ORIGINAL PAPER

Catalytic activity and stability toward methanol oxidation of PtRu/CNTs prepared by adsorption in aqueous solution and reduction in ethylene glycol

Z. H. Zhou · W. S. Li · P. P. Guo · H. Y. Yang · X. D. Xiang · L. Z. Zeng · Z. Fu

Abstract In this paper, we reported an improved process for the preparation of PtRu/CNTs, which involves the adsorption of Pt and Ru ions on CNTs in aqueous solution and the reduction of the adsorbed Pt and Ru ions on CNTs in ethylene glycol. The surface morphology, structure, and compositions of the prepared catalyst were studied by transmission electron microscopy (TEM), X-ray diffraction (XRD), and energy-dispersive spectrometer. TEM observation showed that the particles size of the prepared PtRu alloy was in the range of 2–5 nm, XRD patterns confirmed a face-centered cubic crystal structure. The activity and stability of the prepared catalyst toward methanol oxidation were studied in 0.5 M H_2SO_4+1 M CH_3OH solution by cyclic voltammetry, chronoamperometry, and chronopotentiometry. The electrochemical results showed that the prepared catalyst exhibited higher activity and stability toward methanol oxidation than commercial PtRu/C with the same loading amount of Pt and Ru.

Keywords PtRu alloy · Carbon nanotubes · Methanol oxidation

Z. H. Zhou · W. S. Li (✉) · P. P. Guo · H. Y. Yang · X. D. Xiang · L. Z. Zeng · Z. Fu
School of Chemistry and Environment,
South China Normal University,
Guangzhou 510006, China
e-mail: liwsh@scnu.edu.cn

W. S. Li
Key Lab of Electrochemical Technology on Energy Storage and Power Generation in Guangdong Universities,
Guangzhou 510006, China

Introduction

Direct methanol fuel cells (DMFCs) have attracted worldwide attention because there are many advantages for the practical application of DMFCs, such as low operating temperature, ease of handing liquid fuel, high theoretical energy density of methanol, and little pollution caused [1]. However, there are several drawbacks need to be overcome before their large-scale commercial application. The major problem that limits the further development of DMFC technology is its low energy efficiency currently attainable, which arises from the insufficient activities of the electrode catalysts [2, 3], especially toward methanol oxidation. Platinum is active for the oxidation of methanol but the reaction intermediates, such as CO_{ads}, are poisonous to the platinum catalyst [4]. Thus, considerable efforts have been devoted to develop new catalysts with higher poison tolerance and greater methanol oxidation activity. The activity of platinum toward methanol oxidation can be improved by alloying platinum with one or more other elements such as Ru [1, 5–8], Sn [9–11], and Ni [12, 13] or composites such as H_xMoO_3 [4, 14, 15] and WO_x [16, 17]. Among all the developed platinum alloys, binary PtRu alloy is believed to be the most active electrocatalyst for methanol oxidation [18, 19]. It is well known that the activity of catalysts depends on their preparation technique to a great extent. A number of strategies for the preparation of supported PtRu bimetallic catalysts were developed [20–25]. Among all the proposed preparation methods, conventional impregnation and chemical reduction is the most practical because it is simple and therefore is economical. In this process, as shown in Fig. 1, solutions containing the metal ions are mixed with supports and subsequently reductant is added so that the metals are reduced and
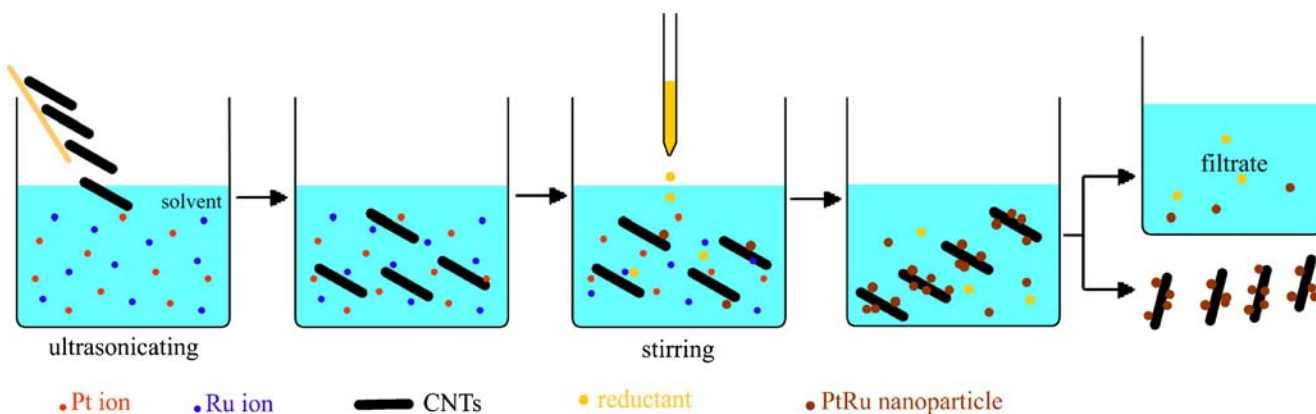
Fig. 1 Scheme of conventional impregnation and chemical reduction method for the preparation of PtRu/CNTs

