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.

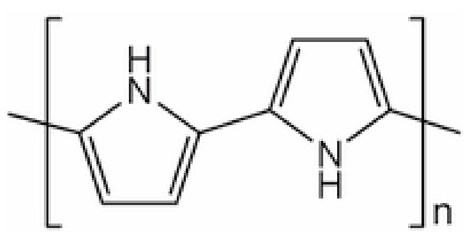
BARRIERS

The Battery Electrodes

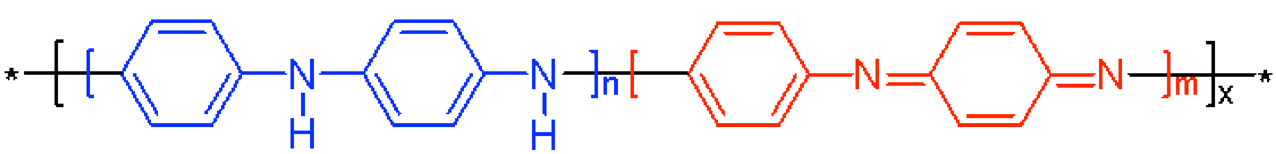
1. **Commercial Considerations**
    - Cost, safety, environmental compatibility
    - Energy density (capacity = range *vs* weight)
    - Power, P = IV (voltage and rate capability)
    - Recharge time (rate capability)
    - Reliability and life (recyclability)
2. **$LiFePO_4$ Cathode**
    - Low cost,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



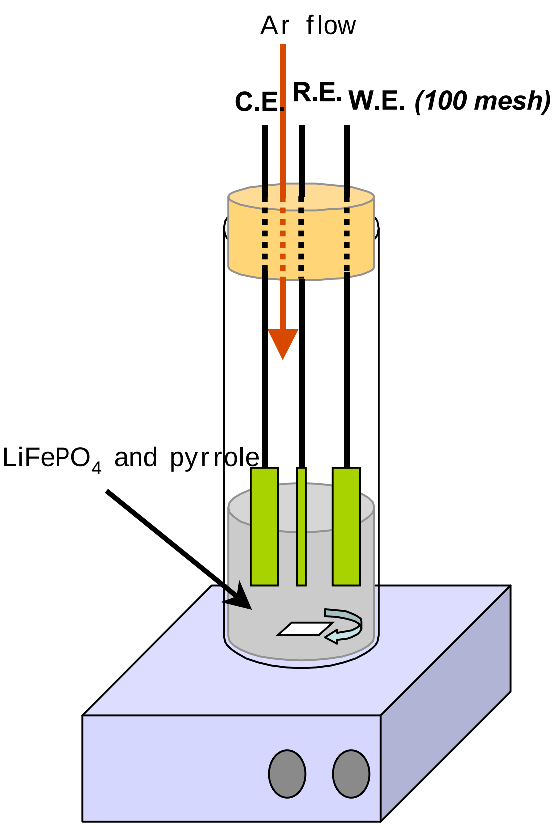
(PANI)

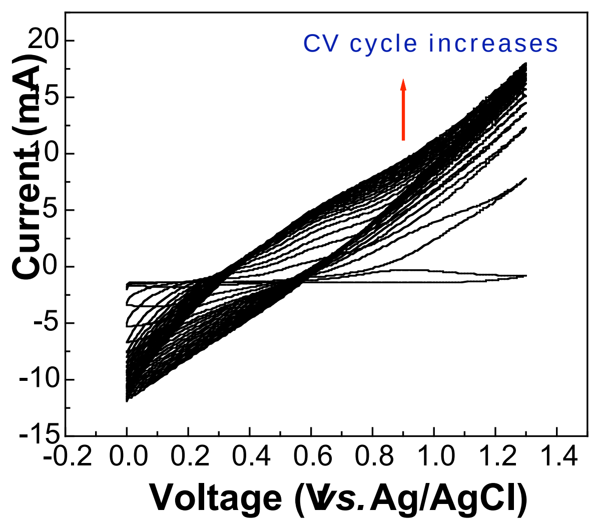
APPROACH

- Select a conductive polymer that is 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

