Supporting Information

Development of Novel Durable Aromatic Anion Exchange Membrane using a Thermally Convertible Precursor

Hafis P.R. Graha, Shinji Ando, Shoji Miyanishi and Takeo Yamaguchi*

*To whom correspondence should be addressed.
Email: yamag@res.titech.ac.jp (T.Y.)

Table of Contents

Materials and Methods

Materials

2,6-dibromoanthracene **(1)** (CAS: 186517-01-1), bis(pinacolate)diboron (CAS: 73183-34-3), 2,5-dibromo-1,4-xylene **(3)** (CAS: 1074-24-4), diethyl azodicarboxylate (40% in toluene, ca. 2.2 mol/L) (CAS: 1972-28-7), azobisisobutyronitrile (AIBN) (CAS: 78-67-1), and NBS (CAS: 128-08-5) were purchased from Tokyo Chemical Industry Co., Ltd. and used as is without further purification. $Pd(PPh_3)_4$ (CAS: 14221-01-3), $Pd(dppf)Cl_2$ (CAS: 72287-26-4), trimethylamine (TMA) (CAS: 75-50-3), K_3PO_4 (CAS: 7778-53-2), and CH_3COOK (CAS: 127-08-2) were purchased from Wako Pure Chemical Industries Ltd. and used as is without further purification.

Instruments

^{1}H and ^{13}C NMR spectra were recorded using a Bruker Avance II NMR instrument at 400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR. Thermogravimetric analysis (TGA) was performed on a PerkinElmer model Pyris 1 TGA, and the heating profile was recorded and analyzed using a PerkinElmer Pyris software system. The TG-DTA/mass profile was recorded using a Rigaku Thermo Mass spectrometer. Infrared (IR) spectra were recorded on a Jasco FT/IR-6200 spectrometer. The weight-average molecular weight (M_w) and the number-average molecular weight (M_n) of the polymers were determined via gel permeation chromatography (GPC) (JASCO LC-200Plus with Shodex Asahipak GF-7MHQ columns). The standard curve used to determine the molecular weight was created from a polystyrene standard solution (TSK, Tosoh Corp.). Titration was done using Hiranuma auto titrator COM-1700. UV-Vis spectra was evaluated with Hitachi U-3310 Spectrophotometer.

Synthesis

(2)

The synthesis of (2) was performed according to the procedure described in literature[S1]. Yield: 85%

^{1}H-NMR: (500 MHz, $CDCl_3$): δ 7.63–7.21 (m, 6H), 6.22 (s, 2H), 4.20–4.07 (m, 4H), 1.22 (t, 6H).

^{13}C-NMR: (125 MHz, $CDCl_3$): δ 157.55, 143.55, 140.37, 138.17, 134.75, 130.75, 128.95, 127.23, 126.36, 124.51, 121.85, 121.01, 62.97, 59.47, 14.42.

(4)

The synthesis of (4) was performed according to the procedure described in literature[S2]. Yield: 30%

^{1}H-NMR: (500 MHz, $CDCl_3$): δ 7.55 (s, 2H), 2.50 (s, 6H), 1.36 (s, 24H).

^{13}C-NMR: (125 MHz, $CDCl_3$): δ 140.52, 136.95, 83.44, 24.87, 21.49.

(PP1)

(2) (1.68 mmol, 0.854 g), (4) (1.68 mmol, 0.6 g), few drops of the aliquot, and 10 mL of toluene were added to a 100-mL three-necked round flask equipped with a reflux condenser. The solution temperature was set to 100 °C. Then, nitrogen was bubbled for 10 min and all of the monomer was

dissolved. K_3PO_4 (5.03 mmol, 1.06) in 15 mL of degassed H_2O was added, followed by the addition of $Pd(PPh_3)_4$ in 5 mL of degassed toluene using a syringe. The mixture was refluxed for 16 h. The reaction solution was then poured into methanol (100 mL with a few drops of conc. HCl) and stirred for 30 min. The white residue was then extracted with acetone to remove the low-molecular weight fractions. The insoluble fractions were extracted with chloroform and then precipitated in methanol (100 mL) to yield a white solid **PP1 (**0.6 g, 74%)

^{1}H-NMR: (400 MHz, $CDCl_3$): δ 7.60–7.05 (m, 10H), 6.40 (s, 2H), 4.16 (q, 4H), 2.25 (s, 6H), 1.40–1.12 (t, 6H)

GPC: (DMF, polystyrene standard, 40°C): M_n = 13,432, M_w = 20,577, PDI = 1.5.

