# Supporting Information

# Highly homogeneous sodium superoxide growth in Na-O<sub>2</sub> batteries enabled by a hybrid electrolyte

Nagore Ortiz-Vitoriano, <sup>a,b\*</sup> Iciar Monterrubio, <sup>a+</sup> Laura Garcia-Quintana, <sup>c+</sup> Juan Miguel López del Amo, <sup>a</sup> Fangfang Chen, <sup>c</sup> Teófilo Rojo, <sup>d</sup> Patrick C. Howlett, <sup>c</sup> Maria Forsyth, <sup>b,c</sup> Cristina Pozo-Gonzalo <sup>c\*</sup>

<sup>a</sup> Center for Cooperative Research on Alternative Energies (CIC energiGUNE), Basque Research and Technology Alliance (BRTA), Parque Tecnológico de Alava, Albert Einstein 48, 01510 Vitoria-Gasteiz, Spain.

<sup>b</sup> Ikerbasque, Basque Foundation for Science, María Díaz de Haro 3, 48013 Bilbao, Spain.

<sup>c</sup> ARC Centre of Excellence for Electromaterials Science, Institute for Frontier Materials, Deakin University, Geelong, Victoria, 3200, Australia

<sup>d</sup> Departamento de Química Inorgánica. Universidad del País Vasco UPV/EHU, P.O. Box 664, 48080 Bilbao, Spain

## **Corresponding Authors**

nortiz@cicenergigune.com

cpg@deakin.edu.au

<sup>+</sup>These authors contributed equally to this work

#### **Experimental section**

#### Materials

*N*-Butyl-*N*-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ([C<sub>4</sub>mpyr][TFSI], Solvionic, 99.9%), Diethylenglycol dimethylether (G2, Sigma-Aldrich, 99.5%) and Sodium bis(trifluoromethylsulfonyl)imide (NaTFSI, Solvionic, 99.9%) were opened and stored inside the glovebox. Two different compositions of electrolyte were prepared inside an Argon glovebox (Korea Kiyon with nominated levels of oxygen and water less than 1 ppm); on one hand [C<sub>4</sub>mpyr][TFSI] electrolyte with 16.6 mol% NaTFSI salt and on the other hand [C4mpyr][TFSI] electrolyte with 35 mol% NaTFSI salt, and were dried before using. The water content in the electrolytes, measure by C20 Karl Fischer coulometer (Mettler Toledo), were less than 15 ppm. For each experiment 300  $\mu$ L of electrolyte was used. The carbon nanofiber mats (CNFs) were synthesized using the method reported in our previous study. <sup>1</sup>

#### Instrumentation and techniques

The Na–O<sub>2</sub> cells consisted of a sodium metal anode and CNF materials as the oxygen electrode (1.13 cm<sup>2</sup>, 2.0–3.5 mg<sub>CNF</sub>). The electrodes were dried at 40 °C and under vacuum overnight and transferred to an Ar-filled glovebox (H<sub>2</sub>O < 0.1 ppm, O<sub>2</sub> < 0.1 ppm, Jacomex, France) avoiding exposure to the air.

For the electrochemical measurements, a pressurized 2-electrode Swagelok-type cell was used. The cells were dried overnight at 70 °C and transferred to the glovebox for assembly. Cell assembly consisted of 11 mm diameter sodium metal (Sigma Aldrich), a carbon-based electrode and Celgard H2010 separators (Celgard, USA, 13 mm diameter) soaked in 100 ml of electrolyte. A 12 mm diameter stainless steel mesh (Alfa Aesar) was used as the current collector. Once assemble, the cells were pressurized with pure oxygen to ~1. Electrochemical experiments were performed using a Biologic-SAS VSP potentiostat after 8h of resting at open circuit voltage. The discharge experiments were performed at an applied current of  $\pm$  75 µA cm<sup>-2</sup>. The air electrode geometric area was 1.13 cm<sup>2</sup>. Cycling experiments were conducted at 75 µA cm<sup>-2</sup> to 0.5 mAh cm<sup>-2</sup>.

Discharged CNF electrodes were washed in the glovebox using dried tetrahydrofuran (THF) prior to scanning electron microscopy (SEM) imaging. The electrodes were transferred to the SEM chamber using a hermetic transfer chamber to avoid exposure to ambient air. SEM measurements were performed using a series microscope and a FEI Quanta 250 microscope operating at 20 kV. The micrographs from JSM IT 300 were obtained in secondary electron mode, with a 5 kV accelerating voltage, 30 nA probe current. In order to get more detail of the discharge products, the SEM micrographs (FEI-Quanta 200 FEG) were obtained using the secondary electron detector (ETD), with a 10kV accelerating voltage and a value for the spot size of 3.

A Bruker AVANCE III 500 MHz (11.7 T) wide bore solid state NMR spectrometer equipped with a 2.5 mm magic angle spinning (MAS) probe was used to collect *ex situ* <sup>23</sup>Na and <sup>1</sup> NMR spectra. After discharge, the carbon paper electrodes were cut into pieces and packed into 2.5 mm outer diameter MAS rotors inside an argon glove box. <sup>23</sup>Na spectra were acquired accumulating 16 scans with a 1.5  $\mu$ s  $\pi/2$  excitation pulse and a recycle delay of 5 s. <sup>23</sup>Na chemical shifts were referenced to a 1M NaCl solution at 0 ppm. The <sup>1</sup>H solid state NMR spectra were recorded using a standard rotor-synchronized echo sequence in order to suppress background signals. 16 scans where acquired for each spectrum and the recycle delay was set to 3 s. All spectra were collected at a MAS rate of 20 kHz at room temperature.

