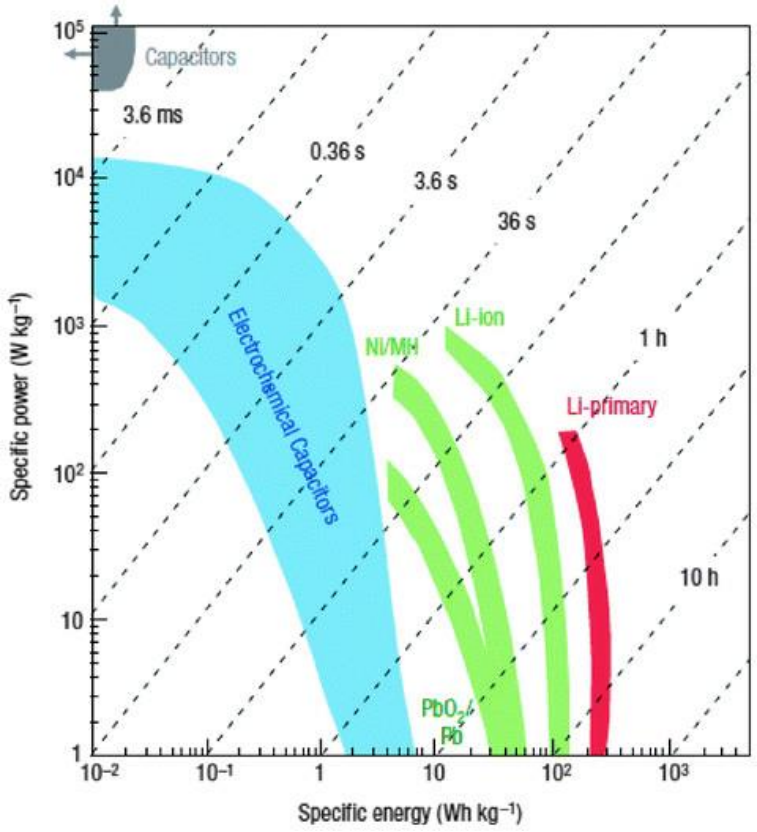
University of Pittsburgh

Adventitious Hydrocarbons and the Graphite-Water Interface

Justin Hurst

April 2020

Electrical Energy Storage



http://dx.doi.org/10.1039/b813846j

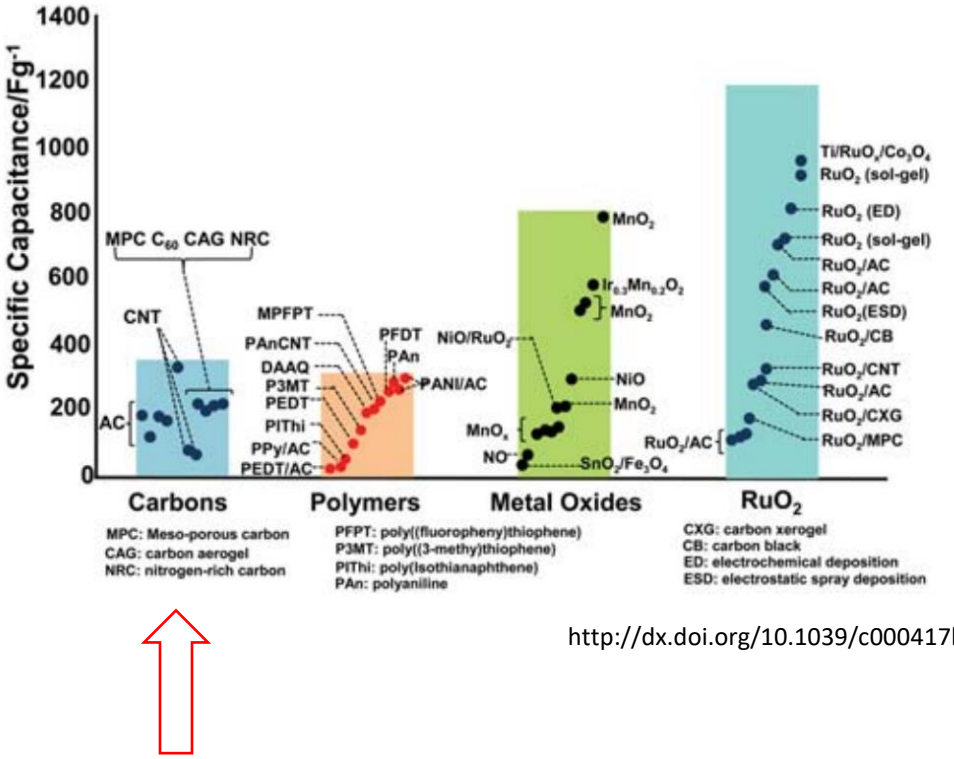
Advantages of electrochemical capacitors:

- Better charge/discharge cycle life than batteries
- Faster charging
- More power density
- Higher charge/discharge efficiency

Disadvantages of electrochemical capacitors:

- Low energy density
- Faster self-discharge rate

Carbon Electrode Materials



http://dx.doi.org/10.1039/c000417k

- Less expensive alternative
- Lightweight
- Materials are less toxic

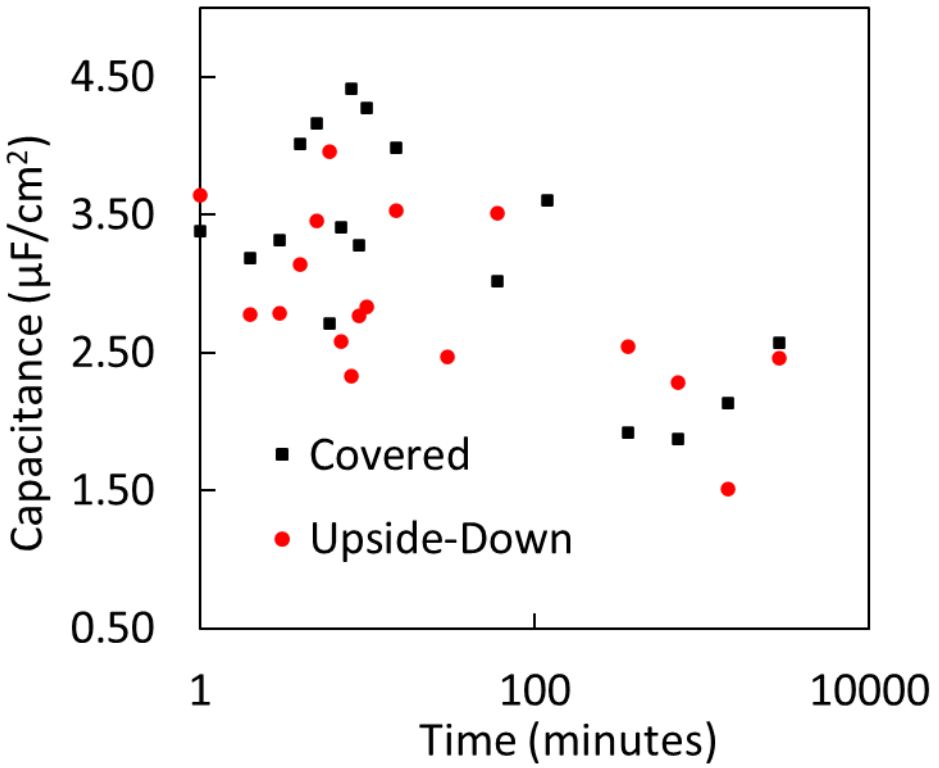
Surface Contamination

We could enhance performance by using cleaner surfaces

- Understanding the intrinsic water wettability of graphite[1]
- Effect of airborne contaminants on the wettability of supported graphene and graphite[2]
- Contamination and Wettability: Rare Earth Oxides[3]

References:
1. Kozbial, A.; Li, Z.; Sun, J.; Gong, X.; Zhou, F.; Wang, Y.; Xu, H.; Liu, H.; Li, L., Understanding the intrinsic water wettability of graphite. *Carbon* **2014,** *74*, 218-225.
2. Li, Z.; Wang, Y.; Kozbial, A.; Shenoy, G.; Zhou, F.; McGinley, R.; Ireland, P.; Morganstein, B.; Kunkel, A.; Surwade, S. P., Effect of airborne contaminants on the wettability of supported graphene and graphite. *Nature materials* **2013,** *12* (10), 925-931.
3. Salim, M. Contamination and Wettability: Rare Earth Oxides. University of Pittsburgh, 2015.

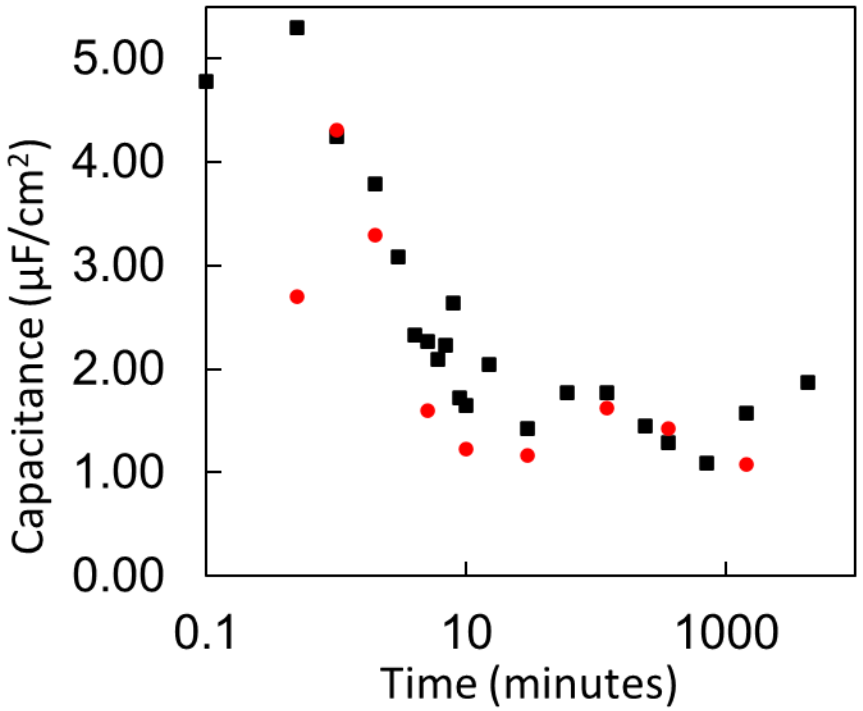
Change in Capacitance with Air Aging



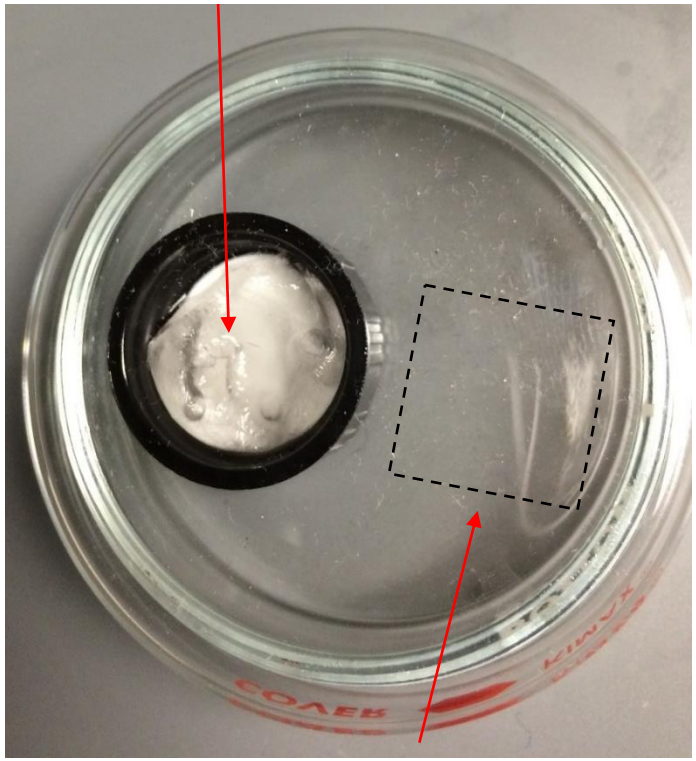
Graphite

- Clean graphite was exposed to air for different time intervals
- Each measurement is a separate exfoliation
- Capacitance reduced by 40% over 24 hours

