Electronic Supplementary Material (ESI) for Analytical Methods.

Supporting Information for:

"Towards improving the robustness of electrochemical gas sensors: Assessment of PMMA addition on the sensing of oxygen in an ionic liquid"

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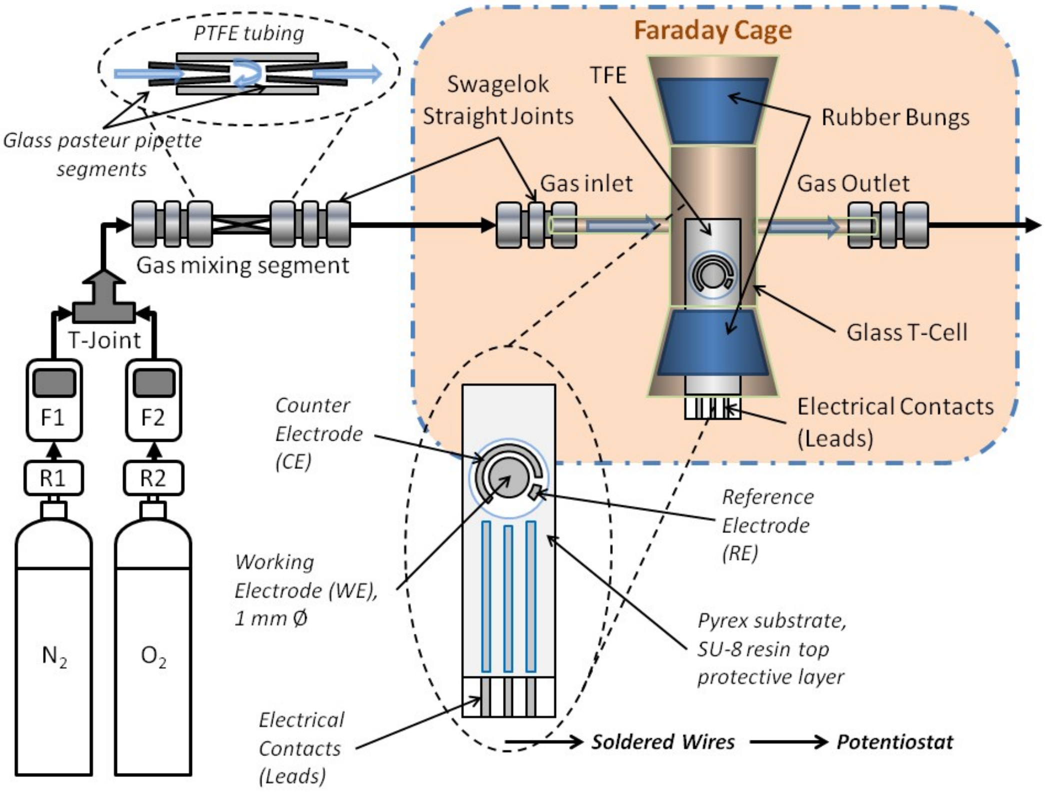

Fig. S1. Schematic of the gas mixing system and glass cell used for voltammetric measurements on thin-film electrodes (TFE) (where F1 and F2 are digital flow meters/controllers, and R1 and R2 are the pressure regulators). The glass cell is situated within an aluminium Faraday cage.

Table S1. Masses of PMMA, m_{PMMA}, and [C_2mim][NTf_2], m_{RTIL}, used to make up samples with total mass, $m_{\mathrm{Tot.}}$, of 1.53 g for each mixture of PMMA-RTIL electrolyte sample. Based on the estimated total volumes, $V_{\mathrm{Tot.}}$, of each mixture sample (assuming that the effective densities of each species remains unchanged after mixing), small volumes of acetone (as shown below) were added to the 30, 40, and 50 % $m_{\mathrm{PMMA}}/m_{\mathrm{Tot.}}$ samples to reduce their viscosity so as to allow them be transferred via a micropipette onto the electrode surface. The volumes of the aliquots used were thus modified accordingly for those PMMA-RTIL mixtures so that the same volume of aliquot was present on the electrode surface.

