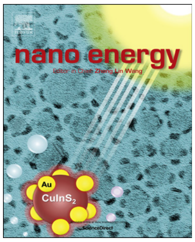
Nano Energy (2015) **15**, 462–469

Available online at www.sciencedirect.com

**ScienceDirect**

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



RAPID COMMUNICATION

# Nanostructured PtRu/C catalyst promoted by CoP as an efficient and robust anode catalyst in direct methanol fuel cells

**Ligang Feng**[*,1,2], **Kui Li**[1], **Jinfa Chang**, **Changpeng Liu**[*], **Wei Xing**[*]

*State Key Laboratory of Electroanalytical Chemistry, Laboratory of Advanced Power Sources, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, PR China*

Received 28 January 2015; received in revised form 24 April 2015; accepted 10 May 2015
Available online 16 May 2015

**KEYWORDS**
PtRu system;
Methanol oxidation;
Fuel cells;
Synergistic effect;
Phosphide material

**Abstract**
Nanostructured PtRu material is considered as the best catalyst for direct methanol fuel cells (DMFCs), but the performance decay resulting from Ru loss seriously hinders the commercial application. Here we demonstrated that the performance of nanostructured PtRu catalyst for methanol oxidation could be significantly improved by CoP material; the presence of CoP could largely slow down the loss of Ru and Pt in PtRu catalyst system, thus promising a highly active and durable performance in DMFCs. Cyclic Voltammetry results showed the peak current is 2.89 times higher than that of state-of-the-art commercial PtRu/C-JM (231.9 mA $mg_{PtRu}^{-1}$) and 3.86 times higher than that of the home-made reference (PtRu/C-H) catalyst (173.6 mA $mg_{PtRu}^{-1}$); kinetics study probed by electrochemical impedance spectroscopy showed a large reduced charge transfer resistance in the rate determining step. The highest maximum power density was achieved on this novel PtRu-CoP/C catalyst among all the evaluated catalysts at different temperatures. Specifically, a maximum power density of 85.7 mW $cm^{-2}$ achieved at 30 °C is much higher than that of state-of-the-art commercial PtRu/C catalyst at 70 °C (63.1 mW $cm^{-2}$). Outstanding catalytic activity and stability observed on this novel PtRu-CoP/C catalyst should be attributed to a synergistic effect between the nanostructured PtRu and CoP, in which the presence of CoP increases PtRu physical stability and anti-CO poisoning ability. The present work is a significant step that opens an avenue in the development of highly active and durable catalysts for fuel cells technology, and makes PtRu catalyst system much closer for commercial application in DMFCs.

---

[*] Corresponding author.
*E-mail addresses:* ligang.feng@chalmers.se, fenglg11@gmail.com (L. Feng), liuchp@ciac.ac.cn (C. Liu), xingwei@ciac.ac.cn (W. Xing).

[1] These authors contributed equally to the work

[2] Present address: Department of Applied Physics, Chalmers University of Technology, SE-41 296, Göteborg, Sweden.
Tel.: +46 0 31 772 3376.

http://dx.doi.org/10.1016/j.nanoen.2015.05.007

## Introduction

Direct methanol fuel cells (DMFCs) are emerged as promising alternative power sources for portable electronics and vehicles over the past few decades [1-4]. Recent progress demonstrated the hopeful commercial application as a kind of alternative green and sustainable power source [5-8]. However, the sluggish kinetics of methanol oxidation severely hinders the mass commercialization of DMFCs. Though lots of inspiring catalyst material has been reported [9-13], a serious problem that performance decay due to the loss of catalyst materials is still there and severely impedes the practical long-term operation [14-18]. Thus, it is highly desired but still a challenge to develop extremely high performance catalyst for DMFC.

Nanostructured PtRu material is thought to be best catalyst with both high activity and stability in DMFCs [19-22]. The outstanding catalytic ability is attributed to the so-called ‘functional mechanism’, in which Ru could provide more oxygen-containing species at lower potential and then accelerate the oxidation process of poisoning intermediates at the adjacent Pt active sites. Based on that principle, some catalytic promoters such as transition metal or metal oxide in combination with PtRu material largely improved the catalytic performances. For example, PtRu-$SnO_2$ [23] hybrid catalysts exhibit superior catalytic properties toward methanol oxidation in terms of catalytic activity and desirable stability; $TiO_2$ [24] combined with PtRu as a multi-functional catalyst showed significantly enhanced catalytic activity and CO tolerance ability compared with a commercial Pt/C catalyst. Unfortunately, a severe problem for this kind of catalytic promoter is unstable; as a result the long-term operation based on that kind of hybrid catalyst is still questionable.