(PP2)

PP1 (0.420 g), NBS (1.90 mmol, 0.338 g), and AIBN (0.043 mmol, 4.3 mg) were dissolved into 5 mL chlorobenzene under an N_2 atmosphere. The reaction was performed for 180 min at 100 °C. After cooling to room temperature, the reaction mixture was added to cold methanol. The suspension was then filtered and washed with methanol several times to yield a pale-yellow solid **PP2** (0.5 g, 90%).

^{1}H-NMR: (400 MHz, $CDCl_3$): δ 7.73–7.2 (m, 10H), 6.46 (s, 2H), 4.43 (s, 4H), 4.20 (q, 4H) 2.28 (s, 6H), 1.40–1.02 (t, 6H)

GPC: (DMF, polystyrene standard, 40 °C): M_n = 13,282, M_w = 24,557, PDI = 1.85.

(P-PAPP)

PP2 (0.45 g) was dissolved in 2 mL DMF; 3.7 mL TMA (2 mol/L) was added to the polymer solution and stirred for 72 h at 50 °C. The solvent was evaporated at 80°C and then ground and dried under vacuum at 80 °C to give **P-PAPP** (0.51 g, 98%).

^{1}H-NMR: δ 8.00–7.42 (m, 10H), 6.62 (s, 2H), 4.76 (b, 4H), 4.06 (q, 4H), 2.89–2.70 (m, 18H), 1.15 (t, 6H).

Degree of bromination and IEC calculation

The degree of bromination (DoB) of PP2 was calculated from the ^{1}H-NMR spectra using the following formula:

$$\text{DoB: } \frac{\frac{A_{\delta 4.43}}{2}}{\frac{(A_{\delta 4.43})}{2}+\frac{(A_{\delta 2.28})}{3}},$$

where $A_{\delta 4.43}$ is the area under the peak δ 4.43, and $A_{\delta 2.28}$ is the area under the peak δ 2.28.

The theoretical IEC of the polymer was calculated using DoB through the following formula:

$$\text{IEC: } \frac{n\ x\ DoB}{M_wS} x 1000,$$

where n is the theoretical number of ion exchange sites and M_wS is the molecular weight of one segment of the polymer.

The IEC of the polymer was measured using titration method with $AgNO_3$ and calculated using the following formula:

$$\text{IEC: } \frac{v\ x\ C_{AgNO_3}}{m} x 1000$$

where v is the volume of $AgNO_3$, C_{AgNO_3} is the concentration of $AgNO_3$, m is the mass of the polymer.

Water uptake

Water uptake of the membranes evaluated with a MSB-ADV-FC equipment (BEL Japan, Inc.). The samples conditioning time for each relative humidity is 2 hours.

Ionic-conductivity measurements

The ionic conductivity σ (S/cm) of the membrane was measured via an AC impedance method using a Solatron 1260 impedance analyzer; two platinum electrodes on a glass plate were used. The impedance spectra were evaluated using the ZPlot/ZView software (Scribner Associates) under an AC perturbation signal of 50 mV in the frequency range of 1 Hz–10 MHz. The ionic conductivity σ (S/cm) of the membranes was calculated using the following formula:

$$\sigma\ (\text{S/cm}) = \frac{D}{R\ x\ L\ x\ T},$$

where R is the membrane resistance (Ohm), D is the distance between the two platinum electrodes (cm), L is the membrane width (cm), and T is the membrane thickness (cm).

Supporting references

S1 T. Uemura, M. Mamada, D. Kumaki and S. Tokito, *ACS Macro Lett.*, 2013, **2**, 830–833.

S2 S. Cao, Y. Wang and X. Peng, *Chem. - A Eur. J.*, 2012, **18**, 3850–3854.

