Nanostructured Electrode and Electrolyte Development for Energy Storage Devices

— SNL, GINER, and ADA
— Electrochemical Storage Program Reviews
— Capacitor Development Activities

Presented by Karen Waldrip
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Albuquerque, NM

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NNSA National Nuclear Security Administration

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Sandia National Labs Program Review
High Voltage Electrochemical Capacitor

presented at

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September 29-30, 2008

PEER Review

Washington, D.C.

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Objective

- Project Began - 7/07
- Increasing the energy of the system
- Energy = 1/2 CV^2
- Four general means to increasing energy
  - Increased surface area - most common approach
    - A - active area of electrode
      - high surface area materials (carbon - typically > 1000 m^2/g)
      - nanomaterials (e.g. carbon multiwalled nanotube)
  - Employ Faradaic processes - psuedocapacitance
    - asymmetric capacitors
    - proton and lithium insertion reactions, eg RuO_x,
  - Increased Voltage - not typically done
      - aqueous based - < 2 V
      - nonaqueous - 2.7 V
    - Working range of electrolyte
      - primary concern - Faradiac processes
        - » oxidation/reduction of electrolyte
        - » corrosion of current collector
        - » oxidation/reduction of active electrode materials
      - Cell Resistance
  - Increased C_d - area specific capacitance
    - not typically done

C_d relatively constant for different systems

TABLE 17.2 Double-Layer Capacitance on Hg

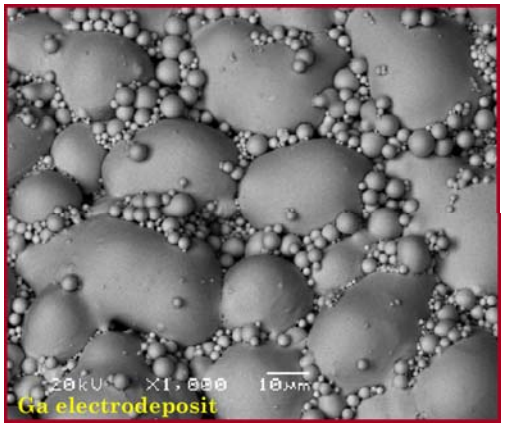
Electrolyte	C_d^{int} ($\mu F\ cm^{-2}$)
$EMIBF_4$	10.6
$EMICF_3SO_3$	12.4
$EMI(CF_3SO_2)_3C$	10.6
$EMI(CF_3SO_2)_2N$	11.7
$EMI(CF_3SO_2)_2N$	12.0[a]
$EMI(CF_3SO_2)_2N$	11.4[b]
1.5 M $EMI(CF_3SO_2)_2N$/PC	9.1
1M Et_4NBF_4/PC	7.0
0.1 M KCl/H_2O	15.1
3 M H_2SO_4/H_2O	14.6

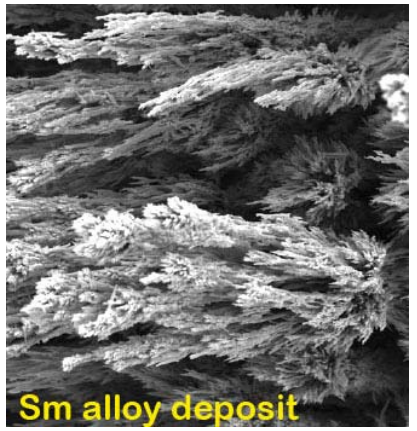
a - glassy carbon
b - SpectraCarb 2220 yarn

