PERFORMANCE ENHANCEMENT OF CATHODES WITH CONDUCTIVE POLYMERS

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The plug-ion hybrid and all-electric vehicles have a huge potential for petroleum displacement.

*This presentation does not contain any proprietary or confidential information.
BARRIERS

The Battery Electrodes

1. Commercial Considerations
   - Cost, safety, environmental compatibility
   - Energy density (capacity = range vs weight)
   - Power, $P = IV$ (voltage and rate capability)
   - Recharge time (rate capability)
   - Reliability and life (recyclability)

2. LiFePO$_4$ Cathode
   - Low cost, safe, environmentally compatible
   - Acceptable capacity (170 mAh/g at 0.5C)
   - Excellent cyclability (many thousands)
   - Acceptable voltage (3.45 V vs Li) with C anode
   - Acceptable rate capability (10C)

3. Can we improve capacity at high rates?
PURPOSE OF WORK

To improve capacity and rate capability of composite LiFePO$_4$/C/PTFE cathodes by replacing inactive C + PTFE with an electrochemically active, conductive polymer, such as polypyrrole (PPy), polyaniline (PANI).

(PPy)

(PANI)
APPROACH

• Select a conductive polymer that is electrochemically active in voltage range of cathode redox center.

• Determine conditions to achieve and maintain good electrical contacts between polymer and cathode nanoparticle as well as polymer and current collector.

• Develop a convenient synthetic route to achieve and maintain electrical contact of polymer with all individual nanoparticles and with the current collector.

• Compare electrochemical versus chemical synthetic routes.

• Test performance to ensure electrolyte has access to all nanoparticles; determine optimal loading.
Method I: Electrodeposition

This method is applicable to C-LiFePO$_4$/PPy composite, but not to C-LiFePO$_4$/PANI composite.

Electrodeposition Condition

(Cyclic voltammetry)
Scan range: 0 ~ 1.3 V vs. Ag/AgCl
Scan rate: 100 mV s$^{-1}$, 20 cycles
Electrolyte: 0.1 mol/L LiClO$_4$ in acetonitrile
Method II: Simultaneous Chemical Polymerization

(1) Synthesis of C-LiFePO₄/PPy composite

pyrrole monomer + sodium p-toluenesulfonate (dopant) + peroxydisulfate ((NH₄)₂S₂O₈, oxidant) + C-LiFePO₄, react at 0–5 °C for 6 h.

(2) Synthesis of C-LiFePO₄/PANI composite

aniline monomer + ammonium peroxydisulfate ((NH₄)₂S₂O₈) + C-LiFePO₄ + HCl, react at 0–5 °C for 6 h.

* C-LiFePO₄ was provided by Phostech, Québec.
Specification of optimal ratio for electrodeposited \((\text{C-LiFePO}_4)_{1-x}(\text{PPy})_x\)

Maximum capacity was obtained in \((\text{C-LiFePO}_4)_{1-x}(\text{PPy})_x\) with weight ratio \(x \approx 0.2\)

Charge and discharge composite capacity vs cycle number for the \((\text{C-LiFePO}_4)_{1-x}(\text{PPy})_x\)
Enhanced capacity and rate capability in electrodeposited C-LiFePO$_4$-PPy composite cathode

Charge at C/10 to 4.1 V, discharge at various rates.

(A) 0.1C/charge, 0.1-20C/discharge;
(B) 0.1-20C/charge, 0.1C/discharge;
(C) 0.1-20C/charge, 0.1-20C/discharge.

* Charging at 10C can reach 94% of full capacity (see B); this composite can endure both fast charging and discharging (C).
The capacity and rate capability of the chemically-synthesized LiFePO$_4$/PPy composite cathode is comparable with the electrodeposited film and higher than the parent LiFePO$_4$. 
Enhanced performance of chemically-synthesized \((C\text{-LiFePO}_4)_{1-x}(\text{PPy})_x\)

High rate capability is also obtained for the chemically-synthesized \(\text{LiFePO}_4/\text{PPy}\) composite cathode.

(A) \(0.1\text{C/charge, 0.1-10C/discharge;}

(B) \(0.1-20\text{C/charge, 0.1C/discharge;}

(C) \(0.1-20\text{C/charge, 0.1-20C/discharge.}

Enhanced performance of chemically-synthesized \((\text{C-LiFePO}_4)_1-x(\text{PANI})_x\)
Comparison of rate capability for the C-LiFePO$_4$/polymer composite cathodes

The composite cathodes show enhanced rate capability especially at high rate. The electrodeposited C-LiFePO$_4$/PPy exhibits the best fast-charging performance.

Rate capability with discharging at 0.1–10C while charging at 0.1C.

Rate capability with charging at 0.1–20C while discharging at 0.1C.
Technology Transfer

Patent has been licensed to Hydro Quebec. PHOSTECH owns license to C-LiFePO$_4$ and supplies nanoparticles.

Worldwide interest in optimizing capacity and rate capability of C-LiFePO$_4$ cathode.
Summary

• **Petroleum displacement**
  (a) Lithium batteries already power tools and small EVs;
  (b) They are under worldwide development for electrical energy storage with alternate energy technologies;
  (c) They show promise for plug-in hybrids and larger EVs.

• **Approach**
  Improve capacity at high rates of the battery cathode for power applications.

• **Accomplishments**
  (a) Demonstrated significant improvement at high rates
  (b) Developed synthetic routes for PPy and PANI
  (c) Electrodeposition of PPy on C-LiFePO$_4$ shown to be superior to chemical deposition of PPy and PANI

• **Technology transfer**
  Patent licensed. Optimal loading demonstrated

• **Future plans**
  Identify new electrodes
Future Plans

Problems for EVs

- Better anode
- Higher-capacity electrodes

Solutions

- Identify a viable framework compound allowing more than one Li/redox center.

**Specification:** (a) No large voltage step
(b) No large volume change

Examples

\[ \text{LiTi}_2(\text{PO}_4)_3 \text{ vs. LiTi}_2(\text{PS}_4)_3 \]

*N.B.* \( \text{Li}_3\text{PX}_4 \) reported to have a 5 V window
Structure of LiTi$_2$(PO$_4$)$_3$ vs. LiTi$_2$(PS$_4$)$_3$
LiT$_2$(PS$_4$)$_3$ (a)

LiT$_2$(PO$_4$)$_3$ (b)

AgT$_2$(PS$_4$)$_3$ (c)

AgT$_2$(PO$_4$)$_3$ (d)
Publications, patents, and presentations

• Publications:


S. B. Schougaard, J. Bréger, M. Jiang, C. P. Grey, J. B. Goodenough, “LiNi_{0.5+δ}Mn_{0.5-δ}O_2 A High-Rate, High-Capacity Cathode for Lithium Rechargeable Batteries,” *Advanced Materials* **18**, 905-909 (2006)


Y.-S. Kim and J.B. Goodenough, “ Lithium Intercalation into ATi_2(PS_4)_3 (A = Li, Na, Ag) (in press)

• Patents:


• Presentations: