Alkaline Stability of Anion-Conductive Ionomer Coated on a Carbon Surface

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ABSTRACT: Anion-exchange membrane fuel cells (AEMFCs) are promising technologies that allow the use of nonprecious metals as catalysts because the oxidation reduction reaction at the cathode occurs readily at the high pH of AEMFCs. However, the insufficient chemical stability of the anion-conductive materials in AEMFCs currently limits their development. We studied the chemical stability of the electrolyte in the catalyst layer of AEMFCs containing cationic dimethyl polybenzimidazole (mPBI). Although degradation was observed in an mPBI membrane under alkaline conditions, mPBI coated on a carbon support showed excellent alkaline stability. Because no glass transition temperature was observed for mPBI after coating on the support, the increase of chemical stability was probably associated with the decrease of polymer flexibility.

1. INTRODUCTION

Polymer electrolyte fuel cells (PEFCs) have been recognized as promising power generation systems because of their high energy conversion efficiency, high power density, compactness, and low pollutant emission.1–5 Proton-exchange membrane fuel cells (PEMFCs) using proton-conductive polymers are the main types of PEFCs because of the ready availability of proton-conductive electrolytes containing anionic groups such as Nafion. A major drawback of PEMFCs is the low stability of the metal catalysts under their highly acidic operating conditions, which limits the catalyst to expensive platinum (Pt) nanoparticles.4 To avoid this problem, increasing attention has been focused on anion-exchange membrane fuel cells (AEMFCs).3,5–7 using cationic electrolytes. The basic environment of AEMFCs is tolerated by various metal catalysts and also promotes the redox reactions of oxygen.5,8–10 Therefore, AEMFCs represent an approach to lower the cost of fuel cells by replacing the Pt catalyst with other less expensive metals.

Polymers with cationic groups such as guanidinium,11 sulfonium,12 pyridinium, imidazolium,13 piperidinium,14 and phosphonium15,16 have been developed as AEMFC electrolytes. Quaternary ammonium cations are used the most often in this role because of their ease of synthesis and higher thermal stability than those of other cations with comparable anion conductivity.17,18 The most critical issue in the development of AEMFCs is the chemical instability of the cationic electrolyte,16,18–25 which typically occurs via the S_{22} reaction, Hofmann elimination, and nucleophilic addition triggered by the OH− attack. Recently, systematic studies to correlate the chemical stability and chemical structures of cationic groups have been conducted,13 and several new membrane structures have been proposed.15,24

These studies mainly focused on the stability of the anion-exchange membrane (AEM); the alkaline stability of the electrolyte in the catalyst layer has not yet been studied. In the catalyst layer, the electrolyte is mixed with carbon materials, which may result in a different morphology from the AEM because of electrolyte adsorption on the carbon surface. In a PEMFC, the polymer electrolyte, typically Nafion, adsorbs on the surface of the electrocatalyst,26 and formation of phase-separated structures is suppressed because of the strong influence of the carbon surface.26 As a result, the polymer electrolyte possesses lower proton conductivity27 and lower water uptake28 than those of a bulk film. The structure and properties of the polymer electrolyte in the catalyst layer of an AEMFC have not been studied to date in detail.29,30 The alkaline stability of the electrolyte in the catalyst layer may be different from that of the AEM in an AEMFC.

In this study, the cationic polymer dimethyl polybenzimidazole (mPBI) is used to study the alkaline stability in the catalyst layer because mPBI is a promising candidate for use as the membrane in AEMFCs due to its high anionic conductivity.31 Another reason for the choice of mPBI is that we found that PBI derivatives strongly and homogeneously adsorbed on the surface of the carbon support such as multilayer carbon nanotubes (MWNTs) to give PBI-wrapped MWNTs (MWNT/PBI) and provided good anchoring sites for Pt loading on the MWNT surface.32 Thus, Pt nanoparticles are immobilized on the surface of MWNT/mPBI to give an electrocatalyst (denoted as MWNT/mPBI/Pt). Alkaline stability of the MWNT/mPBI as well as MWNT/mPBI/Pt...
was investigated by comparing the structure of mPBI after soaking into alkaline solution. It is noted that the use of MWNTs offers a strong measurement advantage when observing the stability of mPBI by transmission electron microscopy (TEM) owing to the good crystallinity of MWNTs. The polarization behavior of the electrocatalyst was also characterized using a membrane electrode assembly (MEA) to check the anion conduction of mPBI in the catalyst layer.

2. RESULTS AND DISCUSSION

PBI was methylated using methyl iodide to afford mPBI, as shown in Scheme 1. In the $^1$H NMR spectrum of mPBI, the signal from the N–H proton of PBI at 13.32 ppm disappeared, and signals from N–CH$_3$ protons at 4.08 and 4.16 ppm appeared (Supporting Information, Figure S1a). Based on the integral ratio of aromatic protons (7.5 to 9.0 ppm) to methyl protons (4.2 ppm), the methylation yield was determined to be 91.8%. Methylation of PBI was also confirmed by FT-IR spectroscopy, which showed a new peak originating from N–CH$_3$ at 1015 cm$^{-1}$ (Supporting Information, Figure S1b). In XPS narrow scans of the N 1s region, the N$^+$–C peak at 400.9 eV was newly observed, while the N–C and N=C peaks at 399.5 and 398.2 eV remained, respectively, indicating the formation of the imidazole cation (Supporting Information, Figure S1c). MWNTs were dispersed in mPBI solution in DMAc without mPBI, including mPBI in the DMAc solution led to effective MWNT dispersion (Scheme 2), suggesting that mPBI was adsorbed on the MWNTs and served as a dispersant, similar to the MWNT dispersion behavior of PBI. The MWNTs were then collected by filtration or precipitation to control the amount of polyelectrolyte (mPBI) around the MWNTs. In the filtration method, the MWNT dispersion was directly filtered, and then the obtained composite (MWNT/mPBI) was washed with DMAc to remove unbound mPBI, giving MWNTs with a coating of a thin layer of mPBI (denoted as MWNT/mPBI-w). In the precipitation method, the MWNT dispersion was precipitated in diethyl ether using a controlled injection rate of 2.0 mL min$^{-1}$ and then collected by filtration (denoted as MWNT/mPBI-p).

Composition ratios of MWNTs to mPBI in the samples were determined by TGA. In TGA measured under air flow, weight loss caused by the thermal decomposition of mPBI starting at around 200 °C was observed, as depicted in Figure 1a. Based on the observed weight losses, it is estimated that MWNT/mPBI-w and MWNT/mPBI-p contained 6.6 and 42.0 wt % mPBI, respectively. Assuming the uniform coating of mPBI on the MWNTs, the thicknesses of the mPBI layers were calculated to be 0.3 and 8.2 nm, respectively, using the surface area of MWNTs (53.7 m$^2$ g$^{-1}$) determined by nitrogen adsorption measurements. Coating of the MWNTs with mPBI was confirmed by TEM measurements. TEM images of MWNT/mPBI-w and MWNT/mPBI-p clearly showed the highly crystalline periodic layered structure together with the amorphous thin layer on the surface in which we assigned the MWNT and mPBI, respectively, based on TGA results (Figure 1a). The measured thicknesses of the mPBI layers were 0.3 ± 0.1 (Figure 1b) and 8.3 ± 0.3 nm (Figure 1c) for MWNT/mPBI-w and MWNT/mPBI-p, respectively.

The alkaline stabilities of MWNT/mPBI-w and MWNT/mPBI-p together with that of the mPBI powder were tested by immersing the materials in 0.01 M KOH solution under gentle shaking for 48 h. Typically, $^1$H NMR spectroscopy is used to monitor the alkaline stability of ammonium or imidazolium cations. In this work, because monitoring the stability by $^1$H NMR spectroscopy was rather difficult due to the insolubility of mPBI/MWNTs and the low mobility of mPBI on MWNT, the degradation was monitored by XPS. In the N 1s scans, peaks assignable to N$^+$–C, N–C, and N=C were observed at 400.9, 399.5, and 398.2 eV, respectively (Figure 2). In the case of the mPBI powder, relative areas of N–C and N=C peaks largely increased, and that of the N$^+$–C peak decreased compared with that of the other samples (Figure 2a, see also the Supporting Information, Table S1a), which indicated the loss of the cation group through the SN2 reaction, as explained in Scheme S1. It is noted that only some of the mPBI powder dissolved and the XPS measurements were obtained from the residual powder. Loss of the methyl group and the increase of the N=C peak intensity were also supported by FT-IR spectroscopy (Supporting Information, Figure S2). For the mPBI film, soaking the film in 0.01 M KOH solution resulted in the decomposition of the film into small pieces after 24 h (Figure 2b), suggesting that the degradation of the mPBI main chain via a hydrolysis reaction followed by ring cleavage to the diamine and carboxylic acid occurred as proposed. Conversely, the XPS profiles for both MWNT/mPBI-w (Figure 2c) and MWNT/mPBI-p (Figure 2d) were almost unchanged.
even after 48 h of immersion in KOH solution. In addition, TEM observations revealed that the thickness of the mPBI layer on the MWNT surface was almost unchanged for both MWNT/mPBI-w (0.3 ± 0.1 nm, Figure 2e) and MWNT/mPBI-p (7.9 ± 0.3 nm, Figure 2f) after immersion in KOH, which also supported the alkaline stability of the mPBI layer on MWNTs.

