# **Supporting information**

## Comparison of ionic conductivity properties of microporous and mesoporous MOFs infiltrated with a Na-ion containing IL mixture

Joshua M. Tuffnell<sup>1,2</sup>, Jędrzej Morzy<sup>1</sup>, Nicola D. Kelly,<sup>2</sup> Rui Tan<sup>3</sup>, Qilei Song<sup>3</sup>, Caterina Ducati<sup>1</sup>, Thomas D. Bennett<sup>1\*</sup> Siân E Dutton<sup>2\*</sup>,

<sup>1</sup>Department of Materials Science and Metallurgy, University of Cambridge, United Kingdom

<sup>2</sup>Cavendish Laboratory, Department of Physics, University of Cambridge, United Kingdom

<sup>3</sup>Barrer Centre, Department of Chemical Engineering, Imperial College London, United Kingdom

## Table of Contents

Characterization and Equipment Details	2
X-ray Diffraction Patterns	4
Pawley Refinements and Crystal Size Analysis	5
$N_2$ Gas Sorption Isotherms	7
Additional Scanning Electron Microscopy Images	9
Thermogravimetric Analysis	10
<sup>1</sup> H Digestive Nuclear Magnetic Resonance Spectra	11
Elemental Analysis	14
Additional Transmission Electron Microscopy Images	15
F/Zn Maps of NalL@MOF Composite Samples	16
Electrochemical Impedance Spectroscopy – Thermal Sweep Protocol	17
Alternating Current Electrochemical Impedance Spectroscopy – Data analysis	18
Electrochemical Impedance Spectroscopy – Fitting Results NaIL@ZIF-8 <sub>meso</sub>	20
Electrochemical Impedance Spectroscopy – Fitting Results NaIL@ZIF-8 <sub>micro</sub>	21
Electrochemical Impedance Spectroscopy – Arrhenius Plot	22
References	23

## **Characterization and Equipment Details**

#### Powder X-ray Diffraction (PXRD)

Room temperature PXRD spectra ( $2\theta = 5-50^{\circ}$ ) were collected on a Bruker D8 Advance DAVINCI diffractometer using Cu K $\alpha$  ( $\lambda = 1.540598$  Å) radiation and a LynxEye EX position sensitive detector in Bragg-Brentano parafocussing geometry. A step size of 0.03 ° and time/step of 1 s/step was used for all samples. Samples were rotated on a Si low background sample holder from Bruker during collection. Topas v5 was used for Pawley and Rietveld refinements.<sup>1–3</sup> A silicon standard was used to obtain the instrumental peak broadening parameters by fitting a Thompson-Cox-Hastings pseudo-Voigt (TCHZ) peak shape. The crystallite size of ZIF-8 was then calculated using the in-built size/strain analysis macro in TOPAS v5.

#### **Nitrogen Gas Sorption**

 $N_2$  gas adsorption isotherm measurements were carried out using a Micromeritics ASAP 2020 instrument. Approximately 50 mg sample was used for each measurement. All samples were degassed at 200 °C for 12 h prior to the measurement. Non-linear density functional theory (NLDFT) analysis of the pore volume was calculated using the provided ASAP 2020 software using a  $N_2$  @ 77 K on Carbon, slit pores model and non-negative regularization method with medium smoothing (0.01).

#### Thermogravimetric Analysis (TGA)

Thermogravimetric analysis was conducted on a Mettler-Toledo TGA 2 SF/1100 with 70  $\mu$ L alumina sample holders. Samples were measured from 25-800 °C at a heating rate of 10 °C/min and under an argon flow (20 mL/min).

#### Scanning Electron Microscopy (SEM)

The samples were imaged using a FEI Nova NanoSEM 450 microscope equipped with a field emission gun, operated at 5 kV accelerating voltage. An Everhart-Thornley secondary electron detector was used. All samples were coated with a thin layer of silver prior to imaging to reduce charging.

