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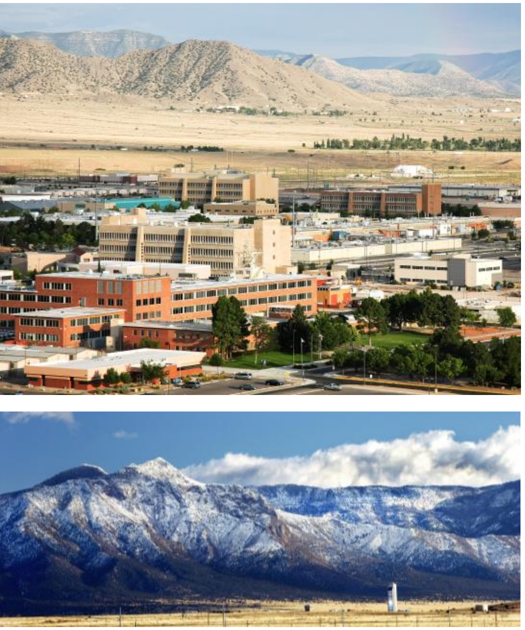
Rechargeable Aluminum Batteries with Conducting Polymers as Active Cathode Materials

Nicholas S. Hudak

Advanced Power Sources Research and Development
Sandia National Laboratories
Albuquerque, New Mexico, U.S.A.



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U.S. DEPARTMENT OF ENERGY

NNSA National Nuclear Security Administration

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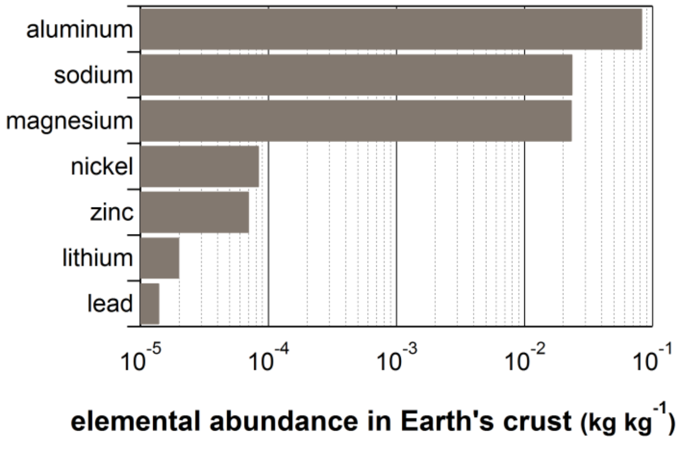
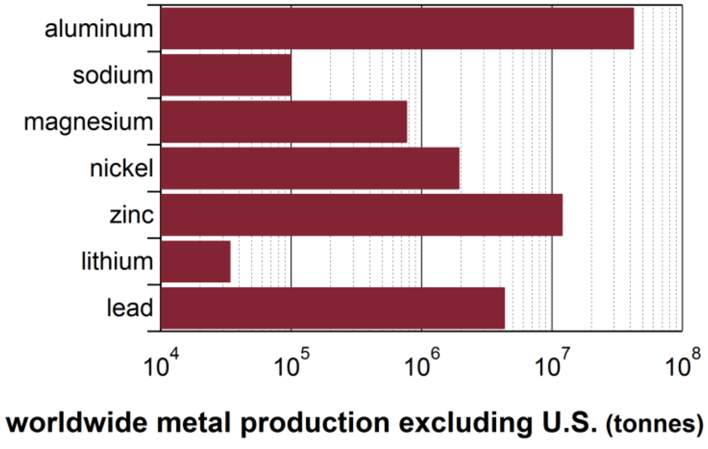
Motivation for Aluminum Batteries