Supplementary figures

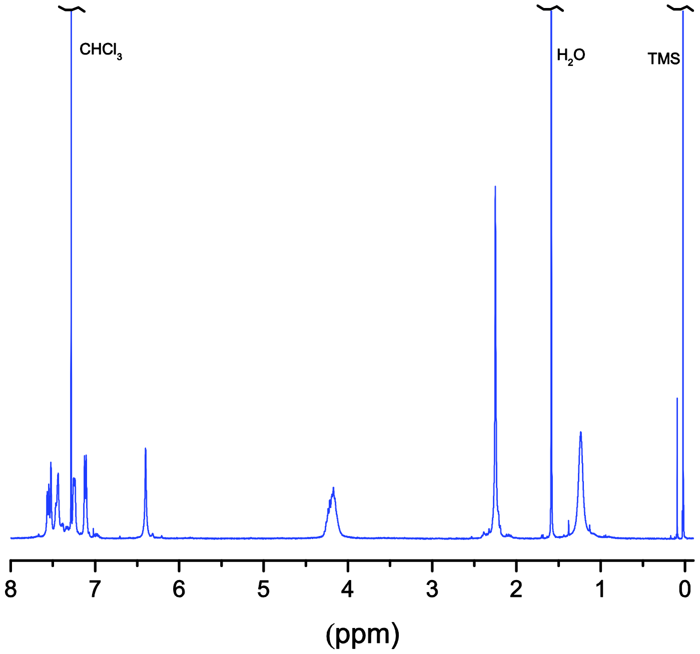

Fig. S1 ^{1}H NMR spectrum of *PP1*.

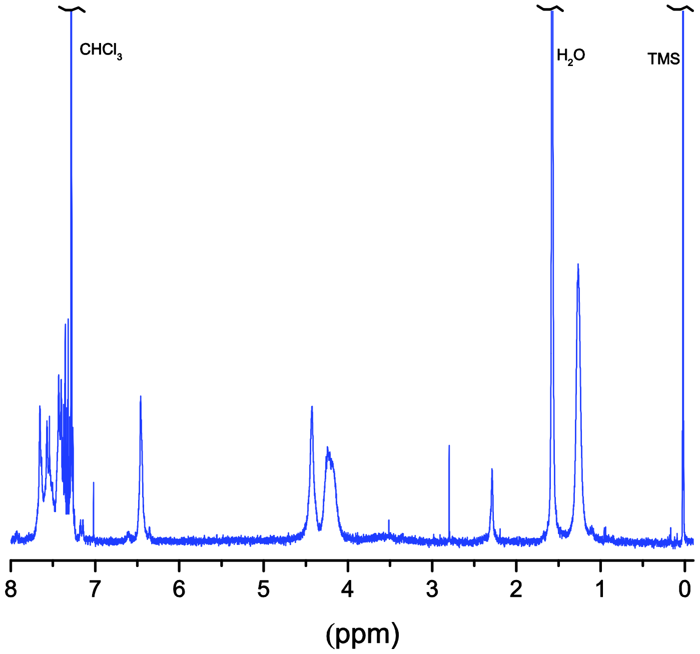

Fig. S2 ^{1}H NMR spectrum of *PP2*.

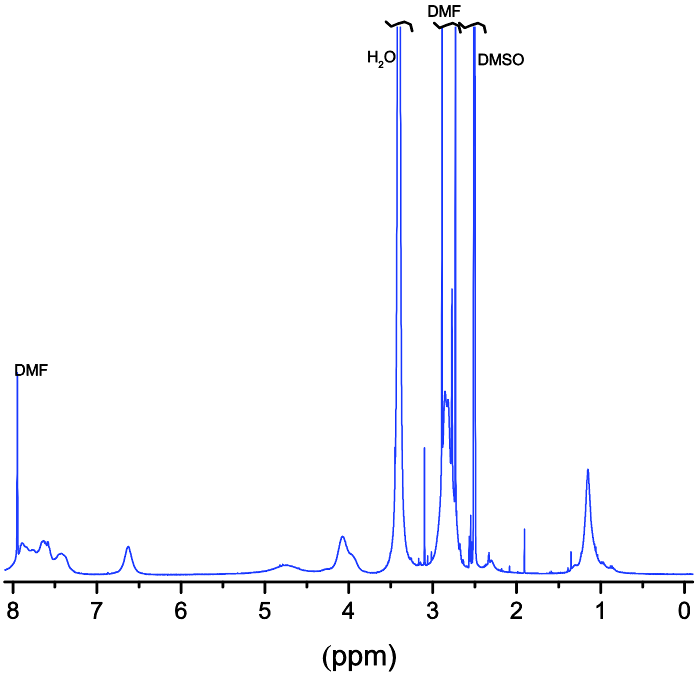

Fig. S3 ^{1}H NMR spectrum of ***P-PAPP***.