Air Aging With 1-Octadecene

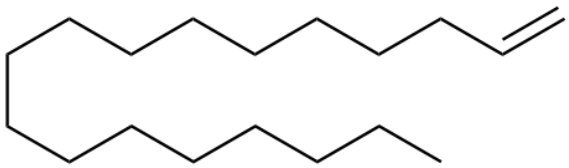


1-Octadecene Reservoir



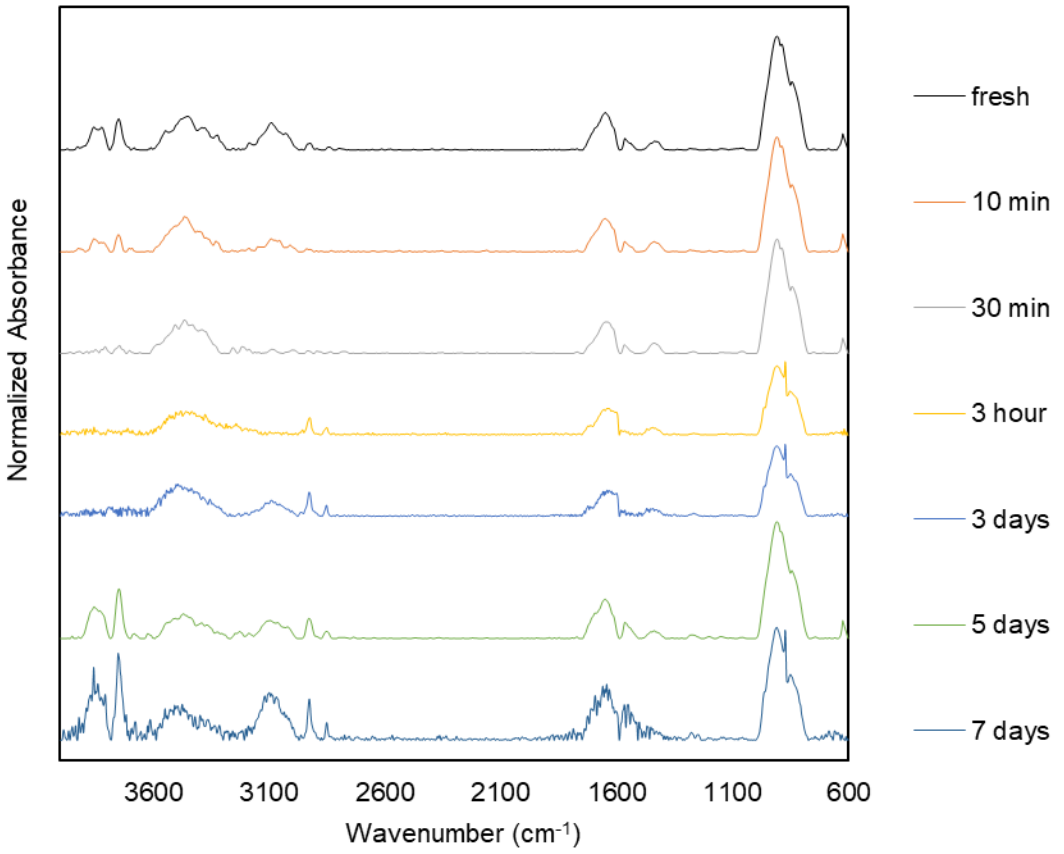
Where graphite is placed

- Clean graphite was exposed to 1-octadecene environment
- Each measurement is a separate exfoliation
- Capacitance reduced by 70% over 10 minutes



