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Conductive Polymers as Positive Electrodes in Rechargeable Aluminum Batteries

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Exceptional service in the national interest

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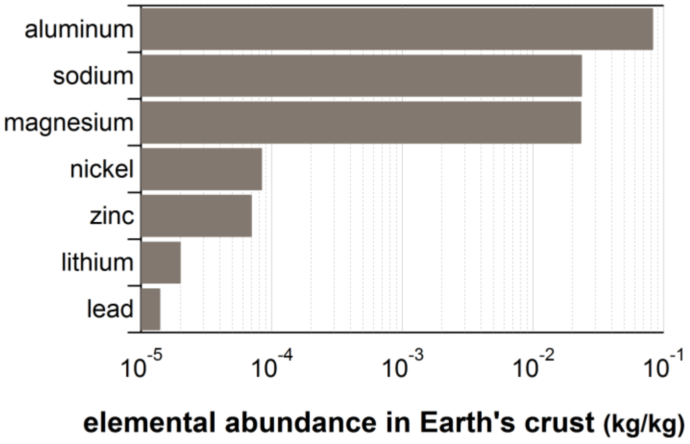
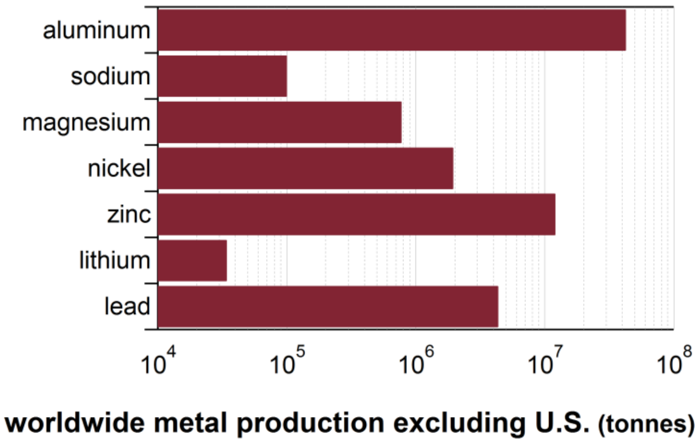
Motivation for Aluminum Batteries

Aluminum is abundant and widely produced compared to other energy-storage metals.

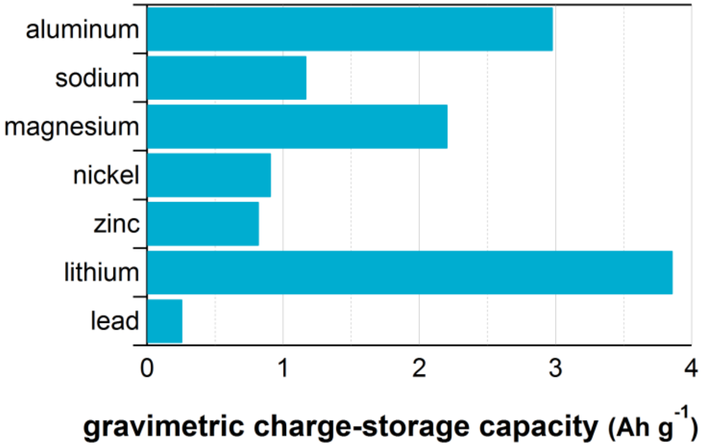


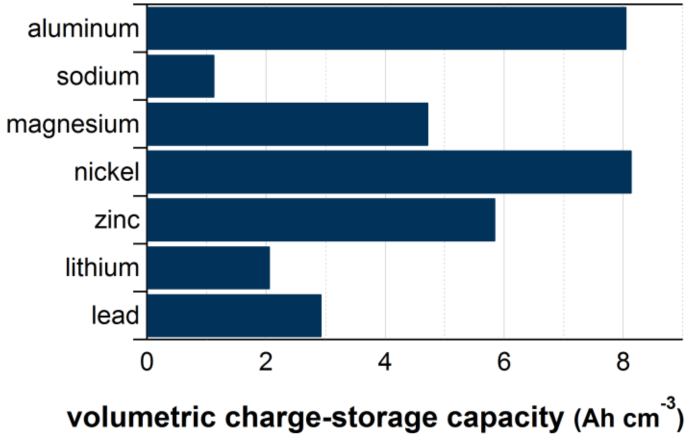
CRC Handbook of Chemistry and Physics



U.S. Geological Survey

Aluminum metal's charge-storage capacity is competitive on gravimetric *and* volumetric scales.





History of Aluminum Batteries

Aqueous Systems

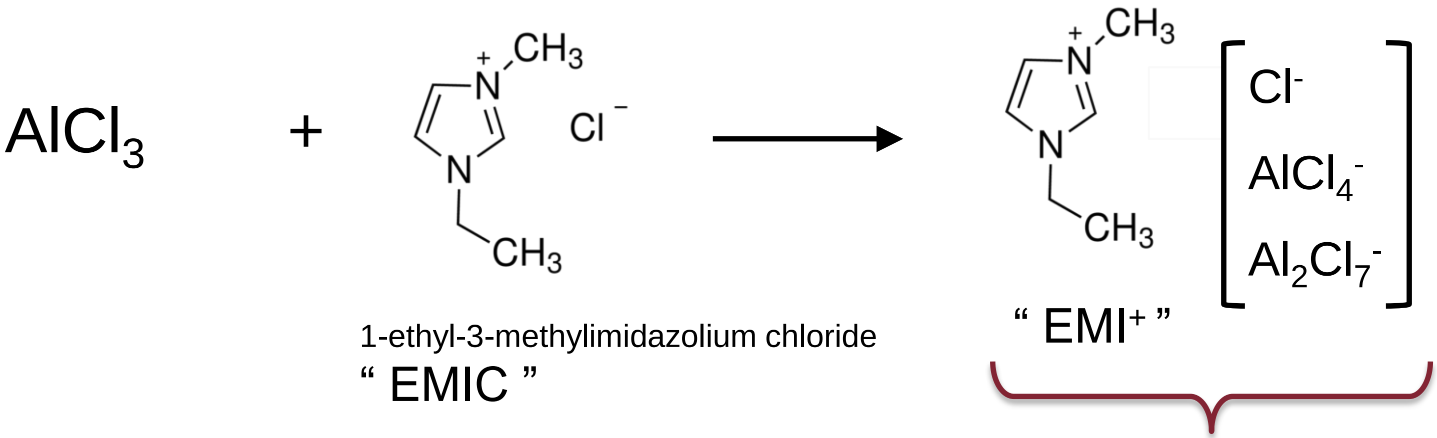
- All primary cells
  - Al metal can not be electrodeposited
  - Al corrodes in alkaline electrolytes
- Aluminum-MnO_2
  - $AlCl_3$ or $Al(OH)_3$ electrolytes
  - Analogous to alkaline primary (Zn) cells
  - Surface oxide → decreased potential
- Aluminum-sulfur
  - K_2S-KOH electrolyte
  - 650 Wh kg^{-1} theoretical
- Aluminum-air
  - Alkaline or saline electrolyte
  - Reduction of oxygen at cathode
  - 2800 Wh kg^{-1} theoretical
  - Mechanical recharging is possible

