Electrochemical Study of Highly Durable Cathode with Pt Supported on ITO-CNT Composite for Proton Exchange Membrane Fuel Cells

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Abstract

In this paper, we describe a highly stable cathode containing a Pt catalyst supported on an indium tin oxide (ITO) and carbon nanotube (CNT) composite. The dependence of cathode performance and durability on the ITO content and the diameter of the CNTs were investigated by electrochemical techniques. The cathode with 30 wt% ITO and CNTs with diameters 10–20 nm in the composite offered preferred locations for Pt stabilization and was very resistant to carbon corrosion (i.e., 82.7% ESA retention and 105.7% mass activity retention after an accelerated stress test for 400 h).

Keywords: proton exchange membrane fuel cells; cathode; catalyst support; Pt; indium tin oxide; carbon nanotube.

Introduction

PEM fuel cells have garnered interest as alternative, auxiliary, and emergency power sources for both automotive and stationary applications, and they are anticipated to replace fossil fuel power sources, such as the internal combustion engine, and many other types of electrical power sources. PEM fuel cells have been extensively studied in academia and industry, leading to remarkable advances in this technology. However, reaching a state of commercial viability of PEM fuel cells is challenging because they lack long-term stability [1,2].

In PEM fuel cells, the membrane-electrode assembly is the core part controlling the performance and lifetime of the cell. As an electrolyte, the membrane provides a protonic pathway that is connected to both catalytic sites at the anode and the cathode. Typically, Nafion has been used as an electrolyte in PEM fuel cells, and the durability of Nafion 120 is reported to be approximately 60,000 h [3]. However, the degradation of Nafion over time is dependent on the membrane properties (e.g., chemical structure, equivalent weight, and thickness) and operating conditions (e.g., temperature, relative humidity, and load cycle) [2]. The electrode includes a catalyst layer (CL) and a gas diffusion layer (GDL). The GDL is primarily responsible for transport processes for both the reactant and the product during operation and the CL is a layered structure of Pt-based catalysts, providing numerous three-phase boundaries (TPBs) that represent triple junctions of the catalyst, ionomer, and reactant [4].

Pt or a Pt alloy is usually supported on high-surface-area carbon to increase the electrochemical surface area of the catalyst [4,5]. The durability of the carbon-supported catalyst strongly depends on the supporting material because the catalyst support determines the dispersion and stabilization of the supported catalyst nanoparticles [6]. The carbon support, however, is vulnerable to oxidation by the sudden potential increase (>1.0 V vs. the standard

hydrogen electrode, SHE) that occur at the cathode during repeated start-up/shut down processes [7–9]. To mitigate carbon corrosion, a variety of alternative carbon supports, such as CNTs, mesoporous carbon, and graphene, have been proposed [6,10–14]. Among these candidates, CNTs have been reported to be very durable compared to carbon black (e.g., Vulcan® XC-72) during long-term stress tests and accelerated stress tests for catalyst supports in single cells [13]. In contrast, metal-based supports, such as titanium oxide with different particle morphologies (spherical, nano-wire, etc.), tin oxide, and tungsten oxide, have also been recently studied in attempts to improve both electrode performance and durability for PEM or direct methanol fuel cell applications [15–20]. However, despite surface modification with metals [21], the relatively poor electrical conductivity and the low specific surface area of metal-based supports still hinders their use as replacements for carbon-based supports in PEM fuel cells [22,23]. Therefore, a different approach to prepare hybrid supports comprised of carbon and metal-based materials, which form metal nanoparticle-decorated carbon scaffold supports [24,25], has been taken. This approach has been adopted by several research groups [25–29], and these hybrid catalyst supports have been shown to be promising. Similarly, Qu et al. synthesized TiO₂-deposited reduced graphene as a Pt nanoparticle support to form a three-phase junction structure for methanol oxidation, [30] and Kim et al. improved catalytic activity for oxygen reduction reaction using Pd-WO₃ on carbon black for use as an electrocatalyst. [31]. Furthermore, we have shown [25] through theoretical calculations and the thin-film disk electrode techniques (TFDE) [32] that a hybrid support increases the stabilization of Pt at the junction of the metal oxide and the carbon support, thereby enhancing the catalyst durability. In this study, based on the assumption that i) for a single catalyst support, Pt nanoparticles are mainly deposited on a carbon because of its higher surface area, higher electrical conductivity, and more defects than in a metal oxide; ii) Pt

