

Supporting Information

Single vs Dual ion UV-crosslinked gel polymer electrolytes for Li-O₂ batteries

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EXPERIMENTAL SECTION

Materials

Poly(ethylene glycol) dimethacrylate (PEGDM, Aldrich, Mn 550), tetraethylene glycol dimethyl ether (TEGDME, Aldrich, $\geq 99\%$) and 2-Hydroxy-2-methylpropiophene (DAROCUR, Aldrich, 97%) were dried by adding activated 4Å molecular sieves (Aldrich, 4-8 mesh) and allowed 5 days for drying effect. Additionally, PEGDM was dried under vacuum for 24 hours and TEGDME was additionally dried at 55 °C under vacuum overnight. The water content, measured by Coulometric Karl Fischer, decreased to 19.9 ppm for PEGDM; and 4.6 ppm for TEGDME (Table S1).

Table S1 Water content by Coulometric Karl-Fischer of initial materials before and after applying a drying method. Theoretical water content of GPEs.

Water content (ppm)			
	As received	Extra dry	<i>Drying Efficiency</i>
PEGDM	1441.6 ± 29.9	17.9 ± 4.6	99%
TEGDME	94.7 ± 1.4	4.6 ± 1.8	95%
LiTFSI in TEDGME ^a	110	16	86%
LiTFSI	850	80	91%
Dual ion GPE ^b	353.9	30.1	92%
Single ion GPE ^{b,c}	255.3	61.6	76%

^a Dilution factor = 20

^b Theoretical GPE water content calculated as $\text{Water}_{\text{GPE}} = \text{Water}_{\text{PEGDM}} \cdot \% \text{wt PEGDM} + \text{Water}_{\text{TEGDME}} \cdot \% \text{wt TEGDME} + \text{Water}_{\text{LiTFSI or LiMTFSI}} \cdot \% \text{wt LiTFSI or LiMTFSI}$

^c Assuming $\text{LiMTFSI}_{\text{Water}}$ at 250ppm in all cases

Lithium 1-[3-(methacryloyloxy)-propylsulfonyl]-1-(trifluoromethylsulfonyl)imide (LiMTFSI) was synthesized as described elsewhere¹ and dried under vacuum for 24 hours. Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, TCI, >98.0%) was dried under vacuum at 100°C for 24 hours. Water contents were also monitored (Table S1).

The liquid electrolytes mixtures were stirred for 2 hours (0.84M LiMTFSI in TEGDME for the single ion GPE, 0.84M LiTFSI in TEGDME for the dual ion GPE), before being mixed with PEGDM at different weight ratios and stirred for another hour. DAROCUR was added at this step at 3% w/w of the monomers. Then, the solution was drop-casted on a silicon mould (Φ 11.28 mm circular voids) and irradiated with a UV-LED lamp (300 – 400 nm wavelength light emission spectrum, with peak at 385 nm. Lightningcure® V3, Hamamatsu) for 6 minutes at a distance of 9 cm. All the steps were done under an argon filled glovebox with levels of $\text{H}_2\text{O} < 0.01$ ppm and $\text{O}_2 < 0.01$ ppm.

Polymeric materials characterization

Chemical characterization was studied via Fourier transform infrared spectroscopy (FTIR ATR, Bruker Alpha I Spectrometer). The measuring probe (solid and liquid samples) was at room temperature (RT) and under air atmosphere.

Thermal degradation was investigated by Thermal Gravimetric Analysis (TGA) employing a TGA Q 500 (TA instruments). About 10 mg of sample were heated from RT

to 600 °C at a heating rate of 10 °C/min under nitrogen flux of 90 mL/min. At 600 °C air flux was introduced for 15 minutes to remove the organic part of the sample.

Mechanical properties were studied by dynamic mechanical thermal analysis (DMTA) in a Dynamic Mechanical Analyzer, Triton 2000 DMA (Triton Technology) at compression. Circular samples of 1 cm² and 2 – 2.5 mm thick were used. Samples were first cooled down to -100 °C with liquid nitrogen and heated till 100 °C at a heating rate of 4 °C/min and a frequency of 1.0 Hz.

