

Supporting Information

Electrochemical Synthesis of Polyaniline in the Micropores of Activated Carbon for High- Performance Electrochemical Capacitors

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1. Chemicals

Aniline (ANI) (Wako Pure Chemical Industries, Ltd.) and the commercial activated carbon MSP20N (Kansai Coke and Chemicals Co., Ltd.) were used as received.

2. Preparation of AC/ANI samples

The experimental setup for the adsorption of ANI into AC is presented in Figure S1. All procedures were conducted under nitrogen atmosphere. AC was dried at 150 °C for 6 h under vacuum to remove any adsorbed water. Dried AC was transferred into a 13.5 mL glass vial, which had been weighed in advance, and the accurate mass of dried AC was obtained by calculating the weight difference. The glass vial was placed in a tailored glass apparatus (Figure S1). ANI was added to a glass tube with an outer diameter of 4 mm and wall thickness of 1 mm. The weight of ANI was accurately adjusted using a microsyringe so as to achieve ANI/AC weight ratios of 5:95, 10:90, 20:80, 30:70, and 40:60. Only the sample saturated with ANI was prepared using an excess amount of ANI. Subsequently, ANI was frozen in liquid nitrogen and placed in the glass apparatus (Figure S1). The reason why ANI was frozen was to prevent the evaporation of ANI under vacuum. Finally, the glass apparatus was vacuumed and sealed and then placed in an incubator at 25 °C for 24 h to complete the adsorption of ANI into AC. For the sample saturated with ANI, the weight percent of ANI was calculated from the weight difference of the dried AC and the obtained AC saturated with ANI.



Figure S1. Experimental setup for sample preparation.

3. Nitrogen adsorption/desorption measurements

The nitrogen adsorption/desorption data for MSP20N were collected with a Micrometrics ASAP 2020 apparatus at $-196\text{ }^{\circ}\text{C}$. The specific surface area (S_{BET}) was calculated by the Brunauer–Emmett–Teller (BET) method using the adsorption isotherm at $p/p_0 = 0.05\text{--}0.20$. The total pore volume (V_{total}) was estimated using the adsorption value at $p/p_0 = 0.96$. The micropore volume (V_{micro}) was determined by the Dubinin–Radushkevich method. The mesopore volume was calculated by subtracting the micropore volume from the total pore volume ($V_{\text{meso}} = V_{\text{total}} - V_{\text{micro}}$). Figure S2 presents the nitrogen adsorption/desorption isotherm for MSP20N. MSP20N shows the typical type I isotherm, confirming the microporous nature of carbon. The BET surface area and pore volume data of MSP20N are summarized in Table S1. As expected from the isotherm, the mesopore volume of MSP20N is negligible.

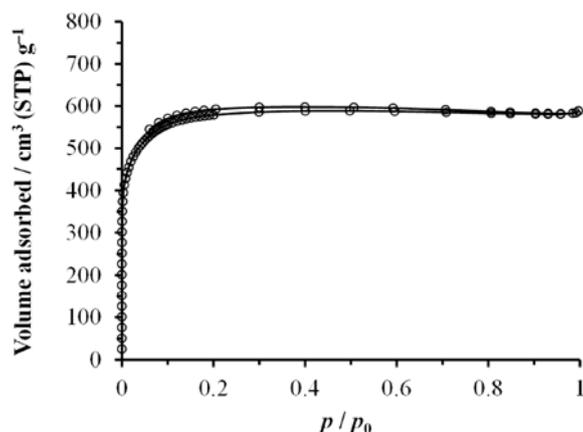


Figure S2. Nitrogen adsorption/desorption isotherm for MSP20N measured at $-196\text{ }^{\circ}\text{C}$.

