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Short communication

Synthesis and characterization of carbon nanotubes supported platinum nanocatalyst for proton exchange membrane fuel cells

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ABSTRACT

Multi-walled carbon nanotubes (MWCNTs) were used as catalyst support for depositing platinum nanoparticles by a wet chemistry route. MWCNTs were initially surface modified by citric acid to introduce functional groups which act as anchors for metallic clusters. A two-phase (water–toluene) method was used to transfer $PtCl_6^{2-}$ from aqueous to organic phase and the subsequent sodium formate solution reduction step yielded Pt nanoparticles on MWCNTs. High-resolution TEM images showed that the platinum particles in the size range of 1–3 nm are homogeneously distributed on the surface of MWCNTs. The Pt/MWCNTs nanocatalyst was evaluated in the proton exchange membrane (PEM) single cell using H_2/O_2 at 80 °C with Nafion-212 electrolyte. The single PEM fuel cell exhibited a peak power density of about 1100 mW cm^{-2} with a total catalyst loading of 0.6 mg Pt cm^{-2} (anode: 0.2 mg Pt cm^{-2} and cathode: 0.4 mg Pt cm^{-2}). The durability of Pt/MWCNTs nanocatalyst was evaluated for 100 h at 80 °C at ambient pressure and the performance (current density at 0.4 V) remained stable throughout. The electrochemically active surface area (64 m^2 g^{-1}) as estimated by cyclic voltammetry (CV) was also similar before and after the durability test.

1. Introduction

Proton exchange membrane fuel cell (PEMFC) is the most promising energy technology for portable and stationary applications due to its advantages such as lower operating temperature and higher power density as compared to other types of fuel cells [1,2]. However, for wide-scale commercialization of PEMFCs, it should overcome several challenges including reducing the cost, maximizing the utilization of platinum catalyst, improving the performance and durability of the membrane electrode assembly [3,4].

Generally, there are two approaches for enhancing the utilization of platinum catalyst in PEMFCs, either by decreasing the particle size of catalyst or by uniform distribution on the surface of support materials. This paper focused on these two approaches simultaneously. Nanosized catalyst particles have unique characteristics such as the high specific surface area and superior catalytic activity, thus exhibit higher performance even at lower catalyst loading. Effective utilization of catalyst is feasible only through homogeneous distribution on a high surface area support material.

Numerous catalyst support materials for PEMFCs have been actively investigated, like various high surface area carbon [5], boron-doped carbon [6], carbon nanofibers (CNFs) [7], multi-walled carbon nanotubes (MWCNTs) [8,9], CNTs directly grown carbon paper [10,11], single-walled carbon nanotubes (SWCNTs) [12], etc. However, MWCNTs and their composites as catalyst support material have wide-scale interest due to their unique properties such as high chemical and oxidative stability, extraordinary mechanical strength, good electronic conductivity, high surface area and relatively simple manufacturing process. Moreover, the highly inert surfaces of MWCNTs necessitate surface modification to enhance the attachment of Pt nanoparticles. The oxidation of CNTs with HNO_3, $KMnO_4$, H_2O_2 or ozone gas is well known to introduce functional groups such as hydroxyl (–OH), carboxyl (–COOH), carbonyl (–CO) and sulfate (–OSO_3H) groups [12–16] on the surface of the CNTs. These groups provide nucleation anchors for the deposition of highly dispersed catalyst particles. In comparison, a mild citric acid (CA) treatment on CNTs was found to be simple and effective [17].

Platinum nanoparticles can be synthesized using different approaches reported in the literature. These approaches include: polyol process [18], electrodeposition [19], sonochemical processes [20], sputter deposition [21], gas reduction [22] and solution reduction method [10,12]. All these methods have been successful in yielding Pt nanoparticles but with wide particle size ranges, essentially due to agglomeration or inefficient control on the growth of nuclei. However, colloidal process has been well established to produce uniform particles with excellent control on nuclei growth

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and morphology [23]. For example, synthesis of gold colloids in solution with a particle size of 1–3 nm was accomplished using 1-dodecanethiol as a protective agent [24].

