Proton Conductive Membranes Based on Two Dimensional Materials

Dhanraj Shinde, Pavan Chaturvedi, Sergei Smirnov (NMSU); Ivan Vlassiouk (GG); Georgios Polyzos (ORNL)

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Why do we need new membranes?

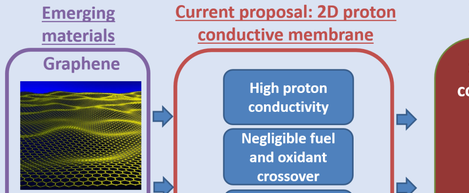
Membranes define the performance and economic viability of many applications: Fuel Cells, RedOx batteries, electrolyzers and others.

Current state of the art proton conductive membranes (e.g. Nafion) have technical and economic limitations:

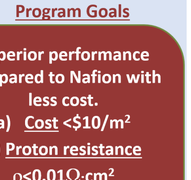
- Hydration is required
- Crossover (low proton selectivity)
- High cost

Nafion is Bulk (3D) Material ➔ Selectivity vs. Conductivity Tradeoff

Nafion chemical structure



Fuel Cell Cost Breakdown

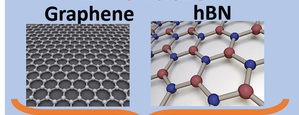


Houchins et al., *Membranes*, **2012**, 2, 855-878;

Proposed Solution: 2D Membranes Based on Atomically Thin Materials

2D Membrane

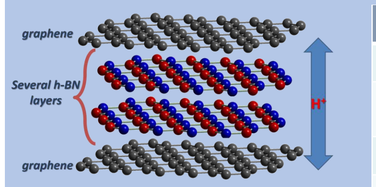
Graphene hBN



Current state of the art: 3D Nafion

Nafion – 3D polymeric membrane. > 25 μm thick

Proposed Membrane Structure



Targets

Metric	State of the Art	Proposed
Operation temperature	<120^{0}C	-50 to 400^0 C
Required humidity levels	>50%	>0%
Methanol crossover	10 mA/cm^2	<0.1 mA/cm^2
Manufacturin	$30/m^2	$1/m^2

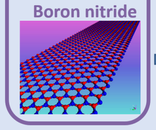
Proposed 2D Membrane is > 1000 times thinner than Nafion

Program Overview

Emerging materials

Graphene

Boron nitride



Current proposal: 2D proton conductive membrane

- High proton conductivity
- Negligible fuel and oxidant crossover
- Chemical and thermal stability
- No humidification requirement

Program Goals

Superior performance compared to Nafion with less cost.

a) Cost <$10/m^2

b) Proton resistance

ρ<0.01Ω·cm^2

c) Operational Temperature

-50^{0}C - + 400^{0}C

d) Crossover <2 mA/cm^2

Proton conductive membranes:10X performance, 1/10 of the cost

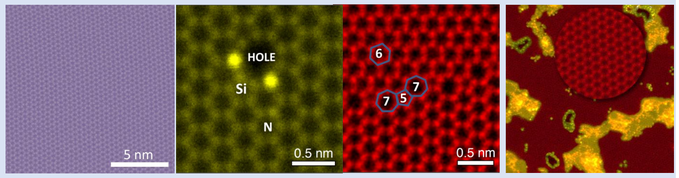
How do we make 2D materials H$^+$ conductive?

Special treatments are required to produce H$^+$ specific defects in the graphene and boron nitride crystal lattices

Various approaches can be used to create defects: Bombardment by particles, plasma treatment, material synthesis at low temperatures as well as employing plasma enhanced synthesis.

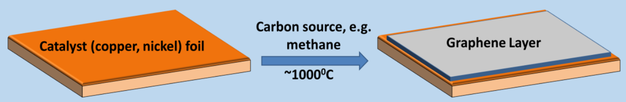
Atomic resolution STEM images of the crystal lattice defects:

Pristine | Vacancies / Substitutions | 5,7,8 carbon cycles | Larger nanopores

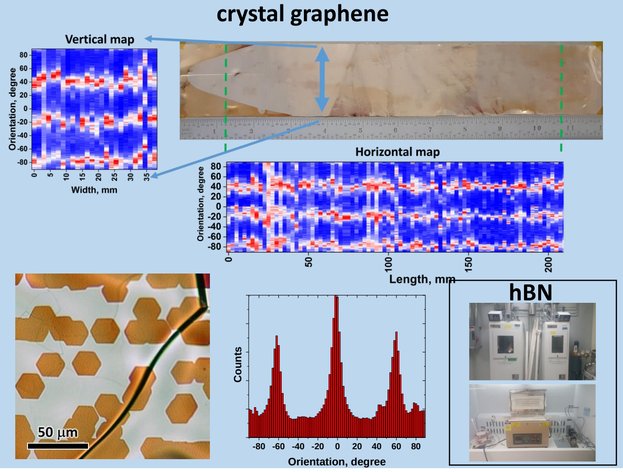


Can we make 2D materials with required quality on a large scale?