Table S1. BET surface area and pore volume of MSP20N

Sample	S_{BET} ($\text{m}^2\text{ g}^{-1}$)	V_{total} ($\text{cm}^3\text{ g}^{-1}$)	V_{micro} ($\text{cm}^3\text{ g}^{-1}$)	V_{meso} ($\text{cm}^3\text{ g}^{-1}$)
MSP20N	2070	0.96	0.93	0.03

4. Electrode preparation

The electrode sheet for the working electrode was prepared by mixing each of the samples with poly(tetrafluoroethylene) (PTFE; PTFE 6-J, Du Pont-Mitsui Fluorochemicals Company, Ltd.) and carbon black (Denka black, Denka Company Ltd.). The weight ratio of AC (i.e., excluding aniline), PTFE, and carbon black in the samples was adjusted to 90:5:5 for all electrodes. The weight of AC in the electrode sheet (i.e., excluding the weight of aniline, carbon black, and PTFE) was fixed to 8.5 mg so that the thickness of the electrode sheet became constant for each working electrode. The electrode sheet was sandwiched by stainless steel mesh (100 mesh, Nilaco) and pressed at 30 MPa. A counter electrode was prepared from activated carbon (MSP20N) using the same procedure as that for the working electrode. Before the electrochemical measurements, the working electrode prepared from AC and the counter electrode were immersed in an electrolyte (1 M H_2SO_4) and vacuumed for 10 min, and then kept

at 40 °C for three days to impregnate the pores of AC with the electrolyte. The working electrodes prepared from the AC/ANI samples were used as prepared without impregnation with the electrolyte.

5. Electrochemical procedures

A three-electrode cell was used for the electrochemical experiments using Ag/AgCl (sat. aqueous KCl) as the reference electrode and 1 M H₂SO₄ as the electrolyte. The electrochemical polymerization and all the electrochemical measurements were performed on a potentiostat/galvanostat instrument (VMP3, Bio-logic) at 25 °C. Cycle lifetimes were also measured using a two-electrode cell in 1 M H₂SO₄ as the electrolyte.

5.1. Cyclic voltammetry for the electrochemical polymerization of AC/ANI

Electrochemical polymerization was conducted by cyclic voltammetry (CV) at a sweep rate of 10 mV s⁻¹ and a potential range of -0.1 to 1.0 V. Figure S3 shows the results of the CV polymerization of AC/ANI. The vertical axis indicates the current per gram of the sample (excluding the weight of carbon black and PTFE). As presented in the voltammograms for AC/ANI (20%) (Figure 1), a large anodic current derived from the polymerization of ANI was observed between 0.7 and 1.0 V in the first cycle. The current decreased with the number of cycles and the anodic and cathodic currents derived from the redox couple of PANI appeared at around 0.6 and 0.4 V for AC/ANI (5%) and AC/ANI (10%), 0.7 and 0.3 V for AC/ANI (30%) and AC/ANI (40%), and 0.8 and 0.2 V for AC/ANI (48%), respectively. The peak currents reached their maximum at around the 15th cycle for all AC/ANI samples, indicating the completion of the electrochemical polymerization of ANI. After CV polymerization, the cells were used in further experiments without electrolyte exchange or any purification process of the electrodes.