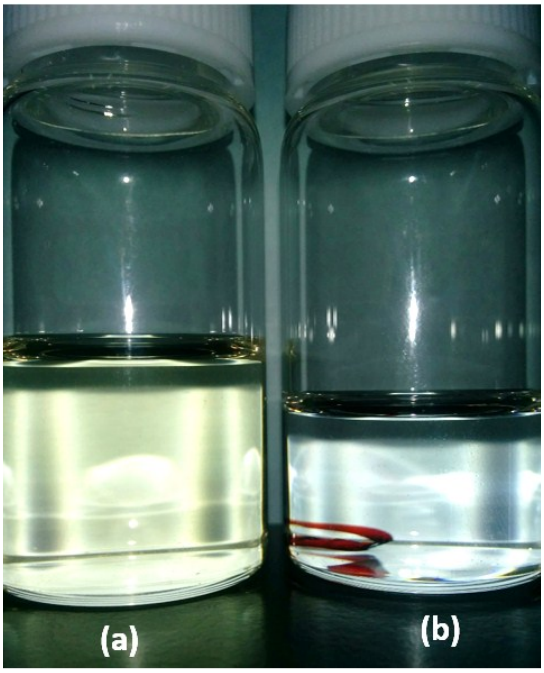

Fig. S4 Solubility test in DMF: **(a) P-PAPP** membrane: membrane dissolved and DMF color turned into yellow **(b) PAPP** membrane: membrane was intact and DMF remained clear.

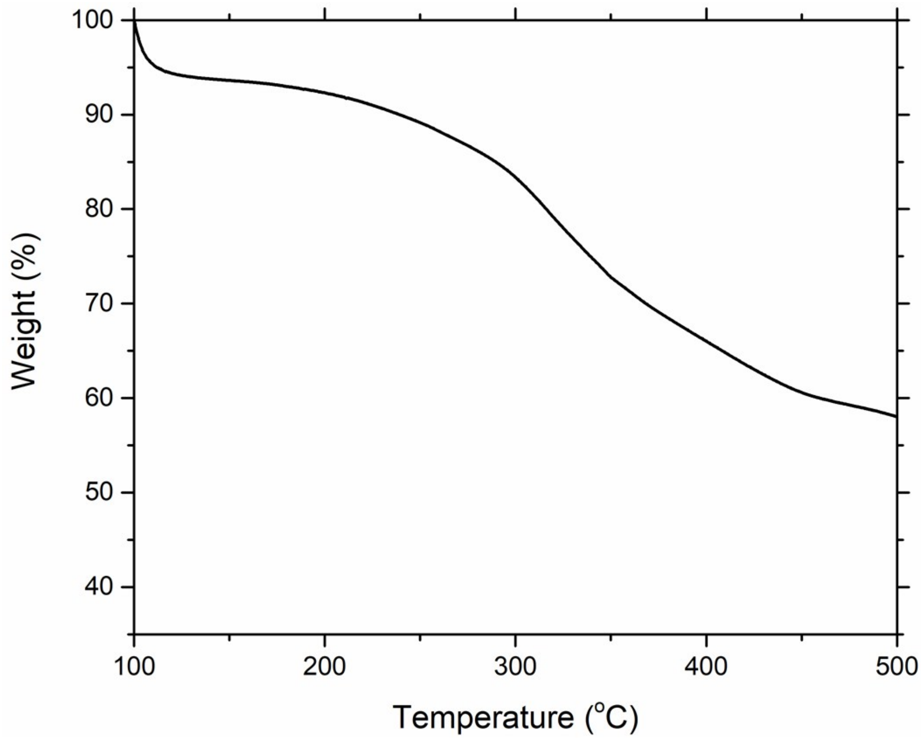

Fig. S5 TG profile of **PAPP** membrane.