#### Transmission Electron Microscopy (TEM)

Specimen powders were scattered onto lacey carbon Cu grids. FEI Tecnai Osiris TEM with a high brightness X-FEG gun operated at 200 kV was used for bright field TEM imaging (BF-TEM), annular dark field scanning TEM imaging (ADF-STEM) and scanning energy dispersive X-ray spectroscopy (STEM-EDX). EDX was performed using the FEI Super-X detector system (4 silicon drift detectors placed symmetrically around the sample). Probe current in STEM mode was about 0.25 nA, dwell time 80 ms. EDX data were analysed using an open source Python package Hyperspy.<sup>4</sup> Cliff-Lorimer method has been used to quantify elemental ratios using k-factors from Tecnai Imaging and Analysis software.

#### <sup>1</sup>H Nuclear Magnetic Resonance (NMR) Spectroscopy

<sup>1</sup>H NMR spectra were recorded at 298 K using a Bruker AVIII 500 MHz Spectrometer with a dual <sup>13</sup>C/<sup>1</sup>H (DCH) helium cooled cryoprobe. Samples were dissolved in a 6:1 ratio of DMSO-d<sub>6</sub> with 0.03 % (v/v) TMS and 35 wt% DCl in D<sub>2</sub>O. Data processing was performed using TopSpin 4.0.8.

#### **Elemental analysis**

CHN analysis was measured on a CE-440 Elemental Analyzer from Exeter Analytical. Samples were combusted at 975 °C in  $O_2$  with He carrier gas and an acetanilide reference. For the elemental analysis of Zn, Na and S, inductively coupled plasma optical emission spectroscopy (ICP-OES) was employed on an iCAP 7000 Series ICP Spectrometer from Thermo Scientific. Samples were dissolved in conc. nitric acid in plastic vessels to avoid sodium leaching from standard glassware and incubated at room temperature for 1 h. Solutions were then diluted with deionised water (5 mL) and further diluted by taking 500 uL aliquots and diluted to a total volume of 10 mL with deionised water to yield solutions with elemental concentrations appropriate for detection. For every 5 samples, a blank (~2 % HNO<sub>3</sub>), standard solutions of a range of concentrations from 0.001 to 20 ppm (in ~2 % HNO<sub>3</sub>) and a 1.0 ppm standard are measured. A calibration curve can be constructed from the diluted standard solutions for each element. A Supleco ICP multi-element standard solution IV was used as the calibration for Zn and Na quantification; for S quantification a single element sulphur standard was used. Data was analysed with Data analysed with Qtegra Intelligent Scientific Data Solution (ISDS) software from Thermo

#### Electrochemical Impedance Spectroscopy (EIS)

Conductivity measurements were performed between 0.05 Hz and 10<sup>7</sup> Hz using the complex impedance method on a Solartron 1260 impedance/gain-phase analyser. The sample pellet is placed in an impedance cell in which the sample is contacted to two stainless steel blocking electrodes. Swagelok PTFE ferrules were used to seal the impedance cell to allow measurements to be carried out in an argon atmosphere as the pellet could be placed in the cell whilst in a glovebox and then sealed before transferring to the furnace. Measurements were taken over the temperature range: 25-125 °C in a Lenton chamber furnace (EF 11/8B) which was monitored using a K-type thermocouple controlled by a Raspberry Pi as described in the following reference.<sup>5</sup> The temperature dependent complex impedance data was fit by modelling as a RC circuit using a Randle model from which the Arrhenius relation could be used to extract the activation energy for ion conduction.

## **X-ray Diffraction Patterns**



**Figure S1.** XRD patterns of ZIF-8<sub>micro</sub> (blue), ZIF-8<sub>meso</sub> (orange), NaIL@ZIF-8<sub>micro</sub> (light blue) and NaIL@ZIF-8<sub>meso</sub> (light orange) samples along with the simulated XRD pattern from the Cambridge Crystallographic Data Centre (CCDC 602542).

## **Pawley Refinements and Crystal Size Analysis**



**Figure S2**. Pawley refinements of ZIF-8<sub>micro</sub> and ZIF-8<sub>meso</sub> in the cubic space group I-43m.<sup>2,6</sup> Red dots are experimental datapoints, black lines are the calculated diffraction patterns, green lines are the difference profiles and blue tick marks indicate the Bragg reflection positions. Tabulated data for this refinement can be found in Table S1.