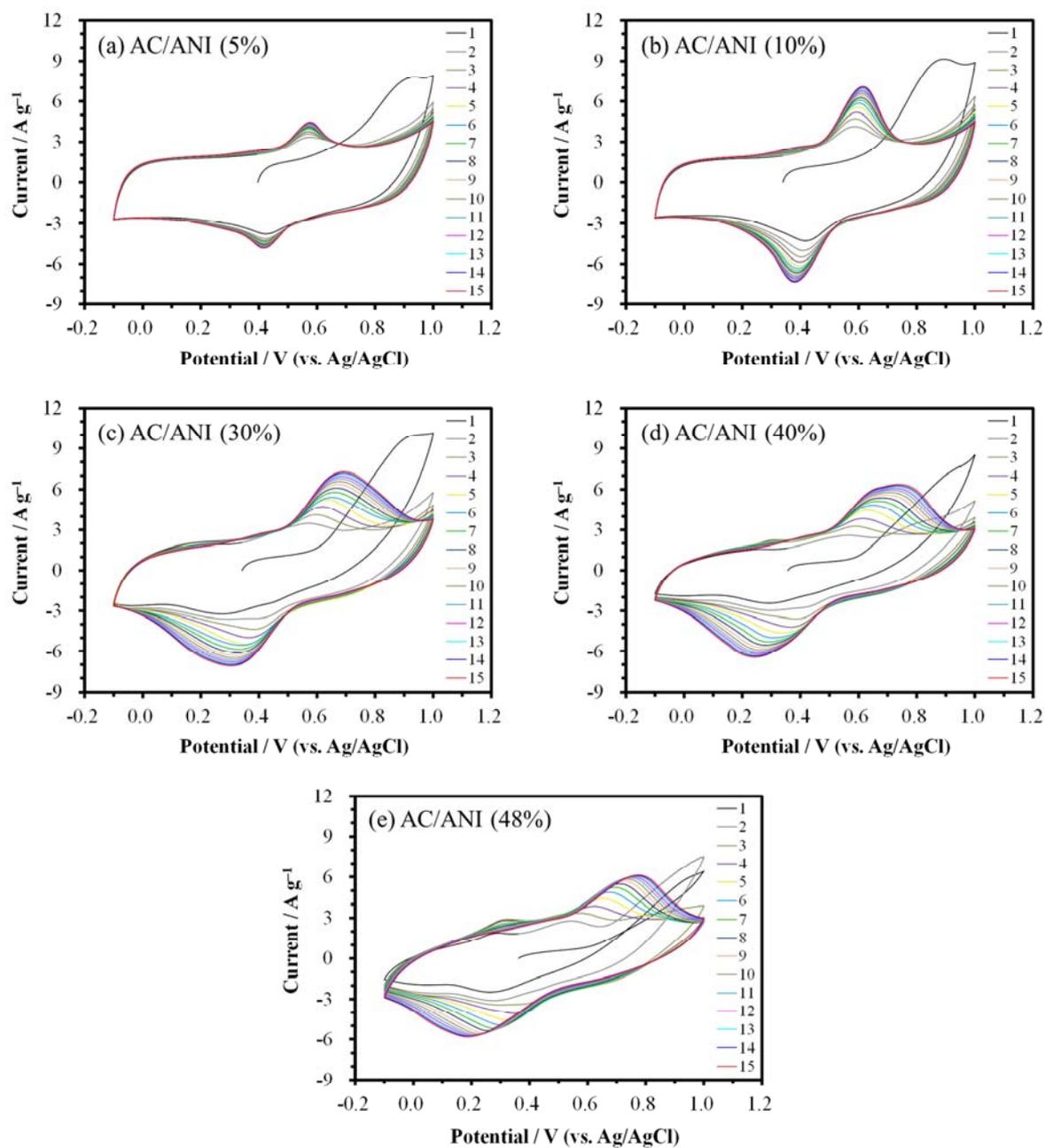


Figure S3. Cyclic voltammograms for the electrochemical polymerization of (a) AC/ANI (5%), (b) AC/ANI (10%), (c) AC/ANI (30%), (d) AC/ANI (40%), and (e) AC/ANI (48%).

5.2. Electrochemical measurements: cyclic voltammetry, electrochemical impedance spectroscopy (EIS), and galvanostatic charge/discharge (GC) analysis

After electrochemical polymerization, cyclic voltammograms were recorded at a scan rate of 1 mV s^{-1} for four cycles and at a potential range of -0.1 to 0.8 V . Subsequently, EIS was conducted at the peak top potential of the anodic current derived from PANI (0.5 – 0.6 V) for each AC/ANI sample and at 0.5 V for AC. GC analysis was conducted at current densities from 0.2 to 5 A g^{-1} and a potential range of -0.1 to 0.8 V . Cycle lifetimes were measured by GC at a current density of 1 A g^{-1} using both two- and three-electrode cells. The cell voltage for a two-electrode cell was 0 to 0.8 V , and the potential range for a three-electrode cell was -0.1 to 0.8 V . For a two-electrode cell, AC/ANIs after the polymerization, which was conducted by using a three-electrode cell, were used as a positive electrode, and the same AC (MSP20N) was used as a negative electrode. For a fair comparison, the amount of the negative electrode was fixed to the same amount of AC in the positive electrode (i.e., 8.5 mg).

