

SYNTHESIS AND CHARACTERIZATIONS OF CORE SHELL NANO-STRUCTURED BIMETALLIC CoPt ELECTROCATALYST BY TRANSMETALLATION FOR OXYGEN REDUCTION REACTION

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Introduction

The slow kinetic of oxygen reduction reaction (ORR) at the cathode of proton exchange membrane fuel cells (PEMFCs) leads to increasing the overpotential of ORR and the power loss of PEMFCs. Up to date platinum (Pt) exhibits the best performances for ORR compared with the other single element electrocatalysts. The electrocatalytic activity of ORR can be promoted by increasing the electroactive area due to the decrease in the Pt particle size, optimizing the Pt crystal structure and using alloying Pt (Pt-M, M = Ti, Co, Cr, Ni Fe) as the cathodic materials [1].

The dissolution of the transition metals from Pt-M used as the cathodic electrocatalysts of PEMFCs results in the decrease in the electroactivity of ORR and the performance of PEMFCs due to the inhibition of ORR by the dissolving M^{m+} in the electrolyte [2-4]. A promising way to overcome the dissolution of transition metal from Pt-M is to prepare the Pt-M with transition metals in core and Pt in shell. To date, several researches indicate that the order of ORR activities is 'Pt-skin' > Pt-M > Pt, i.e. the catalytic enhancement for the 'Pt-skin' being higher than that for pure Pt and Pt-M alloy [5-9]. In this study, the nano-structured core-shell type bimetallic $Co_{rich\ core}-Pt_{rich\ shell}/C$ electrocatalysts were prepared by the thermal decomposition to synthesize Co core and followed by the transmetallation to prepare Pt shell. The characteristics and the electrochemical properties of the home-made nano-structured electrocatalyst were also investigated.

Experimental

In this study, two procedures were used to prepare $Co_{rich\ core}-Pt_{rich\ shell}/C$ electrocatalysts. One of the procedures was prepared Co core on C by the thermal decomposition of cobalt precursor, and followed by the transmetallation method to prepared Pt shell (procedure 1). The other one was prepared Co core by the thermal decomposition, and followed by the transmetallation and polyol reductions in series to prepare a thicker Pt shell (procedure 2). The electroactive areas, characteristics of ORR on $Co_{rich\ core}-Pt_{rich\ shell}/C$ electrocatalysts was studied

by the cyclic voltammetry (CV) and linear sweep voltammetry (LSV) in 0.5 M $HClO_4$ aqueous solution.

Results and Discussion

The particle sizes of Co core and $Co_{rich\ core}-Pt_{rich\ shell}$ on the carbon support were analyzed by TEM to be 1~2 nm. The Pt and Co loadings of $Co_{rich\ core}-Pt_{rich\ shell}/C$ prepared by procedure 1 with transmetallation time of 2, 4, 6 and 8 h were analyzed by atomic adsorption spectrometry (AAs) to be 0.74, 1.34, 2.01, 2.19 % and 12.09, 11.76, 11.68, 10.87 %, respectively. The electroactive area of Pt of electroatylasts prepared by procedure 1 could not be defined due to the unobvious CV peaks for oxidizing the hydrogen adsorbed on Pt surface as shown in Fig. 1(a). The LSVs of ORR on $Co_{rich\ core}-Pt_{rich\ shell}/C$ (procedure 1) in 0.5M $HClO_4$ aqueous solution saturated with O_2 were illustrated in Fig. 1(b). Comparing with the home-made Pt/C, the kinetic controlled region on $Co_{rich\ core}-Pt_{rich\ shell}/C$ electrocatalysts (procedure 1) was located at a relative lower potential region. Consequently the lower mass activity (MA) of ORR was found in Table 1, and revealed that electroactivity of ORR on $Co_{rich\ core}-Pt_{rich\ shell}/C$ (procedure 1) was less than that on Pt/C. The experimental results were inferred to the incomplete protection of Co core by the relative thinner Pt shell, and resulted in the dissolution of Co. Therefore, the polyol reduction step followed by the Pt transmetallation was used to increasing the Pt loading and thickening the Pt shell.

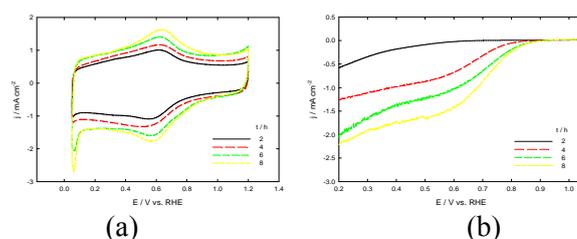


Fig. 1(a) Cyclic voltammograms (b) Linear scan voltammograms of ORR on $Co_{rich\ core}-Pt_{rich\ shell}/C$ (procedure 1) with various transmetallation times for preparing Pt shell.

Table 1 Characteristics of ORR on Co_{rich} core-Pt_{rich} shell/C prepared for various transmetallation times (procedure 1).

t _t ¹ h	OCP ² V	c.d. ³ mA cm ⁻²	MA ⁴ A g ⁻¹
2	0.800	0.001	0.24
4	0.937	0.016	2.08
6	0.978	0.024	2.08
8	0.987	0.027	2.15

¹: transmetallation time, ²: open circuit potential, ³: current density measured at overpotential of 0.1 V, ⁴: mass activity measured at overpotential of 0.1 V.