simultaneously deposited on the supports. To control the particle size of the deposited metals, surfactants or stabilizers need to be introduced in the solution [26]. However, removing the surfactant or stabilizer after reduction is still a complicated problem [27]. On the other hand, the metal ions in the solution cannot be completely deposited on the supports and results in the loss of metals. To reduce the catalyst loss, metal precursors are first adsorbed on supports by immersing the supports in solution containing the metal ions, then the supports are dried and reduced with a hydrogen stream under high temperature (200–700 °C) [28, 29]. Apparently, the use of hydrogen and

the operation under high temperature add cost and complexity to the catalyst preparation.

In this work, we report an improved process to load PtRu nanoparticles on carbon nanotubes (CNTs), which involves two steps—adsorption and reduction, as shown in Fig. 2. Firstly, CNTs were thoroughly dispersed in aqueous solution containing Pt and Ru ions and then the solvent was evaporated. Secondly, the CNTs loaded Pt and Ru precursors were dispersed in ethylene glycol containing $NaBH_4$, a prevalent reductant in impregnation and chemical reduction. Ethylene glycol is used as solvent and also as particle controller [30, 31]. In the first step, the Pt and Ru
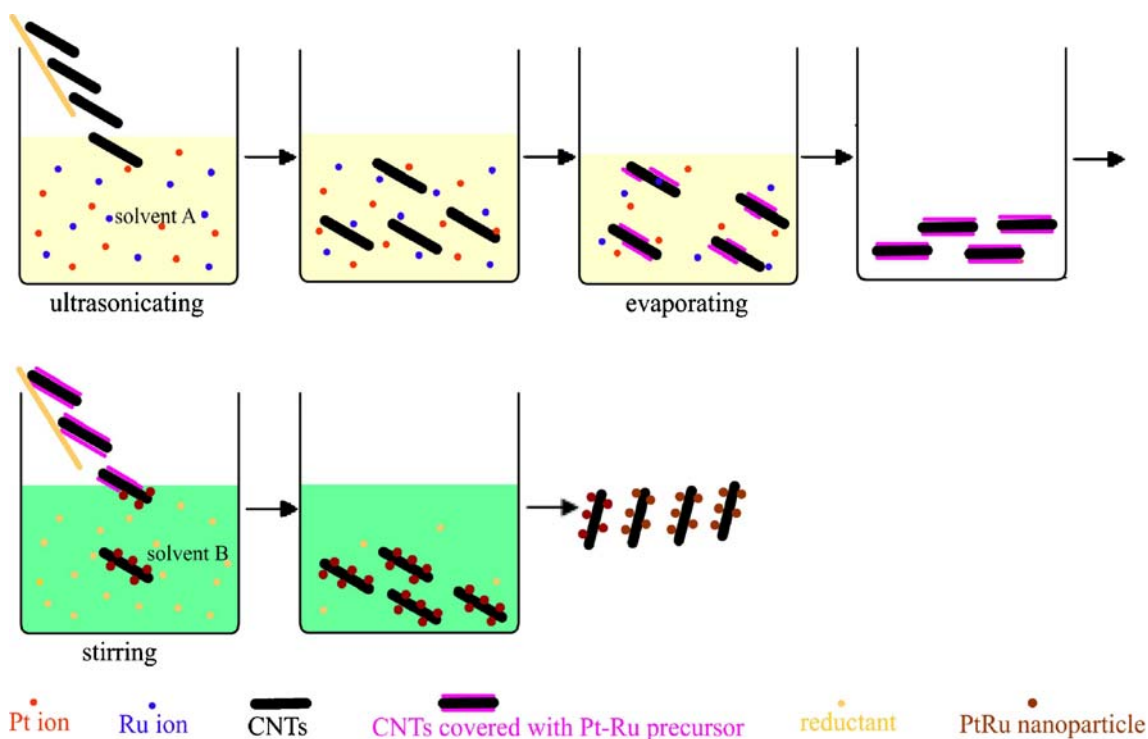

