## **Supplementary information**

# Architecture of imidazolium-based poly(ionic liquid)s-cobalt hexagonal thin nanosheet for high energy density with membrane electrolytes

Abhishek Narayanan<sup>a</sup>, Pavan T<sup>a</sup>, Narad Barman<sup>b</sup>, Nagaraj S Naik<sup>a</sup>, Ranjit Thapa<sup>b</sup>, Chandra Sekhar Rout <sup>*a*, *c*</sup> Mahesh Padaki<sup>a\*</sup>

<sup>a</sup> Centre for Nano and Material Sciences, JAIN (Deemed-to-be) University, Jain Global Campus, Kanakapura, Ramanagara, Bangalore 562112, Karnataka, India.

<sup>b</sup> Department of Physics, SRM University – AP, Amaravati 522502, Andhra Pradesh, India

<sup>c</sup> Department of Chemical Engineering, Chungbuk National University, Cheongju, Chungbuk 28644, Republic of Korea

\*Corresponding author. Mahesh Padaki. Tel.: +918027577212 (186),

Email: sp.mahesh@jainuniversity.ac.in

#### 1. Experimental Section

## 1.1. Chemicals

1-Vinylimidazole (V-imd, 99 %) were purchased from Sigma Aldrich pvt., Ltd.,1-Bromo butane (C<sub>4</sub>H<sub>10</sub>-Br), 1,4-Dioxane (C<sub>4</sub>H<sub>8</sub>O<sub>2</sub>), and Cobalt (II)nitrate hexahydrate (Co(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O were purchased from (SRL) Sisco research limited. Methanol was purchased from Rankem pvt., Ltd. Absolute ethanol was purchased from CH Fine Chemicals, Co., Ltd. Finally, AIBN (Azobisisobutyronitrile) were purchased from Avra Synthesis Pvt. Ltd.

## 1.2 Synthesis of poly(ionic liquid)s (PILs)

#### Scheme S1

Step 1: Synthesis of monomer ((1-butyl-3-vinylimidazolium bromide, ILs)



Initially, 1-Vinylimidazole (10 g, 0.106 mol) and 1-Bromo butane (14.559 g, 0.106 mol) were combined in a two-necked round-bottom flask along with 1,4-Dioxane (50 mL) serving as a solvent. The mixture underwent degassing under dry nitrogen for 1 hour, followed by filling the flask with a nitrogen atmosphere. Subsequently, the setup was immersed in an oil bath at 80 °C for 12 hours with vigorous mechanical stirring. After cooling the reaction to room temperature (RT), the resulting monomer was denoted as BVim-Br. The BVim-Br product was subjected to washing using 1,4-Dioxane and then dried at 80 °C in a vacuum oven for 24 hours. This process yielded a transparent gel-like product, and the overall yield was determined to be 85%.

<u>Step 2:</u> Synthesis of poly(ionic liquid)s (poly(1-butyl-3-vinylimidazolium bromide (poly(ionic liquid)s, PILs)



Initially, BVIm-Br (10.0 g, mmol) was dissolved in Methanol (25 mL). Subsequently, AIBN-Initiator (200 mg) was introduced to the solution, and the resulting mixture underwent degassing with dry nitrogen for 1 hour. The setup was then filled with a nitrogen atmosphere and placed in an oil bath at 80 °C under reflux conditions, maintaining a reaction with vigorous mechanical stirring for 12 hours. After the completion of the reaction, the solution was cooled to room temperature. The polymer, designated as PIL-Br, was precipitated from acetone and subsequently dried at 70 °C in a vacuum oven for 12 hours, resulting in a pale-yellow solid. The overall yield for this process was determined to be 71%, with a final product mass of 7.47 g.

## 2. Characterization and methods

A) Poly(ionic liquid)s were characterized through <sup>1</sup>H NMR analysis using a Bruker Avance 400 S spectrometer, with DMSO-d6 as the solvent and tetramethyl silane (TMS) as the standard.

B) The surface charge of the prepared samples was measured using a Zeta potential instrument (Anton Paar, Litesizer<sup>™</sup> 500), employing a single-frequency laser diode with a wavelength of 658 nm and a power output of 40 mW.

