Published in final edited form as:

Carbon N Y. 2011 April ; 49(4): 1145–1150. doi:10.1016/j.carbon.2010.11.029.

Catalytic Activity of Ultrathin Pt Films on Aligned Carbon Nanotube Arrays

Xin Su, Ji Wu, and Bruce J. Hinds*

Department of Chemical and Materials Engineering, University of Kentucky, Kentucky 40506 (USA)

Abstract

Uniform ultrathin Pt films were electrodeposited onto an aligned array of carbon nanotubes (CNTs) for high-area chemically stable methanol fuel cell anodes. Electrochemical treatment of the graphitic CNT surfaces by diazoniumbenzoic acid allowed for uniform Pt electroplating. The mass activity of the Pt thin film can reach 400 A/g at a scan rate of 20 mV/s and in a solution of 1 M CH₃OH/0.5 M H₂SO₄. A programmed pulse potential at 0V was also seen to nearly eliminate the effects of carbon monoxide poisoning. The mass activity of Pt for methanol oxidation can be maintained at 300 A/g for more than 3000 s, which is 19 times of that under a constant potential of 0.7 V (vs Ag/AgCl).

1. Introduction

Due to increasing energy demands and the possibility of significant methanol production via biomass conversion, there is active research focused on direct methanol fuel cells for electricity generation. The theoretical potential for the standard methanol cell is 1.25V, which is close that for hydrogen cell. Furthermore the theoretical energy density of methanol fuel cell can reach 6.1 kWh/kg [1], which is 10 times higher than that of Li battery [2] which is a critical factor in the transportation sector. However the methanol reaction rate is several orders of magnitude lower than that of hydrogen oxidation on metal electrodes [3].

Methanol fuel cell fabrication thus requires catalytic Pt loading onto the surfaces of electrodes to have useful methanol oxidation rates. Although Pt is an efficient catalyst for methanol fuel cells, it can be the most expensive component. Therefore scientists have been trying to increase the catalytic activity of Pt in fuel cell by reducing the diameters of Pt nanoparticles to as small as 1 nm [4] for the highest surface to volume ratio, by adjusting facet orientations of Pt nanocrystals [5] to be the most reactive faces, or by monolayer growth on nanoporous Au [6]. The ideal system is to have a stable and uniform nm-scale coating of Pt directly on the surface of a high area conductive electrode that is open to the fast mass transport of flowing liquids.

© 2010 Elsevier Ltd. All rights reserved.

*Corresponding author: Fax: 0018593231929. bjhinds@engr.uky.edu (B.J. Hinds).

Publisher's Disclaimer: This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final citable form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

Carbon nanofiber and nanotube mats are the strong candidates for catalyst supports, due to their high surface area, conductivity, and chemical stability [7–9]. Carbon nanotube (CNT) arrays in particular, have high specific surface areas due to the small diameter (10–40nm) of CNTs and high areal density ($\sim 10^9$ /cm²). The chemical inertness of carbon fibers makes the uniform coatings a challenge since Pt will continue to deposit onto an initial Pt nucleation site instead of the high energy graphite surface. In electro-plating, microns to submicron Pt particles thus result with very poor surface to volume ratios reducing the catalytic mass activity. A variety of treatments have been explored on carbon supports to improve Pt catalytic activity by controlling the Pt nanoparticle dispersion onto carbon fibers/tubes [10–13]. These techniques rely on strong oxidation of fibers/tubes by plasma and ozone [11], or hydrogen peroxide [12] and strong oxidizing acids [10, 13] with limited success [10–15]. Recently a general class of CNT surface chemistry based on diazonium salt decomposition has been developed [16]. In this chemistry the diazonium group decomposes to form stable N₂ and a highly reactive carbon cation radical that reacts with graphite. This reaction can be controllably activated by electrochemistry at an electrode surface [17] for precise thickness control. The chemistry of the diazonium group can also be tailored [17, 18] to favor uniform metal ion coordination and, we hypothesize, allow uniform nm-thick Pt electrodeposition on CNTs.

Another difficulty with Pt electrodes in MeOH fuel cells is poisoning of the Pt surface by CO byproducts. Additives such as Ru [19, 20], Ni [21, 22], Au [23] have been used to enhance the activity and stability of catalyst by reduction of CO poisoning. However the surface additives can be etched over time reducing the electrode stability and performance. Needed are alternate methods to eliminate CO poisoning that are stable for indefinite periods of time.