**Table S1**: Rietveld and Pawley refinement details for powder X-ray diffraction data on ZIF-8<sub>micro</sub> and ZIF-8<sub>meso</sub> as well as a silicon standard.<sup>2,3</sup> <sup>a</sup>Volume-weighted column height based on integral breadth; <sup>b</sup>Volume-weighted column height based on full width at half maximum; <sup>c</sup>Assuming a monodisperse distribution of spherical particles.

Material	Silicon	ZIF-8 <sub>micro</sub>	ZIF-8 <sub>meso</sub>
Temperature (K)	298	298	298
Refinement type	Rietveld	Pawley	Pawley
R <sub>wp</sub> (%)	8.13	8.96	4.65
Space group	Fd-3m	I-43m	I-43m
Unit cell length (Å)	5.43163(7)	17.03855(7)	17.046(6)
LVol_IB <sup>a</sup> (nm)	n/a	99(3)	12.4(7)
Mean diameter <sup>c</sup> (nm)	n/a	132(4)	16.5(9)
LVol_FWHM <sup>♭</sup> (nm)	n/a	117(4)	14.5(7)
Mean diameter <sup>c</sup> (nm)	n/a	156(5)	19.3(9)

## N<sub>2</sub> Gas Sorption Isotherms



**Figure S3.** Gravimetric N<sub>2</sub> gas sorption curves at 77 K for ZIF-8<sub>micro</sub> (blue), ZIF-8<sub>meso</sub> (orange), NaIL@ZIF-8<sub>micro</sub> (light blue) and NaIL@ZIF-8<sub>meso</sub> (light orange) samples. Closed squares represent data measured upon adsorption and open squares represents desorption. Solid lines are a guide for the eye. Extracted data is found in Table 1 in the main text. An unphysical small decrease in adsorption capacity at the intermediate range is due to a small leak in the instrument is acknowledged.



**Figure S4**. Gravimetric N<sub>2</sub> gas sorption curves at 77 K for ZIF-8<sub>micro</sub> (blue), ZIF-8<sub>meso</sub> (orange), NaIL@ZIF-8<sub>micro</sub> (light blue) and NaIL@ZIF-8<sub>meso</sub> (light orange) samples. Solid lines are a guide for the eye. Note the semi-log scale on the x-axis to highlight the low relative pressure region.

## Additional Scanning Electron Microscopy Images



Figure S5. SEM images of (a-b) ZIF-8<sub>micro</sub>, (c-d) ZIF-8<sub>meso</sub>, (e-f) NaIL@ZIF-8<sub>micro</sub> and (g-h) NaIL@ZIF-8<sub>meso</sub> samples. Scalebars are inset.

## **Thermogravimetric Analysis**



**Figure S6.** Top: Thermogravimetric analysis (TGA) curves for ZIF-8<sub>micro</sub> (blue), ZIF-8<sub>meso</sub> (orange), NaIL@ZIF-8<sub>micro</sub> (light blue) and NaIL@ZIF-8<sub>meso</sub> (light orange) samples. Measured at a heating rate of 10 °C min<sup>-1</sup> under nitrogen flow of 20 mL min<sup>-1</sup>. Bottom: first derivative of the weight loss curves shown above. Thermal decomposition temperatures are approximated from the onset of the derivative curves.

## <sup>1</sup>H Digestive Nuclear Magnetic Resonance Spectra



**Figure S7.** <sup>1</sup>H NMR spectra from digested samples of (a) ZIF-8<sub>micro</sub> and (b) ZIF-8<sub>meso</sub>. The asterisk identifies a peak assigned to an impurity originating from the plastic pipettes used in the sample preparation.

$$\label{eq:21F-8_micro} \begin{split} \text{ZIF-8}_{\text{micro}} : \ ^1\text{H} \ \text{NMR} \ (d_6\text{-}\text{DMSO}, \ 500 \ \text{MHz}) : \ \delta \ 2.62 \ (s, \ 3\text{H}, \ -\text{CH}_3), \ 7.50 \ (s, \ 2\text{H}, \ -\text{NCHCHN-}). \\ \text{ZIF-8}_{\text{meso}} : \ ^1\text{H} \ \text{NMR} \ (d_6\text{-}\text{DMSO}, \ 500 \ \text{MHz}) : \ \delta \ 2.62 \ (s, \ 3\text{H}, \ -\text{CH}_3), \ 7.50 \ (s, \ 2\text{H}, \ -\text{NCHCHN-}). \end{split}$$



**Figure S8.** <sup>1</sup>H NMR spectra of the NaIL mixture, (Na<sub>0.1</sub>EMIM<sub>0.9</sub>)TFSI. The asterisk identifies a peak assigned to an impurity originating from the plastic pipettes used in the sample preparation.