Thomas et al. 22 reported that introduction of steric hindrance into the PBI structure improved its alkaline stability. Based on this model, it is speculated that the MWNTs provided steric hindrance to suppress the SN2 reaction. Such a mechanism can occur at the interface of the MWNTs and mPBI, but it cannot explain the increased alkaline stability of mPBI located far from the MWNT surface, especially for MWNT/mPBI-p with a thick mPBI coating. XPS analysis revealed that the I 3d peak at around 620 eV observed for mPBI disappeared after KOH treatment for both MWNT/mPBI-w and MWNT/mPBI-p (Supporting Information, Figure S3). This result indicates that hydroxide ions (OH\(^{-}\)) penetrated into the mPBI layer and replaced the iodide ions during KOH treatment regardless of the thickness of the mPBI coating. Therefore, the steric effect of MWNTs was probably not the reason for the increased alkaline stability of MWNT/mPBI compared with that of mPBI.

We suppose that such unexpected stability was achieved because the polymer mobility was lowered by coating on the MWNTs and both the S\(_{2}\)2 and hydrolysis reactions were effectively suppressed by the hardening of the polymer. It is well recognized that the properties of a polymer on a substrate, such as the glass transition temperature (\(T_g\)), 38 thermal expansion, 39 segment dynamics, 40 viscosity, 41 and water uptake, 42 are strongly affected by the polymer/substrate interactions. When the polymer/substrate interfacial interaction is strong, \(T_g\) tends to increase, 43,44 which suggests that the conformation of the polymer chains at the polymer/substrate interface is frozen and relaxation occurs more slowly than that in the bulk polymer. In the case of carbon nanotube (CNT)/polymer composites, \(T_g\) at the CNT/polymer interface has not been studied yet, but the increase of \(T_g\) of CNT/polymer composites compared with that of the polymer alone has often been reported, 45–48 strongly suggesting that the increase of \(T_g\) at the CNT/polymer interface is accompanied by the lowering of the polymer mobility at this interface. To investigate the hardening of the polymer at the MWNT/mPBI interface, we used PBI with a \(T_g\) of around 410 °C 33 instead of mPBI because mPBI did not show a \(T_g\) peak below its thermal decomposition temperature (>230 °C, Figure 1a). 33

Figure 3 shows the differential scanning calorimetry (DSC) profiles of PBI (red line) and MWNT/PBI (black line). We found that MWNT/PBI did not display a \(T_g\) peak at 407 °C from PBI. This is probably caused by the hardening of PBI induced by coating on the MWNTs, which shifted \(T_g\) above the thermal decomposition temperature of PBI (about 450 °C), as reported for other composite systems. 45–48 We assumed that such a hardening of PBI also occurred in the case of mPBI on the MWNT surface and the chemical reactions associated with the volume change might become unfavorable. Such a hardening might also decrease the water uptake of mPBI, resulting in the lower reactivity of the polymer and realizing the longer stability. Similar enhanced alkaline stability was also achieved when carbon black was used as the carbon support instead of MWNTs (see the Supporting Information, Figure S4).