nanoparticles are well dispersed on a carbon in the presence of a metal oxide; and iii) Pt cluster are preferentially anchored at the junction of carbon and metal oxide for a hybrid catalyst support due to a higher interaction energy than Pt cluster on the metal oxide [25]; we have prepared a new Pt catalyst supported on a composite of indium tin oxide (ITO) and CNTs. In addition, we have characterized the catalytic properties and durability of the supported catalyst in a single PEM fuel cell by cyclic voltammetry, polarization analysis, and electrochemical impedance spectroscopy under accelerated stress testing conditions for the catalyst supports. The effects of the ITO content and the diameter of the CNTs in the composite support on the cathode performance and stability were investigated to explore the potential applications of the composite as an alternative catalyst support in PEM fuel cells.

Experimental

2.1. Synthesis of the Pt on ITO-CNT composite

To form ITO nanoparticles with 10 wt% SnO_2 , $\text{In}(\text{acac})_3$ (0.2672 g) and $\text{Sn}(\text{OtBu})_4$ (0.02729 g) were mixed with benzyl alcohol (20 mL) with continuous stirring and transferred to an autoclave. The first step in the preparation of the ITO-CNT composites was to disperse the as-received CNTs (Cheap Tubes, Inc.) in benzyl alcohol at a concentration of 0.0045 g mL^{-1} . The CNTs used in this study had been graphitized and COOH -functionalized (3.86 wt%) by the manufacturer. Then, a designated amount of the CNT/benzyl alcohol mixture was added to the $\text{In}(\text{acac})_3$ and $\text{Sn}(\text{OtBu})_4$ solution, stirred overnight, and heat-treated in an autoclave at 200°C for 17 h. The resultant material was thoroughly washed with ethyl alcohol and chloroform and dried in air. A chemical reduction method was used to load 20 wt% of Pt nanoparticles on the different composite supports: H_2PtCl_6 (0.0525 g) was first dissolved in ethylene glycol (40 mL, EG), and

the pH was adjusted to 12 with a 2 M NaOH/EG solution. To prepare the Pt on ITO-CNT composite (Pt/ITO-CNT), the ITO-CNT (0.1 g) composite was added to the chloroplatinic acid solution, and the mixture was ultrasonically blended for 5 min and heat-treated at 140 °C for 4 h. The products were washed with a large amount of water and dried in air.

2.2. Electrochemical measurements in solution

The electrochemical measurements were made in a standard three-electrode cell using a Pt wire counter electrode and an Hg/Hg₂SO₄ reference electrode at room temperature. To prepare the working electrodes, the catalyst (10 mg) was first added to a solution of 2-propanol (10 mL) and 5.0 wt% Nafion® (45 µL), and the solution was ultrasonically mixed to form a homogeneous catalyst ink. Then, the well-dispersed catalyst ink (15.0 µL) was applied to a polished glassy carbon disk to fabricate thin-film disk electrodes. After drying at room temperature, a 0.05 wt% Nafion solution (10 µL) was applied to the surface of the CL to bind the catalyst particles. Cyclic voltammetry (CV) was performed on the TFDEs between 0 and 1.1 V at 50 mV·s⁻¹ in an N₂-saturated 0.1 M HClO₄ solution until a steady voltammogram was obtained. The accelerated stress tests (AST) for the supported catalyst were performed using the potential step method with an upper potential of 1.4 V for 150 s and a lower potential of 0.85 V for 30 s in each period [33]. The voltammograms were recorded before and after 44 h of AST for each catalyst.