Impedance spectroscopy

Ionic conductivities were measured by electrochemical impedance spectroscopy (EIS) using a Autolab 302N Potentiostat Galvanostat coupled to a Microcell HC temperature controller. Circular membranes (Φ 11 mm) were used for the measurements with a thickness of 500 μ m. The membranes were sandwiched between two stainless steel electrodes and sealed in a Microcell under argon atmosphere in a glove box. The measurements were carried out from 85°C to 25°C, dwell of 30 minutes for temperature stabilization and -10 °C step. The frequency range was set from 0.1 MHz to 0.1 Hz and

10 mV amplitude. According to literature², the ionic conductivity of solid polymer electrolytes (SPEs), including GPEs, can be calculated following the equation:

$$\sigma = \frac{1}{R_b} \cdot \frac{d}{S}$$

where σ is the ionic conductivity ($\text{S}\cdot\text{cm}^{-1}$), d is the thickness (cm) of the GPE, S is the area (cm^2) of electrodes in contact with the GPE and R_b (Ω) is the bulk resistance of GPE, which can be extracted from the Nyquist plot obtained in EIS.

Lithium transference number

The lithium transference number (t_{Li}^+) of both Single ion and Dual ion GPE were calculated following the method proposed by Evans-Vincent-Bruce^{3,4}:

$$t_{\text{Li}}^+ = \frac{I_s(\Delta V - I_0 \cdot R_0)}{I_0(\Delta V - I_s \cdot R_s)}$$

where ΔV is a small DC bias applied to polarize the sample (10 mV) during a chronoamperometry, I_0 is the initial value of the current upon polarization with DC bias, I_s is the current reached in the steady-state for the sample polarized with DC bias. R_0 and R_s are the resistances of the solid electrolyte interface (SEI) before and after the

polarization, respectively, measured via EIS and using a 10mV potential excitation amplitude. All measurements were carried out at 25°C.

Electrodes preparation

All materials preparation is done under argon, inside a glovebox with levels of H₂O < 0.01 ppm and O₂ < 0.01ppm within TME facilities.

Negative electrode. Lithium circular electrodes were punched (Φ 8 mm and 120 μ m thick) from a rolled piece of lithium metal purchased from Rockwood Lithium (USA) and rubbed with a plastic spatula to remove any dust/rust. These lithium thin films were then placed and pressed over a circular piece (Φ 11.28 mm and 20 μ m thick) of electrodeposited NI000320 nickel (0.02 mm thick, GoodFellow, 99.9%). Beforehand, nickel samples were washed with ethanol in an ultrasounds bath for 1 hour at maximum power and dried under vacuum at 100 °C for 24 hours.

Positive electrode. Positive electrodes were formed by a gas diffusion layer (GDL) coated with a slurry containing 0.6%wt of carbon (Ketjen Black 600, Akzonobel), 1.6%wt of binder (LITHion™ dispersion, Ion Power Inc) and 97.8%wt of anhydrous 2-propanol

(IPA, MilliPore Sigma, anhydrous (max. 0.005% H₂O), $\geq 99.9\%$)). The GDL sheets were punched into circular samples ($\Phi 11.28$ mm) that were then dried under vacuum at 120 °C for 24 hours. The carbon was previously dried at 100 °C under vacuum for 24 hours. The binder and IPA were directly used from the supplier after adding activated 4Å molecular sieves and allowed 5 days for drying effect. The water content, measured by Coulometric Karl Fischer, decreased from 252,05 ppm to 218 ppm for the binder; and from 64 ppm to 8 ppm for the IPA after the addition of the zeolites. To make the slurry, all the components were placed in a glass vial and mixed homogeneously using an Ultraturrax IKA T18, at speed 2 for 45 minutes. The slurry was immediately used and 70 μ L of the ink was deposited on each circular GDL. These were covered and allowed to dry at RT for 24 hours. The coated GDLs had an average carbon loading of 0.72 mg·cm⁻².

Lithium symmetrical cells

All symmetrical cells, specifically designed and developed at TME, were prepared inside a glovebox with levels of H₂O < 0.01 ppm and O₂ < 0.01ppm within TME facilities. All

parts were rigorously dried at 60 °C under vacuum for 24 hours before introducing them in the glovebox.

