



Microwave assisted synthesis of surfactant stabilized platinum/carbon nanotube electrocatalysts for direct methanol fuel cell applications

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ABSTRACT

Platinum electrocatalysts deposited on multi-walled carbon nanotubes (CNT) with high loading were prepared using a microwave-assisted polyol reduction method and employed for direct methanol fuel cells (DMFC). A zwitterionic surfactant was used as a stabilizing agent for the formation of Pt nanoparticles. A uniform and narrow size distribution of highly dispersed Pt nanoparticles could be achieved by adjusting the weight ratio of surfactant to Pt precursor allowing for Pt loadings of up to 60 wt%. The heating time and the temperature for the ethylene glycol (EG) oxidation were found to be the key factors for depositing Pt nanoparticles homogeneously on carbon nanotubes. The smallest average particle diameter of 1.8 nm was obtained through microwave heating to 140 °C in 50 s. The structure, amount and morphology of the electrocatalysts were characterized with XRD, TGA, and TEM, respectively. Single cell DMFC measurements were performed in a membrane-electrode assembly (MEA) with 5 cm² active area and very low catalyst loading (0.25 mg cm⁻² of noble metal on both anode and cathode). The DMFC performance of the surfactant stabilized cathode catalyst obtained by the new method described here revealed that the power density was three times higher than for a commercial catalyst used for comparison and two times higher than for an unstabilized CNT supported catalyst.

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1. Introduction

Direct methanol fuel cells (DMFCs) have attracted enormous research interest as portable power sources [1,2]. However, the performance of DMFCs is still much worse than that of hydrogen fuel cells. A key factor for improvement of DMFCs is the development of better catalyst materials [3]. Several ways to increase the amount of platinum that is utilized in the active electrode surface layers have been described [4,5]. However, the costs related to the high noble metal content in DMFCs have to be considered. Promising ways to achieve a larger catalyst utilization are the use of nanosize metal particles and high surface area carbon supports [6,7]. Nanostructured carbon materials such as multi-walled carbon nanotubes (MWNT) and mesoporous carbon spears are potentially useful candidates for such applications [8,9].

It is well known that the catalytic activity of platinum is strongly related to the particle size distribution and the metal dispersion on the carbon support [10]. Pt catalysts with nanometer sized particles and a narrow size distribution should provide high electrocatalytic activity. Therefore, considerable attention has been paid to the synthesis methods and the characterization of catalyst nanoparticles [11,12]. Various approaches are used for the preparation of sup-

ported catalysts, such as wet impregnation [13], ion-exchange [14], physical deposition [15], and colloidal methods [16]. Impregnation-reduction methods have been studied extensively in which the Pt precursor is reduced in a hydrogen atmosphere at high temperature [17]. However, the heat treatments often increase the particle size and reduce the catalytic activity [18,19]. On the other hand colloidal procedures involve several steps with repeated filtering and washing. This leads to lower yield and higher overall catalyst production cost.

Recently, a simple and rapid synthesis method for metal catalysts using microwave irradiation energy has been suggested [20]. The advantage of the microwave irradiation is that it transfers heat to the substance uniformly through the microwave-transparent reaction container (i.e. glass or plastic), leading to a more homogeneous nucleation and shorter crystallization time compared to conventional heating during which unavoidable temperature gradients occur, in particular when large volumes of solutions are used. This gradient of temperature may adversely affect the particle size distribution and yield. In the present paper, we demonstrate that even a simple household microwave oven as a heating source can successfully be used to prepare highly dispersed platinum particles supported on carbon nanotubes.

The use of surfactants as stabilizers is another important parameter for the achievement of uniform and stable nanoparticles. Preferably, water soluble surfactants, i.e. anionic or zwitterionic surfactants, have been used to disperse CNTs and stabilize the Pt

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nanoparticles [21]. With suitable surfactants, the particle size of Pt can be controlled by the surfactant content in the reaction medium [22,23]. Until now, only very few investigations reported the use of surfactants to Pt precursor weight ratio to stabilize nanoparticles supported on carbon nanotubes.

In this work, emphasis was put on the optimization of the surfactant quantity, reaction temperature and heating time for Pt/CNT catalysts prepared by microwave irradiation. The physico-chemical and electrochemical characterizations of the CNT supports and the corresponding Pt/CNTs catalysts are presented. The influence of the Pt deposition conditions on the dispersion and size distribution of Pt particles on CNTs are discussed. Furthermore, the performance of a DMFC based on the new Pt/CNT catalysts was studied.

