Electronic Supplementary Information

Redox-Active Polyimide/Carbon Nanocomposite Electrodes for Reversible Charge Storage at Negative Potentials: Expanding the Functional Horizon of Polyimides

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Synthesis of *N*,*N*'-dimethylpyromellitimide. To a solution of methylamine (5.1 mL, 40% in CH_3OH, ca. 9.8 M) in *N*,*N*'-dimethylacetamide (50 mL) were added pyromellitic anhydride (1.09 g). The resulting solution was heated at 160 °C under argon for 12 h with constant stirring. After cooling to room temperature, the precipitated crude product was collected by filtration, washed with H_2O, and purified by column chromatography using $CHCl_3$ as an eluent (R_f = 0.13) to give *N*,*N*'-dimethylpyromellitimide as a colorless powder (Yield: 81%). MS (*m*/*z*): calcd for M^+ 244.2; found 244.0. IR (KBr, cm^{-1}): 3034 ($\nu_{C\text{-}H}$), 1766 ($\nu_{C=O}$), 1701 ($\nu_{C=O}$). Anal. Calcd for $C_{12}H_8N_2O_4$: C, 59.0; H, 3.3; N, 11.5%. Found: C, 59.2; H, 3.2; N, 11.2%. ^1H NMR ($CDCl_3$, 600 MHz, ppm): δ 3.26 (s, 6H), 8.28 (s, 2H). ^{13}C NMR ($CDCl_3$, 150 MHz, ppm): δ 166.3, 137.3, 118.1, 24.5.

Synthesis of poly(amide-acid):[(4,4'-oxydiphthalic anhydride)-*alt*-(1,4-phenylenediamine)] (3). 1,4-Phenylenediamine (649 mg) was dissolved in *N*,*N*'-dimethylacetamide (12 mL). To this solution was added 4,4'-oxydiphthalic anhydride (1.86 g). The resulting solution was stirred at room temperature for 6 h under argon. The product was precipitated by pouring the resulting mixture into acetone, which was collected by filtration and dried under vacuum to give **3**. Yield: 95 wt%. IR (KBr, cm^{-1}): 1661 ($\nu_{C=O}$). ^1H NMR (DMSO-d_6, 600 MHz, ppm): δ 7.99-7.17 (10H), 10.33 (2H), 12.75 (2H). GPC (polystyrene standard, eluent: DMF): $M_n = 2.6 \times 10^4$, $M_W = 8.2 \times 10^4$.

Synthesis of poly(amide-acid):[(pyromellitic dianhydride)-*alt*-(1,4-phenylenediamine)] (4). 1,4-Phenylenediamine (1.08 g) was dissolved in *N*,*N*'-dimethylacetamide (25 mL). To this solution was added pyromellitic anhydride (2.18 g). The resulting solution was stirred at room temperature for 6 h under argon. After the reactions, the product was precipitated by pouring the resulting mixture into acetone and collected by filtration. The polymer was purified by reprecipitation from the *N*,*N*'-dimethylacetamide solution into acetone repeatedly. After washing the product with acetone and drying under vacuum, the poly(amic acid) **3** was obtained as an yellow powder. Yield: 85 wt%. IR (KBr, cm^{-1}): 1662 ($\nu_{C=O}$). ^1H NMR (DMSO-d_6, 600 MHz, ppm): δ 7.71 (4H), 7.97 (1H), 8.31 (1H), 10.52 (2H), 13.32 (2H). GPC (polystyrene standard, eluent: DMF): $M_n = 2.5 \times 10^4$, $M_W = 7.4 \times 10^4$.

Synthesis of polyimide:[(4,4'-oxydiphthalic anhydride)-*alt*-(1,4-phenylenediamine)] (poly(4,4'-oxydiphthalimido-1,4-phenylene)) (1). A film of **3** on a glass substrate was cast from the *N*,*N*'-dimethylacetamide solution. Cyclodehydration was accomplished by a stepwise heating at 160, 200, 230 and 260 °C for 20 min and finally at 290 °C for 30 min to give a dark yellow film of **1**, which was insoluble in $CHCl_3$, THF, DMF and DMSO. IR (KBr, cm^{-1}): 1775 ($\nu_{C=O}$), 1720 ($\nu_{C=O}$), 1360 ($\nu_{C\text{-}N}$). Anal. Calcd for $C_{22}H_{10}N_2O_5$: C, 69.1; H, 2.6; N, 7.3%. Found: C, 68.4; H, 2.7; N, 7.5%.