The electrolyte samples were prepared for nuclear magnetic resonance (NMR) analysis in a flame-sealed 3 mm capillary placed inside a 5 mm static probe, containing D<sub>2</sub>O with NaF as

the reference. All <sup>1</sup>H, <sup>19</sup>F and <sup>23</sup>Na-NMR measurements were carried out at 11.7 T on a Bruker Avance III 500 MHz wide-bore spectrometer at 20 °C.

### MD simulation details and force field preparation

All-atom classic molecular dynamic simulations were conducted using DL\_Poly Classic software.<sup>2</sup> The 16.6 and 35 mol% IL/G2 systems were created by randomly packed all ions and molecules in the cubic simulation box using Packmol,<sup>3</sup> and the number of each type of ions/molecule is given in Table SI 1. The initial structure was equilibrated first at 500 K and then cooled down to 393 K and equilibrated for more than 1 ns using a NPT ensemble and the Berendsen thermostat and Hoover Barostat (relaxation time is 1.0 ps for both). Then the equilibrated system at 393 K was further equilibrated for another 1 ns using the Nose-Hoover thermostat and Hoover Barostat with relaxation constant of 5.0 and 10.0 ps, respectively. The total energy and volume was checked to make sure the system reaching equilibrium. The production run was continued for another 400 ps for a structural analysis. The pressure was set to 1.0 atm. The time step is 1 fs. The cutoffs for van der Waals force and the real space of Ewald were 12 Å. The Velocity Verlet integration algorithm was adopted. The Ewald summation method with a precision of  $1 \times 10^{-6}$  was used to treat Coulomb interaction in a periodic system. A uniform scale factor of 0.9 is adopted to scale down the net atomic charge of all ions.

The energy potential of ions was described by the OPLS\_AA force field. The parameters for C4mpyr<sup>+</sup>, TFSI<sup>-</sup> and Na<sup>+</sup> were all taken from the CL&P force field,<sup>4</sup> which was developed based on the same potential function of OPLS\_AA. The force field parameters of G2 were generated based on LigParGen force field generator<sup>5</sup> and the atomic charge has slightly modifications so that the structurally equivalent atoms carry the same charge. These force field parameters and G2 structure was shown in Table SI 2, SI 3 and Figure SI 4.

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Systems	C4mpyr	TFSI	Na	G2
16.6 mol% IL/G2	40	140	100	150
35 mol% IL/G2	60	120	60	240

Table SI 2. Atomic charges and Van der Waals parameters for G2 generated based on LigParGen[1].

Atom	Charge	σ/Å	Eps (kJ mol <sup>-1</sup> )
OP	-0.38	2.9	0.58576
СТ	0.01	3.5	0.27614
CN	0.01	3.5	0.27614
СМ	-0.05	3.5	0.27614
HN	0.09	2.5	0.12552
HM	0.08	2.5	0.12552

Bond	Å	K (kJ mol <sup>-1</sup> )		Angle	deg	$\frac{K (kJ)}{mol^{-1} rad^{-2}}$	
C-C	1.529	2242.6		C-C-O	109.5	414.8	
C-H	1.090	2845.1		H-C-O	109.5	292.9	
C-0	1.410	2677.8		С-О-С	109.5	502.1	
				C-C-C	112.7	488.3	
				С-С-Н	110.7	313.8	
				Н-С-Н	107.8	276.1	
	V1	V2	V3		V1	V2	V3
Angle	(kJ mol <sup>-1</sup>	(kJ mol <sup>-1</sup>	(kJ mol <sup>-1</sup>	Angle	(kJ mol <sup>-1</sup>	(kJ mol <sup>-1</sup>	(kJ mol <sup>-1</sup>
	rad <sup>-2</sup> )	rad <sup>-2</sup> )	$rad^{-2}$ )		rad <sup>-2</sup> )	rad <sup>-2</sup> )	rad <sup>-2</sup> )
0-C-C-0	-2.30112	0	0	H-C-C- O	0	0	1.9581
С-С-О-С	2.7196	-1.046	2.8033	H-C-C- H	0	0	1.2552
Н-С-О-С	0	0	3.1798				

Table SI 3. Bond, angle and torsion angle terms for G2.



Figure SI 1. SEM images corresponding to the discharge electrode in Figure 1a, composed of 16.6 mol% NaTFSI in G2.



Figure SI 2. (a) Discharge-charge curves corresponding to 16.6 mol% NaTFSI in IL, G2 and IL/G2, respectively; (b) evolution of discharge capacity (left axis, points denoted as filled symbols) and coulombic efficiency (right axis, points denoted as open symbols) with the number of cycles for all the studied electrolytes. Applied current: 75  $\mu$ A cm<sup>-2</sup> to a limited capacity: 0.5 mAh cm<sup>-2</sup>. Cut-off potential: 1.8 V. Salt concentrations along with the electrolyte composition are indicated in the plot.



Figure SI 3. a) Discharge curves and b) and c) SEM images at different magnifications corresponding to the discharge electrode composed of 16.6 mol% NaTFSI in  $[P_{66614}]$ [TFSI]/G2. Applied current: 75  $\mu$ A cm<sup>-2</sup>. Cut-off potential: 1.8 V.



Figure SI 4. Chemical structure of G2 and atomic type used in forcefield.

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