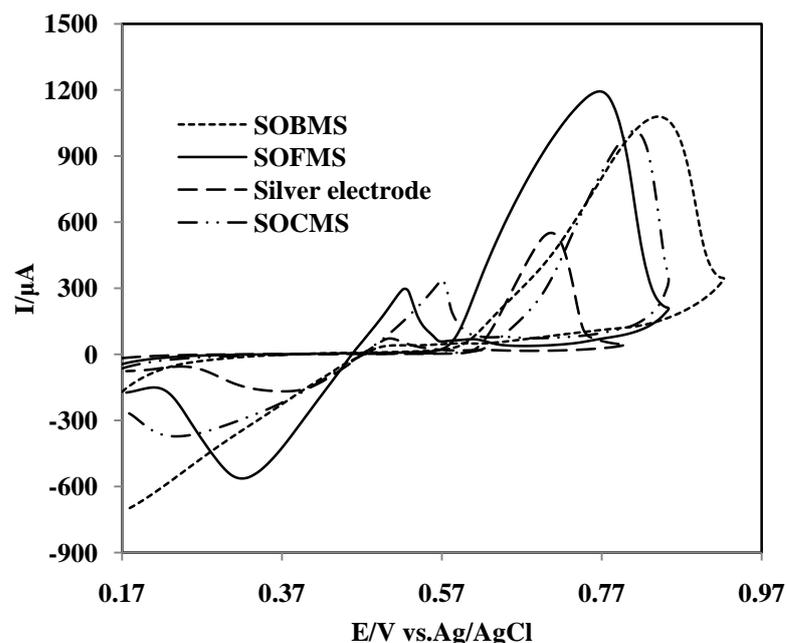


Fig. 2. Cyclic voltammograms of bare silver electrode, SOFMS, SOCMS and SOBMS electrode in 0.1 mol L^{-1} NaOH solution in presence of 20 mmol L^{-1} methanol at a scan rate of 50 mV s^{-1}

With the increase of methanol concentration, the anodic peak current gradually increased (not shown). The characteristic shape of cyclic voltammogram in this potential region indicates that the signal is due to the oxidation of methanol. The catalytic peak current is proportional to the concentration of methanol in the range of 5 to 50 mmol L^{-1} . The linear regression equation is $I (\mu\text{A}) = 15.758 C_{\text{methanol}} (\text{mmol L}^{-1}) + 608.07$ ($R^2 = 0.9953$).

In order to provide more evidence, the effect of the scan rate on the performance of SOFMS electrode was also studied. The peak currents could lead to the information on electron transfer kinetics. Fig. 3A shows the CVs of the electrode prepared in optimum condition at various scan rates when immersed in a solution containing 20 mmol L^{-1} methanol and 0.1 mol L^{-1} NaOH. It can be noted from Fig. 3A that the anodic currents increase and the peak potential shifts toward positive direction with increasing the scan rate, suggesting a kinetic limitation in the reaction between the redox sites of the modifier and the methanol. When peak current values were plotted against $v^{1/2}$ (Fig. 3B), the following linear relationship was obtained, suggesting that the process is controlled by diffusion of analyte as expected for a catalytic system.

$$I_p = 56.203 + 310.61v^{1/2} (\text{mV}^{1/2} \text{ s}^{-1/2}) \quad (1)$$

Moreover, a plot of the scan rate normalized current ($I/v^{1/2}$) versus the scan rate exhibits the typical shape of an electrochemical (EC') catalytic process (Fig. 3C).