Inner configuration (Figure 3c). The synthesized solid electrolyte (Φ 11.28 mm) was sandwiched between two lithium foils (see “Electrodes preparation”) and placed between stainless steel caps. This sandwich was then placed between two electronically isolated stainless steel spacers. This stack was kept vertically aligned through a hollow PEEK cylinder. A set of 3 nuts/bolts/insulator O-rings were used to ensure a good tightening. A Teclock thickness gauge was used to ensure that the thickness of the electrolyte was even all along the electrode | electrolyte contact surface.

Top level configuration. The stack was enveloped by an insulating material and electronically connected with wires to the top part of an external stainless steel container, used to keep the cell under argon atmosphere. The container was finally tight with a hose clamp.

Li-O₂ solid batteries

Li-O₂ Swagelok cells - specifically designed at TME - were assembled inside a glovebox with levels of H₂O < 0.01 ppm and O₂ < 0.01ppm. All parts were rigorously dried at 60 °C under vacuum for 24 hours before introducing them in the glovebox.

Inner configuration (Figure 4b). The electrolyte (Φ 11.28 mm) was sandwiched between the negative and positive electrodes (see “Electrodes preparation”). In the case of liquid Li-O₂ cells, two glass fiber sheets (Φ 11.28 mm) soaked with the liquid electrolyte mixture (500 μL) were placed between the electrodes. The glass fiber sheets (Whatman®, GF/A grade) were previously dried at 150 °C under vacuum for 24 hours. The positive electrode was placed with the coated side facing the electrolyte surface. This stack was then sandwiched between two stainless steel spacers (positive electrode on the O₂ side) and held together with a PEEK Swagelok cell. The cell was tighten manually.

Top level configuration. The Swagelok cell was placed vertically inside a sealed plastic container with the help of an insulated holder, and electrically connected to the outer part of the container. The argon gas inside the container was then purged and replaced by

oxygen gas outside the glovebox (oxygen flow at 0.2 l/min for 30 minutes, Praxair, > 99.5%).

RESULTS

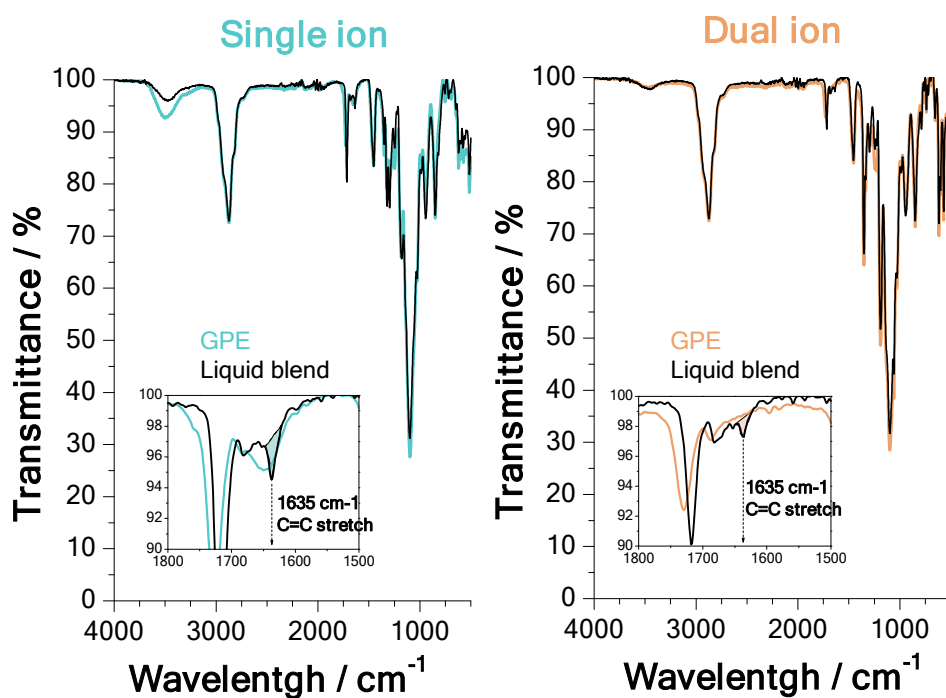


Figure S1. FTIR spectra of the single and dual ion GPEs before (liquid blend) and after curing. The 1635 cm^{-1} band, which is associated to the carbon double bond of methacrylate functionalities⁵, disappeared from the solid GPEs' spectra.

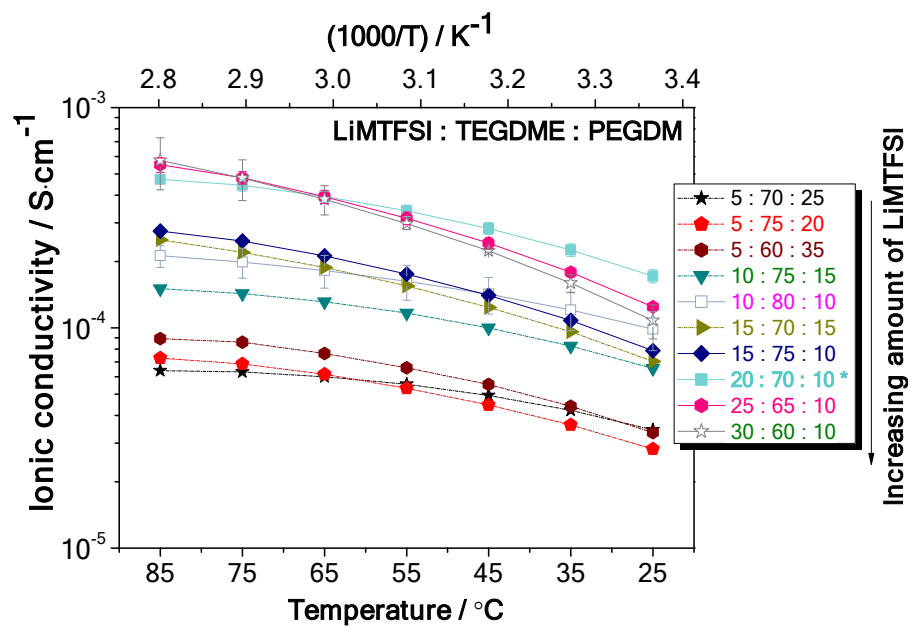


Figure S2. Ionic conductivities against temperature of different single ion membranes at different concentration ratios of LiMTFSI : TEGDME : PEGDM, respectively. * indicates the selected single ion formulation for further testing.

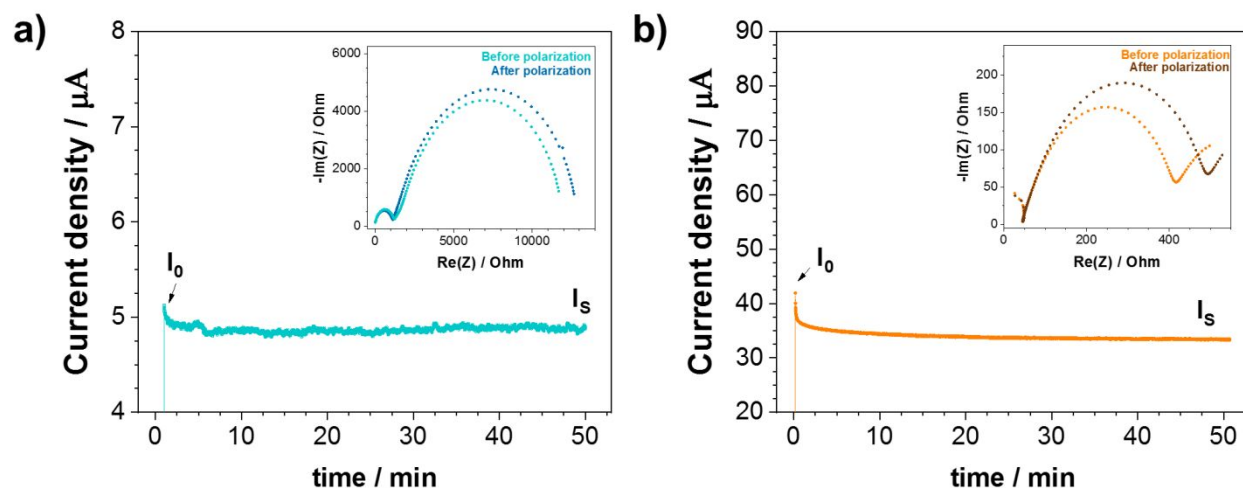


Figure S3. Lithium transference number. Chronoamperometry and EIS curves before and after polarization obtained in lithium symmetrical cells for: a) Single ion GPE and b) Dual ion GPE.

