

**HIGHLY ION-CONDUCTING POLY(IONIC-LIQUID) LAYERS:
ELECTRONIC SUPPLEMENTARY INFORMATION**

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1. EXPERIMENTAL

1.1 Deposition of Poly(ionic liquid) Layers

Pulsed plasmachemical deposition was carried out in an electrodeless cylindrical glass reactor (volume of 480 cm³, base pressure of 3 x 10⁻³ mbar, and with a leak rate better than 2 x 10⁻⁹ mol s⁻¹) surrounded by a copper coil (4 mm diameter, 10 turns), and enclosed in a Faraday cage. The chamber was pumped using a 30 L min⁻¹ rotary pump attached to a liquid nitrogen cold trap. A Pirani gauge was used to monitor system pressure. The output impedance of a 13.56 MHz radio frequency (rf) power supply was matched to the partially ionized gas load via an L-C circuit. Prior to each deposition, the reactor was scrubbed using detergent, rinsed in propan-2-ol, and dried in an oven. A continuous wave air plasma was then run for 30 min (0.2 mbar pressure and 40 W power) in order to remove any remaining trace contaminants from the chamber walls. Substrates used for coating were silicon (100) wafer pieces (Silicon Valley Microelectronics Inc.) and polypropylene sheet pieces (Lawson Mardon Ltd.) which had two evaporated gold electrodes (5 mm length and 1.5 mm separation) for ion conductivity testing. 1-Allylimidazole (+97%, Acros Organics Ltd.) was loaded into a sealable glass tube and degassed using several freeze-pump-thaw cycles. Precursor vapour was allowed to purge the reactor for 5 min at a pressure of 0.18 mbar prior to electrical discharge ignition. Pulsed plasma deposition utilized an optimal duty cycle of 20 μs on-period and 1200 μs off-period in conjunction with a peak power of 30 W. Upon plasma extinction, the precursor vapour was allowed to continue to pass through the system for a further 3 min, and then the chamber was evacuated back down to base

pressure. Typical deposition rates and film thicknesses were $16 \pm 2 \text{ nm min}^{-1}$ and 580 nm respectively. Imidazole ring quaternization entailed exposure of the deposited layers at $70 \text{ }^\circ\text{C}$ to 1-bromobutane vapour (99%, Sigma-Aldrich Ltd, degassed using several freeze-pump-thaw cycles) at a pressure of 4 mbar for 4.5 h. Subsequently, the reactor was evacuated to base pressure prior to venting to atmosphere.

Anion exchange experiments were carried out in the vapour phase by exposing the quaternized films to trifluoroacetic acid (Fluorochem Ltd) vapour for 300 s before evacuating the reactor to base pressure prior to venting to atmosphere.

1.2 Film Characterization

Infrared spectra were acquired using a FTIR spectrometer (Perkin-Elmer Spectrum One) fitted with a liquid nitrogen cooled MCT detector operating at 4 cm^{-1} resolution across the $700\text{--}4000 \text{ cm}^{-1}$ range. The instrument included a variable angle reflection-absorption accessory (Specac Ltd.) set to a grazing angle of 66° for silicon wafer substrates and adjusted for p-polarization.

Surface elemental compositions were determined by X-ray photoelectron spectroscopy (XPS) using a VG ESCALAB II electron spectrometer equipped with a non-monochromated Mg K α X-ray source (1253.6 eV) and a concentric hemispherical analyser. Photoemitted electrons were collected at a take-off angle of 20° from the substrate normal, with electron detection in the constant analyser energy mode (CAE, pass energy = 20 eV). Experimentally determined instrument sensitivity factors were taken as C(1s): N(1s): Br(3d) equals 1.00: 0.66: 0.36. All binding energies were referenced to the C(1s) hydrocarbon peak at 285.0 eV. A linear background was

subtracted from core level spectra and then fitting used Gaussian peak shapes with a constant full-width-half-maximum (fwhm).¹

Film thicknesses were measured using a spectrophotometer (nkd-6000, Aquila Instruments Ltd.). Transmittance-reflectance curves (350–1000 nm wavelength range) were acquired for each sample and fitted to a Cauchy material model using a modified Levenberg-Marquardt algorithm.²

Impedance measurements across the 10 Hz–13 MHz frequency range were carried out using an LF impedance analyser (Hewlett-Packard, 4192A) for coated polypropylene substrates. The low frequency 45° line in the acquired impedance plots was assigned to the Warburg diffusion impedance, and a high frequency arc was fitted in order to extract the resistance of the deposited membrane layer.³ The formula $\sigma = l/(R_S A)$ was used to calculate proton conductivity, where σ is the specific membrane conductivity, R_S is the bulk membrane resistance, l is the distance between the two electrodes, and A is the cross-sectional area of the film.⁴ Humidities of 97% and 75% were achieved by using saturated solutions of potassium sulfate (+99%, Sigma-Aldrich Ltd.) and sodium chloride (+99.5%, Sigma-Aldrich Ltd.) respectively in water.⁵ For measurements at elevated temperatures, the cell was run in a potentiostatic mode (Bio-Logic SP-150) by applying a sinusoidal AC potential around applied DC potentials of 0.3 V, 0.5 V and 0.7 V respectively.

