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Electrocatalytic oxidation of formic acid on nano/micro fibers of poly(*p*-anisdine) modified platinum electrode

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HIGHLIGHTS

- The poly(*p*-anisidine) was synthesized electrochemically.
- The polymer modified Pt used for the first time for FA oxidation in acid medium.
- It shows an enhanced formic acid oxidation.
- The loading level of the polymer is optimized to give maximum rate of the oxidation process.

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ABSTRACT

Poly(*p*-anisidine) (PPA) modified platinum (Pt) electrode shows an extraordinary electrocatalytic activity towards formic acid oxidation in acid medium compared to bare Pt electrode. The Pt/PPA is prepared by electropolymerization of the monomer on Pt electrode in salycilate aqueous solution. The PPA has a fiber-like structure with a thread size of nano- to micrometers. The cyclic voltammogram for formic acid electrooxidation on the Pt/PPA shows no peak for the indirect current and the peak current in the backward sweep is almost equal to that in the forward sweep indicating high electrocatalytic activity for FA oxidation compared to the Pt electrode which shows lower tolerance to CO poisoning. The loading level affects both the onset potential and the peak current of formic acid oxidation. Optimization of the loading level shows that a 5 cycles of polymerization (11.8 μg cm^{-2}) is the best loading level of the PPA under the prevailed experimental conditions. The stability of the Pt/PPA towards FA oxidation confirms the higher tolerance to CO poising. SEM images and data analysis demonstrate the facilitated oxidation of FA on the Pt/PPA. Interpretation of the enhancement of FA oxidation on the Pt/PPA electrode is introduced.

1. Introduction

Fuel cells have been considered for several applications as an important alternative to ordinary energy sources because of its low emission and high power output. Many small organic molecules have shown promising performance as fuels in what is so called direct energy conversion fuel cells. However, some of these small organic molecules show some drawbacks. In direct methanol fuel cell (DMFC), for instance, the methanol concentration cannot exceed some limits (1–2 M), since high rates of fuel crossover reduces the fuel utilization and simultaneously decreases the cell performance [1–3]. Those limitations of methanol caused an increased interest in direct formic acid fuel cells (DFAFCs) [4–6]. Formic acid, on the other hand, is relatively non-toxic and non-explosive compared to MeOH. The DFAFC has an electromotive force (open circuit voltage (OCV)) of ~1.48 V which is higher than either hydrogen or direct methanol fuel cells [7]. Platinum and platinum-based catalysts considered to be unavoidable candidate for efficient and durable catalyst for formic acid oxidation [8–13]. However, the platinum surfaces suffer from lower tolerance to CO adsorption and poisoning. Also, high cost of those catalysts is crucial. That is to say, the above failure problems render the commercialization of the DFAFC less practical. Conducting polymers have been used either as coating onto the platinum surface [14,15] or as a dispersion medium for platinum particles [16–20] for enhancing the catalytic activity of Pt surface towards the electrooxidation of formic acid. In this context, the combination of both Pt surface (either as planar or Pt-particles) with a conducting polymer exhibits a synergetic effect and the electrocatalytic activity of the Pt electrodes toward oxidation of small organic molecules

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can be dramatically increased. Such modification by conducting polymers afforded better catalytic effects than Pt for oxidation of organic fuels and offered many advantages such as its easiness and fast preparation by chemical and electrochemical routes.

In the present study and for the first time, poly(*p*-anisidine) modified Pt (Pt/PPA) is used as an anode for electrochemical oxidation of formic acid (FA) from acid solution and the results are compared to that of bare Pt electrode. Cyclic voltammetry, chronoamperometric curves and SEM will be used to demonstrate the electrocatalytic activity of the Pt/PPA towards FA oxidation in acid medium.

2. Experimental

The monomer, *p*-anisidine and all chemicals (purchased from Merck, Sigma Aldrich) were of analytical grade and were used as received without further purification. The working electrodes were polycrystalline Pt ($d = 1.6$ mm) and GC ($d = 3.0$ mm). They were cleaned by mechanical polishing with aqueous slurries of successively finer alumina powder (down to 0.06 mm) then washed thoroughly with second distilled water. An $Hg/Hg_2Cl_2/KCl$ (sat) (SCE) and a Pt sheet were used as reference and counter electrodes, respectively. Conventional procedure was applied to clean the Pt electrode as described elsewhere [21]. An electrochemical cell with a three-electrode configuration was used in this study. Electrochemical characterizations were performed using system IM6 Zahner electrik Meβtechnik, Germany.

The electropolymerization process was carried out using 0.01 M *p*-anisidine in 0.1 M sodium salycilate aqueous solution. The polymer film was produced by cyclic voltammetry technique in the potential range from −1.0–1.7 V (SCE) for a number of cycles. The polymer then washed with water and dried in air. The catalytic activity of FA oxidation was carried out in an aqueous solution of (0.12 M FA in 0.12 M H_2SO_4). The electrochemical measurements were carried out inside an air thermostat kept at 25 °C (±0.1 °C). Scanning electron microscope (SEM) images were taken using field emission scanning electron microscope, FE-SEM (FEI, QUANTA FEG 250). The loading level of the polymer film was estimated from the total charge passed through the polymerization process.