2. Experimental

2.1. Reagents and pre-treatment of CNTs

All chemicals used in this study were analytical grade. The Pt precursor complex $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ was purchased from Merck, Germany. HNO_3 (ACS grade), NaOH (98.0%) and ethylene glycol (EG) were obtained from Sigma–Aldrich, Germany. All reagents and materials were used without further purification. The necessary solutions were prepared with deionized water having a conductivity of less than $0.5 \mu\text{s cm}^{-1}$.

Multi-walled carbon nanotubes having inner diameters of 5–10 nm and outer diameters of 15–25 nm were kindly provided by Bayer MaterialScience AG, Germany (BayTubes[®], C 150 HP). Oxidation of 40 g CNTs was carried out in 1 L concentrated nitric acid (65%) at 100°C . Before heating the suspension was sonicated for 5 min using an ultrasonic probe (200 W, 20 kHz, Bandelin SONO-PLUS, Germany) to disperse the nanotubes in the mixture and to enhance the uniformity of functionalization. Subsequently, the oxidation was carried out under reflux in nitrogen atmosphere for 5 h. The solution was then diluted with deionized water ($\sim 1\text{--}2\text{ L}$) and centrifuged (Hettich, Rotina 380) at 4000 rpm for 30 min. This step was repeated until the filtrate reached pH 7. Finally, the carbon nanotubes were dried in air at 60°C overnight.

2.2. Preparation of Pt/CNT catalysts

Pt electrocatalysts were prepared by using a microwave-assisted polyol reduction method. The required amount of chloroplatinic acid was dissolved in 20 ml of EG, followed by addition of functionalized CNTs to the precursor solution to attain a nominal metal loading of 60 wt%. The EG here acted as both a reducing medium and a dispersion medium avoiding the agglomeration of CNTs and Pt particles. NaOH pellets were dissolved in EG solution and 1 ml of a saturated solution was used to adjust the pH between 10 and 11. To study the influence of the surfactant on the catalyst properties, a zwitterionic surfactant (3-(*N,N*-dimethyldodecylammonio) propanesulfonate, SB12) was added to the mixture at weight ratios of SB12: Pt = 1:1, 2:1, and 3:1. The reaction mixture underwent ultrasonic treatment for 10 min and was then mechanically stirred for 30 min. Subsequently, the mixture was transferred to a 100 mL Teflon microwave closed vial placed in the centre of the microwave oven (Samsung Prima, 2.45 GHz). The microwave power was fixed at 850 W and the pulse rate was adjusted to reach the desired temperatures ($T = 100, 120, 140, \text{ and } 160^\circ\text{C}$) within different heating times ($t = 50, 100, \text{ and } 150\text{ s}$). In all cases, the sample was afterwards maintained for 1 min at the desired temperature. After the microwave polyol reduction procedure, the suspension was diluted with a surplus amount ($\sim 1\text{--}2\text{ L}$) of ethanol and then separated by using the centrifuge at a speed of 10,000 rpm for 15 min. The procedure was repeated 5–6 times and the catalyst was finally dried in an oven for 24 h.

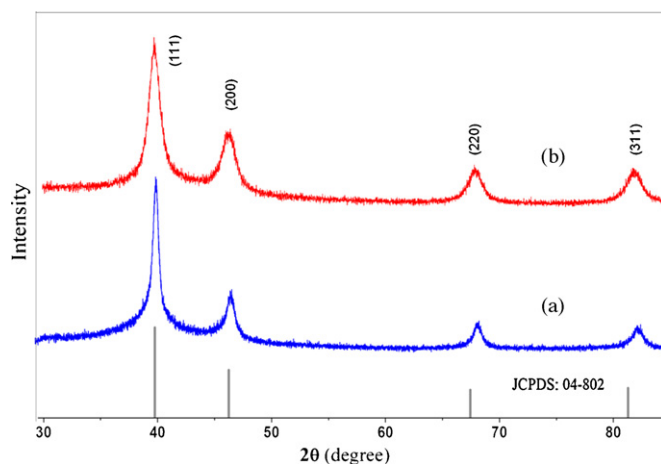


Fig. 1. XRD spectra of Pt/CNT catalyst synthesized by using microwave polyol reduction heated within 50 s to 140°C , (a) no surfactant and (b) SB12 surfactant.