In the present study, we have synthesized platinum nanoparticles on MWCNTs using the two-phase ion transfer followed by solution reduction approach. The Pt/MWCNTs nanocatalyst was characterized using transmission electron microscope (TEM) for particle morphology and distribution. The single cell testing of Pt/MWCNTs based membrane electrode assembly (MEA) with catalyst loadings of 0.4 mg Pt cm^{-2} was performed using Nafion-212 electrolyte and H_2/O_2 at 80 °C. The performance stability and durability of the MEA was also examined using the potentiostatic (0.4 V) polarization tests for about 100 h.

2. Experimental

In the current study MWCNTs (OD 20–30 μm) were obtained from Cheaptubes Co., citric acid (CA) from Spectrum Chemicals, hexachloroplatinic acid ($H_2PtCl_6{\cdot}6H_2O$), tetraoctylammonium bromide (ToAB, $N(C_8H_{17})_4Br$), toluene ($C_6H_5CH_3$) and 1-dodecanethiol ($C_{12}H_{25}SH$, 98%) from Sigma–Aldrich.

2.1. MWCNTs surface modification

Carboxylic acid functionalization of MWCNTs was carried out using citric acid as follows: 200 mg of MWCNTs was added to the citric acid aqueous solution (500 mg of citric acid in 3 cm^3 deionized water) and subjected to 15 min ultrasonic treatment followed by a vigorous stirring for 1 h using magnetic stirrer. The solvent was removed by filtering and the MWCNTs were heat treated in a muffle furnace at 300 °C for 30 min. This treatment improves the wetting characteristics of MWCNTs by incorporating –COOH functional groups on the surface [17]. These groups act as anchors for metal deposition. For comparison purpose both modified and unmodified MWCNTs were used for the Pt deposition step.

2.2. Platinum nanoparticles deposition

Deposition of Pt nanoparticles (20 wt.% on MWCNTs) involves a two-phase transfer of $PtCl_6^{2-}$ followed by reduction in presence of 1-dodecanethiol [24]. Aqueous chloroplatinic acid (133 mg in 3 cm^3 DI water, orange colored) solution was mixed with ToAB (445 mg in 4 cm^3 toluene) solution and vigorously stirred for about 30 min at room temperature (RT). During this process, $PtCl_6^{2-}$ ions are transferred from aqueous solution to toluene with ToAB as the phase-transfer catalyst. The orange colored organic layer is extracted and the surface modified MWCNTs were added with constant stirring for 1 h. Meanwhile, 550 mg of 1-dodecanethiol was added and stirred for another 30 min. Aqueous sodium formate solution (680 mg in 10 cm^3 DI water) was added drop wise to the above dispersion and continued stirring for another 2 h at 60 °C. The mixture was filtered through G4 glass frit crucible to remove solvent and the solid product was thoroughly rinsed with ethanol to remove excess of 1-dodecanethiol and with copious amount of warm DI water to remove the remaining sodium formate. Pt/MWCNTs product was air dried overnight at 100 °C in an air oven and further heat treated at 800 °C for 3 h in a tubular furnace in argon atmosphere.

2.3. Preparation of membrane electrodes assembly

Fabrication of the MEA consisting of commercial catalyst (Pt/C) coated on anode side and Pt/MWCNTs catalyst coated on cathode side of the Nafion-212 membrane (Ion Power Inc., New Castle, DE, USA) was reported elsewhere [10,11]. Briefly, catalyst ink was prepared by adding isopropanol (20 cm^3 for 1 g of electrocatalyst) after purging the Pt/C (for anode) catalyst powder (TKK, Japan) or Pt/MWCNTs (for cathode) in flowing nitrogen gas for about 30 min to avoid any flame/ignition. In order to extend the reaction zone of the catalyst layer, 5 wt% Nafion® (Ion Power Inc., New Castle, DE, USA) dispersion (10 cm^3 for 1 g of electrocatalyst) was added to the catalyst slurry. Catalyst layer on Nafion-212 with 5 cm^2 active area was fabricated as anode by spraying the catalyst ink using the micro-spray method. The catalyst loading on the anode and cathode was about 0.2 and 0.4 mg Pt cm^{-2}, respectively. The catalyst coated Nafion-212 membrane and the MEA were vacuum dried at 30 °C for 15 min before assembling them in the test cell.