6. XRD patterns of AC/ANI samples after CV polymerization

The X-ray diffraction (XRD) patterns of the electrode sheets for the AC/ANI samples after CV polymerization were collected with an XRD-6100 instrument (Shimadzu) with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). PTFE and carbon black, which were used for the preparation of the electrode sheets, MSP20N, and the electrode sheet of MSP20N were also analyzed. CV polymerization of each AC/ANI sample was conducted and the electrode sheets were then analyzed by XRD. After polymerization, the electrode sheets were removed from the stainless steel mesh and thoroughly washed in deionized water under stirring for 24 h to remove the electrolyte, followed by drying at $60 \text{ }^\circ\text{C}$ under vacuum for 24 h . As shown in Figure S4, carbon black and MSP20N exhibited a broad peak at around 25.5° and 44° , respectively, derived from the carbon (002) and (10) diffraction planes, respectively. Note that the sharp peak at around 18° observed for all electrode sheets is ascribed to the PTFE binder. The post-polymerization AC/ANI samples did not exhibit the characteristic peaks of bulk PANI at 14.4° , 19.6° , and 25.4° .¹ Instead, a broad peak at around 20 – 25° was observed, and the peak intensity increased with the amount of ANI in the sample. These results indicate the formation of PANI with an extremely thin structure.

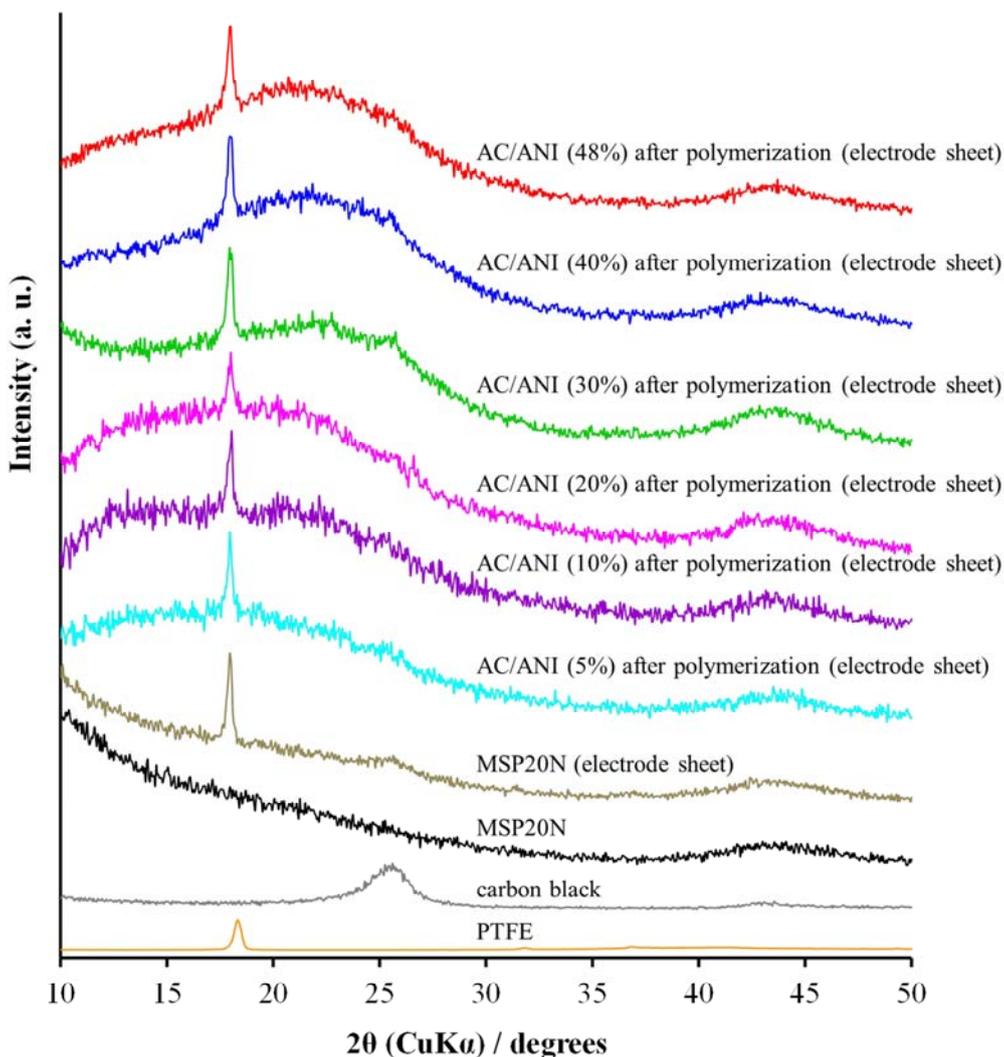


Figure S4. XRD patterns of PTFE, carbon black, MSP20N, the electrode sheet of MSP20N, and the electrode sheets of the AC/ANI samples after polymerization.

