Supporting Information

An Asymmetric Supercapacitor–Diode (CAPode) for Unidirectional Energy Storage

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**Experimental part**

**Materials.** Novoloid based active carbon fiber ACC-5092-10 (C0.87) and ACC-5092-15 (C1.00) were provided by Kynol Europe GmbH. Pitch based active carbon fiber A7 (C0.60) was supplied by AD’ALL Co (Japan). The label subscript x in Cx indicates the peak pore size of the respective carbon materials. C0.87 indicates a peak pore size distribution centered at 0.87 nm. Mesoporous CMK-3 (C4.80) is prepared based on a hard-templating method. The synthesis of CMK-3 (C4.80) was reported elsewhere. Generally, SBA-15 was firstly prepared. Then 2 g of the prepared silica was infiltrated with a solution of 2.5 g sucrose (from AppliChem) and 10 ml deionized water with subsequent adding of 0.28 g concentrated sulfuric acid. Afterwards, the mixture is heated to 100 °C and annealed for 3 h at 100 °C and 160 °C, respectively. This process is repeated in the following step with a solution containing 1.6 g sucrose, 10 mL water and 0.18 g concentrated acid. Hereafter, the obtained black polymer is carbonized at 900 °C for 2 h under Ar atmosphere (150 K h⁻¹) followed by HF etching to remove the silica template. The final product was washed and dried.

All chemicals were used as received.

**Characterization.** Nitrogen physisorption was measured volumetrically at 77 K on a BELSORP apparatus. Ar physisorption experiments were conducted with an AUTOSORB-iQ-C-XR from Quantachrome at 87 K. The Brunauer-Emmett-Teller (BET) method was used to calculate the specific surface area based on the adsorption data in the partial pressure range 0.05 < P/P₀ < 0.20 and the total pore volume was estimated from the cumulative values based on density functional theory (DFT). Micropore volumes were calculated via DFT methods using the cumulative pore volume up to 2 nm. The pore size distributions (PSDs) were calculated using the equilibrium branches of the isotherms based on Non-Localized Density Functional Theory (NL-DFT, slit pores) for microporous carbon and Quenched Solid Density Functional Theory (QSF-DFT, slit/cylindrical pores) for mesoporous carbons. For carbon isotherm analysis, Quenched Solid Density Functional Theory (QSF-DFT, cylindrical pores) for mesoporous carbon was used. Unless it is specifically noticed, the textural properties are derived from N₂ physisorption isotherms. Prior to measurements the samples were degassed at 150 °C for at least 12 h.

**MAS-NMR spectroscopy.** Carbon materials were loaded with an amount of 1M TBABF₄ dissolved in deuterated acetonitrile (d-AN) corresponding to their pore volume by the incipient wetness method. The volume of added electrolyte was calculated to fit the entire pore volume of studied materials. Solid state ¹H, ²H, and ¹¹B spectra were acquired using a Bruker AVANCE 300 spectrometer and 2.5 mm double-resonance (¹H, X) MAS NMR probe head. The ¹H spectra were referenced relative to tetramethylsilane (TMS). For ¹H experiments, 90° single pulse excitation was used with 3.75 µs pulse length and 3 s recycle delay. 8 scans were acquired. ¹¹B and ²H spectra were referenced relative to boron trifluoride and TMS, respectively. For ¹¹B and ²H experiments HPDEC pulse program was taken. Again, 90° single pulse excitation was used with pulse lengths of 4.9 µs and 6.05 µs for ¹¹B and ²H, respectively. 400 scans for ¹¹B experiments and 8 scans for ²H experiments with recycling delays of 3 s were acquired. During signal acquisition, SPINAL ¹H-decoupling was applied. All spectra were acquired at 16 kHz sample spinning rate.

**Electrochemical measurements.** The carbon electrodes were prepared by mixing 85 wt% carbon, 10 wt% carbon black (Sigma Aldrich) and 5 wt% polytetrafluoroethylene binder (PTFE, Sigma Aldrich) to yield a free standing film, of which 10 mm diameter discs were punched out and the thickness for microporous carbon is 50 µm and for mesoporous carbon is 100 µm separated by a glass-fiber separator (GF/D, Whatman) and placed on a carbon-coated titanium current collector (12 mm in diameter). A mass ratio of about 1:1 is used to ensure C₄.80 has enough space to balance the ions adsorbed in C₀.87. For the symmetric cells, the thickness of the electrodes is always maintained at 100 µm.