2.3. Preparation of the membrane-electrode assembly

The catalyst ink for the cathode was prepared by mixing 20 wt% Pt/ITO-CNT catalyst with a 5 wt% Nafion solution (Ion Power, Inc.), deionized water, and methanol for 1 h. The catalyst ink was applied to hydrophobized carbon paper with microporous layers (SGL 10CC, SGL group), followed by drying at 80 °C for 10 min. This process was repeated until a total Pt loading of 0.2 mg cm⁻² was achieved. The catalyst ink for the anode was prepared using commercially available

Pt/C (20 wt% Pt, Electrochem, Inc) and was sprayed on the carbon paper in the same manner. A thin layer of Nafion (0.4 mg cm^{-2}) was applied to both the anode and the cathode surface to enhance the adhesion between the electrode and the membrane. Two gas diffusion electrodes were hot-pressed with a Nafion 117 membrane at 140°C for 3 min. The geometric area of the MEA used for all of the single cell tests was 8 cm^2 .

2.4. Electrochemical measurements in single cells

Polarization curves were obtained at an automated fuel cell test station (Arbin Instrument, Inc.). CV and electrochemical impedance spectroscopy (EIS) measurements were performed with a potentiostat (VersaStat, AMETEK, Inc.). To obtain the CV curves, the cathode was cycled as a working electrode at 50 mV s^{-1} between 0.02 and 1.1 V vs. SHE. The electrochemical surface area (ESA) of the cathode fabricated in this study was determined with the total charge corresponding to the hydrogen atoms desorption peak in the CV, the total charge related to a monolayer of hydrogen atoms ($210 \mu\text{C cm}^{-2}$), and Pt loading on the cathode (0.2 mg cm^{-2}). The EIS experiments were carried out under H_2/O_2 by applying an AC amplitude of 10 mV over a frequency range from 50 mHz to 10 kHz. The impedance data in H_2/O_2 were obtained at 0.9 V and $v_{\text{H}_2} = v_{\text{O}_2} = 100 \text{ cm}^3 \text{ min}^{-1}$. The AST for the catalyst support [2] in this study was conducted in a single-cell fixture by holding the potential at 1.2 V using fully humidified H_2/N_2 at 80°C and 150 kPa for a defined period.

Results and discussion

Fig. 1 displays the initial ESA for the Pt/ITO-CNT with CNT diameters ranging from 10 to 20 nm ($d_{\text{CNT}} = 10\text{--}20 \text{ nm}$) and the ESA retention values after a 44 h AST at various ITO contents using the ITO-CNT composite as the catalyst support. The experiments were performed

in a 0.1 M perchloric acid solution with N₂ bubbled through the solution at room temperature. The ESA obtained using a bare CNT-supported Pt catalyst is also shown in Fig. 1 for comparison. Fig. 1 shows that the formation of the ITO-CNT composite by applying ITO nanoparticles on the CNT surface increases the ESA of the Pt dispersed on the surface. Furthermore, Fig. 1 shows that the catalyst utilization for hydrogen adsorption/desorption through electrochemical processes is dependent on the ITO content of the CNT surface. The Pt/ITO-CNT ESA reaches a maximum at 30 wt% ITO in the ITO-CNT composite, decreasing on further increasing the ITO content, indicating that there exists an optimal ITO loading for Pt utilization. Fig. 1 also shows that the addition of ITO to the CNT improves the catalyst durability, i.e., ITO nanoparticles loaded on the CNT improve the carbon corrosion resistance under potential step changes between 0.85 and 1.4 V (vs. SHE) for 44 h [33]. According to our previous density functional theory calculations [25], Pt and ITO nanoparticles are stable at oxidizing conditions are thermodynamically favored to be deposited on graphene sheets with defects and functional groups. In particular, once Pt and ITO nanoparticles are anchored to the graphene sheets, the interaction energy is much larger than that of respective Pt and ITO on the graphene sheets. Fig. 2 shows a TEM image of Pt nanoparticles on ITO-CNT composite (30 wt% ITO on CNT), demonstrating that ITO nanoparticles are dispersed on the CNTs, whereas Pt nanoparticles are mostly deposited on the CNTs and at the junction between ITO and CNT. Pt nanoparticles are not found in significant quantities on the surface of the ITO nanoparticles. Consequently, we believe that the ITO nanoparticles on the CNTs provide locations for Pt anchoring, resulting in strong interactions between the Pt nanoparticles and the ITO-CNT composite during electrochemical stress. Using electrochemical TFDE tests and TEM analysis, we determined that an ITO loading of 30 wt% was optimal, and we used this loading for the catalyst support for all

