Characterization of Electrical Double Layer Capacitance and Pseudocapacitance in Iron Oxide Supercapacitors

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REU 2018
10 August 2018

Overview

- Aim
- Background
  - Supercapacitors
  - EDLC
  - Pseudocapacitance
- Experimental
  - Supercapacitor Assembly
  - Characterization
- Results
  - EDLC vs. Pseudocapacitance
  - Capacitance
  - Repeatability and Working Material Stability
- Conclusions
- Acknowledgements
- References

Aim

- Characterize electrical double layer capacitance (EDLC) vs. pseudocapacitance.

- Why is this important?
  - Pseudocapacitance greatly enhances overall capacitance of a supercapacitor.
    - Makes supercapacitors “super.”

  - Pseudocapacitance can alter the properties of materials, such as magnetism.
    - Useful to determine when pseudocapacitance occurs in order to track these changes.

Supercapacitors

What is a supercapacitor?

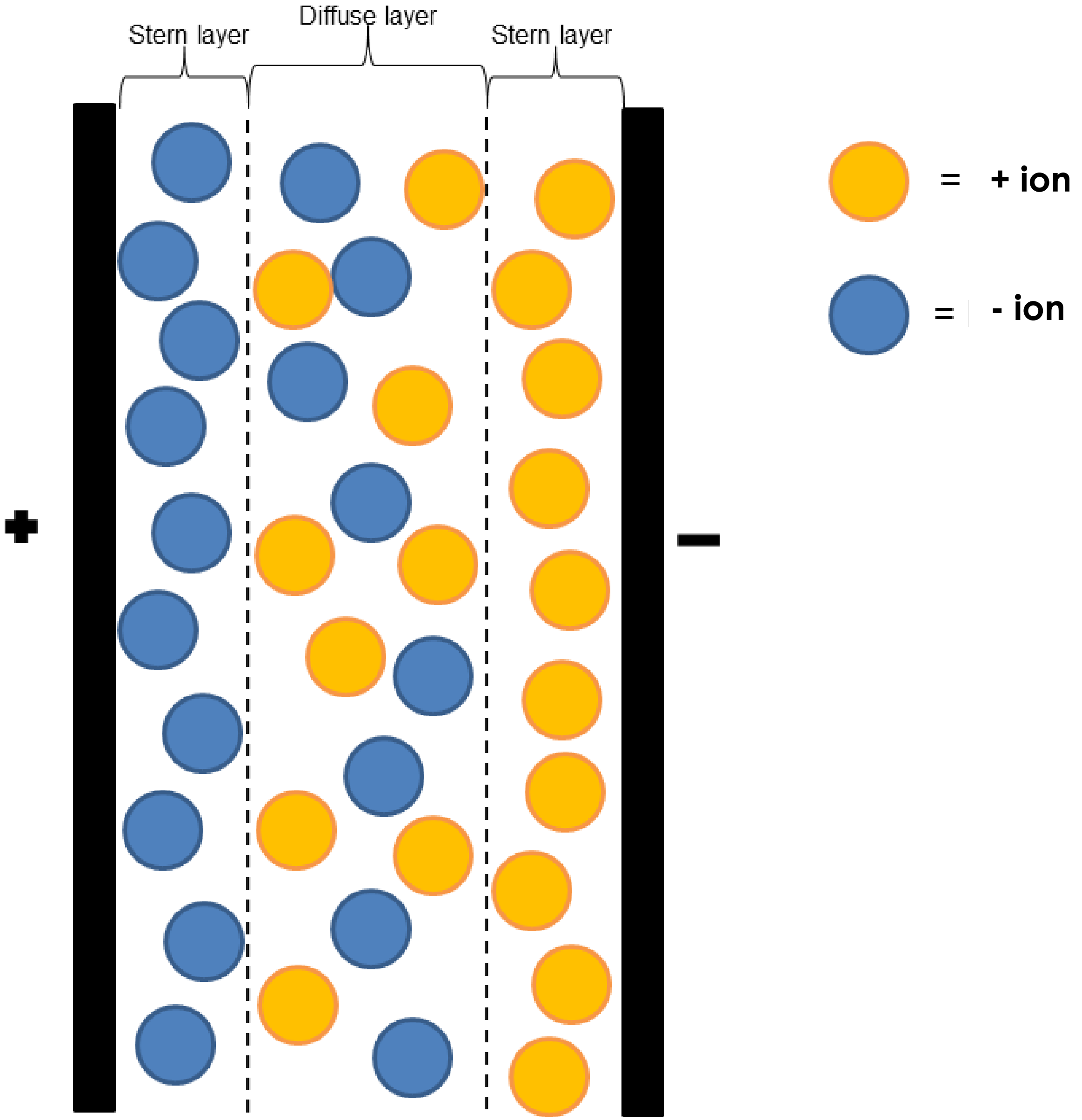
- Everyday capacitor:
  - Stores energy in electric field via electrostatic buildup.

