

HIGHLY EFFICIENT Pt₅₀-Ru₅₀ ELECTROCATALYSTS SUPPORTED BY POROUS CARBONS WITH ORDERED UNIFORM CONTROLLABLE PORES

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Received: June 17, 2005

Abstract. Ordered uniform nanoporous carbons with pore sizes in the range of 10 – 600 nm were synthesized against removable colloidal crystalline templates by carbonization of phenol and formaldehyde as a carbon precursor. The porous carbons have high surface areas, large pore volumes, and three-dimensionally interconnected uniform pore structures, and thus were used as a support of a Pt₅₀-Ru₅₀ alloy catalyst to study their effect on the anodic performance of the catalyst in direct methanol fuel cell. The ordered uniform porous carbon allowed higher degree of dispersion of the catalysts and efficient diffusion of reagents, resulting in much improved catalytic activity for methanol oxidation in the fuel cell. In general, the smaller pore sizes the porous carbons have, the higher surface areas and the better catalytic activity for methanol oxidation they showed.

1. INTRODUCTION

Direct methanol fuel cell (DMFC) has recently attracted great attention for its future potential as a clean and ideal power source. Metal catalysts are generally dispersed as small particles on conductive carbon supports with high surface area in order to give the high dispersion of the catalysts [1,2]. Recently, in addition to the development of new catalysts themselves there also arises a great attention for new carbon materials as supports as well in order to help achieve optimum catalytic performance. High surface area and well-developed porosity are essential for a catalyst support to result in high catalytic activities. Carbon black, called Vulcan XC-72 has been commonly used as a car-

bon support for electrode catalysts in DMFCs [3]. Vulcan XC-72 carbon consists of aggregation of amorphous carbon nanoparticles with size in the range of 30 ~ 60 nm. In fact, commercially available E-TEK catalysts are Pt-Ru alloys supported on the Vulcan XC-72. Several different carbon materials such as graphitic carbon nanofiber [4], carbon nanotubes [5] and mesocarbon microbead (MCMB) [6] were also reported as supports of Pt or Pt alloy catalysts mainly for higher dispersion of the catalysts and for improved synergic effects.

Recently, a remarkable progress has been made in the synthesis of carbons with periodic porous structures using templates, such as ordered mesoporous silicas [7] and silica colloidal crystals

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[8] for the synthesis of ordered mesoporous (2-50 nm) and macroporous (>50 nm) carbons, respectively. Fabrication of new uniform porous carbons with spherical cavities of 50-70 nm in diameter interconnected to each other was reported through colloidal crystalline templates by carbonization of sugars and polymers [9]. In our earlier work, highly ordered uniform porous carbons with spherical cavity of ~ 200 nm in diameter were synthesized by template replication of colloidal crystals [10]. Pt(50)-Ru(50) catalyst supported on these ordered uniform porous carbon increased methanol oxidation activity compared to that of the commercially available Pt-Ru alloy catalyst by about 15%. One of the advantages of the colloidal crystalline template method is that the pore sizes of the carbon structure can be easily controlled in the range of several nm to several μm by varying the silica spheres in the colloidal crystal template. Such pore size control can render porous carbons with regulated surface area, pore volume and structural integrity. Here we report the synthesis of uniform porous carbons with controllable pore sizes through the colloidal crystal templates of silica spheres of 10 ~ 600 nm in diameter and their utilization as supports for Pt-Ru catalysts in DMFC.

2. EXPERIMENTAL DETAILS

Several monodisperse silica nanoparticles in the range of 10 – 600 nm were synthesized using a modification of the procedure described by Osseo-Asare *et al.* and Stober *et al.* [11]. Uniform porous carbon replica was synthesized against a colloidal crystal template by polymerization of phenol and formaldehyde as a carbon precursor according to the reported methods [9-10]. The resulting ordered porous carbons were termed C-X, where X indicates the pore size of the carbons.

The Pt₅₀-Ru₅₀ catalysts were prepared by borohydride reduction method using equal molar solutions of Pt and Ru sources [10]. The metal loading was 60 wt.% for a Vulcan XC-72 like the commercially available E-TEK catalyst, and 80 wt% for the porous carbons, C-Xs. The resulting supported catalysts were named as PtRu-C-X, where X indicates pore size of the carbon support. The Pt-Ru catalyst prepared on Vulcan XC-72 carbon black was named as PtRu-VC.

The nitrogen adsorption and desorption isotherms were measured at 77K using a Micromeritics ASAP 2010 system. X-ray diffraction patterns of the supported catalysts were obtained with a Rigaku diffractometer with Cu K α radiation at a scan rate of

4 °/min. The microscopic features of the sample were observed with a transmission electron microscope (TEM, EM 912 Omega) operated at 200 kV.