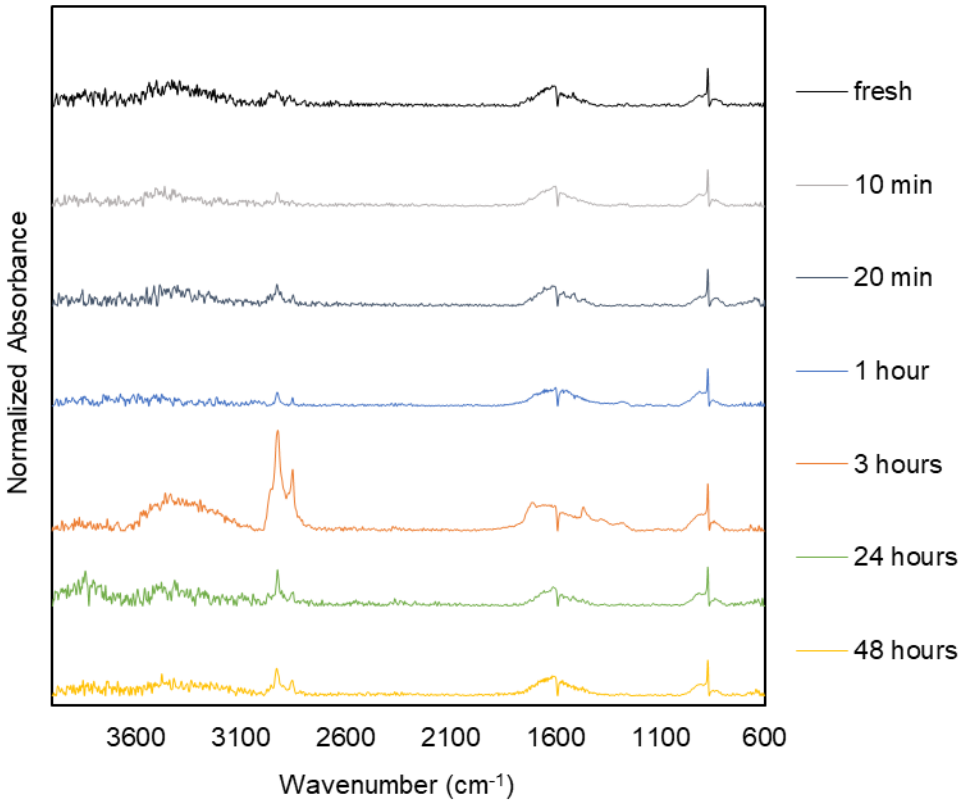
1-Octadecene

FTIR of Graphite After Exposure to Air



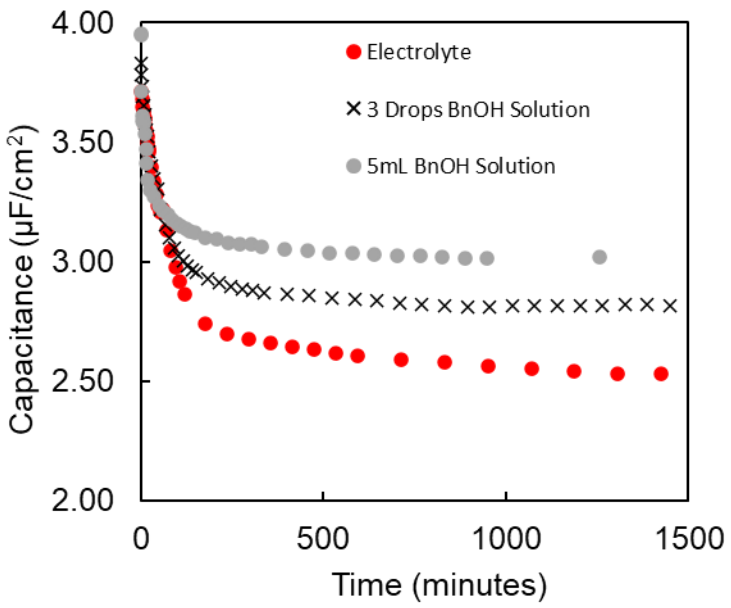
- Clean graphite was exposed to air for 4 hours
- After 10 minutes a C-H stretch peak is visible at ~2900 cm^{-1}
- A large peak at ~1650 cm^{-1} is likely a C=C stretch. There is little noticeable change in this peak over the duration

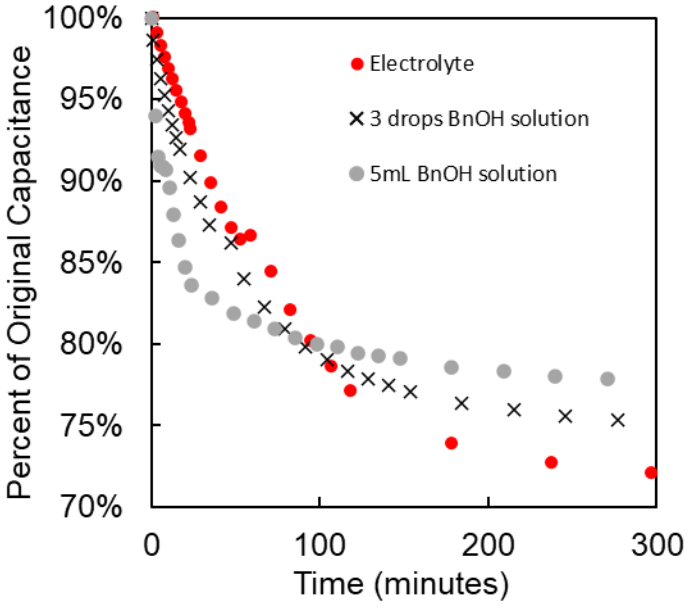
Exposure to 1-Octadecene



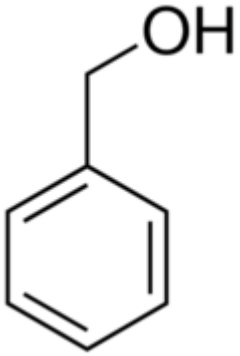
- First visible at 10 minutes
- Large increase after 3 hours - anomaly could not be replicated
- C-H stretch peaks still present after 2 days

