High Voltage Electrochemical Capacitor

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Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed Martin Company,
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Objective

- New Start - 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

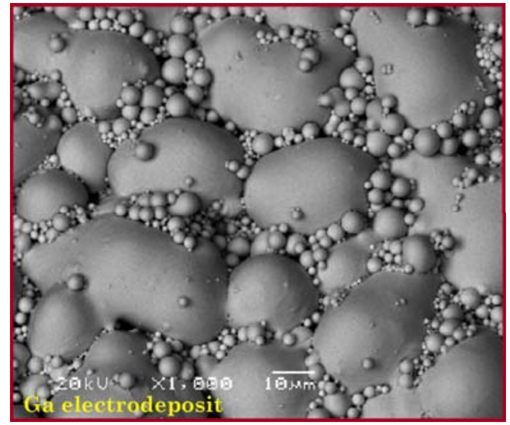
Electrolyte	C_d^{int} ($\mu F\ cm^{-2}$)
$EMIBF_4$	10.6
$EMICF_3SO_3$	12.4
$EMI(CF_3SO_2)_3C$	10.6
$EMI(CF_3SO_2)_2N$	11.7
$EMI(CF_3SO_2)_2N$	12.0[a]
$EMI(CF_3SO_2)_2N$	11.4[b]
1.5 M $EMI(CF_3SO_2)_2N/PC$	9.1
1M Et_4NBF_4/PC	7.0
0.1 M KCl/H_2O	15.1
3 M H_2SO_4/H_2O	14.6

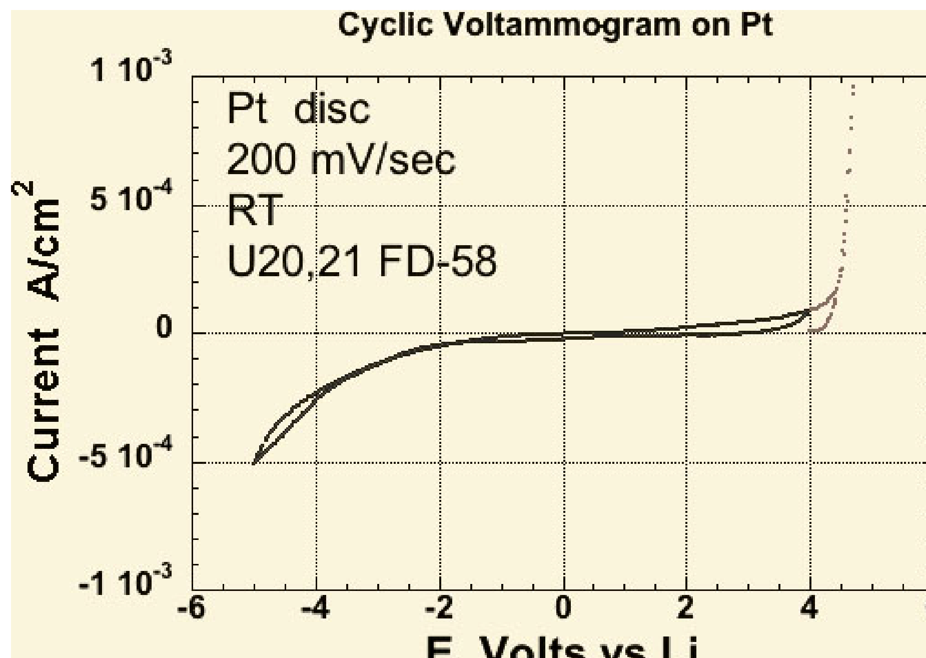
a - glassy carbon
b - SpectraCarb 2220 yarn

