ORIGINAL ARTICLE

Effective anchoring of Pt-nanoparticles onto sulfonated polyelectrolyte-wrapped carbon nanotubes for use as a fuel cell electrocatalyst

Tsuyohiko Fujigaya[1,2], ChaeRin Kim[1], Kazuya Matsumoto[1] and Naotoshi Nakashima[1,2,3]

Sulfonated polymers, such as sulfonated polysulfone and sulfonated polyimide, are promising candidates as a future polyelectrolyte for polymer electrolyte fuel cells (PEFCs). In PEFC cell systems, the same polyelectrolyte material is often added to the electrocatalyst layer as the ionic path. We selected partially sulfonated poly(arylene thioethersulfone) (SPTES) and poly[(2,2′-benzidinedisulfonicacid)-*alt*-(1,4,5,8-naphthalenetetracarboxylic dianhydride)] (BDSA-NTDA) as the electrolytes and wrapped multi-walled carbon nanotubes (MWNTs) with the materials to which platinum nanoparticles (Pt) were attached onto the polyelectrolyte layer to fabricate new electrocatalysts. In these electrocatalysts, the MWNT and Pt serve as the electron path and reaction site, respectively. For both polyelectrolytes, Pt-nanoparticles <5 nm in diameter with a narrow size distribution were observed to be homogeneously dispersed on the polymer-wrapped MWNTs. The electrochemical measurements revealed that MWNT/SPTES/Pt and MWNT/BDSA-NTDA/Pt possessed electrochemically active surface areas (ECSA) of 42.3 and 35.6 m^2/g of Pt, respectively. Such a high ECSA efficiency ensures the use of these composites for the preparation of a future electrocatalyst.

INTRODUCTION

Carbon nanotubes (CNTs) are attractive materials in many fields of science, including materials science, (bio)technology, and electronics, because of their unique structure, outstanding electronic properties, and mechanical stiffness. Among the wide range of applications for CNTs, the metal nanoparticle/CNTs hybrid is an attractive material, especially for use as fuel cell electrocatalysts owing to the large surface areas, remarkable electrical conductivity and excellent electrochemical durability of the CNTs.[1] Various metals, such as Pt and Pd, have been immobilized on CNTs and used for fuel cell applications.[2,3] It is well recognized that pristine CNTs possess insufficient binding sites for anchoring the metal precursors onto their graphitic surfaces, which results in poor dispersion of the particles.[4] To improve the loading efficiency, surface functionalization of CNTs has been investigated. A common approach to introduce an anchoring unit is the strong oxidation of the CNT to generate carboxyl functional groups.[5]

However, such a covalent functionalization causes structural damage and is often accompanied by reducing the intrinsic properties of CNTs, such as high electrical conductivity and electrochemical durability, which are unfavorable as electrocatalysts for fuel cells. For these reasons, metal anchoring onto the surface of CNTs through

non-covalent functionalization is desirable. Several anchoring molecules based on the non-covalent functionalization using 1-aminopyrene,[6] DNA,[7] and polypyrrole[8] have been reported. We have reported that polybenzimidazole (PBI) also serves as an anchoring polymer through the combination of the strong π–π interactions of PBI on the surfaces of CNTs and the coordination of metal ions with the imidazole group.[4,9] PBIs are unique anchoring polymers because they function as a proton conductive polyelectrolyte after acid doping and are considered to be a promising polyelectrolyte for polymer electrolyte fuel cells (PEFCs). As a consequence, the composite of multi-walled carbon nanotubes (MWNTs), PBI and Pt possesses electron conductivity, proton conductivity, and a reaction site, all of which are required for PEFC electrocatalysts.[4,9] We reported that the use of a polyelectrolyte as the anchoring unit that provides a large exposed surface enables a smooth fuel gas access in PEFCs and provides for an ideal triple-phase interface structure.[4,9] To date, perfluorosulfonic acid polymers, such as Nafion, have been widely used as a polyelectrolyte for PEFCs, and the development of the Nafion-based electrocatalysts have been extensively studied. However, because of the cost problem and its mechanical weakness, the post-Nafion is required in PEFCs. Therefore, many extensive studies