Liquid Phase Aging

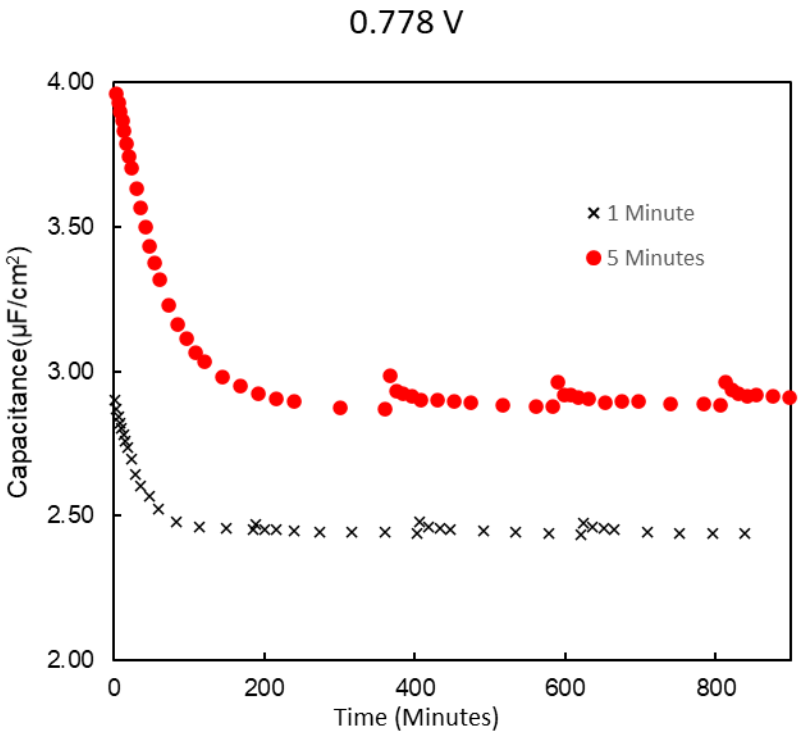


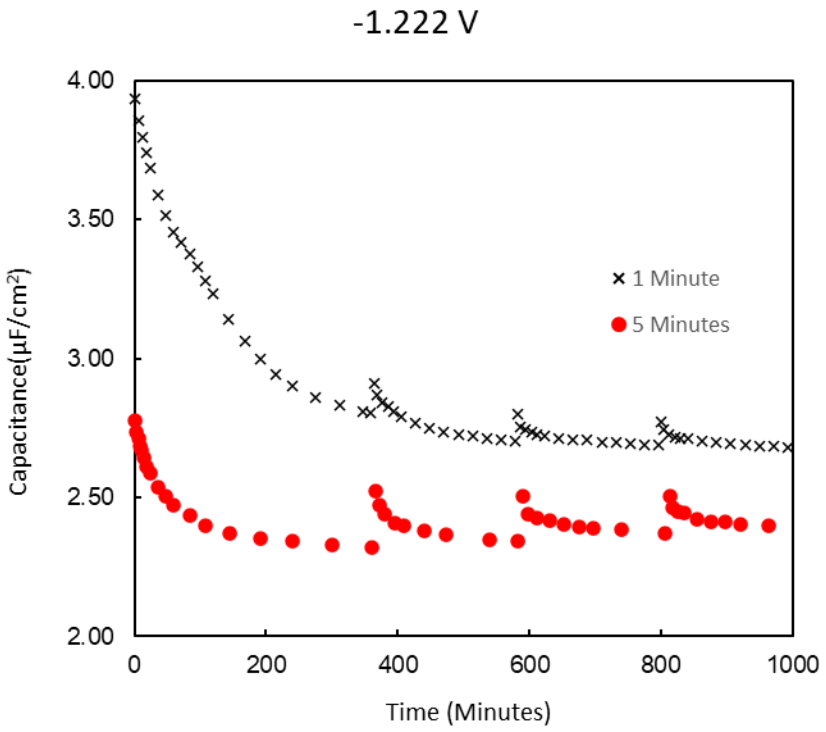


- Comparison of graphite in pure and intentionally contaminated electrolyte solution
- Initial drop in capacitance is faster with more benzyl alcohol
- Addition of 1.5 % benzyl alcohol reduces the impact of contamination



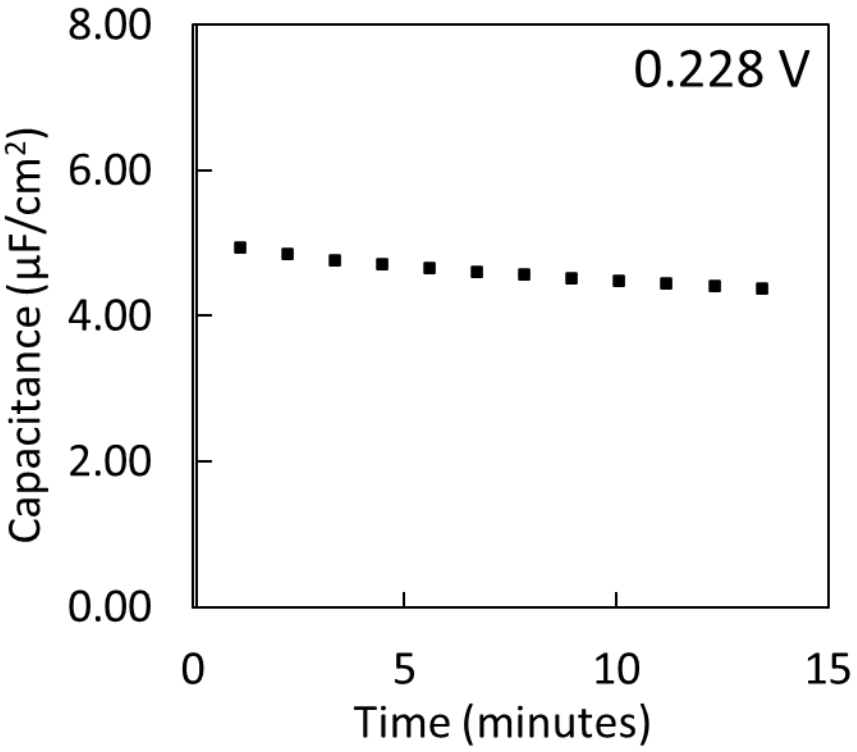
Cell Potential Conditioning

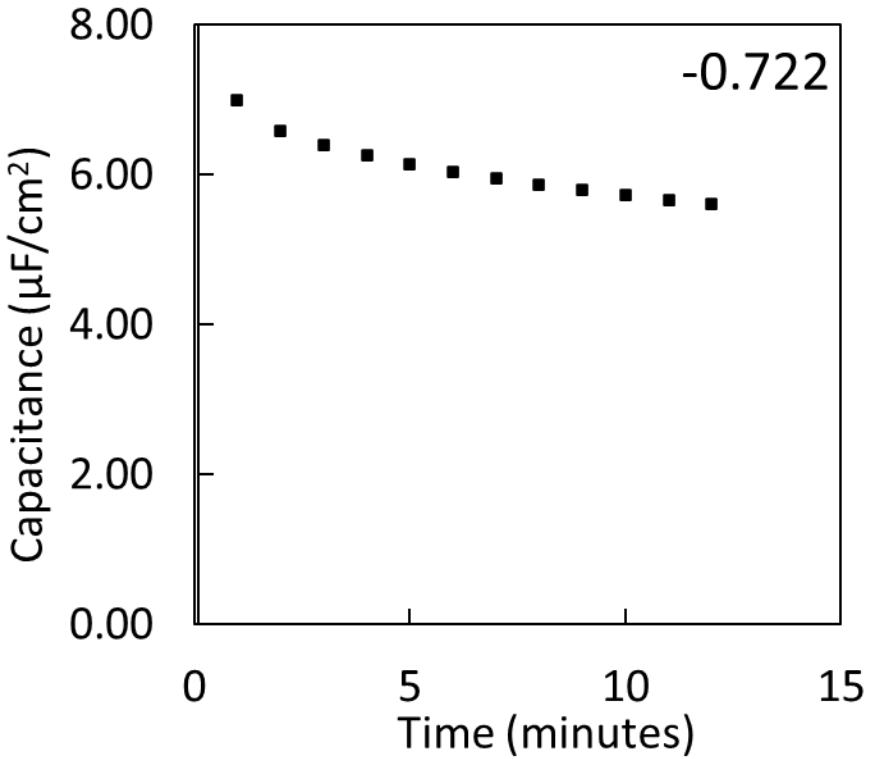




- Investigated the effect of cell potential on the equilibrium capacitance
- The cell was held at 0.778 V or -1.222 V, for either 1 minute or 5 minutes
- Capacitance measurements were taken at -0.222 V

