Electronic Supplementary Information

Alkaline ionomer with tuneable water uptakes for electrochemical energy technologies

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Experimental Details

Preparation of the membrane electrode assemblies (MEA) and fuel cell test conditions.

The aqueous polymer poly(vinylbenzyltrimethylammonium chloride), PVBTMACl, solution (30.22% mass, MW = 400,000, Scientific Polymer Products, Inc., USA) was diluted with ethanol (ethanol:water = 1:1 by volume) and mixed with the commercially available electrocatalyst, HiSpec4000 containing 40%(mass)Pt/C (Johnson Matthey, UK), to form a catalytic ink (PVBTMACl:electrocatalyst = 3:7 by mass). Ethanol was added to aid with satisfactory ink spraying using the equipment available. However, the PVBTMACl can be deposited using only water as solvent if painted onto the electrode. The electrocatalyst was sprayed onto one side of PTFE treated plain Toray 090 carbon paper (Toray Industries, Inc., Japan) to give a Pt loading of 0.53 ± 0.03 mg cm^{-2}. The electrodes (2.4 cm × 2.5 cm) were put in a vacuum oven for 2 h at room temperature and then 2 h at 50°C. The electrodes were then treated in vacuum oven at 190°C for the set periods of time. Subsequently the electrodes were immersed in KOH (aq, 0.5 mol dm^{-3}) for ion exchange of the ionomer to the hydroxide form. The alignment of the electrodes in the MEAs (containing a radiation–grafted anion–exchange membrane of 80 µm fully hydrated thickness)[1] and the positioning of the reference electrodes (RE) are reported in detail in reference[2] and shown diagrammatically in Scheme S1. The potential and impedance of cathode and anode were recorded *vs* REc and REa respectively. The potential and impedance response of the whole cell were recorded directly by the two anionomer–containing electrodes. The fuel cell test conditions (gas flows, gas humidities, fuel cell temperatures etc.) were controlled using a commercial fuel cell test station (Arbin Instrument., USA). The impedance spectra, current densities and potentials were recorded using Solartron 1470E/1450A CellTest® system (Solartron Analytical, UK). The fuel cell test procedures were as previously reported: The non–pressurised and fully hydrated H_2 and O_2 gases were supplied to the anode and cathode, respectively, of the fuel cells, which were heated to 50°C[3].

Ionic conductivity testing of ex situ cast films

The water soluble polymer PVBTMACl solution was further diluted in water to make a 3%(mass) solution. A porous polymeric film (BS095015, Coin Nanotech Innovations Co. Ltd., China) was soaked in this solution and ultrasonicated for 1hr. The porous film containing the polymer electrolyte solution was dried overnight at room temperature to yield the desired membrane. The membranes were thermally treated using the same procedure as the electrodes (the membrane was heated at 190°C or 160°C in vacuum oven for the desired times). The treated membrane was washed in water and converted from chloride form to hydro oxide form by submersion in aqueous KOH (0.5 mol dm^{-3}). The ionic through–plane conductivities of the AAEMs (submerged in water – hence fully hydrated) were obtained from the high frequency *x*–axis intercept in the Nyquist plot impedance spectra collected using a Solartron 1260/1287 frequency gain analyser/electrochemical interface combination with a maximum voltage amplitude of 10 mV and a frequency range from 1 MHz → 1 kHz. Note that the porous polymeric films were required to retain membrane integrity in the conductivity test cells.

The measurement of the linear expansion

The linear expansion of the thermally treated cast as films (off the electrodes and in the chloride form) is calculated as following:

$$\text{Linear expansion \%} = (L_{wet} - L_{dry}) \times 100 / L_{dry}$$

where L is the length of the long edge of a rectangular cast polymer film. L_{dry} was measured after the thermal treatment step and L_{wet} was measured after the polymer film was soaked in water for about 10 min until the shape of the film was unchanged. Note that the porous polymeric films used for through plane conductivity measurements were not used for these ex situ linear expansion tests.

Characterisation of the t–PVBTMACl polymer

Solid State NMR spectra were obtained using a Varian VNMRS 400 spectrometer (USA) operating at 40.53 MHz for ^{15}N and 100.56 MHz for ^{13}C; the spectral referencing was with respect to external undiluted CH_3NO_2 and tetramethylsilane respectively. XPS analyses were performed on a ThermoFisher Scientific (East Grinstead, UK) Theta Probe spectrometer. XPS spectra were acquired using an MXR1 monochromated Al K_α X–ray source (h = 1486.6 eV). An X–ray spot of 400 µm radius was employed. Survey spectra were acquired employing a pass energy of 300 eV. High resolution core level spectra were acquired using a pass energy of 50 eV and 20 scans. Quantitative surface chemical analyses were calculated from the high resolution, core level spectra following the removal of a non–linear (Shirley) background. The manufacturer's Avantage software was used, which incorporates the appropriate sensitivity factors and corrects for the electron energy analyser transmission function. Fourier–Transform Raman spectra of the polymer films were obtained using a combined near infrared (NIR) Raman System 2000 spectrometer (Perkin Elmer, USA).