the MEAs investigated in this study.

Fig. 3 shows the initial ESAs and mass activities of Pt/ITO-CNT electrodes with different CNT diameters in PEM fuel cells. The experiments were carried out using MEAs in a single cell setup at 80 °C and 150 kPa_{abs}. The ESA increases with increasing diameter of the CNTs in the composites. It is possible that the composite of ITO-CNT with larger values of d_{CNT} provides more CNT/ITO junctions for the stabilization of Pt nanoparticles connected to effective protonic pathways. However, the Pt/ITO-CNT with $d_{\text{CNT}} = 10\text{--}20$ nm have a higher mass activity at $E_{\text{cell}} = 0.9$ V than those with d_{CNT} values greater than 20 nm. To understand the different mass activities (or oxygen reduction kinetics) at the cathode, EIS measurements, which yield information about individual electrochemical processes at various relaxation times, were carried out [34]. Nyquist plots of Pt/ITO-CNT of different diameters are illustrated in Fig. 3(b). EIS experiments were performed at $E_{\text{cell}} = 0.9$ V, where the mass activity is estimated. The ohmic resistance, which primarily originates from the membrane resistance, can be determined by the x -intercept at high frequency, and the values of ohmic resistance for the Pt/ITO-CNT in this study are all similar. Next, the polarization resistance, R_p , which characterizes the charge and mass transfer limitations at the TPBs, can be estimated from the difference between the x -intercepts at low and high frequencies. Because the mass transfer effect is assumed to be negligible at $E_{\text{cell}} = 0.9$ V in a typical PEM fuel cell, the value of R_p can be regarded as the charge transfer resistance at the TPBs, and it increases in the same sequence of mass activities shown in Fig. 3(a). Therefore, the relatively high mass activity of Pt/ITO-CNT with $d_{\text{CNT}} = 10\text{--}20$ nm is associated with a smaller charge transfer resistance in the absence of a mass transfer restriction.

Fig. 4 shows the polarization curve for the cathodes prepared with Pt/ITO-CNT with different CNT diameters. The current density estimated at $E_{\text{cell}} = 0.4$ V is relatively high when

the Pt/ITO-CNT with $d_{\text{CNT}} = 10\text{--}20$ nm are used as a catalyst. In general, polarization behaviors are the combined results of individual irreversible losses: activation loss, ohmic loss, and concentration loss. Thus, it is helpful to split the experimental polarization curve into individual overpotentials to elucidate the dominant electrode processes that control the fuel cell performance. The experimental polarization curves have been thus analyzed in stages to investigate how the CNT diameter in the Pt/ITO-CNT catalyst influences oxygen diffusion and oxygen reduction reaction at the cathode [35].

