



Ag supported on carbon fiber cloth as the catalyst for hydrazine oxidation in alkaline medium



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ABSTRACT

Silver particles with microspheric structure are directly electrodeposited on carbon fiber cloth (CFC) substrate by square-wave potential electrodeposition method. The electrocatalytic behaviors of the Ag/CFC electrode toward hydrazine oxidation in alkaline solution are examined by cyclic voltammetry and chronoamperometry. An onset oxidation potential of -0.5 V and a peak current density of 30 mA cm^{-2} are achieved in the solution containing 1.0 mol L^{-1} KOH and 20.0 mmol L^{-1} hydrazine. The microspheric structure of the Ag/CFC electrode provides large electroactive surface area, hence, abundant active sites are vacant for hydrazine oxidation. The calculated apparent activation energies at different potentials show that hydrazine electro-oxidation at higher potential has faster kinetics than that at lower potential. In addition, the transfer electron number of hydrazine oxidation reaction on the Ag/CFC electrode is close to four, suggesting hydrazine is almost completely electrooxidized on the electrode and the full use of hydrazine fuel is basically achieved.

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1. Introduction

Direct hydrazine fuel cell (DHFC) employing carbon-free hydrazine as fuel has gained a great deal of attention due to its several attractive advantages. DHFC has a theoretical potential of 1.56 V, which is higher than other types of fuel cell, such as direct methanol fuel cell [1,2]. No greenhouse gas and only nitrogen and water are generated during hydrazine oxidation [3–5]. Therefore, DHFC is thought to be a zero pollution emission electrochemical device. No intermediates which can poison the electrocatalysts (such as CO) exist in the process of hydrazine electrooxidation [1]. Furthermore, DHFC has high power density and high hydrogen content [6,7].

The anode catalyst plays an important role in enhancing the performance of DHFC. A lot of electrocatalysts have been explored, such as Pt [8,9], Pd and Pd-based composites [10–13], Au [14], Ag [15], Co [2], Ni [16,17] and Cu [18]. Among the above metals, silver has shown more favorable properties including high conductivity, chemical stability, modest price and stability in alkaline media and thus acts as a potential electrocatalyst for hydrazine oxidation. The

catalytic activity of the catalyst depends not only upon the metal nanoparticles of active component but also upon the choice of support material. By now, many literatures concerning silver particles supported on various carbon materials used as catalysts for hydrazine oxidation have been reported [19–22]. For example, Gao et al. prepared multi-walled carbon nanotubes (MWCNTs) supported Ag electrode and the electrode was active for hydrazine oxidation [20]. Tan et al. synthesized carbon black supported silver nanoparticle catalyst (denoted as Ag/CB) by a modified ethylene glycol reduction method and the electrode possessed a superior electrocatalytic activity for hydrazine oxidation [21]. However, literatures concerning carbon fiber cloth (CFC) supported silver catalyst as an electrocatalyst for hydrazine oxidation have not been reported. Compared with the conventional carbon materials, CFC is seen as an excellent support because of the following reasons [23,24]. Firstly, CFC has a large surface area and can improve the dispersion of catalyst, thus can improve the electrocatalytic activity of catalyst. Secondly, CFC has high electrical conductivity and flexibility. Thirdly, CFC has good corrosion resistance in alkaline media.

The structure of catalyst and its catalytic performance are closely related. Until now, several methods have been developed to control the morphology of Ag catalyst [25–27]. But, each approach has its own limitations. For example, the preparation process of

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template method is complex and the structure of the product may be damaged in the process of removing the template. Therefore, it is considerably attractive to propose a simple, rapid and without adding any templates or surfactants method to control the structure of the catalyst and prepare the catalyst with good electrocatalytic performance for hydrazine oxidation.

In the traditional electrode preparation process, the electrical conductivity of the electrode will be reduced due to the presence of binder such as Nafion [28–30]. In this paper, in order to overcome the above limitations, silver was directly deposited onto carbon fiber cloth (CFC) by a simple one-step electrodeposition method. Herein, CFC acted as the support of catalyst and current collector. The electrodeposition solution was composed of AgNO_3 and NaNO_3 and without any additives. Electrodeposition parameters, including oxidation potential, reduction potential, electrodeposition time and frequency have effects on the structure and the electrocatalytic performance of the Ag/CFC electrode. Silver particles with microspherical structure obtained by adjusting the electrodeposition parameters showed promising catalytic activity for hydrazine oxidation.