Fig. 2 Scheme of adsorption and reduction method for the preparation of PtRu/CNTs

precursors were completely and uniformly adsorbed on the supports. In the second step, the adsorbed precursors were reduced and deposited uniformly on CNTs before diffusion into solution, thus there is less loss of Pt and Ru and better combination between the catalyst and the support can be expected than the conventional impregnation and chemical reduction method. The transmission electron microscopy (TEM) results indicated that the prepared PtRu catalyst contained nanosize particles and electrochemical measurement showed better catalytic activity and stability of the prepared catalyst than commercial product.

Experimental details

Preparation

CNTs (purchased from Chengdu Institute of Organic Chemistry of CAS) were refluxed in the mixture of concentrated nitric acid and 95 wt.% sulfuric acid (V_{HNO3}: V_{H2SO4}=3:1) for 5 h, washed and dried at 100 °C in air. The treated CNTs (100 mg) were dispersed in 50 ml aqueous solution containing 2.9 mM H_2PtCl_6 and 2.8 mM $RuCl_3$ (in the amount of 20 wt.% Pt and 10 wt.% Ru for PtRu/CNT) and then the mixture was heated at 70 °C under magnetic stirring. After complete evaporation of water, all the dried mixture was dispersed in ethylene glycol containing excessive amount of 0.06 M $NaBH_4$ solution under vigorous stirring for the complete reduction of Pt and Ru precursor. The mixture was stirred for 1 h at room temperature, filtered, and washed with ethanol and deionized water successively.

Characterization

TEM (JEM-2010 ELECTRON MICROSCOPE) was employed to observe the morphology of the prepared catalyst. The composition of the catalyst was analyzed by energy-dispersive spectrometer (EDS) (Thermal field emission environmental SEM-EDS-EBSD, model Quanta 400 F). X-ray diffraction (XRD) pattern of the prepared catalyst was obtained on a Rigaku D/max 2200 vpc diffractometer operated at 30 kV and 20 mA with Cu Ka radiation.

Electrochemical measurements

The electrochemical experiments were carried out in a three-electrode configuration with a potentiostat (Eco Echemine BV). A rotating glassy carbon (GC) disk electrode with a diameter of 3 mm on an instrument (RDE, model ATA-1B) was used as working electrode, a platinum sheet electrode was used as the counter electrode and an Ag/AgCl/saturated KCl electrode was used as the reference electrode. The potentials

in this paper are with respect to this reference. A commercial catalyst (20 wt.% Pt 10 wt.% Ru/C, Johnson Mattery) was used for comparison. Catalyst powder was ultrasonically dispersed in 0.5% Nafion+C_2H_5OH solution to generate a homogeneous black suspension ink with a content of 1 mg/mL catalyst. Five microliters of this ink was pipetted onto GC electrode surface and dried at room temperature. Before the loading of catalyst, the GC electrode was polished with 0.05 μm alumina, cleaned by ultrasonicating in acetone and distilled water successively, and then cycling in 0.5 M H_2SO_4 between −0.2 and 0.9 V at 50 mV/s.

Results and discussion

Morphology and composition

Figure 3 shows the TEM image of the prepared PtRu/CNT catalyst. It can be seen from Fig. 3 that most of the catalyst is distributed on CNTs uniformly with an average particle size of 2–5 nm. The EDS in Fig. 4 gives the evidence for the presence of Pt and Ru in the composite. The contents of Pt and Ru in the prepared catalyst, estimated by EDS, are 21 and 14 wt.%, respectively. The result is not exactly equal but close to the amount in preparation solution, because the EDS analysis gives the only semiquantitative result.

