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Electronic Supplementary information for

PIM-1-based carbon-sulfur composites for sodium-sulfur batteries that operate without shuttle effect

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Experimental

1. Materials

Potassium carbonate (99.99%, Sigma-Aldrich), dimethylformamide (DMF, Burdick & Jackson), tetrahydrofuran (THF, J. T. Baker), Sulfur (>99.5%, Sigma-Aldrich) and ethanol (95%, SAMCHEN Chemicals) were used as purchased. 5,5’,6,6’-Tetrahydroxy-3,3,3’,3’-tetramethyl-1,1’-spirobisindane (TTSBI, >97%, TCI) was recrystallized by addition of methylene chloride to clear TTSBI solution dissolved in MeOH. Tetrafluoroterephthalonitrile (TFTPN, >98%, Matrix Scientific) was purified by sublimation at 150 °C under low pressure.

2. Synthesis of Polymers of intrinsic microporosity (PIM-1)

PIM-1 was synthesized as described in our previous paper.[45] All the glassware was dried in an oven prior to use. Under a nitrogen atmosphere, a mixture of TTSBI (10.21 g, 30 mmol), TFTPN (6.00 g, 30 mmol), and anhydrous K_2CO_3 (8.29 g, 60 mmol) were dissolved in DMF (210 mL) in a reaction flask, and then it was put into pre-heated oil bath at 55 °C and maintained for 3 days. The mixture was then cooled and THF was added to the flask for removing low molecular fraction. The resulting yellow polymer was dissolved in THF and re-precipitated in methanol and H_2O, respectively. The synthesized PIM-1 powder was dried in a vacuum oven for 3 days. Yield : 10.3 g (74.6%). ^{1}H NMR (500 MHz,$CDCl_3$): δ_H (ppm) = 6.80 (2H, s), 6.41(2H, s), 2.46 - 2.04 (4 H, dd), 1.45-1.16 (12H, br); Molar mass (Determined from GPC): *Mn* = 60 900, *Mw* = 96 200, PDI = 1.58, Anal. Cald for $C_{29}H_{20}N_2O_4$ (wt%) : C, 75.64; H, 4.38;

N, 6.08; O 13.90. Found: C, 74.20; H, 4.40, N, 6.20; O, 14.10%. BET surface area = 735 m^2g^{-1}; total pore volume = 0.57 cm^3 g^{-1} at (p/p^0 = 0.99)

3. Preparation of carbonized PIM-sulfur composites (cPIMS)

The PIM based carbon-sulfur composites were synthesized though one-step heating process. The heating process was divided by following two temperature regions. The first region was melt diffusion process. After mixing the grounded PIM-1 powder and elemental sulfur in a 1:5 weight ratio, the mixture was transferred into an alumina boat and then heated at 155 °C in tube furnace under the inert atmosphere (N_2 flow, 100 cc/min) with a heating rate of 5 °C min^{-1}. After the impregnation of sulfur into the free volume of PIM-1 powder, a second successive heat treatment was proceeded without any transfer process. For cPIMS series, different second temperature was applied to optimize sulfur contents and thermal properties in tube furnace under the inert atmosphere (N_2 flow, 100 cc/min) with a heating rate of 5 °C min^{-1}, denoted as cPIMS-X and where X was the applied second temperature. (see Table S1) In the case of cPIMS-600 sample, the second temperature was set to 600 °C. During these heating process, thermal crosslinking between sulfur and the polymer matrix and carbonization of the polymer was occurred. In addition, by holding at the final temperature of 600 °C, it was intended that residual sulfur, physically confined in micropore but not chemically connected with carbonized PIM matrix, was removed and the only chemically connected sulfur remained in carbon host, where the sulfur content was about 30%, confirmed by elemental analysis (EA). The sulfur carbon composites was denoted as cPIMS-600 for convenience.

