Supporting information to

# Deconstructing Proton Transport Through Atomically Thin Monolayer CVD Graphene Membranes

*Pavan Chaturvedi[a], Nicole K. Moehring[a,b,c], Peifu Cheng[a], Ivan Vlassiouk[d], Michael S.H. Boutilier[e], Piran R. Kidambi[a,b,c,f]\**

*[a] Chemical and Biomolecular Engineering Department, Vanderbilt University, Nashville, TN, 37212, United States*

*[b] Interdisciplinary Graduate Program in Materials Science, Vanderbilt University, Nashville, TN, 37235, United States*

*[c] Vanderbilt Institute of Nanoscale Science and Engineering, Nashville, TN, 37212, United States*

*[d] Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, TN, United States.*

*[e] Department of Chemical and Biochemical Engineering, Western University, London, Ontario, Canada, N6A 5B9*

*[f] Mechanical Engineering Department, Vanderbilt University, Nashville, TN, 37212, United States*

\*Email: piran.kidambi@vanderbilt.edu

**Limiting current for small scale**

Based on the diffusion of protons, the limiting current for a 2μm diameter can be estimated as,

$$I_{limiting} = 4nFDC_o r$$

where n is the charge on the species involved in the process, $F$ is the Faraday constant ~ 96485.3 C/mol, $D \sim 9.31 \times 10^{-9}$ m$^2$/s is the diffusion constant for protons[1] in aqueous solution, $C_o$ is the bulk proton concentration (e.g. 0.1M HCl) and $r$ is the radius (1μm) of exposed area to the solution.

The resulting limiting current ~$0.4 \times 10^{-8}$ A is ~50× larger than measured values for small scale suspended graphene membranes, indicating CVD graphene limits proton transport.

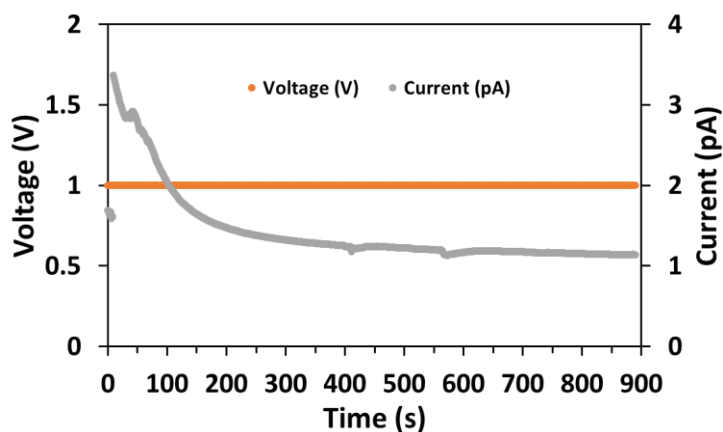**Lower current limit of the small-scale set-up:**



**Fig. S1** Single step chronoamperometry measurement at 1M HCl for a SiNx/Si chip with no open aperture.

A leakage current of ~ 1-3 pA was measured at an applied potential of 1V for a SiNx/Si chip with no aperture, providing the lower limit of the set-up, indicating that the measured currents are above the leakage current of the set-up.