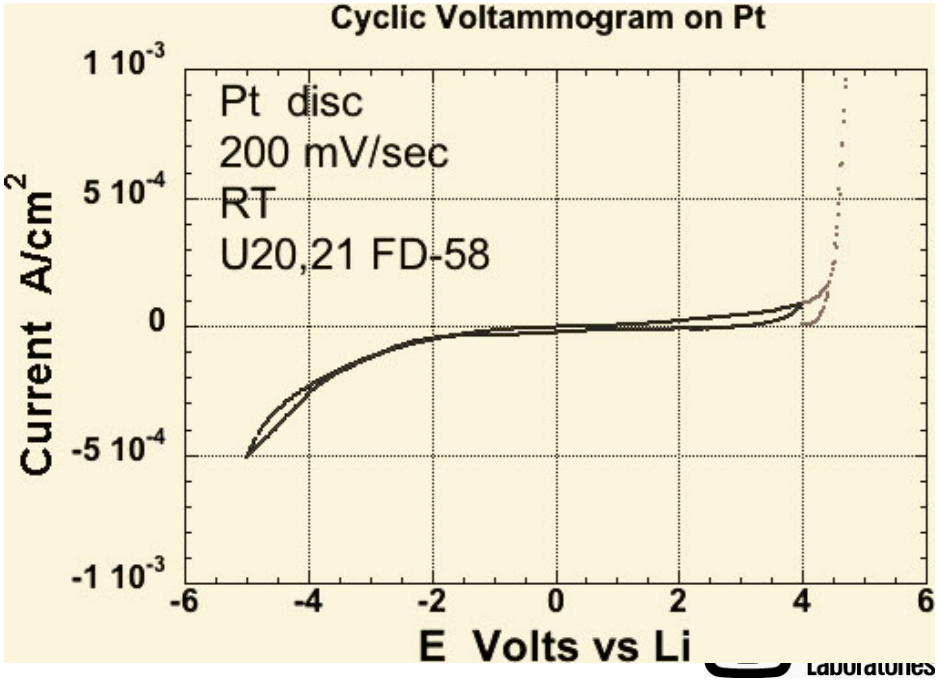
M. Ue, Electrochemical Aspects of Ionic Liquids, H. Ohno ed., Wiley Interscience, 2005.

Motivation

- Previous program - room temperature electrodeposition of reactive metals & alloys. (Joint program with LANL)
  - ***highly*** reactive metals
    - necessitates large electrolyte working range (large voltage)
  - low solution resistance
- ionic liquids (ILs)
  - neat
  - as electrolyte in other solvents
  - typical materials (eg EMI-Im, DMPI-Im)
  - new materials - DMPIpA-Im
  - In general, IL working range is limited & resistance is relatively high.
- Typical battery & capacitor electrolytes
  - LiBOB, LiTFS, $TEABF_4$, etc, in DME, PC
- atypical electrolyte solutions
  - e.g. reactive metal salts in DMSO
- We have observed large working range of some of our systems. (8 V for data shown)





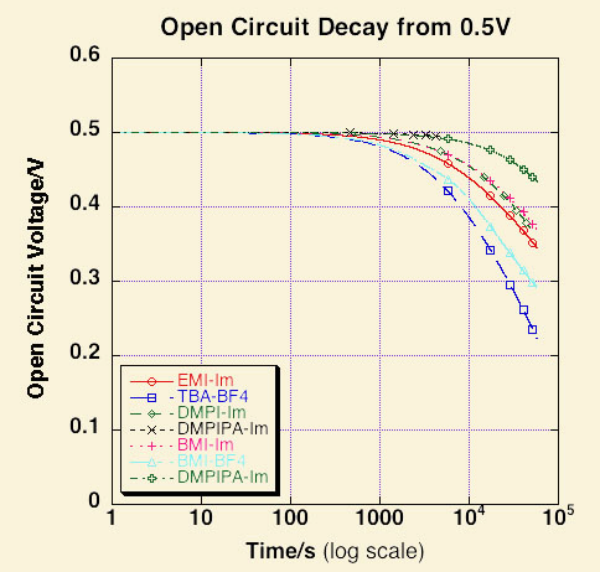


Ionic Liquid Study Conclusions

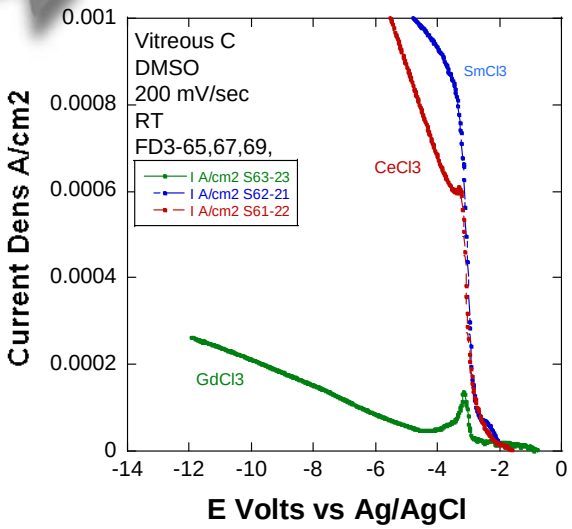
- Large working ranges were observed
- Resistance in cells was high
- Capacitance was low
- Self discharge was fairly high
- Higher voltages did not offset higher cell resistance and lower capacitance
- Determined not to be a viable route at this time for a high energy density capacitor