Q. F. Li and N. J. Bjerrum, *J Power Sources*, **110**, 1-10 (2002)

Non-Aqueous Systems

- Molten-salt electrolytes
  - $NaCl$-$AlCl_3$ or $NaCl$-KCl-$AlCl_3$
  - 100ºC – 300ºC operation
  - Chlorine cathodes
    - Recapture of chlorine at electrode is main challenge
  - Metal-chloride or metal-sulfide cathodes
    - Solubility of these species in electrolyte is main challenge
- Chloroaluminate room-temperature ionic liquids
  - Mixtures of imidazolium chlorides and aluminum chlorides
    - Efficient deposition and stripping of Al
  - Safety: low temperature & non-flammable
  - Metal-chloride or metal-sulfide cathodes
    - Solubility causes self-discharge
  - Cathodes that are hosts for chlorine or chloroaluminate anions

Chloroaluminate Ionic Liquids



1-ethyl-3-methylimidazolium chloride
“ EMIC ”

“ EMI+ ”

liquid at room temperature

Electrodeposition of aluminum metal is possible only when $Al_2Cl_7^-$ ions are present.

$$4Al_2Cl_7^- + 3e^- \xrightarrow{\text{reducing potential}} Al + 7AlCl_4^-$$

(Stripping of aluminum metal occurs in any stable $EMIC/AlCl_3$ mixture.)

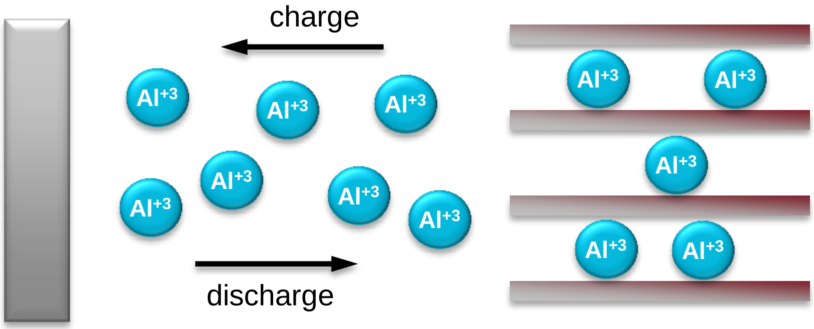
This is the negative electrode in a rechargeable aluminum-metal battery.

Proposed Electrode Reactions

What about the positive electrode in a rechargeable aluminum-metal battery?

Shuttle Mechanism

- Basis for “rocking chair” batteries
- Analogous to lithium-metal batteries
- Solvated Al^{+3} ions are not present in the chloroaluminate ionic liquids
- Intercalation of trivalent species in any host is difficult and has not been successfully demonstrated with this electrolyte system



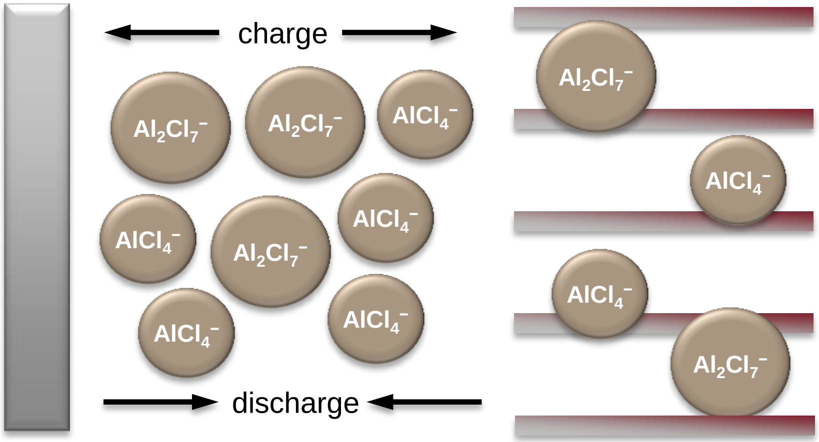
Al metal
(−) electrode

electrolyte

host material
(+) electrode

Anion-Insertion Mechanism

- AKA “dual-ion” system
- Chloroaluminate anions are inserted into positive electrode host during charge
- Amount of electrolyte must scale with the size of the positive electrode
- Demonstrated previously in
  - graphite (via intercalation of anions)
  - **conductive polymers** (via doping)



Proposed Electrode Reactions

"M" ≡ positive electrode active material (host for anions)

Positive Electrode $3(M^{+}\mathrm{AlCl}_4^{-}) + 3e^{-} \longleftrightarrow 3M + 3\mathrm{AlCl}_4^{-}$

Negative Electrode $\mathrm{Al} + 7\mathrm{AlCl}_4^{-} \longleftrightarrow 4\mathrm{Al}_2\mathrm{Cl}_7^{-} + 3e^{-}$

Full Cell $\mathrm{Al} + 3(M^{+}\mathrm{AlCl}_4^{-}) + 4(\mathrm{AlCl}_4^{-}\ \mathrm{EMI}^{+}) \longleftrightarrow \underbrace{3M + 4(\mathrm{Al}_2\mathrm{Cl}_7^{-}\ \mathrm{EMI}^{+})}$

Upper bound for capacity is **49 mAh g^{-1}** (accounting for all electrolyte species).