In this report we describe an electrochemical method to produce uniform nm-scale thick Pt films on a high area array of CNTs. The mass-activity of Pt catalyst is dramatically improved due to its large surface to volume ratio on CNT supports. A new voltage pulse method, between the operational voltage 0.7V and a recovery voltage 0V (vs. Ag/AgCl), was found to eliminate the effects of CO poisoning of Pt electrode without the requirement of potentially unstable additives.

2. Experimental Section

2.1 Materials

Aligned CNTs were grown on quartz slides for 2 h by chemical vapor deposition method which ferrocene / xylene were used as precursors at 700 °C as previously reported [24]. The Buehler epoxycure resin and hardener of formerly expoxide were purchased from Buehler. The chloroplatinic acid hydrate was from Aldrich. The aryl diazonium salt was synthesized in the lab according to the references reported by Belanger et.al [25]. 5 g of p-aminobenzoic acid was dissolved in 20 ml of deionized water at 60°C with magnetic stir. Then 7 ml of concentrated HCl solution was added into it dropwise. The mixture was then cooled down to –3°C and 15 ml of a cold solution of 3 M sodium nitrite were added slowly to it. The whole solution was kept at –3°C one hour for complete reaction. Then the mixture was then filtered. To this, 10 ml of a cold solution of 4.5 M NaBF₄ was added to stabilize the

diazonium salt. About 30% of the water was evaporated under low vacuum. The concentrated solution was cooled down to -3°C for diazonium salt crystallization. The salt was finally vacuum filtered and rinsed by cold water and ether.

2.2 Preparation of the Pt Deposited on Aligned CNTs

The schematic of the process to prepare aligned CNT substrates is shown in Figure 1. The goal was to stabilize an aligned array of CNTs with only the tip region embedded into an epoxy support. At first, an epoxy film was spun coat on a glass substrate at 5000 rpm. The film thickness of the epoxy was about 10 μm . Aligned CNTs (40~120 μm in length) grown on quartz slides were pressed on epoxy film at a weight loading of 25 g/cm^2 . The sample was then kept in a vacuum oven at 60 $^{\circ}\text{C}$ for 16 hours to cure the epoxy. After the epoxy was completely cured, the quartz substrate could be easily separated from the CNTs by mechanical peeling. The aligned CNTs, which were partly embedded in epoxy film coated on glass slide, were used as the working electrode. The electrochemical deposition of Pt on aligned CNTs was performed in three-electrode cell using a potentiostat (PAR Model 263A) with the reference electrode of Ag/AgCl from Bioanalytical. Pt wire was used as the counter electrode. The electrolyte solution for electrochemical depositions were 4.8 mM $\text{H}_2\text{PtCl}_6/0.1$ M HCl/0.3 M NaCl. The solution was purged by Ar gas for 10 minutes before use.

2.3 Surface Modification of CNTs

The surface of CNTs was modified via an approach of aryl diazonium grafting, which had been known to react covalently with CNTs and graphite [16–18]. This was carried out for 40 s, at a potential of -0.6 V (vs Ag/AgCl) and in the solution of 5 mM aryl diazonium salt ($\text{H}_5\text{C}_7\text{O}_2\text{N}_2\text{BF}_4$)/0.1 M HCl/0.1 M KCl. Before diazonium grafting, the electrolyte solution was purged by Ar gas for 20 minutes to remove the oxygen adsorbed on the aligned CNT substrates and in solution. The theoretical monolayer thickness of this functional group grafted on the carbon surface was approximately 0.7 nm.

2.4 Cyclic Voltammogram (CV) and Programmed Pulse Potentials

The CV measurements were carried out in the three-electrode cell using a potentiostat (PAR Model 263A) with a reference electrode of Ag/AgCl. The Pt deposited on aligned CNTs was used as the working electrode and the Pt wire as the counter electrode. The electrolyte solutions were 0.5 M H_2SO_4 and 1 M methanol/ 0.5 M H_2SO_4 . All the solutions were purged by Ar gas for 20 minutes before running CV to remove the adsorbed gas in solution and the surface of sample.

