Electronic supplementary information: Highly water dispersible, mixed ionic-electronic conducting, polymer acid-doped polyanilines as ionomers for direct methanol fuel cells

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1. Experimental

Experimental procedure for the preparation of Polyaniline polymers

Ortho-toluidine, aniline, poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (PAAMPSA), and ammonium peroxydisulfate were procured from Sigma-Aldrich. The following procedure describes the synthesis of PoT-PAAMPSA, and an identical procedure was followed for the synthesis of PANI-PAAMPSA using aniline in the place of ortho-toluidine. 5.8 g (0.028 mol) of PAAMPSA was dissolved in 375 mL of deionized water in a 500 mL beaker with a stir bar. 3 g (0.028 mol) of ortho-toluidine (3 mL) was added to the PAAMPSA solution and stirred at room temperature for 2 h. 5.8 g (0.025 mol) of ammonium peroxydisulfate was dissolved in 25 mL of deionized water. The solutions of PAAMPSA + ortho toluidine and ammonium peroxydisulfate were deoxygenated by bubbling nitrogen and then cooled in an ice bath separately. The ammonium peroxydisulfate solution was then added to the PAAMPSA + ortho-toluidine solution slowly, and the reaction was allowed to take place in an ice bath with stirring for 6 h. After the reaction, the ice bath was removed but stirring was continued for another 36 h when the solution turned green. Acetone was added slowly to the above solution to precipitate the green polymer. The supernatant was decanted, and the green precipitate was filtered and washed with acetone. The solid was then dried in a vacuum oven overnight. Finally, a known weight of the polymer was added to a known volume of deionized water and stirred for two weeks continuously to get a well dispersed polymer.

Membrane-electrode assembly (MEA) preparation and single cell experiments

The performances of PtRu/C-PANI-PAAMPSA, PtRu/C-PoT-PAAMPSA, and PtRu/C-Nafion composite anodes in single cell DMFC were assessed using identical cathodes (Pt/C-Nafion) and membranes (Nafion 115). The anode catalyst ink was prepared by sonicating the required amounts of the catalyst (60 wt. % PtRu on carbon, ETEK Inc.), isopropyl alcohol, deionized water, and Nafion (Electrochem Inc., obtained as 5 wt. % solution) or PANI-PAAMPSA or PoT-PAAMPSA (30 wt. % loading) for 1 h. Cathode catalyst ink was prepared by sonicating required quantities of Pt/C (60 wt .%, ETEK, Inc), isopropyl alcohol, deionized water, and Nafion (25 wt. % loading) for 1 h. The catalyst ink was air sprayed onto a gas-diffusion layer (BASF) followed by drying in air at 90 ^{o}C. The catalyst loading was 2 mg/cm^2 for both the anode and cathode. The weight of the carbon-supported catalyst (60 wt. % Pt or PtRu on carbon) for 5 cm^2 active surface area single cell is 2 mg/cm^2 x 5 cm^2 / 60 % = 16.7 mg. The compositions of the inks for the anode and cathode for the above amount of catalyst are as follows.

Anode:

Component	**Description**	**Weight (mg)**
Catalyst	PtRu (60 wt. % on carbon)	16.7
Water	30 times the weight of the catalyst	501
Isopropyl alcohol	50 times the weight of the catalyst	835
PANI-PAAMPSA or PoT-PAAMPSA or Nafion all obtained as 5 wt. % solution	30 % of the weight of the catalyst	100.2 (5 % solution)

Cathode:

Component	**Description**	**Weight (mg)**
Catalyst	Pt (60 wt. % on carbon)	16.7
Water	30 times the weight of the catalyst	501
Isopropyl alcohol	50 times the weight of the catalyst	835
Nafion obtained as 5 wt. % solution	25 % of the weight of the catalyst	83.5 (5 % solution)

The membrane-electrode assemblies (MEA) were fabricated by hot pressing the anode and cathode onto a Nafion 115 membrane at 120 ^{o}C and 80 psi for 2.5 min. The single cell hardware (Scribner) with serpentine flow-field pattern (5 cm^2 active area) was used for feeding 1 M methanol solution (flow rate: 2.5 mL/min) and humidified oxygen (flow rate: 200 mL/min, without backpressure) at 65 ºC.

