PERFORMANCE ENHANCEMENT OF CATHODES WITH CONDUCTIVE POLYMERS

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

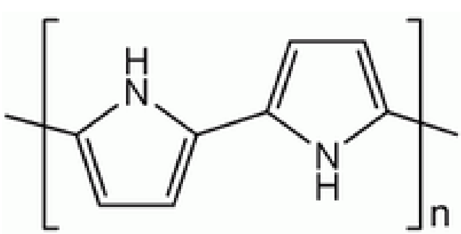
BARRIERS

The Battery Electrodes

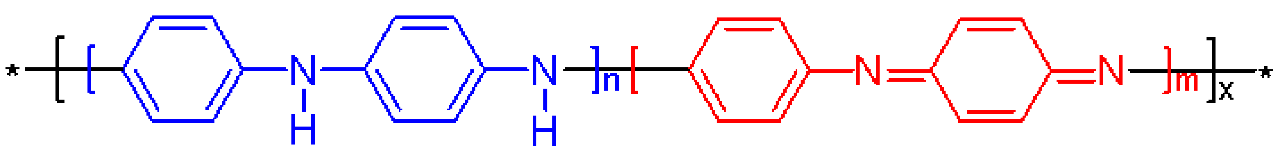
1. **Commercial Considerations**
   - Cost, safety, environmental compatibility
   - Energy density (capacity = range *vs* weight)
   - Power, P = IV (voltage and rate capability)
   - Recharge time (rate capability)
   - Reliability and life (recyclability)
2. **$LiFePO_4$ Cathode**
   - Low cost, safe, 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 electrochemmically 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.

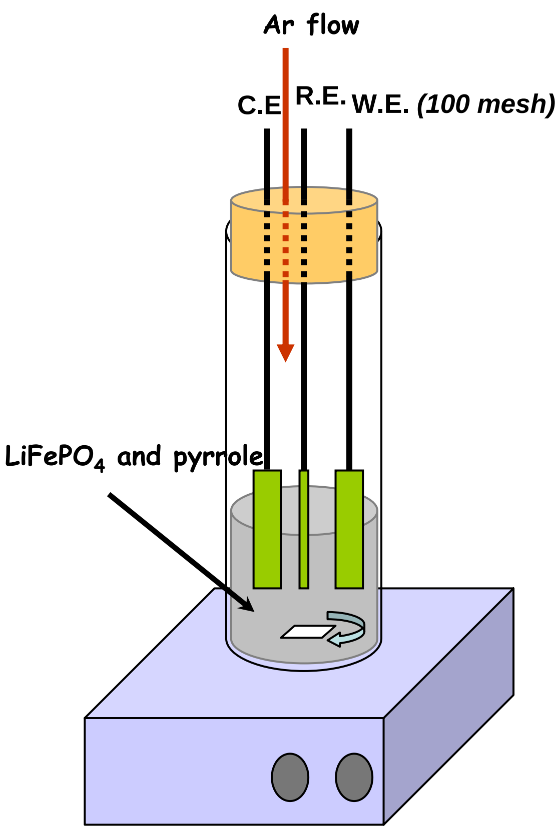
• Develop a convenient synthetic route to achieve and maintain electrical contact of polymer with all individual nanoparticles and with the current collector.

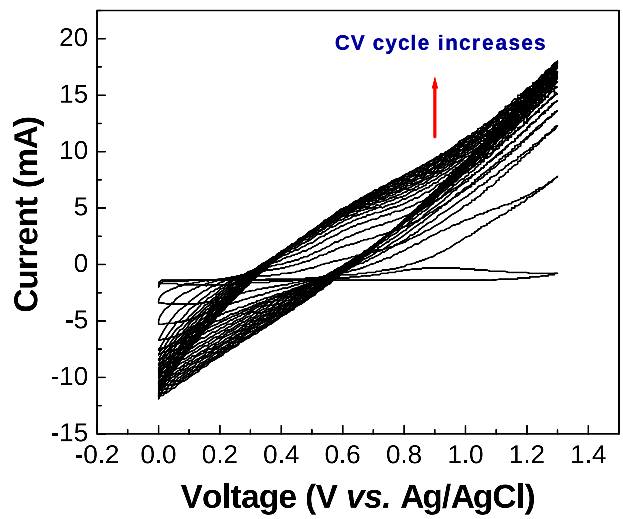
• Compare electrochemical versus chemical synthetic routes.

• 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-$LiFePO_4$/PPy composite

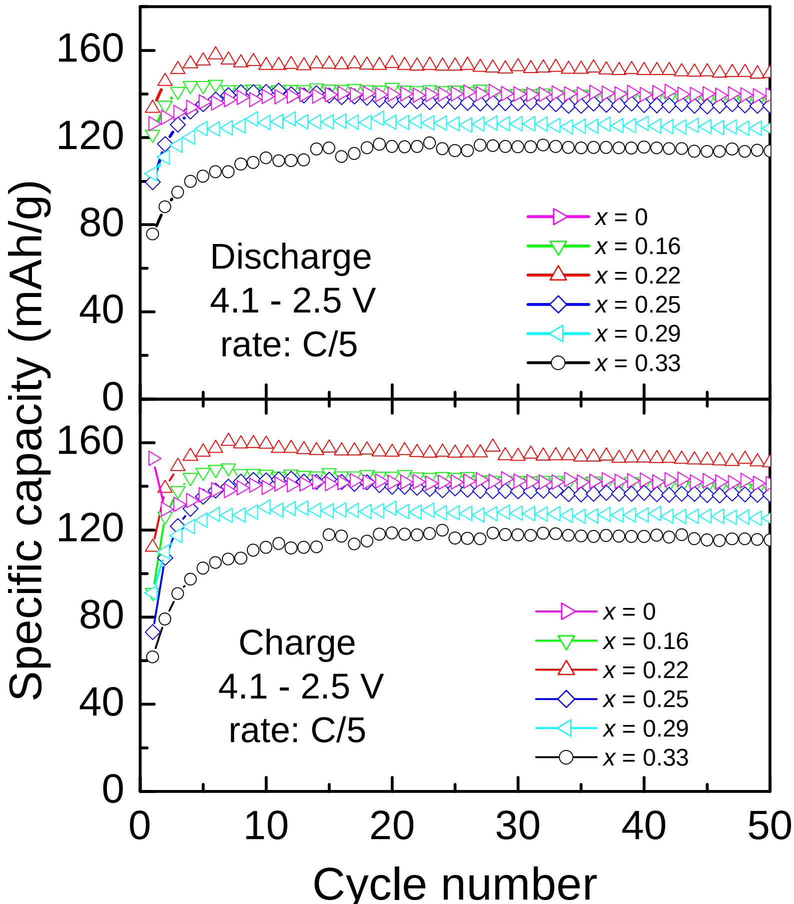
pyrrole monomer + sodium p-toluenesulfonate (dopant) + peroxydisulfate ($(NH_4)_2S_2O_8$, oxidant) + C-$LiFePO_4$, react at 0–5 °C for 6 h.

(2) Synthesis of C-$LiFePO_4$/PANI composite

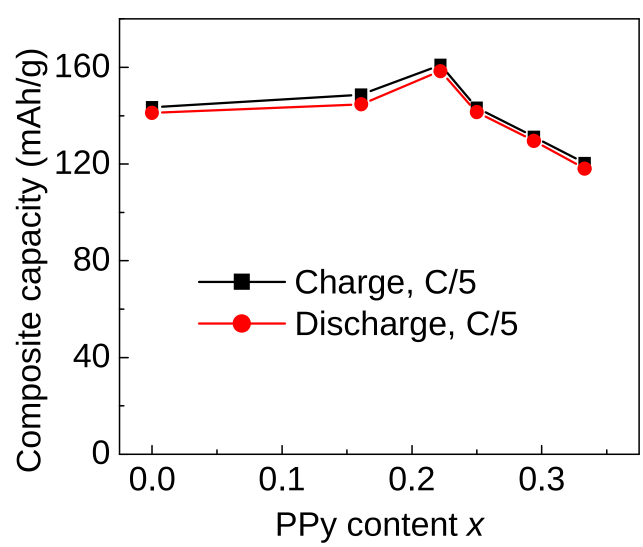
aniline monomer + ammonium peroxydisulfate ($(NH_4)_2S_2O_8$) + C-$LiFePO_4$ + HCl, react at 0–5 °C for 6 h.

* C-$LiFePO_4$ was provided by Phostech Lithium Inc.

Specification of optimal ratio for electrodeposited $(C\text{-}LiFePO_4)_{1-x}(PPy)_x$