The MEA was assembled by sandwiching inside the single test cell (Fuel Cell Technologies Inc., Albuquerque, NM, USA) along with the GDL (fabricated by a wire rod coating method [25]) at both sides. Gas sealing was achieved using silicone coated fabric gasket (Product #CF1007, Saint-Gobain Performance Plastics, USA) and with a uniform torque of 0.45 kg m. The single cell fuel cell performance was evaluated at 80 °C at various gas pressures using Greenlight Test Station (G50 Fuel cell system, Hydrogenics, Vancouver, Canada). The flow rates were fixed at 200 and 400 sccm for H_2 and O_2, respectively. The steady-state voltage values were collected by holding the cell at each current density values for 60 s.

2.4. Characterization

The surface morphology of Pt/MWCNTs was characterized using Philips CM200-FEG TEM. Pt/MWCNTs dispersed in methanol was applied on a lacy carbon grid for TEM characterization to examine the Pt particle size and distribution. Fuel cell durability test was carried out at 0.4 V, 80 °C, with 100% RH and ambient pressure for 100 h. Cyclic voltammetry (CV) was carried out for measuring electrochemical active surface area (ECA) of Pt catalyst using EG&G 2273 PARSTAT potentiostat–galvanostat. The cell was equilibrated for about 2 h with humidified H_2 and N_2 gases at 30 °C prior to voltage scanning. ECA was determined before and after the durability test.

3. Results and discussion

In the current study platinum deposition on MWCNTs was accomplished by the two-phase transfer of Pt ions followed by sodium formate reduction. Brust et al. has reported synthesis of thiol-derivatized colloidal gold nanoparticles in a two-phase liquid–liquid system [24]. In detail, the process involves transfer of $PtCl_6^{2-}$ ions from aqueous to toluene solution using ToAB as a phase transfer catalyst and subsequent reduction using aqueous sodium formate solution in the presence of 1-dodecanethiol to yield platinum nanoparticles. The process is illustrated using the following reactions:

$$\begin{aligned} &PtCl_6^{2-}(aq) + N(C_8H_{17})_4^{+}(C_6H_5Me) \\ &\quad \rightarrow N(C_8H_{17})_4^{+}PtCl_6^{2-}(C_6H_5Me) \end{aligned} \tag{1}$$

$$\begin{aligned} &m PtCl_6^{2-}(C_6H_5Me) + n C_{12}H_{25}SH(C_6H_5Me) + 4me^{-} \\ &\quad \rightarrow 6mCl^{-}(aq) + (Pt_m)(C_{12}H_{25}SH)_n(C_6H_5Me) \end{aligned} \tag{2}$$

where the electrons are provided by $HCOO^-$ from the reducing solution. It was reported that 1-dodecanethiol forms a self-assembled monolayer on the growing nuclei inhibiting agglomeration in the solution [24]. It is expected that 1-dodecanethiol aids in homogeneous distribution of uniform Pt nanoparticles on MWCNTs in the present study. Fig. 1 illustrated the schematic representation of surface modification of MWCNTs and Pt nanoparticles deposition. The major advantage of the CA modification process is that it is simple