NaIL: <sup>1</sup>H NMR (d<sub>6</sub>-DMSO, 500 MHz): δ 1.47 (t, 3H, -CH<sub>2</sub>CH**3**, J = 7.3 Hz), 3.92 (s, 3H, -CH<sub>3</sub>), 4.26 (q, 2H, -CH<sub>2</sub>CH<sub>3</sub>, J = 7.3 Hz), 7.71 (t, 1H, CH<sub>3</sub>NCHCHNCH<sub>2</sub>-, J = 1.7 Hz), 7.79 (t, 1H, CH<sub>3</sub>NCHCHNCH<sub>2</sub>-, J = 1.7 Hz), 9.23 (s, 1H, NCHN).



**Figure S9.** <sup>1</sup>H NMR spectra from digested samples of (a) NaIL@ZIF-8<sub>micro</sub> and (b) NaIL@ZIF-8<sub>meso</sub>. The asterisk identifies a peak assigned to a*n* impurity originating from the plastic pipettes used in the sample preparation.

NalL@ZIF-8<sub>micro</sub>: <sup>1</sup>H NMR (d<sub>6</sub>-DMSO, 500 MHz):  $\delta$  1.44 (t, 3H, -CH<sub>2</sub>CH**3**, J = 7.3 Hz), <u>2.62 (s, 3H, -CH<sub>3</sub>)</u>, 3.90 (s, 3H, -CH<sub>3</sub>), 4.25 (q, 2H, -CH<sub>2</sub>CH<sub>3</sub>, J = 7.3 Hz), <u>7.50 (s, 2H, -NCHCHN-)</u>, 7.72 (t, 1H, CH<sub>3</sub>NCHCHNCH<sub>2</sub>-, J = 1.8 Hz), 7.81 (t, 1H, CH<sub>3</sub>NCHCHNCH<sub>2</sub>-, J = 1.7 Hz), 9.25 (s, 1H, NCHN).

NaIL@ZIF-8<sub>meso</sub>: <sup>1</sup>H NMR (d<sub>6</sub>-DMSO, 500 MHz):  $\delta$  1.44 (t, 3H, -CH<sub>2</sub>CH**3**, J = 7.3 Hz), <u>2.62 (s, 3H, -CH<sub>3</sub>)</u>, 3.90 (s, 3H, -CH<sub>3</sub>), 4.24 (q, 2H, -CH<sub>2</sub>CH<sub>3</sub>, J = 7.3 Hz), <u>7.50 (s, 2H, -NCHCHN-)</u>, 7.72 (t, 1H, CH<sub>3</sub>NCHCHNCH<sub>2</sub>-, J = 1.8 Hz), 7.81 (t, 1H, CH<sub>3</sub>NCHCHNCH<sub>2</sub>-, J = 1.7 Hz), 9.25 (s, 1H, NCHN).

Note: The underlined assignments correspond to proton environments due to the ZIF-8 framework whilst the remainder are associated with the ionic liquid mixture.

## **Elemental Analysis**

Samples		<sup>a</sup> C	<u>"H</u>	<sup>a</sup> N.	<sup>b</sup> Zn	<sup>b</sup> S
ZIF-8 <sub>micro</sub>	Calculated	42.22	4.43	24.62	28.73	-
	Measured	41.95	4.27	23.95	28.98	-
ZIF-8 <sub>meso</sub>	Calculated	42.22	4.43	24.62	28.73	-
	Measured	42.06	4.17	23.15	23.79	-
NalL@ZIF-8 <sub>micro</sub>	Calculated	33.55	3.60	18.06	15.61	7.66
	Measured	31.28	2.85	15.93	13.57	8.90
NalL@ZIF-8 <sub>meso</sub>	Calculated	32.06	3.45	16.93	13.35	8.98
	Measured	29.94	2.98	14.69	10.97	10.06
NalL	Calculated	23.24	2.61	10.25	-	16.76
	Measured	21.61	2.37	9.59	-	16.90

**Table S2**: Elemental analysis of ZIF-8<sub>micro</sub>, ZIF-8<sub>meso</sub>, NaIL@ZIF-8<sub>micro</sub>, NaIL@ZIF-8<sub>meso</sub>, and NaIL. Calculated values are based on the molar ratios from the experimental procedure.

