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

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Aim

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

• Why is this important?
  o Pseudocapacitance greatly enhances overall capacitance of a supercapacitor.
    • Makes supercapacitors “super.”
  o 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.
• **Electrical double layer:**
  
  o 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.
  
  o Second layer: diffuse layer [1].
    • Formed by repulsion of like-charged ions.

  o Each layer acts as parallel plate capacitor.
    • \( C = \frac{k \varepsilon_0 A}{d} \)

  o 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$_3$O$_4$ 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 $\Delta V < 0.8$ V window.

- **Pseudocapacitance:**
  - Occurs in $\Delta V > 0.8$ V window.
  - Redox peaks:
    - Reversible.
    - 0.5 V.
    - -0.06 V.

- **Irreversible redox:**
  - Occurs in $\Delta V > 3$ 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 $\Delta V$:
  - 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:
  o Nearly identical spectra before and after complete cycles.
  o 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:
  o Observed in voltage windows below 0.8 V.

• Pseudocapacitance:
  o Observed in voltage windows above 0.8 V.
  o Redox peaks observed at 0.5 and -0.06 V.
  o 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.
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References