4. Characterization Methods

The morphologies of cPIMS-600 were observed by using a field emission scanning electron microscope (FE-SEM, Carl Zeiss, SigmaHD) and a high-resolution transmission electron microscope (HR-TEM). A field emission transmission electron microscopy (FE-TEM) and energy-dispersive X-ray spectroscopy (EDXS) were used for microstructure characterization and elemental mapping, respectively. ^{1}H nuclear magnetic resonance (NMR) spectra of PIM-1 was recorded on a Bruker AVANCE 500 MHz spectrometer using $CDCl_3$ solvent. Number-average molecular weight (*Mn*), weight-average molecular weight (*Mw*) and polydispersity index (PDI) of PIM-1 were measured by size exclusion chromatography (SEC) in THF, using Shodex columns (KF-800 series) operating at 40 °C. The chromatogram was detected with Wyatt WREX-06 (differential refractive index, RI). Infrared spectra of PIM-1 was recorded as KBr pellet using a Bruker ALPHA-T spectrometer, which was scanned 128 times at a resolution of 4 cm^{-1} in the range 4000 - 500 cm^{-1}. Raman spectra of cPIM-600 and cPIMS-600 samples were characterized using a LabRam Aramis Raman Spectrometer (Horiba Jobin Yvon), equipped with 514 nm Ar-ion laser Elemental analysis was obtained on a Thermo Scientific FLASH EA-2000 Organic Elemental Analyzers. Thermogravimetric analysis (TGA) was performed on Pyris 1 TGA thermogravimetry analyzer. Each sample was heated from ambient temperature to 800 °C under nitrogen flow at heating rate of 10 °C min^{-1}. The X-ray diffraction (XRD) pattern of each polymer was collected on Rigaku Ultima IV Diffractometer, equipped with Graphite-Monochromator and using Cu Kα radiation ($\lambda = 1.5406$ Å). The 2θ scanning range was 10-70° with a scanning speed of 3°/min. The pore characteristics such as surface area and total pore volume of PIM-1, cPIM-600 and cPIMS-600 were calculated with Micromeritics ASAP 2020 instrument. Each sample was dried at 60 °C in vacuum oven and then degassed for 30min at 90 °C and for 24h at 200 °C before analysis. XPS measurements were conducted with AXIS NOVA (KRATOS) with 150 W monochromatic Al-Kα radiation. The time of flight secondary ion mass spectrometer (TOF-SIMS) analysis were conducted using TOF-SIMS5 (IONTOF).

5. Electrochemical characterization

PIM based carbon-sulfur composite electrode was produced by the ratio of 8:1:1 with conducting carbon (Super P) and Polyvinylidene fluoride (PVdF) binder dispersed in NMP. The slurry was casted on aluminum current collector by approximately 1.7 mg cm^{-2}. Galvanostatic cycling and cyclic voltammetry were conducted at 167.5 mA g^{-1} (1/10 C of theoretical capacity of sulfur) and 0.5 mV s^{-1} in the voltage range of 0.5 – 2.8 V (vs. Na/Na^+) using TOYO (TOSCAT–3100, Japan) and WBCS3000 (WonATech, Korea) at 30 °C. Electrochemical impedance spectroscopy was conducted with SP-150 (BioLogic, France). The tests were conducted with 2032 coin type cells with sodium metal (Sigma Aldrich) counter electrode, glass fiber separator and 1.0 M $NaClO_4$ in the mixture solvent of ethylene carbonate (EC) and propylene carbonate (PC) (1:1 v:v) + 2 wt% fluoroethylene carbonate (FEC). FEC was added for protecting sodium metal from electrolyte decomposition.