Anion-Insertion Mechanism

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- Chloroaluminate anions are inserted into positive electrode host during charge
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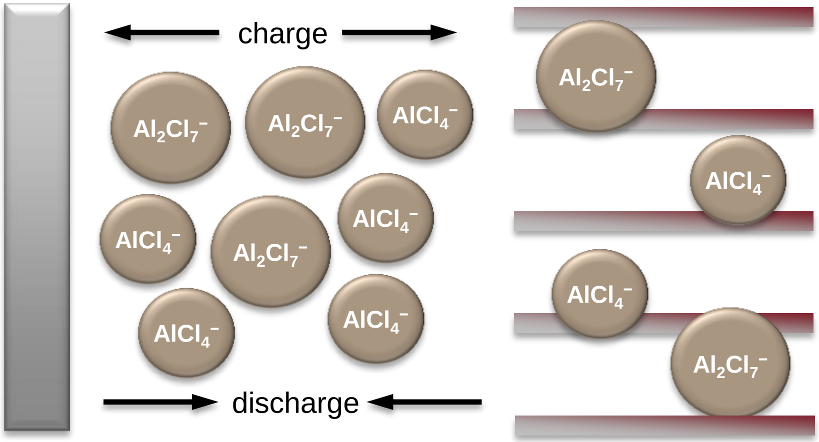


Anion-Insertion Electrodes in Chloroaluminate Ionic Liquids

Polypyrrole

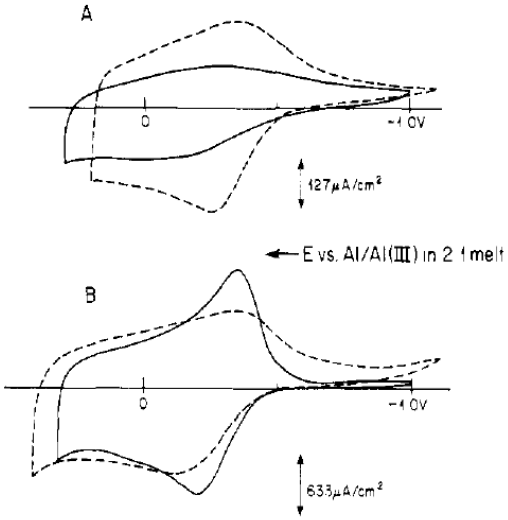
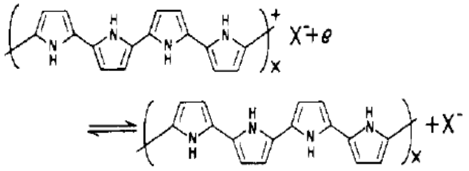


Figure 4. Cyclic voltammetry of Pt/polypyrrole electrodes in 0.8:1 $AlCl_3$:BuPyCl melt (—) and in 0.1 M Et_4NClO_4/CH_3CN (---). (A) 0.06-μm PP film prepared in CH_3CN, (B) 0.20-μm film prepared in neutral melt. Scan speed = 100 mV/s.



Polythiophene

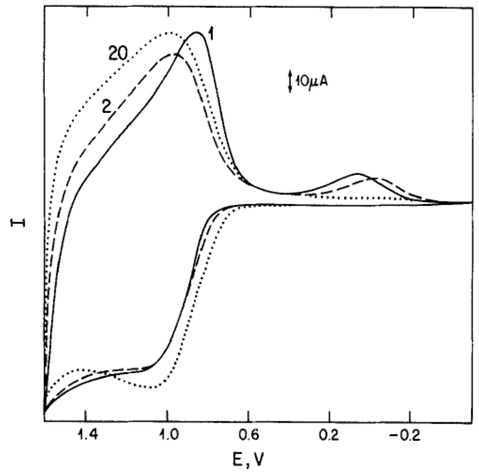
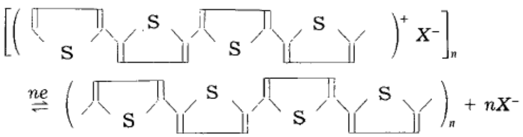


Fig. 3. Cyclic voltammetric curves for 2 × 10^{-2}C film of polythiophene in 1:1 melt; v = 50 mV s^{-1}. Electropolymerization of thiophene was carried out in 0.1M solution of monomer in 1:1 melt at +1.7V. The number on the curve refers to the number of the scan (tungsten electrode, A = 0.12 cm^2).



Polyaniline

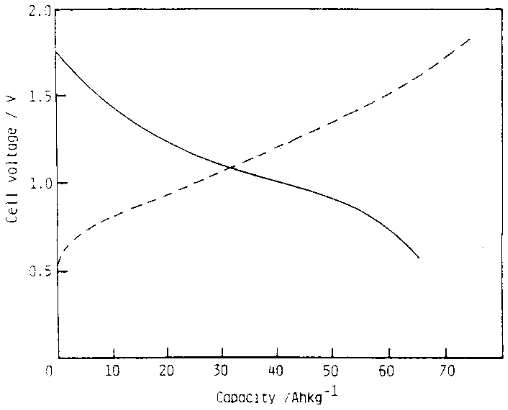
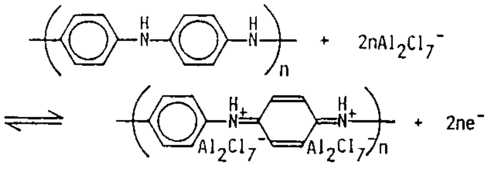


Fig.2 Chrge and discharge curves for the powder electrode of Al/PAn secondary cell. C.D.: 2.0 mAcm^{-2}

----- : charge, ——— : dischrge



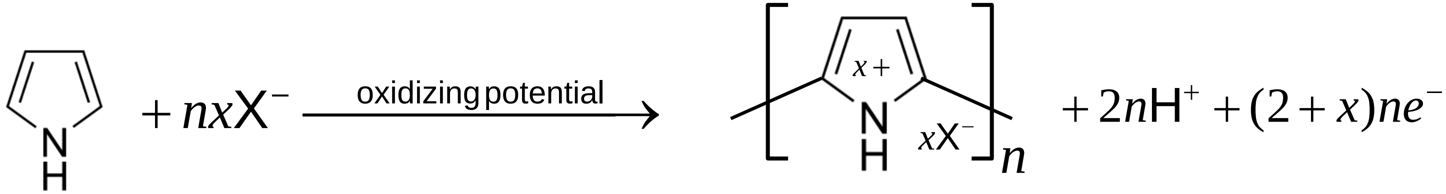
P. G. Pickup and R. A. Osteryoung,
JACS, **106**, 2294-2299 (1984)