The prepared catalyst PtRu/CNTs was characterized by powder XRD and the result is shown in Fig. 5. XRD is a bulk analysis that reveals the crystal structure, lattice constants, and crystal orientation of the supported catalysts. Pure Pt has a face-centered cubic (fcc) crystal structure [32]. With the addition of Ru, which has a hexagonal closed-
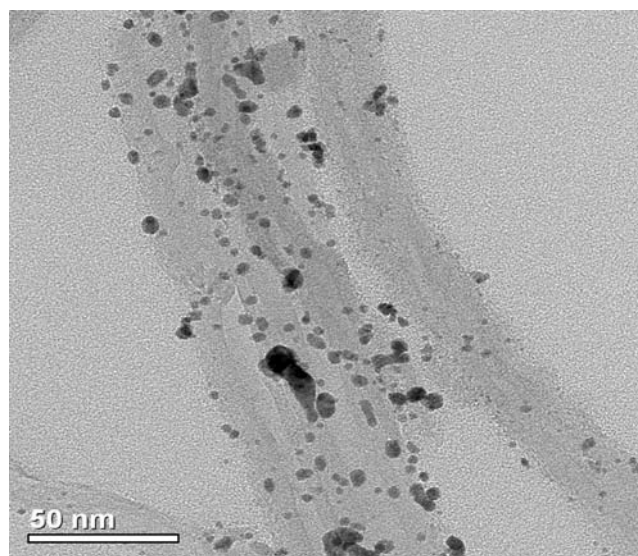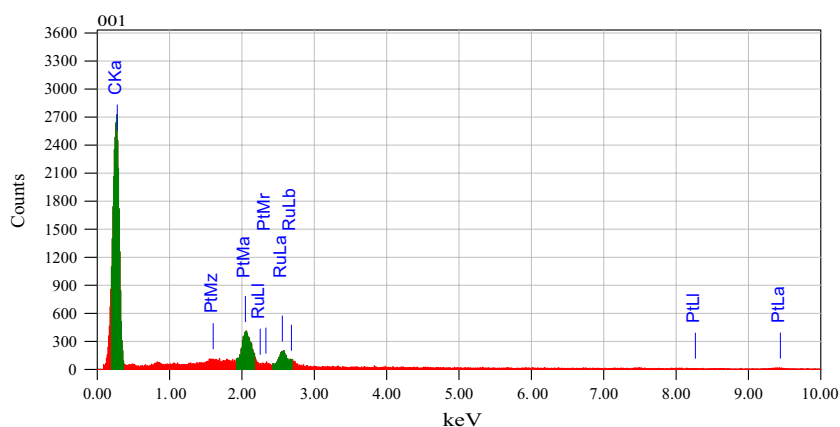

Fig. 3 TEM image of the prepared catalyst PtRu/CNTs

packed (hcp) crystal structure, the diffraction peaks of the PtRu broaden and shift to higher 2θ values [33]. The diffraction peaks of Pt fcc appeared in XRD of PtRu alloys containing up to 52 wt.% Ru [34]. Our result, as shown in Fig. 5, is very consistent with this report. The sharp peak at 2θ≈26° is associated with the graphite-like structure of the CNT support [35, 36]. The peaks at 2θ≈40°, 47°, 68°, and 82° can be attributed to the (111), (200), (220), and (311) crystalline planes of the face-centered cubic structure, which are characteristic of Pt fcc structure. Ru atoms may introduce some decrease of the Pt lattice parameter value due to some Ru insertion into the Pt fcc structure.

Electrocatalytic activity toward methanol oxidation

The electrocatalytic activity of the prepared catalyst PtRu/CNTs toward methanol oxidation was characterized by cyclic voltammertry in 0.5 M H_2SO_4+1 M CH_3OH solution at 50 mV/s. Figure 6 shows the voltammograms of cycle number from 1 to 4 (Fig. 6A) and number 5, 10, 15, 20, and 30 (from a to e in Fig. 6B). The early cycles exhibit a low
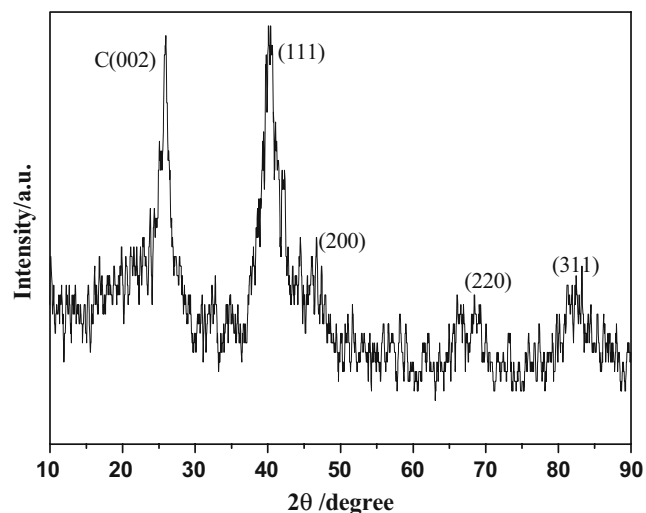
peak current and lower peak potential in the forward scan. As the cycle number increases, the peak potential in the forward scan shifts more positively and the peak current increases gradually. This phenomenon can be ascribed to the leaching of ruthenium during the cycling [5, 37]. Similar results were also observed for the commercial catalyst PtRu/C (Johnson Mattery), as shown in Fig. 6(A′ and B′).

