Unique Li-ion Batteries for Utility Applications

Daiwon Choi, Vilayanur V. Viswanathan, Wei Wang, Vincent L. Sprenkle

Pacific Northwest National Laboratory
902 Battelle Blvd., P. O. Box 999, Richland, WA 99352, USA

DOE Energy Storage Program Review, Washington, DC
Sept. 26-28, 2012

Acknowledgment:
Dr. Imre Gyuk - Energy Storage Program Manager, Office of Electricity Delivery and Energy Reliability
Investigate the Li-ion battery for stationary energy storage unit in ~kWh level.

Fabrication and optimization of LiFePO$_4$/Li$_4$Ti$_5$O$_{12}$ 18650 cell.

Li-ion battery energy storage with effective thermal management.

Improve rate and cycle life of Li-ion battery.

Screen possible new cathode/anode electrode materials and its combinations suitable for large scale Li-ion battery.

Figure 1. (a) first batch LiFePO$_4$/Li$_4$Ti$_5$O$_{12}$ 18650 cell, (b) second batch with various charge/discharge rates at room temperature (measured C-rate).

- Single cell weight 43g with theoretical capacity of 1,100mAh giving cell energy density of 48.6Wh/kg.

- From first batch, theoretical capacity was reduced by 4.5% and cell weight was increased by 13% thus reducing energy density by 15%.
Figure 2. Second batch LiFePO$_4$/Li$_4$Ti$_5$O$_{12}$ 18650 cell under full charge followed by various discharge rates at (a) room temperature of 25°C and (b) 45°C.

- Charge rate is limiting the capacity when tested at same charge/discharge rate.
- More than 1,000mAh was achieved at 5C rate at 45°C.
Second batch 18650 cell shows excellent cycling stability.

- Coulombic Efficiency > 99.8%, Energy Efficiency ~90% at C/4.
- Highest increase in cell temperature was ~15°C at 10C.
Single phase LiMn$_{0.9}$Fe$_{0.1}$PO$_4$, LiFeBO$_3$, and Li$_2$FeSiO$_4$ was synthesized by solid-state reaction.

Lowering carbon content is important to be competitive with other cathodes.

Charge rate is limiting LiMnPO$_4$ cathode for power application.

Figure 4. (a) XRD patterns of the synthesized LiMn$_{0.9}$Fe$_{0.1}$PO$_4$, LiFeBO$_3$, and Li$_2$FeSiO$_4$ and (b) electrochemical voltage profile of LiMn$_{0.9}$Fe$_{0.1}$PO$_4$ electrode.
Single phase LiFeBO$_3$ has been synthesized at 650$^\circ$C but obtained half of the theoretical capacity of 220mAh/g.

Single phase Li$_2$FeSiO$_4$ has been synthesized at 700$^\circ$C but obtained 63% of the theoretical capacity of 166mAh/g (single Li).

More work is required to fully understand LiFeBO$_3$ and Li$_2$FeSiO$_4$ cathode.
Figure 6. (a) XRD patterns Zn$_2$GeO$_4$ with different heat-treatment time and (b) electrochemical voltage profile of Zn$_2$GeO$_4$ anode heat-treated for 1h.

- Zn$_2$GeO$_4$ heat-treated for 1h show amorphous structure compared to extended heat-treatment.
- Zn$_2$GeO$_4$ (heat-treated 1h) show specific capacity >1,000mAh/g close to theoretical capacity of 1,416mAh/g.
**Figure 7.** (a) cycling stability and (b) rate performance of Zn$_2$GeO$_4$ anode electrode heat-treated for 1h.

- Zn$_2$GeO$_4$ heat-treated for 1h delivers stable cycling up to 500 cycles with over 1,000 mAh/g.
- Along with stable cycling, specific capacity of > 400 mAh/g was delivered at 8C rate.
Second batch LiFePO$_4$/Li$_4$Ti$_5$O$_{12}$ based 18650 cell was fabricated.

Initial rate and cycling performance indicate that the second batch show much improved electrochemical response. Further characterization and optimization is underway.

LiMn$_{0.9}$Fe$_{0.1}$PO$_4$, LiFeBO$_3$, and Li$_2$FeSiO$_4$ was synthesized and electrochemically characterized.

Zn$_2$GeO$_4$ anode with specific capacity of ~1,000mAh/g was developed where both the rate and the cycling stability showed promising results.
Future Tasks

- Full characterization and comparison of second batch 18650 cell with commercially available batteries.

- Fabrication of third 18650 cell with enhanced charge rate of 80% SOC at >1C rate based on LiFePO$_4$/Li$_4$Ti$_5$O$_{12}$ chemistry.

- Modify synthesis of LiMn$_{1-x}$Fe$_x$PO$_4$, LiFeBO$_3$, and Li$_2$FeSiO$_4$ based cathodes to achieve higher rate performance.

- Explore other non-commercialized novel high capacity electrode materials suitable for energy form of stationary Li-ion battery.
Acknowledgements

► PNNL
Silas A. Towne
Young Joon Choi
Jun Liu
Alasdair J. Crawford
Ji-Guang Zhang
Larry R. Pederson

► Penn State University
Donghai Wang

► K2 Energy Solution
James D. Hodge