- Hybrid supercapacitor:
  - Stores energy electrically and chemically [1].
  - Electrolytic cell [2].
  - Uses an electrolyte as dielectric material.

  - Capacitance caused by:
    - EDLC:
      - Special type of parallel plate capacitor.
      - Stores charge in an electric field.
    - Pseudocapacitance:
      - Utilizes transition metal oxides to host redox reactions with electrolyte.
      - Stores charge as chemical energy.

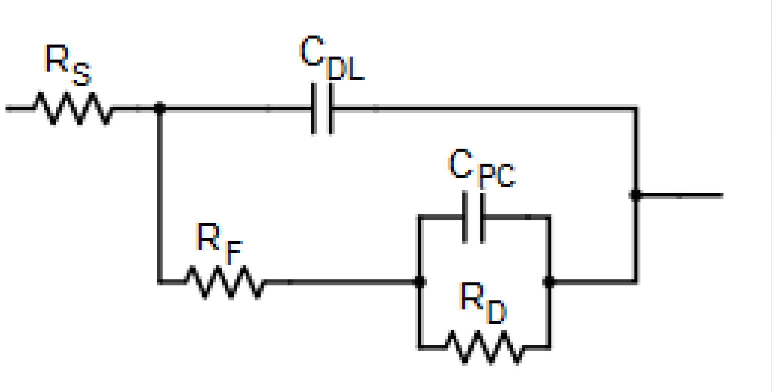
EDLC

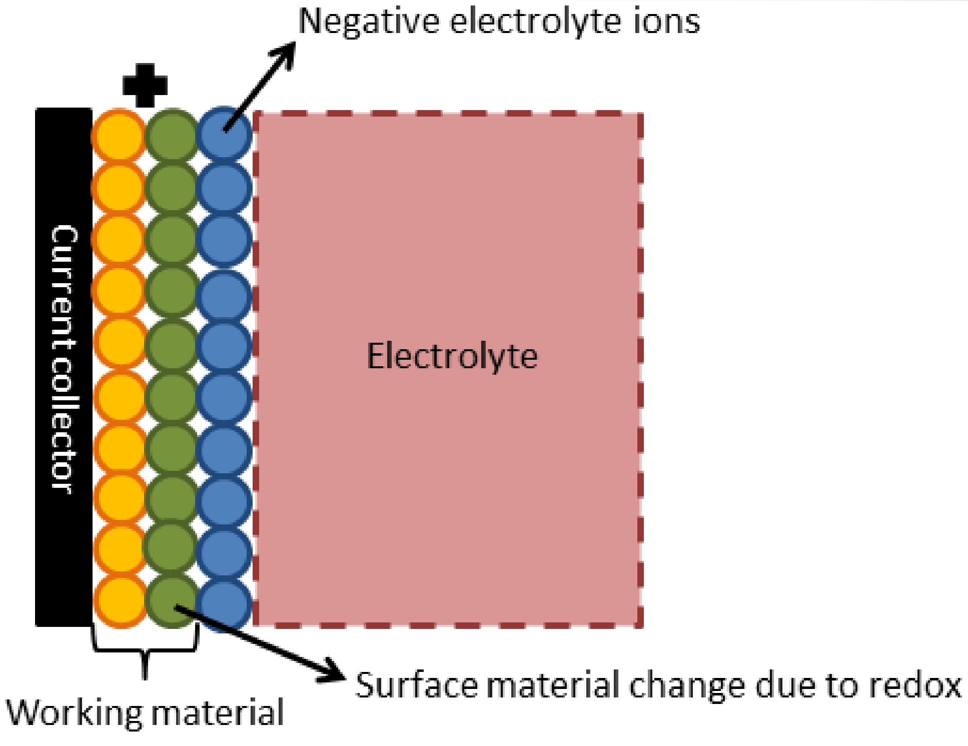
- Electrical double layer:
  - First layer: Stern layer [3].
    - Negative electrolyte ions attracted to positive plate.
    - Positive electrolyte ions attracted to negative plate.
    - Layer of ions adsorbed to electrode surface forms Stern layer.
  - Second layer: diffuse layer [1].
    - Formed by repulsion of like-charged ions.
  - Each layer acts as parallel plate capacitor.
    - $C = \frac{k\varepsilon_0 A}{d}$
  - The two layers are in series with each other.
    - $C_{DL} = \frac{1}{\frac{1}{C_S}+\frac{1}{C_D}}$