[1]Department of Applied Chemistry, Graduate School of Engineering, Kyushu University, 744 Motooka, Nishi-ku, Fukuoka, Japan; [2]International Institute for Carbon-Neutral Energy Research (WPI-I2CNER), Kyushu University, 744 Motooka, Nishi-ku, Fukuoka, Japan and [3]JST-CREST, 5 Sanbancho, Chiyoda-ku, Tokyo, Japan
Correspondence: Professor T Fujigaya or Professor N Nakashima, Department of Applied Chemistry, Graduate School of Engineering, Kyushu University, 744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan.
E-mail: fujigaya-tcm@mail.cstm.kyushu-u.ac.jp or nakashima-tcm@mail.cstm.kyushu-u.ac.jp
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exploring alternative polyelectrolytes, such as PBIs, have been performed. When these polymers are employed as the electrolyte membrane for PEFCs, the same polyelectrolyte is necessary in the electrocatalyst to provide smooth proton conduction between the membrane and electrocatalyst. Hence, the PBI-based electrocatalyst is useful in PEFCs using PBI as a membrane. Indeed, we achieved a high PEFC performance using the composite of MWNT/PBI/Pt as the electrocatalyst, in which the anchored PBI on the MWNTs effectively worked as the proton conducting material in the electrocatalyst.[10,11]

In this study, as shown in Figure 1, we have chosen a sulfonated poly(arylene ethersulfone) and sulfonated polyimide (SPI) (Figure 1) as the polymer anchors because both polymers are also promising alternative polyelectrolytes and have been extensively investigated because of their excellent proton conductivities, mechanical toughness, and low fuel crossover,[12] and we examined their performance as the electrocatalyst for PEFCs.

EXPERIMENTAL PROCEDURE
Materials
N,N-dimethylacetamide (DMAc), ethylene glycol, and hydrogen hexachloroplatinate hexahydrate ($H_2PtCl_6 \cdot 6H_2O$) were purchased from Wako Pure Chemical (Osaka, Japan) and used as received. Sulfonated poly(arylene ethersulfone) (SPES) and poly(arylene thioethersulfone) (SPTES) were synthesized using previously reported procedures.[13–15] SPIs were synthesized using the polycondensation reaction of 2,2′-benzidinedisulfonic acid (BDSA) with carboxylic dianhydride according to a reported procedure.[16] A polytetrafluoroethylene (PTFE) filter (pore size, 0.2 μm; Millipore, Billerica,

MA, USA) was used for filtration. A copper grid with a carbon support (Ouken Shoji, Tokyo, Japan) was used for the TEM (transmission electron microscope) observations. The MWNTs used in this study were kindly supplied by Nikkiso Co. (Tokyo, Japan).

Measurements
The IR spectra were recorded using a Spectrum 100 FT-IR (Perkin-Elmer, Waltham, MA, USA) spectrometer equipped with an ATR. The TGA (thermogravimetric analysis) curves were measured using an SSC 5200 (SII) operated in conditioned air at a heating rate of 5 °C/min. The X-ray photoelectron spectroscopy (XPS) measurements were carried out using an AXIS-ULTRA (KRATOS, Shimadzu, Kyoto, Japan) instrument. The binding energy was calibrated using the C_{1s} peak that appears at 284.5 eV. The TEM measurements were conducted using a JEM-2010 (JEOL, Tokyo, Japan) electron microscope operating at 120 kV.

Wrapping of MWNTs by polyelectrolytes
Five milligrams of the MWNTs were added to SPTES (5.0 mg) dissolved in DMAc (5.0 ml) and sonicated for 60 min using a bath-type sonicator (BRANSON 5510, Sterling Heights, MI, USA). The obtained solution was then centrifuged at $10\,000\,g$ to remove any remaining aggregated sediment. The supernatant was filtered and then washed with DMAc to remove any excess SPTES. The obtained solid, denoted MWNT/SPTES, was then dried under a vacuum. The MWNTs wrapped with NTDA-BDSA were prepared using a similar procedure.