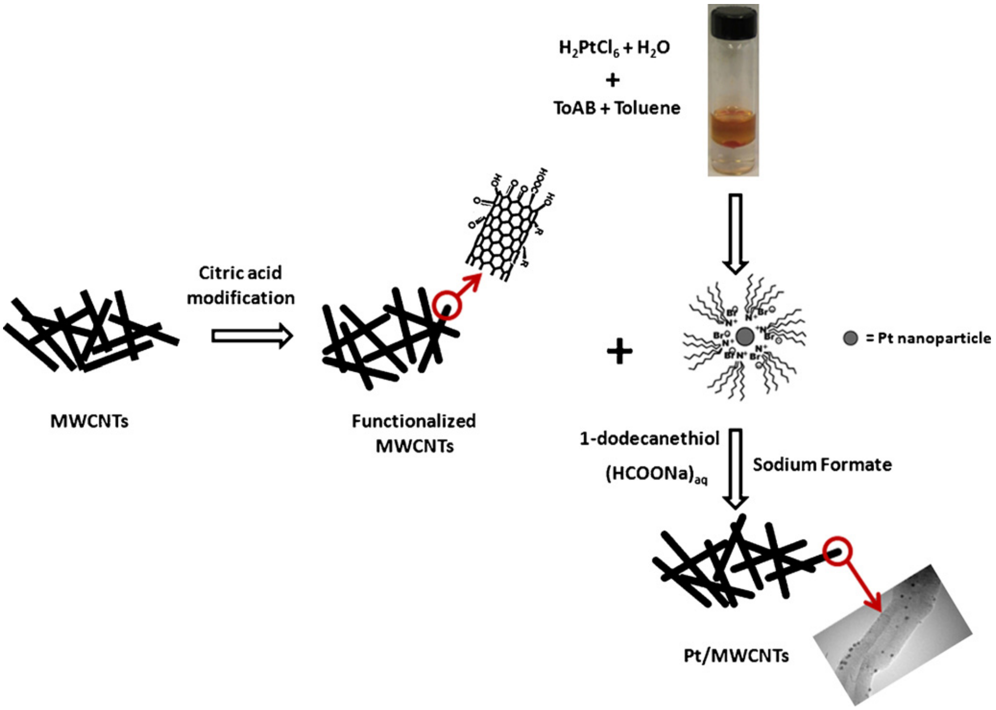

Fig. 1. Schematic representation of surface modification of MWCNTs and Pt nanoparticles deposition.

