Novel synthesis and characterization of Pt-Cu alloy nanoparticles for oxygen reduction reaction in PEMFCs

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Introduction

Pt-M (M=first row transition metal) alloy have been investigated widely to improve the electrocatalytic activity of pure Pt for oxygen reduction reaction [1-2]. In most cases, the Pt alloys had to be prepared at >700°C in order to obtain homogenous alloys that are stable in acidic media. Recently, Pt alloy nanoparticles had also been prepared in situ on high surface area carbon support by aqueous route [3] or by microemulsion [4]. However, thus-obtained Pt alloy nanoparticles had wide size distribution. On the other hand, nanoparticles sitting in the inner pores of carbon support may not be utilized due to the inaccessibility of Nafion electrolyte which is widely used to prepare catalyst layer. Monodispersed Pt alloy nanoparticles can be easily obtained by colloid method [5-6].

In this study, we present the synthesis and characterization of carbon-supported Pt-Cu alloy nanoparticles and its electrocatalytic activity for oxygen reduction reaction in PEMFCs.

Materials and Methods

PVP (Poly(N-vinyl-2-pyrrolidone), MW: 55000), EG (ethylene glycol), $H_2PtCl_6 \cdot 6H_2O$, $CuSO_4 \cdot 5H_2O$, and NaOH were purchased from Sigma. Deionized water (18.2MΩ @25°C) was obtained from Millipore.

PVP-PtCu alloy nanoparticles were synthesized via reduction of $CuSO_4 \cdot 5H_2O$ and $H_2PtCl_6 \cdot 6H_2O$ in ethylene glycol in the presence of PVP under a nitrogen flow. The nanoparticles were separated from solvent by the addition of acetone and centrifugation. The nanoparticles were redispersed in deionized water, iso-propanol and Nafion solution. XC-72 was added in the dispersion and the mixture was ultrasonicated for 2hr. TEM and XRD was used to examine the particle size and structure. Electrocatalytic activity was characterized using rotating disk electrode (PINE instruments) connected with EG&G potentiostat.

Results and Discussion

Fig 1 shows the TEM image and particle size distribution of PVP stabilized PtCu nanoparticles prepared by polyol method. The results show that PtCu nanoparticles are monodispersed and have a very narrow size distribution. The average particle size is around 2.1nm. Fig 2 shows XRD pattern of PVP stabilized Pt, Cu, PtCu and $PtCu_3$ nanoparticles. It indicates that PtCu and PtCu3 nanoparticles are well alloyed with face centered cubic structure, not the simple mixture of Pt and Cu nanoparticles. The volume average particle size obtained from Scherre equation is close to that obtained from TEM image.

Fig 3 compares the electrocatalytic activity of PVP-PtCu nanoparticles supported on XC-72 and Pt/C (20%, E-TEK). As can be seen in Fig 3, PVP stabilized PtCu nanoparticles exhibits higher electrocatalytic activity than Pt/C (20% E-TEK).

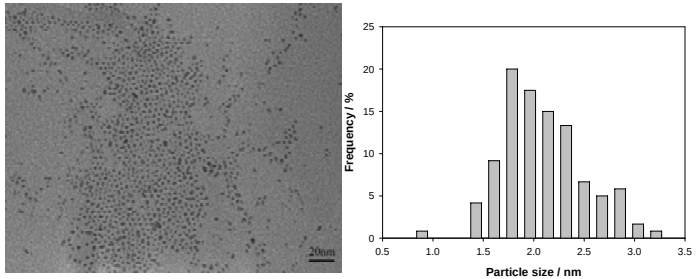

Fig 1 TEM image and particle size distribution of PVP-Pt/Cu nanoparticles

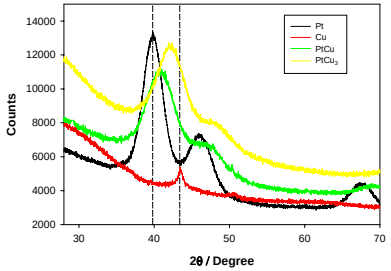

Fig 2 XRD pattern of PVP stabilized Pt, Cu, PtCu and Pt/Cu_3 nanoparticles

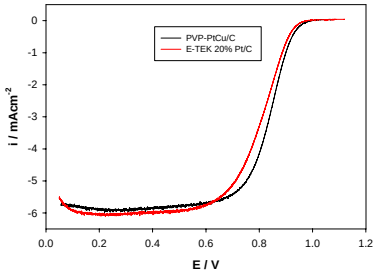

Fig 3 Polarization curves for oxygen reduction reaction on PVP-PtCu/C and E-TEK 20% Pt/C in O_2 saturated 0.1M $HClO_4$ at 25°C

Significance

Monodispersed Pt alloy electrocatalysts supported on high surface area carbon can be prepared colloidal method followed by introducing carbon support. By this method, both the size and composition of the colloidal precursors can be tailored independently of support.

References

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