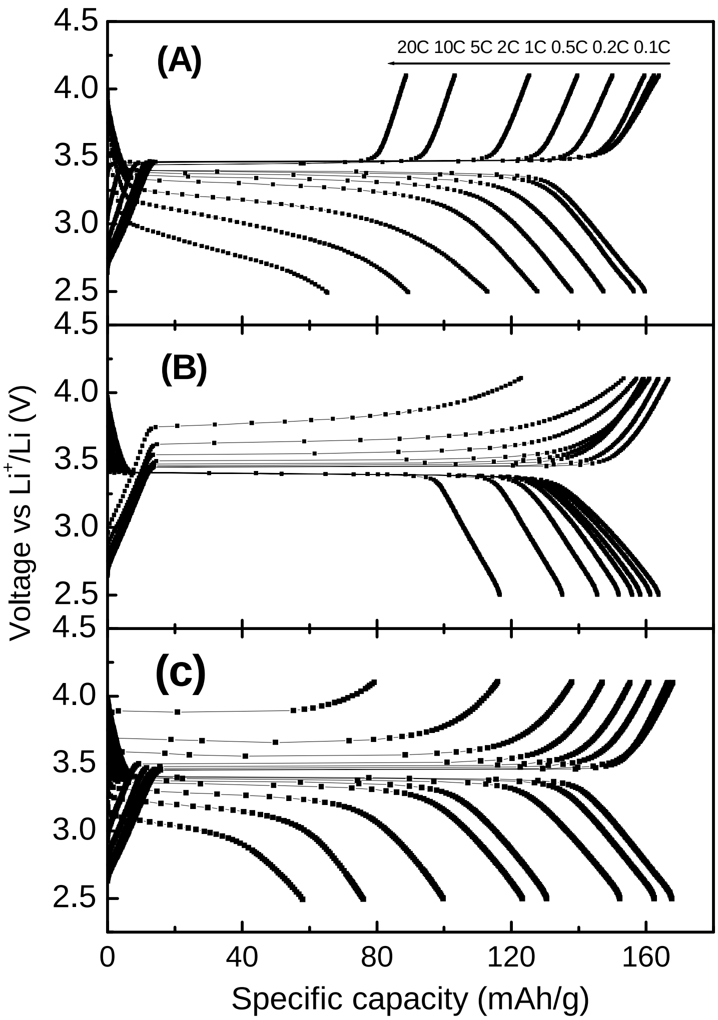


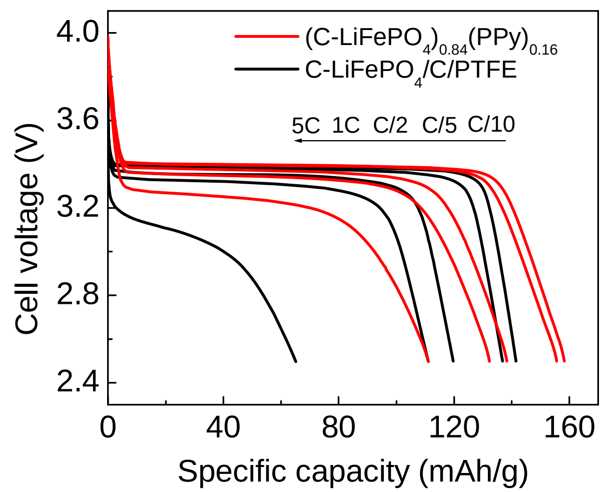
Charge and discharge composite capacity vs cycle number for the $(C\text{-}LiFePO_4)_{1-x}(PPy)_x$



Maximum capacity was obtained in $(C\text{-}LiFePO_4)_{1-x}(PPy)_x$ with weight ratio $x \approx 0.2$

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.

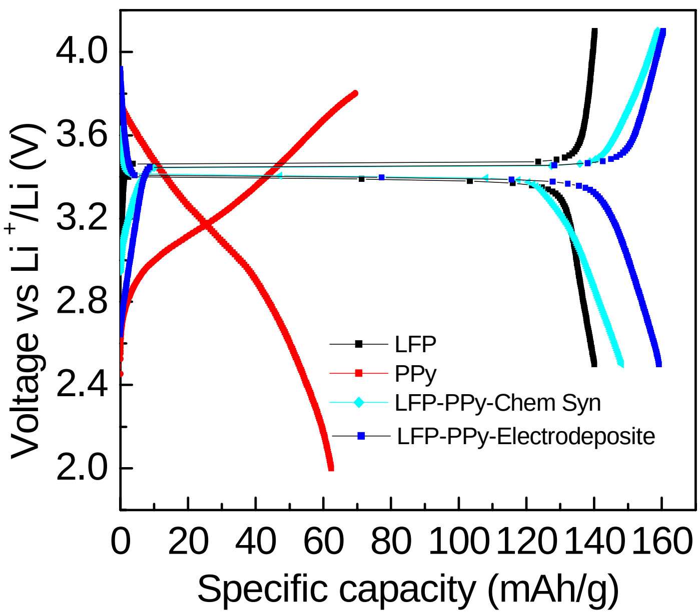
(A) 0.1C/charge, 0.1-20C/discharge;