2.3. Catalyst characterization

X-ray diffraction patterns were measured by using a powder diffractometer (Seifert XRD 3000) equipped with $\text{Cu K}\alpha$ radiation generated at 10 kV and 5 mA at a wavelength of $\lambda = 1.54 \text{ \AA}$ in the Bragg Brentano sample configuration. The scans were run from 30 to $85^\circ 2\theta$ with 0.04° step width and 50–90 s collection time/step. Thermogravimetric analysis (TGA) was performed with a Mettler TGA860 thermo balance in air at a flow rate of $50 \text{ cm}^3 \text{ min}^{-1}$ and a heating rate of 20 K min^{-1} from ambient temperature to 900°C using 5 mg samples. The amount of Pt metal was calculated from the last weight loss step at around 600°C . The microstructure of the samples was studied using transmission electron microscopy (TEM) with a JEOL 2100 (accelerating voltage 200 kV).

2.4. Electrode preparation and DMFC measurements

The cathode catalyst layer was prepared with the CNT based catalyst (loading: 0.25 mg cm^{-2}) prepared with and without surfactant while the anode catalyst layer was prepared by using a commercial catalyst (40 wt% Pt, 20 wt% Ru on Vulcan XC-72 carbon, E-TEK). The catalyst layers were prepared with slurries composing of Pt/C (or

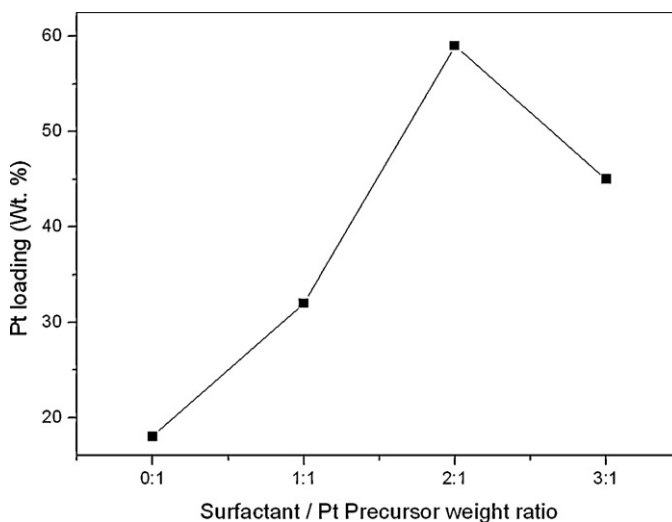


Fig. 2. Achieved Pt loading on CNT for different surfactant to Pt precursor weight ratios. Each catalyst prepared with a nominal metal loading of 60 wt% of Pt precursor at 140°C , 50 s.

Pt/CNT), Nafion solution (15 wt%, DuPont), isopropyl alcohol (IPA) and water at a weight ratio of Pt/C(CNT):Nafion solution:IPA:H₂O of 1:0.5:5:4. The suspensions were uniformly dispersed in an ultrasonic bath for 15 min and sprayed on a Nafion 117 membrane positioned on top of a hot plate at 80 °C. The catalyst coated membranes were hot pressed at 120 °C by using a hydraulic press with 0.14 t cm⁻². In all cases, metal loadings of 0.25 mg cm⁻² were used on both anode and cathode.

DMFC single cell measurements were performed in a self-made test station equipped with a high impedance potentiometer (Delta Elektronika SM3000, The Netherlands) and a computer interface based on LABVIEW (National instruments). Catalyst coated membrane and diffusion layers had an effective area of 5 cm². The diffusion layers consisted of a carbon cloth (Ballard, AvCarb 1071HCB) coated with a layer of carbon black (85 wt%, Ketjen Black EC 300J) and polytetrafluoroethylene (15 wt%, PTFE, Dyneon, Germany). Current density–voltage curves for each cell were measured at 80 °C, a stream of 5 ml min⁻¹ methanol solution (1 M) at the

anode and 200 ml min⁻¹ of pure oxygen (30 mbar overpressure) at the cathode.

3. Results and discussion

Fig. 1 shows the XRD pattern of the Pt/CNT catalyst prepared with and without surfactant by using the microwave polyol reduction method at 140 °C with 50 s heating time. The characteristic peaks of the carbon nanotubes were observed for all the samples at $2\theta = 26.5^\circ$ (not shown in Fig. 1). The other four peaks are characteristic of face-centered cubic (fcc) crystalline Pt, corresponding to the planes (1 1 1), (2 0 0), (2 2 0), and (3 1 1) at 2θ values of 39.8, 46.5, 67.8, and 81.2°, respectively, indicating that the metallic platinum particles are principally single-phase disordered structures. All four peaks can be well indexed with the standard JCPDS data [24]. The average diameters of the Pt particles were calculated from the line broadening peaks by using the Scherrer equation after background