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

Motivation

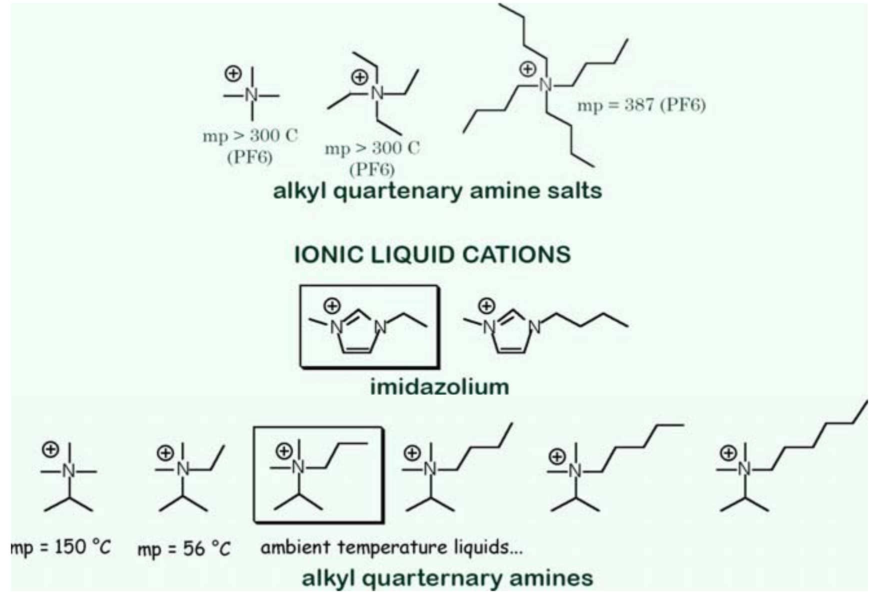
- Ongoing program - room temperature electrodeposition of reactive metals & alloys. (Joint program with LANL)
  - *highly* reactive metals
    - necessitates large electrolyte working range (large voltage)
  - low solution resistance
- ionic liquids (ILs)
  - neat
  - as electrolyte in other solvents
  - 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)

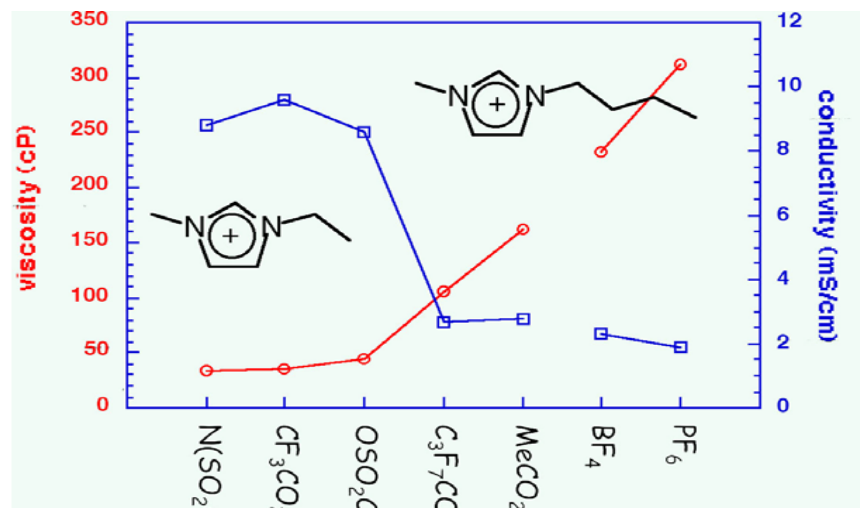




Engineered Ionic Liquids

- Have evaluated a variety of ILs (also utilize literature (eg Ue's work))
- Tailored properties of IL through control of structure
- Both anion and cation must be considered for:
  - stability
  - conductivity
    - viscosity
    - melting point
- Cation
  - small asymmetric species preferred
- Anion
  - smaller anions preferred from C_d standpoint
  - conductivity larger anions preferred