Fig. 5 shows several polarization curves obtained by subtracting each overpotential from the experimental polarization curve of the Pt/ITO-CNT with $d_{\text{CNT}} = 10\text{--}20$ nm. To obtain each polarization curve while assuming that there are negligible anodic contributions and electrical resistance in the CL at the cathode, the ohmic overpotential, excluding the protonic transport resistance in the CL, $\eta_{\text{ohm,non-CL}}$, determined from EIS experiments (i.e., the x -intercept at high frequency in the complex plane), was first subtracted from the experimental polarization curve (E_{cell}), resulting in $E_{\text{iR-free,non-CL}}$. Then, the kinetic-controlled polarization curve E_{kin} was obtained by extrapolating from the linear region at low current densities in the absence of limited oxygen diffusion (i.e., the Tafel region), which quantifies the summation of the concentration overpotential η_{con} at the cathode and the protonic resistance in the CL, $\eta_{\text{ohm,CL}} (= E_{\text{kin}} - E_{\text{iR-free,non-CL}})$. Lastly, the experimentally measured open circuit potential (E_{OC}) assigns the kinetic overpotential, $\eta_{\text{kin}} (= E_{\text{OC}} - E_{\text{kin}})$ [36].

Each overpotential estimated at $i = 0.2 \text{ A cm}^{-2}$ for Pt/ITO-CNT with different d_{CNT} values is illustrated in Fig. 6. As mentioned earlier, the values of $\eta_{\text{ohm,non-CL}}$, which mainly arise from the membrane resistance, are nearly identical among the Pt/ITO-CNT catalysts. Clearly, no appreciable difference is observed among the values of η_{kin} , although the kinetic contribution to

the total overpotential is relatively high (>42% for all samples). Conversely, the value of $\eta_{\text{con}} + \eta_{\text{ohm,CL}}$ for Pt/ITO-CNT with $d_{\text{CNT}} = 10\text{--}20$ nm is smaller than the values of $\eta_{\text{con}} + \eta_{\text{ohm,CL}}$ for CNTs with larger diameters in the ITO-CNT composites. Hence, by comparing each polarization source derived from the experimental polarization curve, we found that non-kinetic losses arising from the mass transport limitation and protonic resistance in the CL predominantly control the fuel cell performance [36].

The long-term catalyst activity is affected significantly by the interaction between the catalytic metals and their supports. It is believed that the weak bonding of Pt clusters on the support may cause Pt nanoparticles to agglomerate via crystal migration [37]. Furthermore, undesirable carbon corrosion at high potentials (>1.0 V) diminishes the Pt nanoparticle stabilization on carbon-based supports [25]. To investigate the Pt metal stability on the ITO-CNT composite during repeated exposure to high potentials (>1.0 V), which can be caused by events in fuel cell electric vehicles such as start-stop cycling and fuel starvation, an AST for the supported catalyst was carried out, in which the potential was held at 1.2 V with the cathode under a nitrogen atmosphere.

Figs. 7(a) and (b) show the normalized ESA retentions and mass activities for cathodes containing different Pt catalysts supported on ITO-CNT composites with $d_{\text{CNT}} = 10\text{--}20$ nm and $d_{\text{CNT}} > 50$ nm. For Pt/ITO-CNT with $d_{\text{CNT}} = 10\text{--}20$ nm, the ESA and the mass activity first increase with increasing hold time, between 30 and 65 h; then, both ESA and mass activity decrease slowly at longer potential hold times, and this trends in ESA and mass activities is similar for Pt/ITO-CNT with $d_{\text{CNT}} > 50$ nm, although the ESAs and mass activities are lower. Similar initial performance improvements have also been reported by Tada et al. [38] Notably, the ESA and mass activity for Pt/ITO-CNT with $d_{\text{CNT}} = 10\text{--}20$ nm remain near their initial levels