Cyclic voltammetry

Cyclic voltammetric experiments were conducted with a CH Instruments potentiostat in a conventional single compartment three-electrode cell having a platinum wire counter electrode and a Hg/$HgSO_4$ reference electrode (in saturated K_2SO_4 solution). The potentials were, however, referenced with respect to the reversible hydrogen electrode (RHE). A glassy carbon (3 mm dia.) electrode was polished to a mirror-like finish with 0.05 μm alumina media (Buehler) and coated with a thin layer of the catalyst to serve as a working electrode. The catalyst ink was prepared by dispersing 2 mg of PtRu (60 wt. % on carbon, ETEK Inc.) in a mixture of deionized water, ethanol, and Nafion (Electrochem Inc., obtained as 5 wt. % solution) or PANI-PAAMPSA or PoT-PAAMPSA by ultrasonic vibration. 2 μL of the resulting ink was drop cast onto the glassy carbon electrode and subsequently dried in air. The conducting polymers or

Nafion form 30 wt. % of the dry catalyst loading. Initially, the electrode potential was scanned between 0.02 and 1.0 V for 10 cycles at a scan rate of 20 mV/s in order to clean the surface in 0.5 M H_2SO_4. Methanol oxidation reaction (MOR) activities of the various electrodes were characterized in a nitrogen saturated 0.5 M H_2SO_4 + 1 M methanol solution at a scan rate of 20 mV/s. The electrochemical activities of PANI-PAAMPSA and PoT-PAAMPSA were characterized in 0.5 M H_2SO_4 with the PANI-PAAMPSA or PoT-PAAMPSA-coated (60 μg/cm^2 loading) glassy carbon working electrode.

UV-visible spectroscopy

10 mg of the conducting polymer was added to 100 mL of deionized water and stirred for two weeks to obtain a solution-like dispersion. The UV-visible spectra were recorded with an Agilent 8453 UV-vis spectrometer in a quartz cuvette. A single band at 875-900 nm and a broad band between 310–460 nm are the characteristic bands for the emeraldine acid.

Impedance analysis

Impedance analysis was carried out with a Solartron 1260 frequency response analyzer and Solartron 1286 potentiostat/galvanostat controlled by ZPLOT2 software from Scribner. The anode and cathode of the single cell were fed with 1 M methanol (flow rate: 2.5 mL/min) and hydrogen (flow rate: 10 mL/min) respectively. The cathode served as a dynamic hydrogen electrode while the anode served as the working electrode. The frequency range explored was from 100 mHz to 5 kHz with an amplitude of 5 mV.

FTIR spectroscopy

The FTIR spectra of PANI-PAAMPSA and PoT-PAAMPSA were obtained with a Nicolet 6700 FTIR spectrometer and were analyzed with OMNIC software. In PAAMPSA, the -S=O and –C=O vibrations occur, respectively, near 1650 and 1550 cm^{-1}. The C-N stretching bands of the benzenoid and quinoid rings appear, respectively, at 1500 and 1590 cm^{-1}. For both PANI-PAAMPSA and PoT-PAAMPSA, the in plane C-H bending vibration appears around 1110 cm^{-1}. The band at 1040 cm^{-1} belongs to the –SO_3H vibration. The band due to the methyl group attached to the ring occurs at 877 cm^{-1} in PoT-PAAMPSA.

Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) images of PANI-PAAMPSA and PoT-PAAMPSA were obtained with a Hitachi S-5500 STEM instrument. Samples were prepared by depositing a dilute dispersion of the polymers on to a lacey carbon grid.

X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopic (XPS) data of the conducting polymers were obtained with a Kratos Analytical XPS instrument using monochromatic Al Kα X-ray source. The spectra were fitted with a Gaussian-Lorentzian function (G:L = 70:30) and a Shirley background function using the CASAXPS software.