Cyclic voltammetric measurements were carried out in a three-electrode cell with Ag/AgCl (in saturated KCl) as a reference electrode and platinum gauze as a counter electrode. Cell performance was evaluated using a DMFC unit cell, and measured with a potentiometer, which can record cell potentials from the circuit voltage under constant current conditions.

3. RESULTS AND DISCUSSION

Fig. 1 shows TEM images of the resulting porous carbons with 25, 68, 245, and 512 nm in pore diameter, respectively. The pores are uniform, close-packed and roughly spherical, resulting in the formation of highly ordered nanoporous carbon framework in the case of the C-68, C-245 and C-512. Each of spherical pores is also three dimensionally interconnected to neighbouring pores through small holes, which were generated at the contact points between silica spheres close-packed in colloidal crystal templates. Such highly ordered structures were predominantly observed for the porous carbons with relatively large pore sizes of 50 nm and higher. However, it is challenging to synthesize uniform silica spheres with diameters less than 50 nm. Usually the size uniformity decreased in such smaller size range. Thus, the degree of uniformity in the preparation of colloidal crystalline arrays also decreased with such smaller silica spheres. The porous carbon with 25 nm in diameter showed decrease in structural order, but still largely maintained overall structural integrity. In the case of 10 nm porous carbon, the structural order was greatly impaired. Overall structural integrity was significantly decreased with nearly structural collapse because the wall separating the pores became too thin to support the rigidity of overall ordered porous structure. The size of the supported Pt-Ru alloy nanoparticles on commercial E-TEK and PtRu-C-68 catalysts was also investigated by TEM and shown in Figs. 1e and 1f. TEM images show homogeneous dispersion of small, spherical and uniform dark spots that correspond to Pt-Ru alloy nanoparticles. Small agglomerates of the metal particles were also sporadically observed in the supported catalysts. The particle sizes measured directly from TEM photographs at randomly selected regions for each sample were approximately 2 - 3 nm.

The ordered porous carbons for C-25 and C-68 exhibited type IV isotherms with a H1 adsorption-

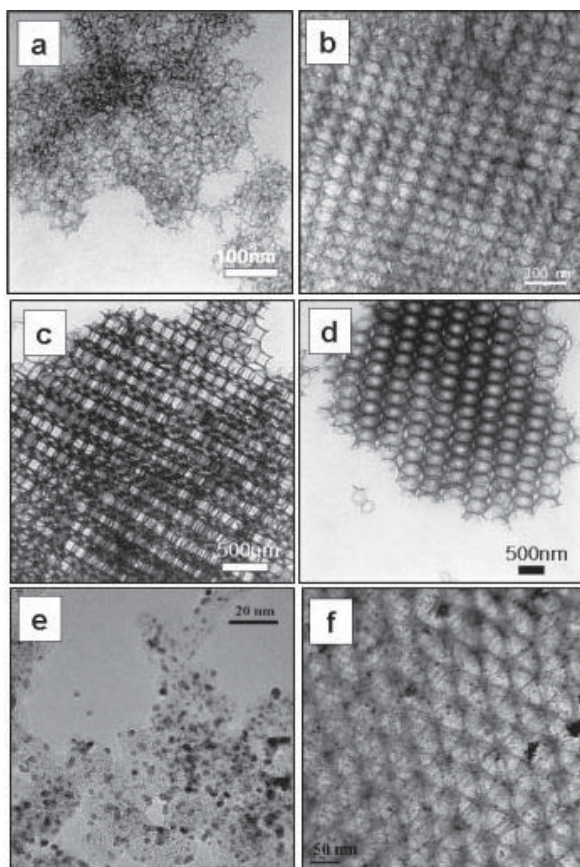


Fig. 1. TEM images of (a) C-25 (b) C-68 (c) C-245, (d) C-512, (e) E-TEK PtRu catalyst and (f) PtRu-C-68. Small dots shown in the figures (e) and (f) correspond to the Pt-Ru alloy catalysts prepared on carbon supports.

desorption hysteresis loop, which are typical for mesoporous materials according to the IUPAC nomenclature in N₂ adsorption and desorption isotherms at 77K. In the case of porous carbons with pore diameters larger than 70 nm, type II isotherms were observed characteristic of macroporous materials. The values for BET surface areas and pore volumes of the porous carbons and the corresponding loaded carbons are summarized in Table 1. In general, the smaller pore sizes the porous carbons have, the higher surface areas and large pore volumes they showed. All the porous carbons showed higher surface area than the Vulcan carbon. The porous carbons have not only meso-/macropores, which are templated by colloidal silica array, but also significant micropores, which are inevitably generated during carbonization of polymer structures. Based on the sorption intensities, both the