Pseudocapacitance

- Electrochemical in nature.
  - Caused by redox reactions at electrode/electrolyte interface [1].
  - Stores energy chemically [4].
  - Oxidation of working material:
    - Increase in cell current due to release of electrons [5].
  - Reduction of working material:
    - Decrease in cell current due to absorption of electrons.
  - Only occurs in sufficiently high voltage windows.
- Greatly increases overall capacitance.
- Pseudocapacitance is in parallel with EDLC.





Characterization

- EDLC vs. pseudocapacitance:
  - Cyclic voltammetry (CV):
    - Varies voltage at constant sweep rate and measures cell current.
    - Ideal EDLC produces rectangular voltammogram.
    - Visible current spikes at certain potentials when redox reactions occur.
      - Indicative of pseudocapacitance.

- Repeatability:
  - Multiple CV cycles over same voltage window.
    - Voltammograms should be consistent and symmetric if redox reaction is reversible.

- Stability of working material:
  - Raman spectroscopy:
    - Should be consistent before and after full cycles.
      - Indicates no change in chemical composition.

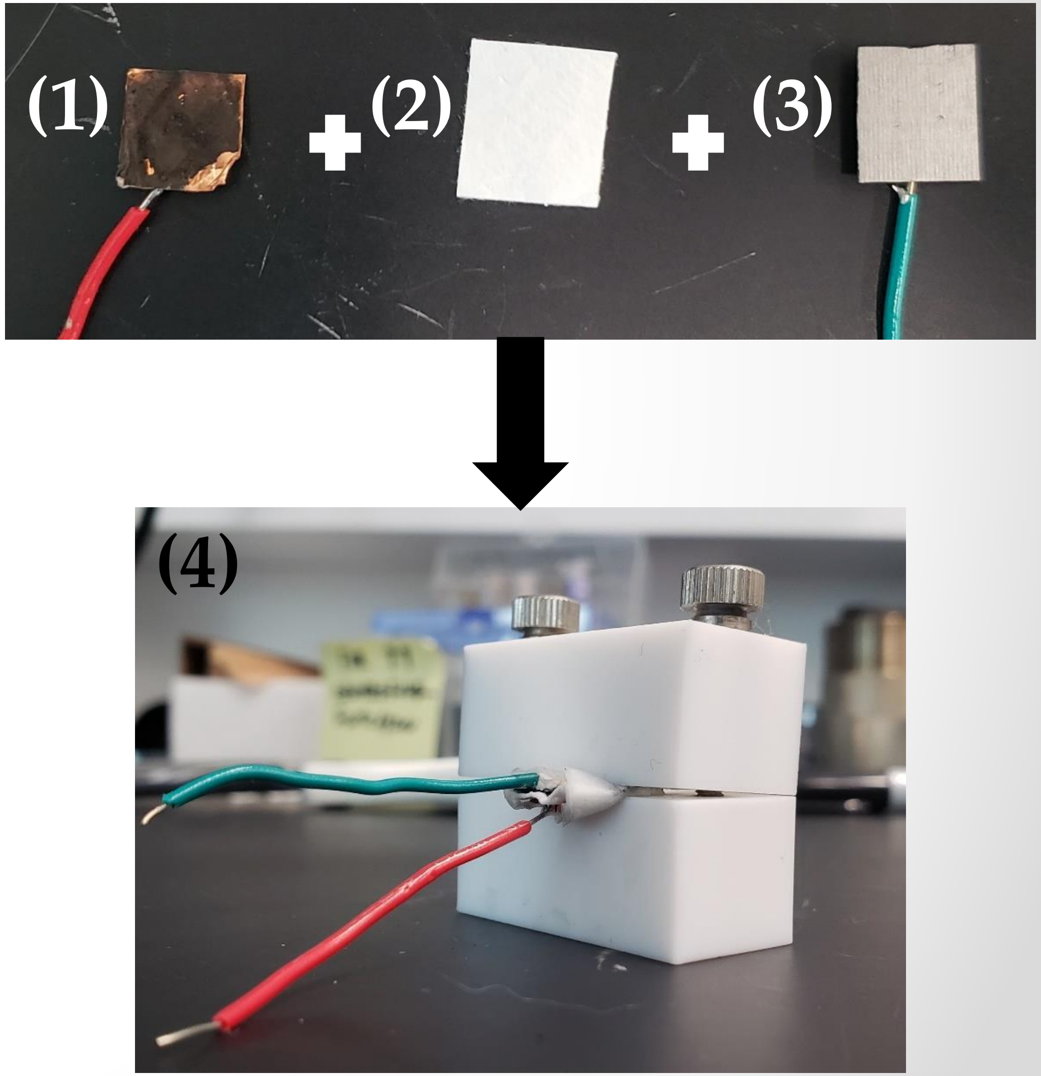
Supercapacitor Assembly

1. Working electrode (anode):
   - Current collector: copper foil.
   - Working material: Fe_3O_4 nanoparticles mixed with PVDF binder slurry (90:10), drop-casted on to copper foil.

2. Dielectric:
   - Glass microfiber paper soaked in 1 M Tetraethylammonium tetrafluoroborate ($TEABF_4$) organic electrolyte.