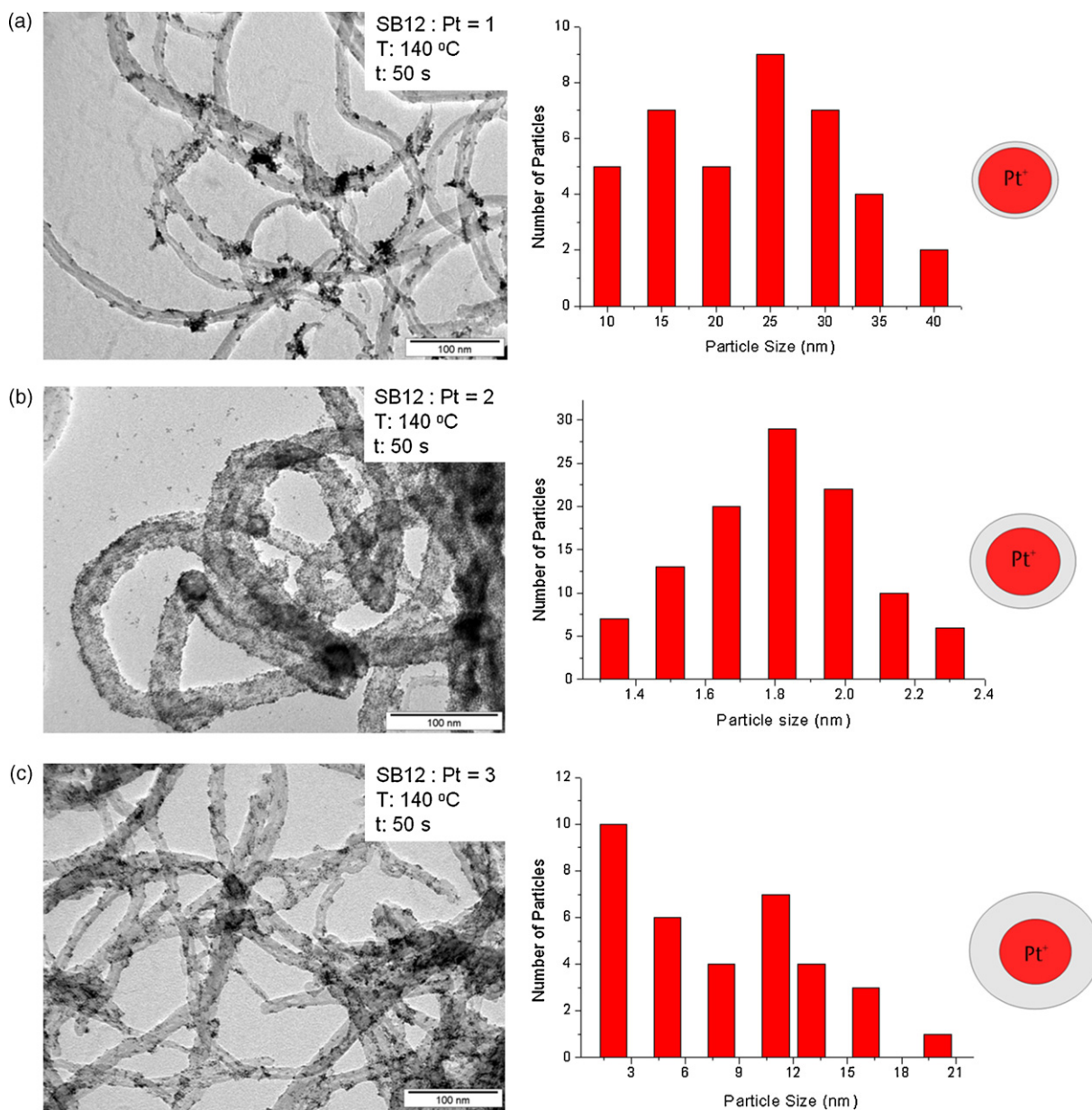


Fig. 3. TEM images, particle size distribution histograms and coverage of the surfactant layers on Pt ion of surfactant stabilized Pt/CNT catalyst synthesized with different surfactant to Pt precursor weight ratio (1:1 top, 2:1 middle, 3:1 bottom).

subtraction [25], and found to be 2.5 nm for the sample with surfactant and 6.3 nm for the sample without surfactant. The results indicate that the surfactant (SB12) plays an important role during the synthesis of the catalyst giving rise to the formation of smaller Pt nanoparticles. It can be assumed that the zwitterionic nature of SB12 stabilizes the size of the Pt particle during the reduction. Guo et al. [26] also reported a similar effect in their preparation of Pt nanoparticles by a reduction method using citric acid as stabilizer.

