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Platinum-macrocycle co-catalyst for electro-oxidation of formic acid

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Abstract

In this work, a new promoter, tetrasulfophthalocyanine (FeTSPc), one kind of environmental friendly material, was found to be very effective in both inhibiting self-poisoning and improving the intrinsic catalysis activity, consequently enhancing the electro-oxidation current during the electro-oxidation of formic acid. The cyclic voltammograms test showed that the formic acid oxidation peak current density has been increased about 10 times compared with that of the Pt electrode without FeTSPc. The electrochemical double potential step chronoamperometry measurements revealed that the apparent activity energy decreases from 20.64 kJ mol^{-1} to 17.38 kJ mol^{-1} after Pt electrode promoted by FeTSPc. The promoting effect of FeTSPc may be owed to the specific structure and abundant electrons of FeTSPc resulting in both the steric hindrance of the formation of poisoning species (CO) and intrinsic kinetic enhancement. In the single cell test, the performance of DFAFC increased from 80 mW cm^{-2} mg^{-1} (Pt) to 130 mW cm^{-2} mg^{-1} after the anode electrode adsorbed FeTSPc.

Keywords: Formic acid; Tetrasulfophthalocyanine (FeTSPc); Platinum electrode; Fuel cell; Electro-oxidation

1. Introduction

Fuel cells are promising power sources due to their high-energy efficiency and density as well as low environmental load. In portable power applications [1], some small organic molecules, such as methanol [2,3], formic acid [4] and ethanol [5], are the fuel candidates. Comparing with hydrogen as fuel, fuel cells with organic molecules as fuel are of two key shortcomings, self-poisoning [2–6] and slow kinetics rate of decomposition of organic molecules [6,7] during electro-oxidation of them on electrode surface, having limited these fuel cells performance. Self-poisoning phenomenon plays a very important role during the electro-oxidation of the small organic molecules, in which some CO_{ad}-like intermediates will occupy the active sites of platinum electrode surface and obstruct the electro-oxidation reaction [8]. In order to remove "poisoning" intermediates with the oxygen content species [2–5,8] that are provided by other elements, Pt electrode was alloyed with other metals such as Sn, Ru, Co and Ni [9]. However, high overpotential must be supplied to ensure the removing reaction of "poisoning" intermediates, resulting in reducing the efficiency of fuel cells. In addition, the foreign adatoms, such as Sb, Bi and Te [10], were found to be helpful to prevent the formation of "poisoning" intermediates during the electro-oxidation. The electro-oxidation of formic acid has been perceived as a clear manifestation of the so-called dual-path mechanism, which was provided by Parsons and others [11–13]. Namely, at double layer potentials, formic acid can decompose to CO_2 rapidly and, in parallel, to chemisorbed CO poisoning the Pt electrode. It is obvious and significant that the reaction rate will become faster if CO_{ad} does not form during the electro-oxidation of formic acid by some manners.

In this work, a new promoter, tetrasulfophthalocyanine (FeTSPc), was found to be very effective in inhibiting self-poisoning, enhancing the electro-oxidation current and improving the intrinsic catalysis activity during the electro-oxidation of formic acid. In addition, comparing the conventional methods [2–4,8], in which poisoning intermediates

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were removed with oxygen content species, the promoter can inhibit the formation of poisoning intermediate and be applied directly to direct formic acid fuel cell (DFAFC). It brings new elicitation and confidence to prevent the electro-oxidation of organic molecules from suffering of self-poisoning.

2. Experimental section

Pt electrode (2 mm diameter), which was polished with an Al_2O_3 water suspension, particle size 0.05 μm and cleaned ultrasonically in high purity water for 5 min, was used in the experiments. The FeTSPc was purchased from Aldrich. The FeTSPc modified Pt electrode was prepared with dropping the clean Pt electrode into 0.1 mg mL^{-1} FeTSPc solution for 1 min, and washed it carefully, then was dried in air for 30 min. The DFAFC anode catalyst layer adsorbed FeTSPc was prepared with pumping 4 μg mL^{-1} FeTSPc into anode channels for 2 h, then washed with 0.5 M H_2SO_4 and water orderly.

The cyclic voltammograms (CVs) for the electrodes were carried out in Parc 273 potentiostat under control of Powersuit Software. A conventional three-electrode cell was used in the experiment. Pt foil and an Ag/AgCl/sat KCl electrode were used as counter electrode and reference electrode, respectively. All potentials in the experiments are quoted against Ag/AgCl/sat KCl, which is 0.196 V versus normal hydrogen electrode at 25 °C. In the measurement pure nitrogen was firstly bubbled in the cell to remove oxygen in the electrolyte solution for 40 min.