L. Janiszewska and R. A. Osteryoung,
J Electrochem Soc, **134**, 2787-2794 (1987)

N. Koura and H. Ejiri,
Denki Kagaku, **58**, 923-927 (1990)

Sample Prep: Electropolymerization

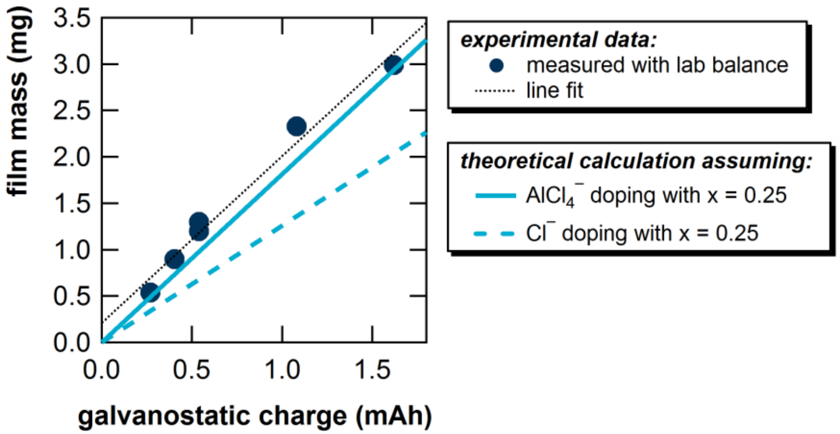
- Pyrrole and other conjugated monomers can be polymerized easily via electrochemical oxidation



n ≡ degree of polymerization (unknown)
x ≡ extent of doping (usually 0.1 – 0.4)

- Note that x can be estimated experimentally by comparing the polymerization charge to the cycling charge (assuming 100% faradaic efficiency of polymerization)

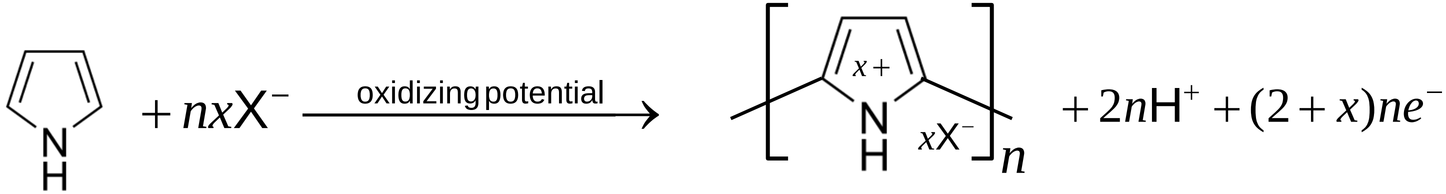
- Electropolymerization of pyrrole, thiophene, and analogs was performed galvanostatically using a 0.3 M solution of monomer in 1:1 $AlCl_3$:EMIC
- Pyrrole polymerization produces a smooth, robust film that peels off the surface
- Other monomers formed solid, adherent films but did not peel off the substrate



Mass data suggest that $AlCl_4^-$ is the dominant anion dopant after polymerization.

Sample Prep: Electropolymerization

- Pyrrole and other conjugated monomers can be polymerized easily via electrochemical oxidation



n ≡ degree of polymerization (unknown)

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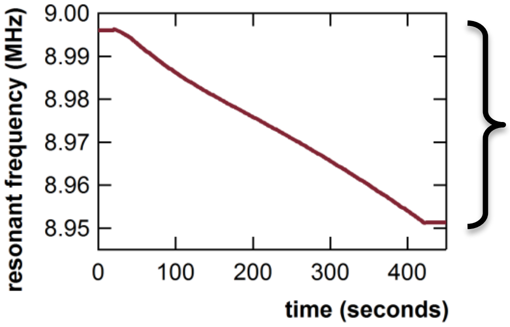
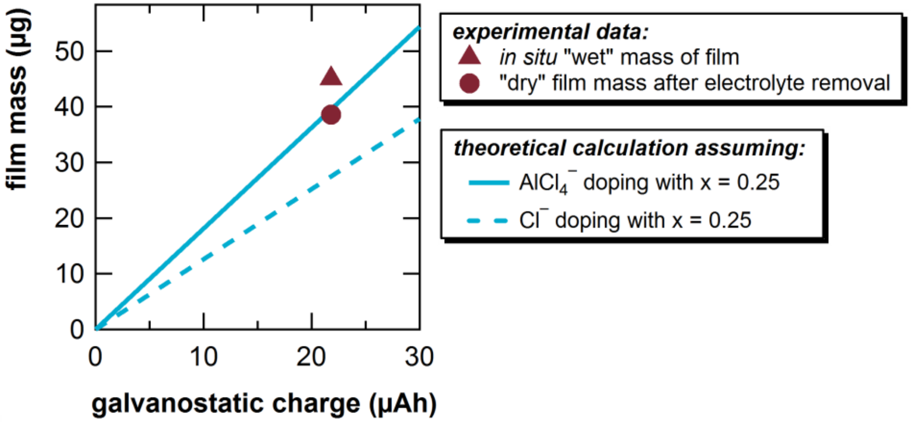
Electrochemical Quartz Crystal Microbalance



Change in frequency during polymerization used to calculate mass of deposited polymer film with the Sauerbrey equation



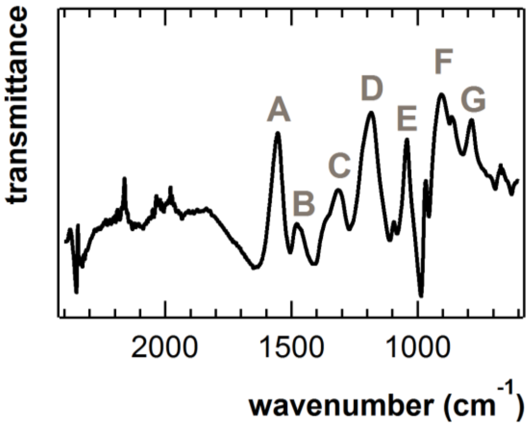
Experimental Conditions:

- Galvanostatic electropolymerization: 1 mA cm^{-2} for 400 seconds
- Electrolyte: 0.3 M monomer in 1:1 (mole:mole) $AlCl_3$:EMI
- Platinum working electrode, aluminum reference and counter electrodes

Calculated cycling capacity of system with polypyrrole at this doping level is **33 mAh g^{-1}**.