C) Morphological features of the materials were studied by Field-Emission Scanning Electron Microscopy (FE-SEM, Jeol JSM-7100F). Samples (1 mg) were ultrasonicated in ethanol, drop-cast on a silicon wafer, and dried. Imaging was conducted at voltages of 5 kV and 8 kV, with a magnification range from 5000 to 80000.

D) Transmission Electron Microscopy (TEM): The internal morphology, SAED pattern, and elemental mapping were done by using TEM analysis (TALOS F200S G2 200 KV, FEG, CMOS Camera 4K x 4K, In Column EDS Detector). Samples were dispersed using ethanol and drop casted on the surface of Cu grid (300 mesh size) and the image was collected 200-5 nm<sup>-1</sup>.

E) Powder X-ray diffraction (p-XRD) analysis was conducted on the synthesized PIL-Co hybrid using a Rigaku X-ray diffractometer, with a  $2\theta$  range of 5 to  $80^{\circ}$  and a ramping rate of  $3^{\circ}$ /min.

F) Fourier-Transform Infrared Spectroscopy (FTIR) analysis was carried out in the frequency range of 4000 to 500 cm<sup>-1</sup> using a Beuker Optik GMBH-FT-IR instrument. Samples were prepared as pellets with KBr powder and subjected to analysis after pressing at 500 Kg/cm<sup>2</sup>.

G) Nitrogen adsorption-desorption isotherms and pore size distribution were analyzed by Brunauer-Emmett-Teller (BET) analyzer (Belsorp-Max, M/s Microtrac BEL, Japan), with degassing at 120 °C and a relative pressure range of 0.1 - 1 Hz.

H) Contact angle measurement to assess hydrophilicity was conducted using a TECH Con-Contact angle measurement instrument (Model No: TECH CON-1200). Contact angles were measured on bare nickel foam and nickel foam with prepared material (PIL-Co).

I) X-ray Photoelectron Spectroscopy (XPS) analysis for elemental composition and chemical/electronic states used a PHI 5000 Versa Probe II (FEI Inc) with Cu (K  $\alpha$ ) radiation.

J) Thermal stability analysis (TGA) was performed using controlled-rate heating in an  $N_2$  environment, recording weight changes with temperature.

K) Electrochemical performance studies, including cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD), were carried out using a Metrohm Auto Lab B.V. in Nova 2.1 software, with 2M KOH aqueous electrolytes and PVDF-HFP/EMIM-TFSI solid-state electrolyte in both three and two-electrode systems.

L) Computational study involved Density Functional Theory (DFT) calculations using the Vienna Ab initio Simulation Package (VASP) with the Projected Augmented Wave (PAW) method, Generalized Gradient Approximation (GGA), and specified convergence criteria.

## 3. Electrochemical measurements

All electrochemical measurements were performed at room temperature using an Autolab instrument with Nova 2.1 software. A three-electrode setup was used to assess the supercapacitor's maximum voltage window. The electrochemical impedance spectroscopy experiments were carried out at open circuit potential under a sinusoidal signal with a frequency range of 100 kHz to 10 mHz.

The capacitance can also be calculated by integration of the CV curves using the equation S1<sup>1</sup>

$$c = \frac{\int I \, dV}{v \, \Delta V}$$
 S1

where I is the discharge current, i.e., the current below the X axis, v is the scan rate, and  $\Delta V$  is the operating discharge potential range.

By using equation S1, the specific capacitance derived from GCD curves was computed.

$$C = \frac{I\Delta t}{m\Delta V}$$
 S2

Where m denotes the quantity of the active materials (g), C denotes specific capacitance (F  $g^1$ ), I represents current density (A), t measures time and V denotes a potential range<sup>2</sup>.

The change in balance for the asymmetric supercapacitor follows the relationship (S2).

The mass ratio of active materials (PIL-Ni-150) and AC is determined using equations S3 and S4, where q + is the change stored in the cathode and q- is the anode<sup>3</sup>.

$$q = C \times \Delta V \times m \qquad S4$$
$$\frac{m^{+}}{m^{-}} = \frac{(C^{-} \times \Delta V^{-})}{(C^{+} \times \Delta V^{+})} \qquad S5$$

Where m (g) is the active material mass of the electrodes, V (V) is the potential window, and C (F  $g^{-1}$ ) is the specific capacitance.