7. SEM observation of the electrodes after CV polymerization

The absence of PANI on the surface of the AC particles was confirmed with a scanning electron microscope (SEM; SHIMADZU SS-550) under an accelerating voltage of 15 kV. Washed electrode sheets were used for SEM imaging (see the previous section). Carbon black and the electrode sheet of MSP20N were also analyzed by SEM. As shown in Figure S5, PANI was not

observed outside the AC particles, indicating that ANI polymerized exclusively in the micropores of AC.

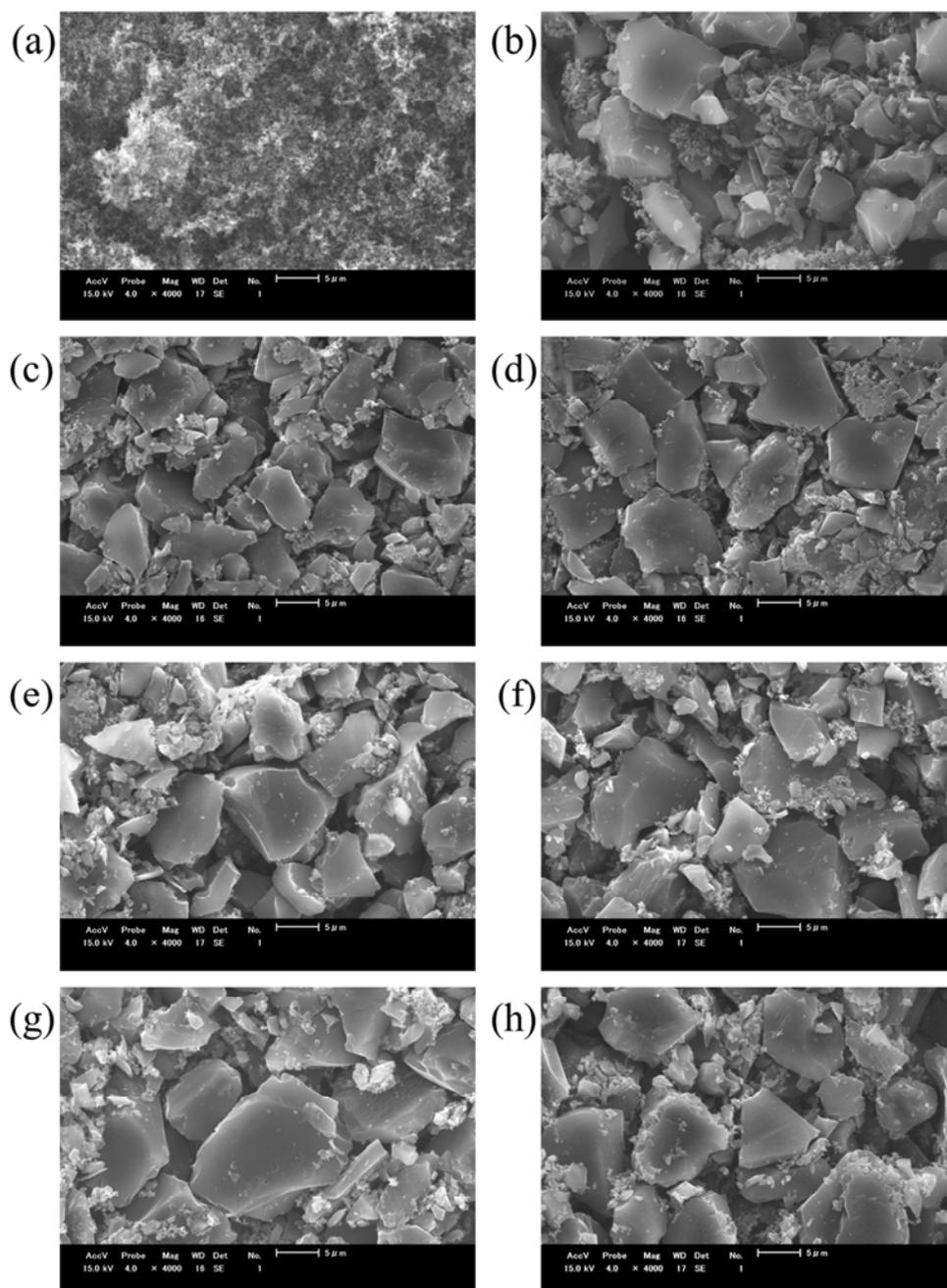


Figure S5. SEM images of (a) carbon black, (b) the electrode sheet of MSP20N, and the electrode sheets after CV polymerization of (c) AC/ANI (5%), (d) AC/ANI (10%), (e) AC/ANI (20%), (f) AC/ANI (30%), (g) AC/ANI (40%), and (h) AC/ANI (48%).

8. X-ray photoelectron spectroscopy (XPS) analysis

To confirm the absence of PANI on the particle surface of AC, XPS analysis was conducted for all the electrode sheets after the polymerization of ANI together with the electrode sheet of AC. All the electrode sheets were the same as those used for the XRD analysis. The analysis was performed on a KRATOS ESCA-3400 instrument using Mg K α radiation (1253.6 eV). Note that XPS spectrum contains the information of approximately several nanometers deep from the surface. Therefore, even if there is no PANI on the surface of AC particles, nitrogen can be detected by the XPS analysis, whereas the resulting molar ratio of nitrogen to carbon (N/C) is expected to be very low. As shown in Figure