Polypyrrole Film Characterization

Attenuated Total Reflectance FTIR

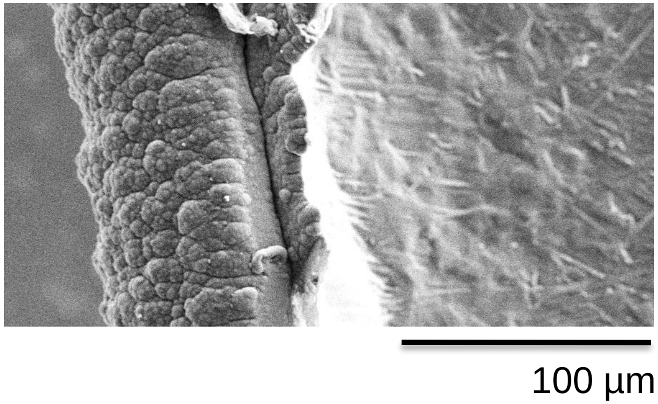


Prominent peaks below 1700 cm^{-1} match published data for doped polypyrrole electropolymerized in organic solvents.

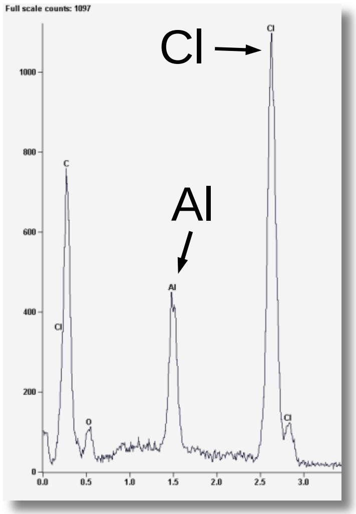
Peak	Approximate Assignment (ref. below)	My Samples	Doped (from Street ref.)	Undoped (from Street ref.)
A	C-C & C=C stretch	1550 cm^{-1}	1550	1530
B	C-N stretch	1480	1470	1440
C	C-H & N-H def.	1310	1300	1300
D	C-N str. & C-H def.	1180	1180	1240
E	C-H deformation	1040	1000	1050
F	?	910	900	960
G	?	790	780	750

Peak assignments: B. Tian & G. Zerbi, *J. Chem. Phys*. **92**: 3886 (1990)

SEM & Energy Dispersive X-ray

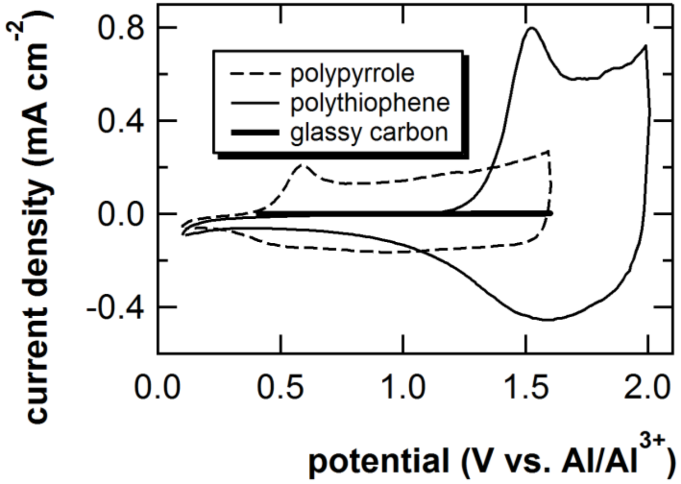


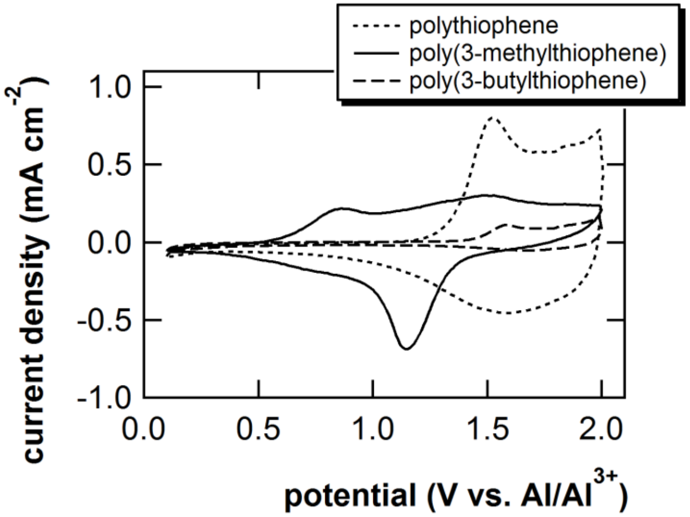
Energy dispersive x-ray spectroscopy shows presence of elemental aluminum and chlorine in all electropolymerized films (polypyrrole, polythiophene, and analogs).



Polymer Electrode Redox Behavior

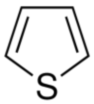
Cyclic Voltammetry at 10 mV s^{-1} of Polymers in Chloroaluminate Ionic Liquids



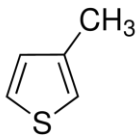


Polythiophene has redox peak-pair at higher potential than polypyrrole (observed previously in other electrolyte solutions).

