Electronic Supplementary Information (ESI)

Quantitative analysis of BF₄⁻ ions infiltrated into micro pores of activated carbon fibers using nuclear magnetic resonance

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1. Additional Experimental Details and Related Discussions

1.1. Characterization of Activated Carbon Fibers

The investigated activated carbon fibers (ACFs) were activated with steam in different ways by the suppliers (Osaka Gas Co. and Toho TENAX Co., Japan), so that the numbers following the acronyms of the suppliers mean the different steam activation conditions.¹

The porosities and chemical compositions of the investigated ACFs were characterized with N₂ adsorption/desorption method (BELSORP-Max, BEL Japan Inc.)

and elemental analysis (Yanako CHN-coder MT-5, Japan), respectively. The contents of C, H, O and N were determined by averaging three replica experimental values, and the assays of O were defined as the difference between the sum of the contents of other elements (C, H and N) and 100%.

Fig. S1 shows the nitrogen adsorption/desorption isotherms. As shown in Fig. S1, the surface area and porosity depended on the degree of steam activation. Specifically, as the degree of activation increased (i.e. OG5A < OG10A and FE100 < FE300), the specific surface area and average pore size increased from ~637 to ~1212 m²/g and from ~0.65 to ~0.78 nm, respectively (See Table 1 in the main text). With the higher degree of steam activation, the amount of oxygen in the ACFs increases, while that of nitrogen decreases. It is notable that the PAN-based FE ACFs were certainly nitrogen-richer than the pitch-based OG ACFs.



Fig. S1. N₂ adsorption/desorption isotherms at 77K of ACFs.

1.2. Electrochemical Measurement in Half-Cell Configuration

Electrochemical measurement in half-cell configuration, i.e., cyclic voltammetry, was performed to understand the electrochemical behavior of the ACFs. The cyclic voltammograms were measured using the conventional three-electrode system (HZ-3000 automatic polarization system, Hokuto Denko, Japan). The working electrode was a dried thin film of a mixture of an ACF (90 wt%) and polyvinylidene fluoride (10 wt%, SOLEF of Solvay Chemicals, Belgium) in N-methyl-2-pyrrolidone (Wako Pure Chemical Industries, Ltd., Japan). The cyclic voltammetry was performed in 1 M (Et₄N)⁺(BF₄)⁻/propylene carbonate (PC, Kishida Chemical Co., Japan) under a nitrogen atmosphere. The potentials were measured using a Ag/AgCl reference electrode ([Cl⁻] = 1 M). Note that Ketjen Black (a conductive material) and polytetrafluoroethylene (PTFE, a binder) was not added to the electrodes in half-cell configuration.

Fig. S2 shows the cyclic voltammograms of the ACFs in 1 M (Et₄N)⁺(BF₄)⁻/PC electrolyte. The ACFs with narrower pores (i.e., OG5A and FE100) did not show any capacitive current, implying that the electrolyte ions did not penetrate into the pores. On the other hand, the ACFs with wider pores (i.e., OG10A and FE300) presented considerable capacitive currents with a distortion between -1.3 and -0.3 V. The particular distortion in cyclic voltammograms may be due to a steric effect: a partial desolvation of the electrolyte ions to be squeezed in pores.^{2, 3} Indeed, OG and FE ACFs with large pores (~1 nm) did not show such a distortion (not shown here), implying no de-solvation.

The capacitance values of the investigated ACFs measured with the configurations of half-cell are listed in Table 1 in the main text. Although the specific values of each

ACF in the scrutinized organic electrolyte slightly depend on the measuring techniques (half-cell versus full-cell), the ACFs with larger pores were generally much more efficient, and the nitrogen-richer ACFs were less effective in capacitive charging.



Fig. S2. Cyclic voltammograms of ACFs in 1 M $(Et_4N)^+(BF_4)^-/PC$. Scan rate: 10 mV/sec

2. ¹¹B NMR Spectra of BF₄⁻ Ions on ACFs

Fig. S3 shows the ¹¹B NMR spectra of BF_4^- ions on ACFs. The sample preparation procedure for the ¹¹B NMR measurements of BF_4^- ions was identical to that for ¹⁹F NMR measurements. The chemical shifts in the ¹¹B spectra in Fig. S3 clearly demonstrate that the BF_4^- ions infiltrated into pores differed from the free ones. See the main text for discussion.