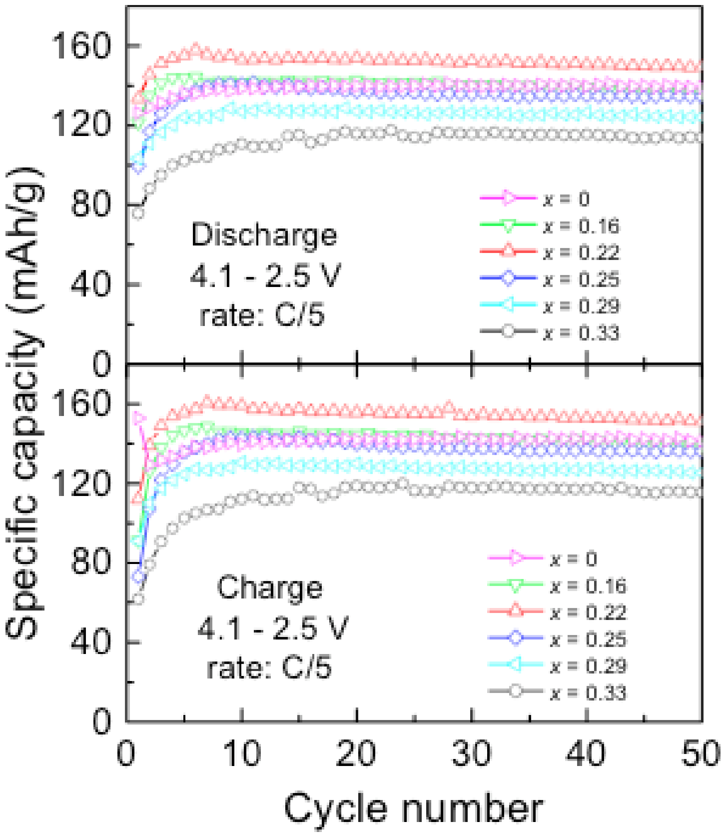
pyrrole monomer + sodium p-toluenesulfonate (dopant) + peroxydisulfate ($(NH_4)_2S_2O_8$, oxidant) + C-$LiFePO_4$, react at 0–5 °C for 6 h.

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

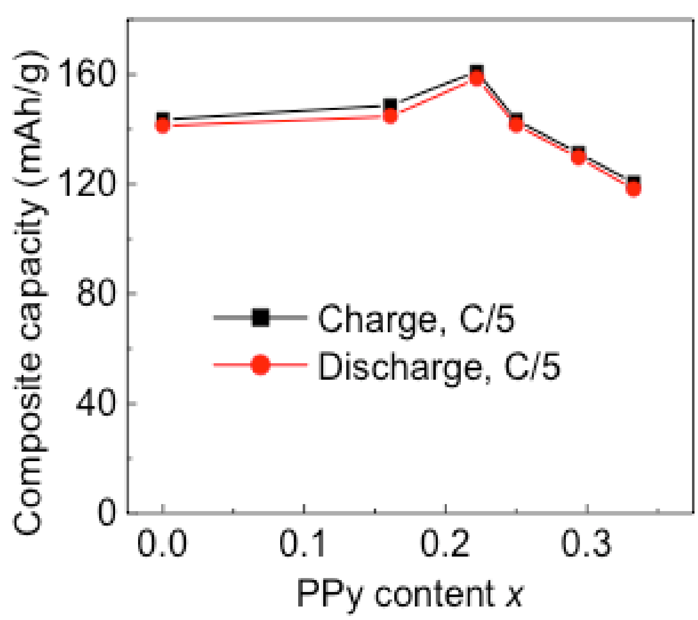
aniline monomer + ammonium peroxydisulfate ($(NH_4)_2S_2O_8$) + C-$LiFePO_4$ + HCl, react at 0–5 °C for 6 h.

* C-$LiFePO_4$ was provided by Phostech, Québec.