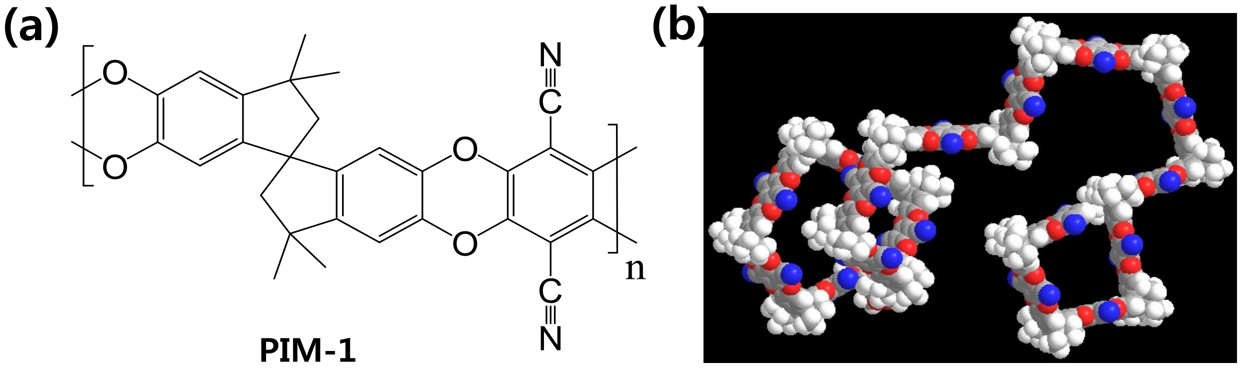


Fig. S1 (a) Chemical structure and (b) 3D structure of PIM-1 (polymers