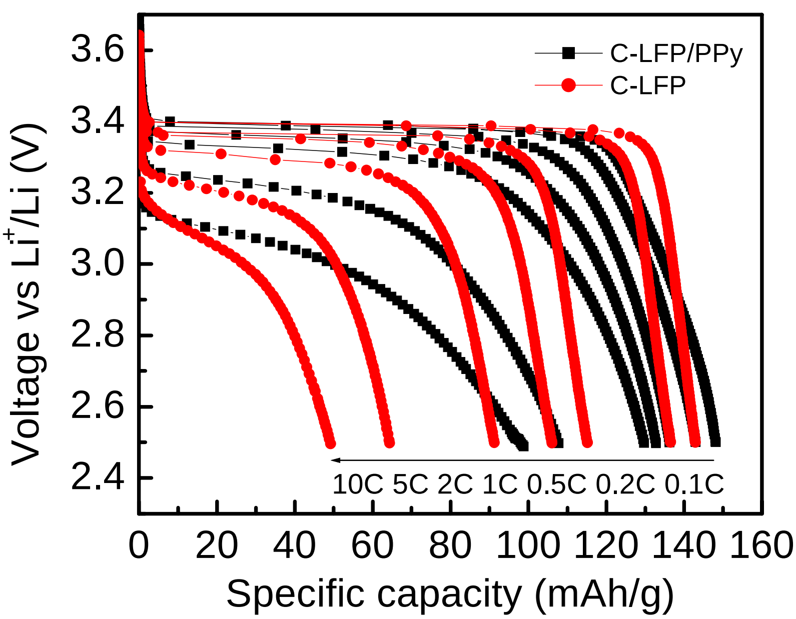
(B) 0.1-20C/charge, 0.1C/discharge;

(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).

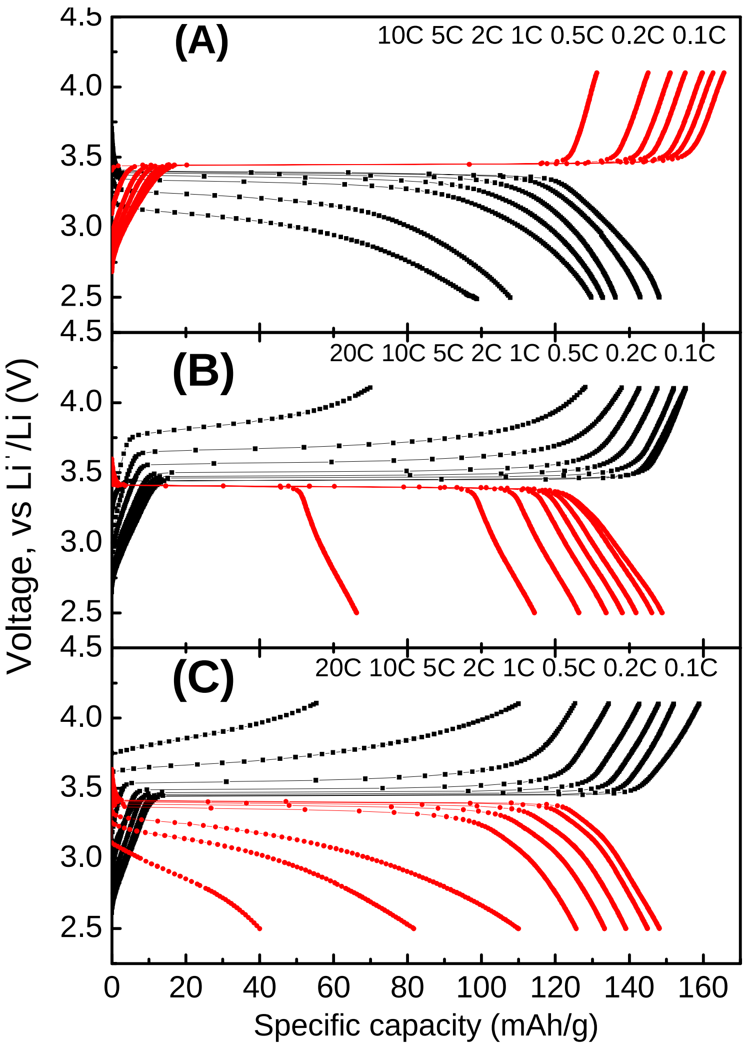
Electrochemical performance of chemically-synthesized $(C\text{-}LiFePO_4)_{1-x}(PPy)_x$

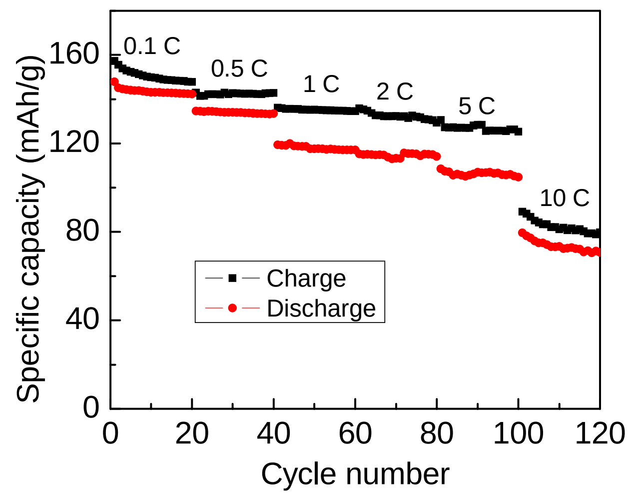




The capacity and rate capability of the chemically-synthesized $LiFePO_4$/PPy composite cathode is comparable with the electrodeposited film and higher than the parent $LiFePO_4$.