m_{PMMA} / g	V_{RTIL} / mL (± 0.001 mL)	m_{RTIL} / g	V_{Acetone} / µL (to reduce viscosity)	PMMA doping mass concentration, %($m_{\mathrm{PMMA}}/m_{\mathrm{Tot.}}$) / % w/v
0	1.000	1.530 ± 0.002	0	0.0 ± 0.1
0.1533 ± 0.0002	0.900	1.377 ± 0.002	0	10.0 ± 0.3
0.3061 ± 0.0001	0.800	1.224 ± 0.002	0	20.0 ± 0.1
0.4591 ± 0.0002	0.700	1.071 ± 0.002	54 (5 % of $V_{\mathrm{Tot.}}$)	30.0 ± 0.2
0.6183 ± 0.0002	0.606	0.927 ± 0.002	113 (10 % of $V_{\mathrm{Tot.}}$)	40.0 ± 0.2
0.7652 ± 0.0003	0.500	0.765 ± 0.002	230 (20 % of $V_{\mathrm{Tot.}}$)	50.0 ± 0.2

Density of [C_2mim][NTf_2] is 1.53 g·mL^{-1} and density of PMMA is 1.18 g·mL^{-1} (from supplier).

Table S2. Contact angles, θ, measured for each PMMA concentration. Error bars correspond to one standard deviation over the number of experimental measurements performed (n).

[PMMA] / % $m_{\mathrm{PMMA}}/m_{\mathrm{Tot.}}$	θ / degrees	cos(θ_{rad})	n
0	30 ± 2	0.87 ± 0.06	38
10	27 ± 2	0.89 ± 0.07	42
20	36 ± 2	0.81 ± 0.04	24
30	48 ± 6	0.67 ± 0.09	54
40	58 ± 7	0.53 ± 0.07	20
50	74 ± 5	0.28 ± 0.02	10

Experimental: Contact angle measurements

Contact angles of PMMA-[C_2mim][NTf_2] mixtures on glass substrates (glass slides – pathology grade, PLAIN 7101-BP, Livingstone, NSW, Australia), were measured using a goniometer (KVS Instruments LTD, Model: CAM 101, Helsinki, Finland). The glass slides were cleaned in aqua regia (hydrochloric acid 32% and nitric acid 70%, from Ajax Finechem Pty Ltd, WA, Australia) before sonicating in Milli-Q grade water for 15 mins, rinsing with acetone, and drying under N_2. They were then subjected to UV-ozone cleaning (~50 W, BIOFORCE Nanosciences, Inc., Model: UV.TC.220 USA) for 10 minutes. The slides were rinsed with acetone, then isopropyl alcohol (meets USP testing specifications, Sigma-Aldrich Pty Ltd., NSW, Australia) and dried under N_2. Approximately 30 % vol. of acetone was added to the 50 % $m_{\mathrm{PMMA}}/m_{\mathrm{Tot.}}$ sample. 6 μL of the PMMA-RTIL samples were transferred onto the glass slides via a micropipette. The goniometer and sample were then enclosed in Perspex to reduce ambient sound-vibrations, drift in temperature, pressure, and humidity, and the deposited droplets were allowed to settle for 3 minutes before the contact angles were measured. Due to the significant viscosity of the PMMA/RTIL mixture at 40 and 50 % $m_{\mathrm{PMMA}}/m_{\mathrm{Tot}}$., aliquots of acetone have to be added (10 and 20 % vol. respectively) to enable the deposition of the highly viscous PMMA-RTIL mixture with a micropipette.

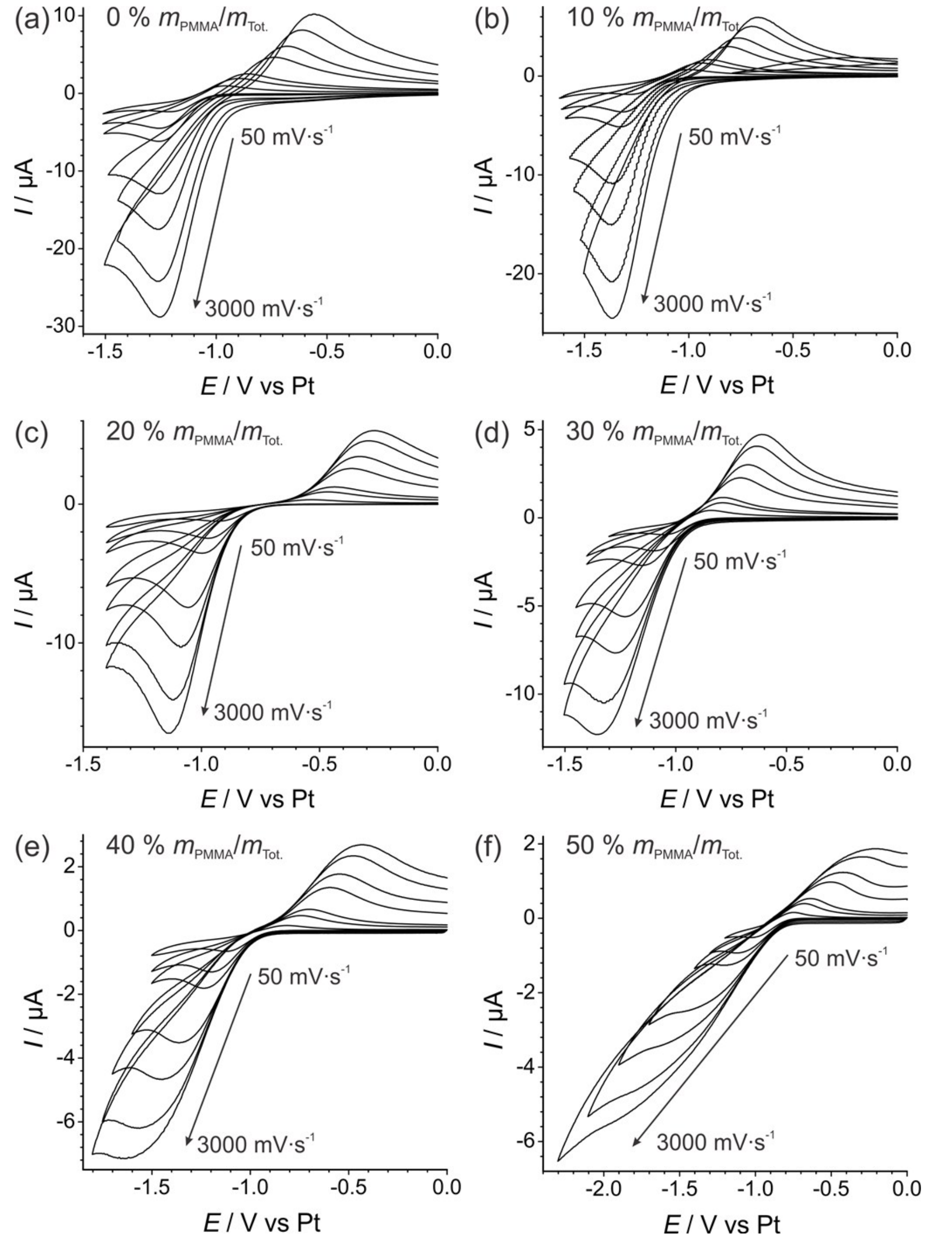

Fig. S2. Cyclic voltammetry of the $O_2/O_2^{\bullet -}$ redox couple at varying scan rates vs. inbuilt Ag pseudo-RE, for different PMMA doping concentrations in [C_2mim][NTf_2] measured at 100 % vol. O_2 flow (flow rate of 500 sccm).

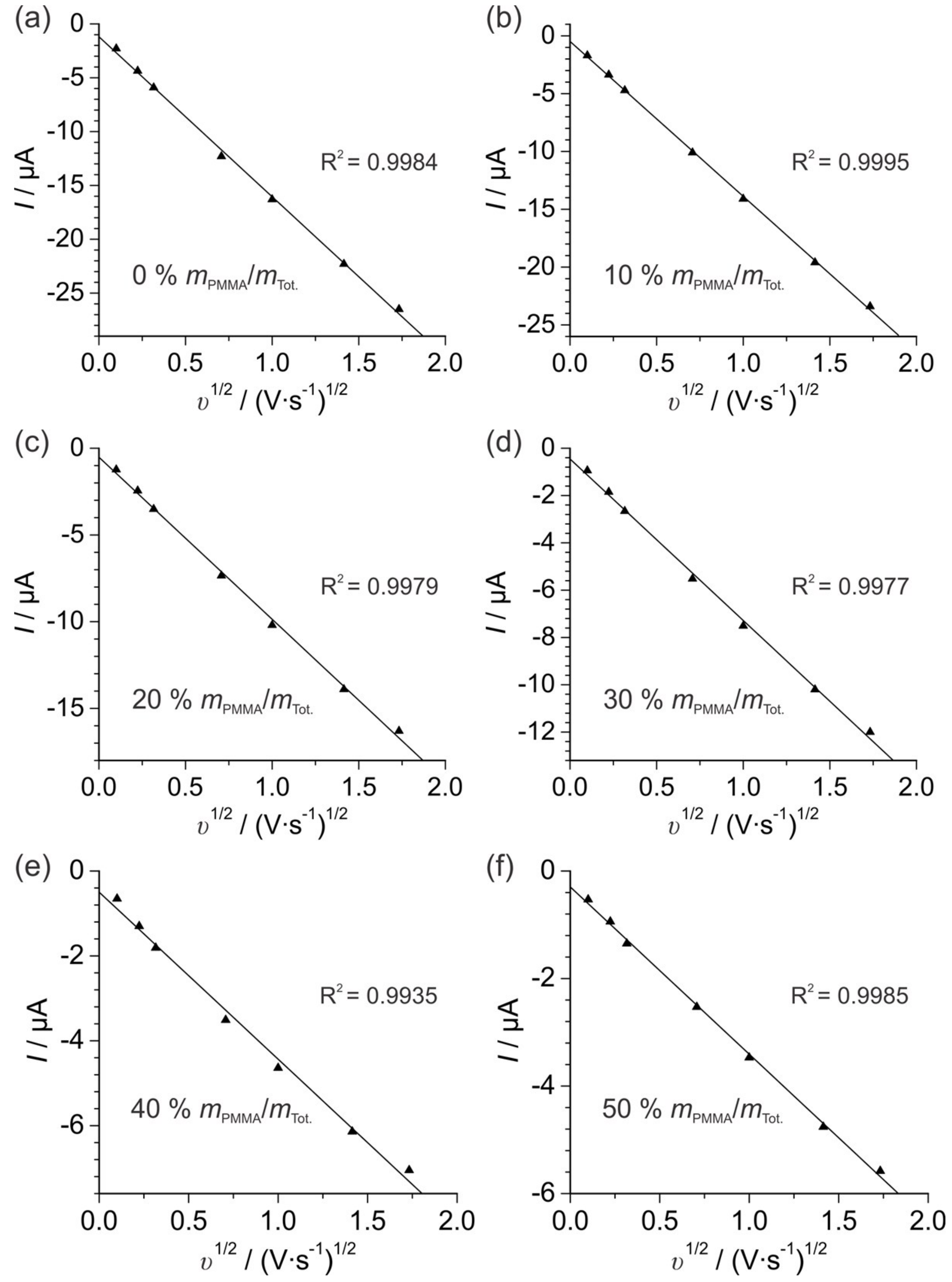

Fig. S3. Plots of peak current, I, vs. scan rates, $\upsilon^{\frac{1}{2}}$ for the cyclic voltammetry presented in Fig. S2, the lines of linear regression fit, and the corresponding R^2 values of the fittings, for each concentration of PMMA doping.