of intrinsic microporosity).

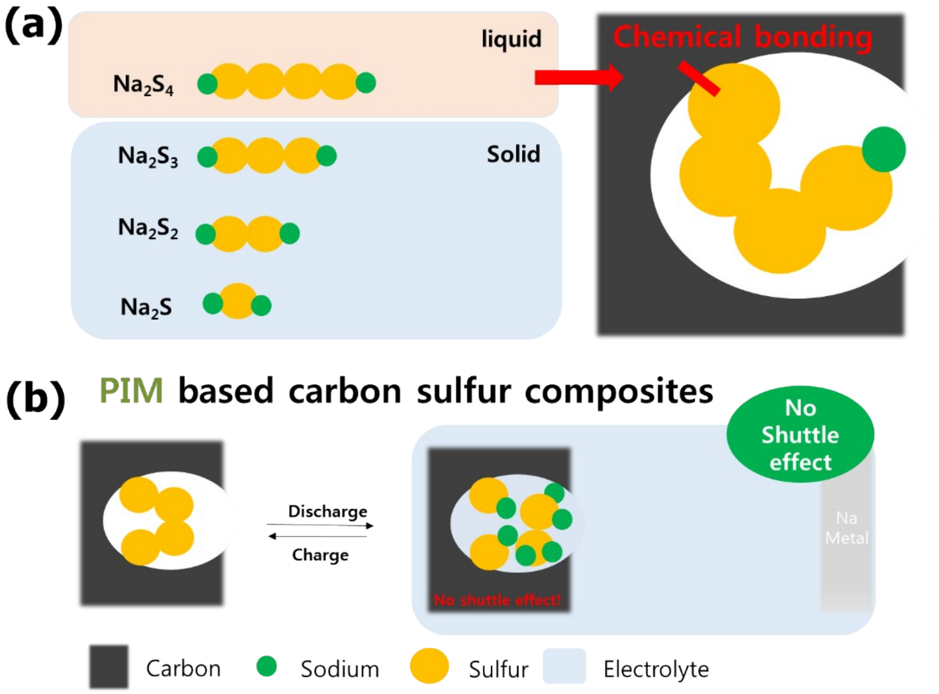
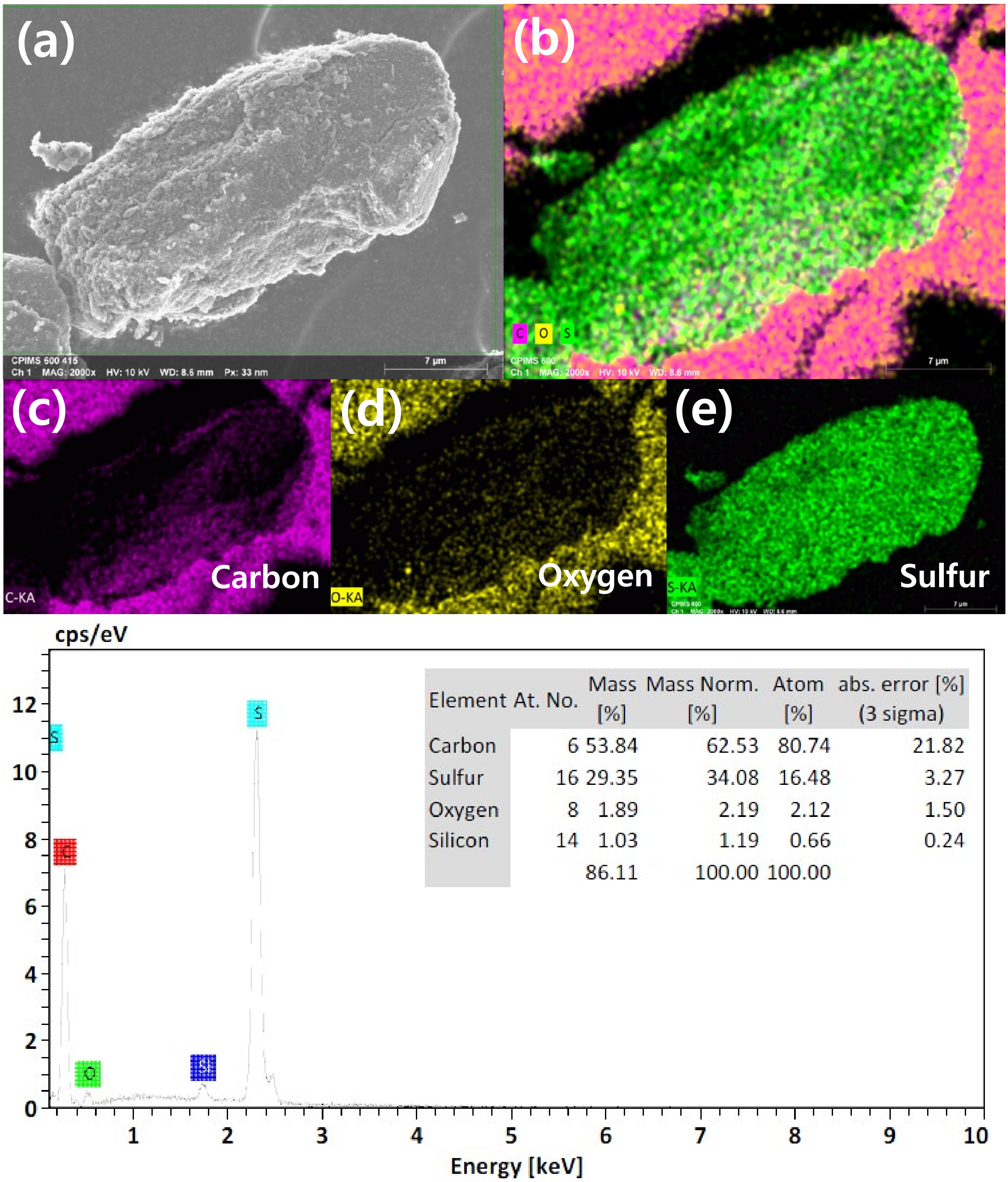


