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Spherical carbon capsules with hollow macroporous core and mesoporous shell structures as a highly efficient catalyst support in the direct methanol fuel cell†

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Carbon capsules with hollow core and mesoporous shell (HCMS) structures were used as a support material for Pt_{50}–Ru_{50} catalyst, and the catalytic performance of the HCMS supported catalyst in the direct methanol fuel cell was described; the HCMS carbon supported catalysts exhibited much higher specific activity for methanol oxidation than the commonly used E-TEK catalyst by about 80%, proving that the HCMS carbon capsules are an excellent support for electrode catalysts in DMFC.

The direct methanol fuel cell (DMFC) that uses liquid methanol directly to an anode as fuel is considered to be a promising candidate for portable power sources because methanol has a high energy density, low price and easy handling, storage and transport. In order to enhance the electrocatalytic activity for methanol oxidation, intense studies have been devoted mainly towards the development of new metal catalysts.[1–3] These catalysts are generally dispersed as nanoparticles on an electrically conducting support such as carbon with high surface area in order to obtain optimum catalyst utilization for methanol electrooxidation by increasing the dispersion of the nanosized catalysts. However, there have been few studies on supporting materials as a means to optimize performance of catalysts. Carbon black, called Vulcan XC-72, has been widely used as a supporting material for electrode catalysts in DMFCs.[4] In fact, commercially available E-TEK catalysts are Pt–Ru alloys supported on the Vulcan XC-72. Recently, in addition to the development of catalysts themselves there has also arisen great attention for new carbon materials as supports as well in order to help achieve optimum catalytic performance.[5] Several different carbon materials such as mesostructured carbon materials,[6] graphitic carbon nanofibers,[7] mesocarbon microbeads[8] and hollow graphitic nanoparticles[9] were reported as supports of Pt or Pt alloy catalysts mainly for higher dispersion of the catalysts and for improved synergic effects. The performance and stability of fuel cells are known to strongly depend on the carbon support used as well as the catalytically active species.[10] Recently, remarkable progress has been made in the synthesis of carbons with periodically ordered porosity by using template replication with zeolites,[11] mesoporous materials[12] and colloidal crystals.[13] In earlier work, we reported a new type of porous carbon supports[14] with three-dimensionally interconnected highly ordered uniform pore structures in the range of 10–500 nm. All the synthesized porous carbon supported Pt–Ru catalysts exhibited much higher specific activity for methanol oxidation than commercial E-TEK Pt–Ru catalyst by about 10–70%. Fabrication of carbon capsules with hollow core/mesoporous shell (HCMS) was also reported by replication through nanocasting of solid core/mesoporous shell silica particles.[15] The HCMS carbon capsules have an interconnected bimodal pore system composed of hollow macroporous core and mesoporous shell and have higher surface area and pore volume compared to the aforementioned porous carbon systems, which are potentially important for support materials. In this paper, the HCMS carbon capsules were employed as supports for electrocatalysts and investigated for the performance of methanol oxidation in the direct methanol fuel cell.

Fig. 1 shows a scanning electron microscope (SEM) image of a HCMS carbon capsule and a transmission electron microscope (TEM) image of HCMS carbon capsules loaded with Pt_{50}–Ru_{50} catalysts. The SEM image showed that the HCMS carbon particles were roughly uniform and spherical with particle diameter of ~300 nm. A broken capsule shown in the inset indicates that it has a spherical hollow core. Both the SEM and TEM images clearly show a hollow core of ~220 nm in diameter and a mesoporous shell with thickness of ~40 nm. The TEM image at high magnification showed randomly distributed mesopores of ~4 nm in the shell. Thus, each of the carbon capsules has a bimodal pore system composed of a spherical macroscopic core and a mesoporous shell. The HCMS carbon capsules revealed a pore size distribution centered at ~3.8 nm, and exhibited a high BET surface area of 1876 m^2/g, and a total pore volume of 1.87 cm^3/g mainly due to the presence of the mesoporous shell (Supporting information Fig. S1). However, the surface properties drastically diminished upon catalyst loading. PtRu-HCMS had a specific surface area of 330 m^2/g and a total pore volume of 0.50 ml/g as indicated also in the decrease of observed sorption intensities. Maximum peak position shifted to about 2.0 nm. As shown in the TEM image in Fig. 1b, most of the Pt–Ru alloy nanoparticles are dispersed homogenously as small, spherical and uniform dark spots over the surface. The size of the metal nanoparticles determined directly from TEM photographs at randomly selected regions for each sample was approximately 2–3 nm. This is further supported by the value calculated through average particle size analysis from a (220) X-ray diffraction peak (Supporting information Fig. S2) of the Pt fcc lattice by a Scherrer equation.[16] The TEM image also indicates that structural integrity was pretty well preserved even after catalyst loading.