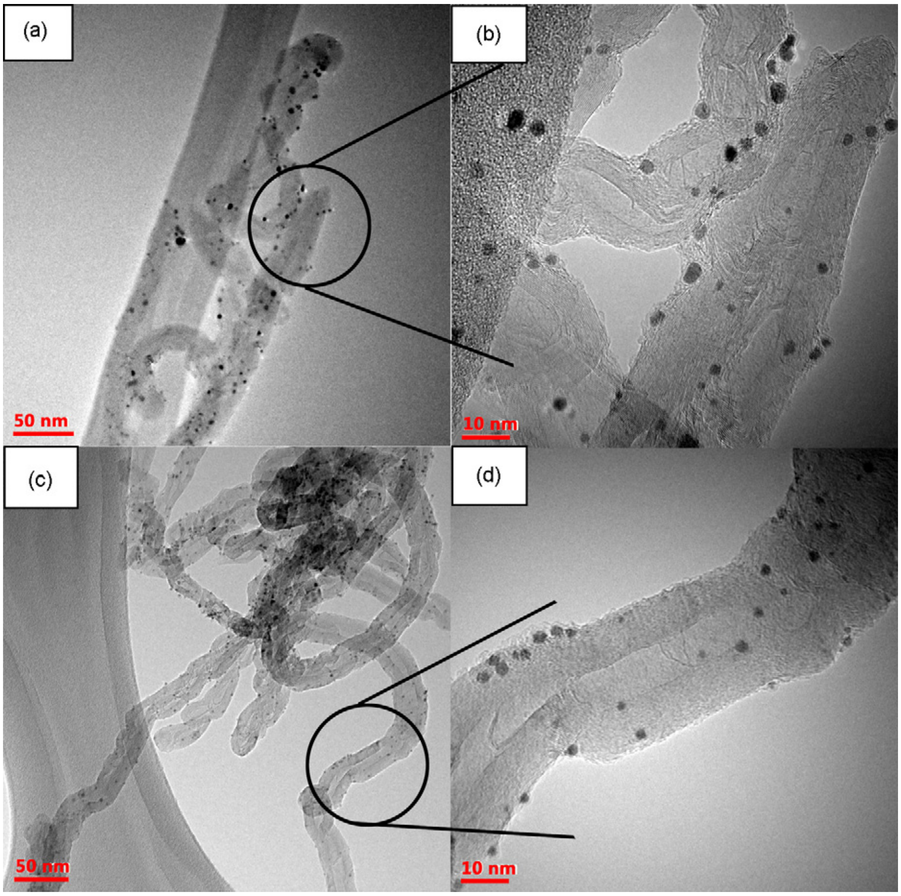

Fig. 2. High-resolution transmission electron micrographs of Pt/MWCNTs at different magnifications: (a and b) images of procedure 1, (c and d) images of procedure 2.

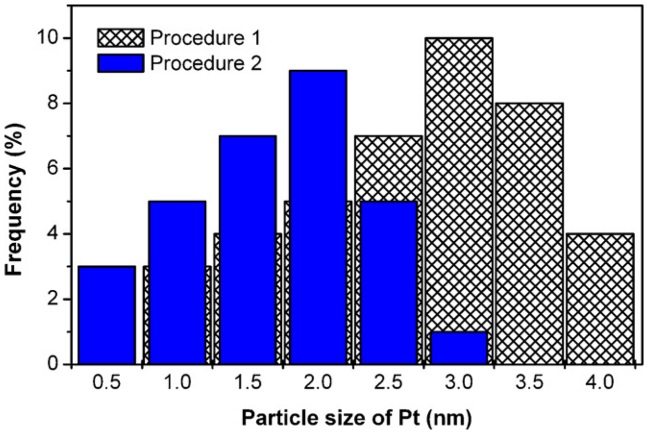

Fig. 3. Particle size distribution of Pt nanoparticles of Pt/MWCNTs made by procedures 1 and 2.

without the multi-stage heating, filtration and washing involved in acid oxidation process [26,27]. Citric acid modification creates functional groups which act as anchors during Pt reduction process. Essentially the functional groups act as defects (nucleation sites) to increase the nucleation rate as compared to growth rate that will lead to particle agglomeration. Hence CA treatment aids in controlling or restricting the particle agglomeration and will indirectly control the particle size.

The effect of surface modification of MWCNTs using CA was investigated by fabricating Pt/MWCNTs with and without the CA modification step. The synthesis approaches were termed as procedure 1: MWCNTs without citric acid treatment and procedure 2: MWCNTs with citric acid treatment. Fig. 2 showed the TEM images of the Pt/MWCNTs fabricated using the two procedures described above. It can be seen that Pt nanoparticles were uniformly distributed on the surface in both the cases. However, the Pt particle size was more uniform in case of CA modified MWCNTs as compared to the unmodified MWCNTs. The statistical particle size distributions of the respective TEM images (Fig. 2b and d) were illustrated in Fig. 3. The median particle size for the unmodified MWCNTs is in the range of 2.5–3.0 nm whereas that for the modified MWCNTs is 1.5–2.0 nm. Hence surface modification of MWCNTs contributes in decreasing the size of particles as well as narrowing the size distribution range. Effective control on the particle size and distribution is essential for enhanced fuel cell performance, durability and reduction in cost of the fuel cell.