Fig. S2 Schematic images of (a) the concepts for PIM based carbon sulfur composites and (b) PIM based carbon sulfur composites that can operate without shuttle effect.



Element	At. No.	Mass [%]	Mass Norm. [%]	Atom [%]	abs. error [%] (3 sigma)
Carbon	6	53.84	62.53	80.74	21.82
Sulfur	16	29.35	34.08	16.48	3.27
Oxygen	8	1.89	2.19	2.12	1.50
Silicon	14	1.03	1.19	0.66	0.24
		86.11	100.00	100.00	

Fig. S3 SEM images and elemental distribution analyses of cPIMS-600 composites: a) SEM image of the cPIMS-600 composite, b) elemental maps for overlay of the carbon, oxygen, and sulfur maps, (c) carbon(magenta), (d) oxygen (yellow), (e) sulfur (green) and (f) EDS elemental composition analysis of the surface of cPIMS-600.

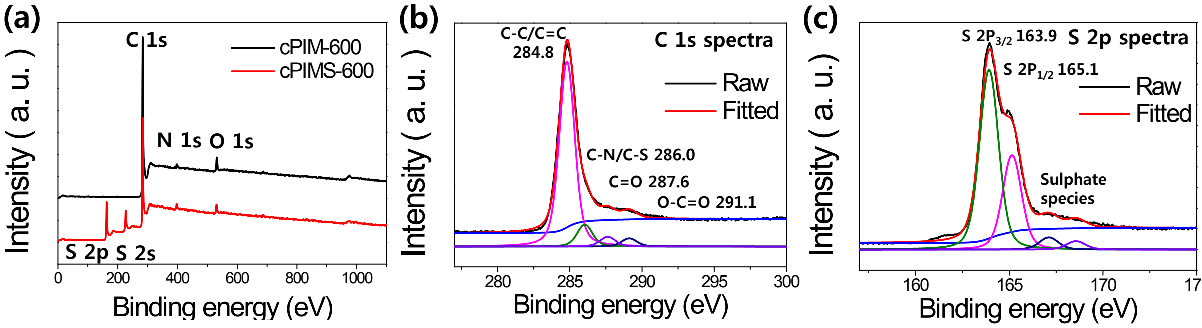


Fig. S4 XPS spectra of cPIMS-600. (a) Survey scan, (b) C 1s spectra and (c) S 2p spectra of cPIMS-600.

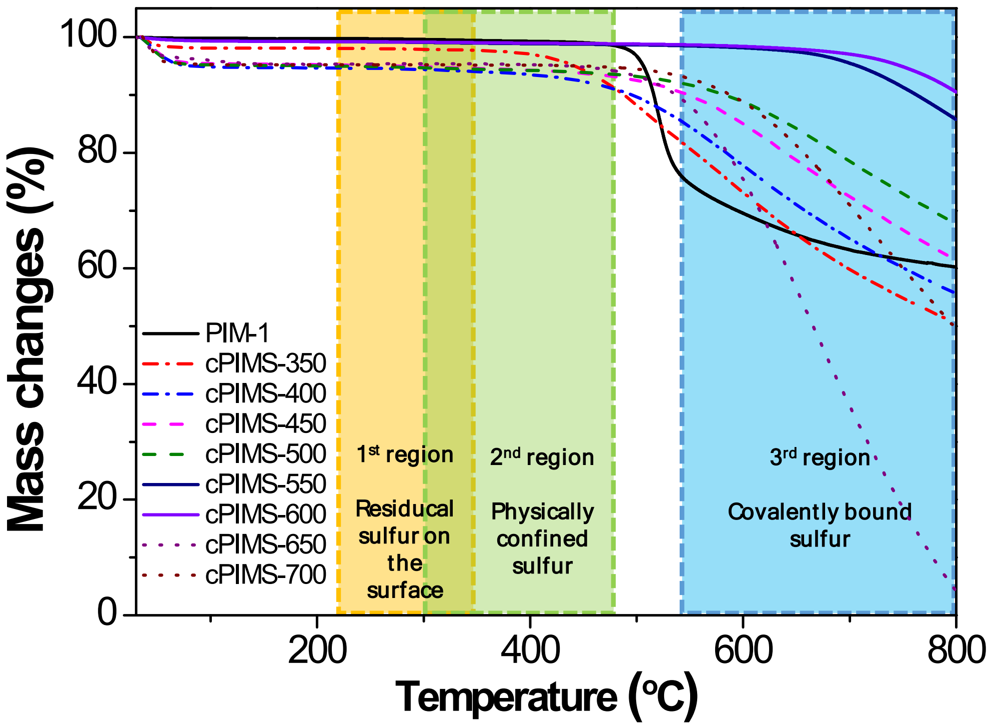


Fig. S5 TGA curves of cPIMS with a final temperature change.