2.5 ICP-OES Analysis

After CV measurement, the sample was rinsed by DI water 6 times and then immersed in aqua-regia (concentrated HCl and concentrated HNO_3 with a volume ratio of 3:1) for 24 h to completely dissolve Pt. The concentration of Pt in the solution was detected by ICP-OES (Varian Vista Pro). For Pt film, the calibration curve for ICP consisted of five datum points and was linear in the range 0.02mg/l to 1mg/l. The detection limit was 0.02mg/l and the sample concentration was near 0.14 mg/l. Meanwhile, for Pt nanoparticles, the calibration

curve for ICP also consisted of five datum points and was linear in the range 0.1mg/l to 10mg/l. The sample concentration was near 7.05 mg/l.

2.6 SEM, EDS and HRTEM

The morphology and composite of the sample were characterized by Scanning Electron Microscopy (SEM), Energy Dispersive Spectroscopy (EDS) (Hitachi S-4300) under the operating voltage of 20 KV and High Resolution Transmission Electron Microscopy (HRTEM), EDS (Jeol-2010f) under the operating voltage of 200 KV. For SEM, portions of the sample were cut and mounted on double sided conductive tape. The electrodes were conductive and no charging effects were seen. For HRTEM, the CNT arrays were ultrasonically dispersed by Branson 1510 in deionized water for 15 minutes. Several drops of solution were placed on the copper TEM grids from Electron Microscopy Science and solvent evaporated.

3. Result and Discussion

The aligned CNT arrays offer significant advantages for fuel cell electrodes since they are highly conductive and have a high active surface area (785 cm² over a nominal 1 cm² substrate area). Though conductive, the graphitic CNTs are chemically stable and highly inert to corrosion. The CNTs used range from lengths of 40 μ m to 120 μ m and have outer diameters of ~50nm. The as grown aligned CNT arrays are transferred to an epoxy polymer film that binds to only the top 10 μ m of CNT tips. The advantages of transferring CNTs to an adhesive layer [26, 27] is to recycle the relatively expensive quartz substrates used in the CVD growth and have a flexible and chemically inert polymer act as the final electrode support. The top view and cross-sectional SEM images of the aligned CNTs substrates are shown in Figure 2 (a) and (b). The conductive CNTs composing the array cross each other within the epoxy and the open electrode volume giving a measured in sheet resistance of 100 ohm/ sq. The sheet resistance of aligned CNTs array decreased to 21 ohm/ sq after uniformly coating with Pt. The sheet resistance can be reduced further by increasing thickness and approach that required for fuel cell applications [28, 29].

The primary hypothesis of this report is that electrochemical grafting of ligands that can coordinate metal ions onto CNTs will aid in the uniform electrodeposition of Pt, thereby increasing Pt mass activity. Graphitic surfaces, such as CNTs, are well known to be chemically inert and uniform coatings are unfavorable compared to island growth onto defects or other nucleation sites. As a control experiment, Pt was first electrodeposited on the unmodified CNTs [30] at a potential of -0.15 V (vs Ag/AgCl) and in a solution of 4.8 mM H₂PtCl₆/0.1 M HCl/0.3 M NaCl for 1.5 h. As shown in Figure 3 (a), the morphology of Pt particles deposited on bare aligned CNT substrates is highly nonuniform with large crystallites and poor surface to volume ratios. The high surface energies of bare CNTs favor the Pt growth onto existing crystals instead of forming a uniform Pt coating on CNTs. The HRTEM image of the unmodified CNT, in a region away from large Pt particles, after electrodeposition, is shown in Figure 3 (b). No uniform coating of Pt is observed on the unmodified CNTs and the deposited Pt is exclusively within the large particles. To have a thin (1–2nm thick) uniform Pt deposition onto CNTs, the surface of CNTs was modified