Pt-anchoring on MWNT/polyelectrolyte hybrids
The Pt-nanoparticles were loaded onto MWNT/SPTES by reducing $H_2PtCl_6 \cdot 6H_2O$ in an aqueous ethylene glycol solution. First, MWNT/SPTES
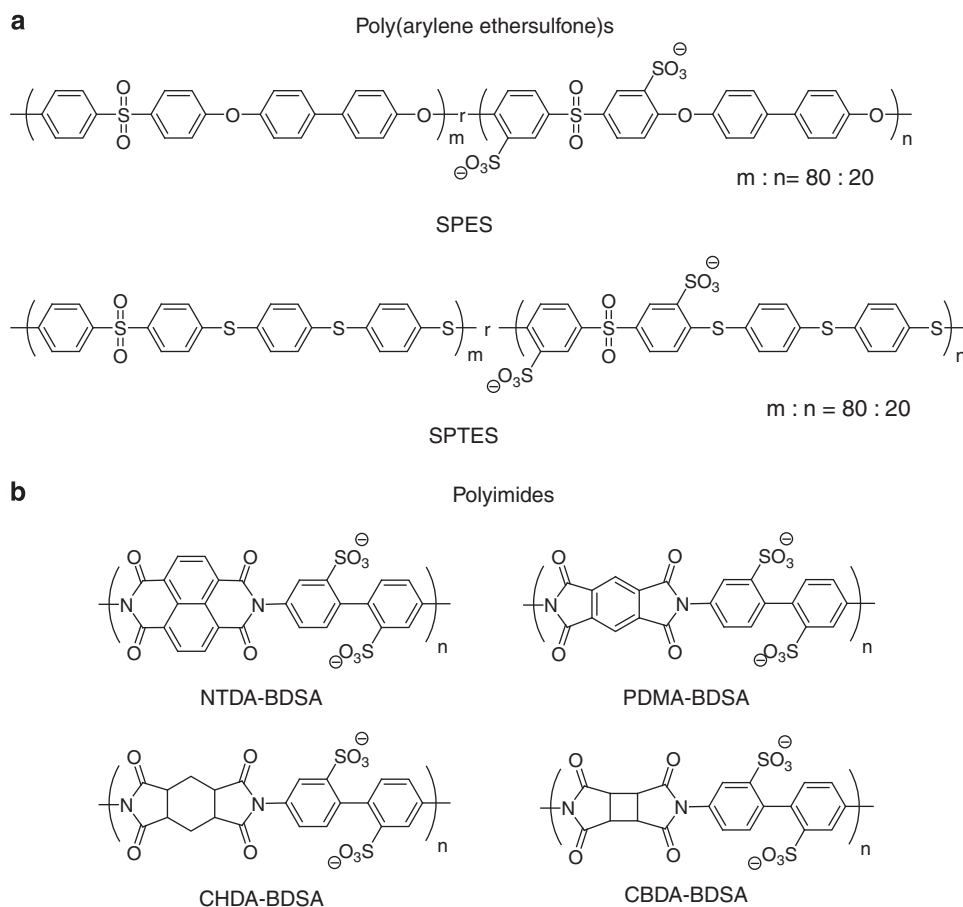

Figure 1 Chemical structures of (a) sulfonated poly(arylene ethersulfone)s and (b) SPIs.

(10 mg) was added to a 60-vol% aqueous ethylene glycol solution (20 ml) and dispersed by sonication. $H_2PtCl_6 \cdot 6H_2O$ (24.0 mg) dissolved in the 60-vol% aqueous ethylene glycol solution (30 ml) was added to the MWNT/SPTES dispersion, and then the mixture was heated at 80 °C for 6 h. The solid material was collected by filtration and washed with water and then dried under vacuum to obtain MWNT/SPTES/Pt. The Pt-loading on MWNT/NTDA-BDSA was carried out using a similar procedure to yield MWNT/NTDA-BDSA/Pt.