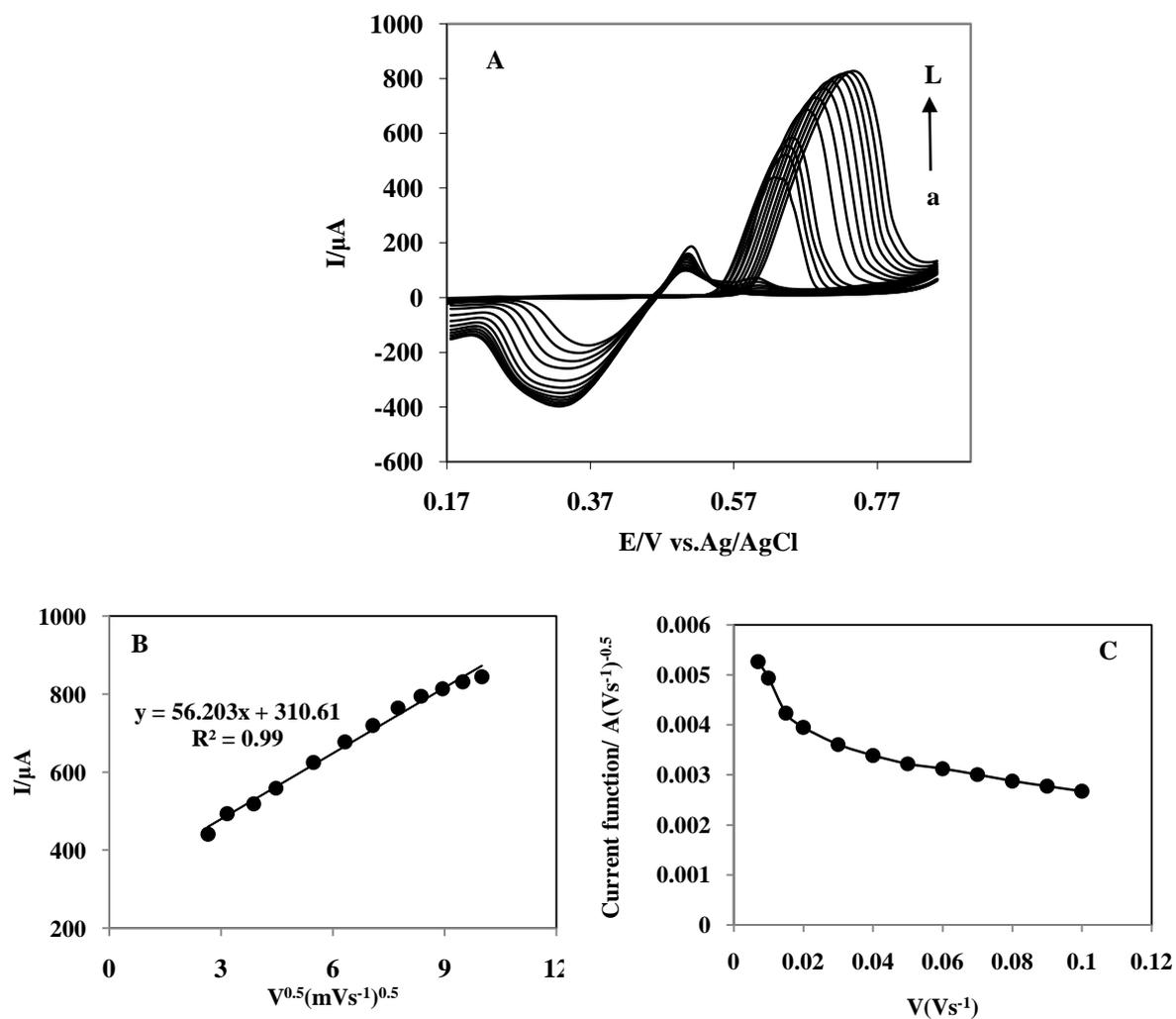


Fig. 3. (A) Cyclic voltammograms of SOFMS electrode in 0.1 mol L^{-1} NaOH containing 20 mmol L^{-1} of methanol at various potential scan rates (from inner to outer) $7\text{--}100 \text{ mV s}^{-1}$. (B) Variation of the catalytic current with the square root of sweep rate. (C) Current function vs. ν for 0.1 mol L^{-1} NaOH solution in the presence of 20 mmol L^{-1} methanol

Fig. 4 shows the Tafel plots recorded for 20 mM methanol on the (A) bare silver, (B) SOBMS (C) SOCMS (D) SOFMS electrodes at a scan rate of 5 mV s^{-1} . The charge transfer coefficient (α), the number of electrons involved in the rate determining step (n_α) and exchange current density (j_0) evaluated from Tafel plots have been given in Table 1. The parameters Tafel slope, α , and n_α are very similar for four electrode reported in Table 1, but the j_0 for SOFMS, SOCMS and SOBMS electrodes are 20.37, 10.38 and 1.61 folds respectively higher than that of bare silver electrode.