Table S2. Lithium transfer number at 25 °C for solid polymer electrolytes (SPE), gel polymer electrolytes (GPE) and liquid electrolytes reported in literature.

<i>Type</i>	<i>System</i>		<i>t_{Li}</i>	<i>Ref.</i>
GPE ^a	Soaked in TEGDME + LiCF ₃ SO ₃	Dual ion	0.5	6
GPE ^a	Soaked in TEGDME + LiTFSI	Dual ion	0.62	7
GPE ^a	Soaked in TEGDME + LiTFSI	Dual ion	0.47	8

<i>Type</i>	<i>System</i>		<i>t_{Li}</i>	<i>Ref.</i>
GPE ^a	Li-Nafion™ soaked in DMSO	Single ion	0.88	9
GPE ^b	LiMTFSI, Propylene carbonate (PC)	Single ion	0.86	10
SPE ^b	SPE-1 (Dual ion, based on LiTFSI)	Dual ion	0.50	11
	SPE-3 (Single ion, based on PLiMTFSI)	Single ion	0.70	
SPE ^b	LiTFSI dissolved in PEO.	Dual ion	0.58	12
	LLZTO nanoparticles added.			
SPE ^b	Single ion, based on LiSTFSI.	Single ion	0.93	13
Liquid ^b	1M LPF ₆ in ethylene- (EC), ethyl methyl- (EMC), and diethyl carbonate (DEC)	Dual ion	0.22	14
Liquid ^b	7M LiTFSI in 1,3 dioxolane (DOL)/ dimethyl ether (DME)	Dual ion	0.73	15

^a Lithium-air / Lithium-O₂ batteries

^b Lithium metal batteries

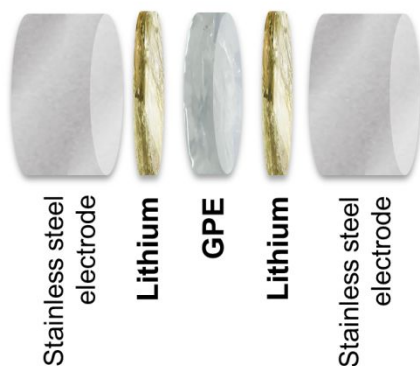


Figure S4. Scheme of lithium symmetric cell configuration.

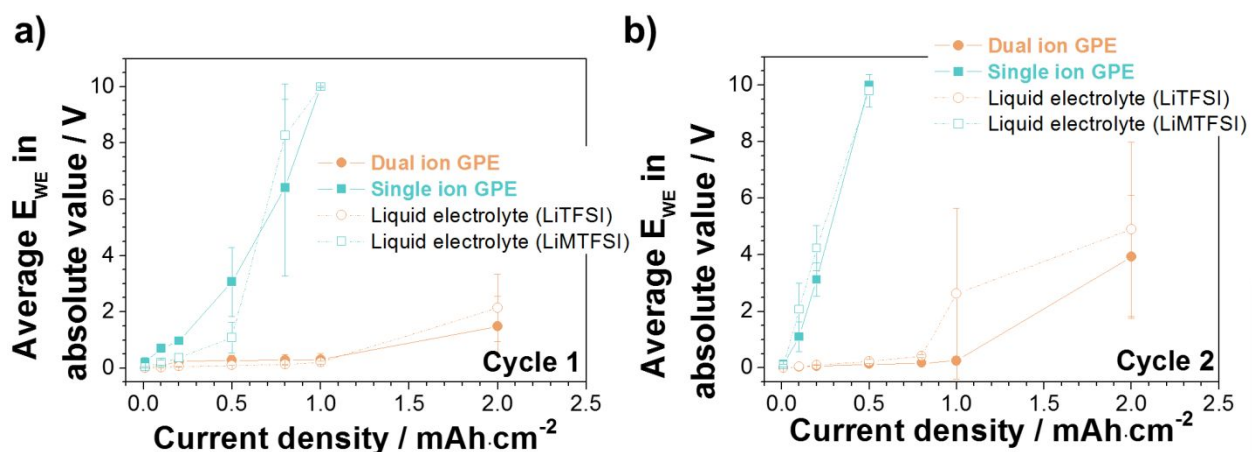


Figure S5. Tests undertaken on lithium symmetric cells. Absolute potential against current density of Dual ion and Single ion GPEs and their respective liquid electrolyte cells

(LiTFSI and LiMTFSI, respectively): a) Cycle 1 and b) Cycle 2. Data extracted from ramp test described in Figure 3a.