We used a VMP300 from Bio-Logic with cyclic voltammetry (CV), galvanostatic cycling with potential limitation (GCPL) and electrochemical impedance spectroscopy (EIS) to investigate the electrochemical performance. A custom-built polyether ether ketone (PEEK) cell with spring loaded titanium pistons was used for both symmetric and asymmetric setup. 1 M Tetraethyllammonium Tetrafluoroborate (TEABF₄, for electrochemical analysis, Sigma Aldrich), Tetrapropylammonium Tetrafluoroborate (TPABF₄, 98%, Sigma Aldrich) and tetrabutylammonium tetrafluoroborate (TBABF₄, for electrochemical analysis, Sigma Aldrich) dissolved in acetonitrile were used as the organic electrolytes (a voltage window from -2 to +2 V was chosen to avoid decomposition of the electrolytes in the negative range because the cations cannot penetrate into the small pores of the used microporous carbon and the charge on the carbon surface cannot be compensated), and 1 M H₂SO₄ (AnalaR NORMAPUR, 95%) as the aqueous electrolyte (-1 to +1 V). CVs were recorded with the respective electrolytes from 5 mV s⁻¹ to 500 mV s⁻¹ and galvanostatic charge-discharge tests for the organic electrolyte with current density from 0.1 A g⁻¹ to 20 A g⁻¹ were carried out in the range of 0 – 2 V and 0 – -2 V, respectively. EIS was conducted in a frequency range between 10 mHz and 100 kHz with a voltage amplitude of 10 mV.

The gravimetric capacitance is calculated via (1):

\[ C_{\text{spec}} = \frac{1}{V} \int_{V_1}^{V_2} \frac{1}{dV} \ dV \]  

(1)
Where \( C_{\text{spec}} \) is the integral specific capacitance (F g\(^{-1}\)) for a single electrode, \( \nu \) is the potential scan rate (mV s\(^{-1}\)), \( m \) is the mass of electroactive materials of a single electrode and \( I \) is the current response during the cycling (for the case of CAPode, the mass of electroactive materials of the working electrode is used). \( V_2 - V_1 \) is the corresponding voltage window used for capacitance calculations. Prior to the data analysis, the electrode was cycled 4 times and each measurement was repeated 4 times. The final calculation is based on the third cycle.

**In situ NMR spectroscopy.** The CAPode cells were prepared in the same way as the cells for electrochemical measurements. Assembled electric double layer capacitors were placed inside the coil of a special, single channel *in situ* NMR probe with a solenoid coil of 1 cm diameter and 2 cm length designed similarly as described by Wang.\(^{[11]}\) The probe was purchased from NMR Services (Erfurt, Germany) and connected to a potentiostat (Iviumstat from Ivium Technologies, Netherlands) with a two-electrode configuration. The capacitors were charged and discharged by applying a constant voltage until equilibrium is achieved. \(^{11}\)B spectra of CAPode cells were recorded. \(^{11}\)B NMR spectra were referenced relative to boric acid solution at 19.6 ppm. Pulse length for the 90° pulse was 7 \( \mu \)s. 400 scans were acquired.

*Figure S1.* Comparison of PSD of the microporous carbons derived from N\(_2\) physisorption.

*Figure S2.* \( \text{Ar} \) physisorption isotherms at 87K and the corresponding PSD for the carbon materials.