Figs. 4 and 5 illustrated the single cell performance of samples fabricated using procedures 1 and 2, respectively at different back pressures. Table 1 compared the FC performance of the two samples. Evidently the surface modified MWCNTs exhibited improved fuel cell performance compared to that of the unmodified MWCNTs at a given back pressure. The current densities at 0.4 V for unmodified and modified MWCNTs were 1800 and 2300 mA cm^{-2}, respectively at 80 °C and ambient pressure. Moreover, the initial drop of cell voltage from the open circuit voltage (OCV) is small for Pt/MWCNTs with CA modification compared to that without CA medication, which is an indication of higher activity (or catalyst utilization) for Pt, at all operating conditions. For example, the voltage drop was ~80 mV (at 50 mA cm^{-2} at 101 kPa) for the CA modified Pt/MWCNTs catalyst (procedure 2) and ~150 mV (at 50 mA cm^{-2} at 101 kPa) for the catalyst prepared without CA modification (procedure 1). Evidently, the CA modification step has significant effect on the activity of the MEA and FC performance. In order to compare the fuel cell performance of the Pt nanocatalyst developed in the present study, an MEA was also fabricated with commercial catalyst (TKK, Japan) based cathode with similar loading and evaluated at 100% RH at ambient pressure. As evident from Fig. 5, the Pt nanocatalyst based MEA performs much better compared to that of the commercial catalyst.

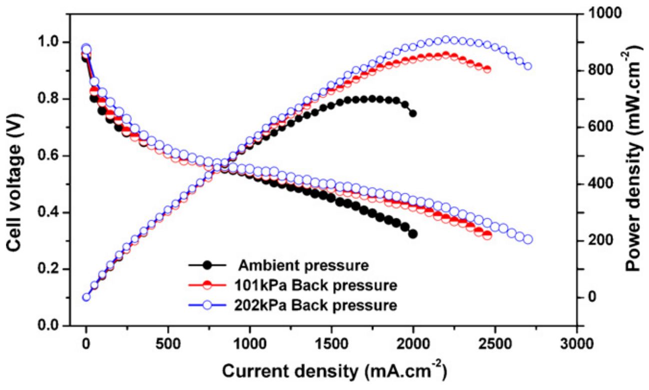

Fig. 4. Fuel cell performance of an MEA with Pt/MWCNTs nanaoparticles prepared by procedure 1 at 80 °C using H_2/O_2 at various operating pressures.

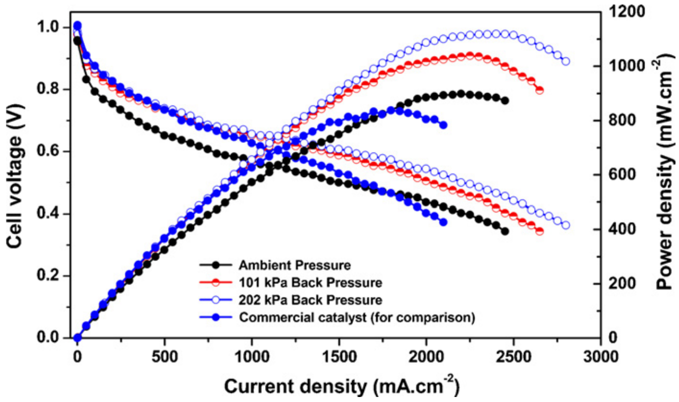

Fig. 5. Fuel cell performance of an MEA with Pt/MWCNTs nanaoparticles prepared by procedure 2 at 80 °C using H_2/O_2 at various operating pressures, along with that for commercial Pt based cathodes at ambient pressure.

Fig. 6 showed the durability study of a single cell, with the MEA fabricated using procedure 2, for a period of 100 h. The current density data was obtained at 1 h intervals at a constant cell voltage of 0.4 V, 80 °C, 100% RH and ambient pressure. The current density was highly stable during the 100 h operation, although it was a very short time to assess the stability of MEA; it gave an indication of the high durability of the MEA. The electrochemical active area (ECA) of the MEA with Pt/MWCNTs (procedure 2 with CA modification) measured before and after 100 h operation and MEA with Pt/MWCNTs (procedure 1 without CA modification) was calculated from the CV patterns shown in Fig. 7. ECA was determined as 64 m^2 g^{-1} for the Pt/MWCNTs made with CA modification (procedure 2), which remained unchanged after the durability test. The stable current density and unchanged ECA of Pt nanocatalyst for

Table 1
Comparison of fuel cell performance of MEAs of Pt/MWCNTs based catalysts prepared by procedures 1 and 2.