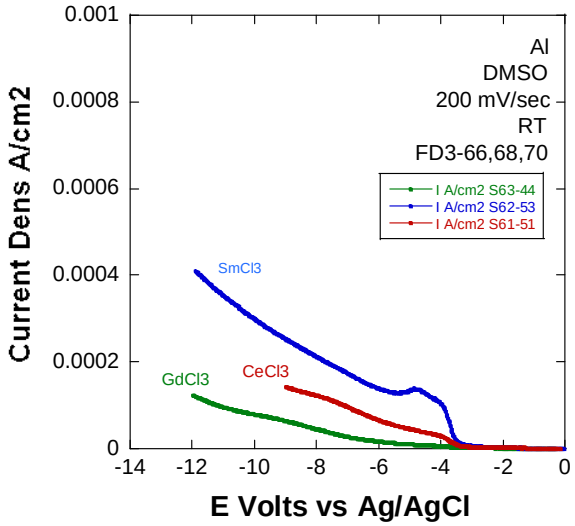
- Returned to DMSO + reactive metal salt electrolyte systems

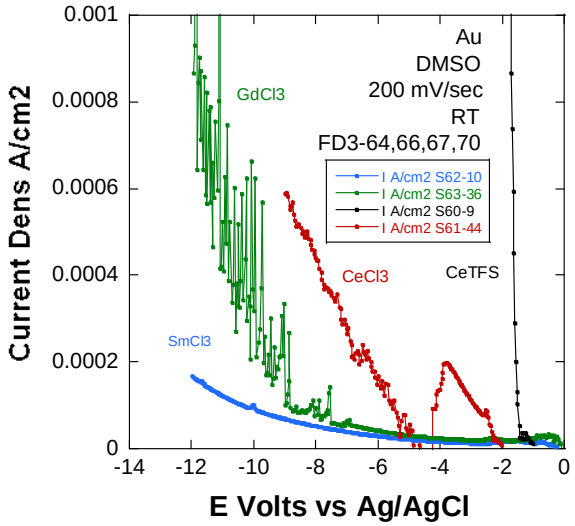
C_d in various ILs	
Electrolyte	$\mu F/cm^2$ BET
EMI-Im	2.5
BMI-Im	2.7
BMI-BF4	2.6
DMPIp-Im	2.5
DMPI-Im	2.7
$TEABF_4$-AN	4.2

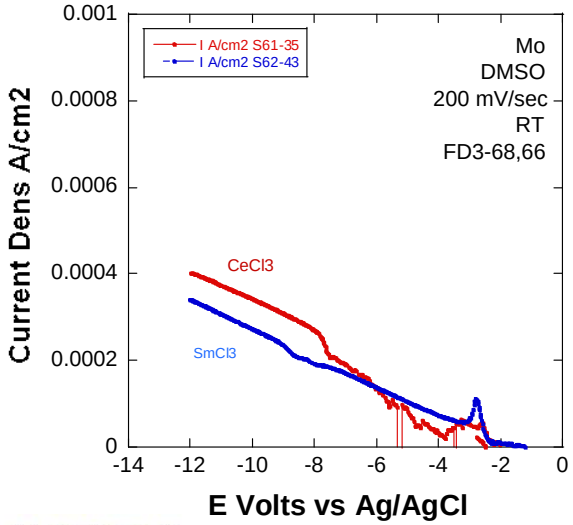


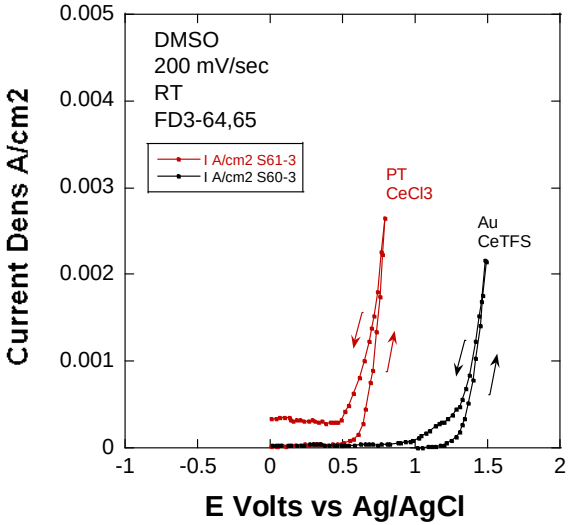
DMSO Electrolyte Working Ranges Depend on Salt and Substrate