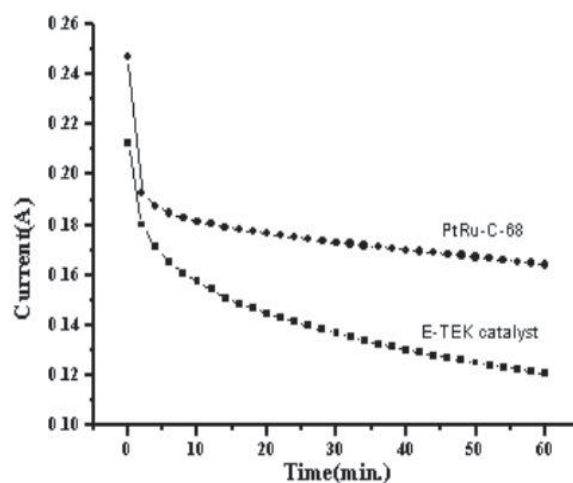


Fig. 2. Chronoamperograms for supported Pt₅₀Ru₅₀ alloy catalysts for E-TEK and PtRu-C-68. The electrodes were first optimized by applying several voltammetric cycles (20 mV/s, from -0.35V to +1.35V, 0.5M H₂SO₄) until a reproducible response was reached. Then, the cyclic voltammograms were recorded at room temperature at a scan rate 20 mV/s in N₂ degassed mixed solution of 0.5M H₂SO₄ and 1.0M CH₃OH from -0.35V to +1.35 V vs. Ag/AgCl reference electrode for 60 min in the mixed solution of 0.5M H₂SO₄ and 1.0M CH₃OH. The effective geometric area of the working electrode was 1 cm² and the electrode had a catalyst loading of 2.0 mg/cm² (metal base).

surface area and pore volume were drastically decreased after the catalyst loading compared to those of the corresponding unloaded carbons. Pure Pt has a face-centered cubic (fcc) lattice structure, while pure Ru has a hexagonal close-packed (hcp) structure. All the supported Pt-Ru catalysts exhibit XRD patterns typical of the fcc structures. The average particle sizes were about 2 - 3 nm as calculated using a Debye-Scherrer equation from the broadening of the (2.2.0) reflection of the Pt fcc lattice [12], which were in good agreement with data in TEM images.

Chronoamperometric (CA) results show the current profiles of methanol oxidation process as a function of time at a fixed potential setting, providing important information regarding reagent diffusion kinetics and electrode stability. Fig. 2 shows different decay patterns of the methanol oxidation cur-

Table 1. Structural parameters of porous carbons and the corresponding carbons with Pt₅₀-Ru₅₀ catalyst loading.

Sample ^a	S_{BET} (m ² /g)	S_{micro} (m ² /g)	$S_{\text{meso/macropore}}$ (m ² /g)	V_{total} (cc/g)	V_{micro} (cc/g)
E-TEK	93	18	75	0.19	0.01
VC	232	87	145	0.32	0.04
PtRu-VC	107	29	78	0.17	0.01
C-10	996	220	776	3.81	0.12
PtRu -C-10	159	13	146	0.55	0.01
C-25	845	195	650	3.66	0.07
PtRu -C-25	213	32	181	0.51	0.01
C-68	691	483	218	1.63	0.12
PtRu -C-68	166	46	120	0.33	0.02
C-245	605	400	205	0.81	0.13
PtRu -C-245	130	20	110	0.24	0.01
C-512	509	313	196	0.75	0.16
PtRu -C-512	118	24	94	0.22	0.02

^aVC indicates a Vulcan XC-72 carbon. C-X and PtRu-C-X, where C and X represent a porous carbon and a pore diameter, respectively. S_{BET} : BET surface area, S_{micro} : micropore area, $S_{\text{meso/macropore}}$: meso and macropore area, V_{total} : total pore volume, V_{micro} : micropore volume.

rent for PtRu-C-68 and E-TEK catalysts at room temperature. Each catalyst loses its catalytic activity fast initially, and then shows slow decrease or nearly steady activity. PtRu-C-68 catalyst exhibited both highest initial and final current densities of methanol oxidation, and also showed better stability as indicated by very slow decrease in current density during the measurement. This indicates that the PtRu-C catalyst can effectively keep up the current density from the electrocatalytic oxidation of methanol for a long period of time.