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

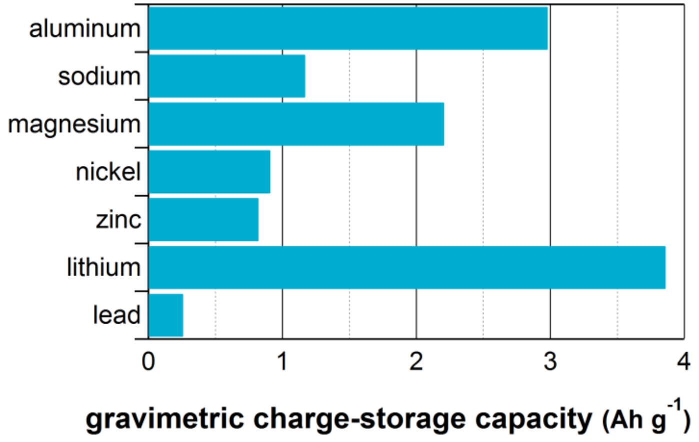


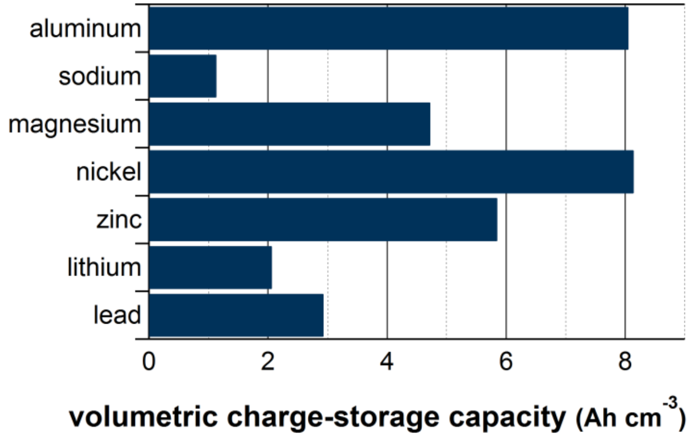
CRC Handbook of Chemistry and Physics



U.S. Geological Survey

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





History of Aluminum Batteries

Aqueous Systems

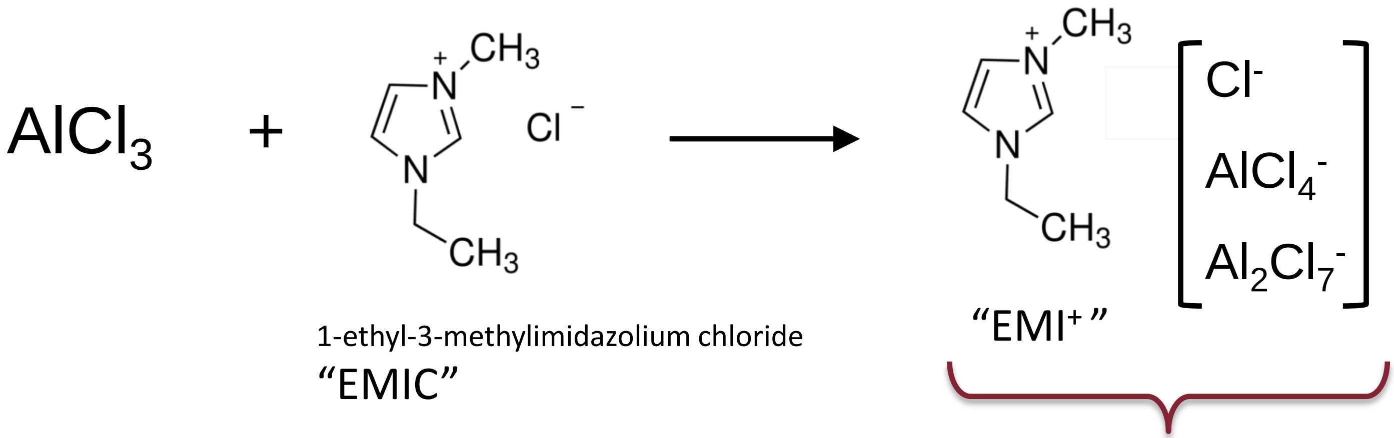
- All primary cells
  - Al metal can not be electrodeposited
  - Al corrodes in alkaline electrolytes
- Aluminum-MnO_2
  - $AlCl_3$ or $Al(OH)_3$ electrolytes
  - Analogous to alkaline primary (Zn) cells
  - Surface oxide → decreased potential
- Aluminum-sulfur
  - K_2S-KOH electrolyte
  - 650 Wh kg^{-1} 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 and 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 $\mathrm{Al_2Cl_7^-}$ ions are present.

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

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

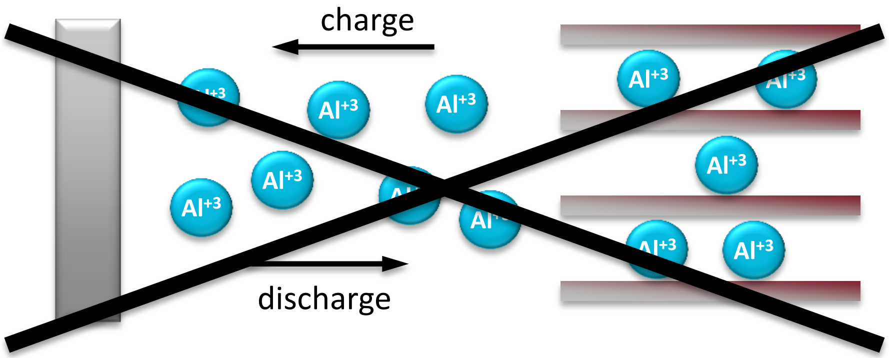
This is the negative electrode in a rechargeable aluminum-metal battery.

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



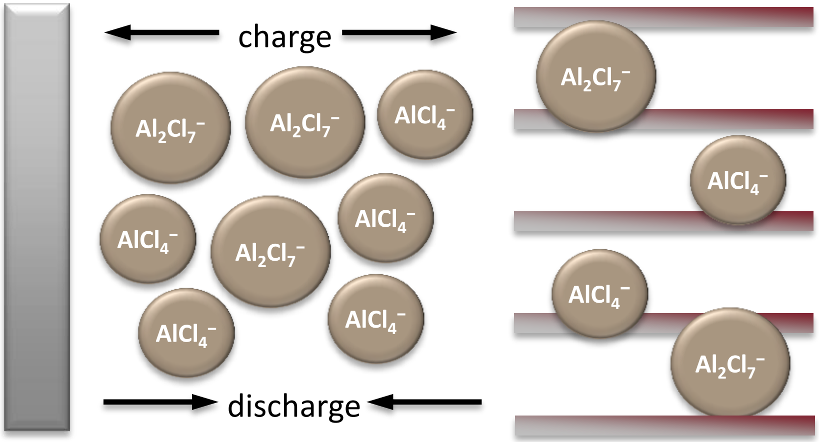
Al metal
(−) electrode

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)
  - **conducting polymers** (via doping)



Proposed Electrode Reactions

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

Positive Electrode $3(M^{+}AlCl_4^{-}) + 3e^{-} \longleftrightarrow 3M + 3AlCl_4^{-}$

Negative Electrode $Al + 7AlCl_4^{-} \longleftrightarrow 4Al_2Cl_7^{-} + 3e^{-}$

Full Cell $Al + 3(M^{+}AlCl_4^{-}) + 4(AlCl_4^{-}\ EMI^{+}) \longleftrightarrow \underbrace{3M + 4(Al_2Cl_7^{-}\ EMI^{+})}$

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

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
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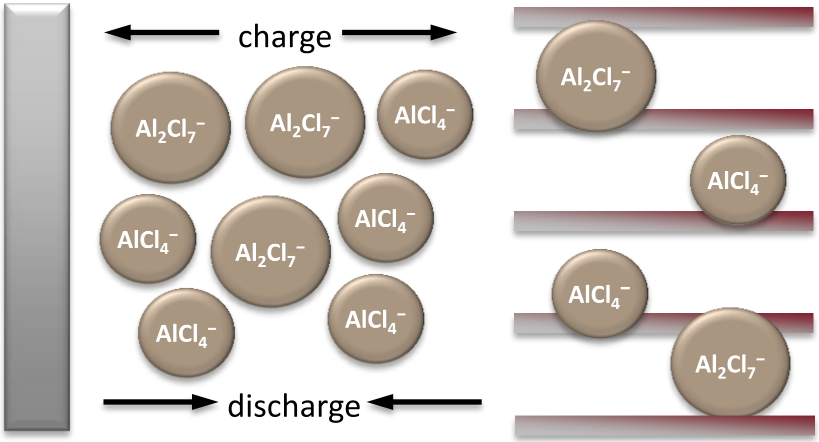


Anion-Insertion Electrodes in Chloroaluminate Ionic Liquids

Polypyrrole

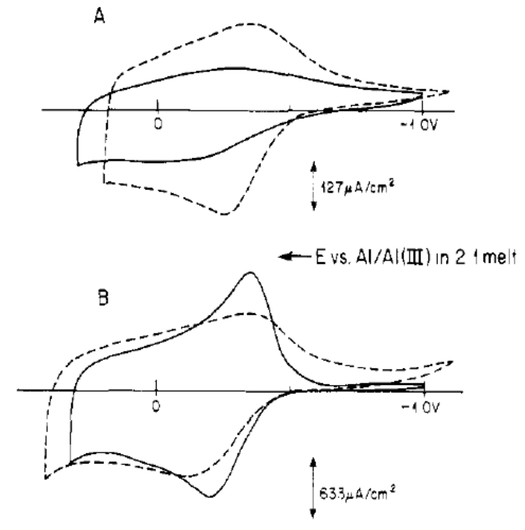
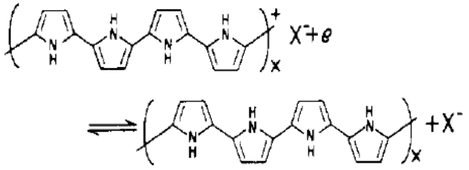


Figure 4. Cyclic voltammetry of Pt/polypyrrole electrodes in 0.8:1 $AlCl_3$:BuPyCl melt (—) and in 0.1 M Et_4NClO_4/CH_3CN (---). (A) 0.06-μm PP film prepared in CH_3CN, (B) 0.20-μm film prepared in neutral melt. Scan speed = 100 mV/s.



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

Polythiophene

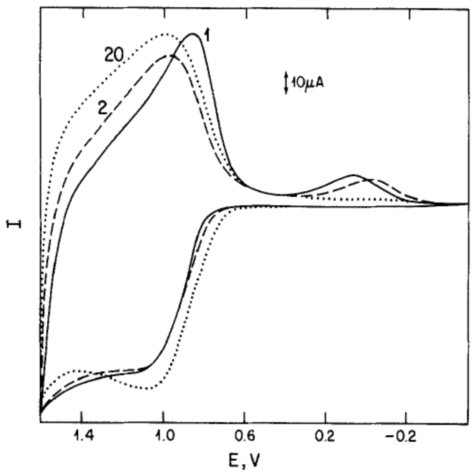
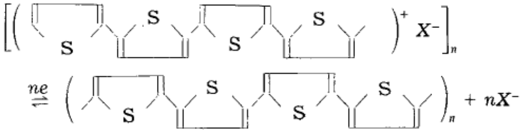


Fig. 3. Cyclic voltammetric curves for 2×10^{-2}C film of polythiophene in 1:1 melt; $v = 50$ mV s^{-1}. Electropolymerization of thiophene was carried out in 0.1M solution of monomer in 1:1 melt at +1.7V. The number on the curve refers to the number of the scan (tungsten electrode, $A = 0.12$ cm^2).



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

Polyaniline

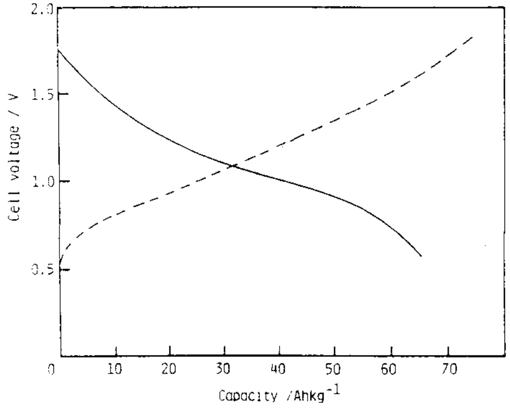
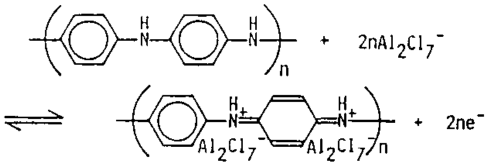


Fig.2 Chrge and discharge curves for the powder electrode of Al/PAn secondary cell. C.D.: 2.0 $mAcm^{-2}$

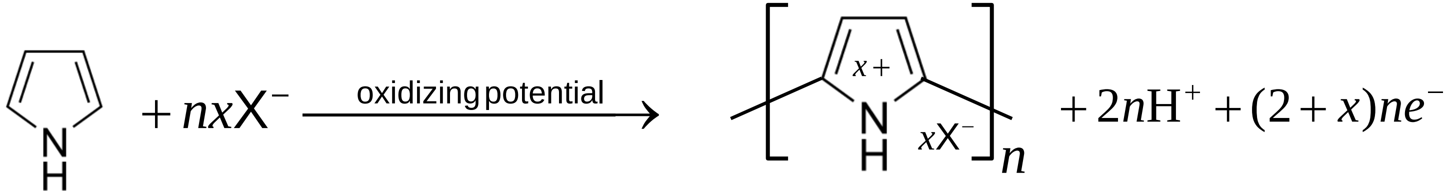
------ : charge, —— : dischrge



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

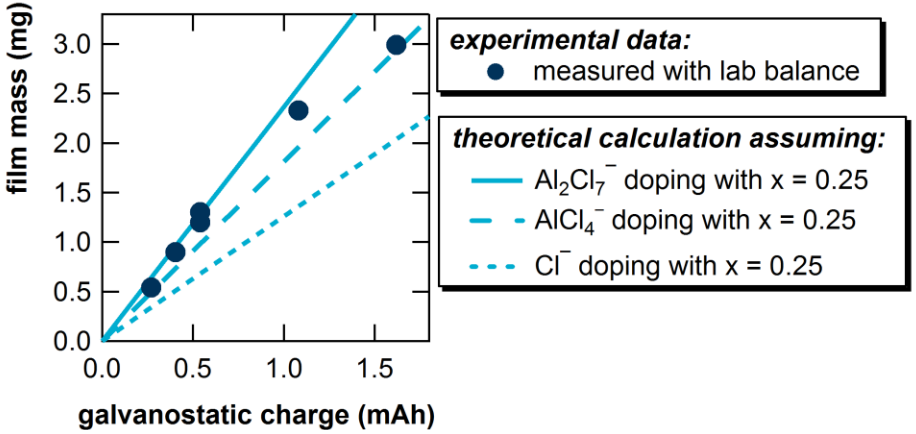
Sample Prep: Electropolymerization

- 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)