Synthesis of polyimide:[(pyromellitic dianhydride)-*alt*-(1,4-phenylenediamine)] (poly(pyromellitimido-1,4-phenylene)) (2). A film of **4** on a glass substrate, prepared by casting from the *N*,*N*'-dimethylacetamide solution, was similarly converted to polyimide by a stepwise heating at 160, 200, 230, 260 and finally at 290 °C to give a dark yellow film of **2**. IR (KBr, cm^{-1}): 1778 ($\nu_{C=O}$), 1732 ($\nu_{C=O}$), 1354 ($\nu_{C\text{-}N}$). Anal. Calcd for $C_{16}H_6N_2O_4$: C, 66.2; H, 2.1; N, 9.7%. Found: C, 65.8; H, 2.1; N, 9.7%.

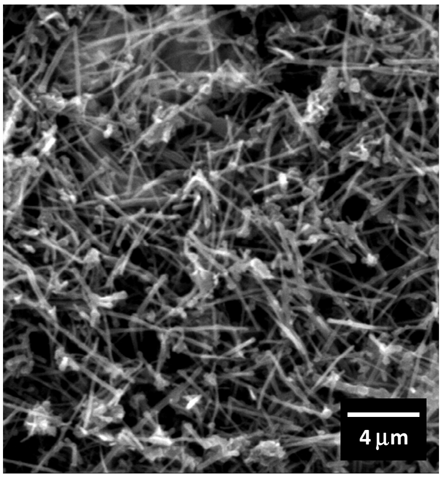

Fig. ESI-1 SEM image of the polyimide **1**/carbon nanocomposite electrode.

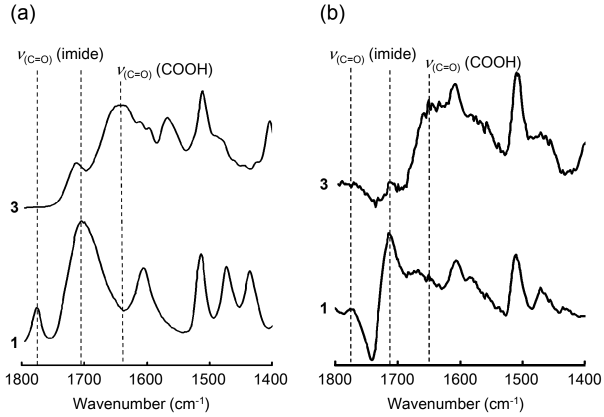

Fig. ESI-2 ATR-IR spectra obtained for the neat films (a) and the polymer/carbon nanocomposites (b) of the polyimide **1** and the corresponding prepolymer **3**.

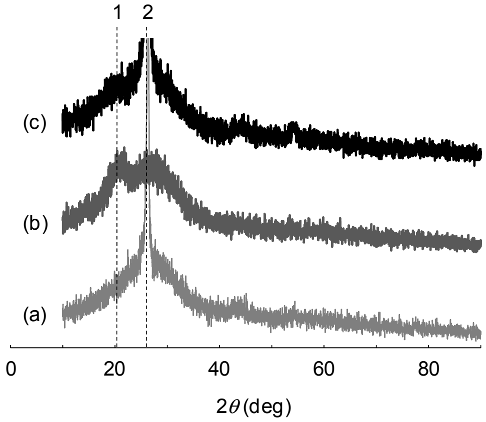

Fig. ESI-3 WAXS intensity profiles (CuKα, λ = 1.5418 Å) of a mixture of carbon and PVdF (a), **2** (b) and the **2**/carbon nanocomposite (c) on a glass substrate. The peak 1 at 2θ = 21.24° (d = 4.18 Å) corresponds to the diffraction from polyimide **2**. The peak 2 at 2θ = 26.30° (d = 3.385 Å), overlapped with the broad halo from the glass substrate, is ascribed to the diffraction from carbon.