3.1. Effect of surfactant to Pt precursor ratio

It is known that the ratio of surfactant to precursor determines the Pt particle size and distribution [27,28]. Therefore, preparations with different surfactant amounts were carried out. Fig. 2 shows the achieved Pt loading as a function of the surfactant to Pt precursor ratio. In all cases, a nominal metal loading of 60 wt% was employed. It can be seen that a Pt loading very close to the nominal value is obtained at a surfactant to Pt precursor ratio of 2:1 while much lower loadings are observed for lower or higher ratios. The lowest Pt content of 18 wt% was observed with the surfactant free Pt/CNT catalyst. Fig. 3 shows TEM images of Pt nanoparticles on CNTs prepared with different ratios of surfactant to Pt precursor and corresponding histograms for the particle size distribution. Particle sizes observed from TEM images are in good agreement with the average particle size calculated from the XRD patterns. It is evident from Fig. 3(top) and 3(middle) that the dispersion of platinum nanoparticles on CNTs is greatly improved upon increase of the weight ratio from 1 to 2. The particle size distribution depicted in Fig. 3(middle) shows a very uniform pattern with almost monodispersed small particles with sizes between 1.2 and 3.0 nm, while a considerable amount of large clusters with 10–40 nm diameter is observed in Fig. 3(top). A previous report [29] also revealed severe aggregation of Pt nanoparticles on carbon Vulcan support when an insufficient surfactant amount was used. Similar results were reported by Sarma et al. [30] for Pt–Ru/C catalysts. Fig. 3(bottom) shows that an uneven distribution of Pt nanoparticles on the CNT surface having sizes in a wide range of 2.0–20 nm is observed for the highest weight ratio of SB12 to Pt precursor of 3.

The effect of the platinum–surfactant interaction and the resulting platinum particle size distribution can be understood if we consider that the formation of metal particles occurs in several steps. The steps involved in the surfactant promoted polyol reduction process are:

- orientation and dispersion of the platinum ions by reaction with the surfactant;
- mass transfer of the reducing agent ethylene glycol through the surfactant layer to the platinum ion, which is trapped by the surfactant;
- chemical reaction of the ethylene glycol to an oxidized molecule, releasing electrons;
- reduction of the platinum by the electrons resulting in the formation of platinum nuclei;
- particle growth of the initially formed metal nuclei.

In our measurements it was observed, that with rising surfactant concentration the metal dispersion improves until an optimum was reached. This can be explained by a better separation of the platinum ions at rising surfactant concentration. Beyond the optimum surfactant content, it could be that the mass transfer of ethylene glycol through the relatively thick surfactant layer becomes the rate determining step. This results in the formation of a smaller number of nuclei that will grow to larger particles until all the platinum is transferred into solid metal particles. This is shown in Fig. 3 that gives a pictorial representation of coverage of the surfactant layers on a Pt ion. Even minor changes towards bigger particle diameters can result in a decreased surface area of the catalyst, which results in lower activity. It should be kept in mind that the single steps during the formation of particles all have their own optimum reaction conditions and that the coupling of the single phenomena involved in the particle formation process cannot easily be determined.

3.2. Effect of heating time and temperature

For the optimum surfactant to Pt weight ratio of 2, the preparation method was studied at different heating times during microwave heating required to reach a temperature of 140 °C. Fig. 4 shows the obtained TEM images of Pt/CNT samples. The most uniform particle size distribution was obtained at the lowest heating time of 50 s (Fig. 4a). Fig. 4b and c shows that an increasingly uneven coverage of Pt nanoparticles on CNT results if longer heating times of 100 or 150 s are employed. The variation in the heating time also influences the particle size. Average diameters of 1.8, 2.0, and 2.4 nm were observed with heating times of 50, 100, and 150 s, respectively. In addition to this slight increase of particle diameter, the uniformity of the distribution and the overall Pt loading decreased with longer heating time (Fig. 5a). In accordance with the