after holding for 400 h at 1.2 V, while the ESA and mass activity for $d_{\text{CNT}} > 50$ nm drastically decreases with increasing potential hold time, resulting in a final cell life of close to 150 h. The impedance behaviors shown in Fig. 7(c) are consistent with the ESA and mass activity trends during the AST. The values of R_p for Pt/ITO-CNT with $d_{\text{CNT}} = 10\text{--}20$ nm at a holding potential are smaller than the initial values of R_p for Pt/ITO-CNT with $d_{\text{CNT}} > 50$ nm. According to a theoretical and experimental study by Setzler and Fuller [40], the inductive loop from intermediate frequency x -intercept (~ 100 mHz) to the low frequency one (~ 1 μHz) in the Nyquist plot is associated with the oxide layer on the Pt surface [39,40]. However, such behavior was not observed in this study, indicating that a Pt oxide layer does not form during the AST [34]. For Pt/ITO-CNT with $d_{\text{CNT}} = 10\text{--}20$ nm, relatively small R_p values were also observed after a 100 h AST, which is consistent with the initial ESA and mass activity improvement in Figs. 7(a) and (b). Therefore, we inferred from the electrochemical experiments that the composite of ITO and CNTs with smaller diameters retain active sites on Pt that are available for the oxygen reduction reaction during carbon corrosion.

Conclusions

An ITO-CNT composite was synthesized for use as a Pt catalyst support for PEM fuel cells, and ex-situ and in-situ electrochemical characterizations of the ITO-CNT supported Pt catalyst (Pt/ITO-CNT) were performed using accelerated stress tests (ASTs), which consist of a potential hold at 1.2 V vs. SHE). The effects of the ITO concentration and the diameters of the CNTs in the hybrid support on the catalyst activity and durability in a PEM fuel cell were examined.

The TFDE experiments for Pt/ITO-CNT with different ITO content showed that 30 wt%

ITO content was optimal, resulting in an ESA and a greater retention of the ESA, indicating that the ratio of ITO and CNTs influences the formation of defects and the Pt deposition on CNTs, thereby controlling the dispersion of Pt nanoparticles and their interactions with the support. Separating the experimental polarization curve using the impedance response and Tafel behavior shows that the CNT diameters determine the oxygen reduction kinetics in addition to the diffusion processes in the CL. Consequently, it is suggested from the in-situ AST that ITO-modified CNTs with smaller diameters ($d_{\text{CNT}} = 10\text{--}20$ nm in this study) are resistant against carbon corrosion and provide superior stabilization of Pt nanoparticles on their surfaces.

Acknowledgments

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References

1. M.L. Perry, T.F. Fuller, J. Electrochem. Soc. 149 (2002) S59.
2. R. Borup, J. Meyers, B. Pivovar, Y.S. Kim, R. Mukundan, N. Garland, D. Myers, M. Wilson, F. Garzon, D. Wood, P. Zelenay, K. More, K. Stroh, T. Zawodzinski, J. Boncella, J.E. McGrath, M. Inaba, K. Miyatake, M. Hori, K. Ota, Z. Ogumi, S. Miyata, A. Nishikata, Z. Siroma, Y. Uchimoto, K. Yasuda, K.I. Kimijima, N. Iwashita, Chem. Rev. 107 (2007) 3904.
3. A. Steck, Proc. 1st Int. Sym., New Materials for Fuel Cell Systems, O. Savagodo, P.

