Supplemental Information

The supplemental information for ‘Mechano-electrochemistry of PPy(DBS) from Correlated Characterization of Electrochemical Response and Extensional Strain’ is organized to provide detailed instructions for the following:

- Substrate fabrication
- Sample fabrication and preparation
- Glass electrode fabrication for shear force imaging
- Shear force imaging for extensional actuation
- Extensional actuation of PPy(DBS) samples from shear force imaging

Substrate Fabrication

Silicon wafers with ≈300nm thick silicon nitride layer and gold pads were fabricated in OSU Nanotech West cleanroom following the procedure discussed in Northcutt and Sundaresan9 and diced into rectangular units. Each unit has two gold pads measuring 5mm × 5mm connected by a 500µm wide gold line. One of the pads is used for electropolymerization of polypyrrole and other as a connector pad for electrical access. An acrylic piece is fabricated with a laser-cutting machine from a stock sheet (McMaster-Carr) and attached to the wafer using epoxy as shown in Figure 9. The acrylic piece serves as the aqueous chamber above the pad during electropolymerization, electrochemical and mechanoelectrochemical characterization. The prepared wafer unit is attached to a 3D printed delrin apparatus with spring loaded connector for electrical access. The delrin apparatus with the wafer is attached to the HEKA ElproScan3 stage with standard set screws and leveled to the stage. The CE and RE were connected to a Pt wire and Ag/AgCl wire and suspended in the solution, and the WE was pinned to the Au pad using a small spring.

Sample Preparation

Electropolymerization: The objective of this article requires deposition of PPy(DBS) of various thickness. This is achieved by potentiostatic electropolymerization of PPy(DBS) to predetermined charge densities (0.1 - 0.8 mC/cm²). PPy(DBS) samples were grown on the gold pads by potentiostatic electropolymerization to a targeted total accumulated charge. The charge accumulated over time during electropolymerization is calculated from chronoamperometry and data for planar PPy(DBS) samples for densities between 0.1-0.8 C.cm⁻² is shown in Figure 9.

For an example charge density (such as 0.1 C.cm⁻²), the number of redox sites can be calculated following Equation 1 as shown below:

\[ N_r = \frac{Q_p}{(\eta_p - \eta_e)F} = \frac{0.025(C)}{7.2 \times 96485(C/mol)} = 3.6 \times 10^{-8} \text{mol} \]  

(7)

SEM Imaging

A comprehensive SEM graphic for the surface features of planar and vesicle-templated samples is given as Figure 10 to demonstrate the presence of nanoscale surface features over a mesoscale range. Images were taken in OSU NanoSystems Laboratory with a FEI Helios Nanolab 600 FIB/SEM with a distance of 4.1 mm between the SEM probe and the samples. The magnification was kept constant between all samples, with a 30 µm scale bar being provided on the bottom right of the image. It can be seen that there is an increased number of morphological features in samples with charge density greater than 0.4 C.cm⁻², with a loss of features occurring at 0.8 C.cm⁻². The images shown in the main article show the samples’ cross-section at a 52° angle for thickness measurement.

![Charge accumulation vs time - Polymer growth](image)

Fig. 9 (top left) Delrin apparatus with nitried silcon wafer shwon in the SECM xy-stage; (top right) Charge data gathered during the fabrication of planar PPy(DBS) membranes; (bottom) Table of fabrication of specifications for PPy(DBS) membranes

Fabrication of Nanoelectrodes

The materials used for nanoelectrode fabrication were quartz capillaries (I.D.: .5 mm, O.D.: 1 mm, L: 10 cm, Sutter Instrument, USA), borosilicate capillaries (I.D.: 1.16 mm, O.D.: 2 mm, L: 20 cm, Sutter Instrument, USA), platinum wire (d: 25 µm, Purity: 99.9%, Hard, Goodfellow, England), silver ink (Stan Rubinstein Assoc., USA), standard copper wire (d: .25 mm), and D-sub connector pins (d: 1mm, RadioShack, USA). The different steps required for the fabrication of the electrode using a Sutter P-2000 puller is shown in Figure 11(a). The various steps in the fabrication are: (i) threading Pt-wire, (ii) sealing glass capillary around Pt-wire, (iii) parting step, (iv) finishing step and (v) polishing. As obtained 1 mm quartz capillaries from Sutter were threaded with the 25 µm platinum wire and placed into a Sutter P-2000 micropipette puller (Sutter Instrument, USA). The capillaries were connected to a vacuum pump at each end through silicon tubing and
**Fig. 10** SEM of planar and vesicle-templated PPy(DBS) membranes for varying charge densities