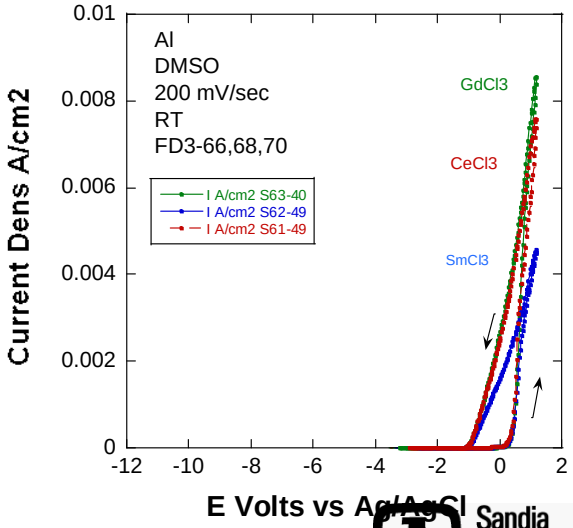












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Observations & Future Work

- Reproduced initial experiments
- Voltage scans limited to working range of potentiostat in some cases
- Electrochemical behavior highly dependent upon substrate and salt composition
- Passive film is extremely thin (specular, shiny electrode surface)
  - May not plug up pores of high surface area carbons
  - May have to increase layer thickness to reduce leakage current due to tunneling (?)
- Perform these experiments on high surface area carbon electrodes (voltage, capacitance, leakage current)
- Evaluate to determine extent of economic advantage for approach

Acknowledgements

- Dr. Imre Gyuk, Department of Energy

- Drs. W.J. Oldham, W. Averill, D.A. Costa and M.E. Stoll
  Los Alamos National Laboratories

“Nano-Engineered Carbon Electrochemical Capacitors”

U.S. DEPARTMENT of ENERGY (DOE)
Contract # DE-FG02-07ER84936
Phase I (June 20, 2007 – March. 19, 2008)

Phase I Study Objective

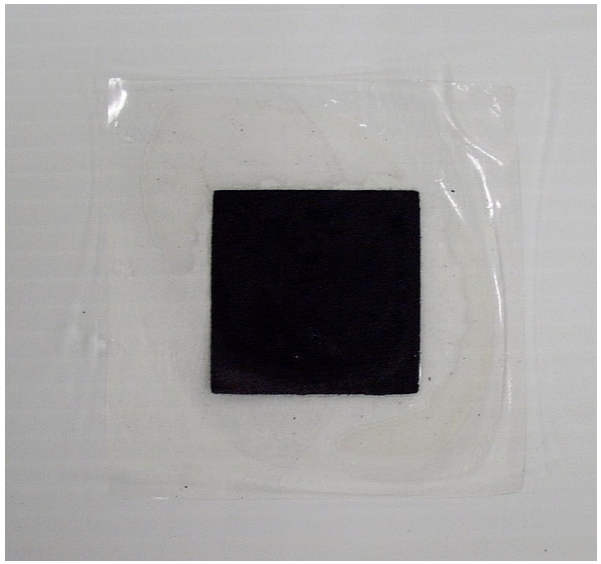
"Design and develop an innovative all-solid-polymer-electrolyte EDLC device consisting of nano-porous carbon, synthesized by selective leaching of metal from metal carbides, and demonstrate its performance."

Specific Objectives Achieved in Phase I

1. High-surface-area (1954 m^2/g) nano-porous carbon powders were synthesized.
2. Single as well as multi cell (5-cell) all-solid-polymer-electrolyte EDLCs, containing no liquid electrolytes, toxic or corrosive materials or precious metals, were fabricated and their performance was successfully evaluated.

Specific Objectives Achieved in Phase I Cont'd

3. High specific capacitance (161.4 F/g) was demonstrated from tested all-solid-polymer-electrolyte EDLCs.
4. High-energy density (greater than 10 watt-h/kg) and high power (greater than 1000 watt/kg) was demonstrated from tested all-solid-polymer-electrolyte EDLCs.