2. Experimental

2.1. Synthesis and characterization of the Ag/CFC electrode

The Ag/CFC electrode was prepared by electrodeposition of Ag onto CFC using a square wave potential method. The electrodeposition was performed in a three-electrode cell using an Autolab PGSTAT302 electrochemical workstation (Eco Chemie, Netherlands). CFC (10 mm \times 10 mm \times 0.3 mm, Shanghai Hesen electric Co. Ltd) was used as the working electrode. A Pt foil (10 mm \times 20 mm) and a saturated Ag/AgCl, KCl electrode worked as the counter electrode and reference electrode, respectively. The Ag/CFC electrode was fabricated in a solution containing 3 mmol L^{-1} AgNO_3 and 0.1 mol L^{-1} NaNO_3 . Under different electrodeposition conditions such as oxidation potential, reduction potential, electrodeposition time and frequency, the morphology and catalytic activity of the Ag/CFC electrode are both varied. When the reduction potential was fixed at -0.15 V, the deposition time was 1000 s, the frequency was 10 Hz, the oxidation potential was varied (0.45 V, 0.5 V, 0.55 V, 0.6 V, 0.65 V, 0.8 V). The effect of oxidation potential on the morphology of the Ag/CFC electrode was studied and the results are shown in Fig. S1. Microspherical-like Ag was formed at 0.45 V. As augmented the oxidation potential, the diameter of Ag microsphere increased gradually. When the oxidation potential reached 0.6 V, Ag particles agglomerated together and Ag microsphere aggregates were formed. The oxidation potential was determined to be 0.45 V. Subsequently, the oxidation potential was set at 0.45 V, the frequency and electrodeposition time remained unchanged, the influence of the reduction potential (0.1 V, 0 V, -0.05 V, -0.1 V, -0.15 V, -0.2 V) was in research (Fig. S2). Sparse clusters of rice-shape Ag particles with

different sizes were first observed. Microspherical-like Ag was formed at -0.05 V. With the decrease of reduction potential, the diameter of Ag microsphere reduced gradually. When the reduction potential reached -0.2 V, Ag microsphere with about 200 nm in diameter was observed. Hence, the reduction potential was determined to be -0.2 V. The effect of electrodeposition time was investigated (Fig. S3). Increasing electrodeposition time resulted in the increase of the diameter of Ag microsphere. Ag particles did not completely cover the CFC surfaces with the reduction of electrodeposition time. In addition, the effect of frequency was also studied (Fig. S4). When frequency was 50 Hz, Ag particles merged together to form petal-like structure. When frequency was 5 Hz, Ag particles did not completely cover the CFC surfaces. Hence, the optimized preparation parameters are as follows: the oxidation potential is 0.45 V, the reduction potential is -0.2 V, the frequency is 10 Hz and deposition time is 1000 s. The Ag loading on the Ag/CFC electrode is $0.1389 \text{ mg cm}^{-2}$. All chemical reagents were of analytical grade and all solutions were made with ultrapure water ($18 \text{ M}\Omega \text{ cm}$, Millipore).

The morphology of the Ag/CFC electrode was obtained using scanning electron microscope (SEM, JEOL JSM-6480). The composition and structure of the electrode were studied by X-ray diffractometer (Rigaku TTR III) with Cu $\text{K}\alpha$ radiation ($\lambda = 0.1514178 \text{ nm}$). The Ag loading on the Ag/CFC electrode was determined by inductive coupled plasma emission spectrometer (ICP, Xseries II, Thermo Scientific). Ag in 1.0 cm^2 electrode was first immersed in a mixture solution containing 7.5 mL HCl and 2.5 mL HNO_3 for 12 h and then diluted to 1000 mL for ICP measurement.

2.2. Electrochemical measurements

The catalytic activities of hydrazine electrooxidation on the Ag/CFC electrode were investigated by cyclic voltammetry (CV) and chronoamperometry (CA) measurements, which were performed in a standard three-electrode cell with the Ag/CFC electrode as the working electrode, a platinum foil (10 mm \times 20 mm) as the counter electrode and a saturated Ag/AgCl, KCl as the reference electrode. All electrochemical tests were carried out by an Autolab PGSTAT302 workstation (Eco Chemie, Netherlands). All potentials in this paper were with respect to the saturated Ag/AgCl, KCl reference electrode. The current densities in this paper were normalized to the geometric area of the electrode. Before the electrooxidation of hydrazine tests, the as-prepared Ag/CFC electrode was cycled in the potential range from -1.2 V to 0.8 V at 50 mVs^{-1} under nitrogen atmosphere in 1.0 mol L^{-1} KOH solution until the stable cyclic voltammogram was obtained.

The gas gathering experiment was conducted at a constant current density of 50, 100, 150, 200, 250 mA cm^{-2} for 1 h in 1.0 mol L^{-1} KOH containing 20.0 mmol L^{-1} hydrazine solution and the volume of generated gas was measured by drainage method.

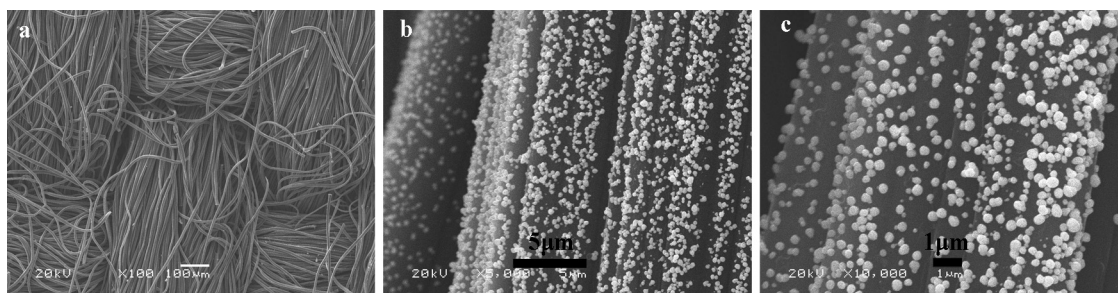


Fig. 1. SEM images of the CFC substrate (a) and Ag/CFC electrode with different magnifications (b–c).

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