Electrochemical measurements

Electrochemically active surface areas (ECSA) measurements were conducted in a nitrogen-deaerated 0.1 M $HClO_4$ solution. An Ag/AgCl and a Pt wire were used as the reference and counter electrodes, respectively. A 17.6-µl aliquot of the DMAc mixture (1.8 ml) and Milli-Q water (0.2 ml) containing 1.0 mg of MWNT/SPTES/Pt or MWNT/NTDA-BDSA/Pt was dropped onto a polished glassy carbon electrode (6.0 mm diameter) and then dried. The cyclic voltammogram (CV) was measured at a scan rate of 50 mV/s at 25 °C using an electrochemical analyzer 1230A (ALS). The electrode was activated by cycling the potential between −0.13 and 1.0 V vs Ag/AgCl for the ECSA measurements.

RESULTS AND DISCUSSION

Dispersion of CNTs using polyelectrolytes

The dispersion abilities of the partially sulfonated poly(arylene ethersulfone)s (SPESs; Figure 1a) and SPIs (Figure 1b) for the dispersion of the MWNTs were investigated. Compared with Nafion, both polymers are known to possess a higher proton conductivity and greater mechanical strength; they are therefore candidates as an alternative polyelectrolyte for PEFCs.[12]

The copolymer ratios (*m:n*) of the partially sulfonated poly(arylene ethersulfone) (SPES) and partially sulfonated poly(arylene thioether-sulfone) (SPTES) synthesized according to reported methods[13–15] were estimated from the ^{1}H-NMR spectra to be 80:20 for both polymers.[13–15] The MWNTs were dispersed in *N,N*-dimethylacetamide (DMAc) solutions containing the polymers by sonication, as described in the Experimental section. Of interest, SPTES produced a gray solution (Figure 2a, right), whereas SPES produced a poor dispersion of the MWNTs (Figure 2a, left). Because both polymers possess similar molecular weights (viscosity of SPES and SPTES are 0.28 and 0.23 dl/g, respectively, in DMAc at 30 °C) and a similar degree of sulfonation, we assumed that the hydrophobic nature of the thioether linkage compared with that of the ether bond reported in literature[17] plays an important role during the dispersion. The importance of the hydrophobic regions during the solubilization of CNTs by the amphiphilic polymers is well recognized because the hydrophobic part is responsible for the adsorption onto the CNT surface, whereas the hydrophilic part allows for solvation to obtain wrapping of the CNT.[18] In the amphiphilic SPTES and SPES, in which the sulfonic acid group serves as a hydrophilic region, the more hydrophobic nature of SPTES was preferable to form the polymer-wrapping structure because of the clear contrast in the amphiphilicity, leading to the better dispersion of CNTs.

We examined the MWNT dispersion ability of a series of SPIs synthesized through the polycondensation of BDSA with four different dianhydrides—1,4,5,8-naphthalenetetracarboxylic dianhydride (NTDA), pyromellitic dianhydride (PMDA), 1,2,4,5-cyclohexyltetracarboxylic dianhydride (CHDA), and 1,2,3,4-cyclobutanetetracarboxylic dianhydride (CBDA)—which are listed in Figure 1b. As shown in Figure 2b, SPIs with an aromatic dianhydride unit—NTDA-BDSA and PMDA-BDSA—exhibited a good MWNT dispersion ability, whereas the SPIs that had an aliphatic unit—CHDA-BDSA and CBDA-BDSA—showed very poor MWNT dispersion in DMAc. The π–π interaction between SPIs and the CNTs is expected to play an important role in CNT dispersion using SPIs. For this study, we chose NTDA-BDSA because this polymer is one of the polyelectrolytes being extensively studied among the various SPIs as a material for PEFCs owing to its excellent chemical stability and mechanical toughness.[19]