Fig. 2 shows the unit cell performance of a direct methanol fuel cell at 30 °C and 70 °C using a PtRu-HCMS catalyst compared to those using Vulcan carbon supported Pt–Ru (PtRu-VC) and E-TEK catalysts. The catalyst loadings were 3.0 mg/cm^2 (metal loading base) for each of the supported Pt–Ru anode catalysts and 5.0 mg/cm^2 for Pt black (Johnson Matthey) cathode catalyst, respectively. At 0.5 V, where the activation polarization is mainly affected by activity of the catalyst, the PtRu-HCMS catalyst showed a current density of 44 mA/cm^2, which corresponds to more than two times those of E-TEK catalyst (15 mA/cm^2) and PtRu-VC catalyst (12 mA/cm^2) at 30 °C, and exhibited a higher maximum power density (83 mW/cm^2) than those of the E-TEK catalyst

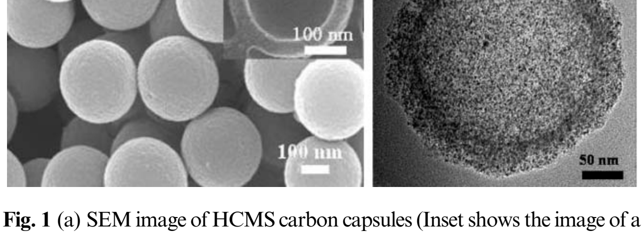

Fig. 1 (a) SEM image of HCMS carbon capsules (Inset shows the image of a broken capsule) and (b) TEM image of an HCMS carbon capsule after catalyst loading. The small black spots represent Pt–Ru catalyst nanoparticles.

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† Electronic supplementary information (ESI) available: experimental section. See http://www.rsc.org/suppdata/cc/b4/b412747c/