Thus, to achieve enhanced alkaline stability, we concluded that the coating of the polymer electrolyte on the solid surface needs to form a strong interaction with the surface and that stability can be increased by adsorption on a support regardless of the inherent alkaline stability of the polymer electrolyte. The MWNT/mPBI-w was loaded with Pt using a polyol method with \(\text{H}_2\text{PtCl}_6\) as a Pt source and EG as a reducing
agent. The inset in Figure 4a shows a TEM image of the obtained composite (MWNT/mPBI/Pt). The Pt nanoparticles with a narrow diameter distribution (3.2 ± 0.5 nm) were homogeneously loaded on the MWNTs (see the Supporting Information, Figure S5). TGA indicated that 45 wt % Pt was loaded on the MWNT/mPBI/Pt composite (Figure 4a), suggesting effective growth of the Pt nanoparticles on MWNT/mPBI-w. An MEA containing 1.0 M KOH-doped MWNT/mPBI/Pt as the electrocatalyst was fabricated on both sides of a commercially available membrane (A2013; Tokuyama) as an anion-conductive membrane. We used an A2013 membrane because of its higher stability (Supporting Information, Figure S6) than that of mPBI (Figure 2b). As shown in Figure 4b, the polarization curve measured at 50 °C under 100% RH showed a power density of 24.6 mW cm\(^{-2}\) (red curve), whereas that of the control MEA containing MWNT/mPBI/Pt without KOH doping was only 9.71 mW cm\(^{-2}\) (black curve). The above comparison clearly indicates that the KOH-doped mPBI layer functioned as an anion-conductive electrolyte in the catalyst layer. This is the first example to demonstrate mPBI serving as the electrocatalyst. It is important to note that MWNT/mPBI/Pt showed excellent alkaline stability after KOH doping, similar to that MWNT/mPBI, which was confirmed by XPS (see the Supporting Information, Figure S7). The above results suggest the possibility of developing AEMFCs with excellent alkaline durability if we have durable AEMs. To check the durability of MWNT/mPBI in an MEA, development of an AEM with excellent durability is necessary where the tests will be conducted with high KOH concentration (>1.0 M) under practical temperature (>60 °C).

3. CONCLUSIONS
We studied the alkaline stability of a polymer electrolyte in the catalyst layer of a LAMFC using mPBI-coated MWNTs with different coating thicknesses of 0.3 to 8.3 nm by soaking the composites in 0.01 M KOH solution. Degradation of MWNT/mPBI was monitored by XPS, which showed that the mPBI coated on MWNTs was remarkably stable, whereas an mPBI film and mPBI powder underwent rapid degradation under the same conditions. Lowering of polymer flexibility upon coating on the MWNTs might suppress the elimination reaction induced by the OH\(^-\) attack. Our novel findings provide important knowledge for not only catalyst layer design but also development of novel alkali-stable membranes.

4. EXPERIMENTAL SECTION

4.1. Materials. Methyl iodide, N,N-dimethylacetamide (DMAC), and ethylene glycol were purchased from Tokyo Chemical Industry Co. Sodium hydride (NaH), N,N-dimethylformamide (DMF), hydrogen hexachloroplatinate-(IV) hexahydrate (H\(_4\)PtCl\(_6\)·6H\(_2\)O), and isopropyl alcohol were purchased from FUJIFILM Wako Pure Chemical, Ltd., Osaka. Potassium hydroxide (KOH) was purchased from Sigma Aldrich. The MWNTs were kindly provided by Nikkiso Co. PBI containing 23.4% DMAC was obtained from Sato Light Industrial.

4.2. Measurements. \(^1\)H nuclear magnetic resonance (NMR) and Fourier transform infrared (FT-IR) spectral measurements were carried out using an AV300 M spectrometer (Bruker Biospin) and Spectrum 65 FT-IR spectrometer (PerkinElmer) equipped with an attenuated total reflection apparatus, respectively. Chemical shifts of protons are reported in parts per million (δ scale) downfield from tetramethylsilane (TMS). Chemical shifts for the carbon resonances are reported in parts per million (δ scale) downfield from TMS. Centrifugation was carried out using a Himac CF 15R centrifuge (Hitachi). X-ray photoelectron spectroscopy (XPS) was performed using an AXIS-ULTRA instrument (Shimadzu, Co., Japan). Thermogravimetric analysis (TGA) was conducted using an Exstar TG/DTA6300 analyzer (Seiko Instruments, Inc.) at a heating rate of 10 °C min\(^{-1}\) under an air flow of 200 mL min\(^{-1}\). Scanning transmission electron microscopy (STEM) and transmission electron microscopy (TEM) measurements were performed using an SU9000 microscope (Hitachi High-Technologies) operated at 30 kV and a JEM-2010 microscope (JEOL) operated at 120 kV, respectively. A copper grid with a carbon support (Okeshoji) was used for the STEM and TEM observations. Gas adsorption (77 K, 1 × 10^{-9} < P/P\(_0\) < 1) measurements were conducted on a Belsorp mini analyzer (BEL Japan Inc.) after pretreatment at 300 °C for 12 h under high vacuum.

