High Methanol Tolerance of PdCo/C Catalysts for Oxygen Reduction

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Abstract: A PdCo/C catalyst was prepared by an organic colloid method using citrate as complexing agent, ethylene glycol (EG) as reducing agent and solvent. And the nanocomposition was characterized by X-ray diffraction (XRD) and energy dispersive X-ray spectroscopy (EDX). XRD patterns showed Pd particles had a face-centered cubic crystal structure and small particle size. It was found that the Pd—Pd distance decreased by the addition of Co, indicating the formation of Pd-Co alloy. The electrocatalytic activities were evaluated by oxygen reduction, which was executed with cyclic voltammetric method with a rotating disk electrode system. The Pd-Co/C catalysts showed higher catalytic activities than Pd/C catalysts and better methanol tolerance than Pt/C (Johnson-Matthey) for the oxygen reduction. The results implied that the Pd-Co/C catalyst might be a good potential cathodic catalyst for direct methanol membrane fuel cell (DMFC).

Key words: electrocatalysts; Pd—Co/C; oxygen reduction reaction; direct methanol fuel cell
CLC number: O643 Document code: A Article ID: 0529-6579 (2007) S1-0058-03

Direct methanol fuel cell (DMFC) have received considerable attention, however, their commercial viability continues to be hindered by several factors, including the poor kinetics of the cathodic reaction, the high cost of the Pt-based electrocatalysts and the crossover of methanol for DMFC[1—2]. To overcome these problems, one strategy is the development of no platinum and methanol tolerant catalyst for the oxygen reduction reaction (ORR)[3]. Pd, less expensive than Pt[4], and its alloys have been widely used as catalysts for many oxidation/reduction reactions and were considered as substitute of Pt for cathode catalyst of DMFC[5—6]. But the high temperature of their prepared process resulted in undesired metal particle growth due to the sintering of metal particles, thus hindering the activity enhancement of the alloy catalysts for ORR.

In the present study, a novel Pd-Co/C catalyst with high activity for ORR and high methanol tolerance was prepared by a modified organic colloid method at moderate temperature. It was found that the addition of cobalt could improve the activity of catalyst significantly.

1 Experimental

Pd-Co/C catalyst was prepared by an organic colloid method in an ethylene glycol (EG) solution. Palladium chloride ($PdCl_2$), cobalt (II) chloride dihydrate and sodium citrate were dissolved in ethylene glycol (EG) and then stirred for 0.5 h. Carbon black Vulcan XC-72R were added to the mixture (Pd metal loading: 20%, and Pd:Co = 2:1 in atomic ratio) under stirring conditions. The pH of the system was adjusted to > 10 with vigorous stirring. The mixture was then placed into a Teflon—lined autoclave and reacted at 160℃ for 6 h. The mixture was then filtered and washed with deionized water 3 to 5 times, followed by drying in air at 90℃. The powders were submitted to a heat treatment conducted in a tubular oven under H_2/N_2 atmosphere at 300℃ for 2 h.

The catalysts were evaluated with oxygen reduction using an IM6e electrochemistry station (Zhnar, Germany). A catalyst coated glassy carbon electrode was used as working electrode, with a platinum wire as counter electrode, and a saturated Ag/AgCl electrode as reference electrode.

X-ray diffraction (XRD) was performed on a XD-3A machine (Shimadzu, Japan) with Cu-Kα radiation.

2 Results and discussion

Fig. 1 compares the XRD patterns of the Pd/C and PdCo/C catalysts prepared by the organic colloid meth-

①收稿日期: 2007-01-10
基金项目: 国家自然科学基金资助项目 (20476034, 20673040)
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od. The diffraction peaks of PdCo/C were characteristic of a face-centered cubic (FCC) lattice, but the reflections were shifted to higher angles compared to that of Pd/C, indicating a contraction of the lattice due to alloy formation. The lattice parameters for the Pd-Co/C catalysts were smaller than those for Pd/C, signaling a progressive increase in the conversion of Co into the alloyed state. It was found that the addition of Co made the average particle size smaller and the specific surface area larger.

