The Contribution of the Electrical Double Layer to Enhance Ionic Currents in Single Walled Carbon Nanotubes.

Samuel L. Bearden and Guigen Zhang
Dept. of Bioengineering, Dept of Electrical and Computer Engineering
Institute for Biological Interfaces of Engineering
Clemson, SC 29634-0905
guigen@clemson.edu

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Enhanced Ionic Conductance in SWCNT

- Ionic conductance through SWCNT has been reported to be enhanced by 2 orders of magnitude.
- Previous explanations have failed to account for all relevant phenomena at the nano-scale.
Electrical Double Layer

- An immobile compact layer forms at the surface due to electrical interactions between materials.
- Mobile diffuse layer carries net charge.
Model Geometry

- SWCNT embedded in $\text{SiO}_2$
- 2D axisymmetric
The Compact Layer

- A cylindrical shell at the interior surface of the SWCNT
- Smoothly varying permittivity

Laplace Equation

\[ \nabla^2 V = 0 \]
The Compact Layer

- Slip at the outer Helmholtz plane
- Validated through observation and modeling
- Combined with the EDL, enables electroosmosis
Governing Equations

- Poisson Equation:
  \[ \nabla^2 V = -\frac{\rho(r, z)}{\varepsilon_0 \varepsilon_r} \]

- Accounts for material potentials, applied potentials, and ionic distributions
Governing Equations

• Nernst-Plank Equation:
  \[ \nabla \cdot \left( -D \nabla c - z \mu F c \nabla V \right) + u \nabla c = R \]

• Accounts for the transport of solvated ions via electrophoresis, electroosmosis, and diffusion
Governing Equations

- Stokes Equation:
  - \( \rho(u \cdot \nabla)u = \nabla \cdot \left[ -PI + \gamma \left( \nabla u + (\nabla u)^T \right) - \frac{2}{3} \gamma (\nabla \cdot u) I \right] + F_v \)
  - \( \nabla \cdot (\rho u) = 0 \)

- Accounts for the effect of a mobile solvent
  - Electroosmosis
    - \( \vec{F}_v = F_c \sum_i (z_j c_j) E \)
Mesh Convergence

- Iteratively refined until the conductance measured at the ends and middle of the channel were equivalent to 3 significant figures.
Mesh Convergence

- Triangular mesh elements were used near the mouth of the channel
Results: Conductance

• The conductance/concentration relationship agreed with experimental output
• 2 orders of magnitude increase compared to bulk conductivity theory
Results: Mechanism

- Electrophoresis at low concentrations
- Electroosmosis at high concentrations
- Net charge increases with concentration

\[ \vec{F}_V = F_c \sum_i (z_j c_j) E \]
Compact Layer Thickness

- Thickness was allowed to vary while the conductance was compared to experimental outputs
- Close to predictions based on assumption of adsorbed molecules
Conclusion

- Demonstrated a stable, rigorous model of electrokinetic flow through SWCNT
- The simulation results agree well with experimental measurements and provide new insight into the unique mechanics of such devices
- Electroosmosis due to increased internal net charge dominates device conductance at higher concentrations
- This study is one of the first to quantitatively define the compact layer thickness

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