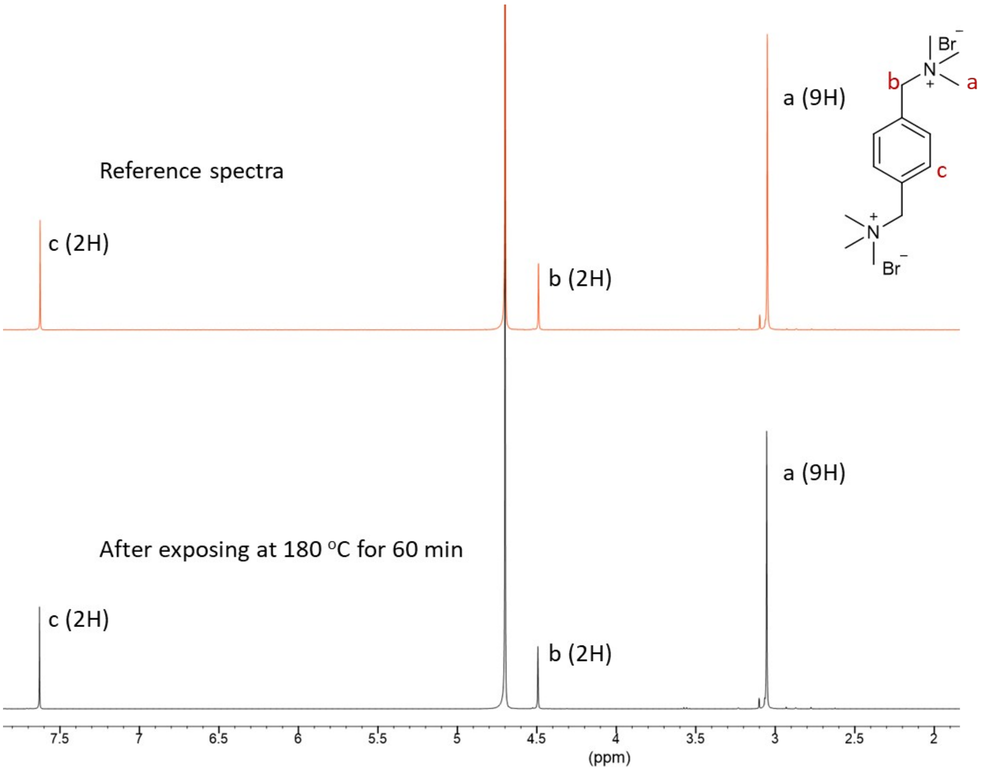

Fig. S6 NMR spectra of model compound to check the stability of BTMA group when heated at 180 °C for 60 min.

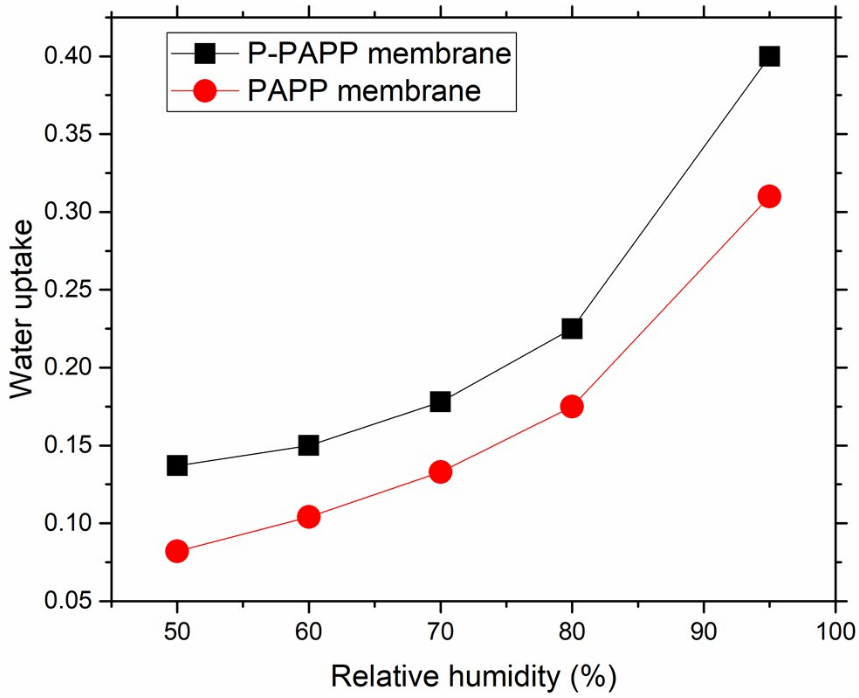

Fig. S7 Water uptake profile of **P-PAPP** and **PAPP** membrane at various relative humidity at 80°C.