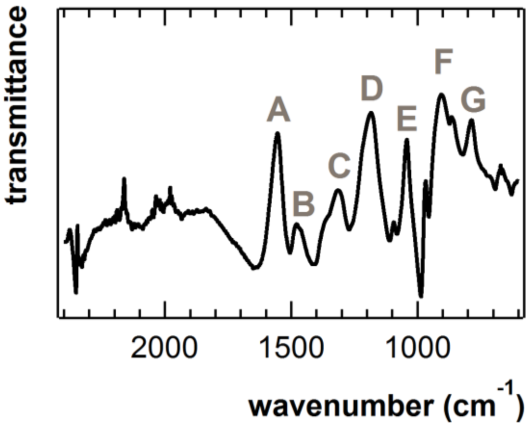
- Electropolymerization of pyrrole, thiophene, and analogs was performed galvanostatically using a 0.3 M solution of monomer in 1:1 $AlCl_3$:EMIC.
- Pyrrole electropolymerization produces a smooth, robust film that peels off the surface.
- Other monomers formed solid, adherent films but did not peel off the substrate.
- All cells were assembled in a glove box (chloroaluminate ionic liquids are air- and water-sensitive).



Mass data show that $AlCl_4^-$ and $Al_2Cl_7^-$ are the anion dopants after polymerization (not Cl^-).

Polypyrrole Film Characterization

Attenuated Total Reflectance FTIR



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

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

G. B. Street, in *Handbook of Conducting Polymers*, ed. T. A. Skotheim, Vol. 1, p. 280 (1986)

N. S. Hudak, *J. Phys. Chem. C* **118**: 5203–5215 (2014)

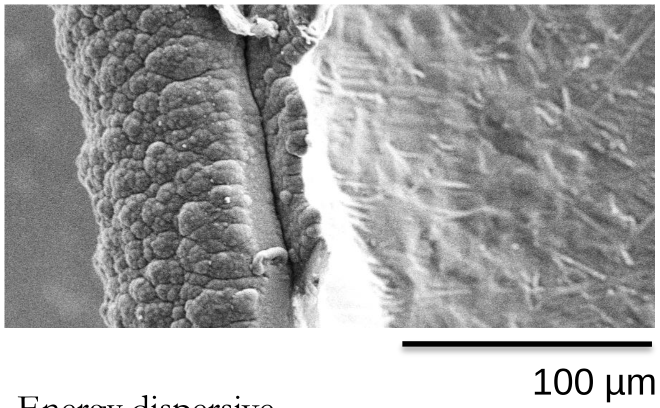
Elemental Analysis of Polypyrrole Films

(micro CHN, ion chromatography, and ICP-MS by ALS Life Sciences)

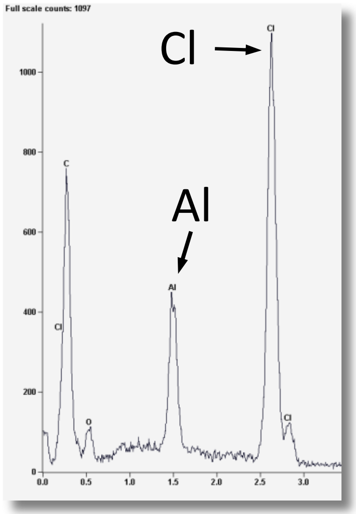
	mass%	mole%	moles per mole of N
carbon	39.54	36.6	3.92
hydrogen	3.67	40.5	4.34
nitrogen	11.76	9.34	1.00
chlorine	34.21	10.7	1.15
aluminum	6.82	2.81	0.301

Values are used to calculate a dopant level of 24.6% (one anion per four monomers).

SEM and Energy Dispersive X-Ray

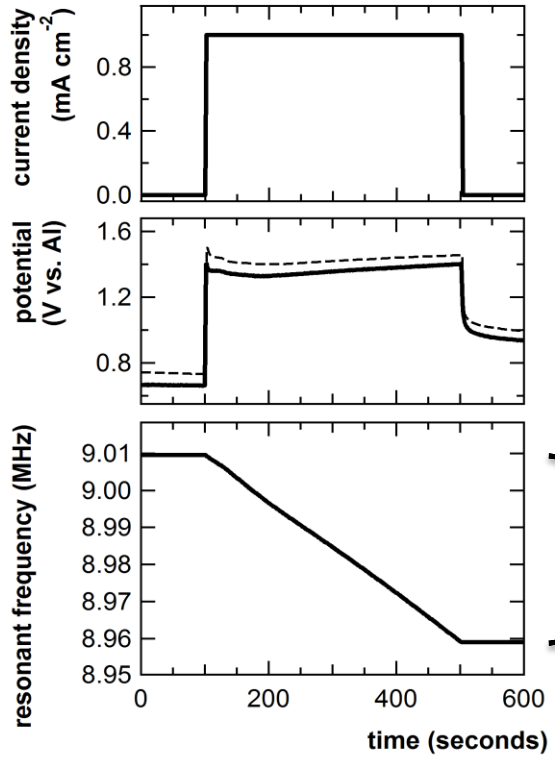


Energy dispersive x-ray spectroscopy shows presence of aluminum and chlorine in all electropolymerized films (polypyrrole, polythiophene, and analogs).