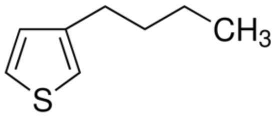
thiophene



3-methylthiophene



3-butylthiophene

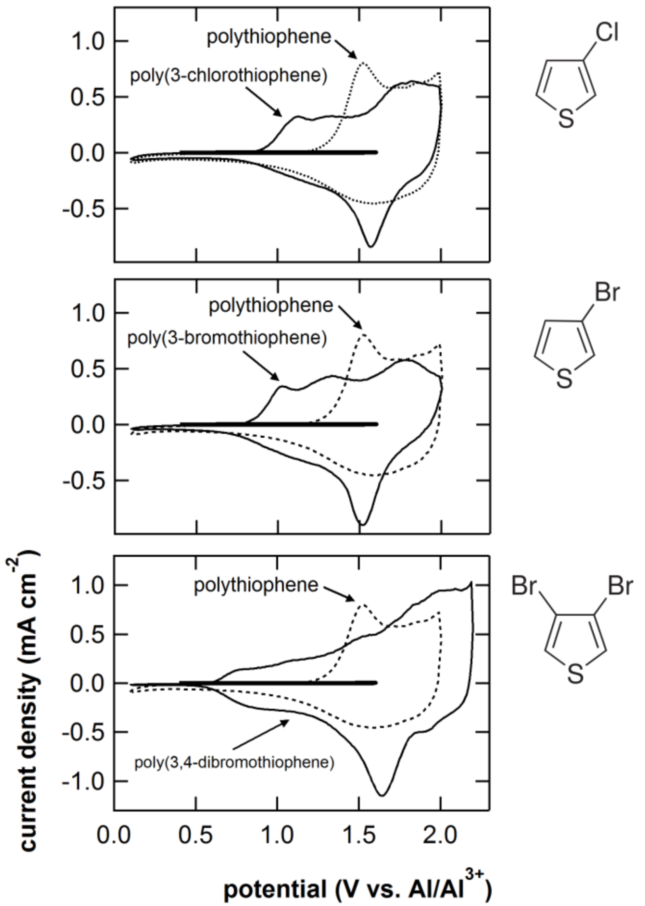


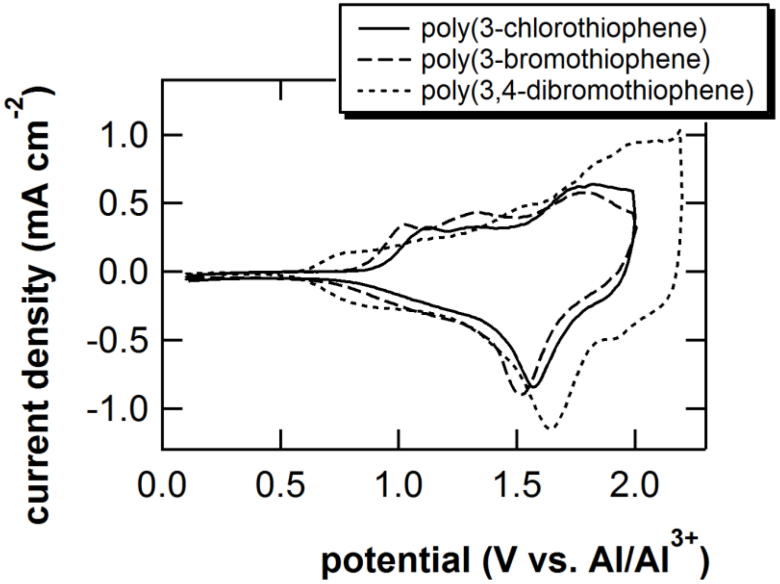
Experimental Conditions:

- All polymer films formed galvanostatically on glassy carbon: 1 mA cm^{-2} for 400 seconds in solution of 0.3 M monomer in 1:1 (mole:mole) $AlCl_3$:EMIC
- Cyclic voltammetry performed in 1.5:1 (mole:mole) $AlCl_3$:EMIC at room temperature with aluminum metal counter and reference electrodes

Polymer Electrode Redox Behavior

Halide Substitution: Cyclic Voltammetry of Polymer Films at 10 mV/s





Halide substitution on thiophene monomer shifts the redox potential of the corresponding polymer to higher values (due to the electron-withdrawing character of the halides).

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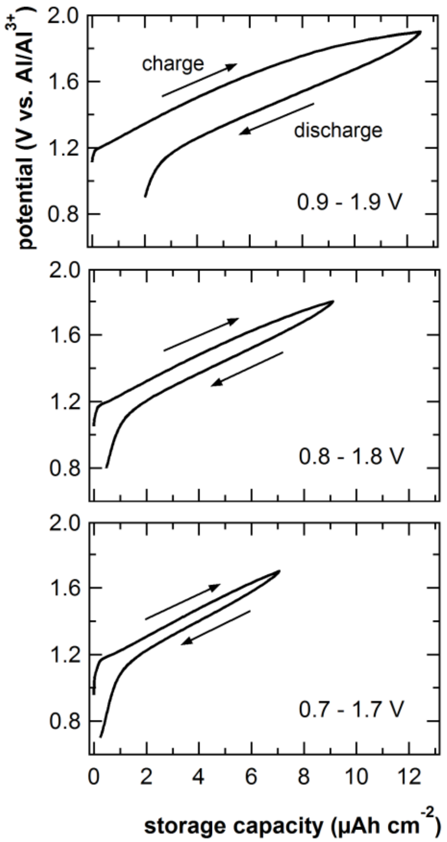
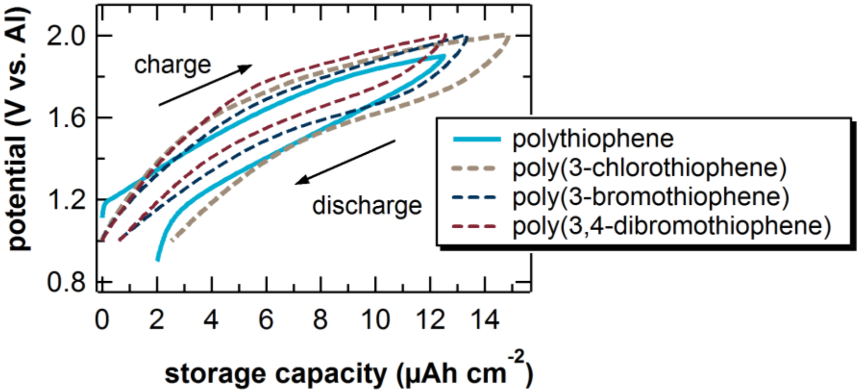
- Cyclic voltammetry performed in 1.5:1 (mole:mole) $AlCl_3$:EMIC at room temperature with aluminum metal counter and reference electrodes

Galvanostatic Cycling

Polythiophene Cycling at 10 μA cm^{-2} (1C – 2C rate)



Effect of Halide Substitution



Halide substitution on thiophene monomer affects cycling potential curve.