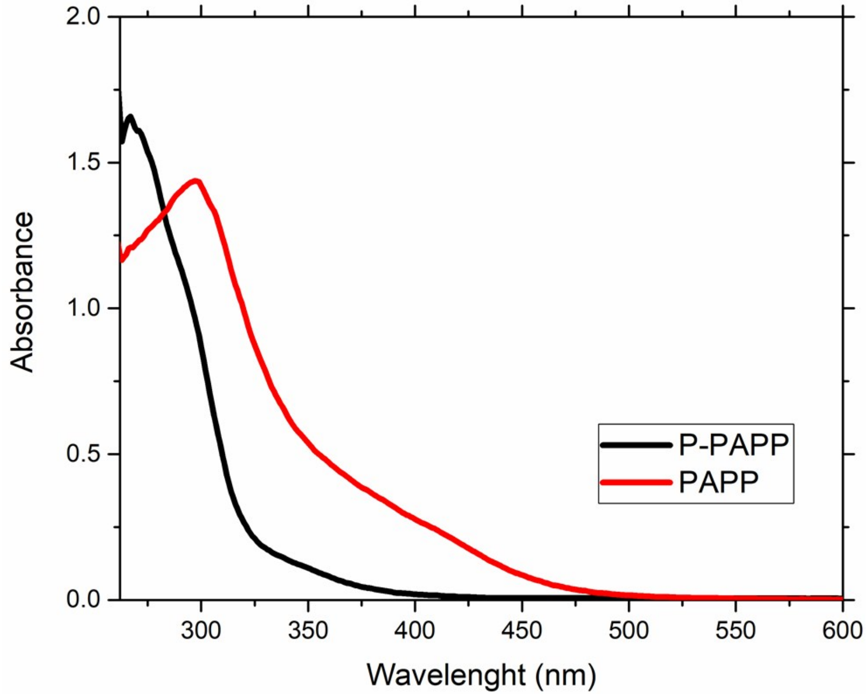

Fig. S8 UV-Vis absorbtion spectra of **P-PAPP** and **PAPP.**

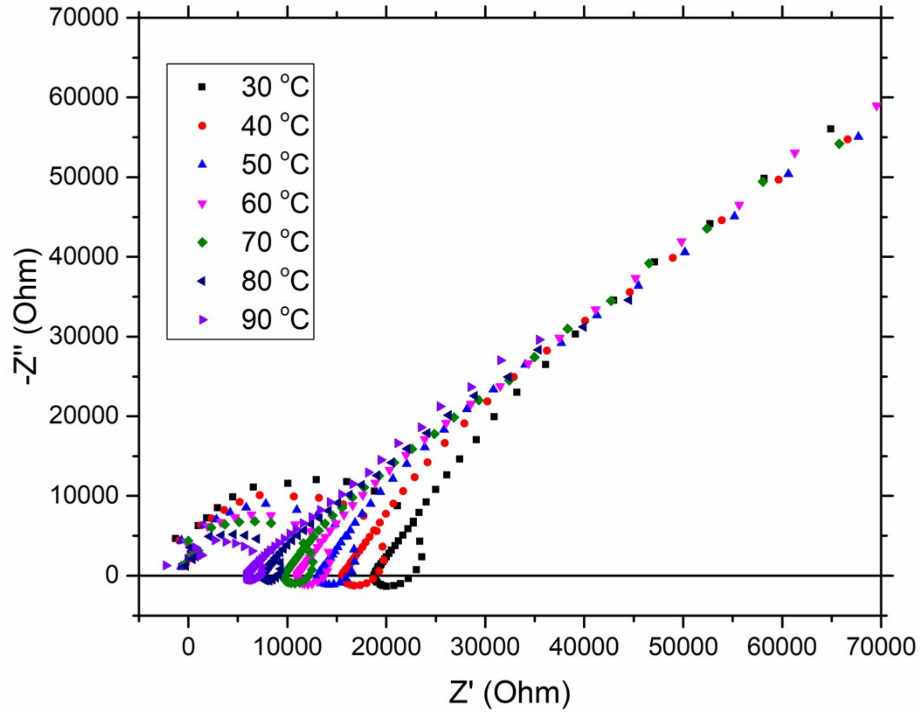

Fig. S9 Nyquist plot for **PPAP** membrane (HCO_3^- form) before durability test.