Hence development of stable catalytic promoter is a smart design strategy to increase the catalyst stability. Phosphide materials, recently, have shown excellent catalytic activity and stability in the electrocatalysis for water splitting [25-27]. The facile adsorption of hydrogen on the phosphide materials might be beneficial to the dehydrogenation during methanol electrooxidation. We also have evidenced the excellent co-catalytic ability of $Ni_2P$ material in fuel cells [28-30]. The encouraging results promoted us to develop more practical catalytic promoter, and thus to promise the potential applications for fuel cell technology. By screening the potential materials, we found that CoP material is a novel effective catalyst promoter for PtRu nanocatalyst in direct methanol fuel cells. Significantly improved catalytic activity and stability were observed on CoP modified PtRu nanocatalyst towards methanol oxidation by cyclic voltammetry measurements. Upon integration into the anode of a direct methanol fuel cell, the highest maximum power density was achieved on PtRu-CoP/C catalyst among all the reference catalysts at different temperatures. Excellent discharge stability was also observed at 0.3 V on PtRu-CoP/C catalyst over 12 h. ICP-AES-MS (Inductivity Coupled Plasma-Atomic Emission Spectroscopy-Mass Spectroscopy) results demonstrated that the presence of CoP could largely slow down the dissolution of Pt and Ru elements, but no Co element was detected. The facile preparation approach of CoP from inexpensive reagents makes it ideally a new member in the catalyst promoter family. The remarkable discharge ability of nanostructured PtRu catalyst in combination with CoP promises a strong potential application, and this finding is a significant step to make PtRu catalyst system much stronger in direct methanol fuel cell technology.

## Results and discussion

The crystal structure of PtRu-CoP/C material was probed by XRD technology, and the patterns are shown in Figure 1. Broaden peaks for Pt face-centred cubic (FCC) structure are observed for all the PtRu catalysts with different CoP loadings. Some CoP diffraction peaks are observed on PtRu catalyst with CoP loading of 40% and 50%, but they are not observed on other samples. The invisible peaks of CoP in the hybrid catalyst are probably due to the coverage of PtRu on the surface or the low CoP contents, because the diffraction peaks of CoP in the CoP/C support could be clearly observed (Figure S1). Alloy between Pt and Ru was formed resulting from the incorporation of the base-metal into the Pt FCC structure, thus $2\theta$ values for PtRu catalysts shift to a higher direction compared with the pure Pt. No distinct diffraction peaks related to the tetragonal $RuO_2$ or hexagonal close-packed Ru phases were observed [31]. It should be pointed out that the formation of PtRuCo(P) alloy is not possible, because CoP itself is firstly prepared and then used as a support that is more stable in the acid condition and during the synthesis ethylene glycol as a weak reduce agent is not able to reduce the CoP itself.

The particle size and lattice parameter were calculated according to Scherrer formula and Vegard's law based on Pt (220) peak, and the alloy degree was calculated based on the formula proposed by Antolini and co-workers [32-34] (see the Supporting information). The relevant parameters are compared in Table S1. The average crystal size is around 3 nm for all the prepared PtRu catalyst, and the lattice parameter is also very close, but it is reduced compared with the pure Pt metal (0.3915 nm) due to the formation of PtRu alloy. The alloy degree of Ru in all the home-made catalyst was around 10%, which is lower than that of the commercial PtRu catalyst. It has been pointed out that the active form of the catalyst is a mixture of phases rather than a bimetallic alloy [35]; thus the less content of the alloyed Ru in the hybrid catalyst might be promising a high activity.

Typical transmission electron microscopy (TEM) images of PtRu/C-JM, PtRu/C-H and PtRu-CoP/C-40% are shown in Figure 2, and those for other samples in Figure S2. It is evident that Pt nanoparticles are observed on the carbon support for all the samples. Specifically, for PtRu-CoP/C-40% catalyst, the average particle size is calculated to be 2.64 nm with a narrow size distribution (Figure 2c), while it is ca. 3.31 and 3.49 nm for commercial PtRu/C-JM and home-made PtRu/C-H catalyst respectively. High Resolution Transmission Electron Microscopy (HR-TEM) was further

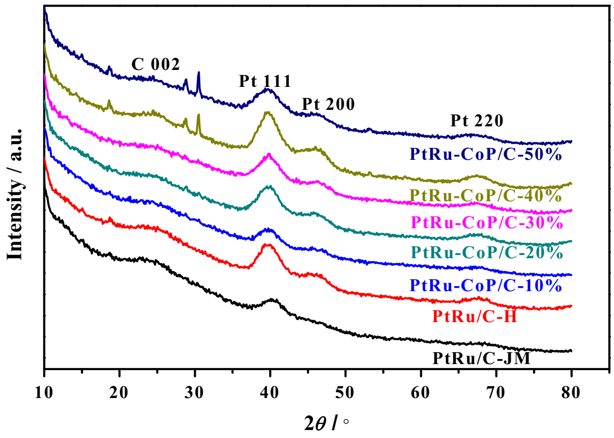


**Figure 1** XRD patterns of PtRu/C-JM, PtRu/C-H and PtRu-CoP/C.