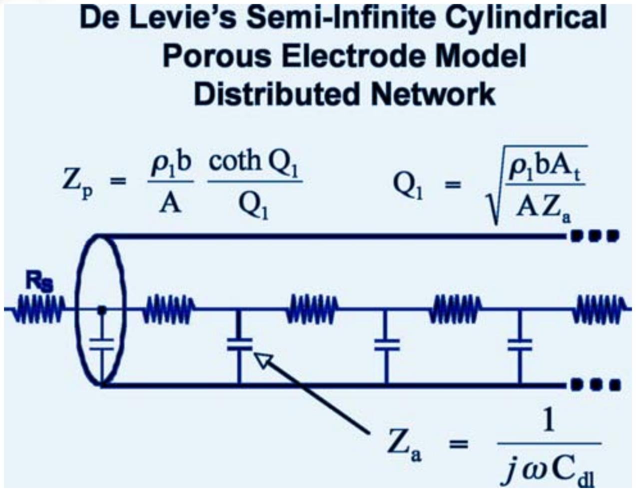


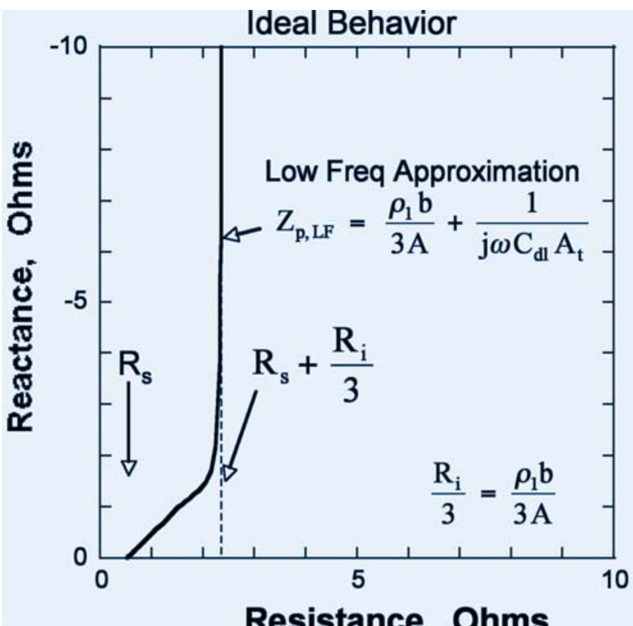


- Bonhote et. al. *Inorg. Chem.* **1996**, *35*, 1168.
- Dupont et. al. *Organometallics* **1998**, *17*, 815.