References

1 J. R. Varcoe, R. C. T. Slade, E. Lam How Yee, S. D. Poynton, D. J. Driscoll and D. C. Apperley, *Chem. Mater.*, 2007, **19**, 2686.

2 R. Zeng, R. C. T. Slade and J. R. Varcoe, *Electrochimica Acta*, 2010, **56**, 607.

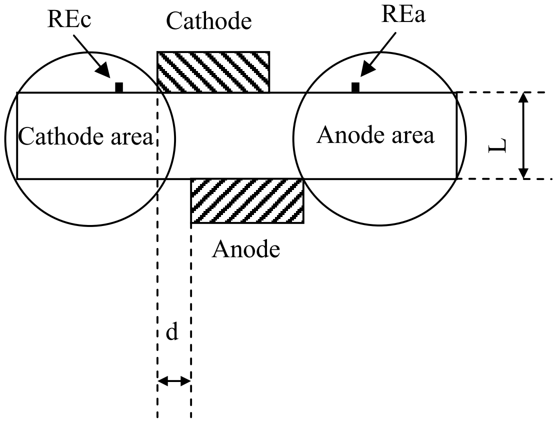
3 J. R. Varcoe and R. C. T. Slade, *Electrochem. Comm.*, 2006, **8**, 839; J. R. Varcoe, R. C. T. Slade, and E. Lam How Yee, *Chem. Commun.*, 2006, 1428.

Additional Tables, Figures and Schemes

Table S1. XPS–based elemental analyses[a] of the polymer films and the ratio of quaternary ammonium (QA) and tertiary amine (TA) N atoms.

Heat–treatment	C(At%)	O(At%)[b]	Cl(At%)[c]	N(At%)[c]	[d]TA/QA ratio
Room temperature	83.79	7.83	3.77	4.61	0
190°C, 10min	88.5	1.84	4.4	5.27	0.27
190°C, 30min	91.51	3.66	1.33	3.51	4
190°C, 1hr	87.27	8.83	0.54	3.36	6.67

[a]Si was observed as a contamination and was not counted for calculation of element concentration. [b]The higher than anticipated concentration of O in the room temperature cast sample is caused by residual water trapped in the hydrophilic polymer. The concentration of O increased as a function of heating time at 190°C due to the oxidation of the polymer. [c]The decreased concentrations of N and Cl showed the loss of N and Cl content at the surface of the polymer due to the degradation of the trimethylammonium functions. [d]The increased ratio of tertiary amine / quaternary ammonium (TA/QA) groups showed the increasing tertiary amine contents, which means the surface of the polymer films became less hydrophilic on increased thermal treatment times.



Va = Anode *vs* REa

Vc = Cathode *vs* REc

d = 1–1.25mm

L = 80 ± 5μm

Scheme S1. The locations of the reference electrodes (RE) and the anode and cathode electrode alignments used for fuel cell testing.