Figure 7 compares the voltammograms of the prepared catalyst PtRu/CNTs and the commercial catalyst PtRu/C with the same loading of Pt and Ru in 0.5 M H_2SO_4+1 M CH_3OH solution at 30th cycle. As can be seen from Fig. 7, the current density of methanol oxidation on PtRu/CNTs is higher than that on PtRu/C at the same potential. For example, at 0.68 V, the peak potential for the forward scan, the current density of methanol oxidation on PtRu/CNTs is 31 mA/cm^2, 55% higher than that on PtRu/C whose current density is only 20 mA/cm^2.

Figure 8 compares the chronoamprometric curves of the prepared catalyst PtRu/CNTs and the commercial catalyst PtRu/C at 0.6 V in 0.5 M H_2SO_4+1 M CH_3OH solution for 1,000 s. It can be seen from Fig. 8 that the PtRu/CNTs maintains a higher current density than does the PtRu/C.

Chronopotentiometry is a useful approach to study the antipoisoning ability of catalysts for methanol oxidation [38]. The chronopotentiometric curve of the prepared catalyst PtRu/CNTs was compared with that of the commercial catalyst PtRu/C. To diminish the influence of current density on the antipoisoning ability of the catalysts, the value of the applied anodic current density is the same as that of the current density at 0.4 V on the forward branch in the corresponding cyclic voltammograms, which is 4.7 mA/cm^2 and 3.6 mA/cm^2 for PtRu/CNTs and PtRu/C, respectively. The results were shown in Fig. 9. It can be seen from Fig. 9 that the potential increases gradually for a long time and then jumps to a higher potential. The reason for this has been given [38, 39]: during the chronopotentio-metric experiment, the poisonous species, mainly CO_{ads} resulting from methanol oxidation, are accumulated on the surface of electrocatalysts and reduce the electrocatalytic
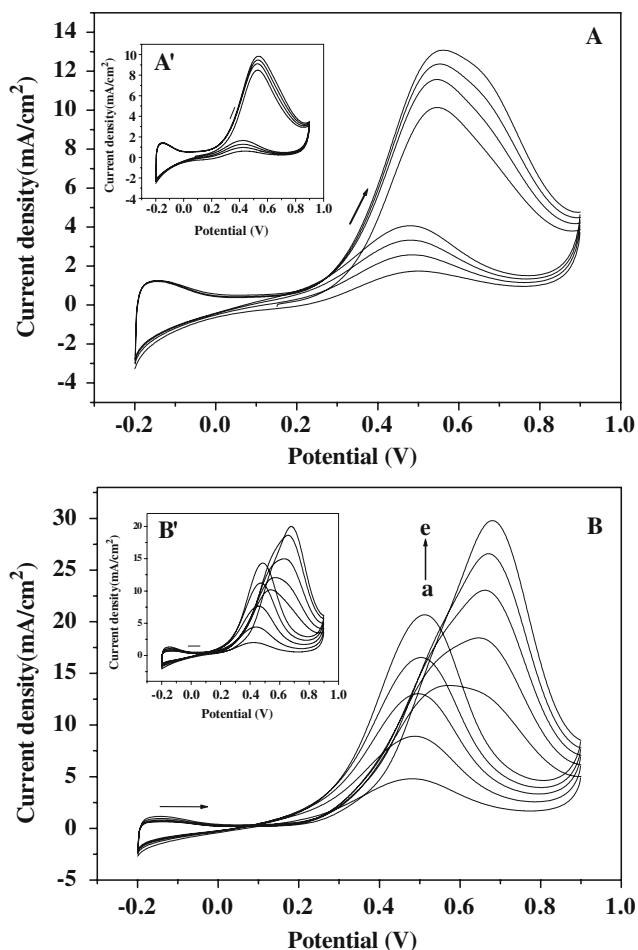

