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Room temperature Sieving of Hydrogen Isotopes Using 2-D Materials

Hydrogen isotope separation is critical to the DOE's mission in environmental remediation and nuclear nonproliferation. Isotope separation is also a critical technology for the NNSA, and the ability to perform the separations at room temperature with a relatively small amount of power and space would be a major advancement for their respective missions. Recent work has shown that 2-D materials such as graphene and hexagonal boron nitride can act as an isotopic sieve at room temperature; efficiently separating hydrogen isotopes in water with reported separation ratios of 10:1 for hydrogen: deuterium separation for a single pass. The work performed here suggests that this technique has merit, and furthermore, we are investigating optimization and scale up of the required 2-D material based membranes.

Awards and Recognition

Intellectual Property Review

This report has been reviewed by SRNL Legal Counsel for intellectual property considerations and is approved to be publically published in its current form.

SRNL Legal Signature

Signature

Date

Room temperature Sieving of Hydrogen Isotopes Using 2-D Materials

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Subcontractor:

Thrust Area: NS

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Recent studies have shown successful separation of protium (H) and deuterium (D) in the aqueous phase using 2-D nanomaterials laminated onto proton exchange membranes (PEMs). In practice an electrochemical pump is built using the membranes where conduction is rate-limited by transport of hydrons (H^+ , D^+ , and T^+) across the 2-D material. The basis for the separation is believed to be quantum tunneling through the graphene which favors the the conduction of H^+ ions over D^+ ions. Previous work has shown an H:D separation factor of ~10:1 under favorable conditions and proper processing of the 2-D material.

The results of this work have shown that there is plausible merit to the claims in these previous studies with our results indicating isotope separation ratios of ~2:1 using a similar technique. Isotope separation measurements on this system are not simple due to experimental artifacts and analytical limitations. Therefore much of the effort in this FY was spent on fabricating membranes and building an apparatus for H:D separation measurements.

FY2017 Objectives

- Fabricate graphene coated Nafion membranes
- Characterize graphene films transferred to Nafion membranes by microscopy and Raman spectroscopy
- Build an apparatus for H/D isotope separation
- Demonstrate H/D separation in an aqueous phase
- Begin development of a membrane scale up approach

Introduction

Traditional techniques for hydrogen isotope separation are all based in kinetic isotope effects that are energy intensive; require low temperatures, a large footprint, or some combination of the three. Recent work has shown that 2-D materials such as graphene and hexagonal boron nitride (hBN) can act as an isotopic sieve at room temperature and, thus, provide a means of efficiently separating hydrogen isotopes. In particular one study has shown successful separation of protium (H) and deuterium (D) in the aqueous phase, with separation ratios on the order of 10:1.¹

This process is believed to be governed by a quantum tunneling mechanism and utilizes continuous sheets of 2-D materials with no holes or defects. This is fundamentally different from the approach taken by most graphene based or intercalated separation membranes which use holes in the structure (i.e., lattice defects) or spaces between nanostructures in a composite. In the electrochemical pumping

configuration, a cell is formed using a proton exchange membrane (PEM) coated with a 2-D material. A potential applied across the PEM drives ions (hydrons) to migrate across the membrane. The separation occurs as ions are then driven (quantum tunnel) across the 2-D material.

Approach

The goal of this project is to investigate the feasibility of 2-D materials as isotopic sieves for separation of hydrogen isotopes while simultaneously investigating the fabrication, optimization, and scale up of 2-D material Proton Exchange Membranes.