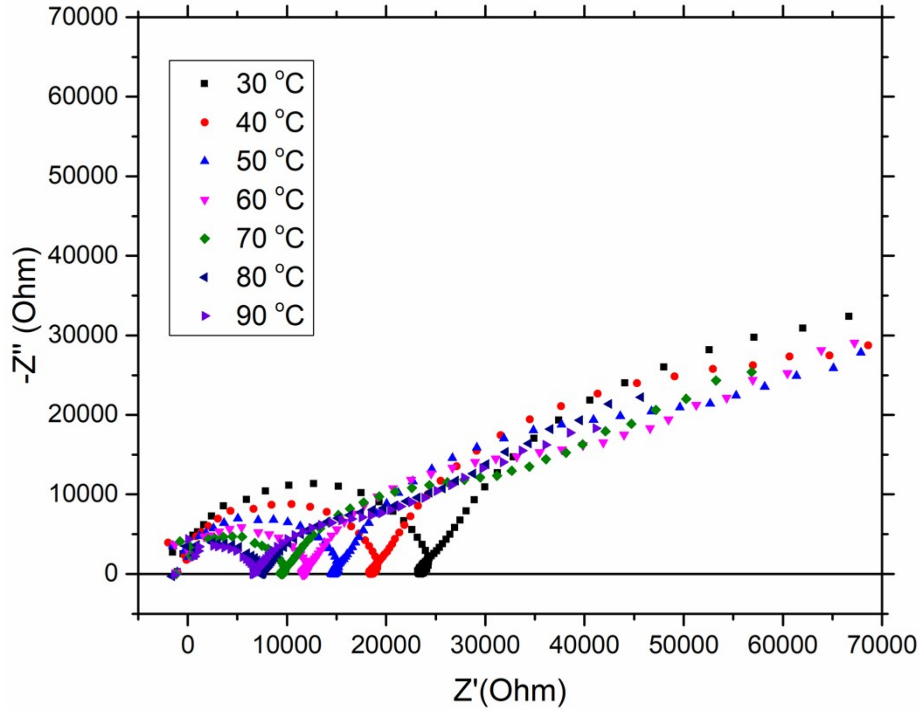

Fig. S10 Nyquist plot for **PPAP** membrane (HCO_3^- form) after alkaline durability test.

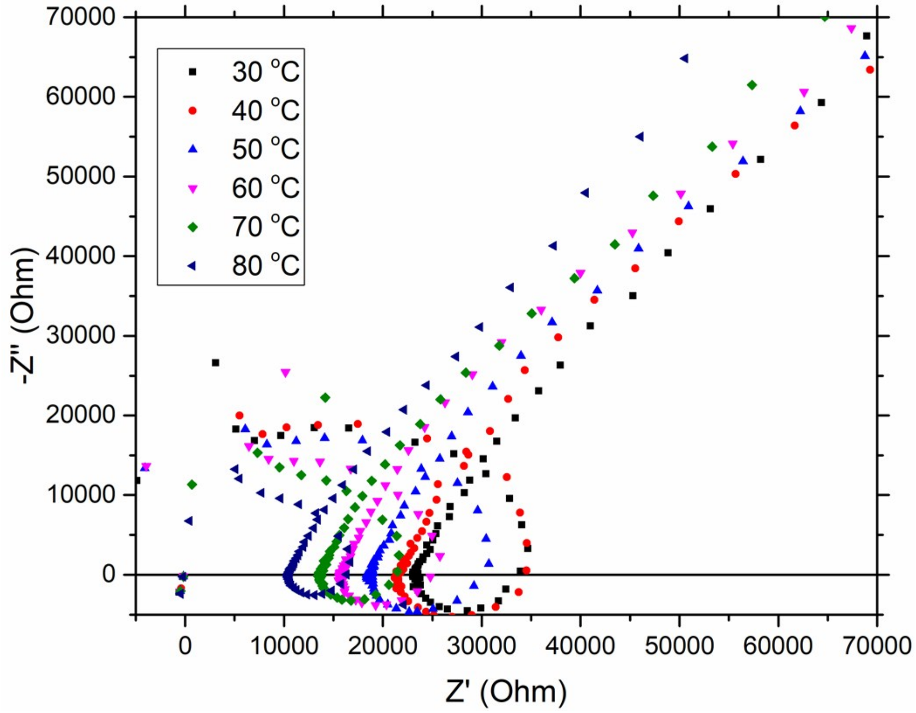

Fig. S11 Nyquist plot for **PPAP** membrane (HCO_3^- form) after oxidative durability test.