Desalination and Contaminant Removal from Water by Capacitive Deionization

DOE/EERE Better Plants Technology Days

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Increasing Water Scarcity: A Global Issue

- 1/6th of the world’s population does not have daily access to fresh water
- 57% of the U.S. experienced drought in 2012

Source: Comprehensive Assessment of Water Management in Agriculture, 2007
Desalination Technology Enables the Utilization of Unconventional Water Resources

- **Sea water**
  - High salinity (35,000 ppm salt)
  - High energy cost
  - Great availability
  - Easy brine management

- **Brackish water**
  - Modest salinity (< 10,000 ppm)
  - Lower availability
  - Brine management challenges

- **Water reuse**
  - Variable salinity (< 1,000 ppm)
  - Intended use specific issues:
    - Hardness
    - Toxic Ions
Trace Contaminants Impair Otherwise Potable Water

Ground Water
As, Se, F, nitrates

Agriculture
nitrates

Industry
nitrates, phosphates, metals, hardness
Exiting Water Treatment Technologies Are Not Optimized for Low Salinity Sources or Selective Removal

Reverse Osmosis (RO)
- Pump (75 atm)
- Semipermeable membrane
- Salt water
- Fresh water
- High pressure brine

Ion selective membranes
- Cation exchange membrane
- Anion exchange membrane

Ion exchange resin

Diagram showing the process and components of water treatment technologies.
Capacitive Deionization Enables Lower Energy Use and Selectivity

CDI removes salt from water using charged electrodes

Impact of selectivity on total removal/energy:

\[ S = \frac{\Delta c_{\text{target}}}{\Delta c_{\text{matrix}}} \]

Selectivity Factor:

\[ R = \frac{c_{\text{target}}}{c_{\text{matrix}}} \]

\( R \) = ratio of target ion concentration to matrix ion concentration in feed stream
LLNL’s Unique Flow-Through Electrode CDI Cell Architecture: Faster Desalination and Lower Energy Use

Flow-Through Electrode Architecture

• Water in electrode does not contribute to desalination
• Slow (60 mins/cycle)
• High energy cost
• Low capacity (~1.5 g/L/charge)

Hierarchical Carbon Aerogel Material (HCAM)

• Entire electrode volume contributes to desalination
• Faster
• Lower energy cost
• Higher capacity (~4.5 g/L/charge)

Desalted Water
FTE-CDI Can Compete With RO at Low Feed Salinities or Small Device Scales (Distributed Water Treatment)

FTE-CDI advantages

- Does not require high pressure
- Size-independent efficiency
- Robust carbon electrode
- Ion selectivity (heavy metals, nitrate)
- Recycle brine to achieve higher recovery
- Projected energy use for brackish water: 0.1-0.2 kWh/m³
A Decade of FTE-CDI Development at LLNL: High-Fidelity Model and Performance Metrics

Model of CDI Cell Operation

Key Performance Metrics
Fair Comparisons

Separation Conditions

\[ WR = \frac{V_{d1}}{V_{c1}} + \frac{V_{d2}}{V_{c2}} \]

Desalination Performance

\[ E_v = \frac{\Delta c_{avg}}{[\text{Wh/m}^3]} \]

\[ P = \frac{V_d}{l} \times w \] [L/h/m²]
A Decade of FTE-CDI Development at LLNL: Operation Modes and Energy Recovery

Operating parameters strongly impact efficiency

Constant Current vs Constant Voltage Charging Mode

- Under identical charge transfer and timespans, **CC achieves similar salt removals but consumes much less energy than CV.**

**Charge transfer in energy recovery circuit**
A Decade of FTE-CDI Development at LLNL: Cell Design and Carbon Aerogel Electrode Material Production

### Tunable HCAM electrode material

<table>
<thead>
<tr>
<th>Act. Time (h)</th>
<th>Mass Loss</th>
<th>BET SA (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>--</td>
<td>--</td>
<td>400</td>
</tr>
<tr>
<td>2</td>
<td>43%</td>
<td>~1500</td>
</tr>
<tr>
<td>3</td>
<td>60%</td>
<td>~2300</td>
</tr>
<tr>
<td>4</td>
<td>70%</td>
<td>~2450</td>
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<tr>
<td>5</td>
<td>75%</td>
<td>~2800</td>
</tr>
<tr>
<td>6</td>
<td>85%</td>
<td>~3200</td>
</tr>
</tbody>
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### Cast “bricks”, cut on band saw

- Up to 8 x 12 cm electrodes

- ACA (1400 m²/g)
- ACA (3100 m²/g)
FTE-CDI Demonstration Project:
Delta Diablo Water Treatment Facility

- Small scale (10 L/h) demonstration project is underway
- Remove 500 ppm from ~750 ppm TDS tertiary treated wastewater for use as heat exchanger cooling water
Understanding the Mechanism for Selectivity: 3 Year LDRD ER

\[ A = \frac{c_{mi,j}}{c_{mi,j}} = \frac{c_{mA,i}}{c_{mA,j}} \exp(\mu_{att,j} - \mu_{att,i}) \exp\left(\frac{q\Delta \phi_{li}}{kT}(z_j - z_i)\right) \]

- Statistical non-selective driving force
- Intrinsic selectivity
- Electrostatic selectivity

Donnan model predicts divalent ions preferentially adsorbed

Cyclic voltammetry of single ion solutions

Energy Statistical non-selective driving force

Intrinsic selectivity

Electrostatic selectivity
Atomistic Simulations of Ion Hydration and Interaction with HCAM Nanopores Help Explain Observed Selectivity

- NO$_3^-$ is a planar, weakly solvated, molecule
- => perfect for fitting into slit pores
Our Team

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- Cheng Zhan
- Patrick Shea
- Jennifer Knipe
- Brandon Wood
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