Pure CO was bubbled in measurement system with the potential of work electrode holding at 0.15 V versus Ag/AgCl/sat KCl, which went on for 30 min to ensure CO saturated adsorption on catalysts followed by saturating the solution with N_2. Then, the potential scan was carried out for two circles with scan rate of 20 mV s^{-1} under temperature of 25 °C.

In order to measure the intermediate, the Pt electrode was kept under 0.2 V for 600 s in 0.5 M H_2SO_4 and 1.0 M HCOOH, and the electrode was put into pure water saturated with purified N_2 gas to wash the electrode for 15 s, then the electrode was put into 0.5 M H_2SO_4 saturated with purified N_2 gas immediately to have a CV test between −0.2 and 1.0 V with scanning rate 20 mV s^{-1}.

In the double potential step chronoamperometry, the potential was kept at 0.80 V (vs. Ag/AgCl) for 1.0 s, where surface CO poison was completely removed, followed by keeping at the hydrogen evolution potential –0.15 V (vs. Ag/AgCl) for 3.0 s. Then, the chronoamperometry measurement was performed for 1.0 s. The temperature of the electrochemical reaction system was controlled by using an ultra-precise thermostat bath (Shanghai Instrument, China), which can guarantee a deviation of temperature from a given value within ±0.1 °C.

The single cell test was performed without back pressure at the cell temperature 60 °C. Formic acid solution with concentration 6 M was fed into the anode from its inlet at flow rate of 1 mL min^{-1} by a peristaltic pump. Non-humidified, pure oxygen was fed into the cathode from its inlet at flow rate of 100 mL min^{-1}. The preparation of the membrane-electrode assemblies (MEAs) referenced to reference [14]. Pt loadings were 0.5 mg cm^{-2} and 1.5 mg cm^{-2} in anode and cathode respectively. Cell potentials were not compensated for series resistance.

3. Results and discussion

Formic acid is a very hopeful candidate fuel for fuel cell as well as methanol, because the electro-activity of formic acid is much higher than that of methanol. Pt and Pd are the most active catalyst for the electro-oxidation of formic acid. The conventional promoters for Pt are bismuth, stibium, tellurium [10], etc. These promoters will desorb from the Pt surface at high potential, and pollute the environment of fuel cell system. If an amount of these promoters were applied widely, the problem of environmental pollution must be considered. Tetrasulfophthalocyanine (FeTSPc), one kind of environmental friendly material, is cheap, easy to synthesize, steady, water-soluble. We found that FeTSPc was a very effective promoter for formic acid electro-oxidation.

3.1. The promoted effect of FeTSPc on the electro-oxidation of formic acid

Fig. 1 shows the cyclic voltammograms for formic acid with glass carbon electrode adsorbed FeTSPc, bare Pt electrode, Pt electrode adsorbed FeTSPc and Pt electrode in FeTSPc solution. From the dashdotted line, it can be seen that the FeTSPc cannot catalyze the oxidation of formic acid alone. From the dot line, it can be seen that there

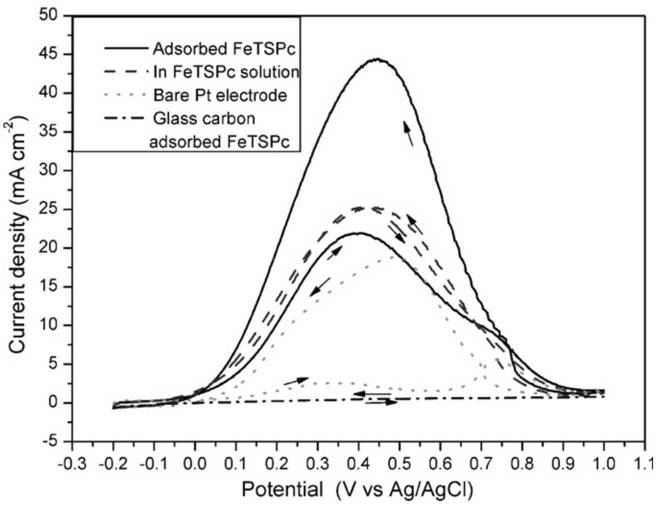

Fig. 1. The cyclic voltammograms of different electrode in 0.5 M H_2SO_4 and 1.0 M HCOOH with scanning rate 100 mV s^{-1} at 25 °C. (–·–·–) glass carbon electrode adsorbed FeTSPc; (……) bare Pt electrode; (—) Pt electrode adsorbed FeTSPc and (-----) Pt electrode in 0.1 mg mL^{-1} FeTSPc solution.