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

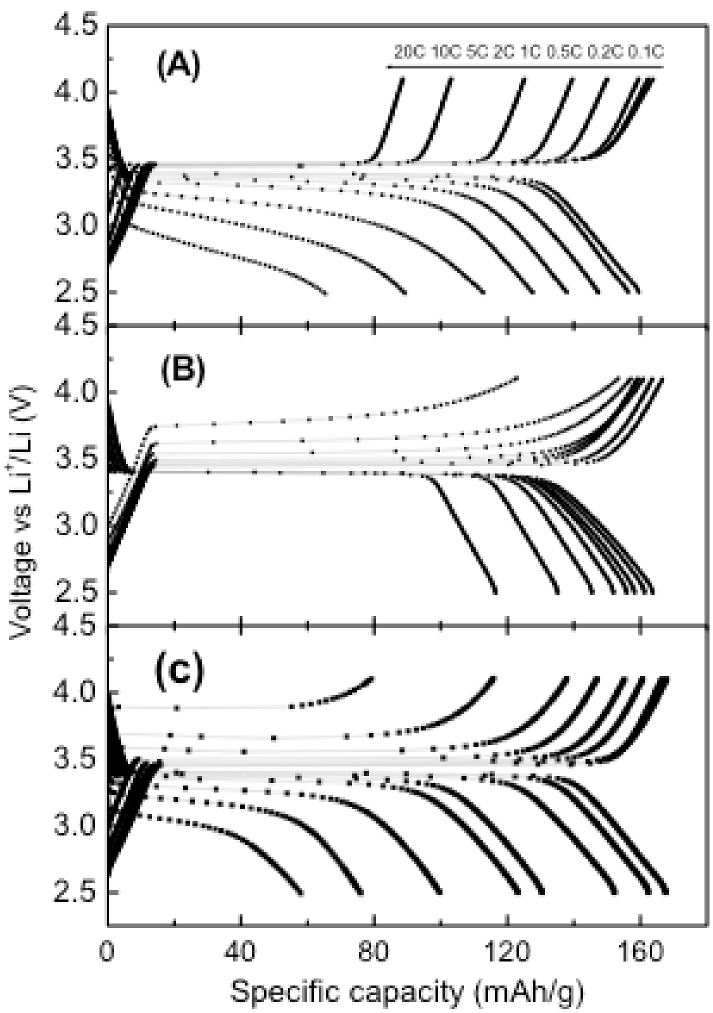


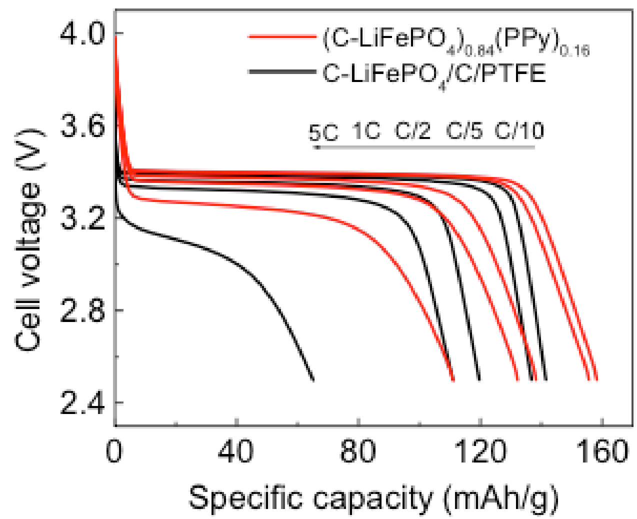
Charge and discharge composite capacity vs cycle number for the $(C\text{-}LiFePO_4)_{1-x}(PPy)_x$



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.

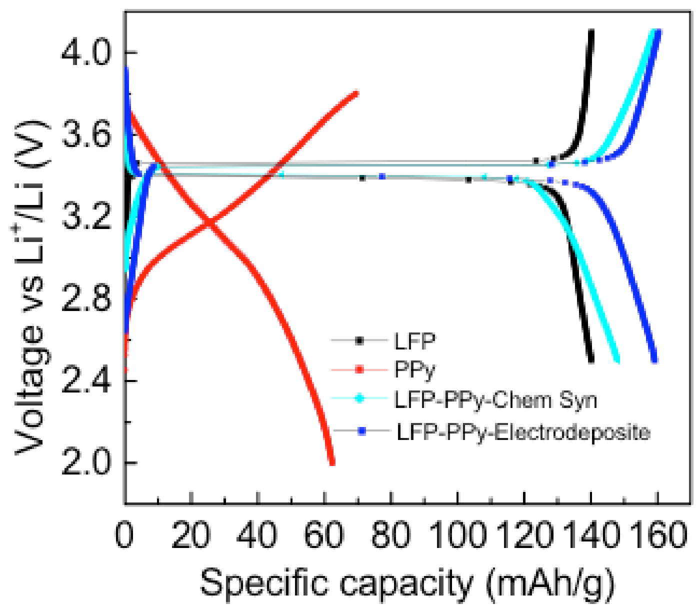
(A) 0.1C/charge, 0.1-20C/discharge;