The carbon 1s signals can be decomposed in to three components. The lower energy peaks (PANI-PAAMPSA = 284.7 eV; PoT-PAAMPSA = 285.0 eV) are due to the C-C, C-H, and C-N groups. The signals at 286.1 eV (PANI-PAAMPSA) and 286.5 eV (PoT-

PAAMPSA) are due to the C=O groups. The shake-up satellites at higher energy end are common for the polymer systems with aromatic rings [1].

The nitrogen 1s signals can be deconvoluted in to two peaks. The lower energy peaks (PANI-PAAMPSA = 399.6 eV; PoT-PAAMPSA = 399.4 eV can be attributed to the amide and amine nitrogens and the ones at higher energy (PANI-PAAMPSA = 401.7 eV; PoT-PAAMPSA = 401.6 eV) can be assigned to positively charged radical nitrogens [2].

Two distinct oxygen species, H_2O and SO_3^-, contributes to the oxygen 1s signals of the conducting polymers. The lower energy peaks (PANI-PAAMPSA = 531.0 eV; PoT-PAAMPSA = 531.2 eV) can be attributed to the H_2O species and the higher energy peaks (PANI-PAAMPSA = 533.5 eV; PoT-PAAMPSA = 533.6 eV) to the SO_3^- groups [3].

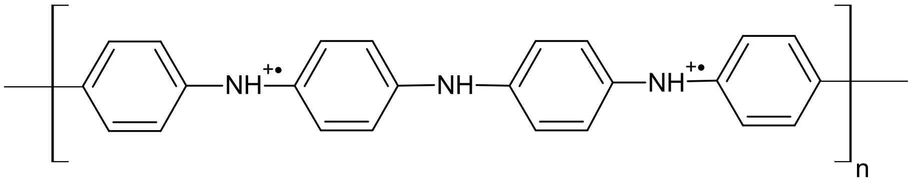
Sulfur 2p signals can be deconvoluted in to two peaks. The lower energy peaks (PANI-PAAMPSA = 167.8 eV; PoT-PAAMPSA = 167.9 eV) can be assigned to $2p_{3/2}$ and the higher energy peaks (PANI-PAAMPSA = 168.9 eV; PoT-PAAMPSA = 169.1 eV) to $2p_{1/2}$ of the sulfur in the sulfonic acid group [4].

References:

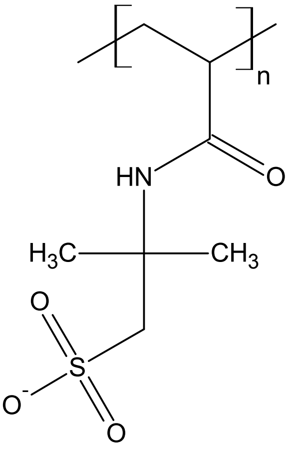
1. R. Rajagopalan and J. O. Iroh, *Appl. Surf. Sci.* 2003, **218**, 58.
2. R. J. J. Jansen and H. Van. Bekkum, *Carbon*, 1995, **33**, 1021.
3. J. Yue and A. J. Epstein, *Macromolecules*, 1991, **24**, 4441.
4. M. M. Nasef , H. Saidi, , *Appl. Surf. Sci.* 2006, **252**, 3073.

2. Structures of PANI-PAAMPSA and PoT-PAAMPSA

PANI-PAAMPSA:

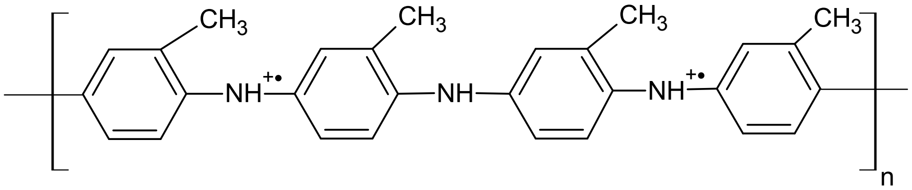


PANI

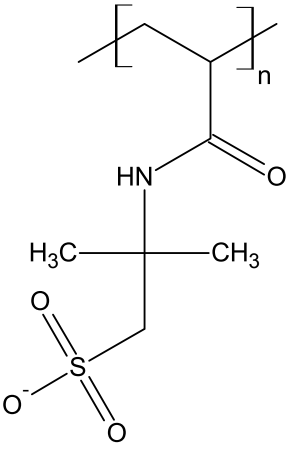


PAAMPSA

PoT-PAAMPSA:



PoT



PAAMPSA

3. Dispersions of PANI-PAAMPSA and PoT-PAAMPSA in water

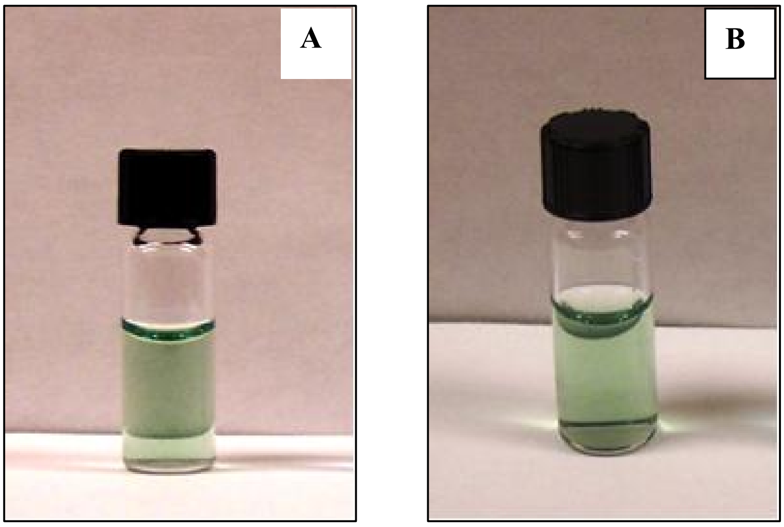


Figure S1. Solution-like clear dispersions of (A) PANI-PAAMPSA and (B) PoT-PAAMPSA in water.

4. FTIR spectra of PANI-PAAMPSA and PoT-PAAMPSA

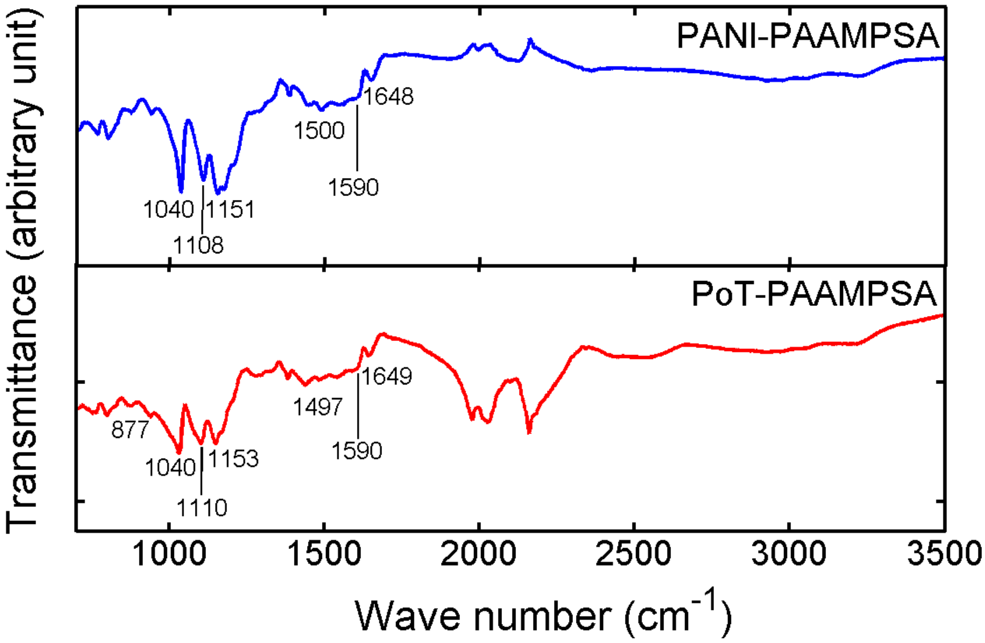


Figure S2. FTIR spectra of PANI-PAAMPSA and PoT-PAAMPSA.