The obtained supernatants from the dispersions (MWNTs in the SPTES and NTDA-BDSA solutions) were filtered and washed with DMAc to remove any unbound polymers to provide polyelectrolyte-wrapped MWNTs (MWNT/SPTES and MWNT/NTDA-BDSA) as gray powders after drying. The TGA of the composites measured under flowing air at a rate of 5 °C/min exhibited a two-step weight reduction starting at ∼200 °C and 600 °C that was attributed to the cleavage of the sulfonyl group[20] and decomposition of remaining composites, respectively (Figure 3a). The X-ray photoelectron spectra (XPS) of MWNT/SPTES and MWNT/NTDA-BDSA exhibited peaks that were attributed to S_{2p} and N_{1s} at ∼165 and 400 eV, respectively (Figure 3b), which suggests a wrapping of SPTES and NTDA-BDSA onto the MWNTs.

Anchoring of Pt on MWNTs wrapped by the polyelectrolytes

Pt-anchoring onto the composites was performed at 80 °C using hydrogen hexachloroplatinate hexahydrate ($H_2PtCl_6 \cdot 6H_2O$) and ethylene glycol as the Pt precursor and reducing agent, respectively.[4] Figures 4a and b show TEM images of the composites after Pt-loading (4a; MWNT/SPTES/Pt and 4b; MWNT/BDSA-NTDA/Pt). Homogenous anchoring of the Pt-nanoparticles with a narrow diameter distribution on MWNT/SPTES/Pt (2.0 ± 0.47 nm) and MWNT/NTDA-BDSA/Pt (2.58 ± 0.42 nm) was achieved (also see Supplementary Figure S1). The XPS of MWNT/SPTES/Pt exhibited peaks that were attributed to the Pt 4 f and S 2p at ∼75 and 165 eV,
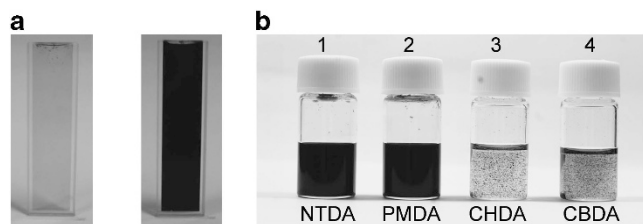

Figure 2 Photographs of DMAc supernatant solutions of the MWNTs dispersed using (**a**) sulfonated polyether sulfones (left: SPES and right: SPTES) and (**b**) SPIs (1: NTDA-BDSA, 2: PMDA-BDSA, 3: CHDA-BDSA, and 4: CBDA-BDSA).
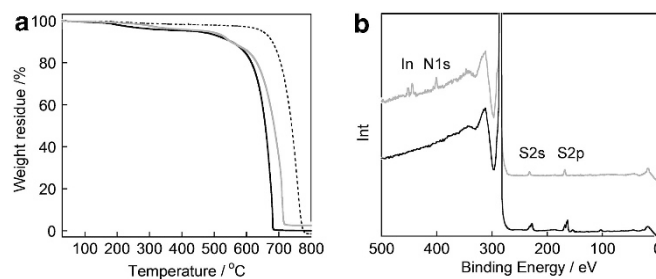