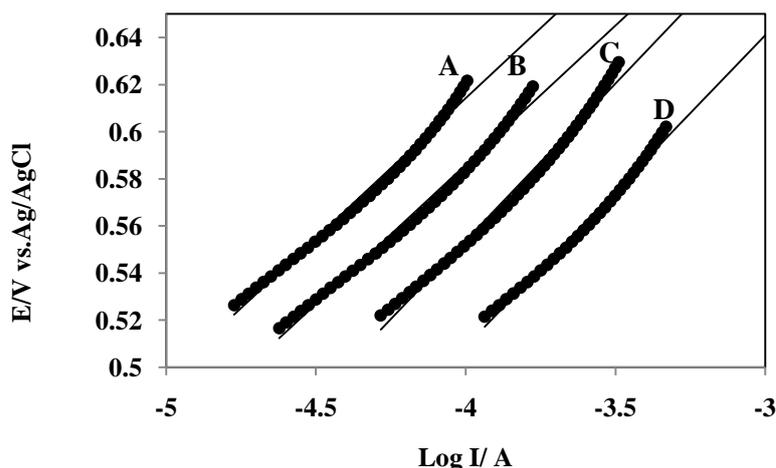


Fig. 4. Tafel plot derived from the rising part of voltammograms recorded at a scan rate 7 mV s^{-1} for 20 mM methanol at (A) bare silver, (B) SOBMS, (C) SOCMS and (D) SOFMS electrodes

Table 1. Kinetic parameters of methanol oxidation at bare silver, SOBMS, SOCMS and SOFMS electrodes

Electrode	Tafel slope	α	n_{α}	$J_0(\text{A cm}^{-2})$
Bare silver	119	0.496	$0.99 - 1$	2.40×10^{-8}
SOBMS	118.1	0.499	$0.999 - 1$	3.87×10^{-8}
SOCMS	133.3	0.44	$0.89 - 1$	2.49×10^{-7}
SOFMS	132	0.45	$0.88 - 1$	4.89×10^{-7}

In order to evaluate the reaction kinetics, the oxidation of methanol on SOFMS electrode was investigated by chronoamperometry. Chronoamperometry, as well as cyclic voltammetry has been employed for the investigation of the processes occurring via an E_rC_i mechanism [23]. Double steps chronoamperograms were recorded by setting the working electrode potentials to desired values and were used to measure the catalytic rate constant on the modified surface. Fig. 5A shows a series of well-defined chronoamperograms for the SOFMS electrode in the absence and presence of different concentrations of methanol at an applied potential of 0.7 V versus Ag/AgCl. The plot of net current with respect to the mines square roots of time presents a linear dependency (Fig. 5B). This indicates that the transient current must be controlled by a diffusion process. The transient current is due to catalytic oxidation of methanol, which increases as the methanol concentration is raised. No significant cathodic current was observed when the electrolysis potential was stepped to 0.00 mV (*vs.* Ag/AgCl), indicating the irreversible nature of the oxidation of methanol. The rate constants of the reactions of methanol and the ensuing intermediates with the redox sites of the SOFMS electrode can be derived from the chronoamperograms according to Eq. (2) [24]:

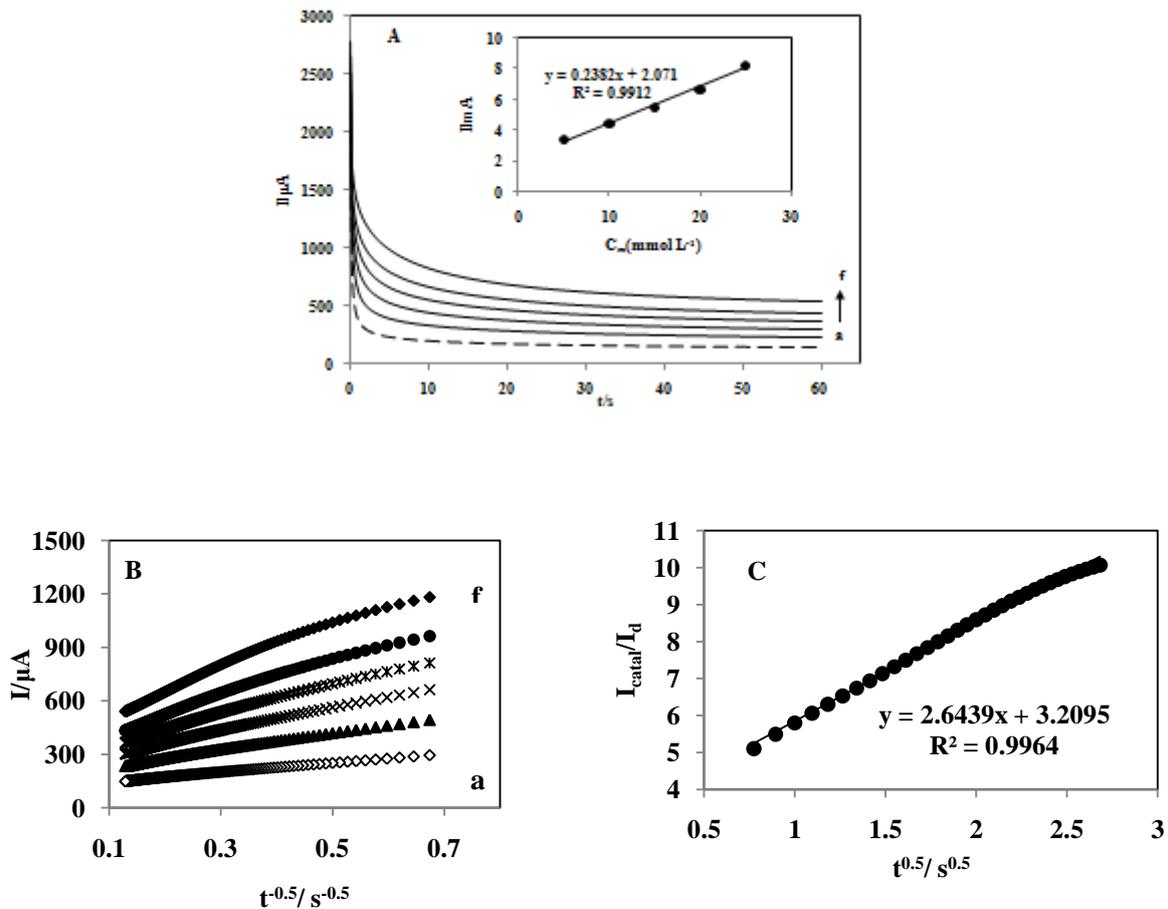


Fig. 5. (A) Chronoamperograms of SOFMS electrode in 0.1 mol L⁻¹ NaOH containing different concentrations of methanol: 0.0, 5, 10, 15, 20, and 25 mmol L⁻¹, from (a) to (f), respectively. Potential steps were 0.7 and 0.0 V, respectively. Insets: Variation of chronoamperometric currents at $t=10$ s vs. concentration of methanol. (B) Plot of i vs. $t^{-1/2}$ obtained from chronoamperometric measurements SOFMS electrode in 0.1 mol L⁻¹ NaOH containing different concentrations of methanol: 0.0, 5, 10, 15, 20, and 25 mmol L⁻¹, from (a) to (f), respectively. (C) Dependency of I_{catal}/I_d on $t^{1/2}$ derived from CAs of (a) and (e) in panel (A)

$$I_{\text{catal}}/I_d = \lambda^{1/2} [\pi^{1/2} \text{erf}(\lambda^{1/2}) + \exp(-\lambda)/\lambda^{1/2}] \quad (2)$$

where I_{catal} is the catalytic current in the presence of methanol, I_d the limiting current in the absence of methanol and $\lambda = kCt$ (k , C and t are the catalytic rate constant, bulk concentration of methanol and the elapsed time, respectively) is the argument of the error function. For $\lambda > 1.5$, $\text{erf}(\lambda^{1/2})$ almost equals unity and Eq. (3) reduces to [25]:

$$I_{\text{catal}}/I_d = \lambda^{1/2}\pi^{1/2}(kCt)^{1/2} \quad (3)$$

From the slope of the I_{catal}/I_d vs. $t^{1/2}$ plot (Fig. 5C), the value of k for 20 mmol L⁻¹ methanol was calculated to be $1.113 \times 10^5 \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

4. CONCLUSION

Silver oxyfluoride modified silver electrode was prepared as a new electrode. The modified electrode successfully used for electrocatalytic oxidation of methanol. The j_0 for SOFMS, SOCMS and SOBMS electrodes are 20.37, 10.38 and 1.61 folds respectively higher than that of the bare silver electrode. For SOFMS electrode, kinetic parameters such as the electron transfer coefficient (α), catalytic reaction rate constant (k) and the number of electrons involved in the rate determining step (n_a) for oxidation of methanol were calculated as 0.45, 1.113×10^5 and 1 respectively.

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