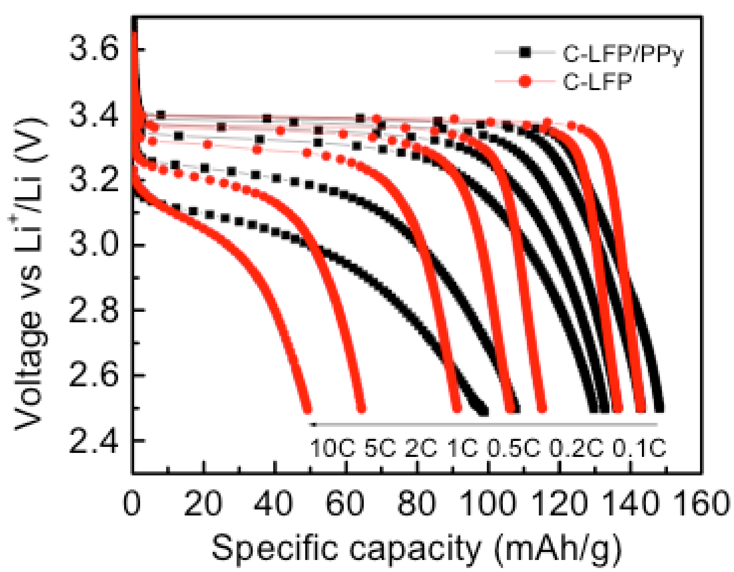
(B) 0.1-20C/charge, 0.1C/discharge;

(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).

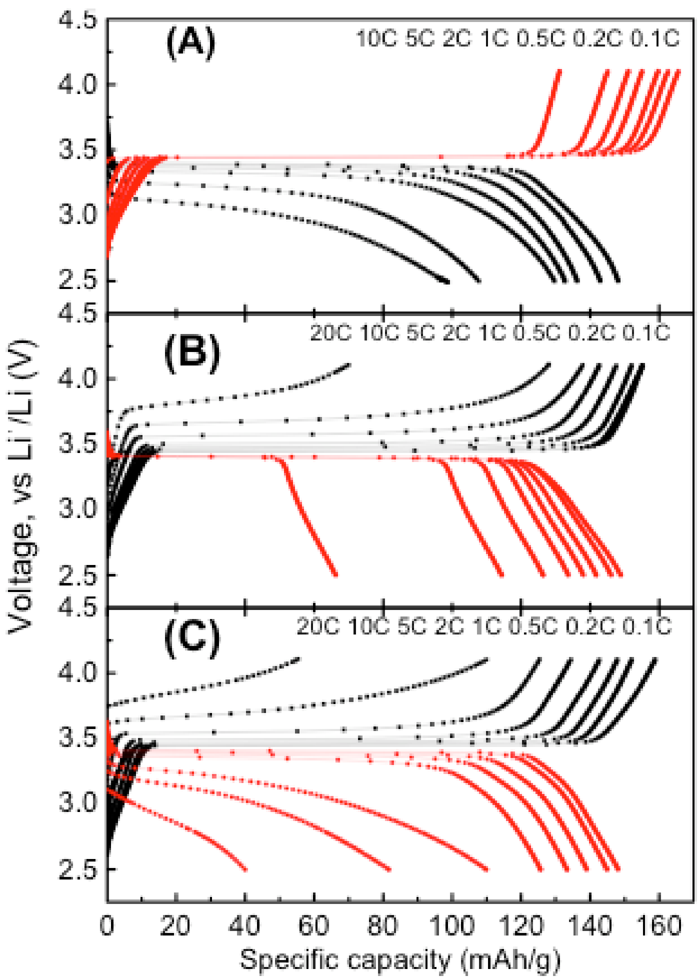
Electrochemical performance of chemically-synthesized $(C\text{-}LiFePO_4)_{1-x}(PPy)_x$

