Supporting Information of

Control of pore distribution of porous carbons derived from Mg²⁺ porous coordination polymers

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Experimental section

Preparation of PCPs

 $[Mg_4(1,3-bdc)_3(HCOO)_2(DMF)_2]_n$ (Mg-C2'), $[Mg_3(1,4-bdc)_3(EtOH)_2]_n$ (Mg-C2), $[Mg_3(btc)_2(DMF)_4]_n$ (Mg-C3), and $\{[Mg_2(btec)(H_2O)_4] \cdot 2H_2O\}_n$ (Mg-C4) were synthesized according to reported procedure.¹ Mg-C2', Mg-C2, and Mg-C4 were degassed at 150 °C, 200 °C, and 150 °C, respectively, for overnight in vaccum oven. Mg-C3 was soaked in methanol for 3 day, during which time the solvent was decanted and freshly replenished three times, and then degassed at 150 °C for overnight in vaccum oven.

Syntheses of porous carbons

Raw carbons were synthesized by carbonization of degassed PCPs under a flow of nitrogen (200 mL min⁻¹) at 800 °C for 5 h. Typically, degassed sample (300 mg) was homogenously placed on a ceramic boat ($16 \times 12 \times 80$ mm) and heated up to the targeted temperature with heating rate of 5 °C min⁻¹. Purified carbons were obtained by stirred in 3 M HCl solution for overnight and washed repeatedly with distillation water.

Characterizations

Powder X-ray diffraction (PXRD) data were collected on a Rigaku RINT 2200 Ultima diffractrometer with Cu $K\alpha$ radiation. Thermogravimetric analyses combined with mass spectrometry (TG-MS) were performed on a Rigaku Thermo plus EVO II equipped with ThermoMass Photo/S by using electron impact ionization (EI) method. All samples were measured from 40 °C to 800 °C with heating rate of 5 °C min⁻¹ under Helium flow

atmosphere. Nitrogen adsorption isotherms were measured at -196 °C (77 K) by BELSORP-mini with a liquid nitrogen dewar. All samples were activated by heating at 180 °C under reduced pressure (< 10^{-2} Pa) for 12 h prior to the measurement. Raman spectra were collected at room temperature by using a LabRAM HR800 (Horiba Jobin Yvon) with a semiconductor laser at 488 nm. Transmission electron microscopic (TEM) observations were performed by using JEOL JEM1400D. TEM specimen was prepared by dropping methanol solution containing the sample on a Cu grid.

Capacitance measurements

The capacitor performance for the carbon samples was performed with two-electrode cell (Hosen Corp.) in 1 M Et₄NBF₄/PC. The working electrode were prepared by mixing the carbon samples with poly(tetrafluoroethylene) (PTFE; M-139, Daikin industries, Ltd.) and carbon black (Denka black, Denki Kagaku Kogyo Kabushiki Kaisha). The weight ratio of carbon sample: PTFE: carbon black = 80: 10: 10. The mixture was dried at 150 °C for 3 h in vaccum and then electrode disk was molded diameter of 10 mm by using a tablet machine under a pressure of 30 M Pa for 5 min. The two electrode cell was fabricated with Al current collector (100 mesh), the electrode disk, a grass paper as separator (ADVANTEC GA-100), and 1 M Et₄NBF₄/ PC under inner atmosphere. The CV curves were recorded by VersaSTAT-4 electrochemical system (Toyo Corp. Ltd.) between 0 and 2.0 V at 2–50 mV s⁻¹. The gravimetric capacitance (C_g) calculated from the CV curve is based on the following equation:

$$C_{\rm g} = 2 \times \Delta Q / (\Delta V \times m)$$

Where ΔQ is the charge integrated from the whole voltage range, ΔV is the whole voltage difference, and *m* is the mass of carbon on electrode. The volumetric capacitance (C_v) were calculated by the equation, $C_v = C_g \rho$, where ρ is the particle density of carbon.²



Figure S1 Simulated (gray line), as-synthesized (solid line) and degassed (dotted line) PXRD patterns of Mg-R, R = (a) C2' (b) C2 (c) C3 (d) C4, respectively.



Figure S2 N₂ adsorption isotherms of C-Mg-R, R = C2' (red circles), C2 (black circles), C3 (blue circles), and C4 (green circles).



Figure S3 PXRD patterns of PC-Mg-R, R = C2' (red), C2 (black), C3 (blue), and C4 (green).



Figure S4 Raman spectra of PC-Mg-R, R = C2' (red), C2 (black), C3 (blue), and C4 (green).

| Table ST fore studence properties of 10 -Mg-K, $K = 02$, 02 , 03 and 04 , and $MS0-50$. | | | |
|---|----------------------------------|--------------------------------|---------------------------------|
| Samples | Surface area ^{<i>a</i>} | Total pore volume ^b | peak pore diameter ^c |
| | (m^2g^{-1}) | $(cm^{3}g^{-1})$ | (nm) |
| PC-Mg-C2' | 968 | 0.95 | 16.4 |
| PC-Mg-C2 | 1013 | 1.66 | 10.9 |
| PC-Mg-C3 | 1108 | 0.97 | 5.0 |
| PC-Mg-C4 | 1996 | 1.84 | 3.5 |
| MSC-30 | 3170 | 1.68 | < 2.5 |

Table S1 Pore structure properties of PC-Mg-R, R = C2', C2, C3 and C4, and MSC-30.

^a The specific surface area was calculated using Brunauer-Emmett-Teller (BET) method.

^{*d*} Total pore volume was calculated using the BET method ($P/P_0 = 0.99$).

^c Peak pore diameter was obtained from Barrett-Joyner-Halenda (BJH) method.



Figure S5 Pore distributions with BJH method between MSC-30 (black dotted) and PC-Mg-R, R = C2' (red), C2 (black), C3 (blue), and C4 (green).

References

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- (2) Itoi, H.; Nishihara, H.; Kogure, T.; Kyotani, T. J. Am. Chem. Soc. 2011, 133, 1165.