Enhanced performance of chemically-synthesized $(C\text{-}LiFePO_4)_{1-x}(PPy)_x$





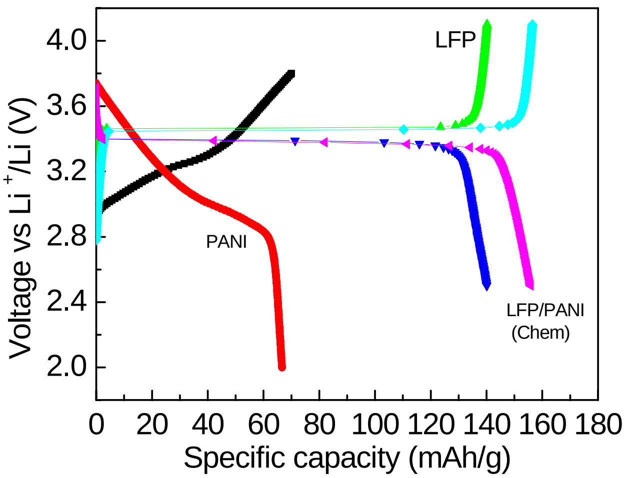
High rate capability is also obtained for the chemically-synthesized $LiFePO_4$/PPy composite cathode.

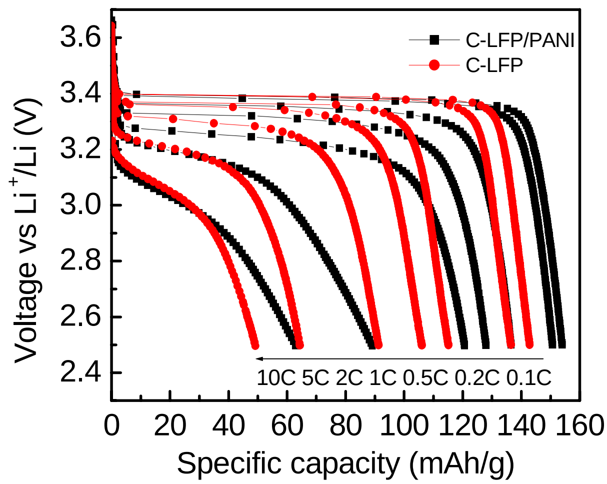
(A) 0.1C/charge, 0.1-10C/discharge;

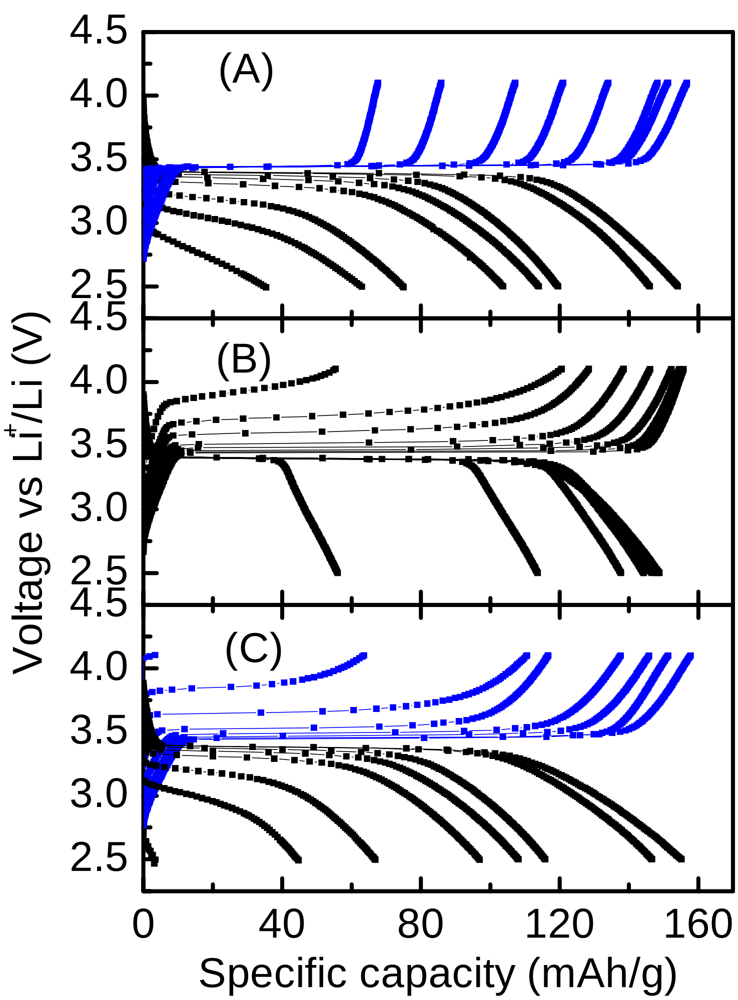
(B) 0.1-20C/charge, 0.1C/discharge;

(C) 0.1-20C/charge, 0.1-20C/discharge.