**Nafion control membranes: N212||N212-K$^+$ sandwich membrane measurements**
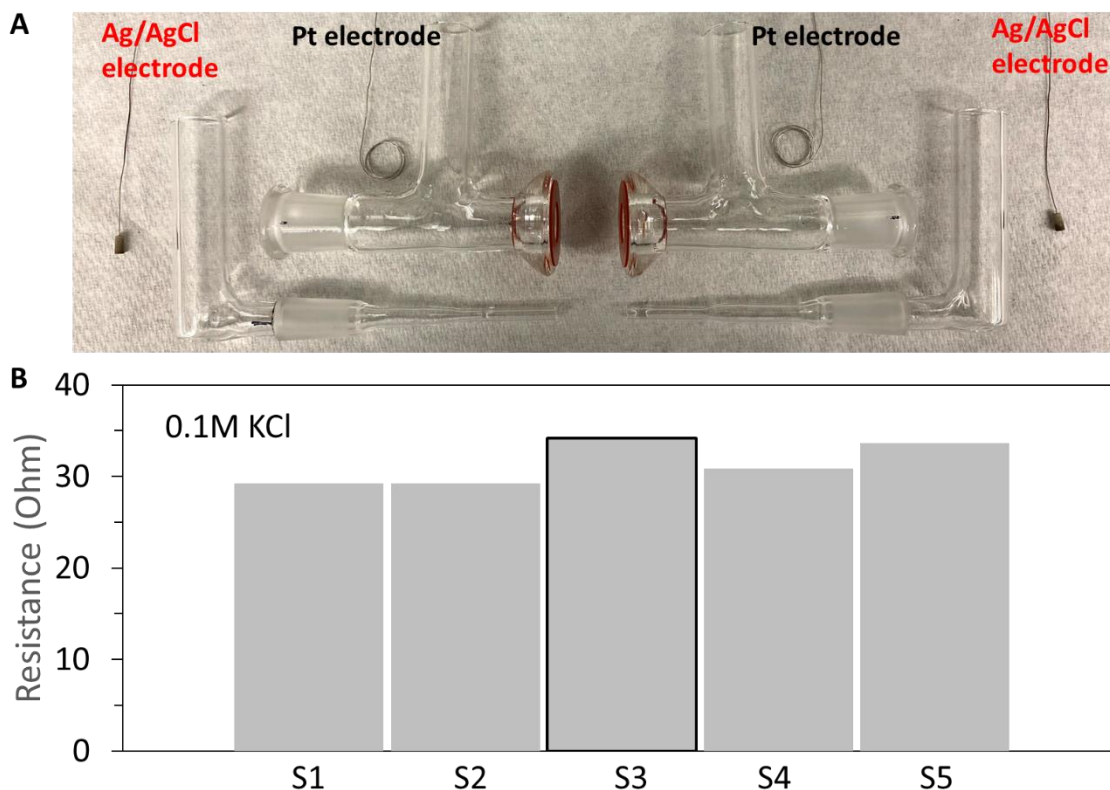
**Fig. S2 A)** Custom made H-cell with electrodes and **B)** Resistance of K$^+$ for different N212||N212 sandwich membranes in 0.1M KCl. Sample # S3 was pretreated with sulfuric acid before converting it to K$^+$-form.

Fig. S2 A, shows the custom-made H-cell cell used for the ionic conductivity measurements. Different control samples were tested for the ionic conductivity measurements as shown in Fig. S2 B. Samples S1 to S5 represents control N212||N212-K$^+$ sandwich membranes prepared using Nafion, N212 converted into K$^+$ form from their initial, as received H$^+$ form. N212 (single ply) was converted to K$^+$ form from their as received H$^+$ form without any pretreatment as described in the main text except sample S3 which was pretreated by soaking in 0.1M H$_2$SO$_4$ at 80 °C for 1h, followed by washing in DI water at 80 °C for 1h before being converted to K$^+$ form via soaking in KCl solution.
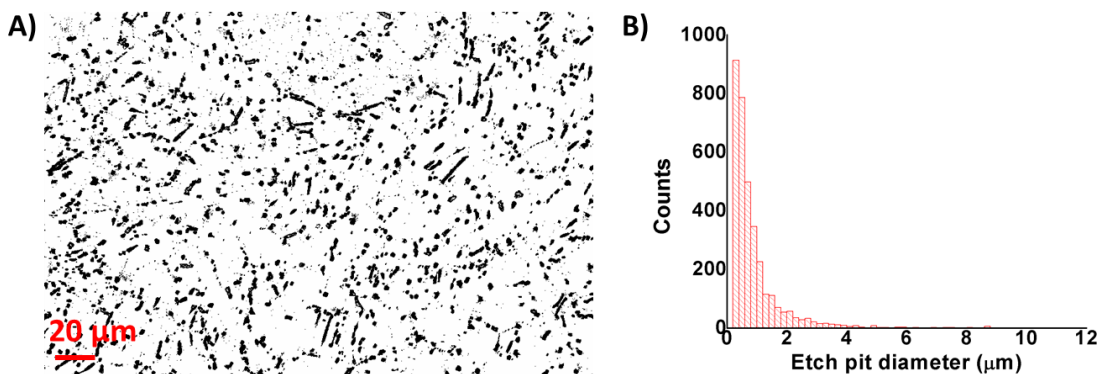
**Etch test of Graphene on Cu foil (Graphene/Cu)**



**Fig. S3  A)** ImageJ analysis of defect density using the SEM images of etch test (performed in 0.1M FeCl$_3$ for 5s) from Fig. 3A. **B)** Etch pit density distribution extracted from SEM images of graphene Cu after electrochemical etch test (1V, 1s in 0.5M CuSO$_4$ solution) using ImageJ color thresholding method.

Fig. S3, presents the ImageJ analysis of the etch test for the graphene/Cu using 0.1M FeCl$_3$ for 5s. Total area of the analyzed figure is ~ 235.9 ×165.27 µm$^2$ and total count of etch pits are ~2790. Assuming each etch pit corresponds to a defect the number of defects/cm$^2$ is ~7.1×10$^6$.