Irreversible oxidative process at higher potential makes the cycling coulombic efficiency highly dependent on upper voltage limit.

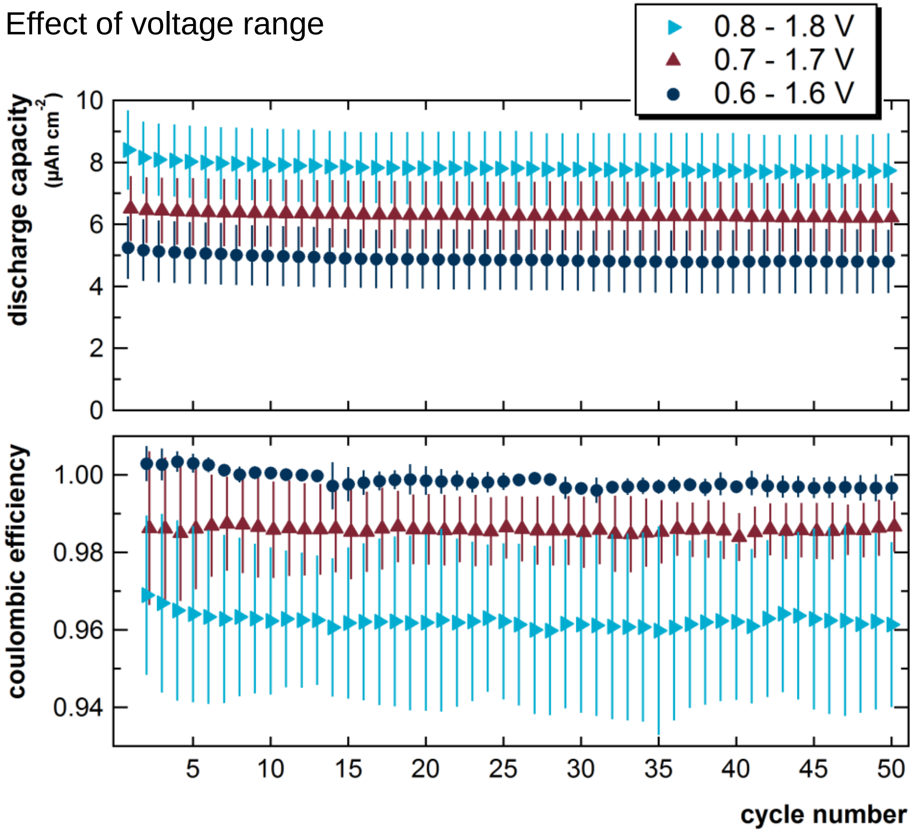
Experimental Conditions:

- All polymer films formed galvanostatically on glassy carbon: 1 mA cm^{-2} for 400 seconds in solution of 0.3 M monomer in 1:1 molar $AlCl_3$:EMIC
- Galvanostatic cycling performed in excess of 1.5:1 (mole:mole) $AlCl_3$:EMIC at room temperature with aluminum metal counter and reference electrodes

Galvanostatic Cycling

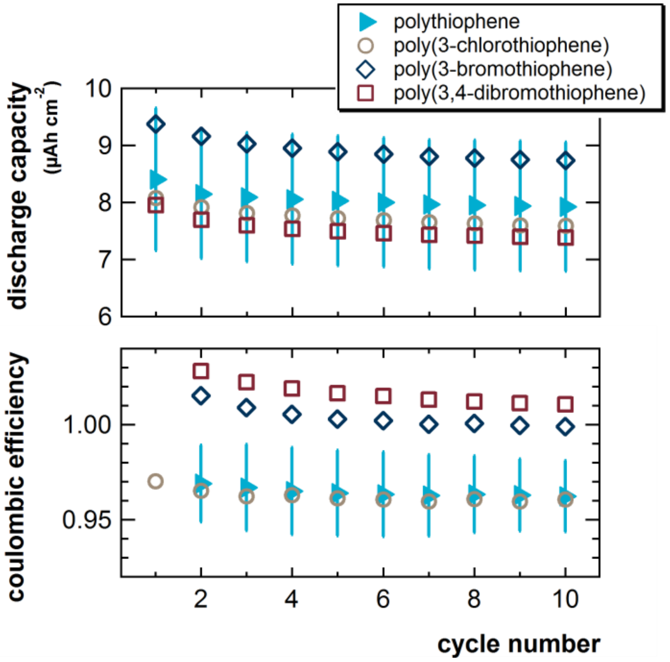
Polythiophene Cycling at 10 µA cm^{-2} (1C – 2C rate)

Effect of voltage range



Effect of Halide Substitution

Voltage range: 0.8 – 1.8 V



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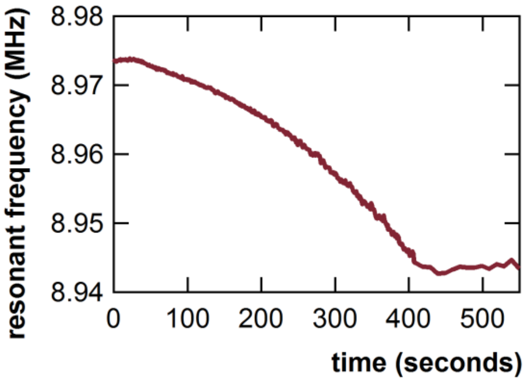
- Galvanostatic cycling performed in excess of 1.5:1 (mole:mole) $AlCl_3$:EMIC at room temperature with aluminum metal counter and reference electrodes
- Markers and error bars are the average and standard deviations, respectively, of three experiments.