Equations S6 and S7 are used to compute the energy density<sup>4,5</sup> (E, Wh kg<sup>-1</sup>) and power density (P, W kg<sup>-1</sup>).

$$E = \frac{\Delta V \times i \times \Delta t}{m}$$

$$P = \frac{\Delta V \times i}{m}$$
S6

where i is the discharge current; V, voltage; t, time in hours; and m, is the mass of the active materials for both electrode materials.

## **Kinetic studies**

To gain deeper insight into the charge storage mechanism, the power law equation, as expressed in equation S8

$$I_p = av^p \qquad \qquad \text{S8}$$

where  $I_p$  represents the peak current (A) as a function of the scan rate, v (V/s). The parameters a and b are variables that define the nature of the charge storage process. The exponent b is determined from the slope of the log-log plot of peak current versus scan rate. A b value of 0.5 signifies a diffusion-controlled process, while a value of 1 indicates a fully capacitive process. If b falls between 0.5 and 1, it suggests a mixed mechanism involving both capacitive and diffusion-controlled contributions.

To further analyze the capacitive contribution, the power law equation can be decomposed into two distinct components—surface capacitive and diffusion-controlled processes- following the Dunn method. This is expressed in **Equation S9**:

$$I_p = K_1 v + K_2 v^{1/2}$$
 S9

where k1 and k2 are constants at a given potential. Here, k1v represents the capacitive contribution, while  $K_2 v^{1/2}$  corresponds to the diffusion-controlled contribution.

#### 4. Computational Details

First-principles calculations are performed using VASP computational code based on density functional theory. Plane-wave basis set<sup>6</sup> we have applied for the total energy calculations, where all the plane waves are expanded within a maximum cut-off energy i.e., a kinetic energy cut-off of 520 eV. To determine the total energy of the given system convergence criteria are set to be 1E-6 eV for the electronic and ionic relaxation and -0.01 eV/Å for the ionic force convergence. The exchange-correlation function is approximated by the well-known Generalized Gradient Approximation type (GGA) with Perdew–Burke–Ernzerhof (PBE13)

functional<sup>7</sup>. The projected Augmented Wave (PAW) method is introduced to treat the interaction between frozen core and valence electrons<sup>8</sup>. Effects of long-range weak Vander Waal forces among H, Co, Br, N, C and O atoms are added in the calculations by introducing the Grimme DFT-D2 dispersion scheme. To improve the interaction of d electrons in the system a correction term U<sup>9</sup> (LDAUTYPE=2) is added. In the reciprocal k-space, to sample the Brillouin zone, we have chosen Gamma centre sampling method, in both cases optimization and DOS calculations of the proposed systems.



Figure S1: Optical photographs of synthesized poly(1-butyl-3-vinylimidazolium bromide).



**Figure S2:** <sup>1</sup>H NMR data of poly(1-butyl-3-vinylimidazolium bromide (poly(ionic liquid)s, PIL-Br).



Figure S3: Photographs of the PIL-Co-150 nanosheets dispersed before and after standing for hours.



Figure S4: Zeta potential for the three prepared PIL-Co composites, which sows the zeta potential in water media in the neutral pH.



**Figure S5:** Contact angle Measurement which clearly shows the decreasing of contact angle by increasing hydrothermal temperature 120°,150° and 180°C.



Figure S6: XRD of PIL-Br which clearly shows the polycrystalline in nature.



**Figure S7:** (a,b) Low and high magnification FE-SEM images of Bare-Co (OH)<sub>2</sub>. (c) FE SEM-EDX colour maping of Bare- Co(OH)<sub>2</sub> showing the distribution of Oxygen and Cobalt.



**Figure S8:** Low and magnification FE SEM-EDX colour mapping of PIL-Co-120 showing the distribution of C, N,O, Br and Co.



**Figure S9:** Low magnification FE SEM-EDX colour maping of PIL-Co-150 showing the uniform distribution of C,N,O,Br and Co.



**Figure S10:** Low magnification FE SEM-EDX colour maping of PIL-Co-180 showing the distribution of C,N,O,Br and Co.



Figure S11: XPS survey spectra of PIL-Co hexagonal crystal revealing the presence of a new peak in C 1s and N 1s regions.



