Electrochemistry Communications 86 (2018) 63–67

Contents lists available at ScienceDirect

Electrochemistry Communications

journal homepage: www.elsevier.com/locate/elecom

Epoxy-sealed single Pt nanoelectrodes: Fabrication and electrocatalytic performance for the methanol oxidation reaction

Hao Wang[a], Yan Gong[b], Yongxin Li[a,*]

[a] Anhui Key Laboratory of Chemo/Biosensing, College of Chemistry and Materials Science, Anhui Normal University, Wuhu 241000, PR China
[b] Nanjing Research Institute for Agricultural Mechanization, Ministry of Agriculture, Nanjing 210014, PR China

ARTICLE INFO

Keywords:
Single Pt nanoelectrodes
Methanol oxidation reaction
Direct fuel cell

ABSTRACT

Epoxy-sealed single Pt nanoelectrodes (SPNEs) ranging in size from 3 to 300 nm have been fabricated by a laser-assisted pulling method and characterized by optical microscopy, transmission electron microscopy (TEM) and electrochemical methods. The prepared SPNEs were used to investigate the methanol oxidation reaction (MOR), and the results show that the electrocatalytic activity of the SPNEs towards MOR depends on the radius of the electrode. In the range of electrode radii tested (3 nm–280 nm), the electrocatalytic activity decreases if the radius of the SPNE is either too small or too large, with optimal electrocatalytic efficiency being observed when the radius is about 4.2 nm.

1. Introduction

The methanol oxidation reaction (MOR) on metal electrodes has received a great deal of attention in recent decades due to potential applications in direct methanol fuel cells [1,2]. Generally, platinum is considered to be the best single metal catalyst for MOR [3], and the oxidation process, which involves a dual path mechanism, has been much discussed [4]. It is well known that the size of platinum particles has a very important influence on the MOR [2,5]. Frelink et al. claimed that the MOR activity decreases as the Pt particle size decreases in the range 1.2–4.5 nm [5]. Nart et al. concluded that the catalytic activity is lost if the particles are either too small or too large [2]. Despite many attempts to address this issue, the effect of the size of Pt nanoparticles on the MOR is still not clearly understood because the properties of Pt nanoparticles modified on the surface of electrodes are complicated. Many issues can affect the catalytic efficiency of Pt, including surface coverage, particle distribution and the interaction of the particles with the supporting material. It is therefore necessary to study the MOR at the single Pt nanoelectrode level.

Compared with normal sized electrodes, nano-sized electrodes have many advantages, including smaller *RC* constant, faster mass-transport rate, and the reduced effect of solution resistance [6,7]. Most single nanoelectrodes have been fabricated by pulling microwires or thin metal films, then either directly polishing the pulled tips prior to electrochemical testing or sealing the tips in a glass tube using a high-temperature hydrogen–oxygen flame [8–10]. However, directly polished tips are fragile and glass-tube-sealed nanoelectrodes crack easily in air. It is necessary to explore new methods of fabricating single nanoelectrodes with good stability, as this is important in both electrochemical studies and real applications. Ludwig et al. found that epoxy-sealed microelectrodes could be polished using alumina paste [11] and this is the approach adopted here.

In this paper, single Pt disk electrodes with radii in the range 3–300 nm have been fabricated using the epoxy-sealing method, and the electrocatalytic activity of the resulting single Pt nanoelectrodes (SPNEs) towards MOR was investigated. It has been found that the catalytic activity towards MOR of the SPNEs is related to the radius of the electrode: the electrocatalytic activity decreases if the radius of the SPNE is either too small or too large, and the optimal catalytic efficiency is obtained when the radius of the SPNE is around 4.2 nm. This is the first investigation of MOR at the single nanoelectrode level, and we believe this study will prove useful in research into Pt-based nanocatalysts for applications in fuel cells.

2. Materials and methods

2.1. Chemicals

Potassium ferricyanide ($K_3Fe(CN)_6$, Acros Organics), hexaammineruthenium (III) chloride ($Ru(NH_3)_6Cl_3$, Aldrich), potassium chloride (KCl, Mallinckrodt Baker), high pure methanol (EMD Chemicals Inc.), and sulfuric acid (EMD Chemicals Inc.) were of reagent grade quality or better and used without further purification.

* Corresponding author.
E-mail address: yongli@mail.ahnu.edu.cn (Y. Li).

https://doi.org/10.1016/j.elecom.2017.11.018
Received 18 October 2017; Received in revised form 17 November 2017; Accepted 17 November 2017
Available online 21 November 2017