- Roberge, T.N. Veziroglu (Eds.) 1995.
4. J. Larminie, A. Dicks, Fuel Cell System Explained, Second ed., John Wiley & Sons, Chichester, 2003.
 5. Y. Shao, G. Yin, Y. Gao, J. Power Sources 171 (2007) 558.
 6. Y. Shao, J. Liu, Y. Wang, Y. Lin, J. Mater. Chem. 19 (2009) 46.
 7. L. M. Roen, C.H. Paik, and T.D. Jarvi, Electrochem. Solid State Lett. 7 (2004) A19.
 8. C.A. Reiser, L. Bregoli, T.W. Patterson, J.S. Yi, J.D. Yang, M.L. Perry, T.D. Jarvi, Electrochem. Solid State Lett. 8 (2005) A273.
 9. H. Tang, Z. Qi, M. Ramani, J.F. Elter, J. Power Sources 158 (2006) 1306.
 10. S.H. Joo, S.J. Choi, I. Oh, J. Kwak, Z. Liu, O. Terasaki, R. Ryoo, Nature 412 (2001) 169.
 11. C. Wang, M. Waje, X. Wang, J. M. Tang, R. C. Haddon, Y. S. Yan, Nano Lett. 4 (2004) 345.
 12. E.S. Steigerwalt, G.A. Deluga, C.M. Lukehart, J. Phys. Chem. B 106 (2002) 760.
 13. S. Park, Y. Shao, R. Kou, V.V. Viswanathan, S.A. Towne, P.C. Rieke, J. Liu, Y. Lin, Y. Wang, J. Electrochem. Soc. 158 (2011) B297.
 14. S. Park, Y. Shao, H. Wan, V.V. Viswanathan, S.A. Towne, P.C. Rieke, J. Liu, Y. Wang, J. Phys. Chem. C 115 (2011) 22633.
 15. P. Zhang, S.Y. Huang, B.N. Popov, J. Electrochem. Soc. 157 (2010) B1163.
 16. K.-W. Park, Y.-W. Lee, J.-K. Oh, D.-Y. Kim, S.-B. Han, A.-R. Ko, S.-J. Kim, H.-S. Kim, J. Ind. Eng. Chem. 17 (2011) 696.
 17. S.Y. Huang, P. Ganesan, B.N. Popov, Appl. Catal. B-Environ. 102 (2011) 71.
 18. M.S. Saha, Y. Zhang, M. Cai, X. Sun, Int. J. Hydrogen Energ. 37 (2012) 4633.
 19. D. Fattakhova-Rohlfing, T. Brezesinski, B. Smarsly, J. Rathousky, Superlattices

- Microstruct. 44 (2008) 686.
20. J. Ju, X. Chen, D. Wu, P. Hua, J. Ind. Eng. Chem. 20 (2014) 1223.
 21. C. Beauger, L. Testut, S. Berthon-Fabry, F. Georgi, L. Geutaz, Micropor. Mesopor. Mat. 232 (2016) 109.
 22. Y. Li, C. Liu, Y. Liu, B. Feng, L. Li, H. Pan, W. Kellogg, D. Higgins, G. Wu, J. Power Sources 286 (2015) 354.
 23. P.K. Biswas, A. De, N.C. Pramanik, P.K. Chakraborty, K. Ortner, V. Hock, S. Korder, Mater. Lett. 57 (2003) 2326.
 24. S. Shanmugam and A. Gedanken, Small 3 (2007) 1189.
 25. R. Kou, Y. Shao, D. Mei, Z. Nie, D. Wang, C. Wang, V.V. Viswanathan, S. Park, I.A. Aksay, Y. Lin, Y. Wang, J. Liu, J. Am. Chem. Soc. 133 (2011) 2541.
 26. L. Zhang, L. Wang, C. M.B. Holt, B. Zahiri, Z. Li, K. Malek, T. Navessin, M.H. Eikerling, D. Mitlin, Energ. Environ. Sci. 5 (2012) 6156.
 27. C. Xu, P. Pietrasz, J. Yang, R. Soltis, K. Sun, M. Sulek, R. Novak, ECS trans. 58 (2013) 1779.
 28. G. Wu, C. Dai, D. Wang, D. Li, N. Li, J. Mater. Chem. 20 (2010) 3059
 29. Q. Li, H. Pan, D. Higgins, R. Cao, G. Zhang, H. Lv, K. Wu, J. Cho, and G. Wu, Small 11 (2015) 1443.
 30. Y. Qu, Y. Gao, F. Kong, S. Zhang, L. Du, G. Yin, Int. J. Hydrogen Energ. 38 (2013) 12310.
 31. I.-T. Kim, M. Choi, H.-K. Lee, J. Shim, J. Ind. Eng. Chem. 19 (2013) 813.
 32. T.J. Schmidt, H.A. Gasteiger, G.D. Stäb, P.M. Urban, D.M. Kolb, R.J. Behm, J. Electrochem. Soc. 145 (1998) 2354.
 33. Y. Shao, R. Kou, J. Wang, V.V. Viswanathan, J.H. Kwak, J. Liu, Y. Wang, Y. Lin, J.

