Supporting Material for

Partially unzipped carbon nanotubes as a superior catalyst support for PEM fuel cells

Donghui Long,^{*a*}* Wei Li,^{*b*} Wenming Qiao,^{*a*} Jin Miyawaki,^{*b*} Seong-Ho Yoon^{*b*}, Isao Mochida^{*b*} and Licheng Ling^{*a*}*

^a State Key Laboratory of Chemical Engineering, East China University of Science and Technology,

Shanghai 200237

^bInstitute for Materials Chemistry and Engineering, Kyushu University, Kasuga, Fukuoka 816-8580,

Japan

*To whom correspondence should be addressed. E-mail: longdh@mail.ecust.edu.cn; lchling@ecust.edu.cn

This PDF file includes:

Experimental details

Figs. S1 to S11

References

Content:

Text:

- 1. Experimental details
- 2. TEM characterization of the PU-CNTs
- 3. ¹³C NMR spectrum of the oxidized CNTs
- 4. Porosity control of the PU-CNTs
- 5. TEM characterization of the Pt/Pu-CNTs
- 6. XRD patterns of the catalysts
- 7. CV testing
- 8. The effect of unzipped degree on the ESA
- 9. The Levich-Koutecky Plots
- 10. Corrosion test of the catalysts
- 11. TG curves of the catalysts
- 12. Photo and SEM images

Fig. S1-S11

References S1-S5

1. Experimental details

1.1 Preparation of the CNTs

The CNTs used here were prepared by CVD growth of CO over unsupported Fe–Ni alloy (6/4, wt. /wt.) catalysts as reported in our previous papers ^{1, 2}. The catalysts were prepared through calcination and reduction of the carbonate precursors. The resulting powdered catalysts were placed in a quartz tube furnace and heated to 640 °C for 1h in flowing a H₂/He (40 ml/160 ml) mixture. Following this reducing anneal, the tube was flushed with He in 15 min and then flushed with the CO/H_2 mixture (40 ml/160 ml) for 30 min. The synthesized CNTs were treated in 10 wt. % HCl until the metal content was less than 0.2 wt. %. The HCl–treated CNTs were used for the further step.

1.2 Preparation of the PU-CNTs

CNTs were oxidized according to the Tour method.³ Typically, 3 g of CNTs was suspended in 300 mL of concentrated H_2SO_4 for 12 h, then 9-15 g of KMnO₄ was added. The reaction mixture was stirred at 40 °C for 30 min and then heated to 70 °C for 1 h. The reaction was quenched by pouring over ice containing 50 mL of hydrogen peroxide (H_2O_2). The solution was separated using a centrifuge at 4800 rpm. The remaining slurry was washed with a 1 M HCl solution and distilled water until the pH was ~4.5. The slurries were then freeze-dried to obtain the O-CNTs.

The O-CNTs were expanded at 300 °C in N₂ atmosphere with a heating rate of 30 °C min⁻¹. The obtained samples were collected at then further heat treated at 900 °C for 3h in N₂ atmosphere with a heating rate of 5 °C min⁻¹ to obtain the PU-CNTs.

The final yield of PU-CNT from the pristine CNT is ca. 75%

1.3 Preparation of the Pt/PU-CNTs

The PU-CNTs supported Pt nanoparticles (Pt/PU-CNTs) were prepared by a ployol reduction method.⁴ In a typical process, 1 g of the carbon supports was ultrasonically dispersed in 350 mL EG for half hour. Then 14.8 mL EG solution of H_2PtCl_6 (33.6 mg Pt/mL) were added with magnetic

stirring. The pH of the solution was adjusted to 11 using EG solution of NaOH (1.0 mol/L). The whole solution was heated at 160 °C for 2 h with magnetic stirring. The catalyst product was vacuum-filtered and washed by a large amount of deionized water, and then dried at 80 °C in an oven. The weight calculation showed that the Pt loading was consistent with the nominal content (40 wt. %), indicating a complete metal loading.

1.4 Characterization

X-ray diffraction (XRD) was performed using a Rigaku X-ray diffractometer with a CuK target. Porosity was measured with nitrogen adsorption–desorption isotherms at 77 K using a surface area analyzer (Sorptomatic 1990, Qunata Instruments). High-resolution solid-state ¹³C nuclear magnetic resonance (NMR) experiments were carried out on a JEOL ECA400 spectrometer operated at 100.53 MHz using the single-pulse decoupling method. The structure was observed under a field-emission scanning electron microscope (FE-SEM; JEOL-6300F) and a high-resolution transmission electron microscope (TEM; JEM-2010F, 200 kV). X-Ray photoelectron spectroscopy (XPS) spectra were acquired using a JPS-9000MC (JEOL) instrument equipped with an Mg Ka X-ray source.