<sup>a</sup> corresponds to CHN combustion elemental analysis and <sup>b</sup> corresponds to ICP-OES analysis.

## Additional Transmission Electron Microscopy Images



Figure S10. TEM images of NaIL@ZIF-8<sub>micro</sub> and NaIL@ZIF-8<sub>meso</sub>. Scalebars inset are 200 nm.

## F/Zn Maps of NalL@MOF Composite Samples



**Figure S11.** Top row: ADF-STEM images of both MOF types. Bottom row: F/Zn ratio maps for the regions highlighted with orange squares. Pixel size of the F/Zn ratio is 5 nm.



### **Electrochemical Impedance Spectroscopy – Thermal Sweep Protocol**

**Figure. S12**. Electrical impedance spectroscopy thermal sweep protocol of two heating and cooling cycles with long thermal equilibration times (blue line) and indication of the three conductivity measurements at each temperature step (red points). Measurements were recorded from 25-125 °C in 20 °C steps.

**Note**: Measurements from the first heating scan are not included in the data analysis as the initial heating curve allows for the removal of adsorbed water on the sample and accounts for changes in pellet dimensions with temperature.

#### Alternating Current Electrochemical Impedance Spectroscopy – Data analysis

#### **Electrochemical Impedance Spectroscopy**

Electrochemical impedance is used to measure the ability of a sample to resist the flow of an applied alternating current (AC) potential over a given frequency range. As with resistance in the Ohm's law equation, the impedance,  $Z(\omega)$  is defined as the ratio of the applied potential,  $V(\omega)$  to the measured current,  $I(\omega)$  i.e.

Impedance, 
$$Z(\omega) = \frac{V(\omega)}{I(\omega)}$$
 Eq. 1

where  $\omega$  is the angular frequency. This applied potential can be written in the form of a sine wave, however, using Euler's relationship ( $e^{j\varphi} = cos\varphi + jsin\varphi$ ), impedance can be expressed as a complex number:

Impedance, 
$$Z(\omega) = Z_0 e^{j\varphi} = Z_0(\cos\varphi + j\sin\varphi)$$
 Eq. 2

where  $Z_0$  is the magnitude, j represents an imaginary unit and  $\varphi$  is the phase shift of the response signal. The expression for  $Z(\omega)$  is composed of a real an imaginary part which can be plotted to show a 'Nyquist' plot in which each point is the impedance at a single frequency. The data can be fit with an empirical model in order to obtain the resistance to ion conduction, R<sub>ion</sub>. The ionic conductivity can then be calculated from the dimensions of the sample pellet and its resistance by the relation:

Ionic conductivity, 
$$\sigma = \frac{l}{R_{ion}A}$$
 Eq. 3

where I is the length of the pellet, R<sub>ion</sub> is the resistance and A is the cross-sectional area. The activation energy for ion conduction can be extracted via the Arrhenius equation:

where T is the temperature of the sample, 
$$\sigma_0$$
 is the pre-exponential factor,  $E_a$  is the activation energy for ion conduction and k is the Boltzmann constant.

#### **Equivalent Circuits**

v

 $\sigma T = \sigma_0 exp - \frac{E_a}{kT}$ 

The empirical models used to fit electrochemical impedance spectra of polycrystalline solid electrolytes utilise a range of resistor-capacitor (RC) circuits. As discussed in text, the RC circuit chosen to model this data is a modified Randle circuit which describes the impedance of an ideal ion conductor with diffusion limited conductivity. The circuit consists of a resistor and two constant phase elements (CPEs), with the total impedance of the circuit corresponding to the sum of the impedance of the phase elements, Z<sub>CPE</sub> and the resistor. Z<sub>CPE</sub> is given by:

where the Y and n are frequency independent parameters which can be fit, j is the imaginary unit, and 0 < n < 1. When n = 1, the system behaves as an ideal capacitor, while the case n = 0 describes a pure resistor.

