Supporting Information

Semi-Interpenetrating Polymer Networks for Enhanced Supercapacitor Electrodes

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Experimental Section

Material Synthesis

Preparation of semi-interpenetrating polymer network (sIPN) films. To synthesize the sIPN films, poly(ethylene glycol) methyl ether methacrylate (PEGM, average Mₙ 500, Sigma-Aldrich) was combined with poly(ethylene glycol) dimethacrylate (PEGDM, average Mₙ 750, Sigma-Aldrich) in a 3:1 ratio. An appropriate quantity of 3,4-ethylenedioxythiophene (EDOT, 99%, Acros Organics) was then added to the mixture; while a range of initial EDOT concentrations were used to produce different films, 50 wt. % EDOT was used to produce the main samples described in this work. Finally, benzoin methyl ether (BME, 99%, Sigma-Aldrich) was added (approximately 2 wt. % with respect to the methacrylate oligomers).

To form flat films, a 100 μL droplet of this mixture was flattened between two glass plates (treated with a hydrophobic coating to facilitate the removal of the film later); plastic spacers were placed on the edges of the glass plates to control the final thickness of the films. The sample was then exposed to ultraviolet light (365 nm) for ten minutes to polymerize the methacrylate oligomers and obtain a poly(ethylene oxide) (PEO) based matrix. The two glass slides were then
pulled apart and the film, which was at this point a freestanding clear gel, was submerged in a 1.5 M aqueous solution of FeCl$_3$ (anhydrous, 98%, Alfa Aesar) for 24 hours. The film was then removed and repeatedly rinsed with methanol until the FeCl$_3$ had been removed (when no more yellow color could be observed in the rinse). This rinsing step also removed unpolymerized EDOT, PEGM, and PEGDM. The samples were then dried at 80ºC under vacuum. The final samples contained 61 wt. % PEDOT; detailed methods for this quantification process are described below.

**Preparation of neat PEDOT control samples.** The neat PEDOT used to benchmark the performance of the sIPNs was synthesized via chemical oxidative polymerization:\textsuperscript{1} 75 μL EDOT was combined with 5 mL of 1.5 M FeCl$_3$ (aq) and stirred for 24 hours. The resulting dark blue powder was isolated using centrifugation, repeatedly rinsed free of FeCl$_3$ with methanol, and dried. Electrodes were created from this powder using a standard procedure:\textsuperscript{2,3} the PEDOT powder was combined with polyvinylidene fluoride (PVDF, M$_w$ = 534,000 g/mol, Sigma-Aldrich) dissolved in N-methylpyrrolidone (NMP, Sigma-Aldrich, anhydrous, 99.5%) and carbon black (CB, Korea Carbon Black Co, Korea) as a binder and conducting agent in a 8:1:1 ratio. Approximately 1 mg of this slurry was uniformly casted on an etched titanium foil using a doctor blade then dried at 100 ºC overnight.

**Characterization of sIPN Films**

Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) were performed on a FEI Nova NanoSEM™. SEM images were acquired using an accelerating voltage of 5.0 kV and a 2.5 nm spot size, while EDX data was collected with an accelerating voltage of 15 kV and a spot size of 4 nm. Samples for cross-sectional imaging were prepared by breaking the films after freezing in liquid nitrogen. All samples were imaged directly, without any additional conductive metal coating. Raman spectra were collected using a silicon-calibrated
Renishaw Ramascope-1000 using a 633 nm laser excitation source. Thermogravimetric analysis (TGA, TA instruments Q500) was performed under nitrogen gas. Samples were heated from approximately 20 ºC to 900 ºC at a rate of 20 ºC/min. Nitrogen adsorption isotherms were undertaken at 77 K using a MicroMeritics TriStar 3000 Porosimeter. Prior to the N₂ adsorption test, all samples were evacuated for 1 hour at 100 ºC under nitrogen flow. The electrical conductivity σ (S/cm) of the films was determined using measurements from a custom-built four-point probe based on the following equation:\(^4\)

\[
\sigma = \left( \frac{k\pi}{\ln(2)} \times \frac{V}{I} \times t \right)^{-1}
\]

where V is the measured voltage (V), I is the applied current (A), t is the film thickness (cm), and k is a correction factor based on the sample dimensions to account for edge effects (k had a value of 1.49 for the samples in this work). Film thickness was measured using a DEKTAK 6M profilometer. Compressive stress-strain curves were obtained using a thermomechanical analyzer (TMA, TA instruments Q400) at room temperature. Compression tests were conducted with a preload force of 0.1 N and force ramp rate of 0.1 N/m. Young’s modulus values were determined using a linear regression over the elastic region of the stress-strain curve.