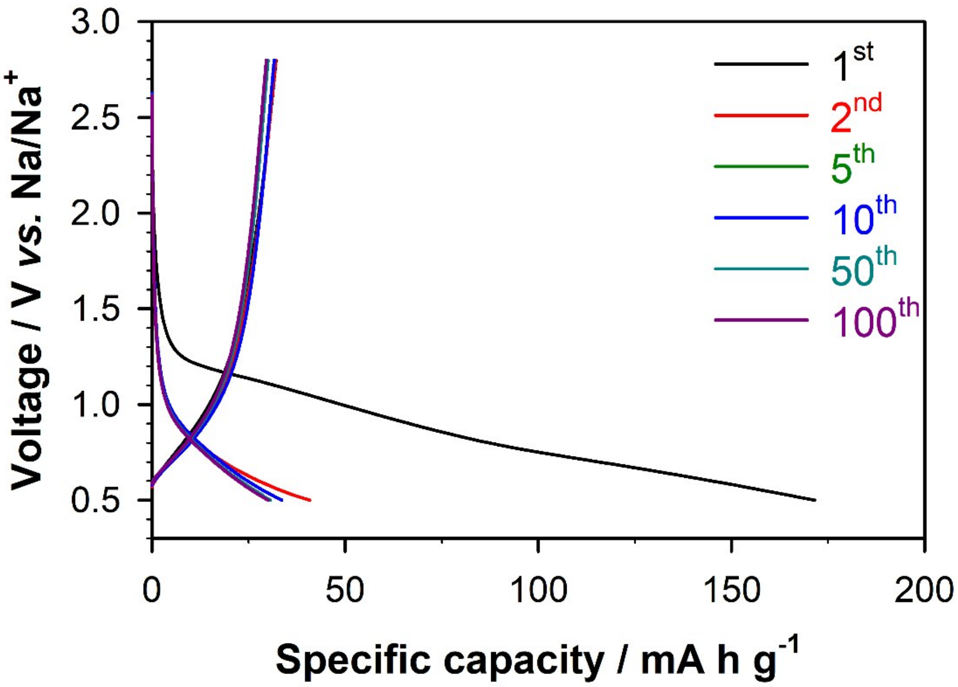


Fig. S6 The voltage profiles of PIM-600 using 1.0 M $NaClO_4$ in EC:PC (1:1 v:v) electrolyte without 2 wt% fluoroethylene carbonate (FEC) for 100 cycles.

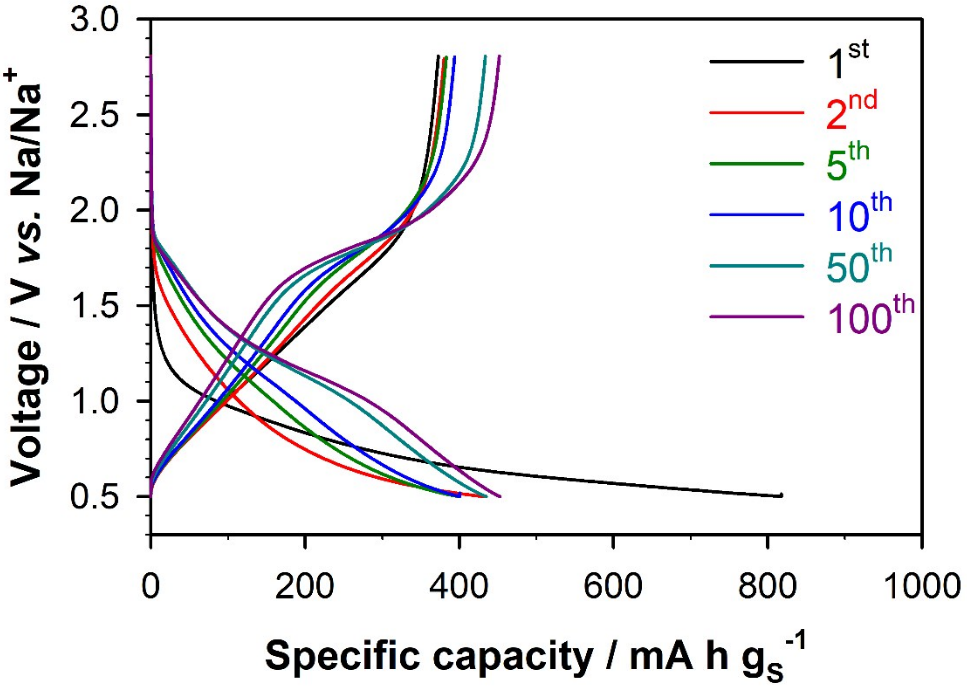


Fig. S7 The voltage profiles of cPIMS-600 using 1.0 M $NaClO_4$ in EC:PC (1:1 v:v) electrolyte without 2 wt% fluoroethylene carbonate (FEC) for 100 cycles at 0.1 C.