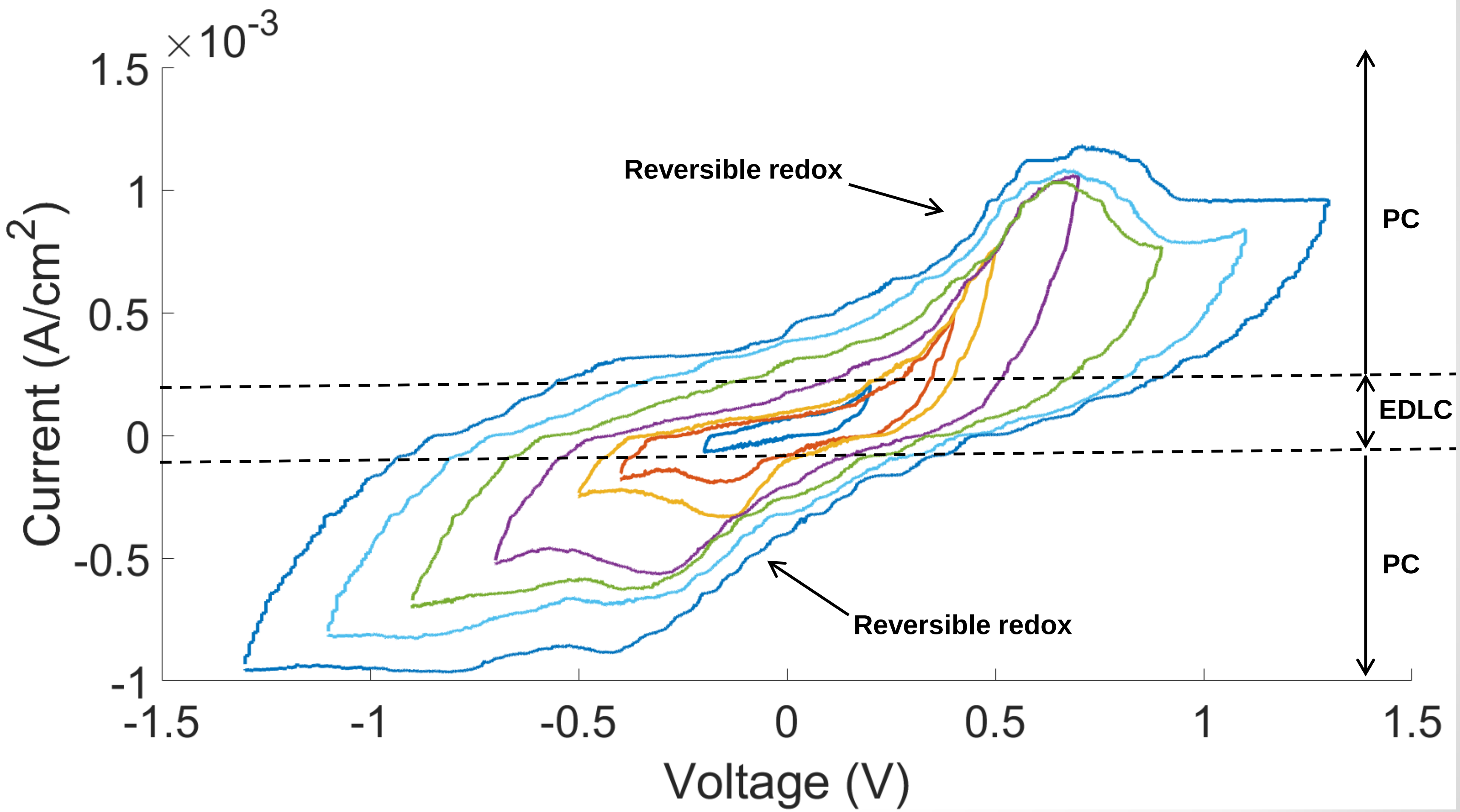
3. Counter electrode (cathode):
   - Graphite sheet.

4. Assembly placed in Teflon clamp for testing



Results: EDLC vs. Pseudocapacitance

- EDLC:
  - Occurs in ΔV < 0.8 V window.
- Pseudocapacitance:
  - Occurs in ΔV > 0.8 V window.
  - Redox peaks:
    - Reversible.
    - 0.5 V.
    - -0.06 V.
- Irreversible redox:
  - Occurs in ΔV > 3 V window.
  - Results in rapid degradation of working material.