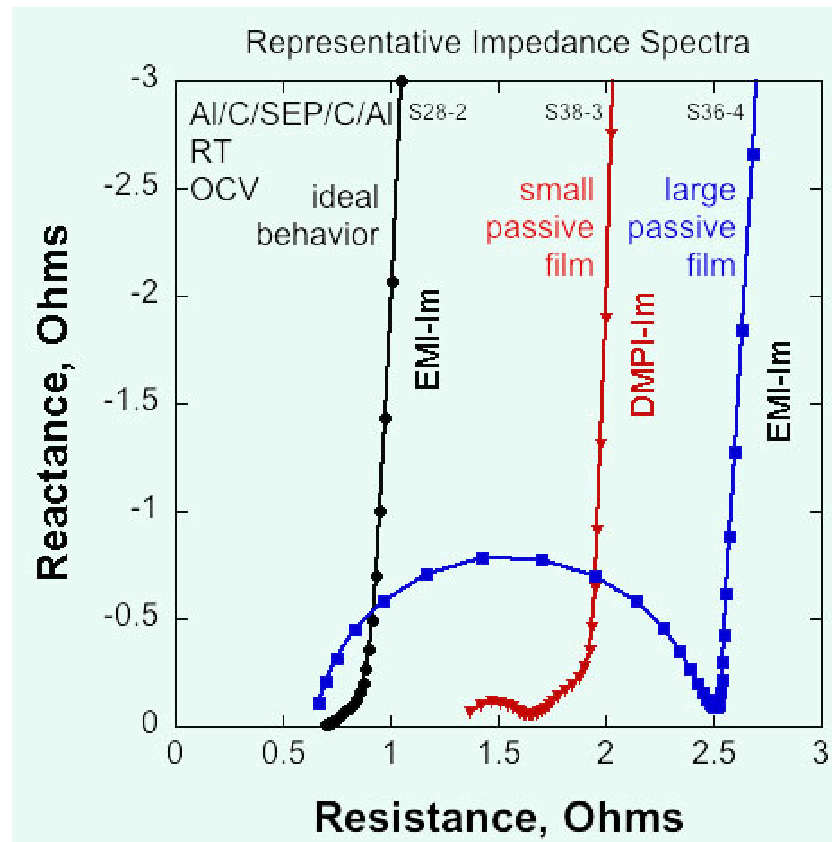
Data Collection and Interpretation

Impedance



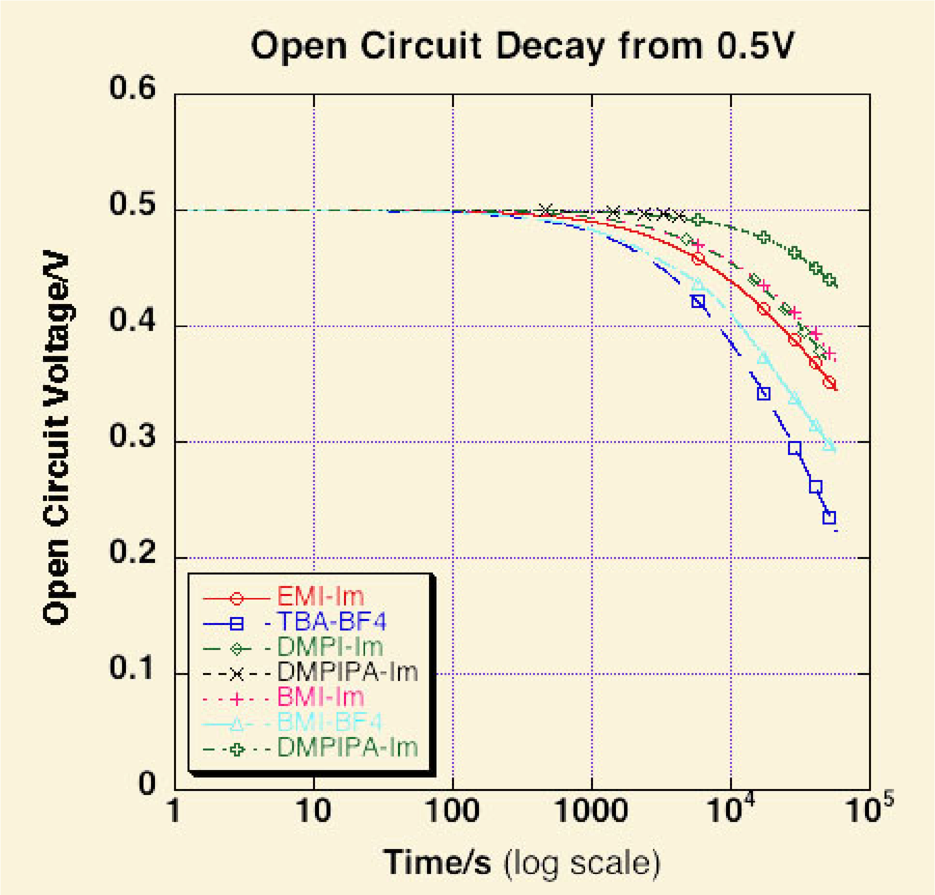


- Experimental data is typically ideal
- observe passive film in some instances
- determination of C_d at low frequency is:
  - not perturbed by passive film
  - frequency independent



C_d and Self Discharge Behavior

- C_d is on the order of 2.5 μF/cm²
  - basal plane graphite - 3-4 μF/cm²
  - edge plane of graphite - 50-75 μF/cm²
    - (Randin and Yeager, JEAC, 58, 313, (1975) and *ibid* 36, 257, (1972))
- graphitic type carbon
  - high conductivity
  - non-reactive basal plane
  - aren't working in restricted pore volume of high surface area carbons
- Of all of the ILs studied, DMPIp-Im (the tailored compound) has the lowest self discharge by an order of magnitude



C_d in various ILs	
Electrolyte	μF/cm² 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

future work

- continue to leverage select reactive metal work to electrochemical capacitors
- evaluate working range limits of tailored IL
- evaluate voltage dependencies of C_d
- fabricate laboratory prototype
- evaluation of laboratory prototype
- develop understanding (thermodynamic and kinetic) of the large working ranges observed

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