Procedure		#1	#2
Ambient pressure	W_p (mW cm^{-2})	696	898
	CD at 0.4 V (mA cm^{-2})	1797	2301
101 kPa BP	W_p (mW cm^{-2})	838	1027
	CD at 0.4 V (mA cm^{-2})	2151	2499
202 kPa BP	W_p (mW cm^{-2})	907	1120
	CD at 0.4 V (mA cm^{-2})	2301	2751
ECA (m^2 g^{-1})		53	64

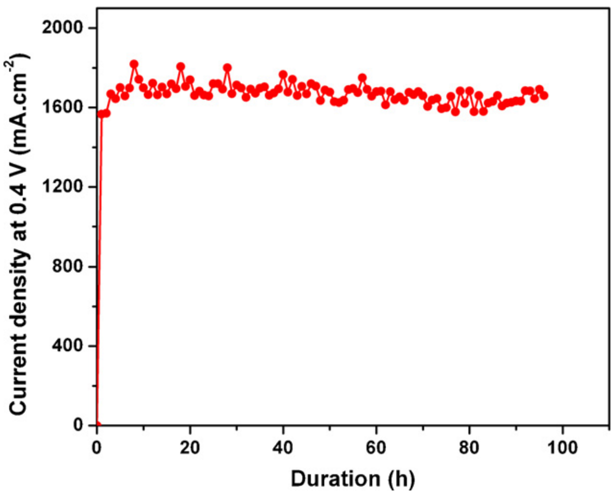

Fig. 6. Durability data of an MEA with Pt/MWCNTs nanaoparticles prepared by procedure 2 at 80 °C using H_2/O_2, 100 % RH and ambient pressure.

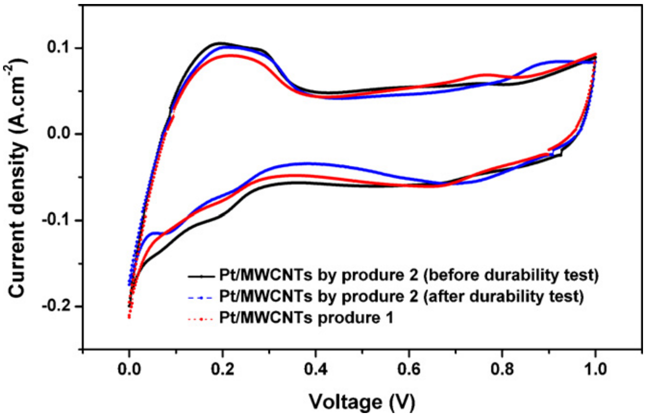

Fig. 7. Cyclic voltammograms of MEAs with Pt/MWCNTs based catalysts prepared by procedures 1 and 2.

100 h were indications of the high stability of Pt/MWCNTs based MEA. The ECA for MEA (procedure 1) was estimated as 53 $m^2 g^{-1}$. Higher ECA value for the Pt/MWCNTs with CA (procedure 2) compared to that without CA (see Table 1) clarified the effect of surface modification on the higher Pt utilization. Further work in lowering the catalyst loading is in progress.

4. Conclusions

The Pt/MWCNTs nanocatalyst was synthesized by the two-phase transfer of Pt salt followed by sodium formate reduction in the presence of 1-dodecanethiol. The effects of surface modification of MWCNTs using citric acid process were also reported. The synthesis technique has the advantages of decreasing the size of catalyst while increasing the chemical activity and stability of the MEA. High-resolution TEM analysis revealed that a highly homogenous dispersion of platinum nanoparticles with a size range of 1–3 nm was deposited on surface modified MWCNTs. The single cell PEMFC with a total catalyst loading of 0.6 mg Pt cm^{-2} (anode: 0.2 mg Pt cm^{-2} and cathode: 0.4 mg Pt cm^{-2}) exhibited high power density of 900 mW cm^{-2} using H_2/O_2 at 80 °C and ambient pressure. High durability and stability of MEA were indicated by comparisons of the electrochemical active area of the Pt catalyst before and after the 100 h durability test.

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