3. Results and discussion

3.1. Electrochemical and surface characterizations

Fig. 1A and B show cyclic voltammograms (CV) for the Pt electrode in 0.1 M sodium salycilate solution in the potential range of −1.0–1.7 V (SCE) in absence and presence of 0.01 M *p*-anisidine (PA), respectively. In Fig. 1A, the peak “a” denotes the reversible oxidation peak of salycilate ion. The peak “c” corresponds to a dissolution peak of Pt-oxide layers. CV in Fig. 1A in monomer-free solution is similar to that found in literature [22]. In Fig. 1B (in presence of the monomer), the oxidation peak “d” at ~0.47 V corresponds to the oxidation of PA and formation of radical cations, which is considered to be the first step in the polymerization of the monomer. The peak at −0.30 V (peak b) is for reduction of the formed polymer. In Fig. 1B and in presence of the monomer, the CV shows similar peaks with those found in literature [23]. The peak height “d” decreases in the consecutive cycles with cycling due to formation of the polymer film which is lower in conductivity than Pt and also due to lower diffusion of the monomer to the Pt surface. The peak “c” increases until the 4th cycle (not shown here) before it decreases to lower currents. In the start, the Pt/PPA enhances the Pt oxides dissolution and then with the increase in cycle number (increase in the thickness), it retards the reduction of the Pt oxides. Note that the peak “a” in Fig. 1A converted to a shoulder in Fig. 1B with the potential cycling pointing to the lower currents of the salycilate oxidation on the modified compared to the bare Pt electrode.

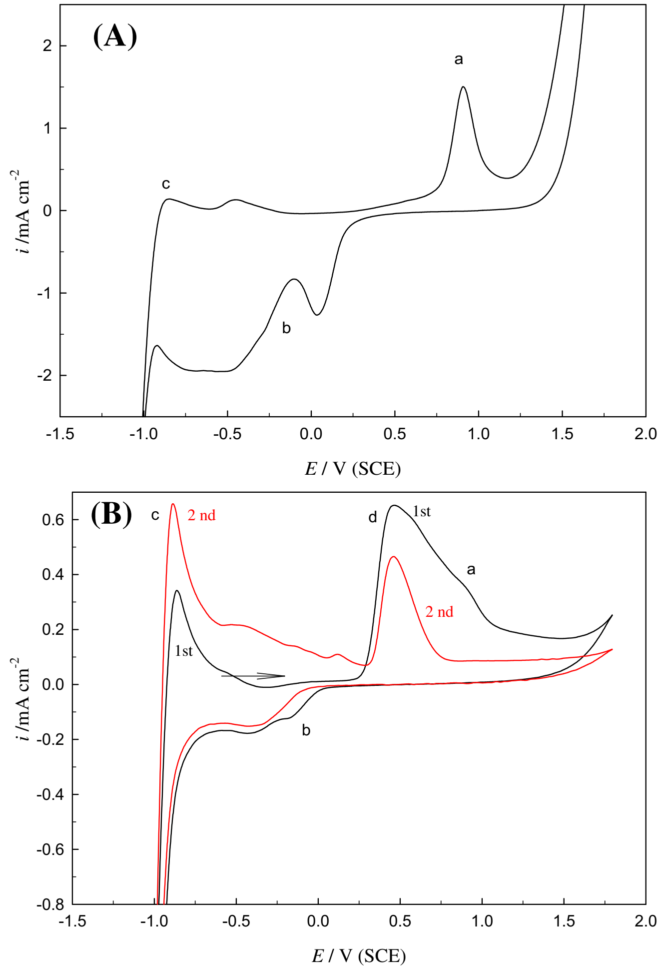

Fig. 1. CVs for Pt electrode in monomer-free 0.1 M sodium salycilate (A) and for electropolymerization of *p*-anisidine from 0.01 M PA + 0.1 M sodium salycilate (B).

The morphology of the formed PPA polymer was examined by taking micro-image using the SEM as shown in Fig. 2. The image was taken for PPA formed after 5 cycles of electropolymerization. The polymer surface is bearing fiber-like structure with a range of thread size from 250 nm to 500 nm (nano- to micro- scale). The small size of the polymer fibers provides high surface area of the polymer with good and uniform distribution of the polymer onto the Pt surface. The Pt surface can be seen as the light areas in the image implying the exposure of the Pt surface to formic acid solution. These features of the Pt/PPA can facilitate the diffusion of liquid fuel to the Pt surface.

3.2. Electrocatalytic oxidation of formic acid

Electrooxidation of formic acid on Pt catalysts follows a well documented dual-pathway mechanism, i.e., direct and indirect oxidation processes involving dehydrogenation and dehydration, respectively [24,25]. In the direct pathway mechanism, i.e., dehydrogenation pathway, HCOOH adsorbed on Pt sites is converted to CO_2 without the formation of poisoning CO_{ads} species:

$$Pt + HCOOH \rightarrow Pt\text{-}(HCOOH)_{ads} \quad (1)$$

$$Pt\text{-}(HCOOH)_{ads} \rightarrow Pt + CO_2 + 2H^+ + 2e- \quad (2)$$