 $Z_{CPE} = \frac{1}{Y \cdot \omega^n} e^{-\frac{\pi}{2}nj}$ 

Eq. 4

Eq. 5

As the model consists of two constant phase elements and a resistor, the overall impedance of the modified Randles circuit is given by:

$$Z_{model} = \left(\frac{1}{R_{ion} + Z_{CPE_1}} + \frac{1}{Z_{CPE_2}}\right)^{-1}$$
 Eq. 6

From Eq. 5 and Eq. 6, we see that  $Z_{model}$  is parameterised by  $R_{ion}$ ,  $Y_1$ ,  $n_1$ ,  $Y_2$  and  $n_2$ .

#### **Fitting Procedure**

A brief explanation of the fitting procedure is explained here. Detailed explanation of the code used can be found in the corresponding thesis.<sup>5</sup>

- 1. At each temperature, three measurements are taken, and the results averaged. Errors are taken as the standard deviation of the three measurements at each temperature.
- 2. The modified Randles model is defined (Eq. 6) and parameterised by R<sub>1</sub>, Y<sub>1</sub>, n<sub>1</sub>, Y<sub>2</sub> and n<sub>2</sub> which will be used for fitting.
- 3. An initial guess for the model parameters is made based on the form of the experimental data. Upper and lower limits are defined.

Initial\_params = [R1,Y1,n1,R2,Y2,n2,Y3,n3] = 6e2, 3e-6, 0.63, 1.3e-9, 0.89 Upper\_limit\_params = [Ru, Yu, Nu] = 1e10, 1e-4, 1 Lower\_limit\_params = [Rl, Yl, nl] = 1e1, 1e-15, 0.01

4. A cost function, f is defined which allows an assessment of the 'goodness of fit' of the model to the experimental data. In its simplest form, this is represented as:

$$f = \sum_{i=0}^{N} |Z_{obs}(\omega_i) - Z_{calc}(\omega_i)|^2$$
 Eq. 7

The impedance of the model,  $Z_{calc}$ , is a function of the model parameters and the experimentally observed impedance of the sample,  $Z_{obs}$ , has a phase and magnitude.

- 5. To ensure the phase and magnitude are equally weighted in the cost function, a pairwise normalisation is carried out. See thesis for normalization details.<sup>5</sup> An additional normalization is required to ensure that when the fitting is carried out, small variations in the model parameters are equivalent for example, small changes in n<sub>1</sub> which ranges from 0 to 1, will not be the same as small changes in R<sub>1</sub> which ranges from 1e1 to 1e10.
- 6. Finally, the model was fit to the data by minimisation of the cost function. To avoid local minima, a Monte Carlo method is utilised via the basinhopping routine from the open source scipy.optimize library. In this method, random perturbations of the model parameters are performed, and the results accepted or rejected based on the cost function and further iterations are carried out. Importantly, perturbations which lead to an increase in cost function are not immediately rejected, as further iterations can lead to relaxation into another local minima (by a gradient decent method).<sup>7</sup>
- 7. The results from the fitting of the composite samples and model parameters are shown below.



#### Electrochemical Impedance Spectroscopy – Fitting Results NaIL@ZIF-8meso

**Figure. S13**. Variable temperature electrical impedance data from NaIL@ZIF-8<sub>meso</sub> collected from 25-125 °C in 20 °C steps. On the left are the magnitude (top) and phase (bottom) of the impedance against frequency. On the right is the Nyquist plot of the observed data. The colour of the data points represents the temperature at which the measurement was recorded. The error bars correspond to the standard deviation for three measurements at each temperature with the average data displayed as closed circles. The solid black lines are the fit to the data using a modified Randles circuit, shown in Fig. 6 and discussed above.