4.3. Synthesis of mPBI. PBI containing 23.4% DMAC (9.07 g) was dissolved in DMAC (300 mL) at 80 °C in a 500 mL flask, and then NaH (1.5 g, 2.1 mmol) was added at room temperature. The solution turned dark red after heating at 80 °C for 6 h. After cooling the solution to room temperature, CH\(_4\)I (9.3 mL, 4.2 mmol) was added, and then the mixture was heated at 80 °C for 20 h. The obtained solid was collected by a polytetrafluoroethylene filter with a pore diameter of 3.0 μm and rinsed with DMAC and methanol. After drying at 100 °C for 12 h, a yellow powder (14.2 g, yield; 99%) was obtained. \(^1\)H NMR (DMSO-d\(_6\)): δ/ppm 8.90–7.80 (m, 10H), 4.16, (s, 6H), 4.09 (s, 6H). \(^{13}\)C NMR (DMSO-d\(_6\)): δ/ppm 149.58, 137.58, 132.64, 114.23, 112.01, 33.62, 33.43. FT-IR 3063 (ν\(_{\text{N-H}}\)), 1516 (ν\(_{\text{C=N}}\)), 1015 cm\(^{-1}\) (δ\(_{\text{C-H}}\)).

4.4. Preparation of MWNT/mPBI. MWNTs (20 mg) were added to mPBI (4.0 mg) dissolved in DMAC (20 mL). The resulting mixture was sonicated for 4 h. The mixture was filtered and then washed with DMAC to remove any unbound PBI. The obtained solid (MWNT/mPBI; 24.1 mg; yield: 100%) was dried under vacuum.

4.5. Preparation of MWNT/mPBI/Pt. H\(_2\)PtCl\(_6\)·6H\(_2\)O (1.4 mmol) in a 60% aqueous ethylene glycol (EG) solution (25 mL) was added to MWNT/mPBI (5.0 mg) dispersed in a 60% aqueous EG solution (10.0 mL). The mixture was heated under reflux at 140 °C for 6 h. The solid material was collected.

Figure 4. (a) TGA curves of MWNT/mPBI (black line) and MWNT/mPBI/Pt (red line). Inset: TEM image of MWNT/mPBI/Pt-w. Scale bar: 50 nm. (b) Polarization curves of MEAs containing MWNT/mPBI/Pt-w with (red) and without (black) KOH doping measured at 50 °C under 100% RH using H\(_2\) (0.1 L min\(^{-1}\)) and conditioned air (0.2 L min\(^{-1}\)) as fuels.
by filtration, washed with water, and then dried under vacuum to obtain the MWNT/mPBI/Pt (8.26 mg).

4.6. MEA Fabrication. MWNT/mPBI/Pt was dispersed in 1.0 M KOH solution (40 mL) by sonication and shaken for 24 h at 25 °C. The solid material was collected by filtration and then washed with water. The obtained solid was dispersed in isopropanol (120 mL) by sonication and then transferred onto a gas diffusion layer (Sigracet GDL 25 BC, SGL Carbon Group) by vacuum filtration. The gas diffusion layer was used as a filter to produce a gas-diffusion electrode (0.45 m² cm⁻²). Gas-diffusion electrodes were laminated on both sides of an AEM (AQ2013, Tokuyama Co.) to fabricate the MEA.

4.7. Single Cell Tests. Polarization curves were obtained at a scan rate of 1.0 mA s⁻¹ and cell temperature of 50 °C using pure humidified H₂ (RH = 100%, flow rate = 100 mL min⁻¹) and conditioned air (RH = 100%, 200 mL min⁻¹) as the fuel gases for the anode and cathode, respectively.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b01466.

*H NMR, FT-IR, and XPS of PBI and mPBI before and after KOH treatment. XPS of MWNT/mPBI-w and MWNT/mPBI-p before and after (red) KOH treatment. XPS of the CB/mPBI and MWNT/mPBI/Pt before and after the KOH treatment. Histogram of Pt diameter on MWNT/mPBI/Pt. Photos of A2013 before and after the KOH treatment. PDF

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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