Figure S12: (a, b) Cyclic voltammetry and charge-discharge curve of PIL-Co-120 at different scan rates and current densities.



Figure S13: (a, b) Cyclic voltammetry and charge-discharge curve of PIL-Co-150 at different scan rates and current densities.



Figure S14: (a, b) Cyclic voltammetry and charge-discharge curve of PIL-Co-180 at different scan rates and current densities.



**Figure S15:** Comparison of specific capacitance for PIL-Co-120, PIL-Co-150 and PIL-Co-180 at different scan rates.



Figure S16: Differentiating capacitance contribution from CV curves at a scan rate of  $50 \text{ mV s}^{-1}$ .



Figure S17: CV and GCD of ACs.



Figure S18: XRD of PIL-Co-150 and PIL-Co-150 after analysis.



**Fig. S19**: (a), (b) and (c) show the binding energy of Br with PIL having one monomer at different positions of Br with respect to PIL. (a) shows more binding than (b) and (c) cases.



**Fig. S20**: (a), (b) and (c) show the adsorption energy of PIL having one monomer, Br and ultrathin layer of Co(OH)<sub>2</sub> at different positions of Br with respect to PIL. (c) shows the better adsorption over (a) and (b) cases.

SI. No	Materials	Morphology	Electrolyte	Specific Capacitance	Current density	Referenc e
1	IL-Co(OH) <sub>2</sub>	Porous	3M KOH	859 F/g	1 A/g	10
		nanostructure				
2	CoNi-	nanoarrays	1M KOH	1430.4 C/g	1 A/g	11
	LDH@PCPs					
3	NiCo-LDH-	nanosheet	0.1M KOH	1489 F/g	1 A/g	12
	graphene					
4	Co <sup>II</sup> Co <sup>III</sup> –	LDH	0.1M KOH	1490 F/g	0.5 A/g	13
	CO <sub>3</sub> LDH	platelets				
5	Nickel-	nanosheet	2M NaOH	1289 F/g	1 A/g	14
	cobalt-					
	aluminium					
	LHs					
6	Co(OH) <sub>2</sub>	Hexagonal	1M KOH	800 F/g	2 A/g	15
		nanosheet				
7	ACT/Co-Al	nanoarrays	6M KOH	977.3 F/g	2 A/g	16
	LDH					
8	Ni–Co	bouquets	3M KOH	714.8 F/g	1 A/g	17
	phosphides					
9	Co(OH) <sub>2</sub>	nanoarrays	1M KOH	1044 F/g	1 A/g	18
	MOF					
10	$Co_3O_4$	nanowires	30 wt %	1199 F/g	1 A/g	19
			КОН			
11	Co-MOF	nanoflakes	2M KOH	150 F/g	1 A/g	20
12	$Co_3O_4$	nanocrystal	2M KOH	742.3 F/g	0.5 A/g	21
13	$Co_3O_4$	nanofilms	2M KOH	1400 F/g	1 A/g	22
14	$Co_3O_4$	3D-nanonet	6M KOH	820 F/g	5  mV/s	23
15	$Co_3O_4$	nanostructure	1M LiOH	1693.2 F/g	1 A/g	24
	@MnO <sub>2</sub>	S	electrolyte			
16	Ph-Co <sub>3</sub> O <sub>4</sub>	nanosheet	6M KOH	1716 F/g	5 mV/s	2

Table S1: Comparison of	of specific capa	citance of PIL	$-Co(OH)_2 \text{ com}$	posite with	different
electrode materials					

17	PIL-	Hexagonal	2M KOH	1758 F/g	2 A/g	This
_	Co(OH) <sub>2</sub>	nanosheet				work

Sample code	$R_{s}\left(\Omega ight)$	$R_{p}\left(\Omega ight)$	C <sub>PE</sub> (µMho*s^N)
PIL-Co-120	2.23	1.82	482
PIL-Co-150	2.16	1.81	455
PIL-Co-180	3.32	1.79	449