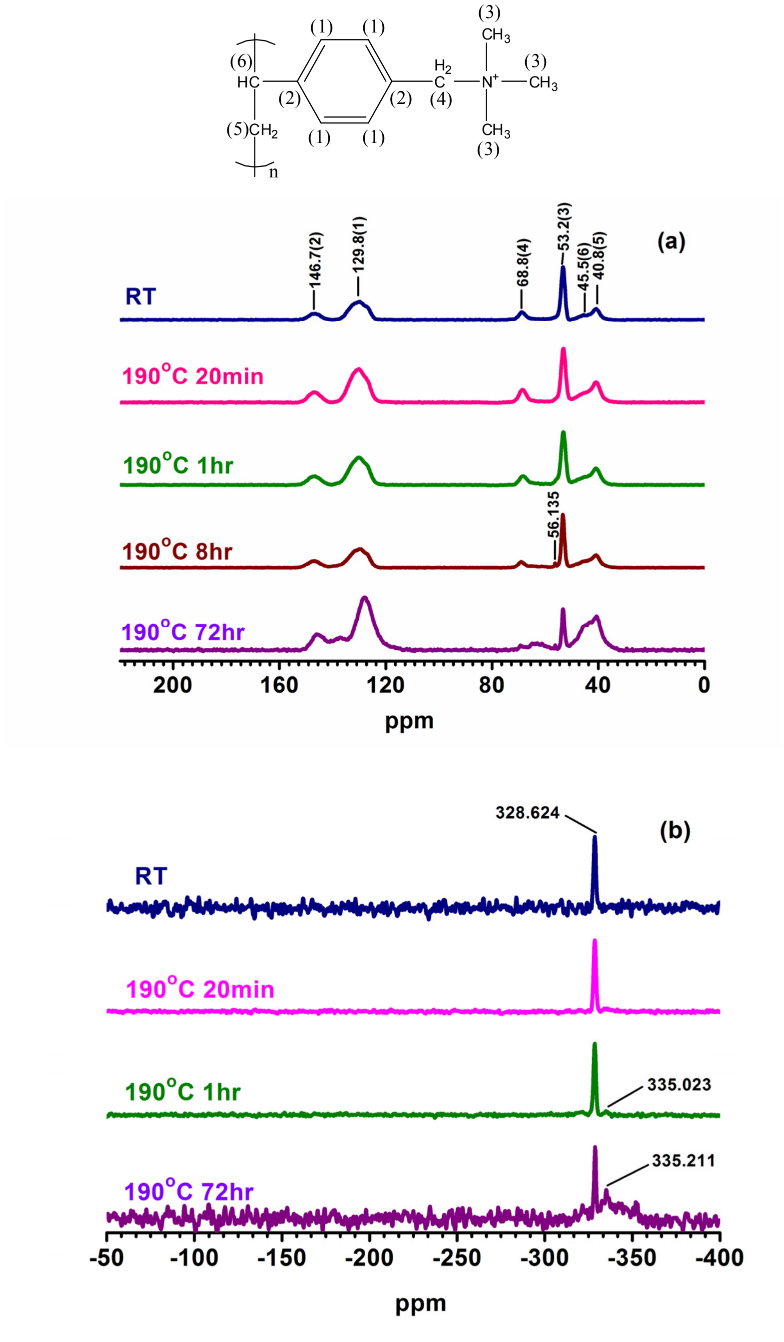


Figure S1. The ^{13}C (a) and ^{15}N (b) NMR spectra of the PVBTMACl polymer films treated at 190°C for increasing lengths of time.

Commentary: No significant changes in the ^{13}C and ^{15}N NMR spectra were observed until the polymer was treated for 72 h at 190°C. A small sharp peak at $\delta = 56$ ppm in the ^{13}C spectra appeared when the polymer was treated for 8 h and this was probably related to an unidentified decomposition product. The aromatic carbon signal at $\delta = 137$ that appeared after 72 h treatment is evidence that there are changes to the aromatic groups. The loss of the $\delta = 53$ and 68 signals suggest loss of trimethylammonium functionality. The poorly defined peak at $\delta = 335$ in the ^{15}N spectra was caused by the presence of tertiary amine functionality.

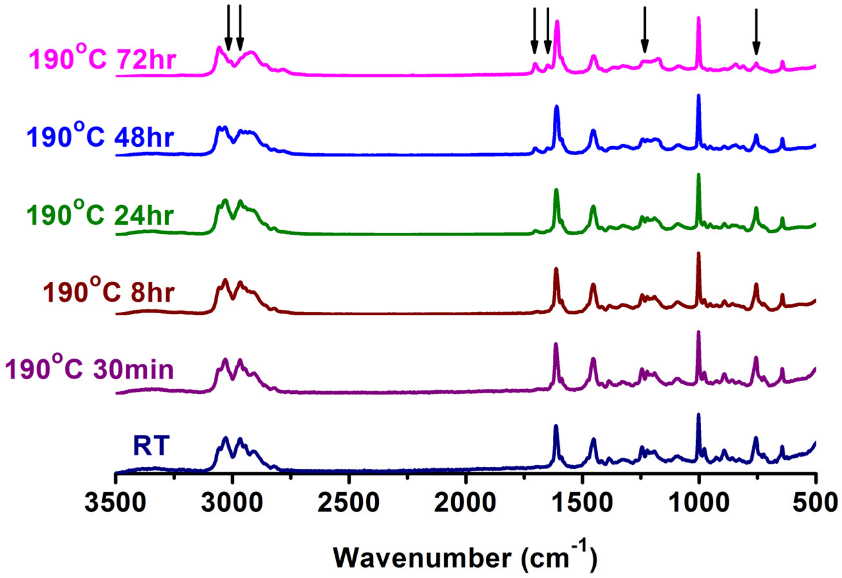


Figure S2. The FT–Raman spectra of PVBTMACl anionomer films that were thermally treated at 190°C. The spectra were normalised by the area of the peak at 1002 cm^{-1}. The arrow highlights the peaks that have changed the most during the thermal treatment process.