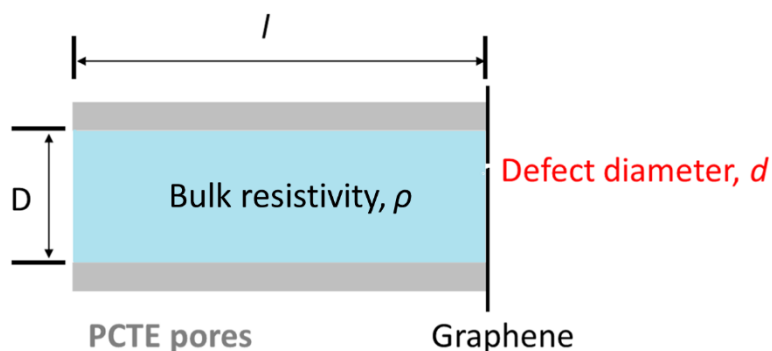**Estimation of an equivalent defect size with conductivity similar to that of an open PCTE support pore:**



**Fig. S4** Schematic of graphene suspended on a single PCTE support pore with a defect of diameter ($d$).

The ~10% porosity of the PCTE support can be used to isolate larger defects and tears in the graphene. Consider a single 200nm diameter pore of the PCTE with graphene suspended over it (Fig. S4). The presence of a defect in this supported graphene can result in increased ionic conductivity and decreased selectivity (H$^+$/K$^+$) compared to pristine graphene.

We estimate the size of a defect in graphene that equates the resistance of a single 200 nm PCTE pore by considering the access hall resistance. A defect size smaller than the estimation will provide significant resistance to ionic flow.

Assuming the pore resistivity to be same as bulk solution resistivity, the bulk resistance of a single PCTE pore, $R_{PCTE\ pore}$ can be written as

$$R_{PCTE\ pore} = \left(\rho * \frac{l}{A}\right) \ \ldots\ldots\ldots\ldots\ldots(1)$$

where, $\rho$, $l$ and $A$ are bulk resistivity of electrolyte, length of the pore and area of the pore, respectively.

Assuming the defect resistivity to be same as bulk solution resistivity, access Hall resistance from graphene with a defect (of diameter d) suspended on PCTE pore, $R_{Graphene}$ can be written as,

$$R_{Graphene} = \left(\frac{\rho}{2*d}\right) \ \ldots\ldots\ldots\ldots\ldots (2)$$

where, $\rho$ is defect pore resistivity and it is assumed to be same as the bulk electrolyte resistivity.

Using additional assumptions such as no presence of surface charge and ionic mobility inside defect being similar to bulk/PCTE pore for simplicity (note the presence of surface charge and distinctly different ionic mobility can lead to a significant deviations in the estimated defect diameter), we equate equation (1) and (2),

$$\rho\frac{l}{A} = \frac{\rho}{2*d} \text{ ----------- (3)}$$

Hence the equivalent defect diameter, d is

$$d = \frac{\pi*D^2}{8*l} \text{ --------------(4)}$$

Using our experimental conditions, $l = 10$ µm (PCTE thickness or support pore length), support pore diameter D = 200nm results in an estimated equivalent defect diameter (d) ~1.6 nm.

Hence, a single defect of ~1.6 nm will show ionic transport characteristic similar to that of an open 200 nm diameter pore of PCTE.

**Table S1. Description of the samples, their conditions and their nomenclature.**

| Sample Name | Description |
|---|---|
| Solution | Open cell (no membrane present) with electrolyte solution of 0.1M KCl or 0.1M HCl |
| N212\|\|N212+Solution<br><br>(Control) | Nafion sandwich i.e. N212\|\|N212 (also referred as control) assembled in the cell with electrolyte solution of either 0.1M KCl or 0.1M HCl. Measurements performed in KCl are referred as N212-K+ form and similarly for N212-H+ form when HCl. |
| N212\|Gr\|N212+Solution<br><br>(Graphene Sandwich Membrane) | Nafion, graphene (Gr) sandwich i.e. N212\|Gr\|N212 assembled in the cell with electrolyte solution of either 0.1M KCl or 0.1M HCl |
| N212\|\|N212 | "N212\|\|N212+Solution" after correcting for "Solution" e.g. $R_{N212\|\|N212}=(R_{N212\|\|N212+Solution})-(R_{Solution})$, where the first term on the right side is experimentally measured resistance when the N212\|\|N212 is assembled in the cell and the second term is solution resistance, which is measured with no assembled membrane. |
| N212\|Gr\|N212 | "N212\|Gr\|N212+Solution" after correcting for "Solution" e.g. $R_{N212\|Gr\|N212}=(R_{N212\|Gr\|N212+Solution})-(R_{Solution})$, where the first term on the right side is experimentally measured resistance when the N212\|Gr\|N212 is assembled in the cell and the second term is solution resistance, which is measured with no assembled membrane. |
| Gr | Refers to "only graphene" estimated values after corrections from solution as well as Nafion itself, as shown in equation (2); $R_{Gr} = R_{N212\|Gr\|N212+Solution} - (2 \times R_S + 2 \times R_{N212})$ |