Fig. 5 XRD pattern of the prepared catalyst PtRu/CNTs

Fig. 6 Cyclic voltammograms of the prepared catalyst PtRu/CNTs (**A**, **B**) and the commercial catalyst PtRu/C (*A′*, *B′*) in 0.5 M H$_2$SO$_4$+ 1 M CH$_3$OH solution during cycles 1-4 (**A**, *A′*) and cycles 5, 10, 15, 20, 30 from *a* to *e* (**B**, *B′*). Scan rate, 50 mV/s

Fig. 8 Chronoamperometric curves for the prepared catalyst PtRu/CNTs and the commercial catalyst PtRu/C in 0.5 M H$_2$SO$_4$+1 M CH$_3$OH solution at 0.6 V

activity of catalysts. The potential must be increased to satisfy the applied anodic current density. When the electrocatalysts are poisoned deeply, the methanol oxidation reaction cannot continue. To satisfy the applied anodic current density, the potential must jump to a higher potential, at which H$_2$O is decomposed.

Here, the time (*T*) at which the electrode potential jumps to a higher potential is introduced to judge the antipoisoning ability of catalysts. The *T* of PtRu/CNTs is 3,000 s, over two times that of PtRu/C, which is less than 1,500 s.

It is obvious that the prepared catalyst PtRu/CNTs shows its better activity and stability toward methanol oxidation than the commercial catalyst PtRu/C that has the same loading amount of Pt and Ru. The improvement in catalytic activity and stability can be ascribed to the uniform distribution of PtRu alloy on support CNTs and the good
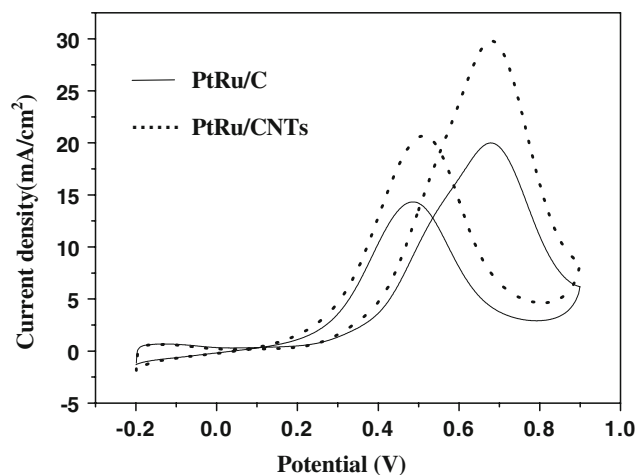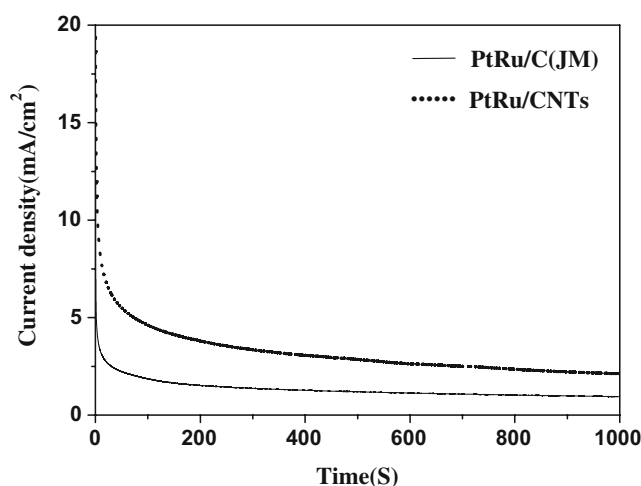