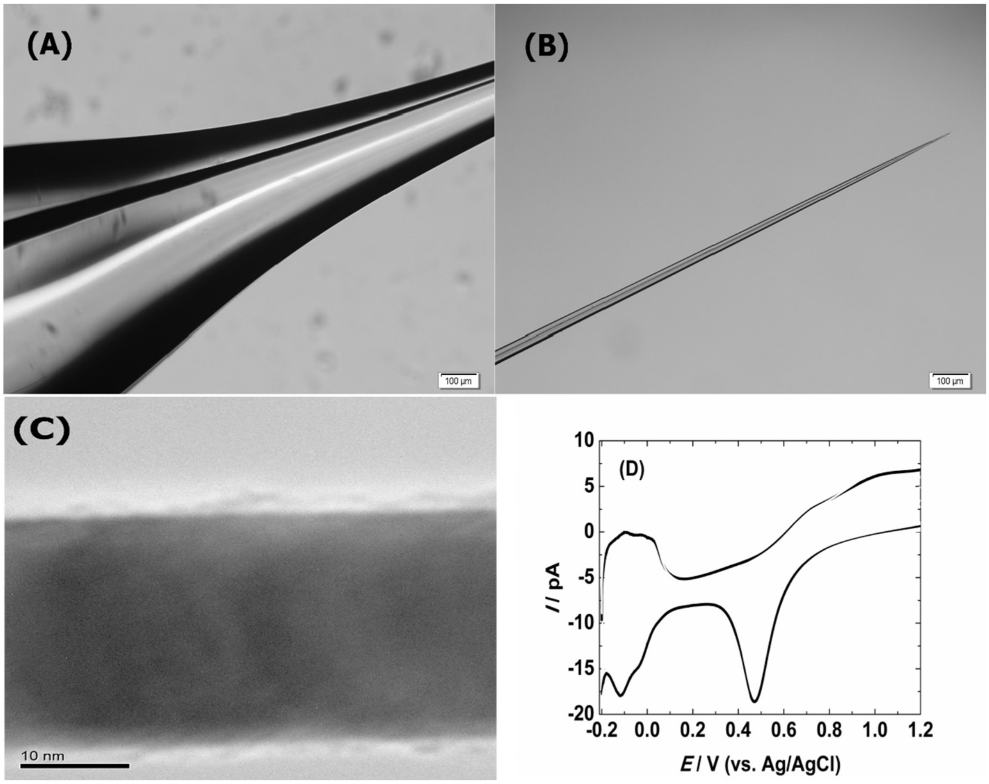

Fig. 1. Optical microscopic images of a pulled Pt nanotip (A) at the bottom position and (B) at the top position; (C) TEM image of a pulled Pt nanotip; (D) CV of a SPNE in 0.5 M H_2SO_4 solution.

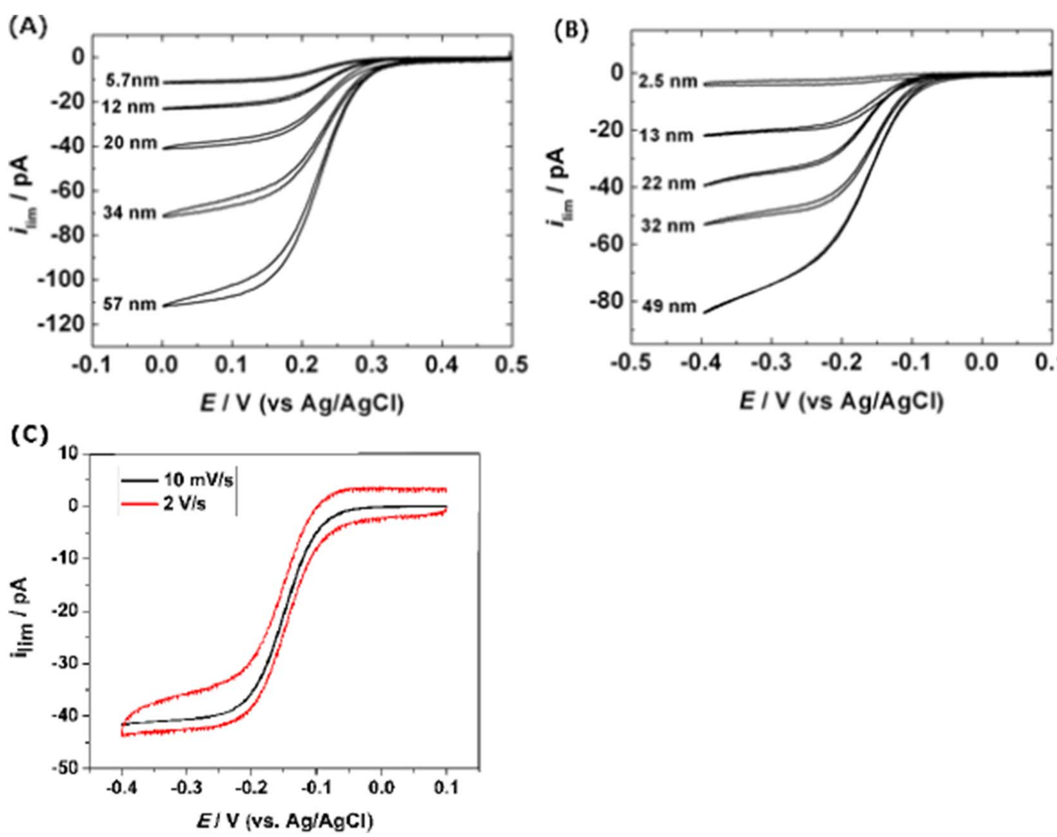

Fig. 2. CVs of SPNEs in (A) 5 mM $K_3Fe(CN)_6$ solution at a scan rate of 10 mV/s; (B) 5.0 mM $Ru(NH_3)_6Cl_3$ solution at a scan rate of 10 mV/s and (C) 5.0 mM $Ru(NH_3)_6Cl_3$ solution at scan rates of 10 mV/s (black curve) and 2 V/s (red curve). Radius, 22 nm; supporting electrolyte, 0.2 M KCl. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)