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Supplemental Information

Preparation of Au-patterned Si-Si3N4 wafer

The substrate microfabrication was conducted in Nanotech West at The Ohio State University. A schematic for the microfabrication of the wafer chips as well as the electrodeposition of PPy(DBS) membranes is included in Figure 7. Silicon wafers were oxidized to various thicknesses (~300nm) of Si-Si₃N₄ using a stoichiometric oxidation process (a). This produced substrates with electrically insulating and chemically inert characteristics. The wafers were patterned using optical lithography. A dehydration bake was performed at 190°C for 5 minutes. LOR2A photoresist was deposited on the wafer and spun at a speed of 3000RPM to form a thin (<1 μ m) film. The wafer was pre-baked at 190°C for 5 minutes. Subsequently, SR1813 photoresist was then deposited onto the wafer and spun at 3000RPM to form another thin (1.4 μ m) film. The wafer was again baked at 115°C for an additional 1



Figure 7: Fabrication steps for a PPy(DBS) membrane

minute. UV light was applied to the wafer with an intensity of 15mW/cm^2 for 2.4 seconds and then the wafer was developed with MF-319 to remove the patterned photoresist (c). Metallization was performed with electron beam evaporation of an adhesive Cr layer (15nm) underneath an Au layer (60nm) at $1\text{x}10^{-6}$ torr. The Au pattern consisted of an Au strip ($500\mu\text{m x}$ 5mm) connected to a large Au pad. Excess Cr and Au were removed using a lift-off technique with hot NMP (d). The individual chips from the wafer were parted and cleaned using isopropyl alcohol, methanol and deionized water. Prior to use and in preparation to electropolymerize PPy, a silicone O-ring was epoxied on to the side with the wafer with Au-patterns to form an aqueous chamber (e).

Mass Calculation for PPy(DBS) Membranes

The following equation is used to calculate the mass of a PPy(DBS) membrane:

$$M_{mem} = \left(\frac{\frac{Q_p}{Q_e}}{(\eta_p - \eta_c)N_A}\right) MW_{PPy(DBS)}$$

Where Q_P , Q_e , η_p , η_c , N_A , and $MW_{PPy(DBS)}$ represent total charge accumulation during polymerization, charge of an electron, number of electrons produced during polymerization, number of electrons consumed by polymerized product, Avogadro's number, and the molecular weight of a 0.33 dopant level PPy(DBS) molecule, respectively. The number of electrons produced/consumed, as well as the molecular weight of PPy(DBS) are based on the Diaz mechanism of polymerization and are 9.4/2.3 and 526 g mol⁻¹, respectively.

This equation has been verified using Faraday's law as presented by Arcila-Velez¹ as

$$m = \left(\frac{It.(M_m + \gamma M_d)}{F(2 + \gamma)}\right)$$

Where I is the current, t is time, M_m is molar mass of monomer, γ is the doping density (0.33 for PPy), M_d is the molar mass of the dopant and F is Faraday's constant.

These equations have a strong agreement of a 11.5 μ g total mass for the PPy(DBS) membranes formed in this article.

Mechanistic Approach for Calculating Accessibility of Redox Sites

The mechanistic model for cation storage in a PPy(DBS) membrane follows the assumption that there is a maximum storage ratio of 1:1 for cation molecules to PPy(DBS)⁻ units in the polymer bulk during reduction. The number of PPy(DBS)⁻ units formed ($N_{PPy(DBS)}$) can be calculated as a function of the charge produced during electropolymerization, as shown by the modified mass equation:

$$N_{PPy(DBS)^{-}} = \left(\frac{\frac{Q_p}{Q_e}}{(\eta_p - \eta_c)N_A}\right)$$

For 100% accessibility of redox sites, $N_{PPy(DBS)} = N_{Cation}^+$. If the number of electrons produced when a cation is inserted into a PPy(DBS) membrane is represented by η_+ (where $\eta_+=1$ for Na⁺ and Li⁺), the maximum charge produced from reversible cation

insertion (Q_{c,max}) is calculated following

$$Q_{c,\max} = \left(\frac{Q_p(\eta_+)}{(\eta_p - \eta_c)}\right)$$

Therefore, the accessibility coefficient (PA) is

$$P_A = \left(\frac{Q_{C^+}}{Q_{C,\max}}\right)$$

where Q_c^+ is evaluated from the maximum charge accumulated in the PPy(DBS) membrane during reversible cyclic voltammetry.

Two-Dimensional cyclic voltammetry plot for a representative data set for PPy(DBS) with a mobile Na^+ cation

A two-dimensional view of the cyclic voltammograms provided in Figure 3 is shown as Figure 8 for convenience.



Figure 8: CV of planar (a) and biotemplated (b) as a function of Na⁺ concentration, CV of planar (c) and biotemplated (d) as a function of Li⁺ concentration



Figure 9: A photograph of the microfabricated substrate and an optical micrographs of the gold pad, planar PPy(DBS) and biotemplated PPy(DBS) membranes demonstrating long-range order

Gold Pad

Planar PPy(DBS)

Biotemplated PPy(DBS)







Figure 11: A high resolution SEM image of a biotemplated PPy(DBS) membrane to demonstrate the long-range order

Compilation of Sodium and Lithium data for various wafer polymerization conditions:

During this study, PPy(DBS) membranes of both planar and biotemplated configurations were produced under varying polymerization conditions. These conditions include changing the monomer solution, with samples produced with 50mM or 100mM DBS or samples produced with 50mM, 100mM, 150mM, 200mM, or 250mM pyrrole. The results of this are presented in Figure 12. There seems to be no correlation

between concentrations so long as they remain above the cmc for DBS and there is enough pyrrole present in the electropolymerization droplet to fully polymerize

 Arcila-Velez, M. R.; Roberts, M. E., Redox solute doped polypyrrole for high-charge capacity polymer electrodes. Chemistry of Materials 2014.



Figure 12: Compilation of planar PPy(DBS) and Biotemplated PPy(DBS) anodic I_{peak} and a Compilation of planar PPy(DBS) and Biotemplated PPy(DBS) cathodic I_{peak}