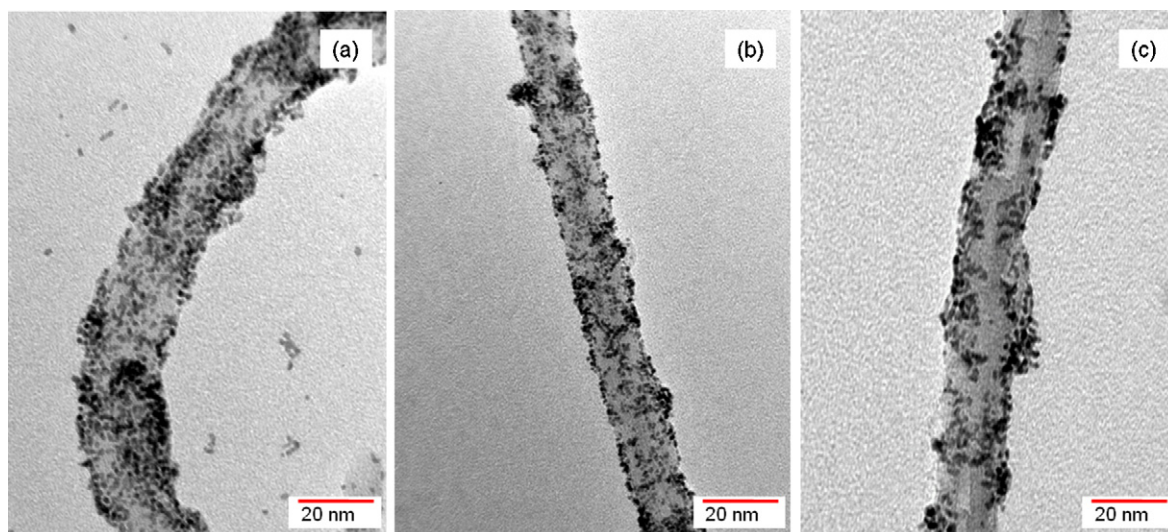


Fig. 4. TEM images of surfactant stabilized Pt/CNT catalyst heated within different times to 140 °C (a) 50 s, (b) 100 s, and (c) 150 s.

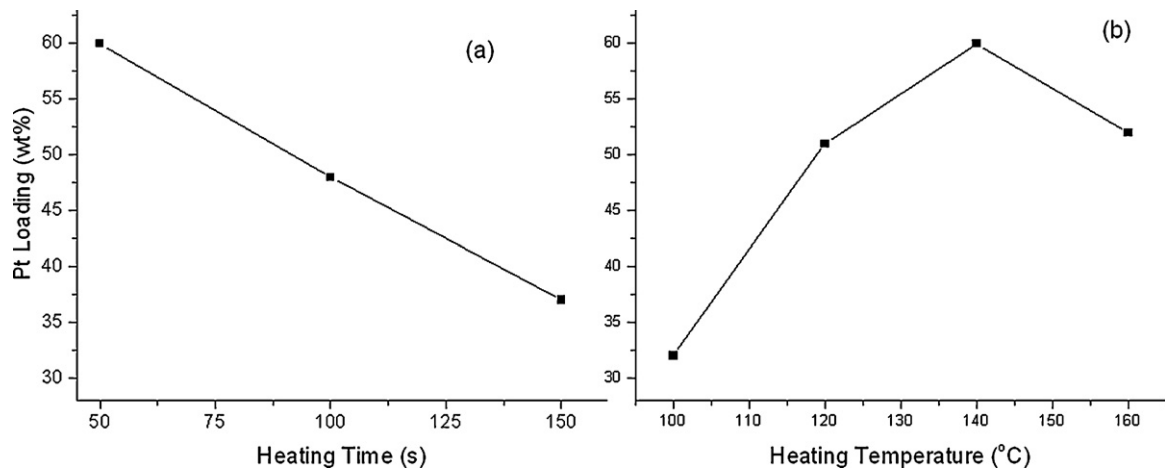


Fig. 5. Achieved Pt loading as a function of heating time at 140 °C (a) and as a function of temperature at a constant heating time of 50 s (b).

literature [31,32], it is observed that the size of metal nanoparticles is determined by the rate of reduction of the metal precursor.

In order to study the effect of the microwave heating temperature, a series of samples was prepared by heating within 50 s to temperatures of 100, 120, 140, and 160 °C, respectively. Fig. 5b reveals that the amount of deposited Pt increases with temperature up to 140 °C, while a further temperature raise again reduces the Pt loading. Fig. 6 shows the corresponding TEM images of Pt/CNT nanoparticles. It can be clearly seen from these images that there is no noticeable difference in the particle size for samples prepared between 100 and 140 °C (Figs. 6a–c). However, the most uniform distribution of the Pt nanoparticles is achieved at 140 °C. The achieved particle size range of 1.2–3.0 nm achieved at these

conditions is close to or better than previously reported values [33,34]. Fig. 6d shows that upon further temperature increase to 160 °C the Pt particles become larger and have an uneven distribution, which can be attributed to agglomeration of nanoparticles.