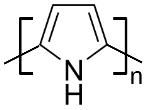


Electropolymerization and QCM

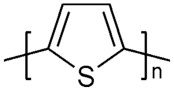
Electrochemical Quartz Crystal Microbalance (EQCM)

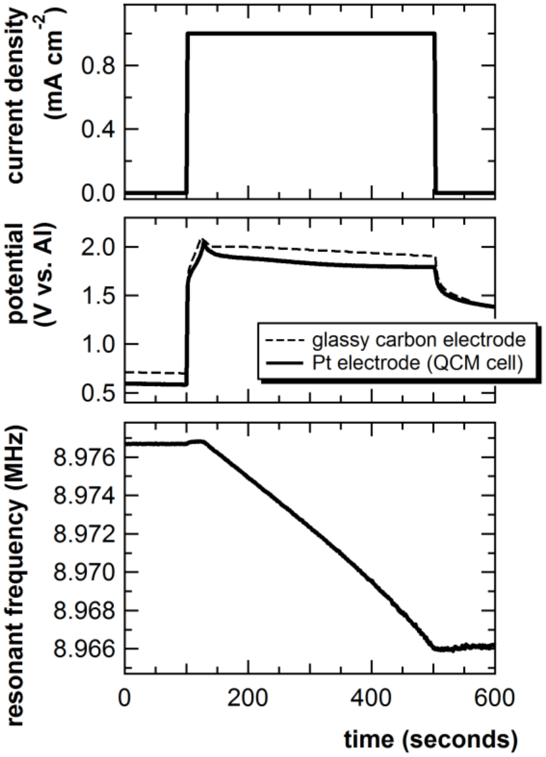


Polypyrrole



Polythiophene





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

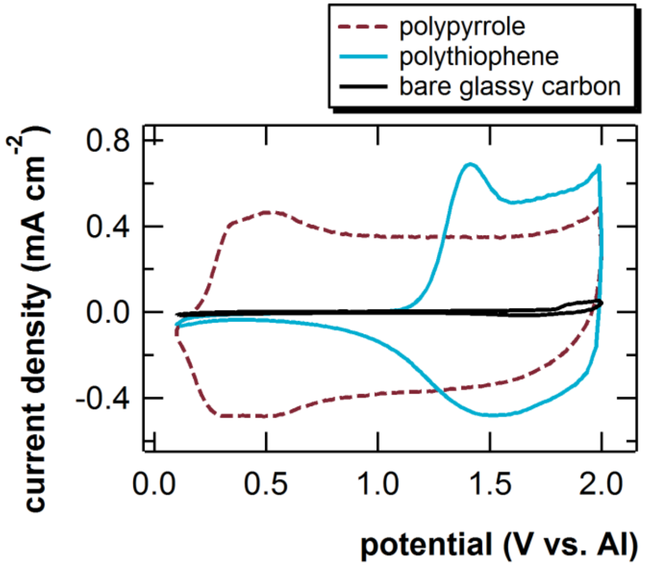
Summary of QCM Results	Δfreq. (kHz)	Δmass (µg)	Δmass/area (mg/cm^2)
polypyrrole *in situ*	50.7	54.4	0.277
polypyrrole *ex situ*	49.7	53.2	0.271
polythiophene *in situ*	10.5	11.2	0.0573
polythiophene *ex situ*	10.6	11.4	0.0580

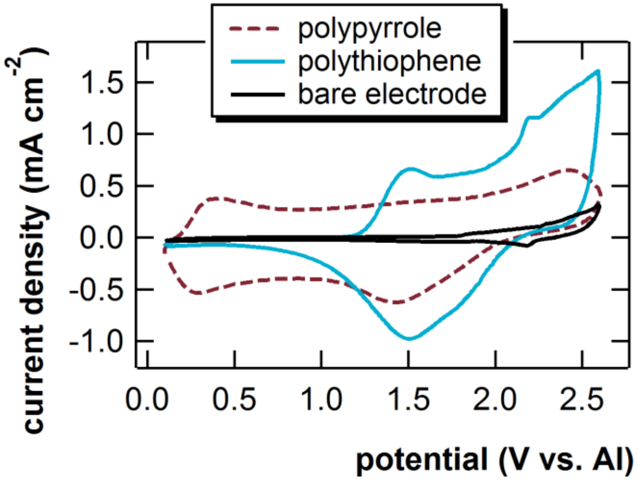
Experimental Conditions:

- 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

Polymer Electrode Redox Behavior

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





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

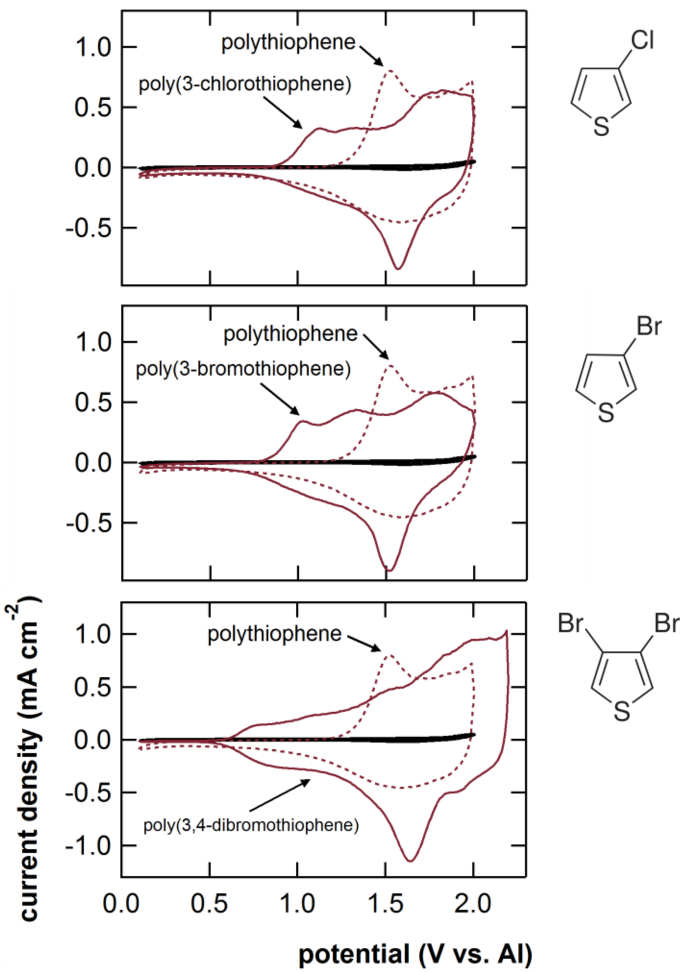
Irreversible processes were observed at potentials above ~1.7 V; these limit the useful potential window of EMIC:$AlCl_3$.