Fig. 3 shows the unit cell performance of direct methanol fuel cell at 30 °C by PtRu-C-Xs compared to those of the PtRu-VC and E-TEK catalysts. The open-circuit voltages (OCV) were 0.646, 0.638, 0.672, 0.662, 0.654, and 0.651V for E-TEK, PtRu-VC, PtRu-C-25, PtRu-C-68, PtRu-C-245 and PtRu-C-512, respectively. The maximum power densities were 33, 30, 58, 46, 42, and 39 mW/cm², respectively. This indicates that the porous carbon supported catalysts exhibited 20 – 75% higher power density than the E-TEK catalyst. Interestingly, the PtRu-VC catalyst prepared in the same condition as the porous carbon-supported Pt-Ru catalysts showed lower activity as well as lower OCV than those of the E-TEK catalyst also supported on the Vulcan carbon. This may indicate that the Pt-Ru

alloy catalyst itself prepared in this work is inferior to the E-TEK catalyst in terms of methanol oxidation activity since the same Vulcan XC-72 carbon was used as a support for both cases. Even then, the activities of the Pt-Ru catalysts supported on the porous carbons are significant in comparison to those on the Vulcan carbon. Thus, such increase in activity may be attributed solely to the supporting effect of the porous carbon. In general, the smaller pore sizes the porous carbons have, the higher surface areas and the better catalytic activity they showed. Based upon the sorption and activity data, the improved activity for the methanol oxidation is considered to be due to the higher surface areas and larger pore volumes that the porous carbon can provide for the higher degree of catalyst dispersion compared to those of the Vulcan carbon. The porous carbon with 10 nm in pore diameter had highest surface area and pore volume studied in this work. The PtRu-C-10 showed very high activity for methanol oxidation, but was found to give a little less activity than PtRu-C-25. The carbon wall particularly in the case of the porous carbon with very small pore size, may become too thin to maintain an integrated porous framework upon metal loading, resulting in the collapse of the porous structures, which can lower the supporting effect. The

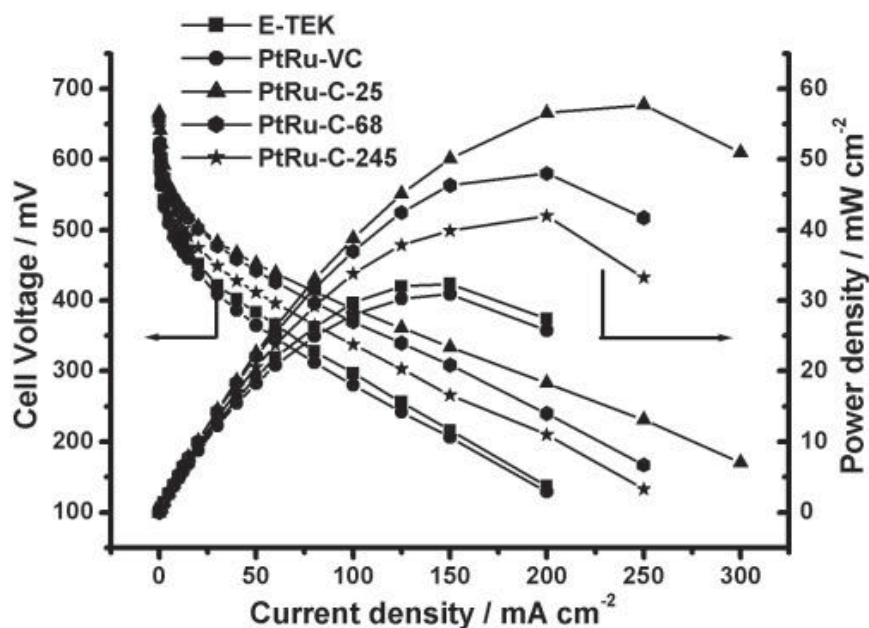


Fig. 3. Voltage and power density responses of the porous carbon supported Pt₅₀-Ru₅₀ alloy catalysts compared to those of the PtRu-VC and E-TEK catalysts in direct methanol fuel cell. The DMFCs were operated at 30 °C with a flow rate of 1.0 ml/min for 2.0 M CH₃OH at anode and 300 ml/min for O₂ gas at cathode and Nafion 117 as electrolyte membrane. Anode: supported Pt-Ru alloy catalyst (3.0 mg/cm²). Cathode: Johnson Matthey Pt black (5.0 mg/cm²).

three-dimensionally interconnected pore system in the porous carbons can also favour efficient fuel and product diffusion as a diffusion layer as compared to that of the Vulcan carbon which has randomly distributed pores of varying sizes and thus make fuel and product diffusion difficult.

4. CONCLUSIONS

The colloidal silica template presented in this work was simple and viable route for production of ordered porous carbons with high surface areas and large pore volumes, whose pore sizes can be easily controlled by monitoring the sizes of the silica spheres. The porous carbon supported Pt-Ru alloy catalysts exhibited a higher catalytic activity for methanol oxidation with 20 ~ 75% increase compared to that of a commercially available E-TEK Pt-Ru alloy catalyst. This is considered to be not only due to the higher surface areas and larger pore volumes, which allow higher degree of catalyst dispersion. but also due to highly integrated interconnected pore systems with periodic order of the porous carbon, which allow efficient diffusion of reagents.

ACKNOWLEDGEMENTS

Author thanks ITEP for its financial support on fuel cell project and the Korean Basic Science Institute for TEM and SEM analyses

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