5. SEM pictures of the conducting polymers

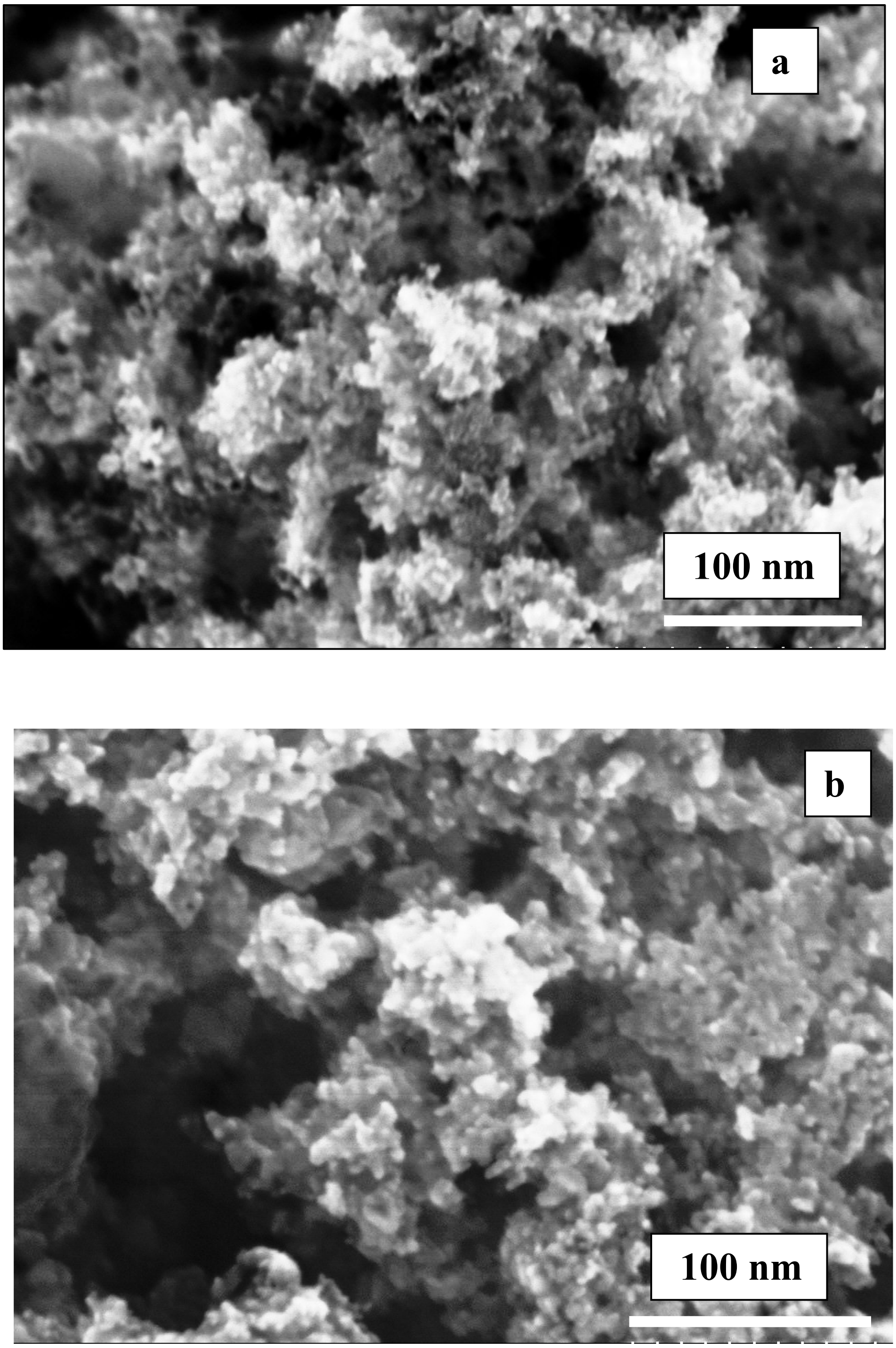


Figure S3. Scanning Electron Micrographs of (a) PANI-PAAMPSA and (b) PoT-PAAMPSA.