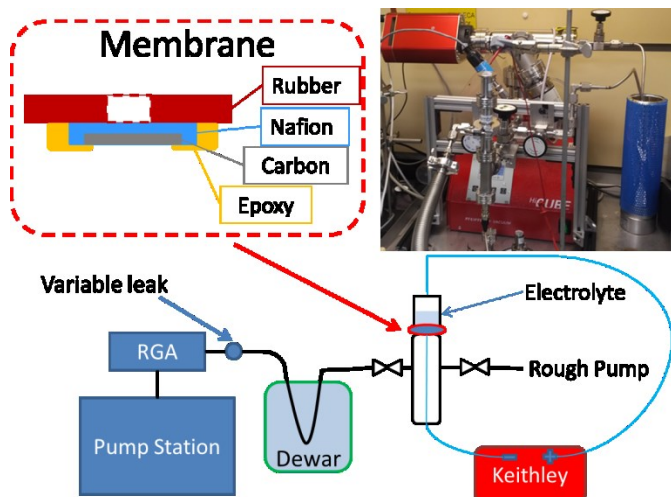


Figure 1. Schematic and picture of the experimental setup for isotope separation.

Initial milestones were to recreate the apparatus discussed in the open literature and to develop greater understanding of the mechanism(s) governing process described in the literature.

Figure 1 shows a diagram and picture of the experimental setup built to measure hydrogen isotope separation. In this configuration hydrons are driven by a potential supplied by Keithley power supply from liquid side of the cell (0.1M HCl/DCl electrolyte) through the membrane into the vacuum chamber. In the vacuum chamber hydrogen is detected using a quadrupole mass spectrometer.

In a limited scope through a Clemson University contract, research methods using graphene and related materials as isotopic sieves in water electrolysis cells have also been explored. Clemson was able to keep a graduate student employed during the summer and the feasibility, scopes, and lab setup needs were investigated for isotopic selectivity on hydrogen evolution with graphene sieving in the Membrane Electrode Assemblies (MEAs) of PEMs. The Clemson group is well known as experts on MEAs and PEMs, and SRNL has benefited from their water electrolysis cell design.

Results/Discussion

Graphene was grown on copper using chemical vapor deposition (CVD) and subsequently transferred to the surface of commercial Nafion membranes. Before transferring the graphene to Nafion membranes its quality and, in particular, the amount of multilayer graphene was characterized using a combination of microscopy and spectroscopy. Scanning electron microscope (SEM) images were collected before and after < 1 nm HfO_2 was deposited on top of the graphene by Atomic Layer Deposition (ALD). The deposited HfO_2 is preferentially deposited on the multilayer regions, grain boundaries, and lattice defects and thus adds contrast to SEM images for these areas. This contrast technique facilitates digital image analysis using ImageJ (Fig. 2a) to quantify the high contrast area. Using this technique multilayer graphene was estimated to cover 14.2% of the sample. To verify the technique Raman spectra were taken and analyzed to estimate the amount of multilayer graphene through deconvolution of the 2-D peak. The Raman maps displayed 14% multilayer in the sample. This agreement between the techniques suggests that the ALD/SEM technique is a viable method to quantify multilayer regions in arbitrarily large graphene samples.