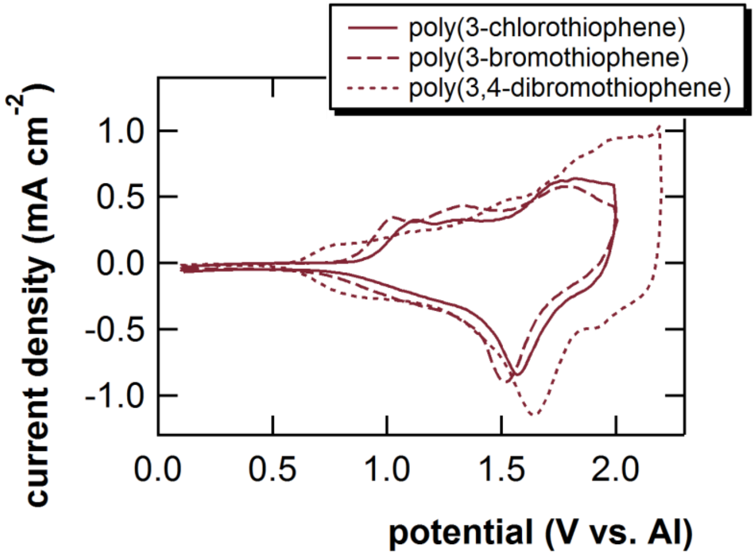
Experimental Conditions:

- 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





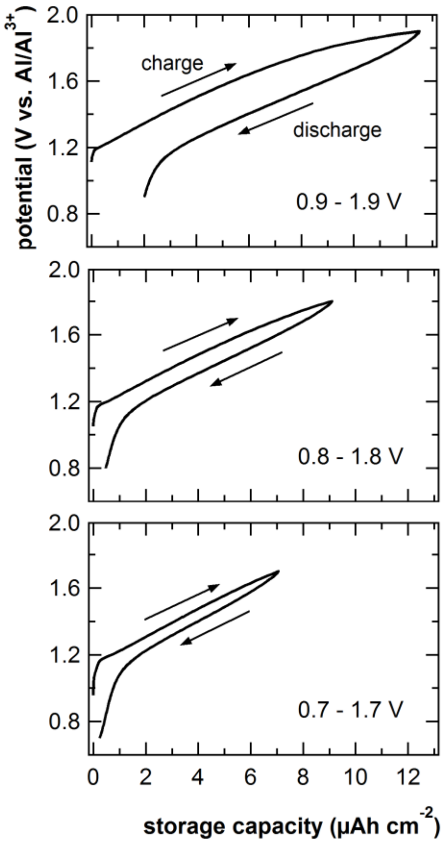
Halide substitution on thiophene monomer shifts the redox potential of the corresponding polymer to higher values (due to the electron-withdrawing character of the halides).

Experimental Conditions:

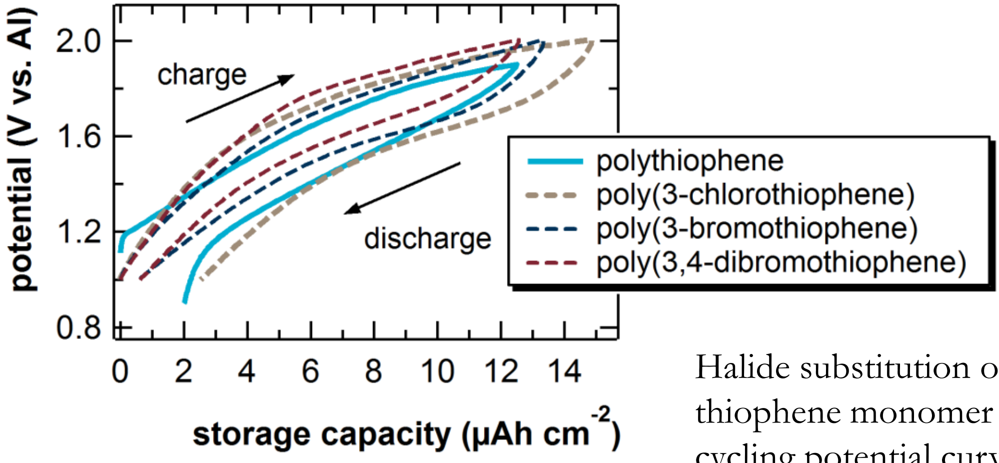
- All polymer films formed galvanostatically on glassy carbon: 1 mA cm^{-2} for 400 seconds in solution of 0.3 M monomer in 1:1 (mole:mole) $AlCl_3$:EMIC
- Cyclic voltammetry performed in 1.5:1 (mole:mole) $AlCl_3$:EMIC at room temperature with aluminum metal counter and reference electrodes

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.

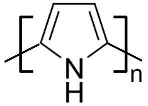
Irreversible oxidative processes at higher potential result in Coulombic efficiency (dishcarge/charge) that is highly dependent on upper voltage limit.