1.5 Electrochemical measurements

The electrochemical measurements were performed on *Gamry PC14/300* electrochemical workstation in a single compartment with three-electrode cell at room temperature. A glassy carbon electrode (GCE) with geometric surface area of 0.089 cm² was used for the preparation of working electrode. A powder sample of 10 mg was dispersed in the solution containing 900 μ L isopropanol and 100 μ L Nafion solution (5wt %, EI DuPont), and then ultrasonically dispersed for 15 min to form a uniform suspension. Then 1.0 μ L portion of the suspension was dropped onto the GCE to form a uniform catalyst layer and then dried at 60 °C for 30 min. Cyclic voltammetry (CV) was used to study the electrochemical active surface areas in 0.5 mol/L H₂SO₄ solution.

Measurements on rotating disk electrode (RDE) were carried out on a BAS RDE-2 rotator (Bioanalytical Systems, Inc.). A Pt wire was used as the counter electrode and Hg/Hg₂SO₄ electrode was used as the reference electrode. All potentials referred in this paper are with respect to the normal hydrogen electrode (NHE).

The durability tests were carried out in N₂-saturated 0.5M H_2SO_4 solution with potential step method (1.4V 10 s to 0.85 V 5 s) for 44 h⁵. After a certain cycles, voltammogram were recorded at a scanning rate of 50 mV/s in N₂ saturated 0.5 M H_2SO_4 . This is an in-house developed accelerated degradation tests (ADT) and has been shown to effectively study the catalyst durability with the emphasis on support corrosion

1.6 Single fuel cell test

The performance of the membrane electrode assemblies (MEAs) in PEMFC with 40 wt % Pt on carbons (0.4 mgPt/cm²), as cathode, was evaluated in a single cell PEMFC. The MEA with a 100 cm² cross-sectional areas was fabricated by decal process and then by hot-pressing (135 °C, 5 MPa, 2 min). The Nafion 212 membrane (DuPont) was used as the membrane. The cell temperature is 70 °C and the stoichiometry of H2/Air is 1.4/2.5.



Fig. S1 TEM images of the PU-CNTs. The tubes were longitudinally unzipped into several graphene nanoribbons. These nanoribbons were not completely isolated because their tips were still linked together.



Fig. S2 The solid ¹³C NMR spectrum of the oxidized CNTs. The spectrum showed five peaks centered at 60, 70, 105, 130, and 165 ppm, corresponding to C–OH, C–O–C epoxide, conjugated double groups, aromatic entities, and carboxylic groups, respectively, which is consistent with a graphite oxide structure.



Fig. S3 The XRD patterns of the oxidized CNTs (a) and the N₂ adsorption-desorption isotherms of the PU-CNTs (b) obtained at different mass ratios of KMnO4/CNTs (R). The porosity could be slightly enhanced by increasing the oxidation degree of the O-CNTs, which were achieved though increasing the mass ratio of KMnO₄/CNTs. In this work, the MP-CNTs with BET specific surface areas of 215 and 247 m^2/g were prepared at the KMnO₄/CNTs mass ratio of 4 and 5, respectively.



Fig. S4 More TEM images of the Pt/PU-CNTs, which indicated that the Pt nanoparticles were highly

dispersed on the surface of the hybrid structure of CNT and graphene sheet.



Fig. S5 XRD patterns of Pt/Pu-CNTs and Pt/CNTs. XRD patterns) indicated that the Pt nanoparticles had a face-centered cubic structure. The mean crystallite sizes estimated from the Scherer's formula were 3.2 nm, in consistent with the particle sizes observed in the corresponding TEM images, confirming the presence of single crystals. The diffraction peak at 26° of the catalysts was ascribed to the graphite (002), which was originated from the support. As shown in the Figure 2a, the graphite 002 peak of the PU-CNT was significantly wider and weaker than that of the pristine CNT. This is due to the split of the CNT tube into several graphene nanoribbons, resulting in the decrease of the crystalline domain.



Fig. S6 Cyclic voltammograms of the catalysts in 0.5 M H₂SO₄ solution saturated by N₂ with a scan rate of 50 mV s⁻¹. The electrochemically active surface areas (ECSAs) of the catalysts were determined by H adsorption using CV. Characteristic peaks in the negative region were attributed to atomic hydrogen adsorption on the Pt surface. The ESAs of all catalysts are obtained to be 129 (Pt/PU-CNTs), 64 (Pt/CNTs) and 71 (Pt/Vulcan) m² g⁻¹ of Pt. The high surface area and strong affinity for the catalyst particles to ensure their efficient immobilization in a well dispersed way should be the reason for highest ECAs obtained for PU-CNTs support.



