Highly Active Core-shell PtSnOx Nanocatalyst

Synthesis, Characterization and Performance as Anode Catalysts for Direct Alcohol Fuel Cell

Luhua Jiang[1], Gongquan Sun[1], Qin Xin[1], Zhenhua Zhou[2], Bing Zhou[2],*

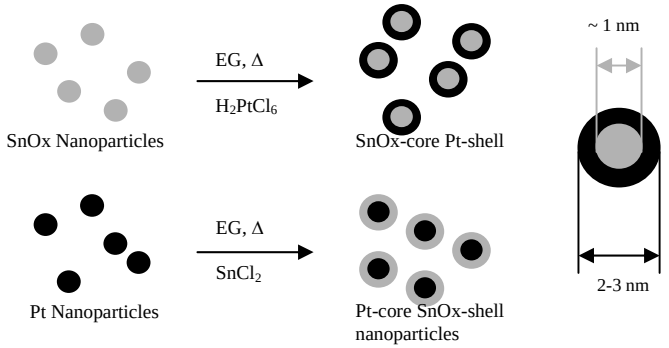
1. Direct Methanol Fuel Cell Laboratory, Dalian Institute of Chemical Physics, P.O. Box 110, Dalian, 116023,
2. Headwaters Inc., 1501 New York Avenue, Lawrenceville, NJ 08648, USA
E-mail: bzhou@headwaters.com

Introduction

In recent decades, direct alcohol fuel cells (DAFCs) are extensively studied and considered as possible power sources for portable electronic apparatus and vehicles in the near future. [1] As a green fuel, ethanol is safer and has higher energy density than methanol and considered to be a potential fuel for low temperature fuel cells. However, the complete oxidation of ethanol to CO2 involves 12 electrons per molecule. Thus many adsorbed intermediates and byproducts are produced during the process of ethanol oxidation. Moreover, the cleavage of the C-C bond is difficult at low temperature (< 100 ^{o}C). It is urgent to develop novel catalysts with high electrocatalytic activity for ethanol oxidation. Most of previous research on ethanol fuel cells employed the state-of-the-art PtRu catalyst, since it is the best catalyst for methanol electro-oxidation. However PtRu performed low activity for ethanol electro-oxidation. Recent research [2-6] showed that PtSn catalysts presented higher activity for ethanol oxidation than PtRu catalysts. Especially, the activity of PtSn catalysts depends on a few factors, including the particle size and composition, the preparation procedure and so on. Herein we prefer to explore the effect of the microstructure of PtSnOx nanoparticles on the performance of ethanol electro-oxidation. In the present paper, two PtSnOx catalysts with different nanostructures, including Pt-core SnOx-shell and SnOx-core Pt-shell were designed and synthesized (Scheme 1). The physical (XRD, TEM, XPS) and electrochemical characterization (IV, Cyclic Voltammetry, Chronoamperometry) of the two PtSnOx/C catalysts were carried out. The superior activity and stability were achieved by using the well-defined Pt (shell)-SnOx (Core) nanoparticles as anode electrocatalyst in DEFC.

Results and Discussion

PtSnOx/C catalysts were prepared by a modified ethylene glycol (EG) method via different depositing orders. The first one includes preparing Pt nanoparticles with 1-2 nanometer by reducing hexachloroplatinc acid by EG [7], and then depositing SnOx onto Pt nanoparticles (denoted as (Pt+SnOx)/C). Reversely, the second one was prepared by coating Pt onto as-synthesized SnOx nanoparticles (denoted as (SnOx+Pt)/C). XRD patterns of the two catalysts reveal that apart from an fcc pattern of Pt, the Pt+SnOx/C sample displays an apparent SnO2 phase, while no prominent tin oxide signal in SnOx+Pt/C sample. TEM images show the metal particles in both catalysts are uniform and small particle size of 2-3 nm with sharp distributions. XPS analysis of the two samples reveals that tin exist in oxide. For the metal particle is small, the analysis of the XPS should be attributed to the bulk not to the surface of particles. The half-cell tests in acid solution show that SnOx+Pt/C has the higher electrochemical surface area than its counterpart. It is deduced that SnOx covered the Pt surface and blocked the Pt active sites in the Pt+SnOx/C sample. The catalytic activities for ethanol electro-oxidation of the two catalysts were characterized by cyclic voltammetry and chronoamperometry on a half-cell. They were also adopted as anode catalysts for direct ethanol fuel cell. The performance of fuel cell with the nanostructured (SnOx+Pt)/C core-shell catalyst was significantly improved from 22.5 mW/cm^2 to 79.5 mW/cm^2 compared to the reversely nanostructured nanocatalyst. The performance enhancement by Pt-coated PtSn nanoparticles is mainly attributed to electronic effect rather than geometric effect. More importantly, the novel structure is very stable in acidic working condition due to high corrosive resistance of out-layer Pt.



Scheme 1 Synthesis of PtSnOx Nanoparticles with Different Nanostructures

Significance

This abstract presents a novel fuel cell nanocatalyst with specific core-shell nanostructure which provides superior activity for breaking C-C bond at low temperature.

References

1. Ren, X.; Zelenay, P.; Thomas, S.; Davey, J.; Gottesfeld, S. *J. Power Sources 86*, 111 (2000).
2. Lamy, C.; Belgsir, E. M.; Leger, J.-M. *Appl. Electrochem.* 31, 799 (2001).
3. Delime, F.; Leger, J.-M.; Lamy, C. *J. Appl. Electrochem.* 27, 28 (1998).
4. Zhou, W.; Zhou, Z.; Song, S.; Li, W.; Sun, G.; Tsiakaras, P.; Xin, Q. *Appl. Catal. B* 46, 273 (2003).
5. Zhou, W.; Zhou, B.; Li, W.; Zhou, Z.; Song, S.; Sun, G.; Xin, Q.; Douvartzides, S.; Goula, M.; Tsiakaras, P. *J. Power Sources* 126, 16 (2004).
6. Lamy, C.; Lima, A.; LeRhun, V.; Deline, F.; Coutancear, C.; Leger, J.-M. *J. Power Sources* 105, 283, (2002).
7. Zhou, Z.; Wang, S.; Zhou, W.; Wang, G.; Jiang, L.; Li, W.; Song, S.; Liu, J.; Sun, G.; Xin, Q. *Chem. Comm. 3*, 394, (2003).