3.3. Comparison of catalysts during DMFC measurements

Pt/CNT catalysts synthesized under microwave irradiation were used as oxygen reduction catalyst at the cathode of a DMFC. A Pt loading of 0.25 mg cm^{-2} was employed in all cases while the same amount of a commercial PtRu/C catalyst was applied on the anode. A comparison of single cell DMFC polarization curves obtained with catalysts Pt/XC-72, Pt/CNT and surfactant stabilized Pt/CNT at the

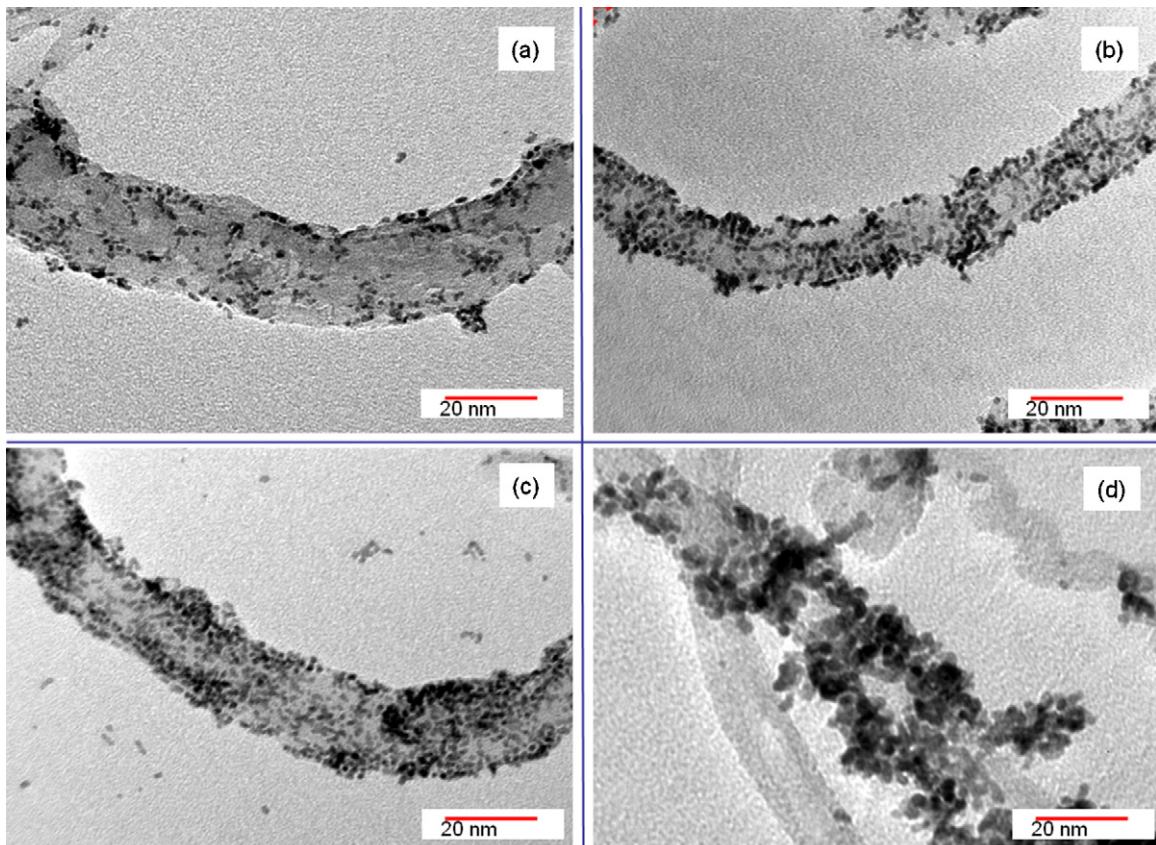


Fig. 6. TEM images of surfactant stabilized Pt/CNT catalyst synthesized at different temperatures (a) 100 °C, (b) 120 °C, (c) 140 °C, and (d) 160 °C. Heating time: 50 s.