(a) Electrode Fabrication Steps

- Insertion of Pt-wire
- Sealing step: Sutter P-2000 puller
- Parting step: Sutter P-2000 puller
- Finishing step: Borosilicate capillary, Electrical contacts and Polishing
- Attaching dither & receiver piezos (for shear force imaging)

(b) Electrode Characterization - CV

(c) Electrode Characterization – Shear force spectra

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**Fig. 11** (a) Schematic to outline the procedure for SECM-SF imaging nanoelectrode fabrication; (b) CV for electrode in 1mM FcMeOH and 100mM NaCl solution; (c) Shear force spectra from the receiver piezo between 600kHz and 700kHz on and 100µm above the sample.
the capillary holders were restrained by an elastomer band and jaw restraints. The first process is several heating cycles to ensure that the quartz melts around the Pt wire until it is fully bonded at a singular point in the center, creating an hourglass shape. During this time, the capillaries were heated with a 40 second on, 20 second off duty cycle (Heat: 660 °C) with a large filament length (Filament: 5) for 5 cycles (until quartz melted and fused with the Pt wire). The seal was verified via microscopy to ensure that the Pt wire did not snap or otherwise detach at the center. The quartz capillary with a continuous Pt-wire running along the neck formed from the sealing step was then returned to the micropipette puller and held in the jaws of the P-2000 puller bars. A reference point is added to the capillary to return it to the same location in the puller. The capillary was then pulled (Heat: 780 °C) over a small filament length (Filament: 2). The base of the resultant piece was then electrically connected with silver ink to a copper wire and inserted into a 2 mm borosilicate capillary to reinforce and seal the electrical connections. The tip of the electrode was polished using a HEKA microelectrode polisher (MHK 1) to expose the Pt core and produce a smooth, even surface.

**Nanoelectrode Characterization**

**Cyclic Voltammetry:** The finish and quality of the electrode prepared for SECM-SF imaging is characterized by the built-in microscope in HEKA ElProScan ELP3 and cyclic voltammetry in a ferrocene methanol (FcMEOH) solution. An example CV for a well conditioned electrode is shown in Figure 11(b). For a clean platinum surface on a flat surface there is a diffusion limited region on the oxidation and reduction peaks as shown below 0.1V and above 0.4V, limited hysteresis, and insignificant signal noise. This diffusion limited current can be calculated using Equation 8,

\[
I_\text{ct} = knFrD[C^\text{t}] \beta
\]

in which \(k\) is a geometric constant (4 for a disc), \(n\) is the number of electrons, \(F\) is Faraday’s constant, \(r_\text{t}\) is the electroactive area, \(D\) is the diffusion coefficient, \(C^\text{t}\) is the concentration of electroactive species in bulk solution, and \(\beta\) is a function of \(r_\text{t}\). Based on this, the size of the exposed platinum of the Pt-nanoelectrode is calculated empirically. It is important to note that despite having an electrochemically active surface, the application of the nanoelectrodes in this article was limited to shear-force imaging and no potential was applied across the platinum core during any characterization of PPy membranes. The ReMEOH solution and platinum were used between trials in order to keep a consistent surface condition and then electrically disconnected once the electrode was placed in the vicinity of the PPY-sample.

