Olivines for HEV and PHEV Applications

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Outline

- Li-Ion system and technology choice
- Experimental part
- LiFePO₄ characterization with std electrolyte
- LiFePO₄ performance with gel polymer
- LiFePO₄ performance with ionic liquid
- Summary
The barriers to commercialization of PHEVs are: batteries life, safety and cost.
Experimental

The primary particle size ranges from 50nm to 250nm

- Laminated cell with 4cm² active surface area.
- Counter and reference electrodes: Li metal for half cell
- Electrolyte: 1M LiPF₆ in EC/DEC = 3/7
- Rate capability (Charge – 0.25C, Discharge – 0.1C to 40C)
- IL: N-Methyl-N-propyl-pyrrolidininium bis(fluorosulfonyl) imide (Py13[FSI]), EMI(FSI), Salts: LiFSI or LiPF₆
ARC test on cathode materials

![Graph showing the dT/dt vs. Temperature for different cathode materials: LiNi_{0.8}Co_{0.15}Al_{0.05}O_2, LiCoO_2, and LiFePO_4.]

- **LiNi_{0.8}Co_{0.15}Al_{0.05}O_2**
- **LiCoO_2**
- **LiFePO_4**
LiFePO$_4$: particle size effect on safety

No particle size effect on the safety of LiFePO$_4$

Test data from Junwei Jiang and Jeff Dahn, LiFePO$_4$ from Hydro-Québec
LiFePO$_4$: Rate Capability

25°C

![Graph showing the rate capability of LiFePO$_4$ at 25°C](image)

- **1st cycle**
- **0.1C**
- **0.5C**
- **1C**
- **2C**
- **5C**
- **8C**
- **12C**

**Potential (V vs. Li/Li$^+$)** vs. **Capacity (mAh/g)**

- **0.1C**
- **0.5C**
- **1C**
- **2C**
- **5C**
- **8C**
- **12C**

**Note:** The graph illustrates the variation in capacity with different rates (C rates) and the 1st cycle performance. The potential range is from 1.8 to 4.3 V vs. Li/Li$^+$. The capacity is measured in mAh per gram.
LiFePO₄: Temperature Effect

Graph showing the capacity (mAh/g) of LiFePO₄ at different temperatures and discharge rates. The graph includes lines for discharge rates of 0.02C, 0.05C, 0.1C, 0.2C, 0.5C, 1C, and 2C. The capacity increases with higher discharge rates and temperatures.
LiFePO₄ : 60°C cycling

- After 400 cycles, Q=98.2% of the rated capacity.
- The coulombic efficiency remains constant during cycling at 99.6%.
- The capacity decreased only by 0.004% /cycle.

At 10C: 120 mAh/g
At 25C: still delivers 73 mAh/g
ARC Test: gel vs. liquid electrolyte

![Graph showing temperature change over time for different electrolyte types. The graph compares the rate of temperature change (dT/dt) with temperature (°C) for PP + liquid, PP + gel, and hard gel (free PP).]
Gel Electrolyte

- No free liquid in the cell
- Cross linking reaction takes place only by heating at 60°C or even at 25°C (20h).
- Cell assembling process is similar with that of liquid electrolyte cell.
- Resulting stable chemical gel even at higher temperature.
LiFePO$_4$: New gel electrolyte

2%wt polymer

- High first coulombic efficiency, with the gel polymer.
- Gel formed at 60°C gives lower reversible capacity.
- Gel formed at 25°C shows the a comparable performance as standard electrolyte.

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LiFePO₄: New gel electrolyte

- At low rates, gel polymer perform as well as liquid electrolyte.
- Liquid and gel (formed) at 25°C cells have comparable performance up to 15C discharge rate.
Room Temperature Ionic Liquid (RTIL)

- No vapor pressure & Good electrochemical stability
- Solvent for many salts and polymers
- Good resistance to oxidation > 5V vs. Li°
- Cost still high, some problem on passivation layer (SEI)
- Combination with Polymer:
  - Shape flexibility & Decrease of IL content

(a) EMI-FSI

(d) Py13-FSI
ILs stability

5 V cathodes:
- LiCoPO_4
- LiMnPO_4
- LiNiPO_4

From M. Kikuta
Symposium "Science of Ionic Liquid", October 5, 2005
- FSI-ionic liquid is well adapted for LiFePO$_4$ cathode and graphite anode.
- ICL is higher when ionic liquid is used as electrolyte.
- Reversible capacity with ionic liquid is comparable to liquid electrolyte.
- LiFSI salt shows very promising data 115 mAh/g at 10C rate.
- Ionic liquid shows acceptable performance until 2C rate.
Vacuum & temperature effect on the IL

Vacuum and temperature have improved the cell performance

LiFePO₄/Py13(FSI)+0.7MLiFSI/Li

Rate (C)

Cathode Capacity (mAh/g)
Summary

- LiFePO₄ material shows promising result on cycling and power with nano-particles (50-250nm) even at 60°C.
- At -10°C, 138mAh/g can be obtained from LiFePO4 cells at discharge rate of 0.02C. However, improvement in the high rate capacity at low temperature is still needed (only about 90mAh/g at 2C at -10°C).
- LiFePO₄ has demonstrated good performance with the gel and with IL (intermediate rates).
- Safety must be the first priority with large Li-ion batteries for transportation application; then the configurations:
  - graphite/Gel polymer/ LiFePO₄ and
  - graphite/Py13(FSI)-LiFSI/ LiFePO₄
  may be considered as potential choice for capacity and safety battery.
- Lithium-ion LiFePO₄ is considered the most commercially viable chemistry for PHEVs – due to the potential for power densities and acceptable energy and safety.
- Further improvements are needed before a larger market penetration of HEVs and PHEVs can take place.