Fig. S3. ¹¹B NMR spectra of BF_4^- ions on (a) OG5A, (b) OG10A, (c) FE100 and (d) FE300 after impregnation and positive charging.

3. Quantification of BF₄⁻ Ions Infiltrated into Pores of ACFs

For measuring the ¹⁹F peak areas of the infiltrated BF_4^- ions, the spectra in Fig. 2 were de-convoluted as shown in Fig. S4. The reason for the manipulation is that the peaks for the infiltrated BF_4^- ions on FE300 were close to the peaks of the free BF_4^- ions. The normalized peak areas of the infiltrated BF_4^- ions were summarized in Table S1.



Fig. S4. Deconvoluted ¹⁹F NMR spectra of (a) impregnated OG10A and (b) positively charged OG10A, and (c) impregnated FE300 and (d) positively charged FE300.

	chemical shift (ppm)	normalized peak area	species
OG10A (impregnated)	-118	1.00	PTFE
	-148	0.61	free BF ₄ -
	-153	0.45	infiltrated BF4-
OG10A (positively charged)	-118	1.00	PTFE
	-148	0.69	free BF ₄ -
	-155	0.81	infiltrated BF4-
FE300 (impregnated)	-118	1.00	PTFE
	-148	0.40	free BF ₄ -
	-151	0.21	infiltrated BF4-
FE300 (positively charged)	-118	1.00	PTFE
	-148	0.50	free BF ₄ -
	-151	0.79	infiltrated BF4-

Table S1. The normalized peak areas of the infiltrated BF_4^- ions on OG10A and FE300.

The concentrations of the BF₄⁻ ions in pores were calculated using the normalized peak areas of BF₄⁻ ions as follows. The weight of the PTFE internal standard (10 wt%) was converted to the concentration of PTFE monomer (-C₂F₄-), which was 1.1×10^{-3} mol/g_{electrode}.

The NMR peak area of an element X is expressed as follows⁴⁻⁶:

$$A = k \cdot n \cdot [X]$$

where A is peak area, [X] is a concentration of X, *n* is the number of the atoms in a molecule X to be detected with NMR, and *k* is a sensitivity factor. Then, the specific relations for BF_4 - ion and PTFE are as follows:

$$A_{BF_{4}} = k \cdot n_{F(BF_{4})} \cdot [BF_{4}] \text{ and } A_{PTFE} = k \cdot n_{F(PTFE)} \cdot [PTFE]$$

The following is the relation between the concentrations of infiltrated BF_4^- ions and PTFE and their peak areas:

$$\frac{A_{BF_{4}}}{A_{PTFE}} = \frac{n_{F(BF_{4})}}{n_{F(PTFE)}} \cdot \frac{\left[BF_{4}\right]}{\left[PTFE\right]}$$

After rearrangement, the concentration of infiltrated BF₄⁻ ions is expressed as follows:

$$\begin{bmatrix} BF_{4}^{-} \end{bmatrix} = \frac{A_{BF_{4}^{-}}}{A_{PTFE}} \cdot \begin{bmatrix} PTFE \end{bmatrix} = A^{normalized} \cdot \begin{bmatrix} PTFE \end{bmatrix}$$

Note that the numbers of the fluorine atoms in a BF₄⁻ ion and PTFE monomer (-C₂F₄-) (i.e., $n_{F(BF_4^-)}$ and $n_{F(PTFE)}$) are 4.

4. Conversion of Capacitance to Electron Concentration

The specific capacitance of a coin cell can be converted to the stored electron concentration during charging by following equation:

 $[electron](mol/g_{electrode}) = Q(coul/g_{electrode})/F(coul/mol) = C(farad/g_{electrode}) \cdot V(volt)/F, where F$ is Faraday constant (96485 coul/mol) and V is the charging potential (volt).

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