**Shear Force Imaging:** For shear force imaging techniques, piezoelectric plates (HEKA Elektronik Dr. Schulze GmbH) were connected to the Pt-nanoelectrode on the quartz capillary, with a 1 cm spacing and approximately 90° rotation between them. The Pt-nanoelectrode was positioned in the x,y plane directly above the PPy(DBS) membrane with a joystick, and brought into contact with the sample by moving in the -z direction until an abrupt change in the shear force signal was observed. This signal indicates contact with the PPy(DBS) membrane. The curve resulting from measuring deviations in the receiver piezo during membrane approach is typically not smooth until calibration. The shear force signal applied during approach curves for oxidized and reduced conditions was selected based on shear force spectra scans. An example SF-spectra plot is shown as Figure 11(c). Contact was established as the point in the approach curve where a discontinuous spike in the receiver piezo potential and a 10 µm distance was chosen as a sufficient distance away from surface hydrodynamic forces. The 667kHz frequency was selected as the point in which the greatest signal deviation between boundary conditions and conveniently was a resonance of the vibrational natural frequency. The shear force spectra was retaken every instance the electrode was polished or the piezoelectric plates were replaced after cleaning to verify the continued response.

A list of specific experimental steps to perform a mechanoelectrochemical analysis of faradaic materials is as follows:

- Mount the electrode to z-stage
- Mount the sample to x,y-stage, add electrolytic solution and apply an oxidation signal to the sample (ring electrode)
- Use zz-motors to position electrode tip into solution and x,y-motors to position the electrode tip above the sample
- Use “Tip Down” procedure with current regulation (10%) to approach the sample until the electrode is in the immediate vicinity
- Use the “2D Scan” with z-piezo motor selected to approach the sample at a rate of -0.05 µm/sec while simultaneously monitoring current and shear force signals
- Upon reaching the “Contact Condition” (characterized by a discontinuous current response or shear response) manually “Stop” the “2D Scan”
- Perform “Shear Force Spectra” procedure with the electrode maintained at “Contact” position
- Set origin in ElProScan: Motors window
- Perform the “Distance Calibration” procedure for with a 2.5 µm distance with a 3 nm step size
- Perform the “Shear Force Spectra” procedure with the electrode maintained at the “Non-Contact” position
- Overlay the two shear force spectra plots to select an operational frequency
• Perform a CA with the PGF generator to reduce the sample while monitoring the current

• After fully reduced, use the “2D Scan” procedure with the z-piezo motor selected to approach sample at a rate of -0.05 μm/sec while monitoring shear force - stop at “Contact”

• Use the “Go Back” option to return the electrode to a position of 2.5 μm above sample

• Perform a CA with the PGF generator to oxidize the sample while monitoring the current

• After fully oxidized, use the “2D Scan” procedure with the z-piezo motor selected to approach sample at a rate of -0.05 μm/sec while monitoring shear force - stop at “Contact”

• Check resultant data to ensure full CA and Approach Curve data satisfies measurement criteria - repeat as necessary

• Remove the electrode from solution by moving zz-motors in the positive direction before turning off the software

**Comprehensive Approach Curve Data**

The complete set of results from SF approach curves for planar and vesicle-templated PPy(DBS) membranes is presented in Figures 12, 13. The point of contact was an unreliable metric to measure the deviation in thickness due to redox processes, as the modulus of elasticity varies with electrochemical boundary conditions, as seen in the slope of the shear force spectra. This deviation of Young’s modulus in a soft material causes the shear force to be insufficiently sensitive to contact, as seen in both planar and vesicle-templated samples. Therefore, the sense length of the electrode was used as the detection criteria for the PPy-membrane surfaces. A nanoelectrode sense length is dependent on the diameter of glass electrode tip and was measured as the point in which a 5% deviation in the non-contact signal during approach. This technique is significantly more accurate as it is unaffected by the material properties of the surface during approach and reliant only on the distance in which the shear force profile from the nanoelectrode begins acting on the surface. It is noted that the 0.8 C.cm⁻² samples followed a different behavioral trend during approach. This is due to a difference in shear force spectra behavior as a result of polishing. This change caused the most sensitive frequency to occur at 672.4 kHz, and produced an approach curve with biphasic behavior. As the sense length is independent of frequency, this trend difference does not affect measurement accuracy.
Fig. 12 Approach curves for planar PPy(DBS) membranes for varying charge densities

Fig. 13 Approach curves for vesicle-templated PPy(DBS) membranes for varying charge densities