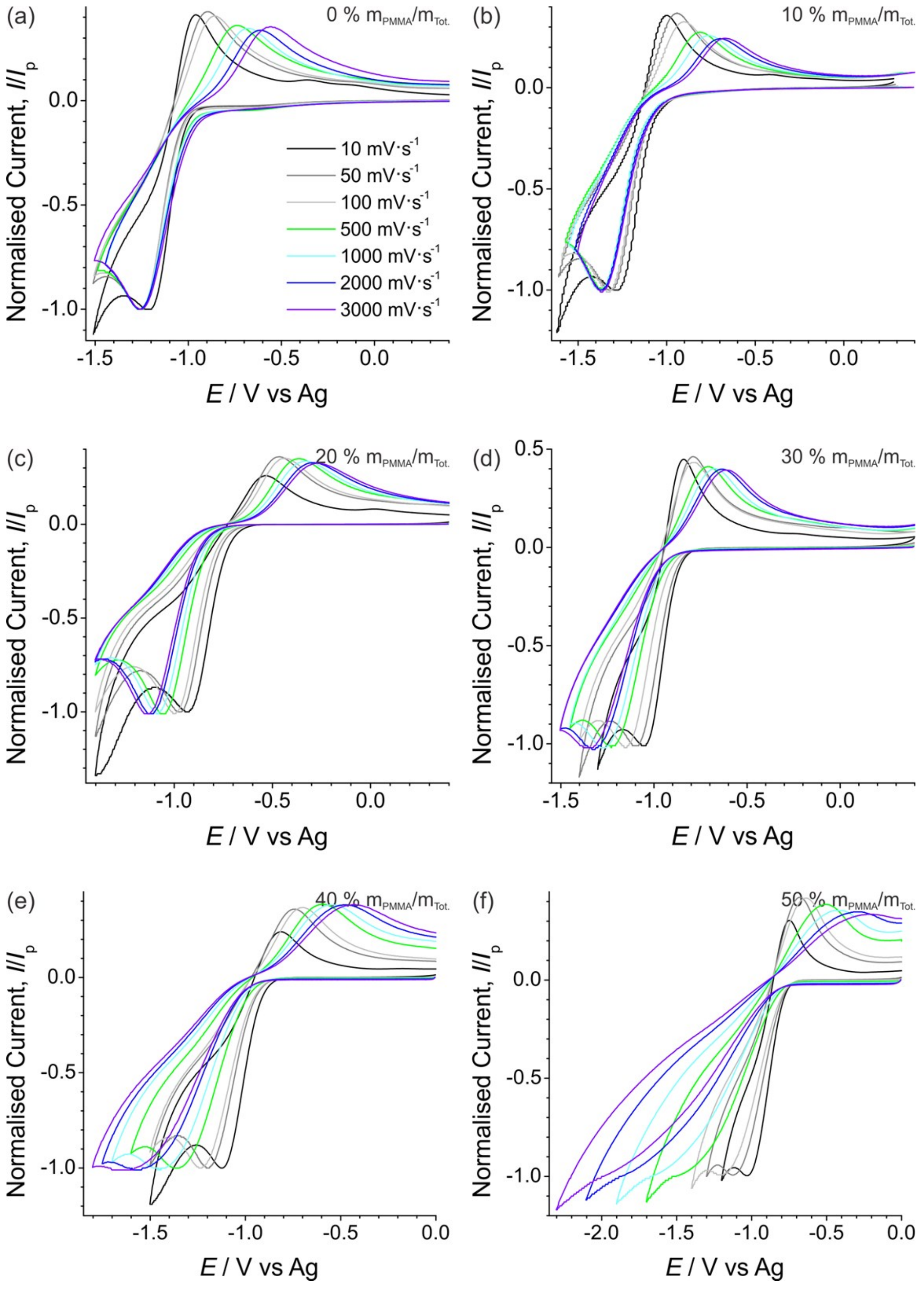

Fig. S4. Voltammograms as presented in Fig. S2., but with the oxygen reduction peak currents all normalized to unity to allow for a qualitative comparison of the stability of the electrogenerated superoxide. The results are presented at different PMMA doping concentrations in $[C_2mim][NTf_2]$, measured at 100 % vol. O_2 flow (flow rate of 500 sccm).

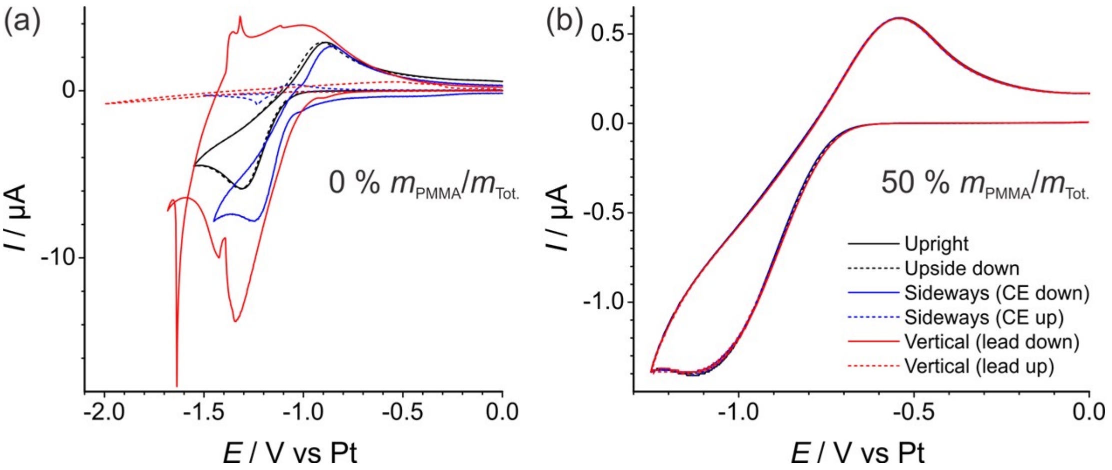

Fig. S5. Overlaid cyclic voltammograms for the $O_2/O_2^{\bullet-}$ redox couple using a PMMA doping concentration of: **(a)** 0 % and **(b)** 50 % $m_{\text{PMMA}}/m_{\text{Tot.}}$ in [C_2mim][NTf_2], for Pt thin-film electrodes positioned in different orientations (i.e. upright, upside down, sideways (CE down), sideways (RE down), vertical (lead down), vertical (lead up)). Scans were measured at 100 % vol. O_2 flow (500 sccm flow rate) at a scan rate of 100 mV·s^{-1}. The thin-film Pt-electrodes were held at the respective orientations for at least 30 mins before measurements were commenced. The 50 % $m_{\text{PMMA}}/m_{\text{Tot.}}$ results show no change in response for all orientations.