Fig. 7 Cyclic voltammograms of the prepared catalyst PtRu/CNTs and the commercial catalyst PtRu/C in 0.5 M H$_2$SO$_4$+1 M CH$_3$OH solution at the 30th cycle. Scan rate, 50 mV/s
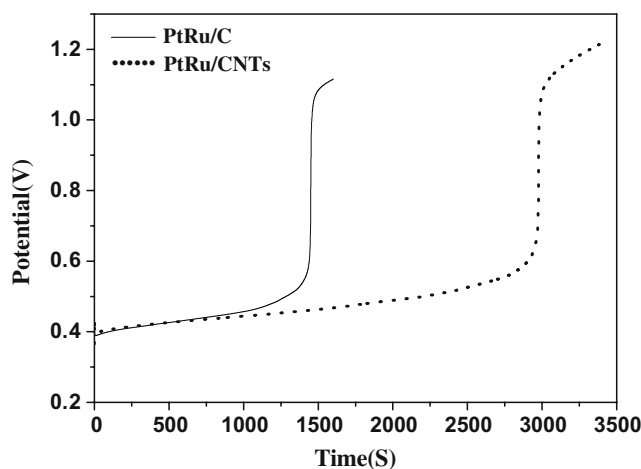

Fig. 9 Chronopotentiometric curves for the prepared catalyst PtRu/CNTs and the commercial catalyst PtRu/C in 0.5 M H$_2$SO$_4$+1 M CH$_3$OH solution

combination between PtRu alloy and the support CNTs. The mechanism for the methanol oxidation on the prepared catalyst should be the same as that on the conventional PtRu catalyst, which has been well understood [40–43].

Conclusions

A catalyst PtRu/CNTs, which has better activity and stability toward methanol oxidation than a commercial catalyst PtRu/C with the same loading amount of Pt and Ru, can be prepared by an improved process on the base of conventional impregnation and chemical reduction. This method is simple and operated under mild condition with little loss of precious metals. The first adsorption of Pt and Ru ions on the support and following reduction of adsorbed Pt and Ru precursors on the support contribute the more uniform distribution of PtRu alloy on the support and better combination between PtRu alloy and support, resulting in better catalytic activity and stability of the catalyst toward methanol oxidation.