CVD batch synthesis approach was used to synthesize 40'' films



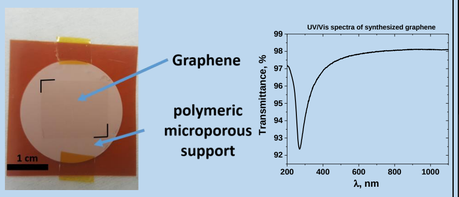
Example of R2R single crystal synthesis: 1 foot single crystal graphene

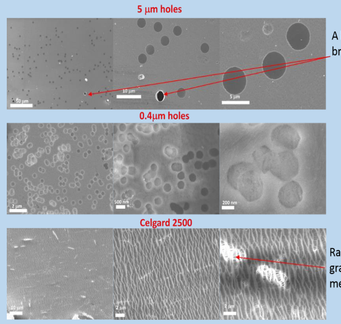


Results

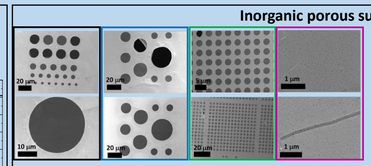
Transferred graphene on variety of porous supports

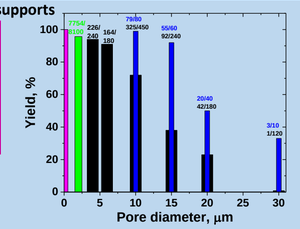
Polymer porous supports

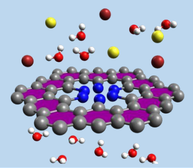




Inorganic porous supports

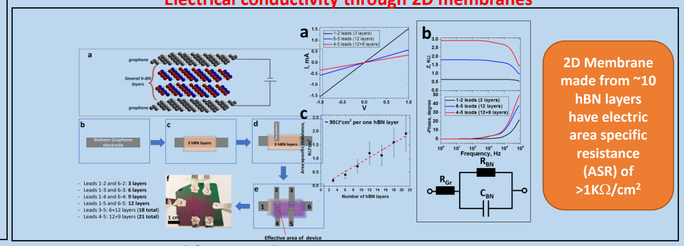






2D Membranes – universal platform for variety of separations.

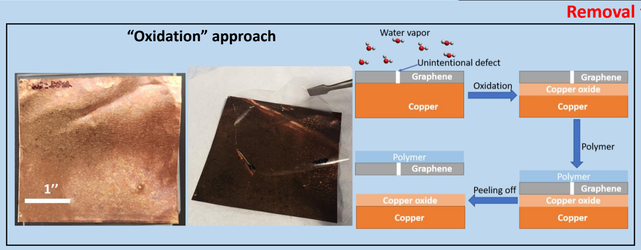
Electrical conductivity through 2D membranes



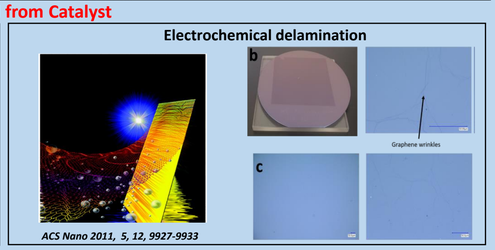
2D Membrane made from ~10 hBN layers have electric area specific resistance (ASR) of >1KΩ/cm^2

Removal from Catalyst

"Oxidation" approach

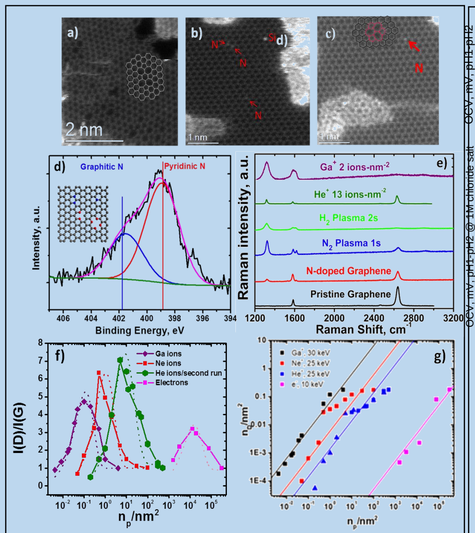


Electrochemical delamination



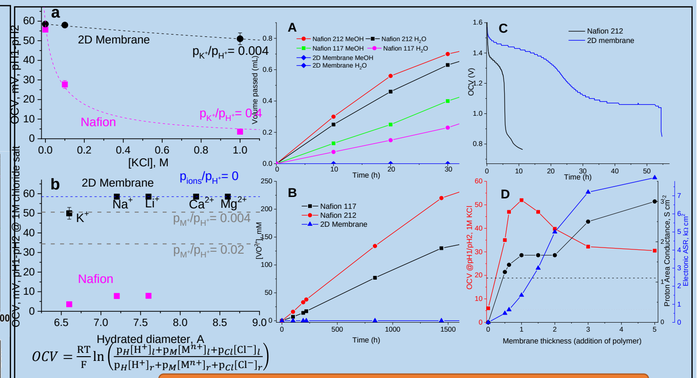
ACS Nano 2011, 5, 12, 9927-9933

Introduction of defects



Bombardment by various species (e, He$^+$, Ne$^+$, Ga$^+$) and plasma treatments (N_2, H_2) are efficient ways for defects creation

Composite 2D Membrane performance



$$OCV = \frac{RT}{F}\ln\left(\frac{p_H[H^+]_I + p_M[M^{n+}]_I + p_{Cl}[Cl^-]_I}{p_H[H^+]_r + p_M[M^{n+}]_r + p_{Cl}[Cl^-]_r}\right)$$

Composite 2D membrane outperform PFSA in most aspects.

Membrane	Thickness (μm)	Area proton resistance (Ω cm^2)	VO^{2+} crossover (10^{7}cm^2/min)	MeOH crossover (10^{7}cm^2/s)	Water crossover (10^{8}cm^2/min)
Nafion 212	50*	0.75 ± 0.3	1.2 ± 0.1	1.4 ± 0.1	6.9 ± 0.2
Nafion 117	183*	2.2 ± 0.3	2.2 ± 0.2	2.2 ± 0.2	7.8 ± 0.3
Composite 2D Membrane	11±1	0.6	0	0	0