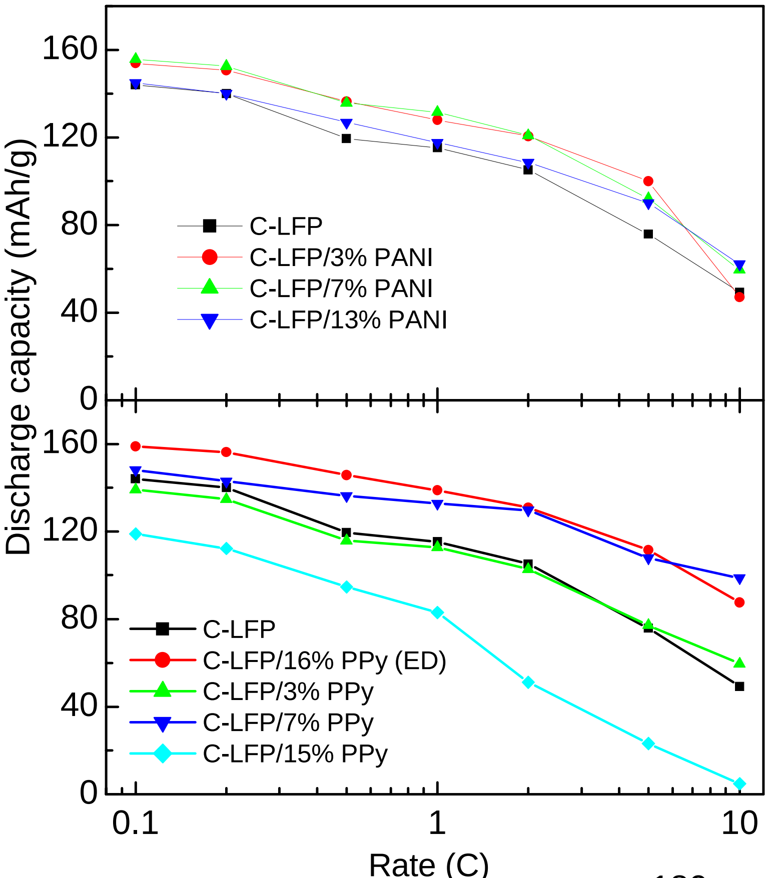
Enhanced performance of chemically-synthesized $(C\text{-}LiFePO_4)_{1-x}(PANI)_x$





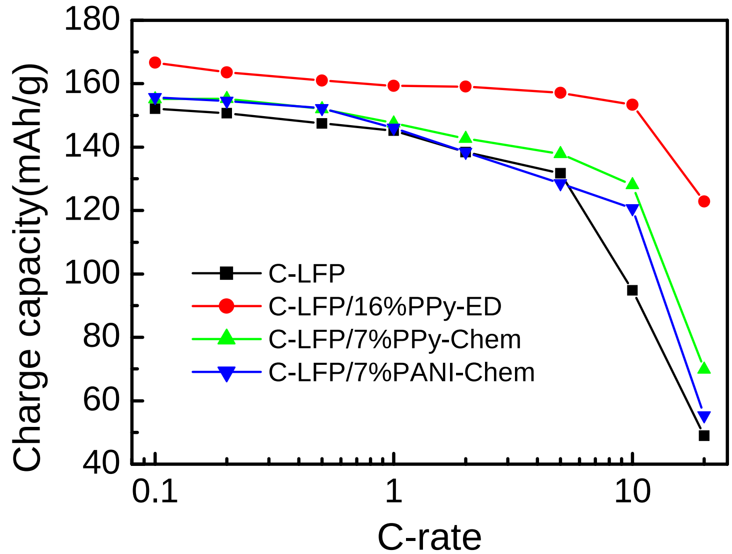


Comparison of rate capability for the C-$LiFePO_4$/polymer composite cathodes



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

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 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 worlwide 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

(Youngsik Kim)