S6, all the AC/ANI samples, with the exception of AC/ANI (48%), do not show any peak in their spectra. On the other hand, only AC/ANI (48%) shows a small peak at around 400 eV with almost the same binding energy as a reported value,² and its N/C ratio is calculated to be only 0.023 while the theoretical N/C ratio of PANI is 0.167. Of note here is that the XPS analysis was conducted using the electrode sheets which contain PTFE and carbon black. However, the weight percent of PTFE and carbon black for AC/ANI (48%) is calculated to be only 5.5%, which does not have a large effect on the N/C ratio for this discussion. The weight percent of ANI in AC/ANI (48%) is ca. 50%, and the particle size of AC reaches more than 10 μm at most (Figure S5). Thus, if a small portion of PANI in AC/ANI (48%) deposits on the particle surface of AC, the thickness of the deposited PANI easily reaches several nanometers, resulting in the much higher N/C ratio than the experimental value.

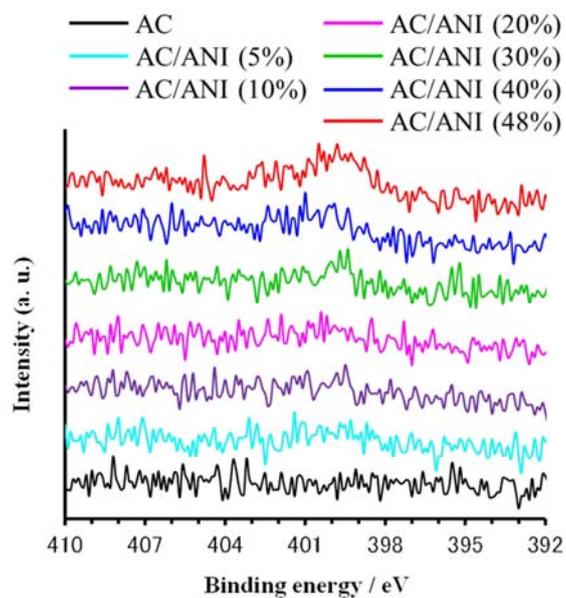


Figure S6. XPS spectra for the electrode sheets of AC/ANIs after the polymerization of ANI and AC. Analysis was performed on a KRATOS ESCA-3400 instrument using Mg $K\alpha$ radiation (1253.6 eV).

9. Calculations

The gravimetric capacitance (C_g F g⁻¹) was calculated from the following equation,

$$C_g = \frac{I\Delta t}{m\Delta V}$$

where I is the current, Δt is the time from -0.1 to 0.8 V (vs. Ag/AgCl), m is the active material mass (i.e., the weight of AC and ANI) in the working electrode, and ΔV is the potential window.

The capacitance per one gram of AC, C_{AC} (F g_{AC}⁻¹), was calculated from the following equation,

$$C_{AC} = C_g \times \frac{100}{(100 - X)}$$

where C_g is the gravimetric capacitance and X is the weight percent of ANI in the sample.

The particle density of active materials, ρ , was calculated with the following equation,

$$\rho = \frac{1 + \frac{X}{100 - X}}{V_{\text{total}} + 1/\rho_{\text{carbon}}} = \frac{\frac{100}{100 - X}}{V_{\text{total}} + 1/\rho_{\text{carbon}}} \left(\propto \frac{100}{100 - X} \right)$$

where V_{total} is the total pore volume of AC estimated from the N₂ isotherm (77 K) and ρ_{carbon} is the true density of carbon (2.0 g cm⁻³).

The volumetric capacitance, C_V (F cm⁻³), was calculated using the gravimetric capacitance and the particle density of the active material as follows:³

$$C_V = C_g \rho = C_g \times \frac{\frac{100}{100 - X}}{V_{\text{total}} + 1/\rho_{\text{carbon}}} = \frac{C_{AC}}{V_{\text{total}} + 1/\rho_{\text{carbon}}}$$

As such, C_V was found to be proportional to C_{AC} . This is confirmed by simply comparing C_{AC} (Figure 3) with C_V (Figure S7). The calculated particle densities for the samples are summarized in Table S2.

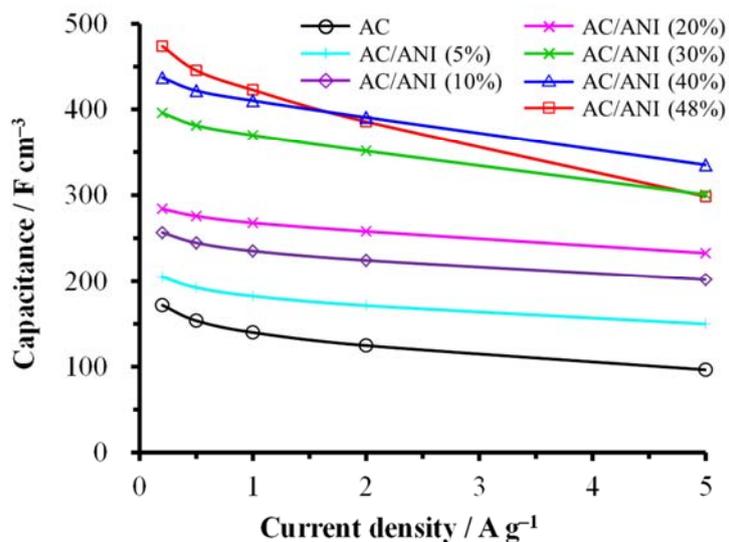


Figure S7. Volumetric capacitance (C_V) for AC and AC/ANI samples plotted at current densities of 0.2–5 A g⁻¹.

Table S2. Particle densities of AC and AC/ANI

Samples	Aniline	Particle density
	X (wt%)	ρ (g cm ⁻³)
AC (MSP20N)	0	0.69
AC/ANI (5%)	5	0.72
AC/ANI (10%)	10	0.76
AC/ANI (20%)	20	0.86
AC/ANI (30%)	30	0.98
AC/ANI (40%)	40	1.14
AC/ANI (48%)	48 ^a	1.32

^a Maximum adsorption of ANI in AC.

10. Cyclic voltammetry experiments to confirm the desorption of PANI from AC

To confirm the desorption of PANI from the micropores of AC, the same CV polymerization and measurements were conducted as described above. Afterward, the potential was held at 0.8 V for 1 min during the subsequent CV cycle. This process was repeated five times. As shown in Figure S8, the anodic and cathodic peak intensity decreased with the increasing number of cycles for AC/ANI (48%), indicating the desorption of PANI from the AC particles. In contrast, AC/ANI (30%) and AC/ANI (40%) exhibited a very small decrease in their anodic and cathodic peaks, while the other AC/ANI samples did not show any decrease in their peak currents.

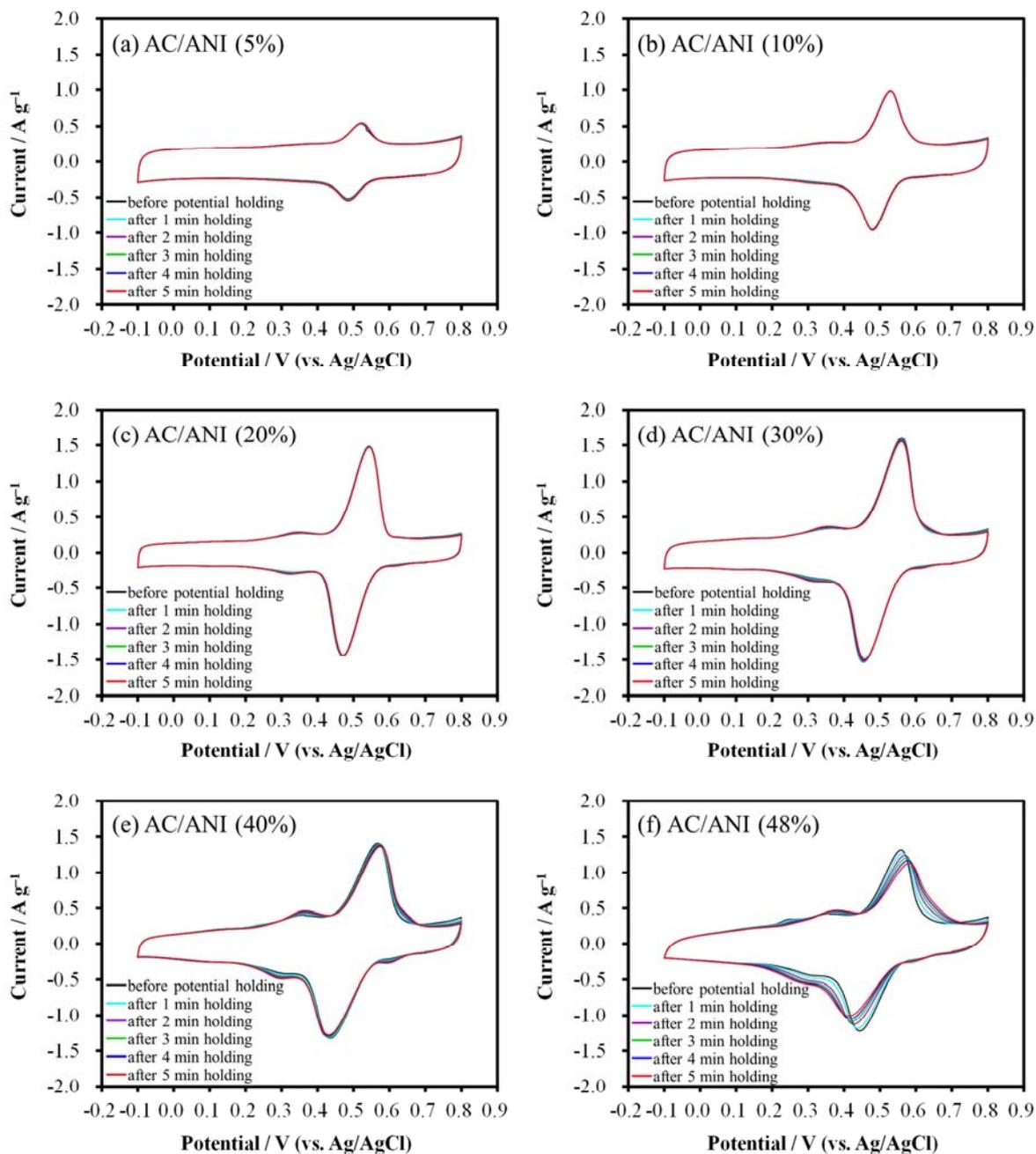


Figure S8. Cyclic voltammograms for AC/ANI collected at a sweep rate of 1 mV s^{-1} after CV polymerization and potential holding at 0.8 V for 1 min . The potential holding procedure was repeated five times.

Reference

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