with functional carboxyl groups via a diazonium grafting method [16–18]. After the surface modification of CNTs with carboxyl groups, Pt was electrodeposited under the same condition as described above. The SEM image in Figure 3 (c) shows that the surface modification of the CNTs with the carboxyl groups can prevent the formation of large Pt particles during the electrochemical deposition. From the corresponding HRTEM and EDS data in Figure 3 (d) a uniform Pt coating of ~2nm is seen on top of a polybenzoic acid film (~2nm). EDS spectra in the inset confirms the presence of Pt in the image. ICP analysis of a solution of Pt dissolved from the CNT array quantifies 6.9 μg Pt that had been deposited on the aligned CNT array (0.3 cm^2 planar sample surface area). Cyclic Voltammogram (CV) was used to evaluate the catalytic activity of the Pt nano-coatings on CNTs which were modified with carboxyl groups. The CV was first performed for hydrogen reduction in a solution of 0.5 M H_2SO_4 and at a scan rate of 100 mV/s. The CV curve is similar to classic curve of Pt nanostructure reported by Wallace et.al [5]. Methanol oxidation by the Pt coated CNTs was then studied by CV with a solution of 1 M CH_3OH /0.5 M H_2SO_4 at a scan rate of 20 mv/s. From the current level in Figure 4 (b) and the mass of Pt measured by ICP, we observe a mass activity for methanol oxidation above 400 A/g (blue line), which is much higher than that of Pt nanoparticles on bare CNTs ~20A/g (red line), due to the ultra-thin and uniform coating on the CNTs having a much larger surface to volume ratio. This is also a significant improvement compared to the reports by Liu et al. of 181 A/g [8]. Furthermore, from the insert in Figure 4 (b), the experimental curve of peak currents ratios vs different scan rates from 20mv/s to 100mv/s matched the calculated curve from Randles–Sevcik equation: $I_p = 2.69 \times 10^5 \text{ AD}^{1/2} n^{3/2} v^{1/2} \text{C}$. This demonstrates that there is no apparent mass-transport limitation of methanol through the CNTs arrays.

The CV of Figure 4 (b) shows a CO oxidation peak at 0.55 V (vs Ag/AgCl) and a methanol oxidation peak at 0.75 V (vs Ag/AgCl). It is well known that CO generated during methanol oxidation can poison the Pt catalyst surface [20]. As shown in Figure 5 (a), the current density for methanol oxidation on Pt/CNT electrode at 0.7 V (vs Ag/AgCl) dropped quickly due to the CO poisoning. During the course of control experiments, we found that we can recover the current almost entirely by applying a short voltage pulse at 0V (vs Ag/AgCl). These pulse potentials at 0V eliminated the effect of CO poisoning and hence dramatically improved catalyst activity at the operating voltage of 0.7V. This new recovery pulse method has significant application in fuel cell operations since additives such as Ru, which can corrode with time, are not needed. From Figure 5 (a), the current density of the Pt nanostructure under the pulse potentials can be maintained at 300 A/g for more than 3000 s, which is about 19 times of that under a constant potential of 0.7 V (vs Ag/AgCl). The sequence of operational (0.7V, 10 s) and recovery (0V, 1–10 s) pulses is shown in Figure 5 (b). As shown in Figure 5 (c), the optimal recovery time was found to be between 5 and 7 seconds. This would give an overall efficiency of 62% of operating current accounting for lost current production during the recovery time. The pulse potential method can be used with two or more cells in tandem with programmed switching. This would result in continual energy output while retaining the high mass activity of catalyst. Here, the pulse potential appears to remove absorbed CO very efficiently from the surface of the catalyst during the recovery time and the mechanism is currently under investigation.

4. Conclusions

Development of a high area, conductive and chemically stable catalyst support is important for fuel cell development. The surface modification of CNTs via diazonium grafting of a metal coordinating functional groups significantly improved the morphology of Pt, achieving uniform 2 nm-thick coatings. The thin organic layer does not impede electrical conductivity and the mass activity of Pt reached 400 A/g, which is a significance enhancement over other reports of high area carbon electrode supports [8, 10, 13]. It was also demonstrated that by applying a simple recovery pulse potentials, the current density of methanol oxidation can be maintained at a value as high as 300 A/g for 3000 s, which is about 19 times of that using a constant potential of 0.7 V (vs Ag/AgCl). This recovery method can eliminate the need for chemically unstable additives to prevent catalyst poisoning.

Acknowledgments

The authors would like to thank Rodney Andrews and Dali Qian from the Center for Applied Energy, University of Kentucky, for supplying MWCNTs. Facility support was provided by the Center for Nanoscale Science and Engineering and Electron Microscopy Center at the University of Kentucky. Financial support from DOE EPSCoR (DE-FG02-07ER46375), NSF CAREER (0348544), and NIH NIDA (R01DA018822) is greatly appreciated by the authors.