Power Sources 185 (2008) 280.

34. A. Lasia, Electrochemical Impedance Spectroscopy and its Applications, in: J.O.M. Bockris, B.E. Conway, R.E. White (Eds.), Modern Aspects of Electrochemistry, Kluwer Academic/Plenum Publishers, New York, 1999, Vol. 32.
35. M.V. Williams, H.R. Kunz, J.M. Fenton, J. Electrochem. Soc. 152 (2005) A635.
36. S. Park, Y. Shao, V.V. Viswanathan, J. Liu, Y. Wang, Int. J. Hydrogen Energ. 37 (2012) 8451.
37. Y. Shao-Horn, W.C. Sheng, S. Chen, P.J. Ferreira, E.F. Holby, D. Morgan, Top. Catal. 46 (2007) 285.
38. T. Tada, Y. Yamamoto, K. Matsutani, K. Hayakawa, T. Namai, Current Progress of Electrocatalyst R&D in TKK, in: T. Fuller, K. Shinohara, V. Ramani, P. Shirvanian, H. Uchida, S. Cleghorn, M. Inaba, S. Mitsushima, P. Strasser, H. Nakagawa, H. Gasteiger, T. Zawodzinski, C. Lamy (Eds.), Proton exchange membrane fuel cells 8, 2008, pts 1 and 2, pp. 215
39. B.P. Setzler, T.F. Fuller, J. Electrochem. Soc. 162 (2015) F519.
40. E.L. Redmond, B.P. Setzler, F.M. Alamgir, T.F. Fuller, Phys. Chem. Chem. Phys. 16 (2014) 5301.

Figure captions

Figure 1. Electrochemical surface area of the Pt/ITO-CNT and its retention after 44 h potential cycling as a function of the ITO content in the hybrid support. The thin film disk electrode was cycled at 50 mV s^{-1} between 0.02 and 1.1 V *vs.* SHE.

Figure 2. TEM image of Pt/ITO-CNT (30 wt% ITO in the hybrid support).

Figure 3. (a) Electrochemical surface area and mass activity at 0.9 V of the cathode prepared using Pt/ITO-CNT with different CNT diameters. The cathode was cycled at 50 mV s^{-1} between 0.02 and 1.1 V *vs.* SHE. (b) ac-impedance spectra of the cathodes, which contain Pt/ITO-CNT with different CNT diameters at $E_{\text{cell}} = 0.9 \text{ V}$.

Figure 4. Polarization curves of the PEM fuel cells using Pt/ITO-CNT with different CNT diameters. The experiments were performed in the constant flow rate mode with $v_{\text{H}_2} = v_{\text{O}_2} = 100 \text{ cm}^3 \text{ min}^{-1}$.

Figure 5. Analysis of the polarization curve of the PEM fuel cell using Pt/ITO-CNT with $d_{\text{CNT}} = 10\text{--}20 \text{ nm}$.

Figure 6. Overpotentials at 0.2 A cm^{-2} of the PEM fuel cell using Pt/ITO-CNT with different CNT diameters.

Figure 7. (a) Normalized electrochemical surface area, (b) normalized mass activity, and (c) ac-impedance spectra of the cathodes consisting of Pt/ITO-CNT as a function of the hold time at 1.2 V

Figure 1**S. Park et al.**

Figure 2

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Figure 3(a)**S. Park et al.**

Figure 3(b)**S. Park et al.**

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Figure 5

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Figure 6**S. Park et al.**

Figure 7(a)**S. Park et al.**

Figure 7(b)**S. Park et al.**

Figure 7(c)

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