		CPE1		СР	_	
T /℃	R1 /Ω	$Y_1$ / $\Omega^{-1}$ s <sup>n</sup>	Exponent n <sub>1</sub>	$Y_2$ $/\Omega^{-1} s^n$	Exponent n <sub>2</sub>	σ <sub>ion</sub> /S cm <sup>-1</sup>
25	1289	3.4E-06	0.66	8.1E-10	0.92	8.39E-06
40	683	3.8E-06	0.70	1.4E-09	0.88	1.59E-05
56	381	3.8E-06	0.75	6.8E-09	0.76	2.84E-05
72	236	4.2E-06	0.77	8.9E-07	0.38	4.58E-05
88	154	5.2E-06	0.78	1.1E-09	0.03	7.04E-05
105	107	6.3E-06	0.80	1.0E-15	0.25	1.02E-04

Table S3: Fitting parameters from the NaIL@ZIF- $8_{meso}$  sample and corresponding ionic conductivity value at each temperature.



#### Electrochemical Impedance Spectroscopy – Fitting Results NaIL@ZIF-8micro

**Figure. S14**. Variable temperature electrical impedance data from NaIL@ZIF-8<sub>micro</sub> collected from 25-125 °C in 20 °C steps. On the left are the magnitude (top) and phase (bottom) of the impedance against frequency. On the right is the Nyquist plot of the observed data. The colour of the data points represents the temperature at which the measurement was recorded. The error bars correspond to the standard deviation for three measurements at each temperature with the average data displayed as closed circles. The solid black lines are the fit to the data using a modified Randles circuit, shown in Fig. 6 and discussed above.

		CPE1		С		
т /°С	R1 /Ω	$\gamma_1$ $/\Omega^{-1} s^n$	Exponent n1	$Y_2$ $/\Omega^{-1} s^n$	Exponent n <sub>2</sub>	σ <sub>ion</sub> /S cm <sup>-1</sup>
24	850	3.7E-06	0.91	3.4E-10	0.97	1.58E-05
39	481	4.3E-06	0.91	4.4E-10	0.94	2.79E-05
54	289	5.2E-06	0.91	8.1E-10	0.84	4.64E-05
70	192	6.1E-06	0.90	1.7E-09	0.01	6.97E-05
86	139	6.3E-06	0.91	3.1E-15	0.01	9.66E-05
104	105	6.5E-06	0.92	1.0E-15	0.06	1.28E-04

Table S4: Fitting parameters from the NaIL@ZIF- $8_{meso}$  sample and corresponding ionic conductivity value at each temperature.



#### **Electrochemical Impedance Spectroscopy – Arrhenius Plot**

**Figure S15.** An Arrhenius plot for the NaIL@ZIF-8<sub>micro</sub> (blue) and NaIL@ZIF-8<sub>meso</sub> (orange) samples. The dotted lines with open circles represent impedance measurements taken when cooling from 125 to 25 °C and solid lines with closed circles when heating. Lines show a linear fit of the data from which the activation energies are calculated. Note the use of a natural log and temperature factor on the y-axis for a linear plot which follows the Arrhenius relationship.

### References

- 1 A. A. Coelho, J. Appl. Crystallogr., 2018, **51**, 210–218.
- 2 G. S. Pawley, J. Appl. Crystallogr., 1981, 14, 357–361.
- 3 H. M. Rietveld, J. Appl. Crystallogr., 1969, 2, 65–71.
- F. de la Peña, E. Prestat, V. T. Fauske, P. Burdet, P. Jokubauskas, M. Nord, T. Ostasevicius, K. E. MacArthur, M. Sarahan, D. N. Johnstone, J. Taillon, J. Lähnemann, V. Migunov, A. Eljarrat, J. Caron, T. Aarholt, S. Mazzucco, M. Walls, T. Slater, F. Winkler, P. Quinn, B. Martineau, G. Donval, R. McLeod, E. R. Hoglund, I. Alxneit, D. Lundeby, T. Henninen, L. F. Zagonel and A. Garmannslund, 2019.
- 5 J. Hodkinson, University of Cambridge, 2019.
- K. S. Park, Z. Ni, A. P. Cote, J. Y. Choi, R. Huang, F. J. Uribe-Romo, H. K. Chae, M. O'Keeffe and O. M. Yaghi, *Proc. Natl. Acad. Sci.*, 2006, **103**, 10186–10191.
- 7 S. Goedecker, J. Chem. Phys., 2004, **120**, 9911–9917.