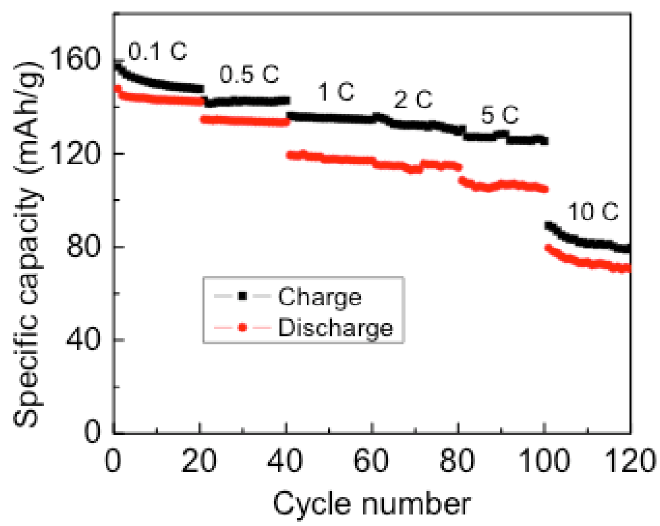




The capacity and rate capability of the chemically-synthesized $LiFePO_4$/PPy composite cathode is comparable with the electrodeposited film and higher than the parent $LiFePO_4$.

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





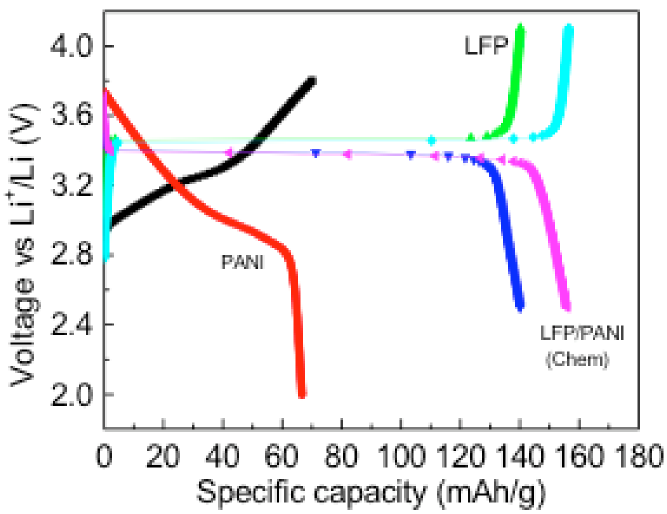
High rate capability is also obtained for the chemically-synthesized $LiFePO_4$/PPy composite cathode.

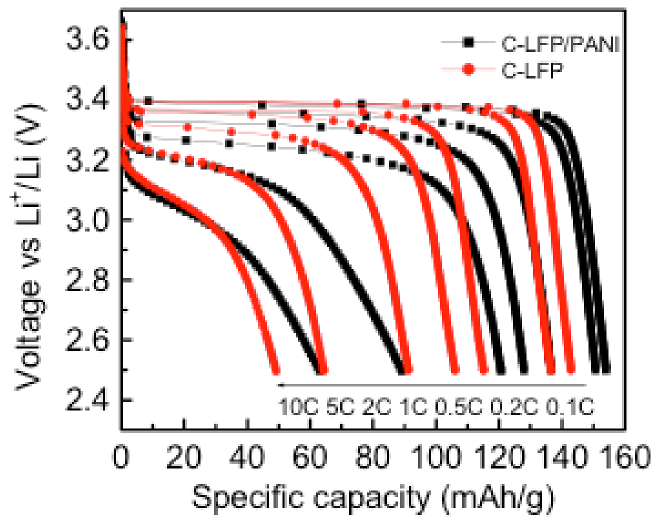
(A) 0.1C/charge, 0.1-10C/discharge;