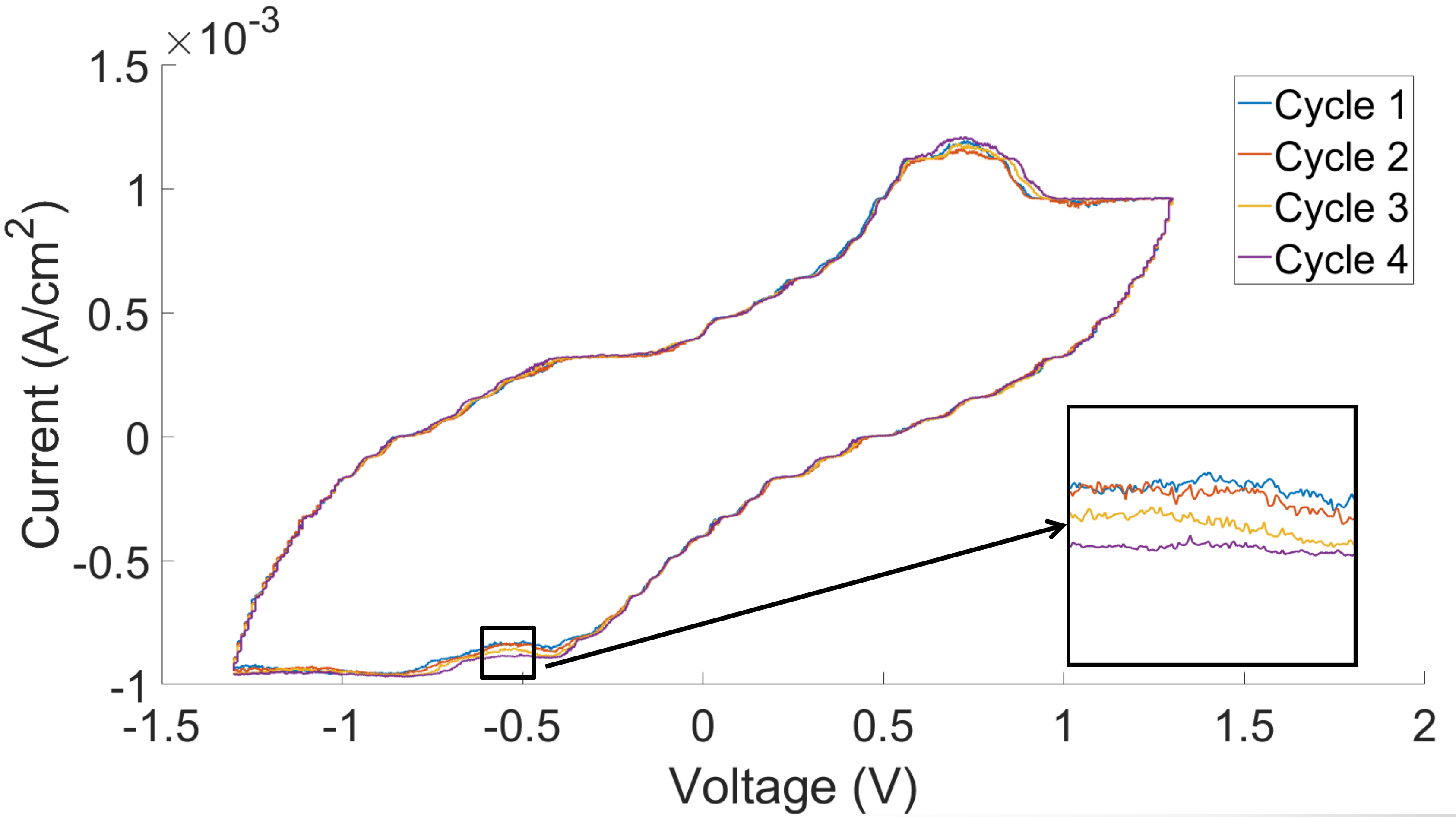


Results: Capacitance

- EDLC specific capacitance:
  - 155 mF/g
- Total specific capacitance with EDLC and pseudocapacitance:
  - 239 mF/g
  - Total capacitance increases significantly with pseudocapacitance.

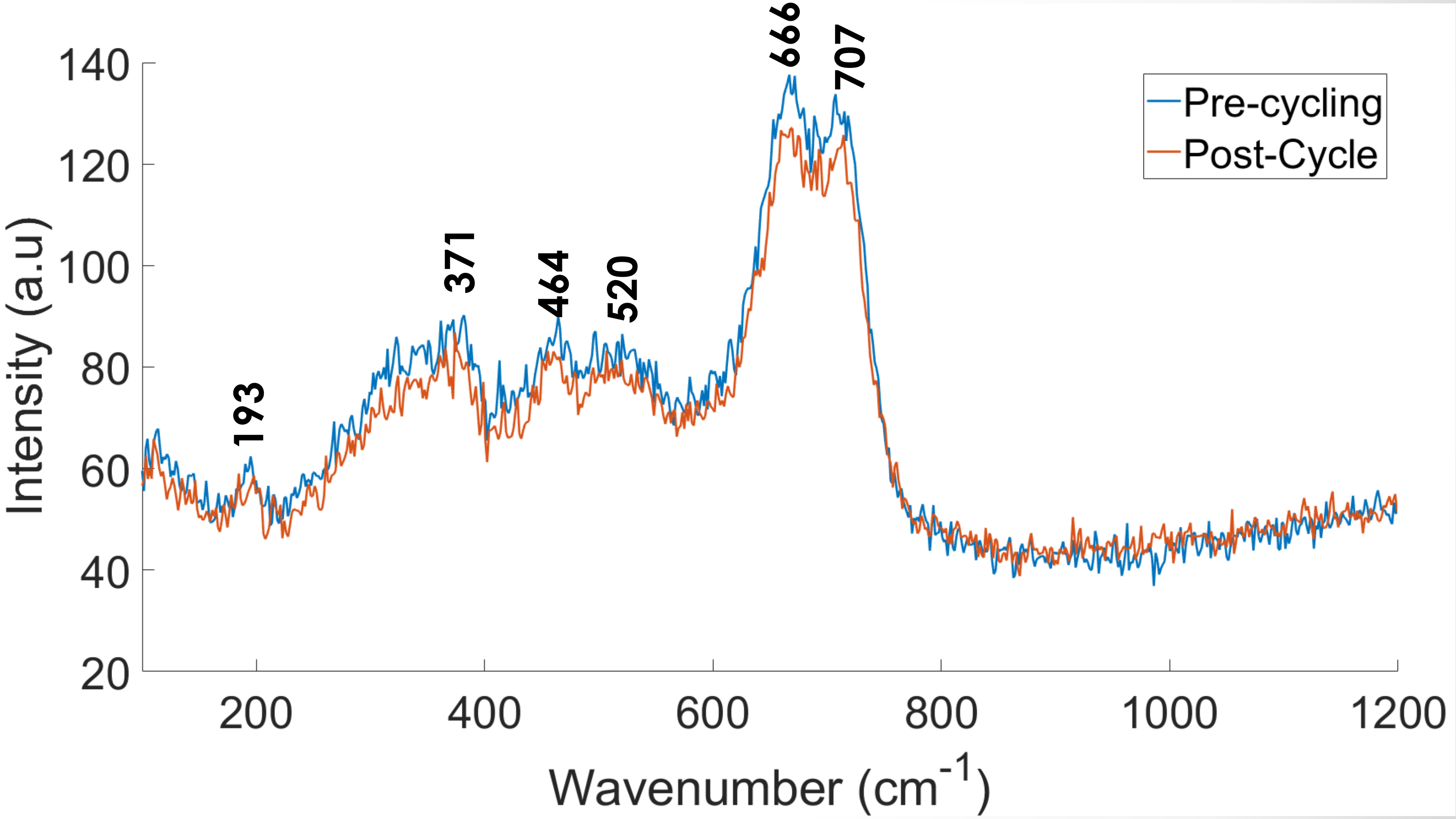
Results: Repeatability

- Multiple cycles over same ΔV:
  - Voltammograms are consistent.
  - Redox peaks occur at same voltages.
  - Results are consistent and repeatable.
  - Consistency also indicates occurrence of reversible redox reactions.