Commentary: The Raman spectra of the anionomer films did not visibly change after heat treatments for up to 8 h at 190°C. The changes observed for heat treatments of more than 8 h indicate the loss of methyl groups (decreased intensity of the 2966 cm^{-1} peak), the formation of C=N (or C=C) and C=O groups (peaks at 1648 and 1702 cm^{-1} respectively), and the occurrence of aromatic rearrangement (changes in the peaks at in the range 3000 – 3100 cm^{-1}).

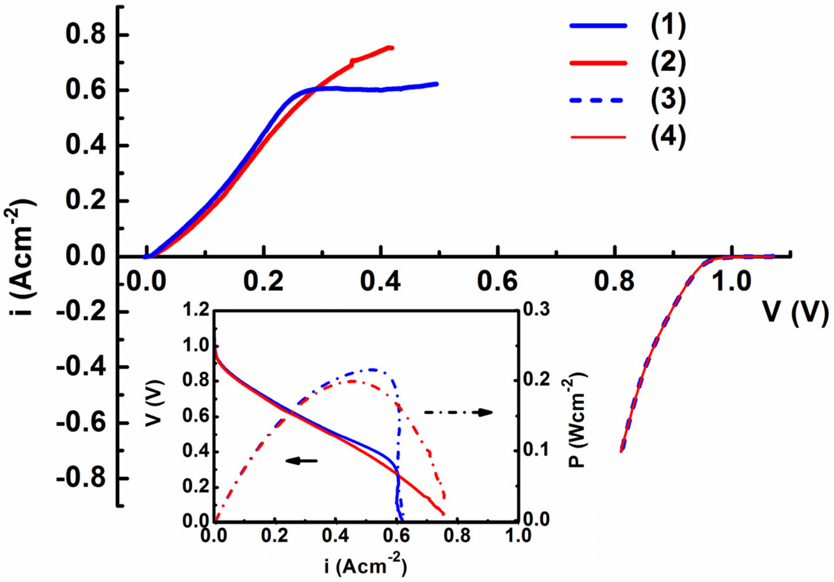


Figure S3. The anode and cathode potentials (main graph) and the *V vs. i* and power density curves (inset graph) for an identical fuel cell with the following gas flow rates: (1) Anode potential H_2 400 cm^3 min^{-1} (ccpm) and O_2 400 ccpm; (2) Anode potential H_2 800 ccpm O_2 400 ccpm; (3) Cathode potential H_2 400 ccpm O_2 400 ccpm; (4) Cathode potential H_2 400 ccpm O_2 800 ccpm. Scan rate 2 mV s^{-1}.

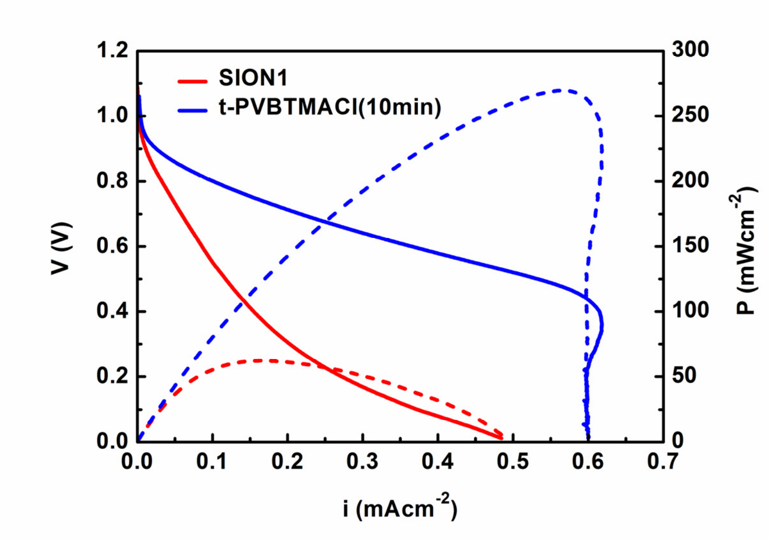


Figure S4. A comparison test between a MEA containing Surrey's first generation anionomer (SION1) and a MEAs containing the novel anionomer introduced in this study. Scan rate 2 mV s^{-1}.