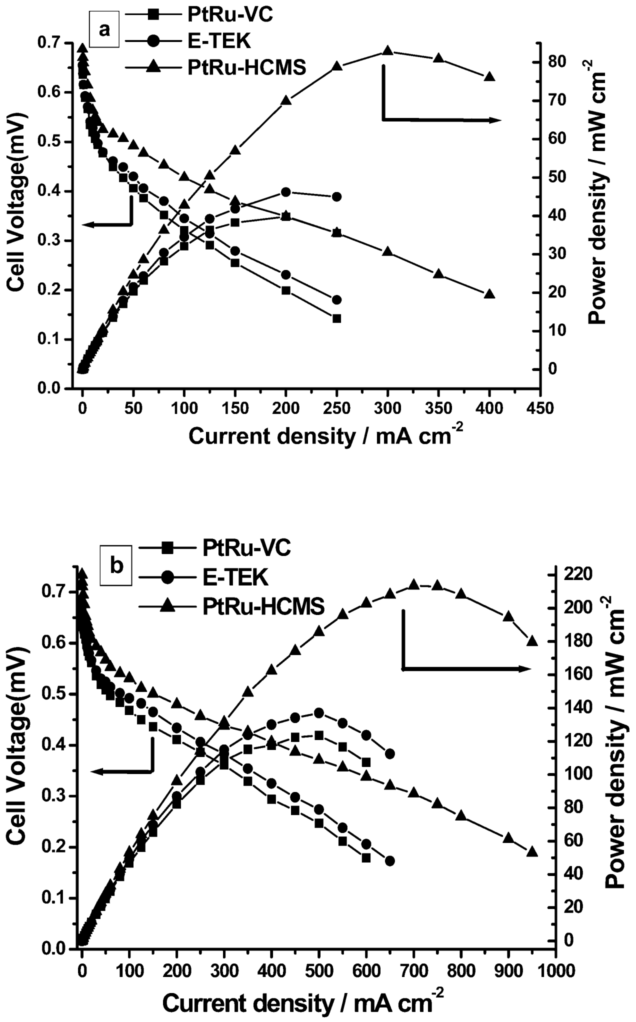

Fig. 2 The polarization curves for a direct methanol fuel cell using a PtRu-HCMS catalyst (▼), a PtRu-VC catalyst (■) and a commercial E-TEK catalyst as an anode (●) determined (a) at 30 °C and (b) at 70 °C, respectively.

(46 mW/cm^2) and the PtRu-VC catalyst (42 mW/cm^2) as shown in Fig. 2a. This corresponds to 80% and 98% increase in methanol oxidation activity for the PtRu-HCMS catalyst compared to those of E-TEK catalyst and PtRu-VC catalyst, respectively. Similar trends were also observed at 70 °C as shown in Fig. 2b. At 70 °C, the PtRu-HCMS catalyst exhibited the maximum power density of 214 mW/cm^2. In comparison, E-TEK catalyst and PtRu-VC catalyst showed the maximum power density of 137 and 124 mW/cm^2, respectively. This also corresponds to better performance by about 56% in comparison with the E-TEK one. The PtRu-HCMS catalyst maintained stable and constant catalytic activity over 150 h in the unit cell. Interestingly, the Vulcan XC-72 supported Pt–Ru catalyst prepared in the same conditions as the PtRu-HCMS catalyst showed lower oxidation activity than that of the commercial E-TEK catalyst also supported on the Vulcan carbon. Even then, the PtRu-HCMS catalyst showed much better performance than the E-TEK counterpart. Thus such increase in activity may be attributed solely to the superb supporting effect of the porous carbon. This can be considered as really significant progress in the DMFC. Such great improvement may be related to the unique structural properties of the HCMS carbon capsules; in part due to the higher surface areas and larger pore volumes of the HCMS carbon capsules, which can allow for a greater degree of catalyst dispersion, and also in part due to the well-combined bimodal nanoporous structures with the mesopores in the shell open to outer surface and inner hollow macroporous core, which provide an open highway network around the active catalyst for a facile diffusion of fuels and products moving into and out of the catalyst. In addition, there are three-dimensionally interconnected large interstitial spaces between the packed spherical carbon particles, to which the mesopore channels are open. Thus, significant portions of the reactants and products can diffuse easily through the interstitial spaces. This argument is also supported by the chronoamperometric results for methanol oxidation of the PtRu-HCMS and E-TEK electrodes polarized at 0.4 V for 4 h (Supporting information Fig. S4). The HCMS catalyst exhibited both higher initial and final current density of methanol oxidation and more stability within the time period. This is also due to the unique structural properties of the HCMS carbon capsules. The core size, shell thickness and porosity and surface morphology of the HCMS carbon capsules can be controlled by monitoring the size of the silica sphere core, the amount and ratio of TEOS and C_{18}-TMS added, thermal treatment and carbon precursors and their blend.[15,17]

In this work, HCMS carbon capsule supported Pt–Ru catalyst exhibits an exceptionally high electrocatalytic activity for methanol oxidation compared to the commonly used commercial E-TEK catalyst. This is considered to be due to unique structural properties of the HCMS carbon including high surface area and well-developed interconnected bimodal porosity. Based on the results obtained, the HCMS carbon capsules are an excellent support for electrode catalysts in the DMFC. Work on the stability and durability of the supported catalysts is under way.

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