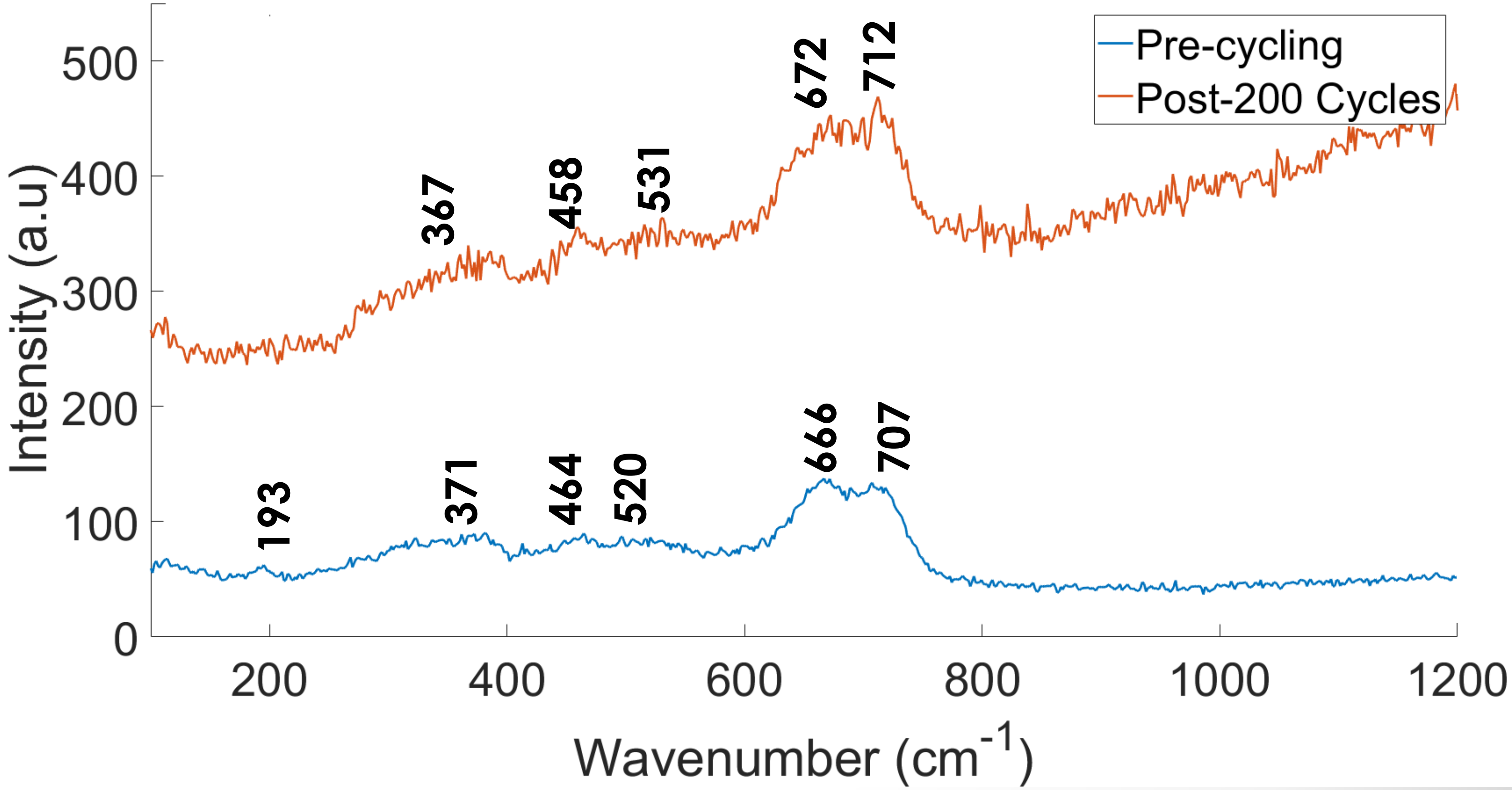
Results: Working Material Stability

- Raman, single cycle:
  - Nearly identical spectra before and after complete cycles.
  - Indicates no chemical change after cycling.



Results: Working Material Stability

- Raman, 200 cycles:
  - Some change in Raman spectra.
  - Indicates changes in chemical composition and degradation of working material.



Conclusions

- EDLC:
  - Observed in voltage windows below 0.8 V.
- Pseudocapacitance:
  - Observed in voltage windows above 0.8 V.
  - Redox peaks observed at 0.5 and -0.06 V.
  - Irreversible redox reactions occur in voltage windows above 3 V.
- Results are repeatable over many cycles.
- Working material is stable for several cycles, but will degrade over many cycles.

Acknowledgments

This work was performed under the auspices of the National Science Foundation (NSF) and Dr. Jun Jiao at Portland State University. Special thanks go to Kavita Meduri, John Yuzon, and Nathan Jansen for their guidance and assistance in completing this research.

Award #: 1560363

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