2. RESULTS

Table S1: XPS elemental ratios of pulsed plasma deposited poly(1-allylimidazole) films before and after quaternization.

Film	Elemental Composition / %			
	C	N	O	Br
Pulsed plasma deposited poly(1-allylimidazole)	72 ± 1	25 ± 1	3 ± 1	—
Pulsed plasma deposited poly(1-allylimidazole) quaternized with 1-bromobutane	72 ± 1	19 ± 1	3 ± 1	6 ± 1

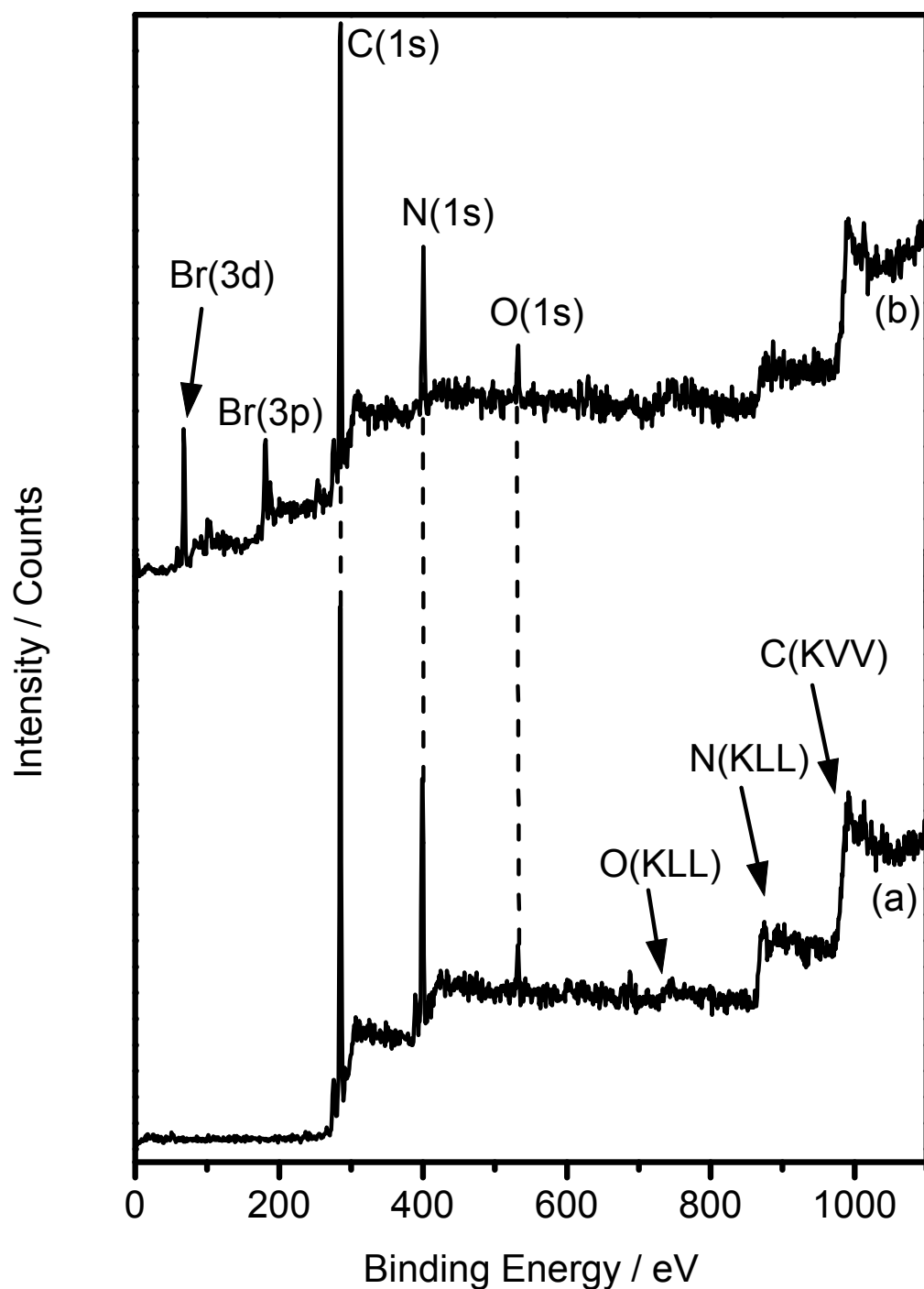


Figure S1: X-ray photoelectron wide scan spectra for (a) pulsed plasma deposited poly(1-allylimidazole) and (b) pulsed plasma deposited poly(1-allylimidazole) quaternized with 1-bromobutane.