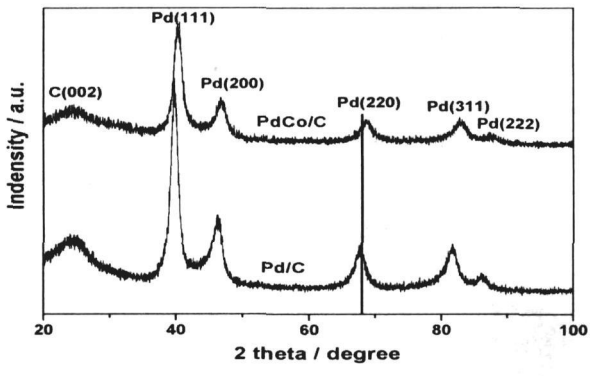

Fig. 1　X-ray diffraction (XRD) patterns for the Pd/C and PdCo/C alloys electrocatalysts

Fig. 2 shows the cyclic voltammograms of the Pd/C and PdCo/C. The hydrogen adsorption and desorption peaks were located at about −0.1 V and the Pd redox peaks were at about 0.6 V for Pd/C and 0.9 V for Pd-Co/C, respectively. It was found that the areas of the hydrogen adsorption and desorption peaks for the Pd-Co/C catalysts were larger than that for the Pd/C catalysts, indicating the electrochemically active surface area of the Pd-Co/C catalyst was larger than that of Pd/C catalyst.

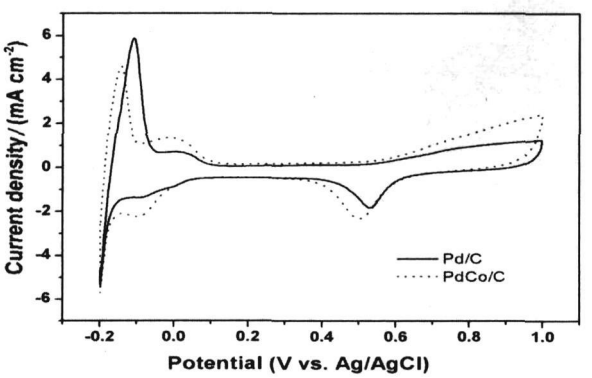

Fig. 2　Cyclic voltammograms of Pd/C and PdCo/C in 0.1 mol/L $HClO_4$ under N_2 atmosphere, scan rate = 50 mV/s, 20℃

Fig. 3 shows the slow sweep voltammograms on the Pd/C, Pt/C (Johnson-Matthey) and PdCo/C in 0.5 mol/L $HClO_4$ + 0.5 mol/L methanol under O_2 atmosphere. The Pt/C exhibited a large anodic current at about 0.6 V vs Ag/AgCl due to the methanol oxidation. The methanol oxidation caused the onset of a net cathodic current to shift cathodically by ca. 250 mV due to the formation of a mixed potential which should negatively affect the cathode performance of the DMFCs. The PdCo/C electrocatalyst showed no mixed potential in the presence of both oxygen and methanol. It was also observed that the methnol oxidation peaks on Pd-Co catalysts shifted to more positive potentials as compared to the Pd/C catalyst, indicating Pd-Co catalysts showed higher activity for methanol-tolerant oxygen reduction.

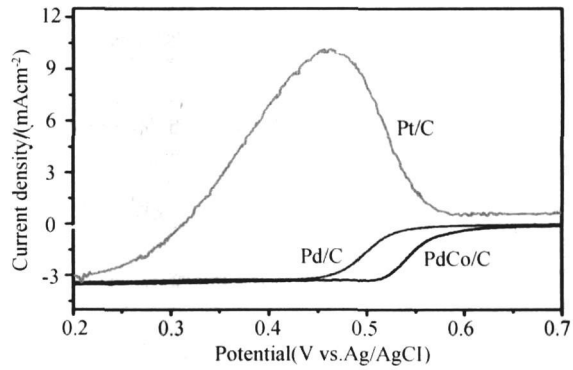

Fig. 3　Slow sweep voltammograms for Pt/C, PdCo/C and Pd/C in 0.5 mol/L $HClO_4$ + 0.5 mol/L methanol under O_2 atmosphere

3　Conclusion

PdCo/C electrocatalyst was synthesized by a modified organic colloid method in an ethylene glycol (EG) solution. The formation of Pd-Co alloy enhanced the activity for the ORR significantly compared to a pure Pd/C, and this catalyst showed good methanol tolerance, which may make it a good potential cathodic catalyst for DMFC.

Acknowledgment

We would like to thank the State Natural Science Foundation of China for the financial support (Project No. 20476034).

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PdCo/C氧还原催化剂及其抗甲醇性能

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摘 要: 以柠檬酸钠为络合剂, 在乙二醇体系中采用有机溶胶法制备出了 PdCo/C催化剂, XRD研究结果表明催化剂具有面心立方结构, 粒度小, 分散性好, 同时元素钴的加入使催化剂的 Pd—Pd间距缩小。采用电化学方法评价了催化剂对于氧气还原反应的活性, 结果表明: PdCo/C催化剂具有比 Pd/C要好的氧还原活性, 同时具有 Pt/C催化剂无法比拟的抗甲醇中毒能力。

关键词: 电催化剂; 氧还原反应; Pd-Co/C; 直接甲醇燃料电池

中图分类号: O643