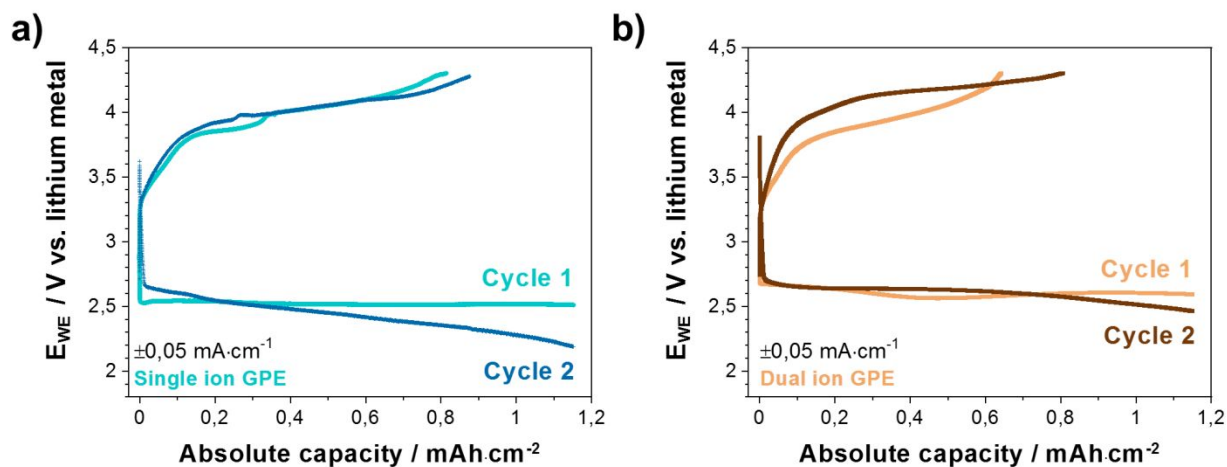


Figure S6. Potential against absolute capacity during galvanostatic discharge/charge at $\pm 50 \mu\text{A}\cdot\text{cm}^{-2}$ at 25 °C for Li-O₂ cells: a) Single ion GPE and b) Dual ion GPE. Discharge/charge steps restricted to 1.15 mAh·cm⁻² absolute capacity, unless limiting potential was achieved (4.3 V for charge and 2 V for discharge).

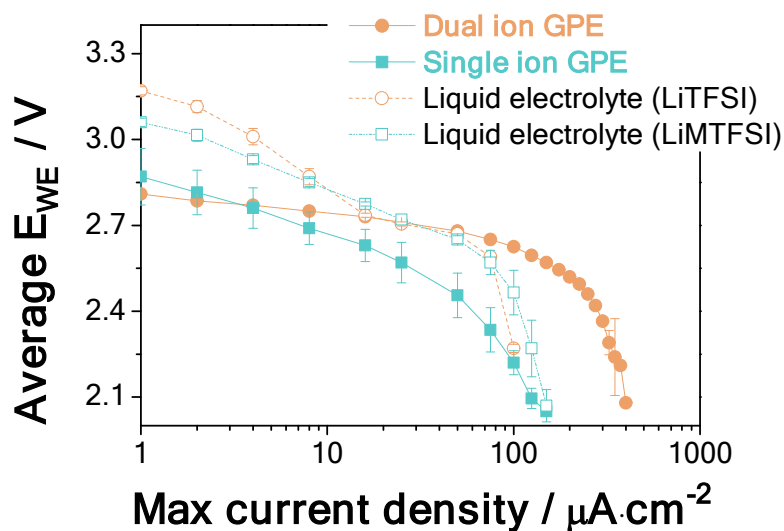


Figure S7. Tests carried out on Swagelok cells adopted to Li-O₂. Average potentials reached at each current density during the first loop on dynamic discharge using single and dual ion GPEs and solid electrolytes.

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