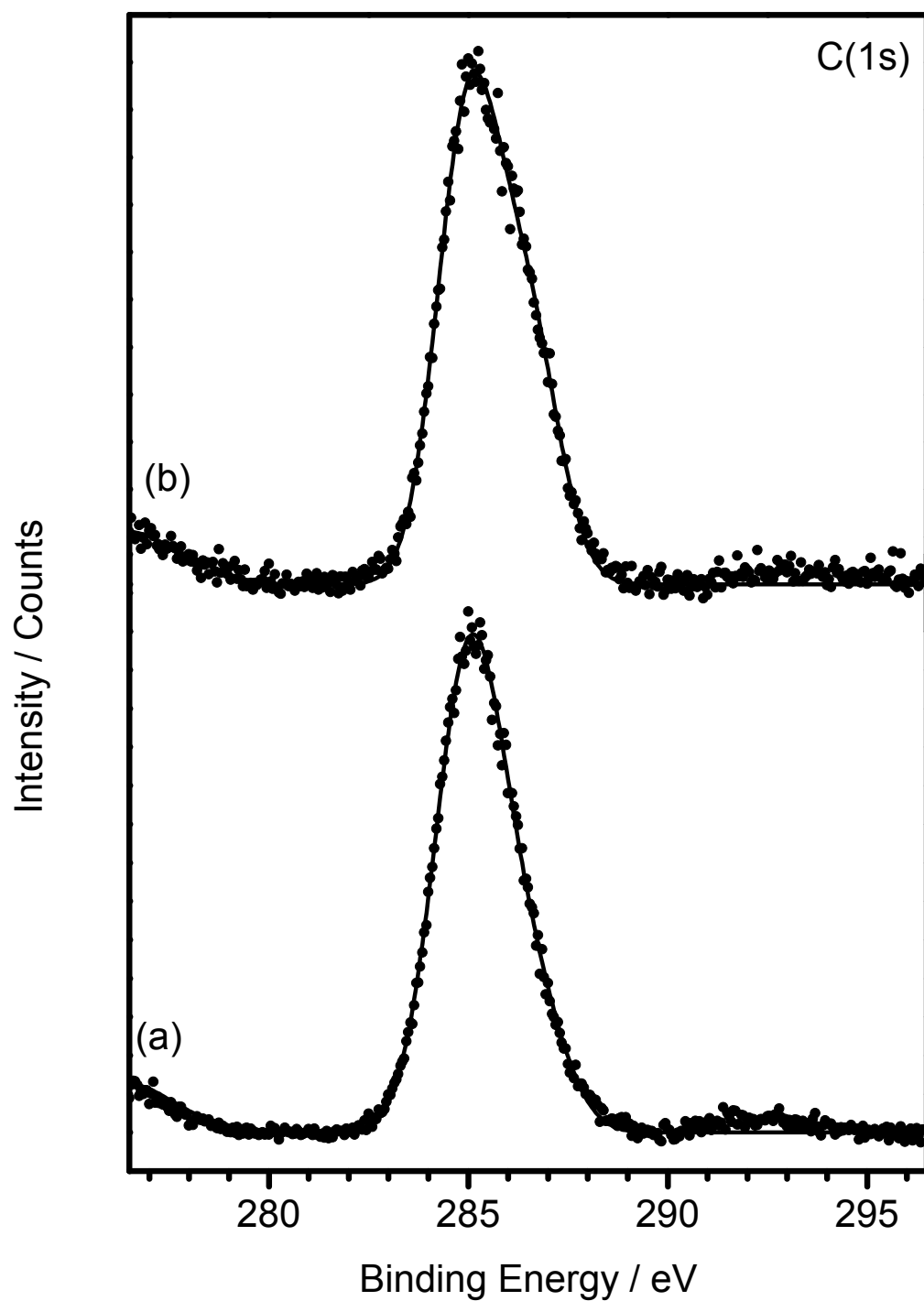


Figure S2: X-ray photoelectron C(1s) spectra for (a) pulsed plasma deposited poly(1-allylimidazole) and (b) pulsed plasma deposited poly(1-allylimidazole) quaternized with 1-bromobutane.

3. REFERENCES

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