References

1. Li HQ, Sun GQ, Gao Y, Jiang Q, Jia ZQ, Xin Q (2007) J Phys Chem C 111:15192. doi:10.1021/jp073072m
2. Bang JH, Han K, Skrabalak SE, Kim H, Suslick KS (2007) J Phys Chem C 111:10959. doi:10.1021/jp071624v
3. Lu QY, Yang B, Zhuang L, Lu JT (2005) J Phys Chem B 109:1715. doi:10.1021/jp0461652
4. Wu YM, Li WS, Lua J, Dua JH, Lua DS, Fu JM (2005) J Power Sources 145:286. doi:10.1016/j.jpowsour.2005.01.065
5. Lin YH, Cui XL, Yen CH, Wai CM (2005) Langmuir 21:11474. doi:10.1021/la051272o
6. Bensebaa F, Farah AA, Wang DS, Bock C, Du XM, Kung J, Page YL (2005) J Phys Chem B 109:15339. doi:10.1021/jp0519870
7. Liu ZL, Lee JY, Chen WX, Han M, Gan LM (2004) Langmuir 20:181. doi:10.1021/la035204i
8. Yang B, Lu QY, Wang Y, Zhuang L, Lu JT, Liu PF (2003) Chem Mater 15:3552. doi:10.1021/cm034306r
9. Stalnionis G, Tamašauskaitė-Tamašiūnaitė L, Pautienienė V, Jusys Z (2004) J Solid State Electrochem 8:900. doi:10.1007/s10008-004-0516-y
10. González MJ, Peters CH, Wrighton MS (2001) J Phys Chem B 105:5470. doi:10.1021/jp0045336
11. Emerilis C-R, Volpe DJ, Alden L, Lind C, Downie C, Terannie V-A, Angelo ACD, DiSalvo FJ, Abruña HD (2004) J Am Chem Soc 126:4043. doi:10.1021/ja038497a
12. Park K-W, Choi J-H, Sung Y-E (2003) J Phys Chem B 107:5851. doi:10.1021/jp0340966
13. Liu F, Lee JY, Zhou WJ (2004) J Phys Chem B 108:17959. doi:10.1021/jp0472360
14. Li WS, Lu J, Du JH, Lu DS, Chen HY, Li H, Wu YM (2005) Electrochem Commun 7:406. doi:10.1016/j.elecom.2005.02.004
15. Li WS, Tian LP, Huang QM, Li H, Chen HY, Lian XP (2002) J Power Sources 104:281. doi:10.1016/S0378-7753(01)00961-2
16. Park K-W, Ahn K-S, Nah Y-C, Choi J-H, Sung Y-E (2003) J Phys Chem B 107:4352. doi:10.1021/jp022515d
17. Shafia Hoor F, Ahmed MF, Mayanna SM (2004) J Solid State Electrochem 8:572. doi:10.1007/s10008-004-0501-5
18. Aricò AS, Srinivasan S, Antonucci V (2001) Fuel Cells (Weinh) 1:133. doi:10.1002/1615-6854(200107)1:2<133::AID-FUCE133>3.0.CO;2-5
19. Garcia G, Baglio V, Stassi A, Pastor E, Antonucci V, Aricò AS (2007) J Solid State Electrochem 11:1229. doi:10.1007/s10008-007-0274-8
20. Liang YM, Zhang HM, Yi BL, Zhang ZH, Tan ZC (2005) Carbon 43:3144. doi:10.1016/j.carbon.2005.06.017
21. Spinacé EV, Neto AO, Linardi M (2004) J Power Sources 129:121. doi:10.1016/j.jpowsour.2003.11.056
22. Che GL, Lakshmi BB, Martin CR, Fisher ER (1999) Langmuir 15:750. doi:10.1021/la980663i
23. Missiroli A, Soavi F, Mastragostino M (2005) Electrochem Solid-State Lett 8:A110. doi:10.1149/1.1847686
24. He ZB, Chen JH, Liu DY, Zhou HH, Kuang YF (2004) Diam Relat Mater 13:1764. doi:10.1016/j.diamond.2004.03.004
25. Yang CW, Hu XG, Wang DL, Dai CS, Zhang L, Jin HB, Agathopoulos S (2006) J Power Sources 160:187. doi:10.1016/j.jpowsour.2006.05.015
26. Guo JW, Zhao TS, Prabhuram J, Chen R, Wong CW (2005) Electrochim Acta 51:754. doi:10.1016/j.electacta.2005.05.056
27. Tu H-C, Wang W-L, Wan C-C, Wang Y-Y (2006) J Phys Chem B 110:15988. doi:10.1021/jp061638l
28. Carmo M, Paganin VA, Rosolen JM, Gonzalez ER (2005) J Power Sources 142:169. doi:10.1016/j.jpowsour.2004.10.023
29. Yang B, Lu Q, Wang Y, Zhang L, Lu J, Liu P (2003) Chem Mater 15:3552. doi:10.1021/cm034306r
30. Tsai M-C, Yeh T-K, Tsai C-H (2006) Electrochem Commun 8:1445. doi:10.1016/j.elecom.2006.07.003
31. Li WZ, Liang CH, Zhou WJ, Qiu JS, Zhou ZH, Sun GQ (2003) J Phys Chem B 107:6292. doi:10.1021/jp022505c
32. Solla-Gullón J, Vidal-Iglesias FJ, Montiel V, Aldaz A (2004) Electrochim Acta 49:5079. doi:10.1016/j.electacta.2004.06.017
33. Liu ZL, Ling XY, Su XD, Lee JY (2004) J Phys Chem B 108:8234. doi:10.1021/jp049422b
34. Deivaraj TC, Lee JY (2005) J Power Sources 142:43. doi:10.1016/j.jpowsour.2004.10.010
35. Wu T-M, Lin Y-W, Liao C-S (2005) Carbon 43:734. doi:10.1016/j.carbon.2004.10.043
36. Li WZ, Liang CH, Zhou WJ, Qiu JS, Zhou ZH, Sun GQ, Xin Q (2003) J Phys Chem B 107:6292. doi:10.1021/jp022505c
37. Holstein WL, Rosenfeld HD (2005) J Phys Chem B 109:2176. doi:10.1021/jp048955h
38. Krausa M, Vielstich W (1995) J Electroanal Chem 399:7. doi:10.1016/0022-0728(95)04249-0
39. Chen JH, Wang MY, Liu B, Fan Z, Cui KZ, Kuang YF (2006) J Phys Chem B 110:11775. doi:10.1021/jp061045a
40. Breiter MW (1967) Electrochim Acta 12:1213. doi:10.1016/0013-4686(67)80036-7
41. Iwasita T (2002) Electrochim Acta 47:3663. doi:10.1016/S0013-4686(02)00336-5
42. Watanabe M, Motoo S (1975) J Electroanal Chem 60:267. doi:10.1016/S0022-0728(75)80261-0
43. Iwasita T, Hoster H, John-Anacker A, Lin WF, Vielstich W (2000) Langmuir 16:522. doi:10.1021/la990594n