Figure 3 (**a**) TGA curves of the MWNT (dotted line), MWNT/STPES (black bold line) and MWNT/NTDA-BDSA (gray line). (**b**) XPS survey scans of MWNT/STPES (black bold line) and MWNT/NTDA-BDSA (gray line).
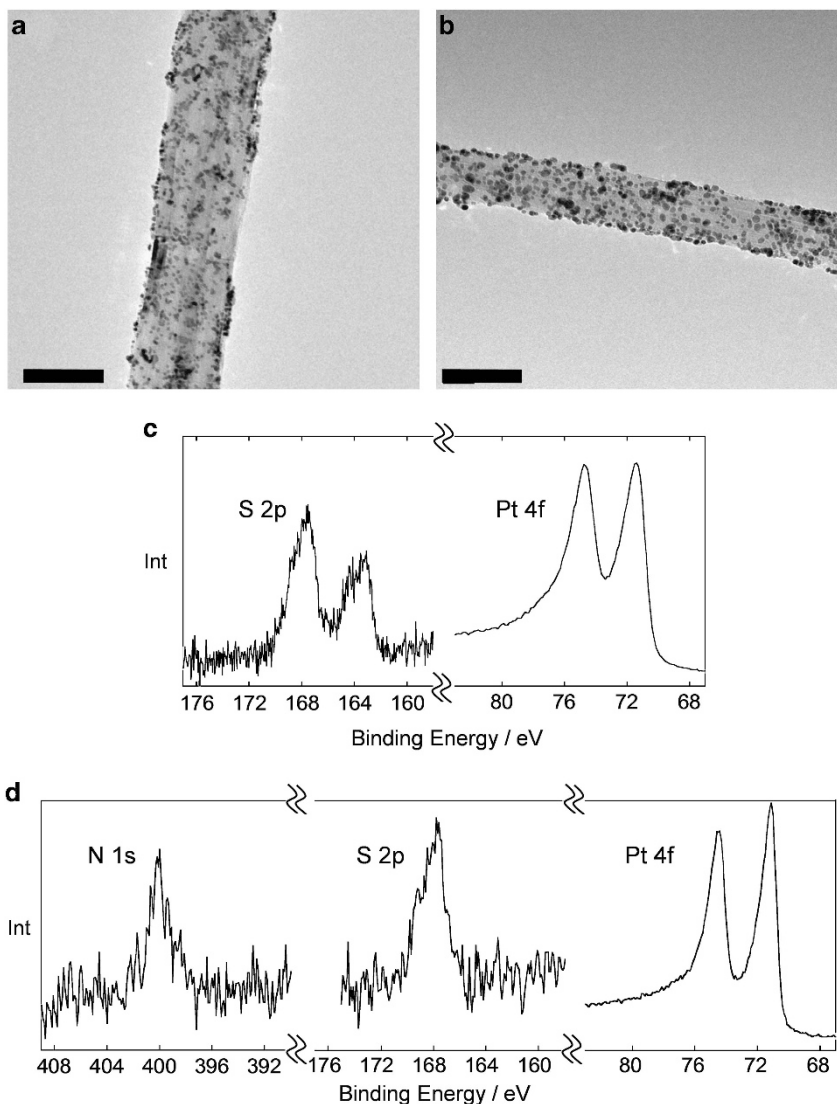
Figure 4 (a) TEM image of MWNT/SPTES/Pt. (b) TEM image of MWNT/NTDA-BDSA/Pt. (c) XPS narrow scan of MWNT/SPTES/Pt for the S2p and Pt 4 f regions. For survey scans, see Supplementary Figure S2. (d) XPS narrow scan of MWNT/NTDA-BDSA/Pt for the S2p, N 1s and Pt 4 f regions. For the survey scan, see Supplementary Figure S2.

respectively (Figure 4c), suggesting the successful formation of an assembly of SPTES and Pt (for a wide scan, see Supplementary Figure S2).

For MWNT/NTDA-BDSA/Pt, the additional N 1s peak at ~400 eV confirmed the presence of SPI in the composites (Figure 4c). Narrow scans for the Pt 4 f region exhibited doublet peaks at 71.1 and 74.3 eV, which were attributed to Pt^0 (4f$_{7/2}$) and Pt^0 (4f$_{5/2}$), respectively, indicating that the dominant valency of Pt is zero for both composites.[21] The TGA of the composites measured under air flow at a rate of 5 °C/min exhibited a two-step weight reduction starting at 200 °C and 400 °C that was attributed to the cleavage of the sulfonyl group[20] and the decomposition of the remaining MWNT/polymer composite, respectively (Figure 5a). The onset temperature for the oxidation of the composite decreased markedly as a result of the catalytic effect of the metal nanoparticle. The 46 wt% of the residual corresponds to the amount of the Pt loaded onto the MWNTs, and it was calculated that as much as ca. 98% of the fed Pt was loaded onto the surfaces of the MWNTs.