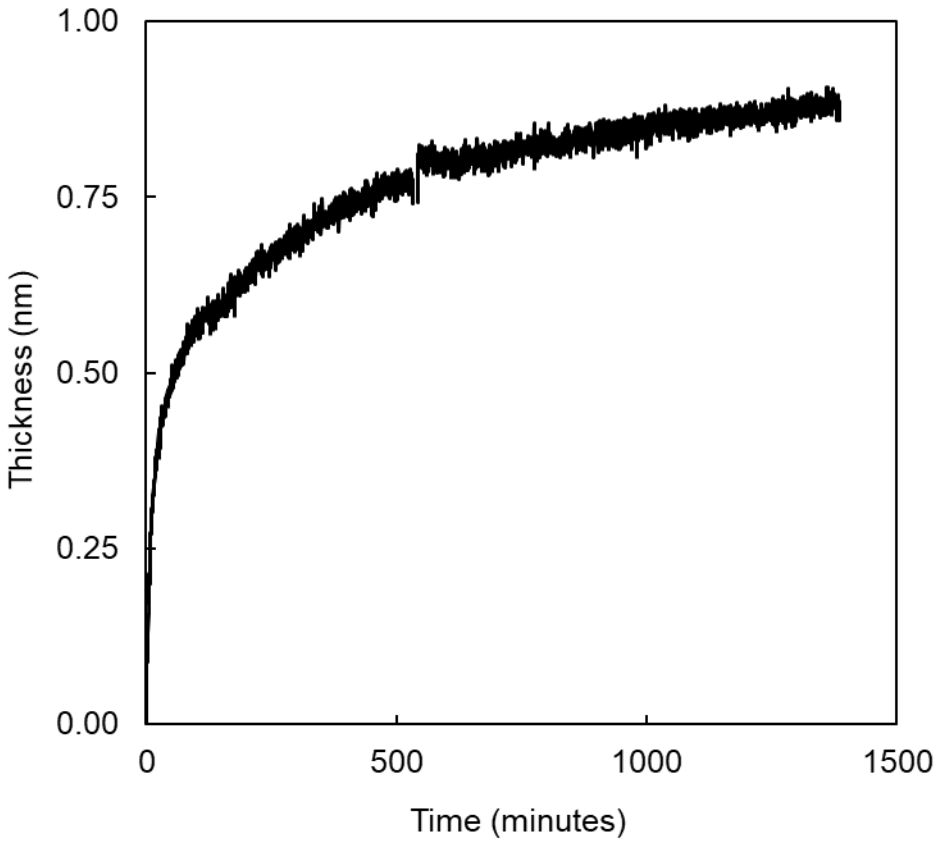
Aging at Different Cell Potentials





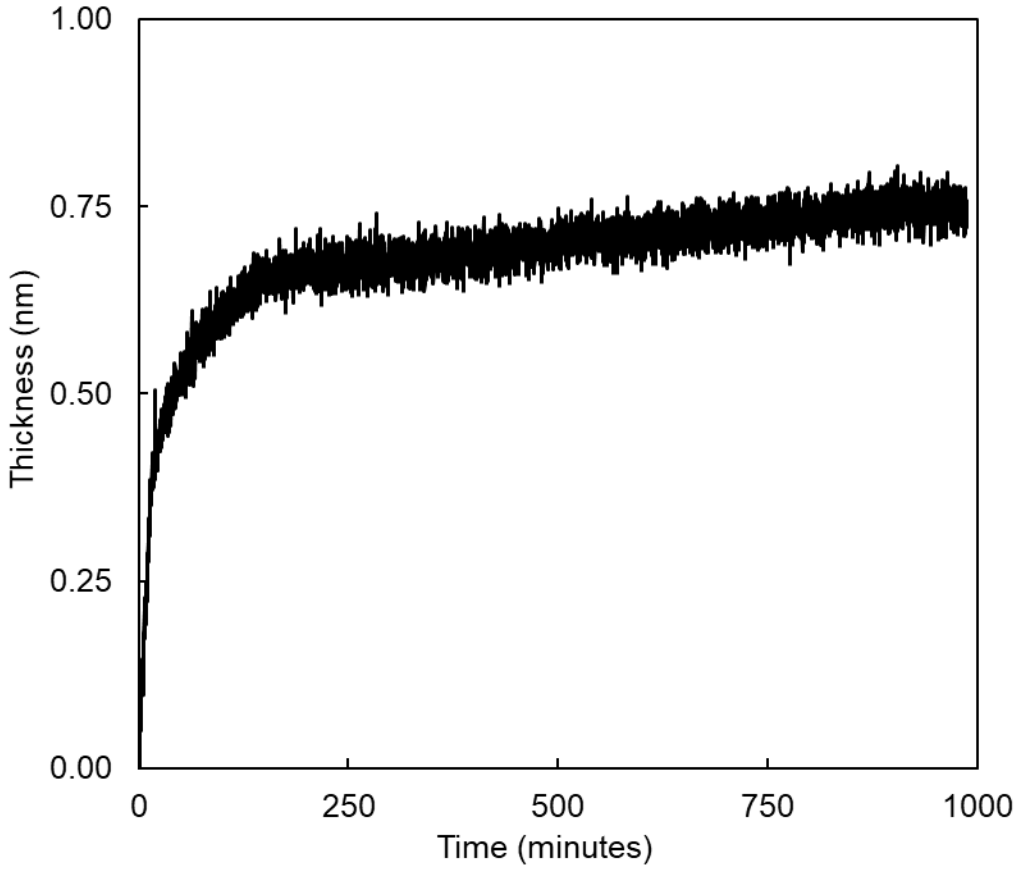
- The aging effect is observed at different cell potentials as well
- Higher initial capacitance, but sharper decrease with negative cell potential