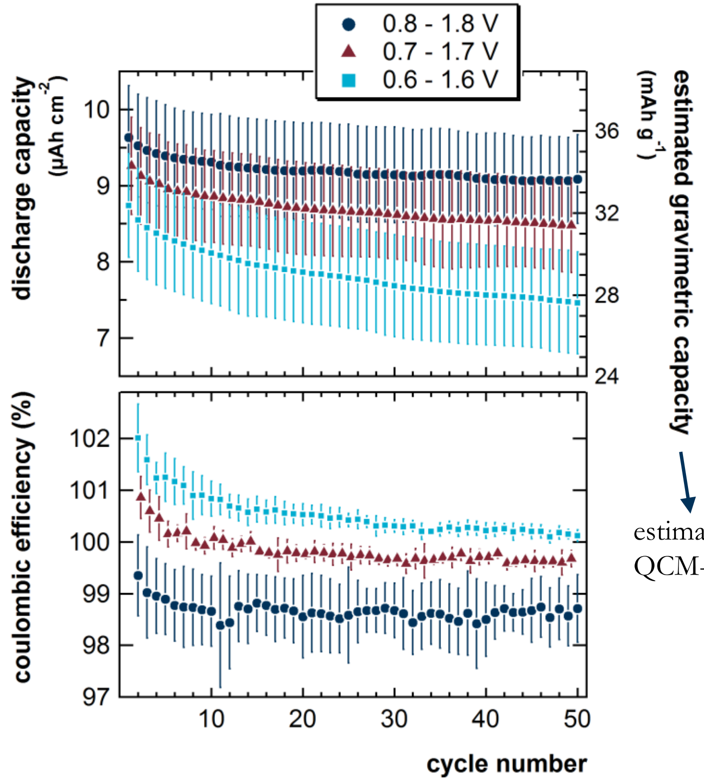
Experimental Conditions:

- 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 temp. with aluminum metal counter and reference electrodes

Galvanostatic Cycling

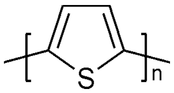
Polypyrrole Film

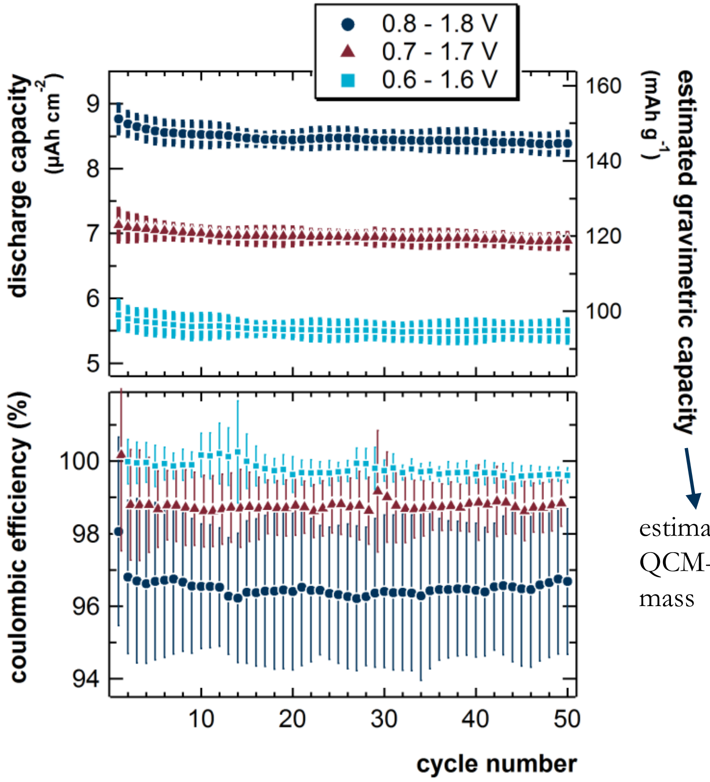




estimated with
QCM-determined mass

Polythiophene Film





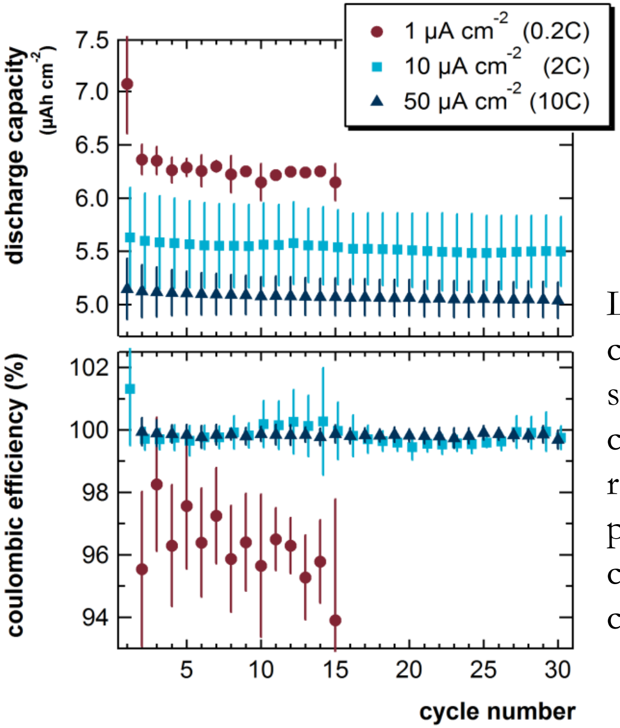
estimated with
QCM-determined
mass

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 at 10 µA cm^{-2} performed in excess of 1.5:1 (mole:mole) $AlCl_3$:EMIC at room temp. with aluminum metal counter and reference electrodes
- Markers and error bars are the average and standard deviations, respectively, of four experiments.