6. XPS spectra of PANI-PAAMPSA

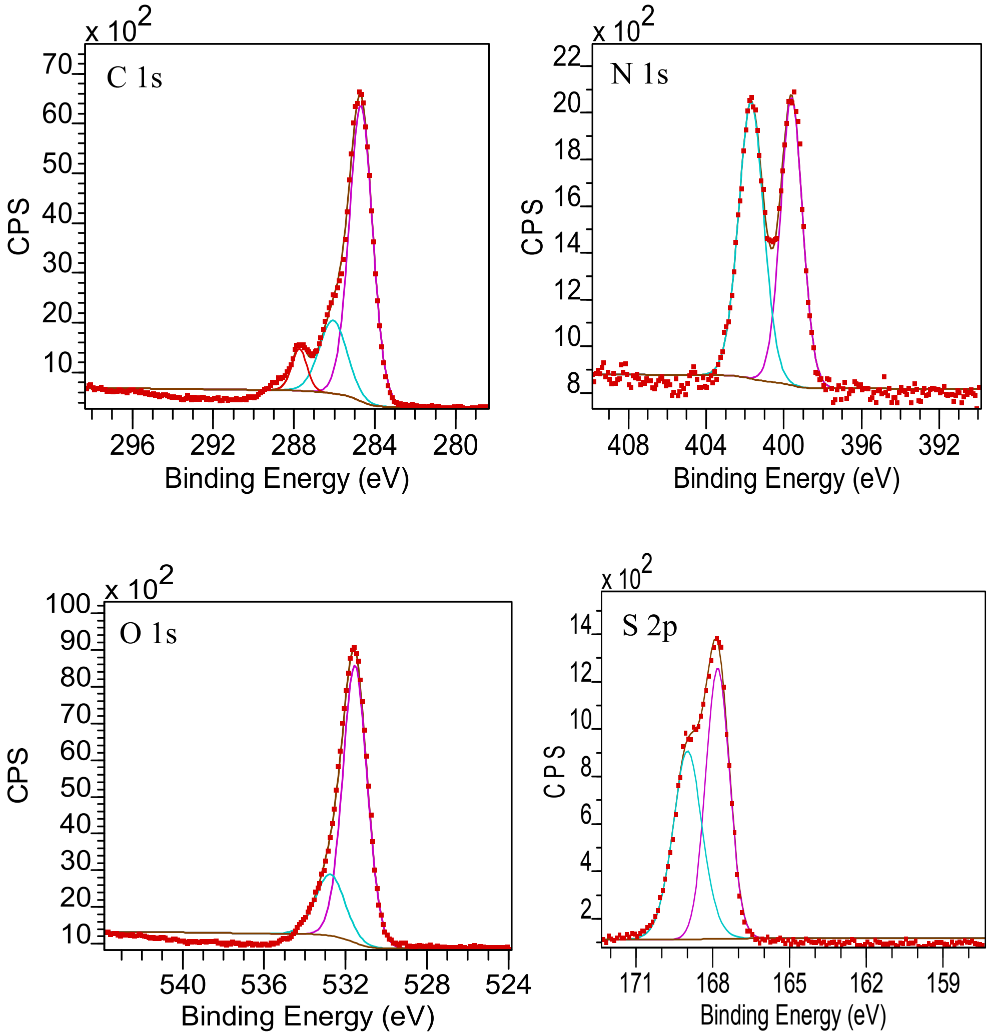


Figure S4. XPS spectra of C 1s, N 1s, O 1s and S 2p signals of PANI-PAAMPSA.