Layer Growth in Ultrapure Water



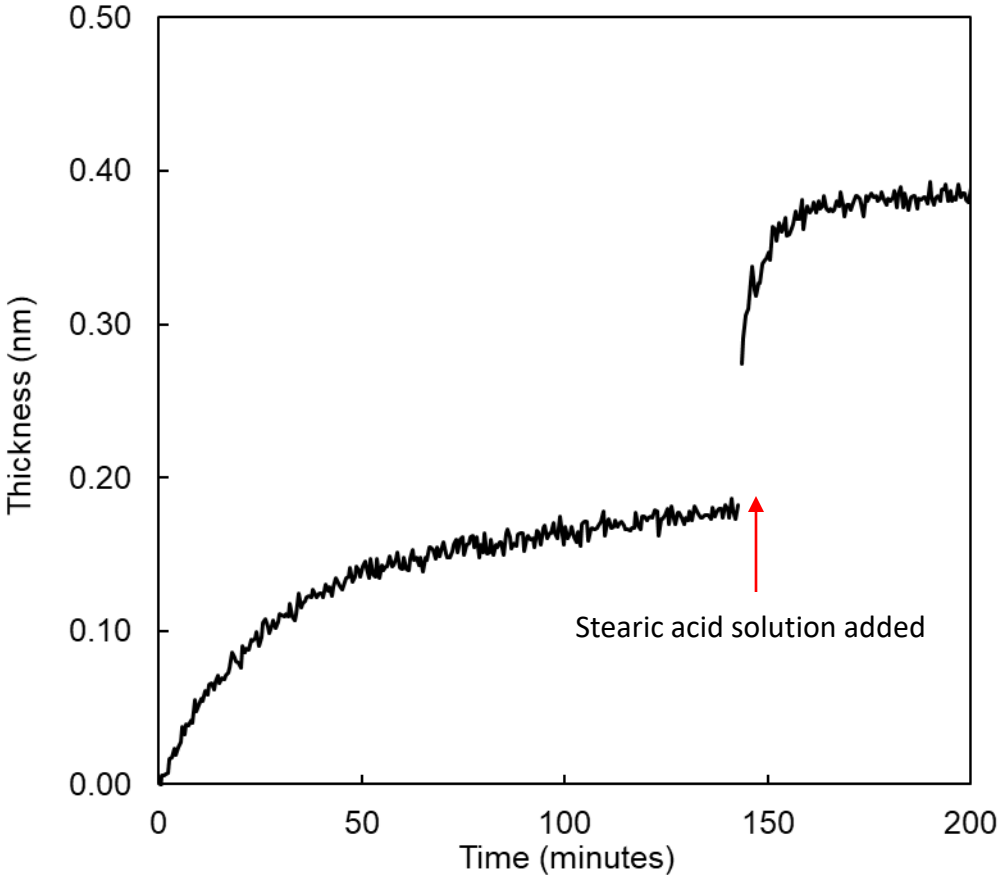
- Clean graphite in ultrapure water
- Implements rinsed with acetone, isopropyl alcohol, and water
- 0.8 nm layer grows in 16 hours

Layer Growth in Ultrapure Water

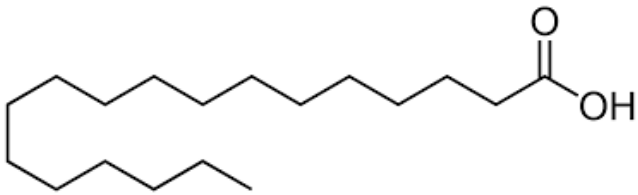


- Clean graphite in ultrapure water
- Implements cleaned with either piranha solution or UV/Ozone
- 0.75 nm layer grows over 16 hours

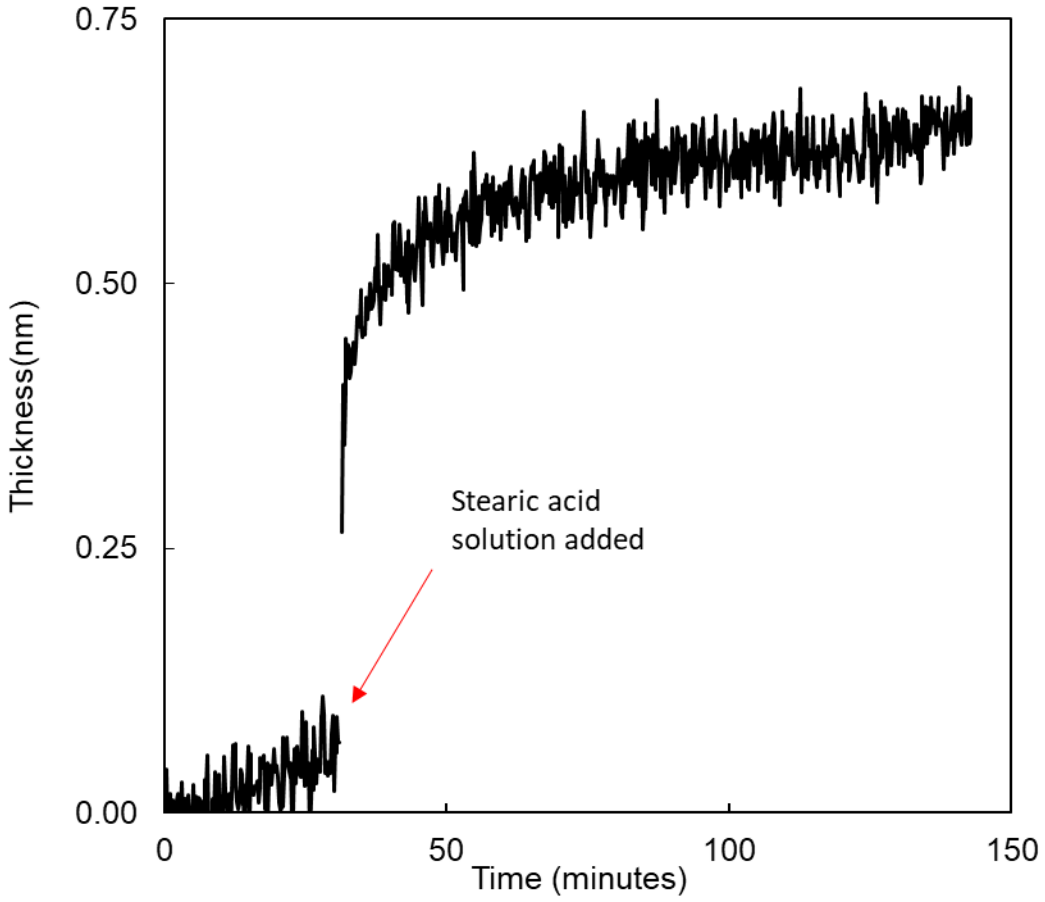
Layer Growth with Added Stearic Acid



- Clean graphite in ultrapure water
- Saturated stearic acid solution added (~10^{-2} M) around 140 minutes
- Rapid layer growth of an additional 0.2 nm over one hour.