Cyclic voltammetry (CV), charge-discharge tests, and electrochemical impedance spectroscopy (EIS) were performed with a potentiostat/galvanostat (Ivium Stat XRi). All of these tests were carried out in a three-electrode cell in 1 M lithium perchlorate (LiClO₄, Alfa Aesar, 98%) using a platinum foil counter electrode and Ag/AgCl reference electrode. The sIPN films were cut into pieces of approximately 5x3 mm² and connected to the external circuit using Ti foil clamps then submerged in solution.
**PEDOT quantification in sIPN films**

The quantity of PEDOT within the sIPN films \( M_{\text{PEDOT,final}} \) was evaluated by performing a simple mass balance on the reaction:

\[
M_{\text{PEDOT,final}} = M_{\text{EDOT,initial}} - M_{\text{PEDOT,precip}}
\]  

(2)

The value of \( M_{\text{EDOT,initial}} \) is the mass of EDOT impregnated in the PEO matrix (Figure 1f), dictated by the initial EDOT content of the reagent mixture (Figure 1e). TGA was used to determine the precise weight percent of EDOT at this stage, as exemplified in Figure S1.

![TGA of a PEO-based film impregnated with EDOT.](image)

**Figure S1.** TGA of a PEO-based film impregnated with EDOT.

While the majority of this impregnated EDOT remained in the PEO matrix as it polymerized, some diffused into the FeCl\(_3\)(aq) solution over the course of the 24-hour polymerization, forming PEDOT precipitates in solution. These precipitates were isolated using centrifugation, repeatedly rinsed with methanol to wash away all FeCl\(_3\), and dried overnight in air; their final weight gave the value of \( M_{\text{PEDOT,precip}} \) to be used in the above equation. Note that any
loss of precipitate in this centrifugation process would increase the calculated PEDOT concentration in the film; this quantification method should thus give conservative estimates of the specific capacitance of these materials.

**Preparation of Solid-State Device**

Full solid-state supercapacitor devices were fabricated using a PEO-based gel electrolyte. The synthesis of this gel was directly analogous to that of the sIPN electrodes: PEGM and PEDGM were combined in a 3:1 ratio with approximately 2 wt. % BME. This mixture was polymerized between two glass slides (as described above) for ten minutes under exposure to 365 nm ultraviolet light, producing freestanding gel films. To assemble the supercapacitor, a gel film was placed between two sIPN electrodes; these three components were all briefly submerged in 1 M LiClO\(_4\) (aq) immediately before assembly. This trilayer structure was then sandwiched between two Ti foil current collectors and clamped together to ensure good contact between the electrodes and electrolyte. The calculated capacitance and energy/power densities of these devices were based on the mass of the PEDOT in the electrodes, excluding the mass of the current collector and electrolyte.

**Calculations for Electrochemical Characterization**

In the three-electrode configuration, specific capacitance (C, F/g) was calculated from cyclic voltammetry data based on the following equation:\(^5\)

\[
C = \frac{Q}{2(E_2 - E_1)m}
\]

(3)

where Q is the total voltammetric charge passed in the CV scan, \(E_1\) and \(E_2\) are the lower and upper potential bounds (V), and \(m\) is the mass of the PEDOT in the electrode (g). The total charge Q is given by \(\int_{E_1}^{E_2} i \, dE\), where \(i\) is the instantaneous current and \(v\) is the scan rate (V/s). The factor of two
in the denominator takes into account the charging that occurs in both the cathodic and anodic sweeps of the CV.

Charge-discharge test data was used to calculate specific capacitance according to:

\[ C = \frac{I \times \Delta t}{\Delta V \times m} \]  

(4)

where \( I \) (A) is the constant charge/discharge current, \( \Delta t \) (s) is the discharge time, and \( \Delta V = E_2 - E_1 \) is the electrochemical potential window. Both \( \Delta t \) and \( \Delta V \) are analyzed after the initial voltage drop.