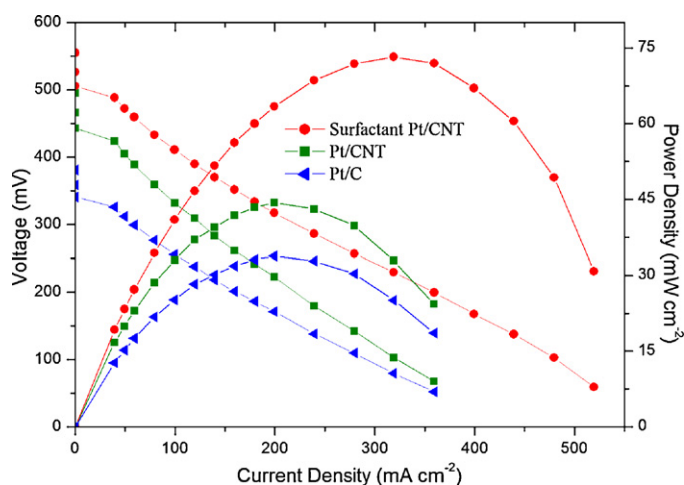


Fig. 7. Single cell DMFC polarization curves of various cathode catalysts synthesized with and without surfactant. Cathode: 0.25 mg cm^{-2} Pt; anode: PtRu/C (E-TEK), 0.25 mg cm^{-2} ; temperature: 80°C ; methanol: 1.0 M , 5 ml min^{-1} ; oxygen: 200 ml min^{-1} .

cathode under identical operating conditions is shown in Fig. 7. Much higher power densities are observed for the two samples with CNT as support compared with the Vulcan carbon supported catalyst. The maximum power density of the DMFC with the surfactant stabilized Pt/CNT catalyst was 74 mW cm^{-2} , while only 30 mW cm^{-2} could be achieved with the commercial catalyst. In order to know the stability of the Pt particles on the cathode catalyst of the surfactant stabilized electrode after 200 potential cycles. It was observed that no significance changes in the average particle size but a slight distorted structure of the CNT caused a detachment of few particles from the support. The Pt particles on the CNT might have detached mechanically during the electrode preparation.

Additional results obtained with catalysts heated for different times (50, 100, and 150 s) under microwave irradiation at 140°C are depicted in Fig. 8. The three MEAs show a systematic enhancement in the power densities with values of 74 mW cm^{-2} (50 s, 60 wt% Pt), 60 mW cm^{-2} (100 s, 48 wt% Pt), and 47 mW cm^{-2} (150 s, 37 wt% Pt). The variation in the DMFC performance of those catalysts can be understood from the Pt particle size and loading on the CNT carrier. A drift in the open circuit voltage (OCV) of the three cells is due to the small variation in the particle size of the three catalysts evident from the TEM images (Fig. 4). In addition, the variation in the

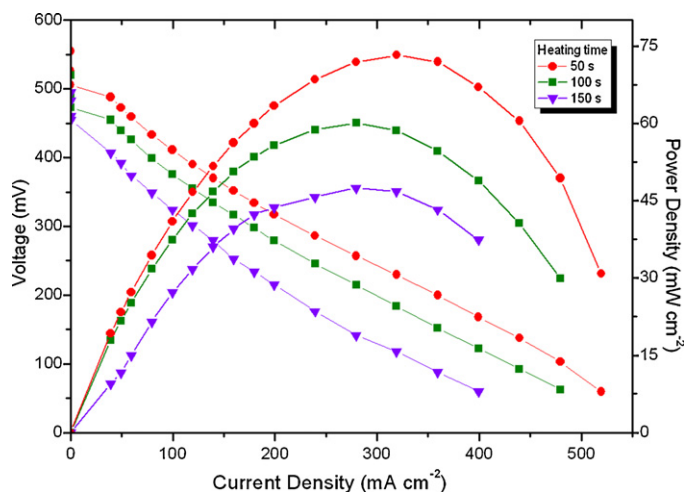


Fig. 8. Single cell DMFC performance of surfactant stabilized Pt/CNT catalyst synthesized with different heating times. Conditions as given in Fig. 7.

Pt loading (Fig. 5a) leads to changes in the thickness of the catalyst layer (5, 9, and $16 \mu\text{m}$ for samples with Pt contents of 60, 48, and 37 wt%, respectively) that was estimated by considering the thickness of the protonated Nafion membrane of $180 \mu\text{m}$ and that of the anode layer of $4 \mu\text{m}$. Consequently, the mass transfer properties of the catalyst layer are equally altered and a slight change in the slope of the polarization curves is observed. However, the main improvement in the performance results from the higher electrocatalytic activities of the smaller Pt particles.

4. Conclusions

A simple, rapid and energy efficient method has been successfully developed for the synthesis of Pt nanoparticles in highly active electrocatalysts by using microwave irradiation during the well known polyol reduction process. A uniform, small and spherical Pt nanoparticles decorated CNT surface is obtained using 3-(*N,N*-dimethyldecylammonio) propanesulfonate as a stabilizer. The amount, size and distribution of nanoparticles were optimised by varying the weight ratios of SB12 to Pt precursor, heating times, and heating temperatures. Single cell DMFC tests revealed that the surfactant stabilized Pt/CNT catalyst allows to achieve higher power density than samples prepared without stabilizing surfactant, and than MEAs prepared with a commercial catalyst.

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