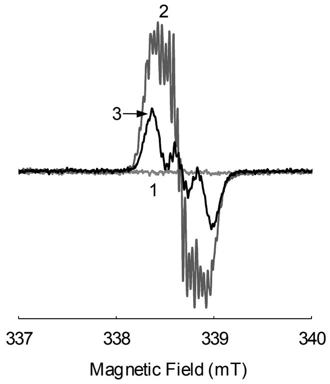

Fig. ESI-4 Electrolytic ESR spectra for 1 mM *N*,*N*'-dimethylpyromellitimide in DMF containing 0.1 M $TBAClO_4$. The spectra were recorded at electrode potentials of -0.3 (curve 1), -1.3 (2), and -2.0 (3) V vs. Ag/AgCl under anaerobic conditions.

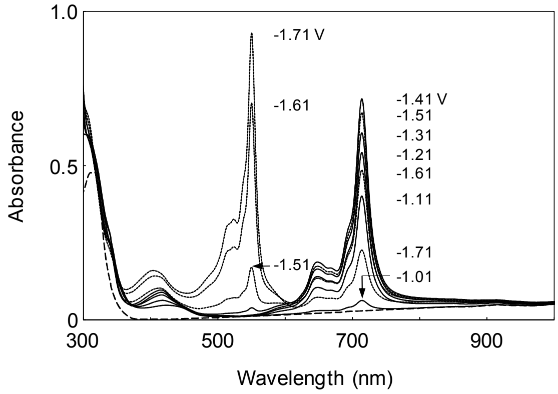

Fig. ESI-5 Electrolytic UV-vis-NIR spectra for 1 mM *N*,*N*'-dimethylpyromellitimide in DMF containing 0.1 M $TBAClO_4$. The electrode potentials were set at -1.01, -1.11, -1.21, -1.31 and -1.41 V vs. Ag/AgCl with the ascending order of absorbance at 714 nm (solid curves) and at -1.51, -1.61 and -1.71 V vs. Ag/AgCl with the ascending order of absorbance at 648 nm (dotted curves). Dashed curve represent the spectrum obtained from the pristine imide (i.e., before applying the electrode potential).

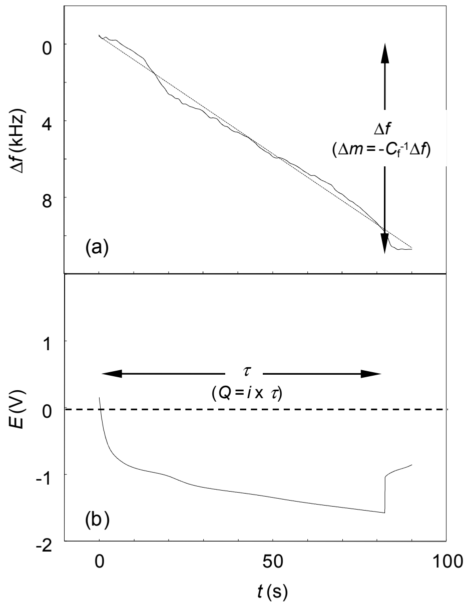

Fig. ESI-6 Resonance frequency changes (Δf) recorded during the galvanostatic reduction of the **2**/carbon layer electrolyzed at 100 μA (a) and the corresponding chronopotentiogram (b). The **2**/carbon layer was prepared on a gold disk with an area of A = 0.196 cm^2 at the surface of the QCM assembly. The supporting electrolyte was 0.1 M $TBAClO_4$ in propylene carbonate. Dotted line in (a) represent the least-squares fitted line, demonstrating the occurrence of mass transfer at a constant rate during the galvanostatic electrolysis. The sensitive factor in the Sauerbrey equaction was C_f = 1.068 Hz/ng. The equivalent weight (M_{eq}) or the mass change relative to the redox capacity, formulated by $\Delta mF/Q$ where F was the Faraday's constant, was M_{eq} = 138 g/mol, which was slightly smaller than the formula weight of the electrolyte cation (tetrabutylammonium cation: 185 g/mol), suggesting a concurrence of a back diffusion of the electrolyte anion.