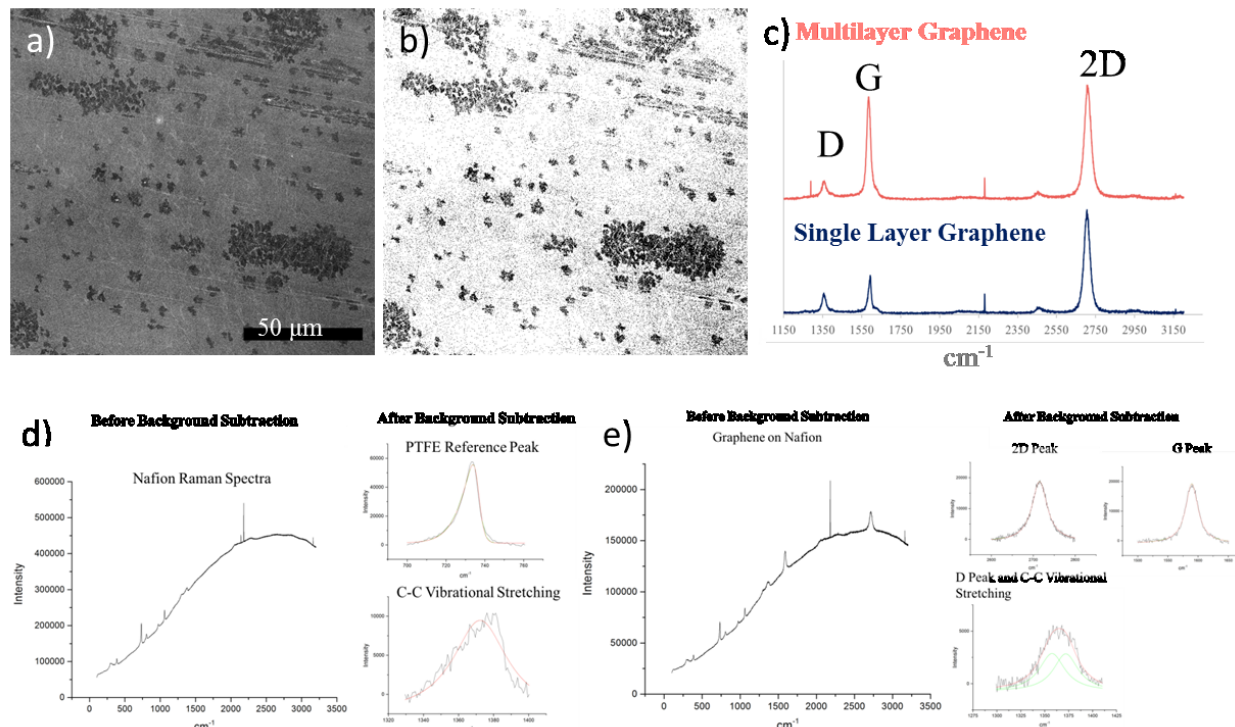


Figure 2. An ImageJ analysis (b) of SEM images (a) can quantify the density of multilayer regions and is confirmed by Raman map scans (c). Raman Maps: 14 % multilayer SEM: 14.2% multilayer. (d) Raman spectra Nafion without graphene. (e) Raman spectra of graphene on Nafion.

Generally, graphene transfer methods are optimized for hard surfaces where overall cleanliness of the final product is the governing criteria. In this case however, we had to optimize the transfer conditions to minimize stress on the graphene in order to avoid the introduction of defects into the membrane. Raman spectroscopy was used to characterize the graphene after the transfer. It is well known that graphene can be characterized using Raman spectroscopy; however, the underlying substrate plays a large role in properly measuring the characteristic peaks.² In the case of graphene-Nafion composites the large background signal from Nafion results in low intensity peaks and difficulty focusing both of which make measurements of the graphene quality particularly difficult. Furthermore, Nafion has several characteristic Raman peaks (Fig. 2d), one of which is a low intensity, broad peak found at ~ 1380 cm^{-1} , very close to the D peak of the graphene, thus necessitating peak fitting to resolve any usable information about the D peak (Fig 2d and e, note: the sharp lines near ~ 2200 cm^{-1} are an artifact of the Raman measurement).^{3,4}

Figure 3a shows a sample $\text{H}_2\text{O}:\text{D}_2\text{O}$ data set, collected with the experimental setup shown in Figure 1, where each plateau corresponds to a data point in the ion

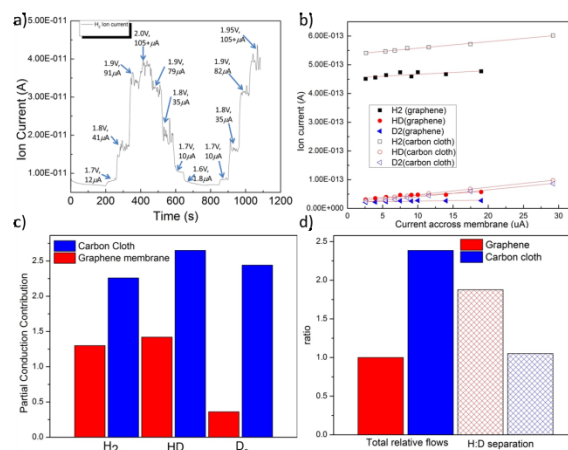


Figure 3 a) Sample raw data set b) Ion current as a function of cell current measured using the same solution with both carbon cloth membrane and graphene membranes. c) Partial conduction contributions, and d) total flow and