**Electrochemical performance of the symmetric supercapacitors**

**Symmetric cells of the individual materials.** In order to investigate the behavior of the individual materials, symmetric cells of \( C_{0.87} \) and \( C_{4.80} \) were built. Due to the well-defined mesoporous structure, \( C_{4.80} \) has a distinct rectangular CV characteristic for double layer capacitors (Figure S3a). Even at 200 mV s\(^{-1}\), the initial capacitance can still be 100% maintained (Figure S3c), manifesting the excellent rate capability of \( C_{4.80} \). Therefore, we can assume that ions can easily enter the pores. However, in the case of \( C_{0.87} \) (Figure S3b), the scenario changes completely. \( C_{0.87} \) has almost no capacitance (4.5 F g\(^{-1}\) at 5 mV s\(^{-1}\)). This is reasonable as most of the pores of \( C_{0.87} \) are smaller than TBA\(^+\) cations and only very few larger pores and external surface area contributes to capacity. Figure S3c and Table S2 also show the huge difference of the two materials in their electrochemical performances. The impedance spectroscopy in Figure S3d illustrates that the two electrode materials have almost the same internal resistance.
Figure S3. Electrochemical performance of the symmetric supercapacitors for C_{4.80} and C_{0.87}. (a) Cyclic voltammetry curves at different scan rates for C_{4.80}. (b) Cyclic voltammetry curves at different scan rates for C_{0.87}. It shares the same legend with a. (c) The capacitance comparison between C_{4.80} and C_{0.87} at varying scan rates. (d) Impedance spectra for both electrode materials.

In the case of C_{0.80} (Figure S4a), comparable electrochemical characteristics can be observed as for C_{0.87}, with tiny capacitance at very low voltage, corresponding to the small part of larger micropores (Figure S1, larger than C_{0.87}). The subsequent saturation of this small amount of larger pores leads to a decreased current, resulting in a negligible capacitance. However, for C_{1.00} (Figure S4b), the cell delivers a high capacitance, especially in the range of 0 – 1 V, but a highly distorted CV curve is detected in the whole measured range. Above 1 V, the capacity is significantly decreased, correlating well with the limited volume of large pores in C_{1.00} (Figure S1) and consequently the saturation. For the same reason, we observe an abrupt decrease of capacitance as the scan rate rises.

Figure S4. Electrochemical performances of the symmetric supercapacitors. (a) Cyclic voltammetry curves at different scan rates for C_{0.60}. (b) CV curves for C_{1.00} at varied scan rates.
Electrochemical performance of CAPode

Figure S5. Schematic illustration of charging mechanism for \( C_{0.87} \) taking into account partial accessibility for the large cations in larger pores.

Figure S6. Diode performance of CAPode \( C_{4.80} | TBABF_4(AN) | C_{0.87} \). (a) Rectification ratio I of the CAPode, the current for calculation chosen here is at 2 V and -2 V for positive charging and negative charging, respectively. (b) The capacitance ratio (Rectification ratio II) of the positive range to the whole voltage range at different scan rates for the CAPode.

Figure S7. Cycle stability of CAPode \( C_{4.80} | TBABF_4(AN) | C_{0.87} \) for 10th and 100th cycles.

Figure S8. Charging/discharging performance of CAPode \( C_{4.80} | TBABF_4(AN) | C_{0.87} \). (a), Galvanostatic charge-discharge curves at 0.1 A g\(^{-1}\) in for positive and negative bias, respectively. (b), the corresponding capacitance for comparison.
Figure S9. Electrochemical and diode performances of CAPode C_{4.80} | TBABF_{4}(d-AN) | C_{0.60}. (a) The capacitance ratio (Rectification ratio II) of the positive range to the entire voltage range at different scan rates for CAPode. (b) Comparison of the capacitances between symmetric supercapacitors and the CAPode at different scan rates. The capacitance for the CAPode is based on the positive part (0 - 2 V).

Figure S10. Configuration of the CAPode inside the NMR coil, only one electrode can be measured.

Figure S11. (a) $^{11}$B NMR spectra of CAPode (C_{4.80} | TBABF_{4}(d-AN) | C_{0.87}). The electrode C_{4.80} is studied. (b) Normalized integral of the $^{11}$B signal as a function of the applied voltage.

Table S1. Ion dimensions of cations and ions used as electrolytes

| Electrolyte | Ion size (without solvation shell) / nm |
|-------------|--------------------------------------|
| TBA$^+$     | 1.1$^{2, 3, 8}$, 1.26$^7$            |
| TPA$^+$     | 0.92$^8$                             |
| TEA$^+$     | 0.68$^{8, 8}$                        |
| BF$_4^-$    | 0.48$^{6, 6}$, 0.43$^5$              |
| H$^+$       | 0.12$^8$                             |
| SO$_4^{2-}$ | 0.29$^8$                             |
Table S2. Electrochemical characteristics of the respective symmetric cells and CAPode