7. XPS spectra of PoT-PAAMPSA

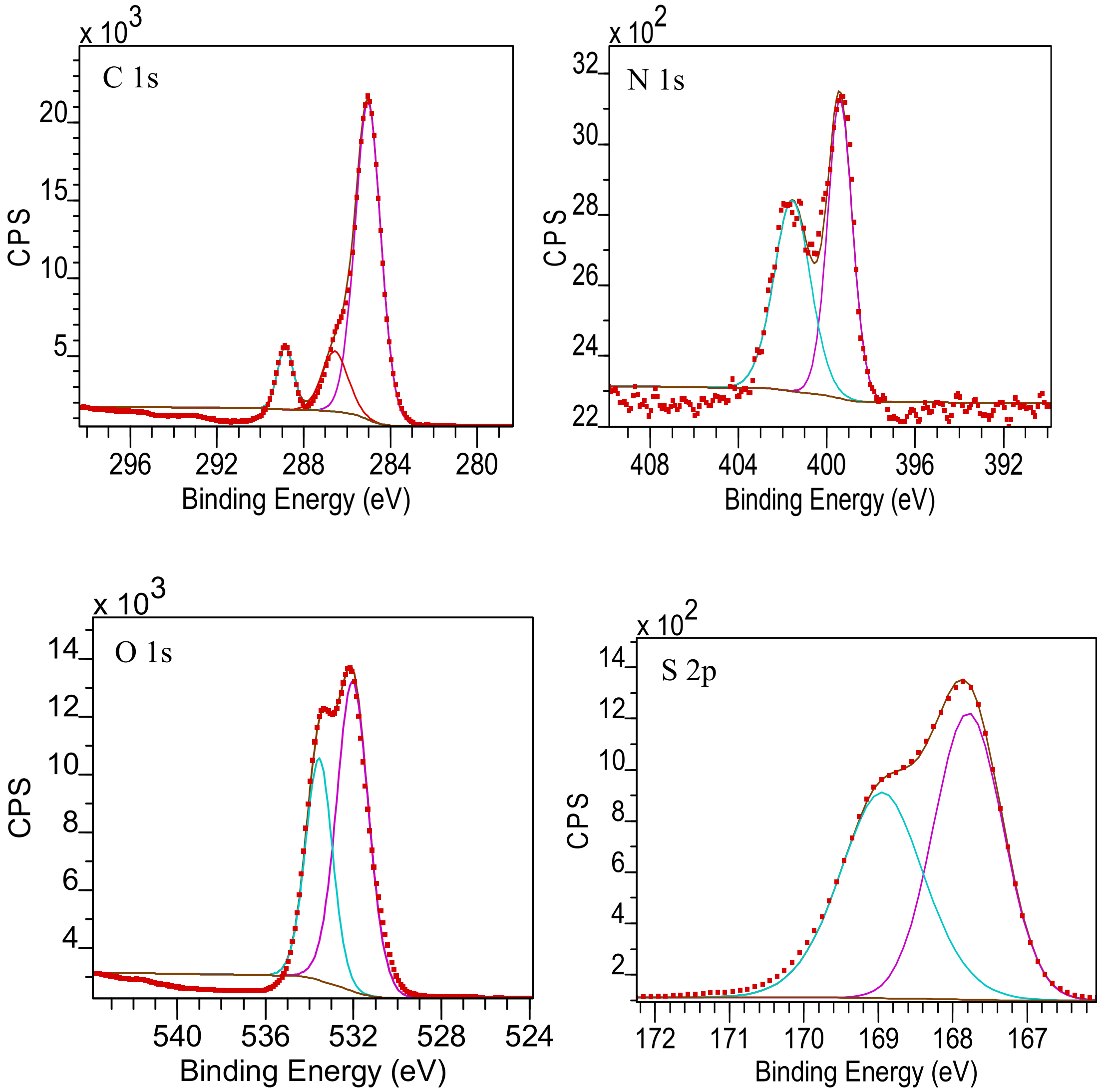


Figure S4. XPS spectra of C 1s, N 1s, O 1s and S 2p signals of PoT-PAAMPSA.