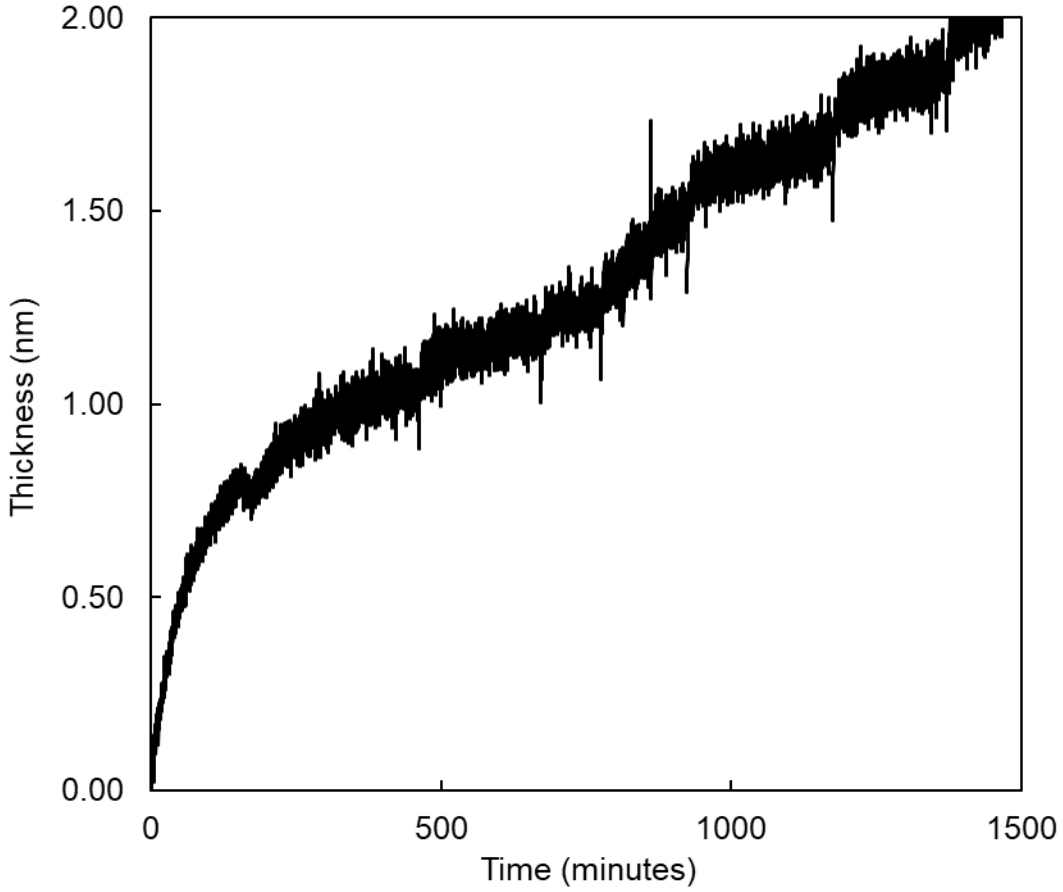


Layer Growth with Added Stearic Acid



- Clean graphite in ultrapure water
- Saturated stearic acid solution added (~10^{-2} M) around 140 minutes
- Rapid layer growth of an additional 0.6 nm over one hour.

Layer Growth in Electrolyte Solution



- Clean graphite in electrolyte solution
- A 2 nm layer grows over 16 hours
- The electrolyte used adds contamination as well

Conclusions

- Contamination from air can reduce the capacitance in as little as 10 minutes
- Intentional contamination reduced the capacitance by as much as 70%
- Water borne contamination from the electrolyte reduced the capacitance by about 30%
- Ellipsometry showed that about ~ 0.5 nm of contamination can grow within an hour in water or electrolyte.
- FTIR studies showed the existence of hydrocarbons on the surface within the appropriate timeframe

Future Directions

Confirming the contamination effect on other carbon materials:

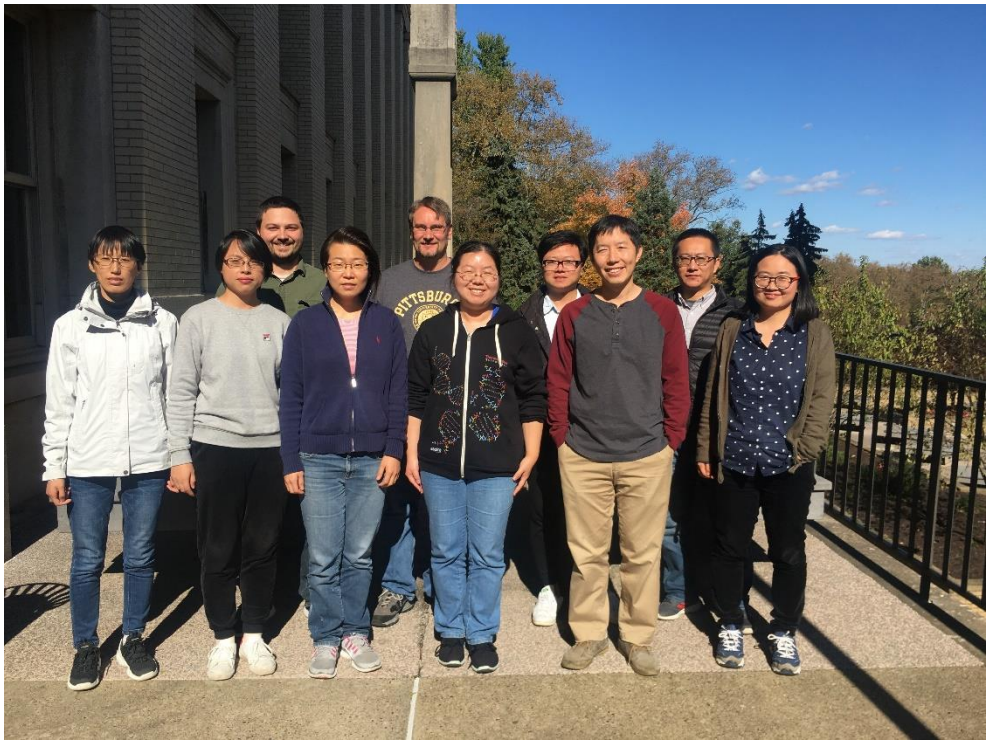
- Graphene
- Activated carbon
- Carbon nanotubes

Investigating the behavior of a manufactured carbon capacitor:

- Double layer/Electrolytic
- Aqueous/ionic liquid

Determination of a dielectric material to competitively inhibit adsorption of contaminants on carbon surfaces

Acknowledgements



Dr. Haitao Liu & group members.

Prof. Shigeru Amemiya and Dr. Andrew Kozbial for helpful comments and assistance.

This work is supported in part by ONR (N00014-15-1-2520).