current v membrane current plot shown in Figure 3b. Figure 3b shows the ion current as a function of cell current measured using the same solution with both a carbon cloth membrane (baseline, where no 2-D material based separation should be occurring) and a graphene membrane. Using the same solution with both a carbon cloth membrane and a graphene membrane allowed for the direct comparison of data without having to consider differences in detector efficiency for different isotopes in our mass spectrometer. Figure 3c shows the partial conduction contribution from different species taken as the slopes of the data in b to remove contributions from the chamber background, because the expected H_2 background in the chamber is an order of magnitude larger than the HD or D_2 background. Finally, Figure 3d shows the total hydron flow and separation ratios for the setup. As expected the total hydron flux across the carbon cloth membrane is significantly larger than the graphene membrane due to the increased conductivity. The measured separation factor of ~ 2 is significantly smaller than the 10 reported in the literature, and can most likely be attributed to imperfections in our membranes from the transfer and fabrication process.

FY2017 Accomplishments

- Synthesis:
 - Single layer graphene sheets have been synthesized via CVD
 - CVD graphene has been transferred to Nafion
- Characterization
 - Raman spectra collected on as-synthesized graphene, and graphene on Nafion
 - New method for estimating the amount of multilayer graphene over large areas
- Separation measurements
 - Designed and built a setup to test isotope separation in the electrochemical pumping configuration
- Membrane scale up
 - Investigating direct growth of graphene on Cu coated Si-N grids
 - If successful, this route would represent a “transferless” membrane fabrication technique

Future Directions

- Optimization and scale up of the graphene transfer and membrane fabrication process
- Characterization
 - Continue studying Raman spectra collected on as-synthesized graphene, and graphene on Nafion
- Separation measurements
 - H/D/T separation measurements

FY 2017 Publications/Presentations

1. J. Velten, D. Hitchcock, T. Krentz, M. Young, and E. Vogel (September, 2017) “Two Dimensional Nanomaterials for Water Detritiation and Isotope Separation” presented at the 2nd Asia-Pacific Symposium on Tritium Science (APSOT-2), Livermore Valley, CA
2. K. Young, C. Joiner, D. Hitchcock, S. Serkiz, E. Vogel. (November, 2017) “A Facile Approach to Mapping Graphene Grain Boundaries and Multilayer Regions on Copper” Accepted for presentation at the fall MRS meeting, Boston, MA

References

1. Lozada-Hidalgo *et al.*, "Sieving hydrogen isotopes through two-dimensional crystals" Science 351, 6268, 68-70 (2016) List any references used in the report.
2. Z. Ni, *et al.*, "Raman Spectroscopy and Imaging of Graphene," Nano Res. 1 (2008) 273-291.
3. A. Gruger, *et al.*, "Nanostructure of Nafion membranes at different states of hydration an IR and Raman study," Vibrational Spectroscopy 26 (2001) 215-225.
4. J. Zeng, *et al.*, "In Situ Surface-Enhanced Raman Spectroscopic Studies of Nafion Adsorption on Au and Pt Electrodes," Langmuir 28 (2012), 957-964.

Acronyms

ALD: Atomic Layer Deposition

CVD: chemical vapor deposition

MEA: membrane electrode assemblies

PEM: proton Exchange Membrane

SEM: scanning electron microscope

hBN: hexagonal boron nitride

Intellectual Property

none

Total Number of Post-Doctoral Researchers

One postdoctoral researcher (Josef Velten), and one graduate student (Katie Young, GA Tech) were involved with this project.