Gravimetric Energy Density

QCM: Convert Area-Specific Capacity of Polythiophene to Gravimetric Capacity

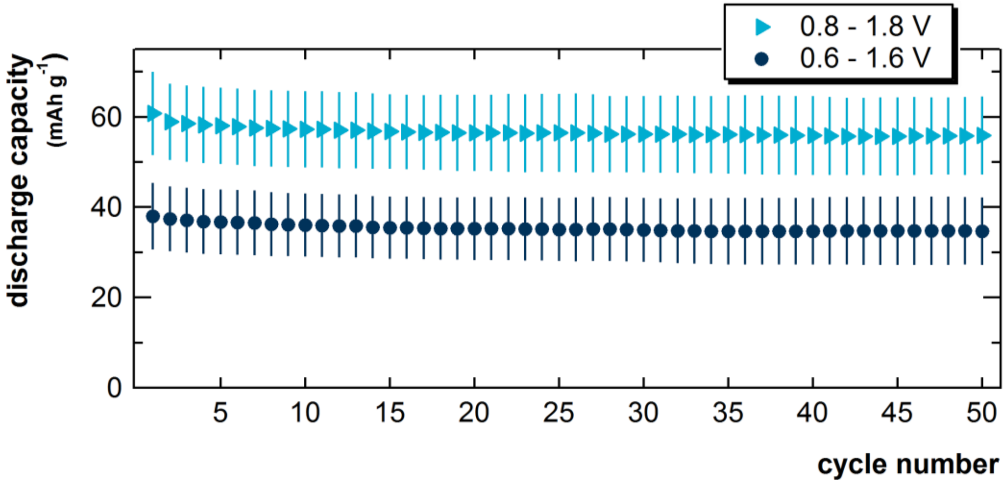


QCM frequency measurement during thiophene electropolymerization shows inefficient polymerization.

Ex situ frequency shift used with Sauerbrey equation to calculate deposited mass

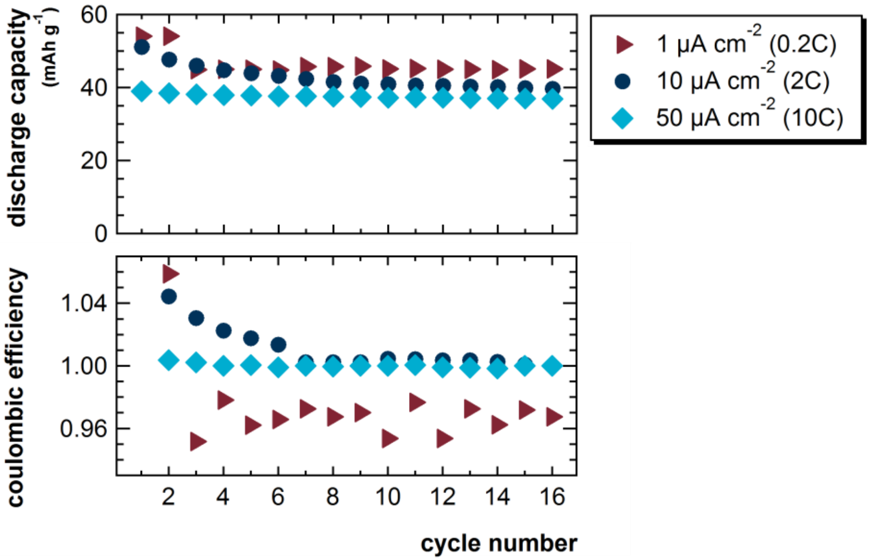
0.14 mg cm^{-2} deposited for a 400-second thiophene polymerization at 1 mA cm^{-2}

- Capacity on plot is specific to doped polymer mass
- Correponds to doping level of 0.29 (approx. one anion per 3 thiophenes)
- Accounting for mass of electrolyte and aluminum metal electrode, effective capacity is 30 mAh g^{-1}
- Specific energy density: 50 Wh kg^{-1}
  - Competitive with flow batteries and other systems for grid-scale storage

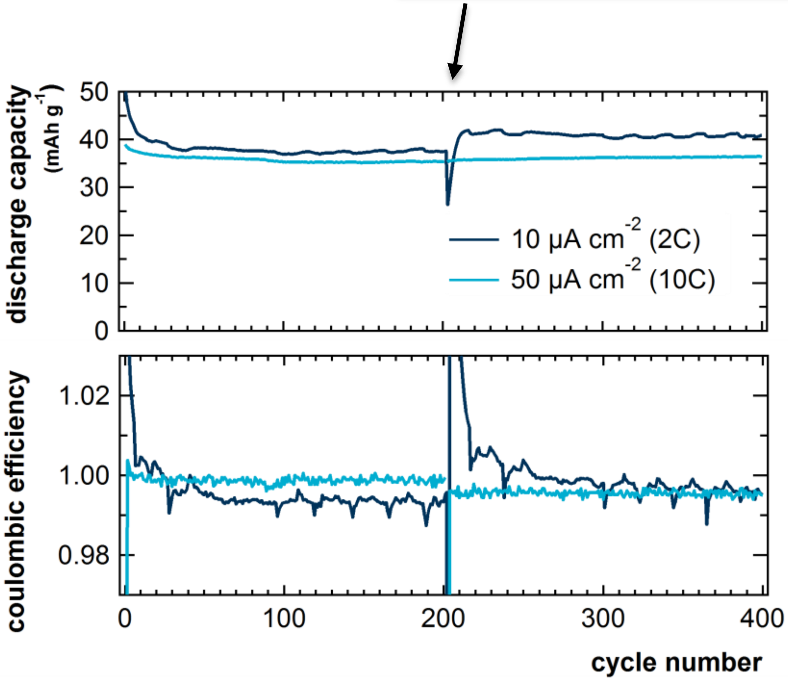


Rate Capability & Long-Term Cycling

Polythiophene Cycling Performance at Various Rates



Pause in cycling: electrode was removed from electrolyte and stored in glove box for 4 months before cycling was resumed.



Large changes in cycling rate resulted in small effect on capacity. The lowest rate tested (0.2C) produced increased capacity but lower coulombic efficiency.

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- Voltage range for cycling: 0.6 – 1.6 V

Conclusions and Acknowledgements

- Cycling of rechargeable aluminum batteries at room temperature with chloroaluminate ionic liquid electrolyte demonstrated
    - Conductive polymers (polythiophene and analogs) as active materials for the positive electrode
    - Aluminum metal as negative electrode
- Electrochemically synthesized polymer films used for initial demonstration
- Energy density of ~50 Wh kg^{-1} is competitive for stationary storage applications
- Steady capacity maintained for at least 400 cycles at 2C and 10C rates

- Acknowledgements
    - Bonnie McKenzie, Sandia National Laboratories (SEM & EDS)
    - Tom Wunsch, Sandia National Laboratories (manager of Advanced Power Sources R&D department)
    - *Funding*: Laboratory Directed Research & Development (LDRD) program at Sandia National Laboratories