**Table S2: Resistance, areal resistance and areal conductance values for centimeter-scale sandwich membranes.**

| Samples | Resistance ($\Omega$) | | Areal Resistance ($\Omega$-cm$^2$) | | Areal Conductance (S/cm$^2$) | |
|---|---|---|---|---|---|---|
| | 0.1M KCl | 0.1M HCl | 0.1M KCl | 0.1M HCl | 0.1M KCl | 0.1M HCl |
| Solution | 8.584 | 2.576 | 5.837 | 1.752 | 0.171 | 0.571 |
| N211\|\|N212+ Solution | 30.838 | 3.497 | 20.970 | 2.378 | 0.048 | 0.421 |
| N212\|Gr\|N212+ Solution | 61.728 | 4.344 | 41.975 | 2.954 | 0.024 | 0.339 |
| Gr | 30.890 | 0.848 | 21.005 | 0.576 | 0.048 | 1.735 |

Gr denotes graphene.

The areal resistance and conductivity values were estimated using:

Areal resistance = Resistance × 0.68 cm$^2$

Areal Conductance = 1/Areal Resistance

Resistance of Graphene (Gr) was calculated by subtracting (N212\|\|N212+Solution) from N212\|Gr\|N212.

**Table S3: Resistance, areal resistance and areal conductance values for PCTE membranes.**

| Samples | Resistance ($\Omega$) | | Areal Resistance ($\Omega$-cm$^2$) | | Areal Conductance (S/cm$^2$) | |
|---|---|---|---|---|---|---|
| | 0.1M KCl | 0.1M HCl | 0.1M KCl | 0.1M HCl | 0.1M KCl | 0.1M HCl |
| PCTE+Solution | 8.580 | 2.575 | 0.583 | 0.175 | 1.714 | 5.711 |
| PCTE+Nafion+ Solution | 30.820 | 3.488 | 2.096 | 0.237 | 0.477 | 4.216 |
| PCTE+IP+Nafion+ Solution | 272.319 | 17.120 | 18.518 | 1.164 | 0.054 | 0.859 |
| PCTE+Gr+Nafion+ Solution | 41.246 | 3.971 | 2.805 | 0.270 | 0.357 | 3.704 |
| PCTE+Gr+IP+Nafion+ Solution | 195.263 | 7.959 | 13.278 | 0.541 | 0.075 | 1.848 |

Area of the PCTE membrane is 0.068 cm$^2$.

**Thickness of PCTE + IP + Nafion Membrane**

A digital micrometer was used to measure the thicknesses of PCTE membranes subjected to interfacial polymerization (IP) and dip coated in Nafion. The measured thickness was ~14 ± 2 μm. Cross-sectional SEM images also thickness ~13.5 μm (see Fig. S5) in agreement with the measured thicknesses from micrometer experiments.
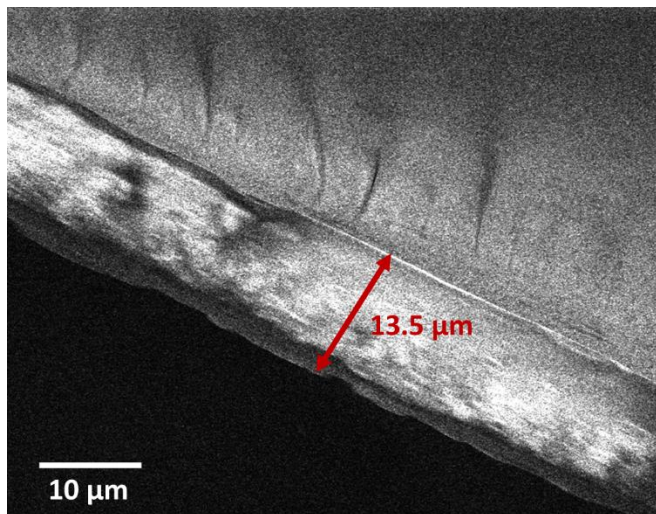


**Fig. S5** Cross-sectional SEM image of a PCTE + IP + Nafion membrane.

**References:**

(1)    Vanysek, P. Ionic Conductivity And Diffusion at Infinite Dilution. In *CRC Handbook of Chemistry and Physics*; CRC Press: Boca Raton, FL, 2000; Vol. 83, pp 76– 78