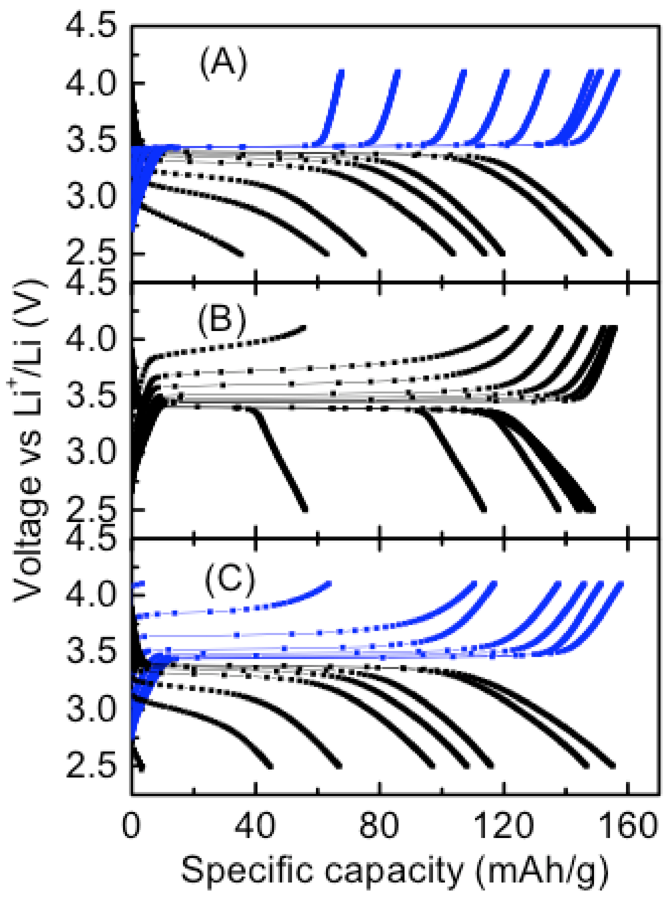
(B) 0.1-20C/charge, 0.1C/discharge;

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

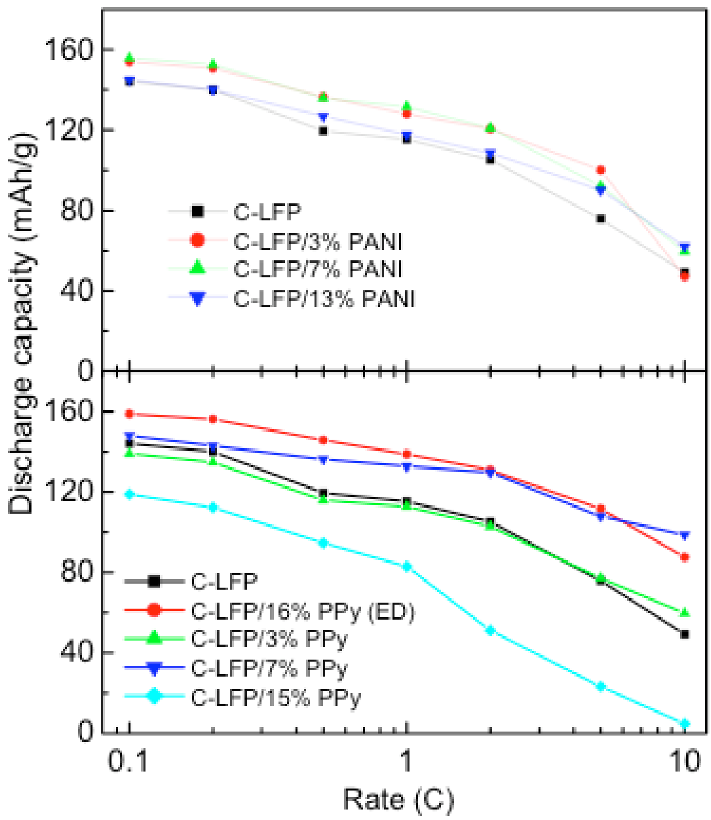
Enhanced performance of chemically-synthesized $(C\text{-}LiFePO_4)_{1-x}(PANI)_x$