(a) (b)

Figure 1. (a) single-cell (14.5 cm^2 active area) all-solid-polymer-electrolyte EDLC; (b) EDLC test hardware

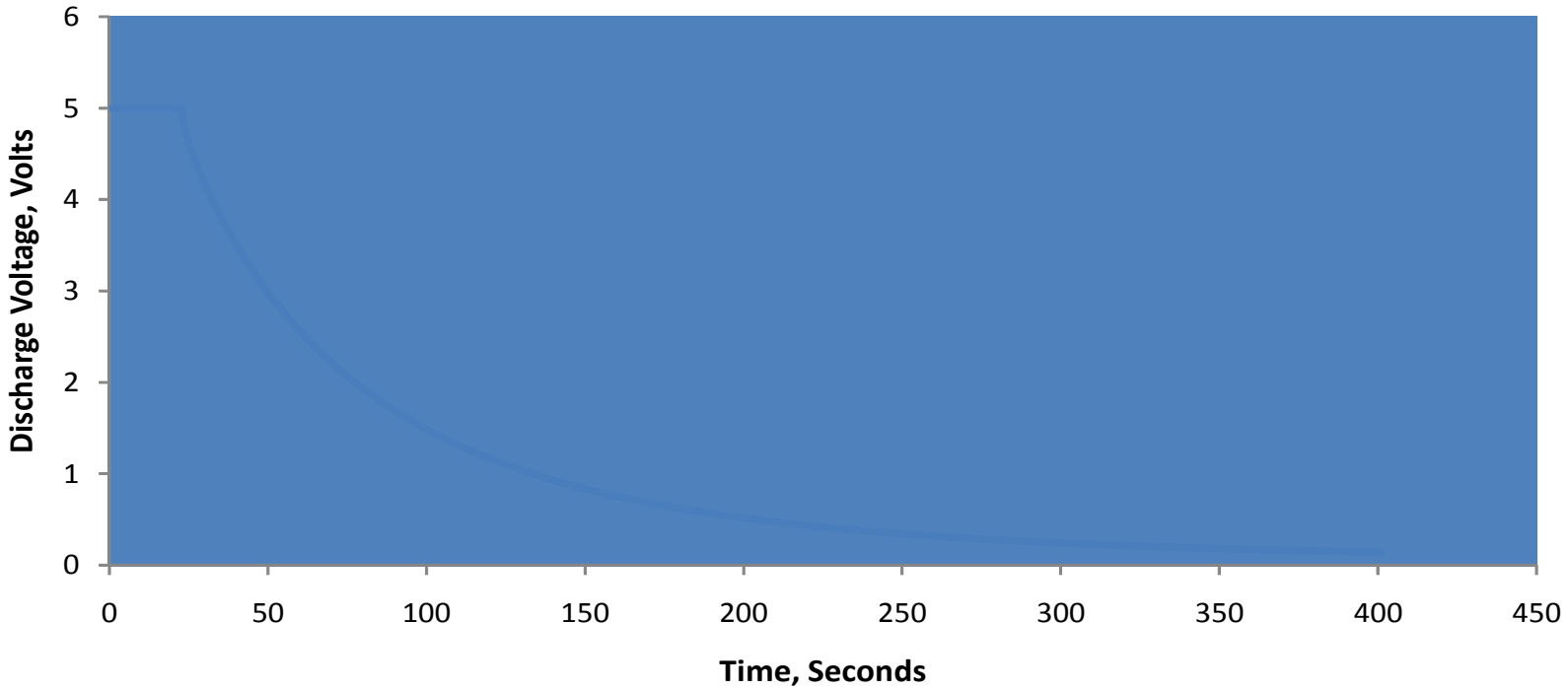


Figure 2. Discharge curve of Giner 5-cell all-solid-polymer-electrolyte EDLC charged to 5.0 volts.

ADA - DoE SBIR Phase I program

- **Project Title:**

  High Performance Carbon Nanomaterials for Electrochemical Capacitors

- **DoE SBIR Phase I Grant Award #:**

  DE-FG02-07-ER84688

- **Principal Investigator:**

  Wen Lu, Ph.D.