References

1. McGrath KM, Prakash GKS, Olah GA. Direct methanol fuel cells. *Journal of Industrial and Engineering Chemistry*. 2004; 10(7):1063–1080.
2. Li HQ, Wang YG, Na HT, Liu HM, Zhou HS. Rechargeable Ni-Li Battery Integrated Aqueous/Nonaqueous System. *Journal of the American Chemical Society*. 2009; 131(42):15098–15099. [PubMed: 19803514]
3. Iwasita T. Electrocatalysis of methanol oxidation. *Electrochimica Acta*. 2002; 47(22–23):3663–3674.
4. Mu YY, Liang HP, Hu JS, Jiang L, Wan LJ. Controllable Pt nanoparticle deposition on carbon nanotubes as an anode catalyst for direct methanol fuel cells. *Journal of Physical Chemistry B*. 2005; 109(47):22212–22216.
5. Tian N, Zhou ZY, Sun SG, Ding Y, Wang ZL. Synthesis of tetrahedral platinum nanocrystals with high-index facets and high electro-oxidation activity. *Science*. 2007; 316(5825):732–735. [PubMed: 17478717]
6. Wang RY, Wang C, Cai WB, Ding Y. Ultralow-Platinum-Loading High-Performance Nanoporous Electrocatalysts with Nanoengineered Surface Structures. *Advanced Materials*. 2010; 22(16):1845–1848. [PubMed: 20512959]
7. Tang H, Chen JH, Nie LH, Liu DY, Deng W, Kuang YF, et al. High dispersion and electrocatalytic properties of platinum nanoparticles on graphitic carbon nanofibers (GCNFs). *Journal of Colloid and Interface Science*. 2004; 269(1):26–31. [PubMed: 14651891]
8. Liu Y, Chen J, Zhang WM, Ma ZF, Swiegers GF, Too CO, et al. Nano-Pt modified aligned carbon nanotube arrays are efficient, robust, high surface area. *Electrocatalysts. Chemistry of Materials*. 2008; 20(8):2603–2605.
9. Prehn K, Adelung R, Heinen M, Nunes SP, Schulte K. Catalytically active CNT-polymer-membrane assemblies: From synthesis to application. *Journal of Membrane Science*. 2008; 321(1):123–130.
10. Hull RV, Li L, Xing YC, Chusuei CC. Pt nanoparticle binding on functionalized multiwalled carbon nanotubes. *Chemistry of Materials*. 2006; 18(7):1780–1788.
11. Brandl W, Marginean G. Functionalisation of the carbon nanofibres by plasma treatment. *Thin Solid Films*. 2004; 447:181–186.