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

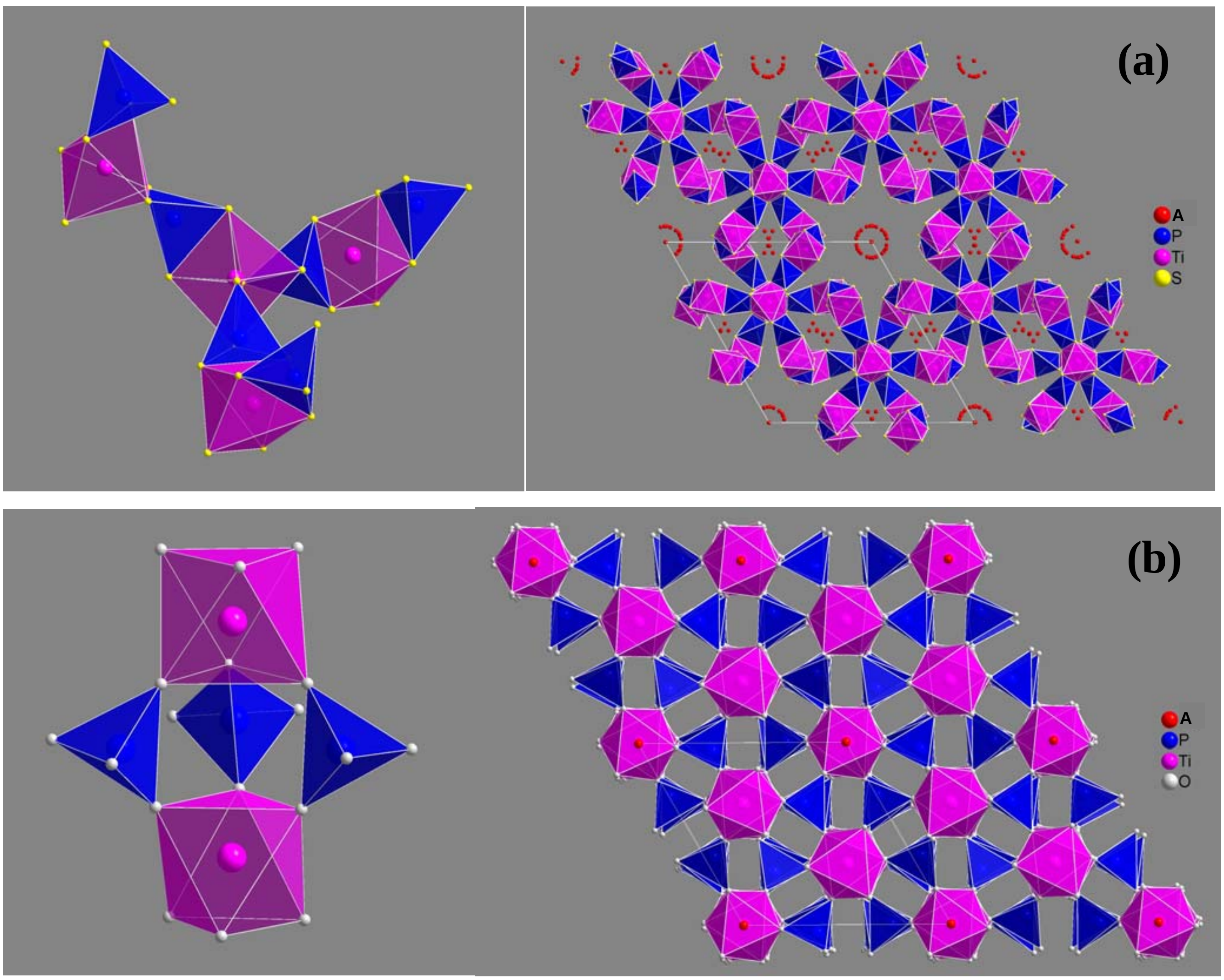
(b) No large volume change

Examples

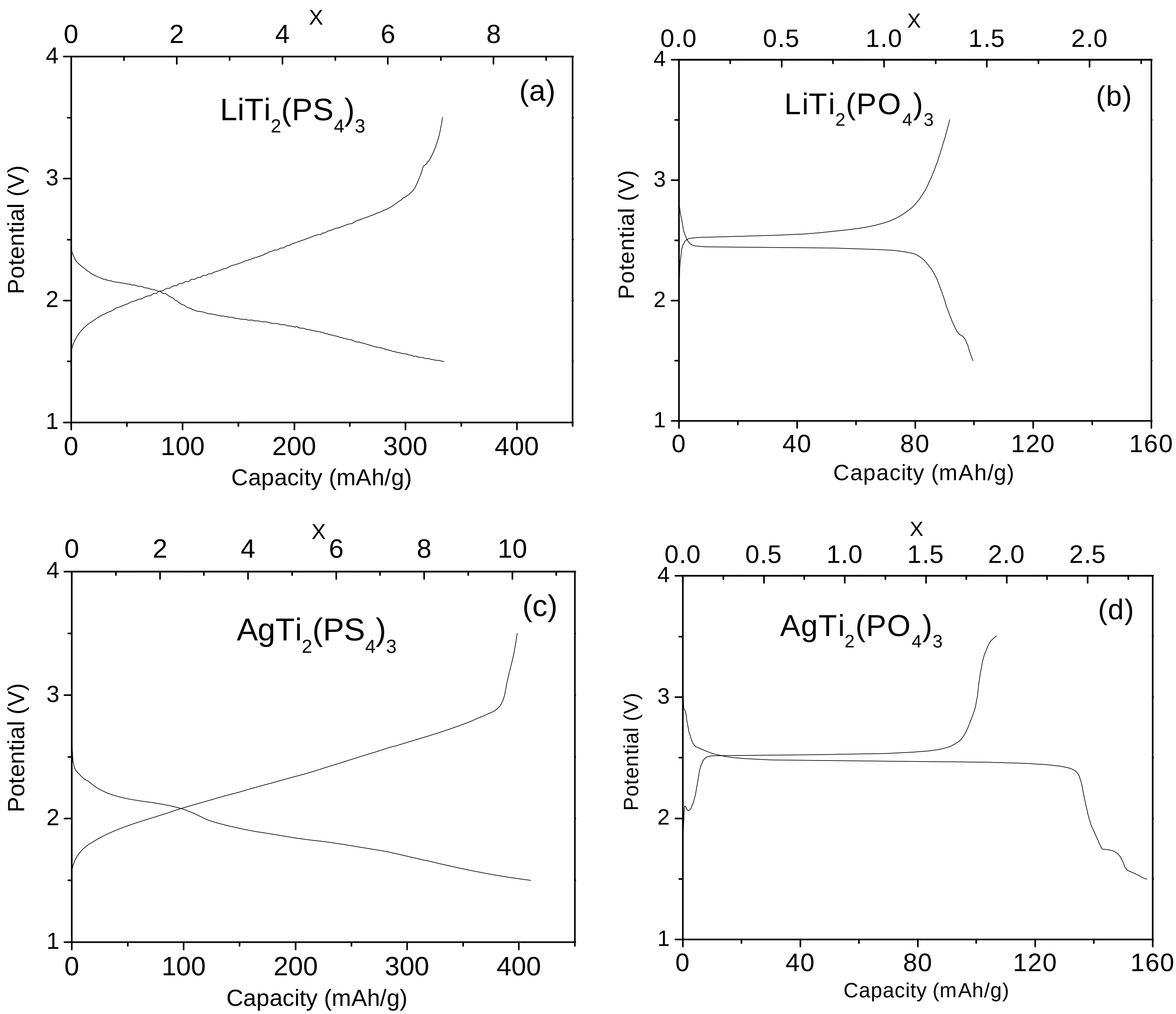
$LiTi_2(PO_4)_3$ vs. $LiTi_2(PS_4)_3$

N.B. Li_3PX_4 reported to have a > 5 V window

Structure of $LiTi_2(PS_4)_3$ vs. $LiTi_2(PO_4)_3$



$ATi_2(PS_4)_3$ vs. $ATi_2(PO_4)_3$ (A = Li, Ag)



New Anode Materials

Insertion Compound vs Displacement Reaction

- want smaller volume change

Redox Couples

- Ti^{3+}/Ti^{2+}, V^{3+}/V^{2+}, Cr^{3+}/Cr^{2+}, Nb^{5+}/Nb^{4+}

Findings

- Cr^{3+}/Cr^{2+} gives too large a volume change
- With sulfides and sulfochlorides, smallest voltage vs Li is ca. 1V
- With oxide and oxyfluorides, what is role of metal-metal bonding ?
  e.g. $Li[Ti_2]O_3F \rightarrow Ti_2O_3 + LiF$

Publications, patents, and presentations

- Publications:

Y.-H. Huang, K.-S. Park, and J.B. Goodenough, "Improving lithium batteries by tethering cathode oxides to conductive polymers," *J. Electrochem. Soc*. **153** (12) A2282-A2286 (2006)

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

K.-S. Park, S.B. Schouguaard, and J.B. Goodenough, "Conducting-Polymer/Iron-Redox- Couple Composite Cathodes for lithium Secondary batteries," *Adv Mater.* **19**, 848-851 (2007)

K. Zaghib, N. Ravet, M. Gauthier, F. Gendron, A. Mauger, J.B. Goodenough, and C.M. Julien, "Optimized electrochemical performance of $LiFePO_4$ at 60°C with purity controlled by SQUID magnetometry," *Journal of Power Sources* **163**, 560-566 (2006)

Y. Kim, N. Arumugam, and J.B. Goodenough, "3D Framework Structure of a New Lithium Thiophosphate, $LiTi_2(PS_4)_3$ as Lithium Insertion Hosts," Chem. Mater. **20(2)**, 470-474 (2008)

Y. Kim and J.B. Goodenough, " Lithium Intercalation into $ATi_2(PS_4)_3$ (A = Li, Na, Ag)" Electrochemical Communications (in press)

- Patents:

J.B. Goodenough, Kyu-Sung Park, and Steen Schougaard, "Cathode for Rechargeable Lithium-ion Batteries."

- Presentations: