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Microwave-assisted synthesis of carbon supported Pt nanoparticles for fuel cell applications

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Spherical and uniform Pt nanoparticles 3.5-4.0 nm supported on carbon were prepared by microwave irradiation and exhibited very high electrocatalytic activity in the room-temperature oxidation of liquid methanol.

Pt and Pt alloys are catalytically active in several room-temperature electro-oxidation reactions of interest to fuel cell applications. It is well known that the metal catalytic activity is strongly dependent on the particle shape, size and the particle size distribution.[1] Conventional preparation techniques based on wet impregnation and the chemical reduction of metal precursors do not provide satisfactory control of particle shape and size.[1] Consequently there has been continuing effort to develop alternative synthesis methods based on microemulsions,[2] sonochemistry,[3,4] and microwave irradiation,[5–8] all of which are in principle more conducive to produce colloids and clusters on the nanoscale, and with greater uniformity.

Microwave heating through dielectric losses is fast and simple, uniform, energy efficient, and has been used in preparative chemistry and materials synthesis.[9] Recently, there has been more reported successes in using microwave irradiation to prepare high purity nanoparticles with narrow particle size distributions. For example, polymer stabilized Pt, Ru, Ag and Pd colloids were prepared from the microwave heating of ethylene glycol solutions of dissolved metal salts.[5–8] Metal oxide nanoparticles (*e.g.* CeO_2, ZrO_2) could likewise be obtained using microwave irriadation.[10,11]

In this communication, a simple microwave procedure for preparing Pt metal nanoparticles supported on carbon is reported. Pt/carbon nanocomposites containing 10, 15 and 20 wt% of Pt were successfully prepared by microwave irradiation. TEM imaging showed a uniform dispersion of spherical Pt nanoparticles 3.5–4.0 nm in diameter and with a narrow particle size distribution on the carbon surface. Laboratory tests showed that these Pt/carbon catalysts were more electrochemically active in the room-temperature oxidation of liquid methanol than commercially available catalysts. To the best of our knowledge, we are not aware of any other report on the rapid and direct synthesis of electrochemically active Pt nanoparticles supported on carbon using microwave irradiation.

In a 100 mL beaker, 1.0 mL of an aqueous solution of 0.05 M $H_2PtCl_6\cdot 6H_2O$ (Alrdich, A.C.S. Reagent) was mixed with 50 mL of ethylene glycol (Mallinckrodt, AR), and 0.5 mL of 0.8 M KOH was added dropwise. 0.040 g of carbon XC-72 with a specific surface area (BET) of 250 $m^2\ g^{-1}$ and an average particle size of 40 nm were uniformly dispersed in the mixed solution by ultrasound. The beaker was placed in the center of a microwave oven (National NN-S327WF, 2450 MHz, 700 W) and heated for 60 s. The resulting suspension was filtered and the residue was washed with acetone. The solid product was dried at 393 K overnight in a vacuum oven. Catalysts with varying amounts of Pt from 10–20 wt% were prepared by varying the H_2PtCl_6 content in the ethylene glycol solution. A mole ratio of KOH/Pt = 8 was used throughout to induce small and uniform Pt nanopartcle formation.[5] The size and morphology of samples were characterized by TEM imaging (JEOL JEM 2010). The Pt contents were determined by EDX (JEOL JSM-5600LV).

Electroactivities were measured by cyclic voltammetric and chronoamperometry using an EG&G model 273 potentiostat/galvanostat and a three-electrode test cell at room temperature. The working electrode was a thin layer of Nafion-impregnated Pt/C composite cast on a vitreous carbon disk electrode.[2] A Pt gauze and a saturated calomel electrode (SCE) were used as the counter and reference electrode, respectively. The electrolyte was a solution of 2 M CH_3OH (Tedia, HPLC) in 1 M H_2SO_4 (J. T. Baker, A.C.S. Reagent).

EDX measurements indicated Pt loadings of 9.5, 13.6 and 18.6 wt% for three samples prepared for the nominal loadings of 10, 15 and 20 wt%, respectively. A commercially available Pt/C catalyst from E-TEK with a nominal Pt loading of 20 wt% (18.8 wt% by EDX) was used as a benchmark. Repeated TEM examinations showed that the Pt nanoparticles are uniformly distributed on the carbon surface. All samples have about the same Pt particle size and the difference between them is the particle density on the carbon surface. Fig. 1 shows the TEM image of the 18.8 wt% sample in comparison with the commercial E-TEK Pt/C catalyst. The microwave assisted heating of $H_2PtCl_6/KOH/H_2O$ in ethylene glycol had evidently facilitated a more uniform dispersion of Pt nanoparticles on the carbon surface. When poly(*N*-vinyl-2-perrolidone) (PVP) was used to substitute for carbon XC-72 in the preparation of nanoparticles (an established methodology to stabilize nanoparticles against agglomeration[5–7]), the resulting polymer-stabilized nanoparticles were hardly dispersible on the carbon. It is suspected that the strong affinity between PVP and Pt nanoparticles had resulted in poor adhesion property of either of them with a foreign surface. More importantly, Fig. 1 shows that the microwave-synthesized Pt nanoparticles are spherical with significantly smaller mean diameters and a narrower particle size distribution than those in the E-TEK catalyst. The diameters for the majority of the particles are between 3.5 and 4.0 nm, with only a few particles larger than 5.0 nm. The E-TEK catalyst, by comparison, has Pt particles about 5.1 nm in diameter, and a broad particle size distribution ranging from about 2–10 nm. It is generally agreed that the size of metal nanoparticles is determined by the rate of reduction of the metal