Fig. S7 (a) Cyclic voltammograms of the Pt/PU-CNTs in 0.5 M H2SO4, where the PU-CNTs were prepared at different KMnO4/CNT ratios (R). (b) Typical TEM image of Although the PU-CNTs with R ratio of 4 and 5 had high BET specific surface areas of 215 and 247 m²/g, respectively, the corresponding Pt loading catalysts exhibited ESAs only about 114 and 95 m² g⁻¹ of Pt. The TEM image revealed that the catalyst Pt/ PU-CNT (R=5) was nearly aggregated, leading to the degradation of the electrocatalytic performances.



Fig. S8 Levich-Koutecky Plots for the ORR on Pt/PU-CNTs at various potentials; current densities normalized to the geometric electrode area. The slope of the lines, the so-called *B* factor, allows us to check the number of the transfer electron for consistency. The figure presents a plot of i^{-1} vs $\omega^{0.5}$ for various potentials. $\frac{1}{j} = \frac{1}{jk} + \frac{1}{J_{alff}} = \frac{1}{jk} + \frac{1}{J_{alff}} = \frac{1}{jk} + \frac{1}{J_{alff}} = \frac{1}{jk} + \frac{1}{B\omega^{4/2}}$, in which $B = \frac{0.62 mF C_0 D_0^{0/2}}{\eta^{4/2}}$ where J_k is the kinetic current density and J_{diff} the diffusion limiting current density, *n* is the overall number of electrons transferred, *F* is the Faraday constant, C_0 is the O₂ concentration in the electrolyte $(1.26 \times 10^{-3} \text{ molL}^{-1})$, D_0 is the diffusion coefficient of O_2 in the H₂SO₄ electrolyte $(1.93 \times 10^{-5} \text{ cm}^2 \text{ s})$, and η is the viscosity of the electrolyte $(1.009 \times 10^{-2} \text{ cm}^2 \text{ s})$. The number of electrons calculated from the slop is 3.6 for Pt/PU-CNTs. This indicates that there is a nearly complete

reduction of O₂ to H₂O, a four-electron process.



Fig. S9 Corrosion test of the Pt/PU-CNTs (a), the Pt/CNTs (b) and the commercial Pt/Vucan catalysts (c). The Pt surface area decreased by 65%, 38% and 11% after testing for Pt/Vulcan, Pt/PU-CNTs and Pt/CNTs, respectively. Compared to carbon black supported catalyst, CNT based catalyst showed remarkable durability enhancement.



Fig. S10 TG curves of the catalysts measured in air atmosphere with a heating rate of 10 ° C/min. The thermal decomposition onset temperatures are 350, 400 and 440 °C for Pt/Vucan, Pt/PU-CNTs and Pt/CNTs, respectively. This result indicates that the CNTs as the support exhibit highest anti-oxidation properties, followed by the PU-CNTs and then Vucan72 carbon blacks. This should be one of basic reasons for good durability for the CNT based catalysts. The noble metal nanoparticles are generally oxidized leading to a weight gain, thus, the quick weight loss caused by carbon combustion was hampered. Consequently, an inflection point occurred at for all catalysts. However, the Pt/PU-CNTs exhibited a much abnormal weight loss around 500 °C, reflecting their high activity.





Fig. S11 Photo image of the MEA electrode (a), and the SEM images of the cross section of the MEA membrane, showing the porous network assembled.

References

- 1. A. Tanaka, S. H. Yoon and I. Mochida, Carbon, 2004, 42, 1291.
- 2. A. Tanaka, S. H. Yoon and I. Mochida, I. Carbon, 2004, 42.
- 3. D. V. Kosynkin, A. L. Higginbotham, A. Sinitskii, J. R. Lomeda, A. Dimiev, B. K. Price and J. M. Tour, Nature, 2009, 458, 872.
- 4. B. Z. Fang, N. K. Chaudhari, M. S. Kim, J. H. Kim, and J. S. Yu, J. Am. Chem. Soc., 2009, 131, 15330.

5. Y.Y. Shao, R. Kou, J. Wang, V.V. Viswanathan, J.H. Kwak, J. Liu, Y. Wang, Y.H. Lin, J. Power Sources, 2008, 185,280.