Background and Motivation

Deteriorating air quality has led to a growing need for rechargeable micro-power sources, such as energy sources for acceleration in hybrid-electric vehicles. The high density of electrochemical micro-supercapacitors (high surface area electrodes, covered with an electrolyte) has led to increased attention from the engineering and researching communities. In order to better understand the underlying mechanism of supercapacitors, a model to construct a description of the effect of electrolyte properties on the behavior of electrical thin double layers.

The components of the micro-supercapacitors (μSCs) used in this study were graphite petal electrodes with a Ti/Au covering on a SiO₂ base, soaked in a PVA and H₂SO₄ polymer gel or aqueous electrolyte.

An electrical thin double layer (EDL) forms when a voltage is applied to a solid immersed in an aqueous electrolyte. It consists of two thin quasi-equilibrium layers of ions, first a compact or condensed layer of mostly counterions and then a diffuse layer of co- and counterions [1] (see figure above). This is similar to the electrodes in a μSC with a few simplifying assumptions, such as a flat electrode surface.

Three different models of EDLs were studied. The Poisson-Boltzmann equation (PB) is the most simplistic. It breaks down under very small applied potentials (potential must be small enough that the compact layer is only one layer of ions deep), and does not account for finite ion volume (steric effects). This is compared to a modified version of the Poisson-Boltzmann equation (MPB) and a composite-diffuse layer model (CDL), both of which account for steric effects. Using the CDL model, the transition from the condensed to the diffuse layer is sharply defined. This distance is defined as $l_c$ [1].

Objectives

- To determine how electrolyte properties affect supercapacitors
- To determine how electrolyte properties affect thin double layers
- To relate thin double layers to supercapacitors
- To create an easy-to-use nanoHUB tool that demonstrates electrolyte property effects above
- To predict supercapacitor entropy generation and cooling, using above simulation

Methods

- Derived PB, CDL, and MPB equations [1]
- Created MATLAB code
- Compared dimensionless results to previous research [1]
- Ex. $I/A $ vs. $ |\Psi|/kT$
- Re-dimensionalized equations
- Ex. $I/\Psi$
- Created user interface in Rappture (xml) and integrated MATLAB code
- Published on nanoHUB.org

Experimental

Sample creation:
- Graphite petals were grown using microwave plasma chemical vapor deposition
- $\text{SiO}_2$ base, approximately 15 mm x 6 mm x 2 mm
- Plasma power = 600 W for 30 minutes
- Sheets were shaped into a interdigitated configuration using photolithography
- Petals were covered with a 600 nm layer of Ti/Au for enhanced light reflectance and then oxidized for 15 min
- Electrodes were soaked in an electrolyte
  - Aqueous: 1 M H₂SO₄ in H₂O, or
  - Solid state polymer gel: H₂SO₄ in PVA
- Thermofluctuation measurements:
  - Used system of wide-field LED illumination and CCD camera to capture thermal data
  - Must use polymer gel electrolyte, ripples in aqueous create extremely high noise level
  - Performed a base measurement with device off to capture background noise
  - Applied 0-1 V voltage waveform shown below

Simulation

- Differential capacitance reaches a maximum then decreases when accounting for steric effects
- The temperature of the EDL simulation shows several trends, such as:
  - Steric effects have a large impact, usually leading to opposite results of PB model [1]
  - Differential capacitance reaches a maximum then decreases when accounting for steric effects [1]
- The cause of the μSC cooling is still unknown, one possibility is the electrocaloric effect

Results and Discussion

Differential capacitance ($C_D$) is $dq/d|\Psi|$, where capacitance is $|\Psi|$. $C_D$, $C_P$ is graphed for each model.

Future work

- The EDL simulation shows several trends, such as:
  - Steric effects have a large impact, usually leading to opposite results of PB model [1]
  - Differential capacitance reaches a maximum then decreases when accounting for steric effects [1]
- The cause of the μSC cooling is still unknown, one possibility is the electrocaloric effect
- Find the cause of the cooling in μSCs
- [2] uses volume of condensed layer to calculate $\Delta S$ and from that $\Delta T$ in μSCs
- Apply EDL model to μSCs to find volume of condensed layer
- Use that to calculate $\Delta T$ observed in experiments

Conclusions

References


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