Table S2: Comparison of EIS spectra for PIL-Co composites

## References

- 1 Y. Shao, M. F. El-Kady, J. Sun, Y. Li, Q. Zhang, M. Zhu, H. Wang, B. Dunn and R. B. Kaner, *Chemical Reviews*, 2018, **118**, 9233–9280.
- T. Zhai, L. Wan, S. Sun, Q. Chen, J. Sun, Q. Xia and H. Xia, *Advanced Materials*, 2017, 29, 1–8.
- 3 X. Chen, S. Wang, G. Qiao, G. Lu, H. Cui and X. Wang, *Energy and Fuels*, 2020, **34**, 16783–16790.
- J. S. Wei, C. Ding, P. Zhang, H. Ding, X. Q. Niu, Y. Y. Ma, C. Li, Y. G. Wang and H.
   M. Xiong, *Advanced Materials*, 2019, **31**, 1–7.
- 5 M. D. S. Michael, K. S. Kesavan and S. R. S. Prabaharan, *Energy Technology*, 2021, 9, 1–12.
- 6 G. Kresse and J. Furthmüller, *Computational Materials Science*, 1996, **6**, 15–50.
- J. P. Perdew, K. Burke and M. Ernzerhof, *Physical Review Letters*, 1996, 77, 3865– 3868.
- 8 A. Allouche, *Journal of computational chemistry*, 2012, **32**, 174–182.
- 9 S. Dudarev and G. Botton, *Physical Review B Condensed Matter and Materials Physics*, 1998, **57**, 1505–1509.
- B. G. Choi, M. Yang, S. C. Jung, K. G. Lee, J. G. Kim, H. Park, T. J. Park, S. B. Lee,
   Y. K. Han and Y. S. Huh, ACS Nano, 2013, 7, 2453–2460.

- W. Wang, Y. Lu, M. Zhao, R. Luo, Y. Yang, T. Peng, H. Yan, X. Liu and Y. Luo, ACS Nano, 2019, 13, 12206–12218.
- J. Yang, C. Yu, C. Hu, M. Wang, S. Li, H. Huang, K. Bustillo, X. Han, C. Zhao, W.
   Guo, Z. Zeng, H. Zheng and J. Qiu, *Advanced Functional Materials*, 2018, 28, 1–11.
- P. Vialat, C. Mousty, C. Taviot-Gueho, G. Renaudin, H. Martinez, J. C. Dupin, E. Elkaim and F. Leroux, *Advanced Functional Materials*, 2014, 24, 4831–4842.
- X. Wang, C. Yan, A. Sumboja, J. Yan and P. S. Lee, *Advanced Energy Materials*, 2014, 4, 1–7.
- T. Deng, W. Zhang, O. Arcelus, J. G. Kim, J. Carrasco, S. J. Yoo, W. Zheng, J. Wang,
  H. Tian, H. Zhang, X. Cui and T. Rojo, *Nature Communications*, ,
  DOI:10.1038/ncomms15194.
- Z. Gao, C. Bumgardner, N. Song, Y. Zhang, J. Li and X. Li, *Nature Communications*, 2016, 7, 1–12.
- 17 B. Li, Y. Shi, K. Huang, M. Zhao, J. Qiu, H. Xue and H. Pang, *Small*, 2018, 14, 1–7.
- 18 T. Deng, Y. Lu, W. Zhang, M. Sui, X. Shi, D. Wang and W. Zheng, Advanced Energy Materials, 2018, 8, 1–7.
- R. B. Rakhi, W. Chen, D. Cha and H. N. Alshareef, *Nano Letters*, 2012, 12, 2559–2567.
- F. Meng, Z. Fang, Z. Li, W. Xu, M. Wang, Y. Liu, J. Zhang, W. Wang, D. Zhao and
   X. Guo, *Journal of Materials Chemistry A*, 2013, 1, 7235–7241.
- X. Wang, A. Sumboja, E. Khoo, C. Yan and P. S. Lee, *Journal of Physical Chemistry* C, 2012, 116, 4930–4935.
- C. Feng, J. Zhang, Y. He, C. Zhong, W. Hu, L. Liu and Y. Deng, ACS Nano, 2015, 9, 1730–1739.
- 23 Y. Wang, Y. Lei, J. Li, L. Gu, H. Yuan and D. Xiao, ACS Applied Materials and Interfaces, 2014, 6, 6739–6747.
- 24 D. Kong, J. Luo, Y. Wang, W. Ren, T. Yu, Y. Luo, Y. Yang and C. Cheng, Advanced Functional Materials, 2014, 24, 3815–3826.