When Co_{rich} core-Pt_{rich} shell/C was prepared by procedure 2 with the designed Co/Pt atomic ratios of 2.75, 5.52 and 8.25, the Co loadings of 8.87, 8.87, 22.08 %, the Pt loadings of 12.75, 8.2, 7.94 %, and the Co/Pt atomic ratios of 2.29, 5.74 and 9.19 were experimentally obtained. The good dispersive of the preparing electrocatalysts were obtained, and the particle size of Co_{rich} core-Pt_{rich} shell with Co/Pt atomic ratio of 5.74 was found in the range of 1~4 nm (Fig. 2). The electroactive areas of Co_{rich} core-Pt_{rich} shell/C (procedure 2) with Co/Pt atomic ratios of 2.29, 5.74 and 9.19 were obtained from Fig. 3(a) to be 21.09, 24.57 and 23.33 m² g⁻¹, respectively. The potential for kinetic controlled region of ORR on Co_{rich} core-Pt_{rich} shell/C (procedure 2) found from LSV (Fig. 3(b)) was moved to a more positive value than that obtained on electrocatalysts prepared by procedure 1. The maximum c.d., MA and SA of ORR measured from the LSVs at the overpotential of 0.1V on Co_{rich} core-Pt_{rich} shell/C (procedure 2) were obtained to be 0.93 mA cm⁻², 19.40 A g⁻¹ and 78.95 μA cm⁻², respectively, for Co/Pt ratio of 5.74 (Table 2).

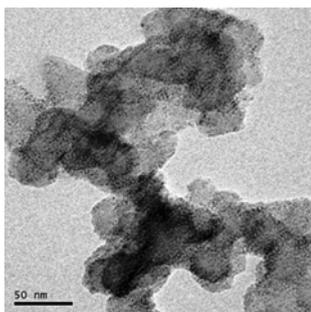


Fig. 2 TEM micrograph of Co_{rich} core-Pt_{rich} shell/C (procedure 2) with Co/Pt atomic ratio of 5.74.

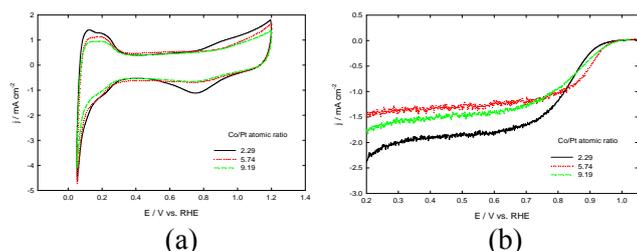


Fig. 3(a) Cyclic voltammograms (b) Linear scan voltammograms of ORR on Co_{rich} core-Pt_{rich} shell/C (procedure 2) with various Co/Pt atomic ratios.

Table 2 Characteristics of ORR on Co_{rich} core-Pt_{rich} shell/C (procedure 2) with various Co/Pt atomic ratios.

atomic ratio of Co/Pt	OCP V	c. d. ¹ mA cm ⁻²	MA ² A g ⁻¹	SA ³ μA cm ⁻²
2.29	0.987	0.36	4.87	23.09
5.74	1.004	0.93	19.40	78.95
9.19	0.991	0.72	15.61	66.09

^{1,2,3}: values measured at overpotential of 0.1 V.

Conclusions

Compared with Co_{rich} core-Pt_{rich} shell/C prepared by procedure 2 the less electroactivities of ORR on electrocatalysts prepared by procedure 1 was inferred to be a faster Co dissolution rate caused by a lower Pt loading and thinner Pt shell. The maximum MA and SA of ORR measured at the overpotential of 0.1V on Co_{rich} core-Pt_{rich} shell/C were obtained to be 19.40 A g⁻¹ and 78.95 μA cm⁻², respectively, for the electrocatalysts prepared by procedure 2 with Co/Pt atomic ratio of 5.74. Furthermore these maximum MA and SA values of ORR were 1.80 and 5.25 folds of home-made Pt/C with the similar Pt loadings.

References

- Alonso-Vante N. and Tributsch H., Nature, (1986) 323, 431-432
- Okada T., Ayato Y., Yuasa M. and Sekine I., J. Phys. Chem. B., (1999) 103(17); 3315-3322.
- Adžić R. R. and Wang J. X., Electrochimica Acta (2000) 45, 2403–2421.
- Greeley, J.; Norskov, J. K, Electrochimica Acta (2007) 52(19), 5829-5836.
- Ma, Y. and Balbuena, P. B., Surface Science (2008) 602(1), 107-113.
- Stamenkovic, V. R., Mun, B. Simon., Mayrhofer, K. J. J.; Ross, P. N. and Markovic, N. M, Journal of the American Chemical Society (2006) 128(27), 8813-8819.
- Mun, B. S., Watanabe, M., Rossi, M., Stamenkovic, V.; Markovic, N. M. and Ross, P. N., Jr., Journal of Chemical Physics (2005) 123(20), 204717/1-204717/4.
- Teliska, M., Murthi, V. S., Mukerjee, S. and Ramaker, D. E., Journal of the Electrochemical Society (2005) 152(11), A2159-A2169.
- Stamenkovic, V.; Schmidt, T. J.; Ross, P. N. and Markovic, N. M., Journal of Electroanalytical Chemistry (2003) 554-555 191-199.