The capacitance of the full symmetric device, \( C_D \), was determined from CV tests based on:

\[ C_D = \frac{Q}{(E_2 - E_1)M} \]  

(5)

where \( M \) is the combined mass of the PEDOT in both electrodes. The energy density (\( E \), Wh/g) and power density (\( P \), W/g) of the devices are calculated using:

\[ E = \frac{C_D \Delta V^2}{2 \times 3600} \]  

(6)

\[ P = \frac{3600 \times E}{\Delta V / \nu} \]  

(7)
**Effect of PEDOT loading on sIPN performance**

To demonstrate the tunability of the electrode fabrication process, sIPNs were fabricated with a variety of PEDOT concentrations ranging from 4 wt. % to 61 wt. % (the samples described in the main text have 61 wt. % PEDOT). As illustrated by the data in Figure S2, the specific capacitance of the sIPNs increases as PEDOT loading increases.

![Figure S2](image_url)

**Figure S2.** Electrochemical characterization of sIPNs with a range of PEDOT concentrations. (a) Charge-discharge data at 1 A/g. (b) Rate capability based on cyclic voltammetry tests.

At lower concentrations, the electrode capacitance was most likely limited by poor continuity of the PEDOT phase. These samples consequently experienced increased electrical resistance, which introduced kinetic limitations that decreased specific capacitance. Indeed, the Nyquist plots in Figure S3a indicate that samples with lower PEDOT concentrations have both higher bulk resistance (the x-intercept of the plot, which reflects resistance from the electrolyte and internal resistance of the electrode) and higher charge-transfer resistance (indicated by the increased diameter of the RC semicircle). Furthermore, this trend is supported by the electrical conductivity of the film surfaces as measured by four-point probe (Figure S3b).
Figure S3. Demonstration of the increasing internal resistance of the sIPN electrodes as PEDOT concentration decreases. (a) Nyquist plots of sIPNs with 61 wt. %, 49 wt. %, and 34 wt. % PEDOT. (b) Four-point probe measurements of electrical conductivity versus PEDOT concentration.

Based on these trends, we would in theory expect sIPN electrodes with even greater PEDOT content (above the 61 wt. % fabricated here) to have even greater specific capacitance; we might predict a PEDOT loading which yields maximum performance, above which we observe negligible improvements in ionic conductivity due to the low PEO content. However, samples with greater PEDOT concentration could not be fabricated due to the mechanical instability of the PEO matrix, which is required to produce the freestanding films. This issue appears in the first step of our synthesis, forming an EDOT-impregnated PEO matrix (Figure 1f). If the EDOT content in the original reagent mixture is too high, the PEO-based oligomers are too dilute to create a stable gel film. The resulting product is too mechanically weak to be transferred to the iron chloride solution used to polymerize the EDOT.
Figure S4. Nitrogen adsorption isotherm for a representative sIPN sample. The sIPN films exhibit a Type II nitrogen adsorption isotherm, indicating that the surface is nonporous. Note that while the overall shape of this isotherm gives insight into the sIPNs’ lack of porosity, the film surface area could not be accurately calculated due to the very low overall quantity of gas adsorbed.
Figure S5. Nyquist plots of the sIPN and neat PEDOT electrodes, with an inset magnifying the high frequency region. The neat PEDOT exhibits an ESR of 6.9 Ω, compared to the sIPN value of 14.6 Ω.
Effect of Film Thickness on sIPN Performance

Figure S6. sIPN specific capacitance (measured by cyclic voltammetry at 5 mV/s) versus film thickness.

To explore the material utilization efficiency of the PEDOT in our sIPN films, we study the effect of film thickness on specific capacitance. Ideally, if all PEDOT is fully utilized, we should expect constant specific capacitance regardless of film thickness – if this is the case, even PEDOT in the bulk of a thick film behaves with the favorable ion transport properties of a thin film. Indeed, we see in Figures S6 that our sIPN electrodes follow this trend up to a thickness of approximately 130 μm (the thickness of the electrodes summarized in the main text), at which point specific capacitance cannot be significantly increased by decreasing film thickness.