It is noteworthy that the direct attachment of Pt onto the MWNTs provided a higher amount of aggregation of the Pt-nanoparticles only because of the lack of binding sites for the metal salts on the CNT surfaces.[4] In previous studies,[4] we revealed that the coordination of the Pt ions to the imidazole group in PBIs is a key step for efficient and homogeneous Pt-loading on CNTs. The sulfonate moiety in the polymers was expected to provide the anchoring sites on the composites, as reported for the metal-loading on CNTs wrapped by sodium dodecyl sulfonate[22] and poly(stylene sulfonate).[23]

Figure 5b shows the CV of MWNT/SPTES/Pt (black bold line) and MWNT/NTDA-BDSA/Pt (gray line). Characteristic peaks in the negative region (from −0.2 to 0.1 V vs Ag/AgCl) that are attributable to atomic hydrogen adsorption and desorption on the Pt-nanoparticle surfaces were detected. This result reveals the electronic communication between Pt and MWNTs. The electrochemically active surface
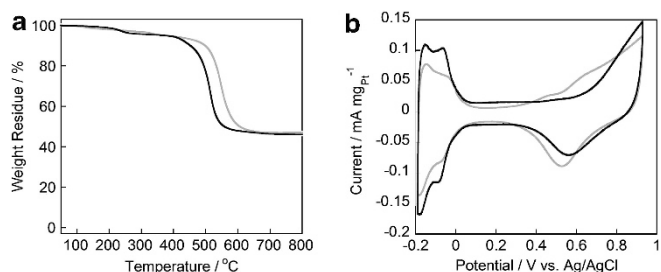
Figure 5 (**a**) TGA curve of MWNT/SPTES/Pt (black bold line) and MWNT/NTDA-BDSA/Pt (gray line) measured at a rate of 5 °C/min under flowing air. The loading amount of Pt on MWNT/SPTES/Pt and MWNT/NTDA-BDSA/Pt was estimated to be 46 wt% and 47 wt%, respectively. (**b**) CVs of MWNT/SPTES/Pt (black bold line) and MWNT/NTDA-BDSA/Pt (gray line) measured in a N$_2$-saturated 0.1 M HClO$_4$ solution at a scan rate of 50 mV per second.

area (ECSA) was calculated using Equation 1:

$$ECSA = Q_H/(210 \times Pt \text{ loading on electrode}) \tag{1}$$

where Q_H is the charge exchanged during the electroadsorption of H on Pt (from -0.13 to 0.2 V vs Ag/AgCl). The amounts of Pt loaded onto the electrode were determined from the amounts of the composite solutions cast onto the electrodes. The ECSA of MWNT/SPTES/Pt and MWNT/NTDA-BDSA/Pt was calculated to be 42.3 m^2/g for Pt and 35.6 m^2/g for Pt, respectively. Such high ECSA values are the consequence of the large exposed Pt surfaces on the MWNTs and indicate the formation of an ideal triple-phase boundary structure that enables an excellent catalyst efficiency, as previously reported.[24]

CONCLUSIONS

We found that the sulfonated poly(arylene thioethersulfone) and SPI served as effective polymeric anchors for CNTs to immobilize Pt-nanoparticles. It was revealed that the hydrophobic thioethersulfone unit functioned as a CNT anchor and that the sulfonate moiety performed as a Pt anchor for SPTES. Decreasing the hydrophobic unit allowed the delamination of the anchoring unit. However, the fully sulfonated SPI functioned as a stable Pt anchor for the MWNTs, probably as a result of the strong affinity of the fused aromatic unit in the SPI. This finding is quite useful, not only for designing the polymeric anchor but also for the development of a practical PEFC for next generation materials. Fabrication of a PEFC cell using the obtained composites as an electrocatalyst is currently in progress in our laboratory.

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Supplementary Information accompanies the paper on Polymer Journal website (http://www.nature.com/pj)