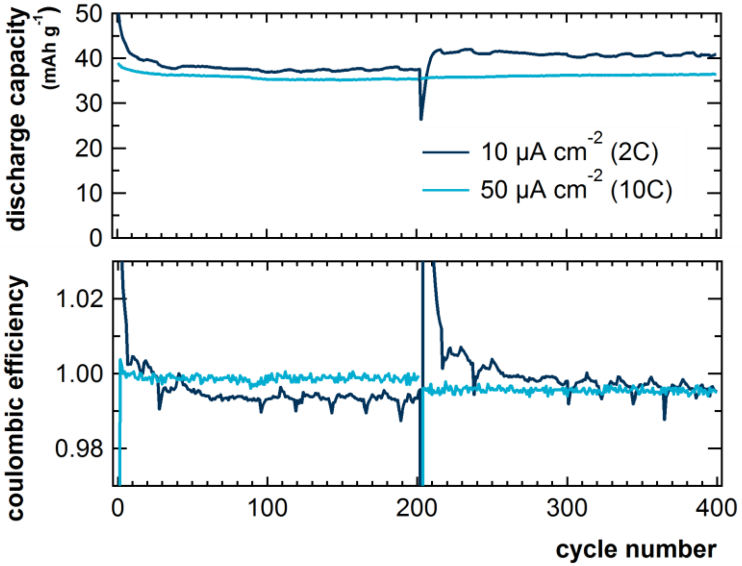
Rate Capability & Long-Term Cycling

Polythiophene Cycling Performance at Various Rates



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

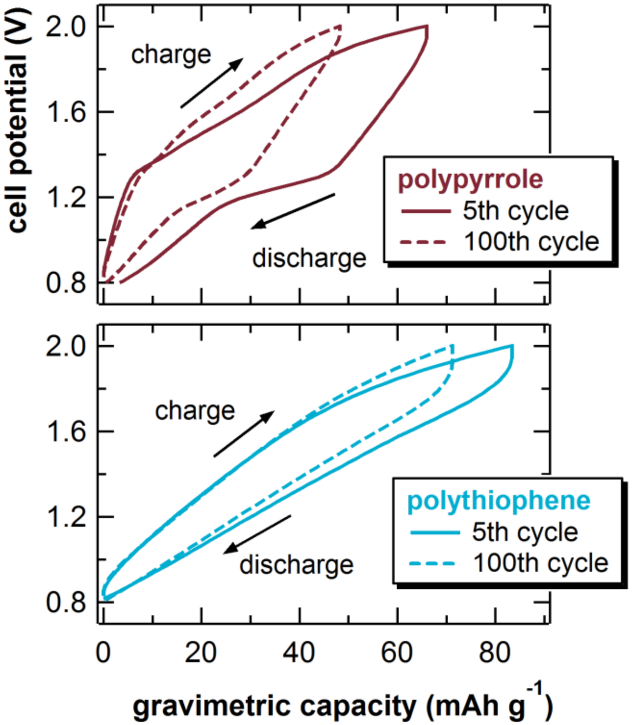
Pause in cycling: electrode was removed from electrolyte and stored in glove box for 4 months before cycling was resumed.

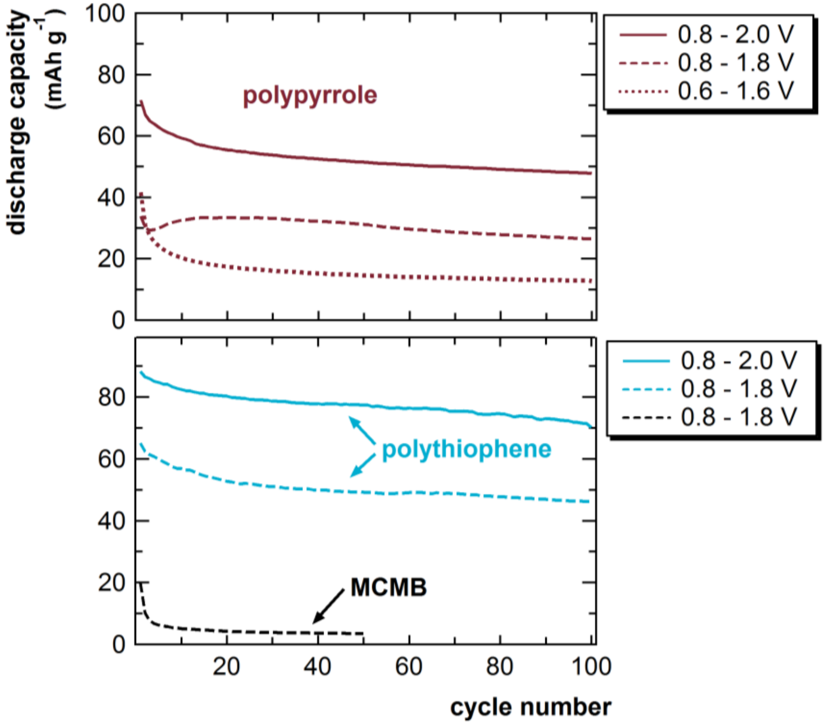


Experimental Conditions:

- 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 temp. with aluminum metal counter and reference electrodes
- Voltage range for cycling: 0.6 – 1.6 V

Electrode Tapes: Cycling in Sealed Cells





For polythiophene, theoretical capacities for 25% doping level (79.6 mAh g^{-1}) were achieved in film *and* tape electrodes.

Experimental Conditions:

- Casting suspension formed by mixing the conducting polymer powder, Kynar 2801 binder, SP carbon black, and dibutyl phthalate plasticizer in acetone with a stir bar for up to 48 hours; tape casting performed on Mylar film followed by heating to 130°C and removal of plasticizer
- Swagelok-type cell assembled in glove box with electrode tape, Whatman GF/D separator soaked in 1.5:1 $AlCl_3$:EMIC, and aluminum disk
- Current collectors made of glassy carbon (positive electrode) and copper (negative electrode) to avoid incompatibility with electrolyte
- Cells cycled galvanostatically at 160–200 mA g^{-1} (specific to active material mass)

Conclusions and Acknowledgements

- Cycling of rechargeable aluminum batteries at room temperature with chloroaluminate ionic liquid electrolyte was demonstrated.
- Conducting polymers (especially polythiophene) undergoing insertion/removal of chloroaluminate anions are effective as active materials in the positive electrode.
- Initial demonstration with electrochemically synthesized conducting polymer films allowed quantification of gravimetric capacity (30 – 100 mAh g^{-1}) and operating voltage (1.0 – 2.0 V).
- Steady capacity was maintained for at least 400 cycles at 2C and 10C rates.
- Cycling of tape electrodes in sealed Swagelok-type cells was also demonstrated, and the observed capacity was 80 mAh g^{-1} relative to polythiophene mass.
- Based on experimental results, estimated energy density of polythiophene-aluminum cell is 44 Wh kg^{-1} relative to all active cell components, including electrolyte. This is competitive for grid-scale energy storage.

- Acknowledgements
  - David Ingersoll, Sandia National Laboratories (project mentor)
  - Bonnie McKenzie, Sandia National Laboratories (SEM & EDS)
  - Laboratory Directed Research & Development (LDRD) Early Career program at Sandia National Laboratories

- This work is summarized in a recent publication:
  - N. S. Hudak, *J. Phys. Chem. C* **118**: 5203−5215 (2014)