- **Company Information**:

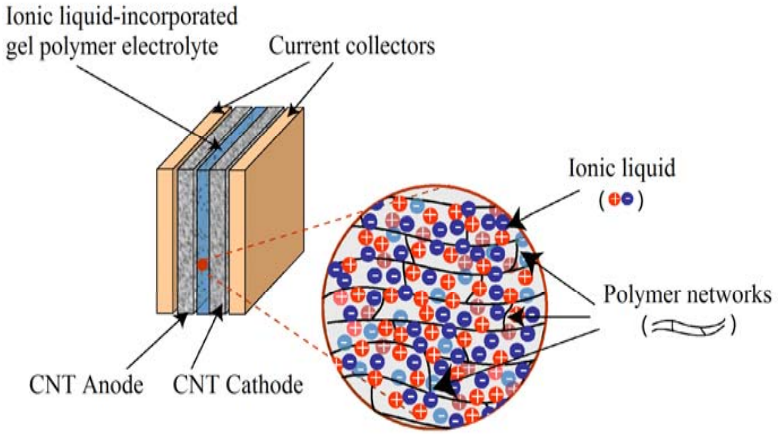
  ADA Technologies, Inc.
  8100 Shaffer Parkway, Suite 130
  Littleton, Colorado 80127-4107

Overall Goal & Approach of the Project

Utilize the unique properties of carbon nanotubes (CNT), high-surface-area activated carbons (AC), and environmentally benign ionic liquids (IL) to fabricate high performance CNT composite electrodes and combine them with ionic liquid electrolytes to develop advanced electrochemical capacitors for utility applications.

- **Phase I proof-of-concept**
  completed using liquid form of the ionic liquids

- **Phase II prototype demonstration**
  will use a solid-state ionic-liquid--incorporated gel polymer electrolyte (ILGPE) to further improve safety and lifetime of the capacitors



Why CNT Composite Electrodes

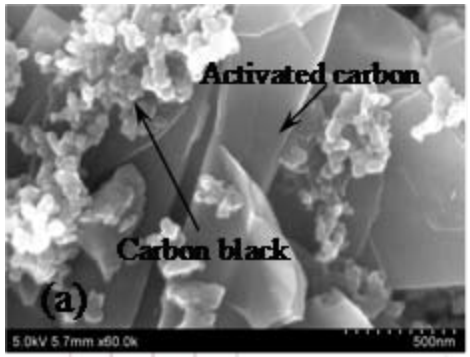
Roles of components in an AC/CNT/IL composite

- *AC* to provide high surface area
- *CNT* to avoid aggregation of CB (of a conventional AC/CB electrode) and to provide a highly conductive and highly electrolyte accessible network
- *IL* to untangle CNTs, serve as plasticizer, and reduce polymer binder content

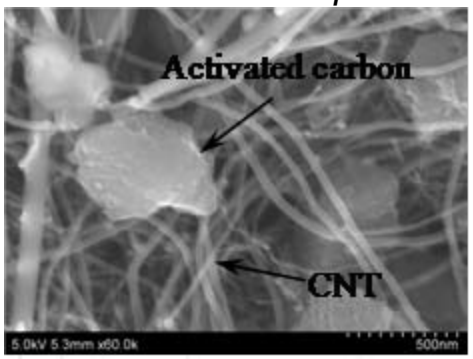
AC/CNT/IL composite electrodes

- Enhanced charge storage / delivery capability in ionic liquids over AC/CB electrodes
- Large-scale and low-cost production capability similar to AC/CB electrodes

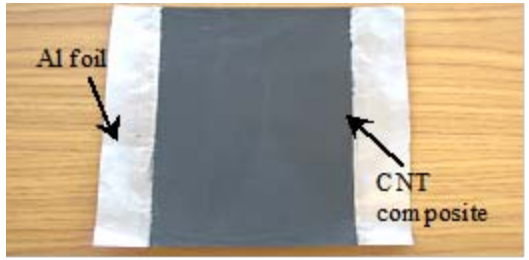
Conventional AC/CB



AC/CNT/IL composite



AC/CNT/IL- Al electrode



Phase I electrode sample (composite coating: 22 cm × 10 cm) prepared manually, which will be scaled up by a automatic coating machine in Phase II.

Why Ionic Liquid Electrolytes

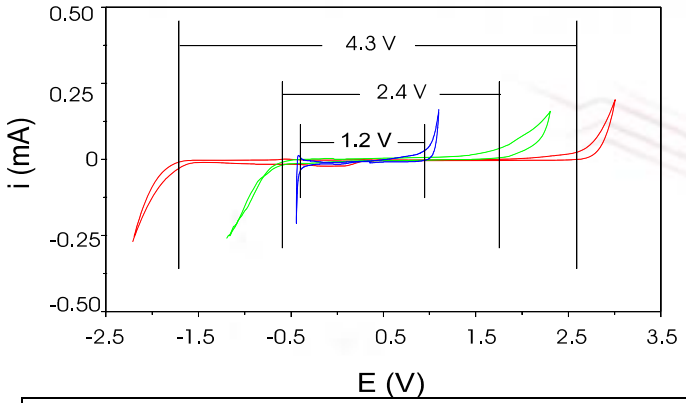
Properties of ionic liquid electrolytes

- High ionic conductivity
- Large electrochemical window
- Wide liquid-phase range
- Non-volatility
- Non-flammability
- Non-toxicity

Improved performance for ultracapacitors

- High cell voltage
- High energy density
- High power density
- High safety
- Long lifetime

Electrochemical windows of different electrolyte systems



1.2V: 38 wt % H2SO4 (current aqueous electrolyte)
2.4V: 1 M Et4NBF4/ACN (current organic electrolyte)
4.3V: ionic liquid [EMIM]Tf2N]

Performance of a ultracapacitor

Maximum energy: $E_{max} = 1/2(CU^2)$

Maximum power: $P_{max} = U_0^2 / 4R$

Enhanced Performance of CNT Composites in Ionic Liquids

Conventional AC/CB in ionic liquids

- Slow charge / discharge kinetics
- Low capacitance (62 F/g)

Conventional CNT paper in ionic liquids

- Fast charge / discharge kinetics
- Low capacitance (20 F/g)

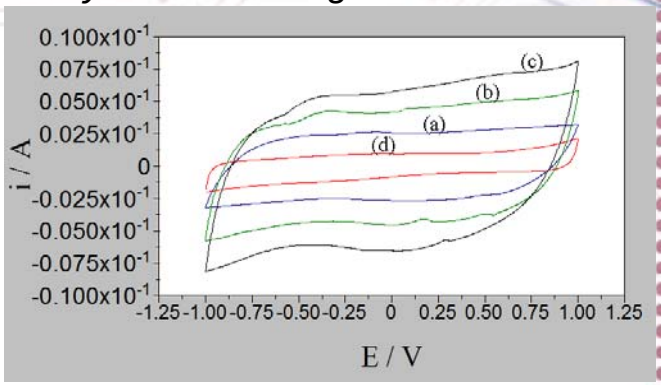
AC/CNT composite in ionic liquids

- Fast charge / discharge kinetics
- Enhanced capacitance (142 F/g)

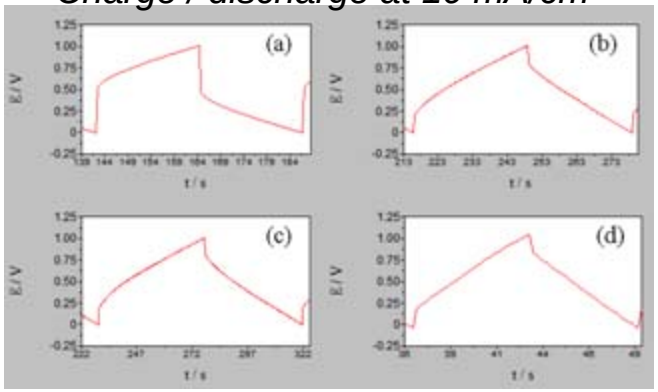
AC/CNT/IL composite in ionic liquids

- Fast charge / discharge kinetics
- Further enhanced capacitance (188 F/g)

Cyclic voltammogram at 20 mV/s



Charge / discharge at 10 mA/cm²



(a): a conventional AC/CB electrode.
(b): an AC/CNT composite electrode.
(c): an AC/CNT/IL composite electrode.
(d): a conventional CNT paper electrode.

Ultracapacitor Performance of CNT Composites with Ionic Liquids against Conventional Electrode Materials

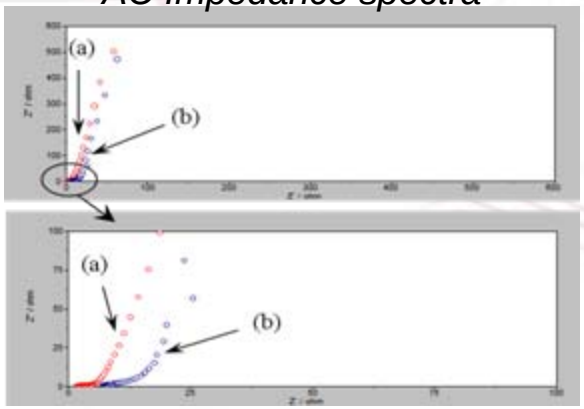
AC - IL capacitors (b)

- *Conventional AC/CB electrode*
- *Ionic liquid electrolyte*
- Slow charge / discharge kinetics
- High ESR
- Small knee frequency
- Poor capacitor performance

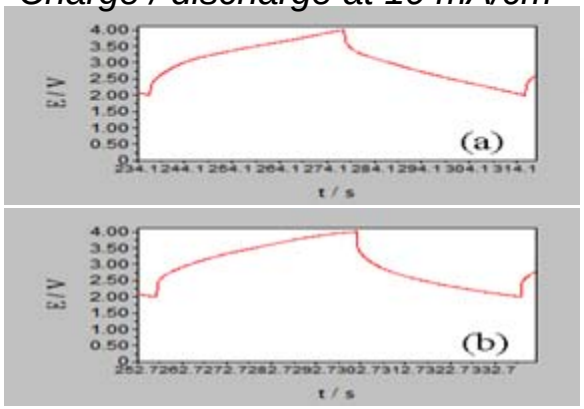
CNT composite - IL capacitors (a)

- *AC/CNT/IL composite electrode*
- *Ionic liquid electrolyte*
- Fast charge / discharge kinetics
- Low ESR
- Large knee frequency
- Excellent capacitor performance

AC Impedance spectra



Charge / discharge at 10 mA/cm²



(a): CNT composite - IL capacitor incorporating AC/CNT/IL composite electrode and ionic liquid electrolyte
(b): AC - IL capacitor incorporating conventional AC/CB electrode and ionic liquid electrolyte

High Performance of CNT Composite - Ionic Liquid Ultracapacitors against Current Ultracapacitor Technology

Current ultracapacitor technology (*AC electrode, organic electrolyte*)

- Low cell voltage
- Limited performance (energy/power density)
- Limited safety
- Limited cycle life

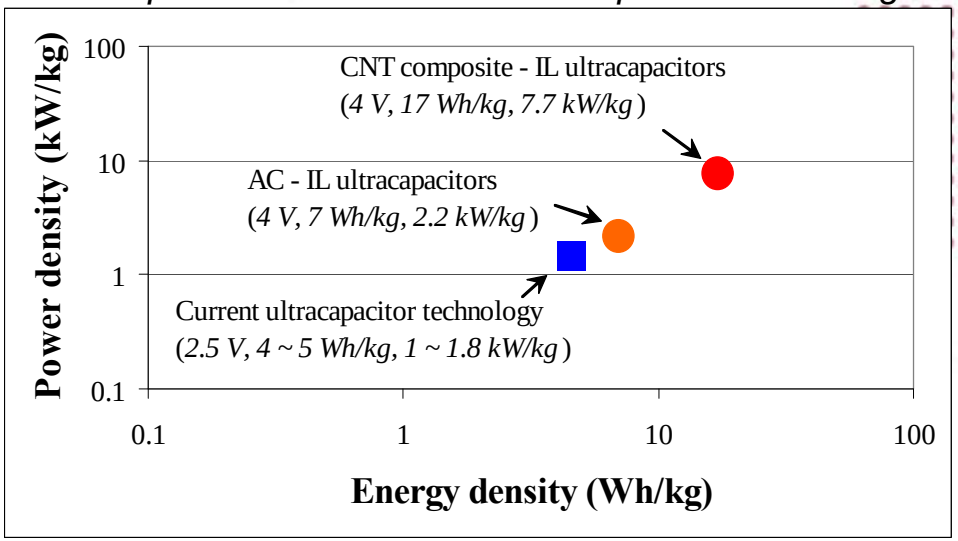
AC - IL capacitors

- AC/CB electrodes function poorly with ionic liquids
- Slightly improved performance

CNT composite - IL capacitors

- High cell voltage
- AC/CNT/IL composite electrodes function well with ionic liquids
- Significantly enhanced performance
- Improved safety
- Improved cycle life

CNT composite - IL vs. current ultracapacitor technologies



Outline of Proposed Phase II Program

- Continue optimizing AC/CNT/IL composites to further improve ultracapacitor performance
- Produce optimized AC/CNT/IL composite electrode in large scale suitable for fabricating industrial ultracapacitors
- Design, fabricate, and evaluate industrial packaged ultracapacitors. Leverage our established ILGPE technology to further improve safety and lifetime for the capacitors
- Integrate individual ultracapacitors to design, fabricate, and evaluate modules and power systems for utility applications. Demonstrate the superior performance (voltage, power, and energy) of the proposed system over the current technology
- Document the design parameters for larger capacitors, modules and power systems of utility scale applications beyond Phase II