12. Morenocastilla C, Ferrogarcia MA, Joly JP, Bautistatoledo I, Carrascomarin F, Riverautila J. Activated carbon surface modifications by nitric-acid, hydrogen-peroxide, and ammonium peroxydisulfate treatments. *Langmuir*. 1995; 11(11):4386–4392.
13. Guha A, Lu WJ, Zawodzinski TA, Schiraldi DA. Surface-modified carbons as platinum catalyst support for PEM fuel cells. *Carbon*. 2007; 45(7):1506–1517.
14. Li ZJ, Yan WF, Dai S. Surface functionalization of ordered mesoporous carbons - A comparative study. *Langmuir*. 2005; 21(25):11999–12006. [PubMed: 16316145]
15. Ye JL, Liu JG, Zhou Y, Zou ZG, Gu J, Yu T. High catalytic performance and stability of Pt/C using acetic acid functionalized carbon. *Journal of Power Sources*. 2009; 194(2):683–689.
16. Bahr JL, Yang JP, Kosynkin DV, Bronikowski MJ, Smalley RE, Tour JM, et al. Functionalization of carbon nanotubes by electrochemical reduction of aryl diazonium salts: A bucky paper electrode. *Journal of the American Chemical Society*. 2001; 123(27):6536–6542. [PubMed: 11439040]
17. Combellas C, Kanoufi F, Pinson J, Podvorica FI. Time-of-flight secondary ion mass spectroscopy characterization of the covalent bonding between a carbon surface and aryl groups. *Langmuir*. 2005; 21(1):280–286. [PubMed: 15620315]
18. Majumder M, Zhan X, Andrews R, Hinds BJ. Voltage gated carbon nanotube membranes. *Langmuir*. 2007; 23(16):8624–8631. [PubMed: 17616216]
19. Prabburam J, Zhao TS, Liang ZX, Chen R. A simple method for the synthesis of PtRu nanoparticles on the multi-walled carbon nanotube for the anode of a DMFC. *Electrochimica Acta*. 2007; 52(7):2649–2656.
20. Yang H, Yang Y, Zou S. In situ surface-enhanced Raman spectroscopic studies of CO adsorption and methanol oxidation on Ru-modified Pt surfaces. *Journal of Physical Chemistry C*. 2007; 111(51):19058–19065.
21. Service RF. Chemistry - Platinum in fuel cells gets a helping hand. *Science*. 2007; 315(5809):172–172. [PubMed: 17218499]
22. Choi JH, Park KW, Kwon BK, Sung YE. Methanol oxidation on Pt/Ru, Pt/Ni, and Pt/Ru/Ni anode electrocatalysts at different temperatures for DMFCs. *Journal of the Electrochemical Society*. 2003; 150(7):A973–A978.
23. Zhang J, Sasaki K, Sutter E, Adzic RR. Stabilization of platinum oxygen-reduction electrocatalysts using gold clusters. *Science*. 2007; 315(5809):220–222. [PubMed: 17218522]
24. Andrews R, Jacques D, Qian DL, Rantell T. Multiwall carbon nanotubes: Synthesis and application. *Accounts of Chemical Research*. 2002; 35(12):1008–1017. [PubMed: 12484788]
25. D'Amours M, Belanger D. Stability of substituted phenyl groups electrochemically grafted at carbon electrode surface. *Journal of Physical Chemistry B*. 2003; 107(20):4811–4817.
26. Huang S, Dai L, Mau AWH. Patterned Growth and Contact Transfer of Well-Aligned Carbon Nanotube Films. *The Journal of Physical Chemistry B*. 1999; 103(21):4223–4227.
27. Hinds BJ, Chopra N, Rantell T, Andrews R, Gavalas V, Bachas LG. Aligned multiwalled carbon nanotube membranes. *Science*. 2004; 303(5654):62–65. [PubMed: 14645855]
28. Wilde PM, Mandle M, Murata M, Berg N. Structural and Physical Properties of GDL and GDL/BPP Combinations and their Influence on PEMFC Performance. *Fuel Cells*. 2004; 4(3):180–184.
29. Yang H, Tu HC, Chiang IL. Carbon cloth based on PAN carbon fiber practicability for PEMFC applications. *International Journal of Hydrogen Energy*. 2010; 35(7):2791–2795.
30. Wu G, Chen YS, Xu BQ. Remarkable support effect of SWNTs in Pt catalyst for methanol electro oxidation. *Electrochemistry Communications*. 2005; 7(12):1237–1243.

Highlights

Diazonium grafting of benzoic acid allows favorable surface energy for Pt coatings on carbon nanotubes. This can be applied to numerous metal systems

Observed over 2 fold increase in the mass activity of Pt to 400 A/g, thereby reducing the amount of Pt required

A new pulse sequence is found to eliminate CO poisoning

Figure 1.
Schematic of the process for preparing the aligned CNT array electrodes

Figure 2.
SEM images of aligned CNT electrodes after epoxy transfer (a) top view; (b) cross sectional view.

Figure 3.

(a) SEM image of Pt particles electrodeposited on the untreated CNTs; (b) HRTEM image of CNT away from large Pt particles showing absence of thin Pt layer; (c) SEM image of Pt electrodeposited onto the CNTs with surface treatment of carboxyl groups from electrochemical diazonium grafting; (d) HRTEM image of uniform ~2 nm thick Pt coating on treated CNTs.

Figure 4.

(A) Cyclic Voltammogram of Pt nanofilm deposited on CNTs grafted with carboxyl groups in a solution of 0.5 M H_2SO_4 and at a scan rate of 100 mV/s; (B) Cyclic Voltammogram of Pt nanofilm (blue) and Pt nanoparticles (red) on untreated CNTs in a solution of 1 M $\text{CH}_3\text{OH}/0.5 \text{ M } \text{H}_2\text{SO}_4$ and at a scan rate of 20 mV/s. Insert figure is the experiment (red) and calculation (blue) showing Randles–Sevcik behavior of peak currents ratios vs scan rates from 20mv/s to 100mv/s.

Figure 5.

(A) The steady state current densities of methanol oxidation vs time (i) applying programmed pulse potential, with a recovery time of $t=7$ s, (ii) applying constant potential of 0.7 V (vs Ag/AgCl) on the sample; (B) Diagram of programmed pulse potentials with recovery pulses for Pt catalyst activity; (C) Steady state current densities of methanol oxidation vs. the recovery time of programmed pulse potentials.