Inevitably, after some threshold thickness, we observe decreases in specific capacitance due to the slow kinetics of ion diffusion in the PEO gel relative to liquid electrolyte. However, the fact that we do not observe these diffusion limitations in films as thick as 130 μm is quite impressive given that many electrode films reported in the literature are one to two orders of
magnitude thinner.\textsuperscript{8–11} The formation of supercapacitor electrodes which can maintain both their specific capacitance and flexibility even when very thick is a crucial challenge in developing devices for practical applications.\textsuperscript{12}
Figure S7. Coulombic efficiency (discharge time / charge time) of the sIPN over long-term cycling.
**Figure S8.** Demonstration of sIPN electrode flexibility. (a) Digital images of an electrode bent around a wire with radius of 180 μm. Inset shows a top-down view of the wrapped electrode. (b) Cyclic voltammograms (20 mV/s) of sIPN electrodes before and after 1,000 cycles of bending and unbending.
Figure S9. Compressive stress-strain curves of sIPN and PEO network films.

Based on the data of Figure S9, the Young’s modulus of the PEO-based network used as a framework for the sIPN is 13.2 MPa; this is highly consistent with the value of 11 MPa reported for similar PEO networks reported in the literature. In contrast, the sIPN exhibits more robust mechanical properties, with a Young’s modulus of 60.1 MPa. Thus, as expected, we observe that the interpenetrated PEDOT/PEO sIPN yields intermediate mechanical properties between those of neat PEO and neat PEDOT (the latter of which typically has a Young’s modulus near 2 GPa).
Figure S10. Characterization of a symmetric solid-state supercapacitor formed using sIPN electrodes. (a) Schematic illustration of the device structure. (b) CV scans of the device, which exhibit the nearly symmetric shape characteristic of an ideal capacitor. (c) Digital image of two supercapacitors in series lighting a 1.7 V LED.
Table S1. Performance of PEDOT-based supercapacitors in the literature.

| Electrode Material          | Fabrication                  | Test Conditions                | Specific Capacitance | Cycling Stability     |
|-----------------------------|------------------------------|--------------------------------|----------------------|-----------------------|
| PEDOT powder16              | Chemical oxidative polymerization | 2-electrode cell (1 M LiClO₄) | 73 F/g at 0.5 A/g   | 75% after 1,000 cycles|
| PEDOT nanofibers17          | Vapor phase polymerization   | 2-electrode cell (EMIBF₄/PVDF-co-HFP) | 80 F/g at 0.5 A/g | 90% after 10,000 cycles|
| PEDOT powder1               | Chemical Oxidative Polymerization | 2-electrode cell (1 M H₂SO₄) | 100 F/g at 5 mV/s   | 85% after 1,000 cycles|
| PEDOT film18                | Vapor phase polymerization   | 3-electrode cell (0.5 M H₂SO₄) | 92 F/g at 0.2 A/g   | 70% after 600 cycles |
| PEDOT film19                | Electrochemical deposition   | 2-electrode cell (BMIBF₄/PVDF-co-HFP) | 85 F/g at 1 mA/cm² | 69% after 10,000 cycles|
| Coral-like PEDOT20          | Chemical Oxidative Polymerization | 3-electrode cell (1 M H₂SO₄) | 174 F/g at 1 A/g   | 74% after 1,500 cycles|
| PEDOT film21                | Vapor phase polymerization   | 2-electrode cell (3 M BMI-BF₄/PC) | 134 F/g at 1 A/g   | --                    |
| PEDOT film22                | Chemical Oxidative Polymerization | 2-electrode cell (1 M LiPF₆/EC+DMC+EMC) | 69 F/g at 0.2 A/g | 72% after 1,500 cycles|
| PEDOT nanofibers23          | Vapor phase polymerization   | 2-electrode cell (6 M HCl)     | 160 F/g at 1 A/g   | 94% after 1,000 cycles|
| PEDOT film24                | Electrochemical deposition   | 3-electrode cell (1 M H₂SO₄)   | 51 F/g at 1 A/g    | 72% after 1,000 cycles|
| 3D flowerlike PEDOT25       | Chemical Oxidative Polymerization | 3-electrode cell (1 M LiClO₄) | 111 F/g at 0.2 A/g | 73% after 1,000 cycles|
| PEDOT/PEO sIPN film (this work) | Chemical Oxidative Polymerization | 3-electrode cell (1 M LiClO₄) | 182 F/g at 1 A/g | 97.5% after 3,000 cycles|
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