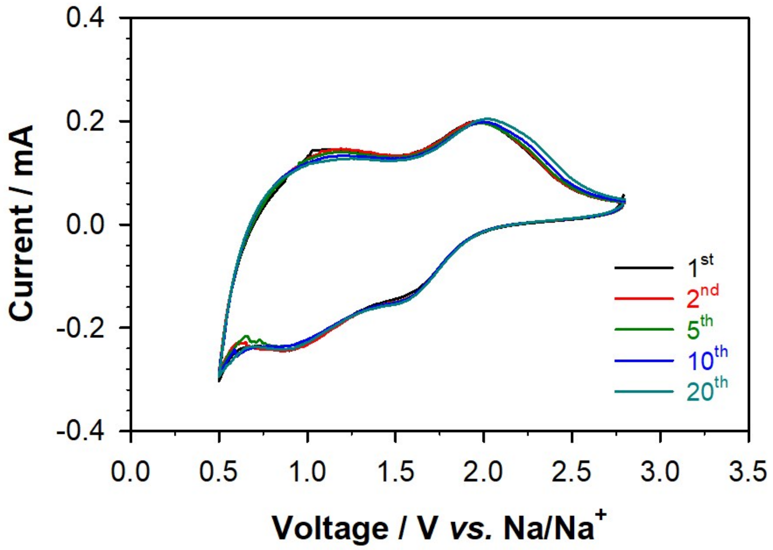


Fig. S8 Cyclic voltammetry of cPIMS-600 after 10cycle with a scan rate of 0.5 mV s^{-1}.

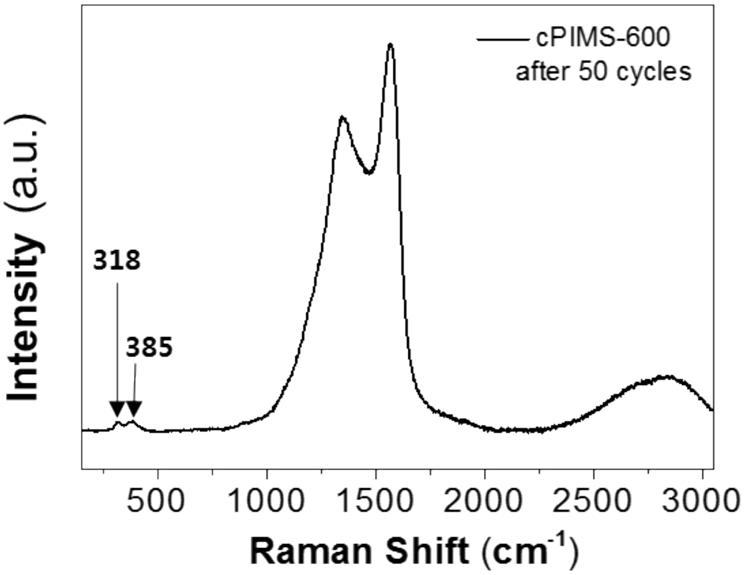


Fig. S9 Raman spectra of cPIMS-600 after 50 cycles.

Table S1. Variation in the chemical composition of cPIMS samples with a final temperature change

	C(%)	**H(%)**	**N(%)**	**S(%)**	**O(%)**	**Total**
cPIMS-350	64.6	2.4	5.3	11.8	11.7	95.8
cPIMS-400	62.3	1.5	4.5	16.3	10.6	95.2
cPIMS-450	62.7	1.2	3.6	19.7	6.1	93.3
cPIMS-500	63.6	0.9	3.4	23.4	5.2	96.5
cPIMS-550	62.1	0.6	3.4	29.5	2.5	98.1
cPIMS-600	63.5	0.4	3.6	29.2	1.3	98.0
cPIMS-650	78.5	1.1	2.5	13.6	6.5	102.2
cPIMS-700	77.8	0.5	1.9	14.6	6.2	101.0

Table S2. Pore characteristics of cPIM-600 and cPIMS-600

	S_{BET} (m^2 g^{-1})	S_{micro} (m^2 g^{-1})[a]	V_{micro}(cm^3 g^{-1})[a]	V_{total}(cm^3 g^{-1})[b]
PIM-1	735	632	0.357	0.573
cPIM-600	387	361	0.156	0.247
cPIMS-600	219	185	0.067	0.16

a) Micropore surface area and volume calculated from t-plot method.

b) Total pore volume.