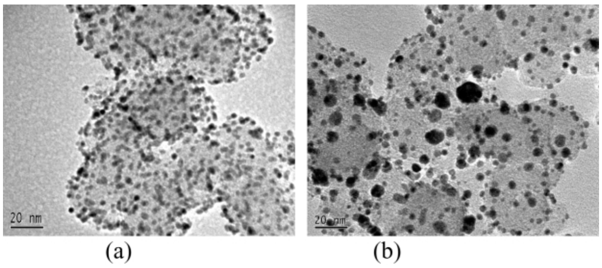

Fig. 1 TEM images of (a) microwave-synthesized Pt nanoparticles supported on Vulcan carbon XC-72 and (b) commercially available E-TEK Pt/C catalyst (nominal Pt loading 20 wt%).

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precursor. The dielectric constant (41.4 at 298 K) and the dielectric loss of ethylene glycol are high, and hence rapid heating occurs easily under microwave irradiation. In ethylene glycol mediated reactions (the 'polyol' process), ethylene glycol also acts as a reducing agent to reduce the metal ion to metal powders.[12]

The fast heating by microwave accelerates the reduction of the metal precursor and the nucleation of the metal clusters. The easing of the nucleation-limited process greatly assists in small particle formation. Additionally the homogeneous microwave heating of liquid samples reduces the temperature and concentration gradients in the reaction medium, thus providing a more uniform environment for the nucleation and growth of metal particles. The carbon surface may contain sites suitable for heterogeneous nucleation and the presence of a carbon surface interrupts particle growth. The smaller and nearly single dispersed Pt nanoparticles on carbon XC-72 prepared by microwave irradiation can be rationalized in terms of these general principles.

Fig. 2 shows the cyclic voltammograms of methanol oxidization under acidic conditions (2 M CH_3OH/1 M H_2SO_4) catalyzed by the microwave-synthesized Pt/C catalyst and the E-TEK Pt/C catalyst, respectively. The voltammetric features are in good agreement with most published work.[13,14] The current peak at about 0.70 V (*vs.* SCE) in the forward scan is attributed to methanol electrooxidation on the Pt/C catalyst. Fig. 2 clearly shows that this peak is significantly higher in the microwave-synthesized Pt/C catalyst than in the E-TEK Pt/C catalyst. Fig. 2 also shows that the electro-oxidation of methanol began at 0.3–0.4 V *vs.* SCE where the current density was 0.18 A $(\mathrm{mg\ Pt})^{-1}$ for the microwave-synthesized Pt/C, and 0.12 A $(\mathrm{mg\ Pt})^{-1}$ for the E-TEK Pt/C catalyst. The difference is significant enough that the current density at 0.4 V can be used as an indicator of the catalytic activity of the catalysts under moderate polarization conditions. The Pt/C catalysts were therefore biased at 0.4 V *vs.* SCE and the changes in their polarization currents with time were recorded (Fig. 3). Besides a higher activity, the microwave-synthesized Pt/C catalyst also displays the same, if not better, fade rate (indicating catalyst deactivation) in comparison with the E-TEK catalyst. These experimental measurements prove unmistakably a greatly improved Pt/C electrocatalyst for the room temperature electro-oxidation of liquid methanol. The significant improvement in the catalyst performance derives directly from the better utilization of Pt when the latter exists as uniform small particles stabilized on a carbon substrate.

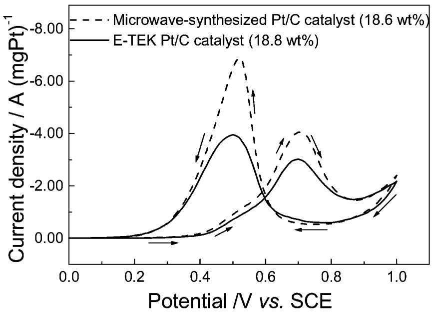

Fig. 2 Cyclic voltammograms of Pt/C electrode in 2 M CH_3OH/1 M H_2SO_4 electrolyte at 20 mV s^{-1} at room temperature.

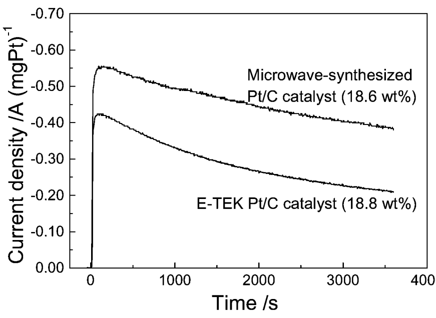

Fig. 3 Polarization current *vs.* time plots for the electrooxidation of methanol in 2 M CH_3OH/1 M H_2SO_4 electrolyte at 0.4 V (*vs.* SCE) at room temperature.

In conclusion, a microwave assisted rapid heating method has been successfully developed for the preparation of Pt/C catalysts with high electrocatalytic activities in direct methanol fuel cell applications. The Pt nanoparticles, which were uniformly dispersed on carbon, were 3.5–4.0 nm in diameter and had a very narrow particle size distribution. The preparation method is simple, fast and energy efficient. It can be used as a general method to prepare other supported metal particles from metal precursors which are susceptive to the polyol process.[15,16]

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