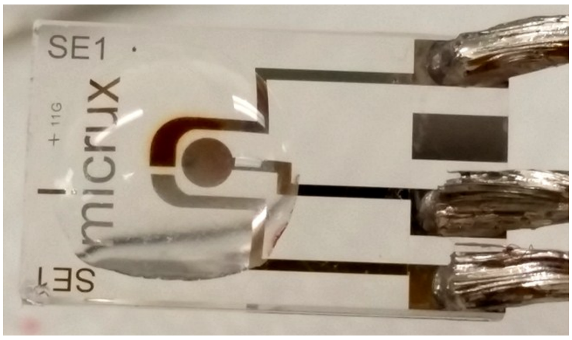

Fig. S6. Photo taken of a Pt TFE with 30 % $m_{\text{PMMA}}/m_{\text{Tot.}}$ PMMA-[C_2mim][NTf_2] electrolyte after long-term scanning in the presence of 100 % vol. O_2 flow. Sign of accumulation of counter electrode reaction product on the CE and WE is clearly visible.

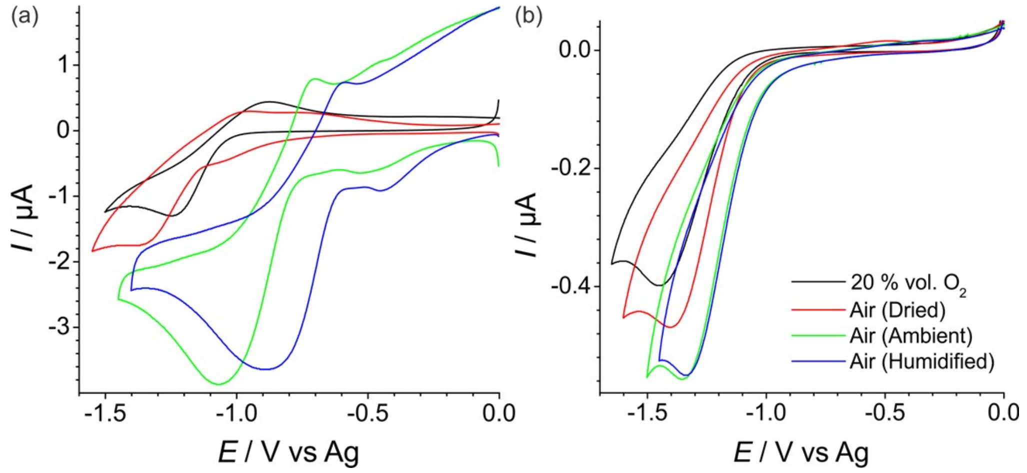

Fig. S7. Cyclic voltammetry for oxygen reduction in different environments: 20 % vol. O_2 in nitrogen, dried air that has been passed through regular building air scrubber/filtration system (i.e. no specific lab-based preparation of the air was employed), ambient air, and humidified air (by bubbling air vigorously through a container of water), in **(a)** neat [C_2mim][NTf_2] and **(b)** in 50 % $m_{PMMA}/m_{Tot.}$

Table S3. Values of the oxygen reduction peak potentials, E_p, and currents, I_p, extracted from the CVs presented in Fig S7 for experiments conducted in different environments (20 % O_2 in nitrogen, dried air, ambient air, and humidified air).

Atmosphere	**Neat [C_2mim][NTf_2]**		**50 % $m_{PMMA}/m_{Tot.}$ PMMA in [C_2mim][NTf_2]**	
	E_p / V vs Ag	**I_p / μA**	**E_p / V vs Ag**	**I_p / μA**
20 % vol. O_2	-1.25	-1.30	-1.45	-0.398
Air (Dried)	-1.55	-1.84	-1.41	-0.469
Air (Ambient)	-1.07	-3.87	-1.35	-0.557
Air (Humidified)	-0.89	-3.64	-1.34	-0.550