| Cells          | Capacitance F g⁻¹ at |
|---------------|----------------------|
|               | 5 mV s⁻¹ | 10 mV s⁻¹ | 20 mV s⁻¹ | 50 mV s⁻¹ | 100 mV s⁻¹ | 200 mV s⁻¹ | 500 mV s⁻¹ |
| C₄.₈₀ | TBABF₄(AN) | C₄.₈₀  | 52.0  | 52.8  | 55.0  | 53.0  | 52.3  | 51.0  | 48.8  |
| C₀.₈₇ | TBABF₄(AN) | C₀.₈₇  | 4.5   | 4.0   | 3.1   | 2.5   | 2.4   | 2.0   | 1.5   |
| C₄.₈₀ | TBABF₄(AN) | C₀.₈₇  | 69.8  | 67.9  | 63.9  | 51.7  | 32.3  | 15.1  | 8.7   |

* the capacitance calculated is based on the mass of C₀.₈₇ and in the positive scan range (0 - 2 V)

Table S3. Physical and chemical properties of the used organic electrolytes.

| Electrolyte | Limiting molar conductivity ¹⁰, S cm² mol⁻¹ | standard partial molar volume ¹¹, cm³ mol⁻¹ | voltage window in mesopore*, V | voltage window in micropore*, V | transport rate ¹² |
|-------------|---------------------------------------------|---------------------------------------------|-------------------------------|-------------------------------|-------------------|
| TBA⁺        | 61.6                                        | 270.2                                       | -2.2                          | -2                            | slow              |
| TPA⁺        | 70.2                                        | 208.9                                       | -1.9                          | -1.7                          | intermediate      |
| TEA⁺        | 85.2                                        | 143.6                                       | -1.8                          | -1.6                          | quick             |
| BF₄⁻        | 108.5                                       | 49.7                                        | 0.7                           | 0.7                           |                   |

* the voltage window refers to a gold electrode, detailed in literature ¹³

References

[1] S. Jun, S. H. Joo, R. Ryoo, M. Kruk, M. Jaroniec, Z. Liu, T. Ohsuna, O. Terasaki, J. Am. Chem. Soc. 2000, 122, 10712-10713.
[2] J. M. Griffin, A. C. Forse, H. Wang, N. M. Trease, P. L. Taberna, P. Simon, C. P. Grey, Faraday Discuss 2014, 176, 49-68.
[3] M. E. Light, P. A. Gale, M. B. Hursthouse, Acta Cryst. E 2001, 57, a705-a706.
[4] J. Chmiola, C. Largeot, P. L. Taberna, P. Simon, Y. Gogotsi, Angew. Chem. Int. Ed. 2008, 47, 3392-3395.
[5] J. Huang, B. G. Sumpter, V. Meunier, Chem. - Eur. J. 2008, 14, 6614-6626.
[6] G. W. Sun, W. H. Song, X. J. Liu, D. H. Long, W. M. Qiao, L. C. Ling, Electrochim. Acta 2011, 56, 9248-9256.
[7] Y. Li, S. Roy, T. Ben, S. Xu, S. Qiu, Phys. Chem. Chem. Phys. 2014, 16, 12909-12917.
[8] J. D. Xu, Q. M. Gao, Y. L. Zhang, Y. L. Tan, W. Q. Tian, L. H. Zhu, L. Jiang, Sci. Rep. 2014, 4, 5545.
[9] C. Zhong, Y. Deng, W. Hu, J. Qiao, L. Zhang, J. Zhang, Chem. Soc. Rev. 2015, 44, 7484-7539.
[10] K. Gong, Q. Sang, S. Gu, S. F. Y. Li, Y. Yan, Energy Environ. Sci. 2015, 8, 3515-3530.
[11] Y. Marcus, Biophys. Chem. 1994, 51, 111-127.
[12] H. Banda, S. Pérelé, B. Daffos, L. Dubois, O. Crosnier, P. Simon, P.-L. Taberna, F. Duclainoir, Electrochim. Acta 2019, 296, 882-890.
[13] G. Moreno-Fernandez, S. Perez-Ferreras, L. Pascual, I. Llorente, J. Ibañez, J. M. Rojo, Electrochim. Acta 2018, 268, 121-130.