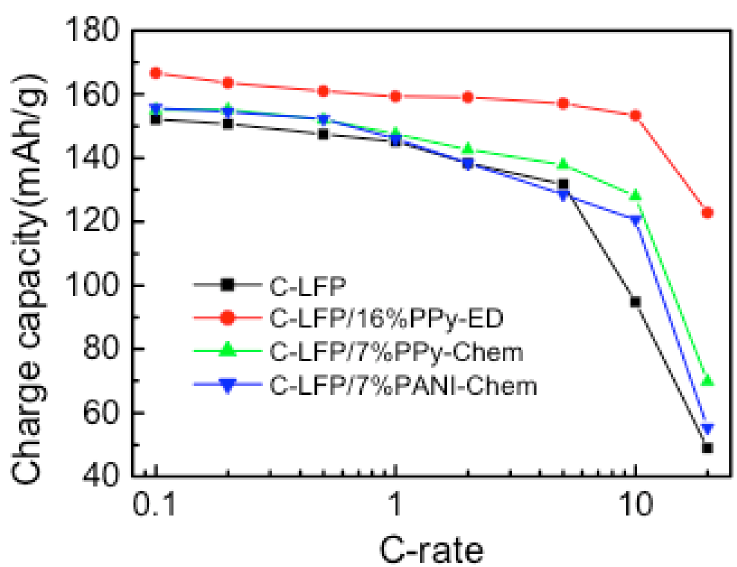


Comparison of rate capability for the C-LiFePO$_4$/polymer composite cathodes



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

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

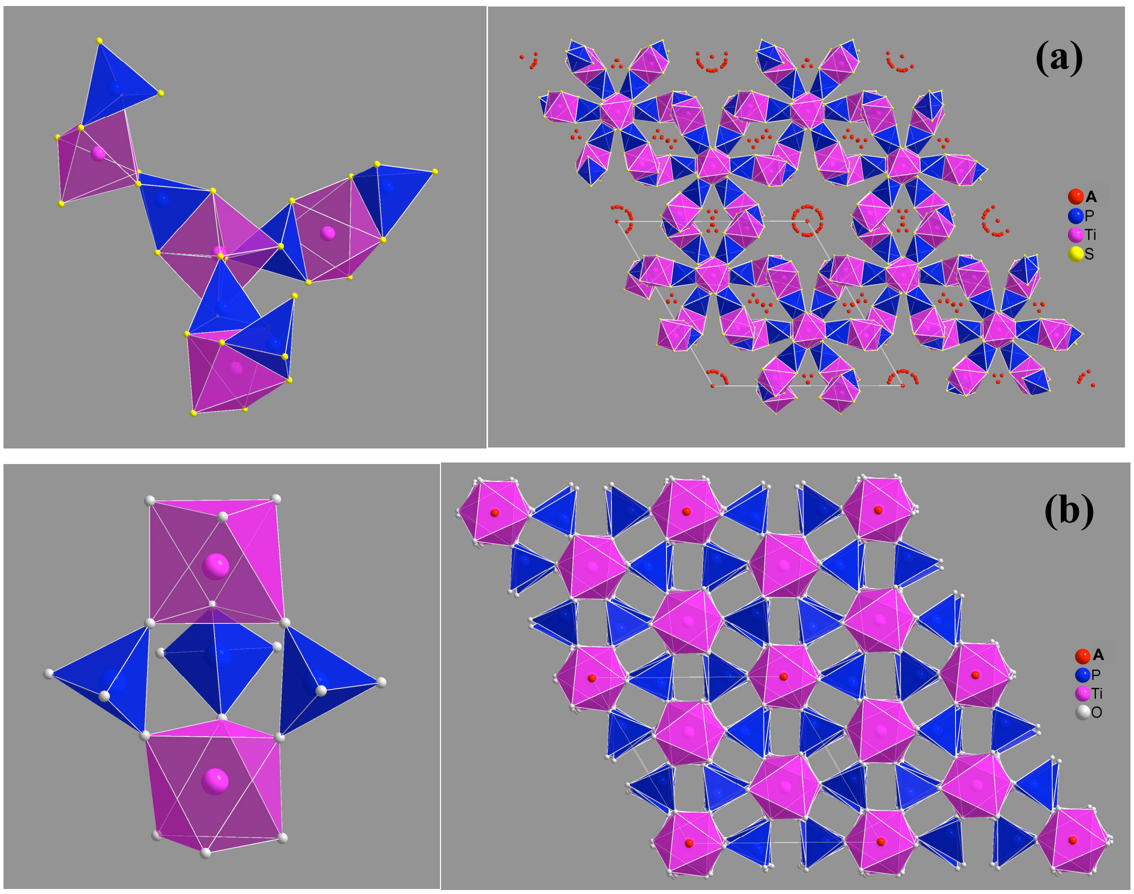
(b) No large volume change

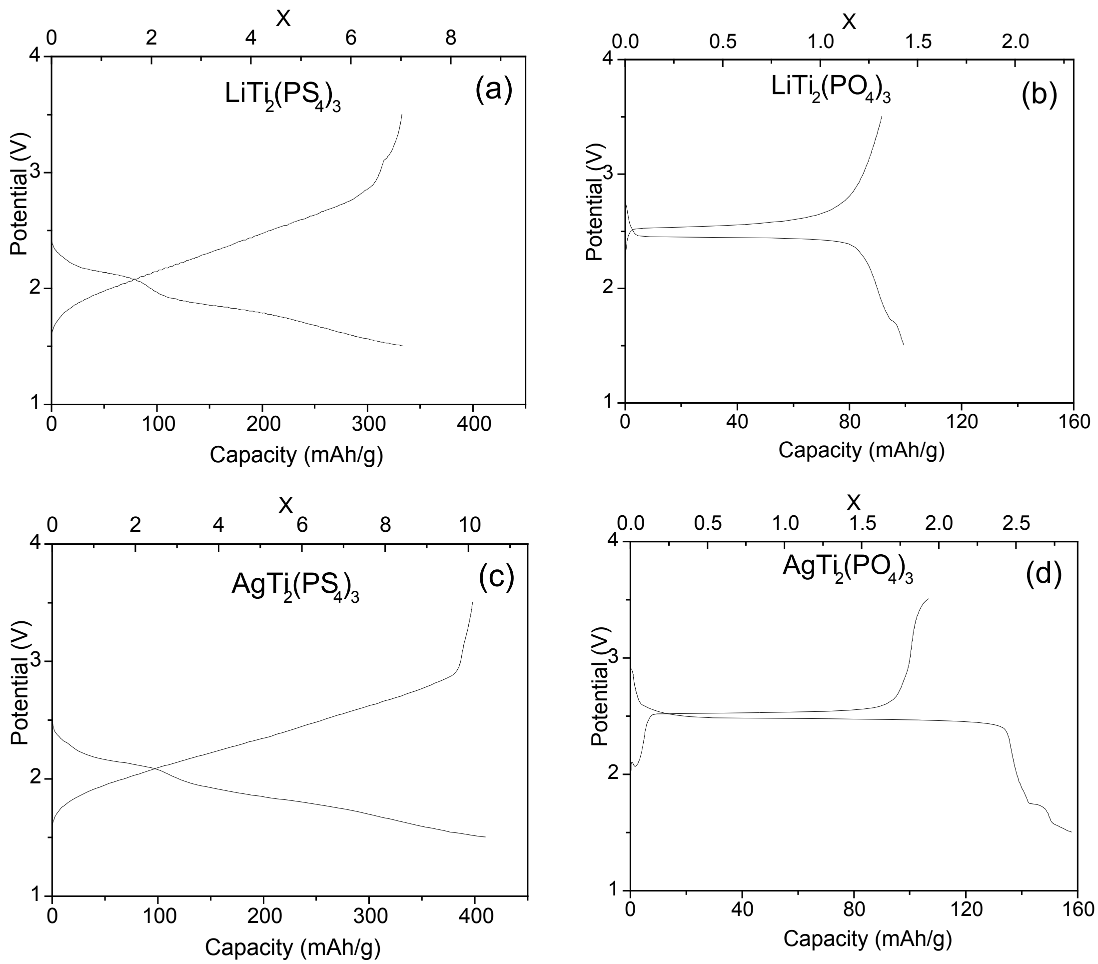
Examples

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

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

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




LiTi2(PS4)3
(a)
LiTi2(PO4)3
(b)
AgTi2(PS4)3
(c)
AgTi2(PO4)3
(d)
X
Potential (V)
Capacity (mAh/g)

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

- Patents:

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

- Presentations: