

# Unique Li-ion Batteries for Utility Applications

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

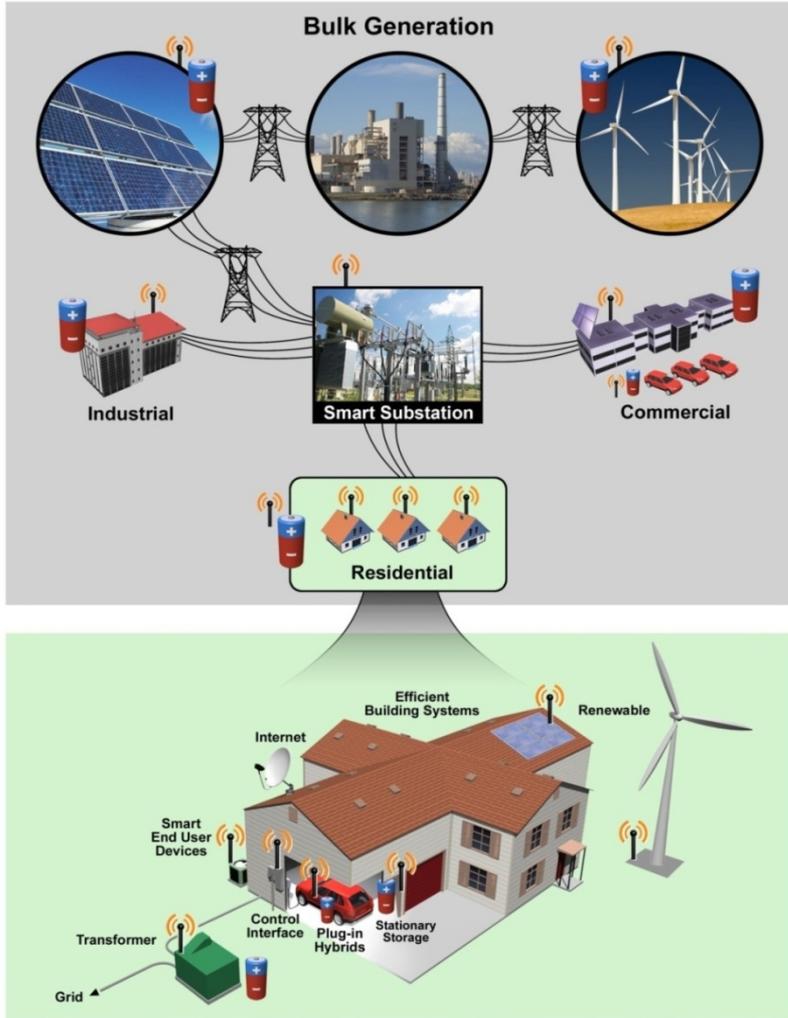
Pacific Northwest National Laboratory  
902 Battelle Blvd., P. O. Box 999, Richland, WA 99352, USA

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

## **Acknowledgment:**

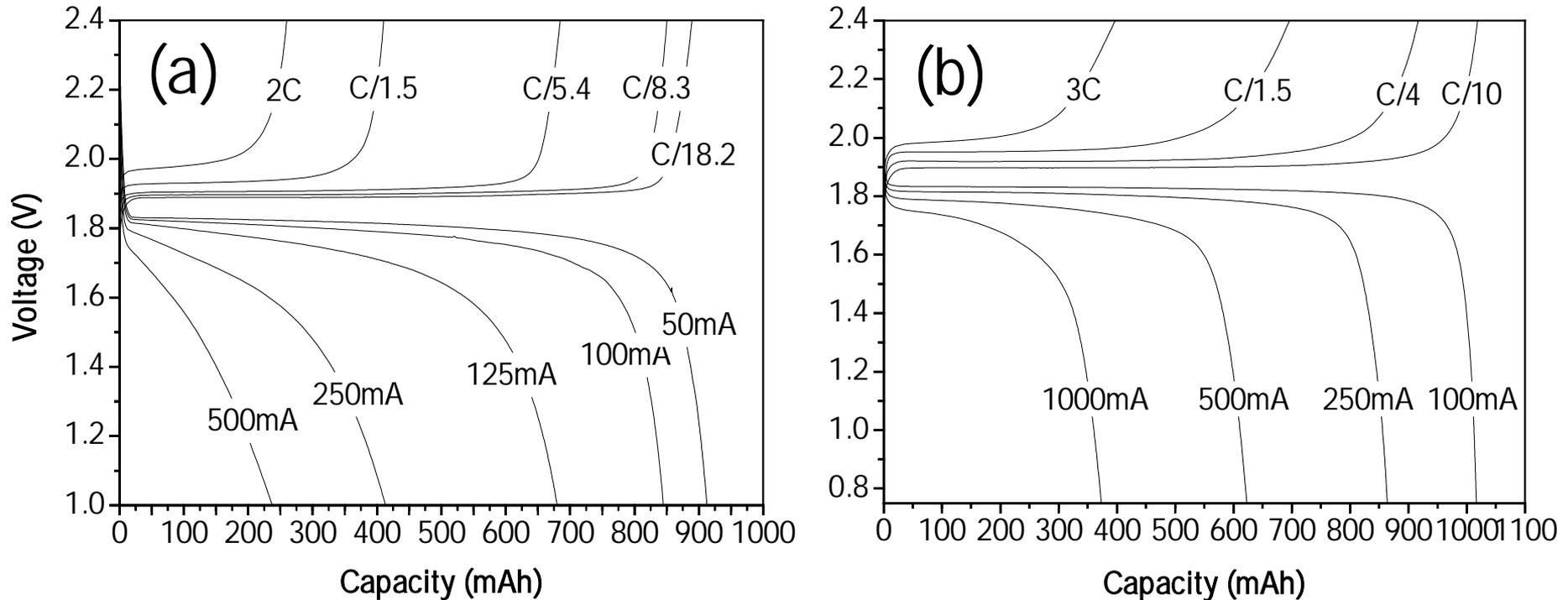
**Dr. Imre Gyuk - Energy Storage Program Manager, Office of Electricity  
Delivery and Energy Reliability**

# Objectives



- ❑ Investigate the Li-ion battery for stationary energy storage unit in ~kWh level.
- ❑ Fabrication and optimization of  $\text{LiFePO}_4/\text{Li}_4\text{Ti}_5\text{O}_{12}$  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.

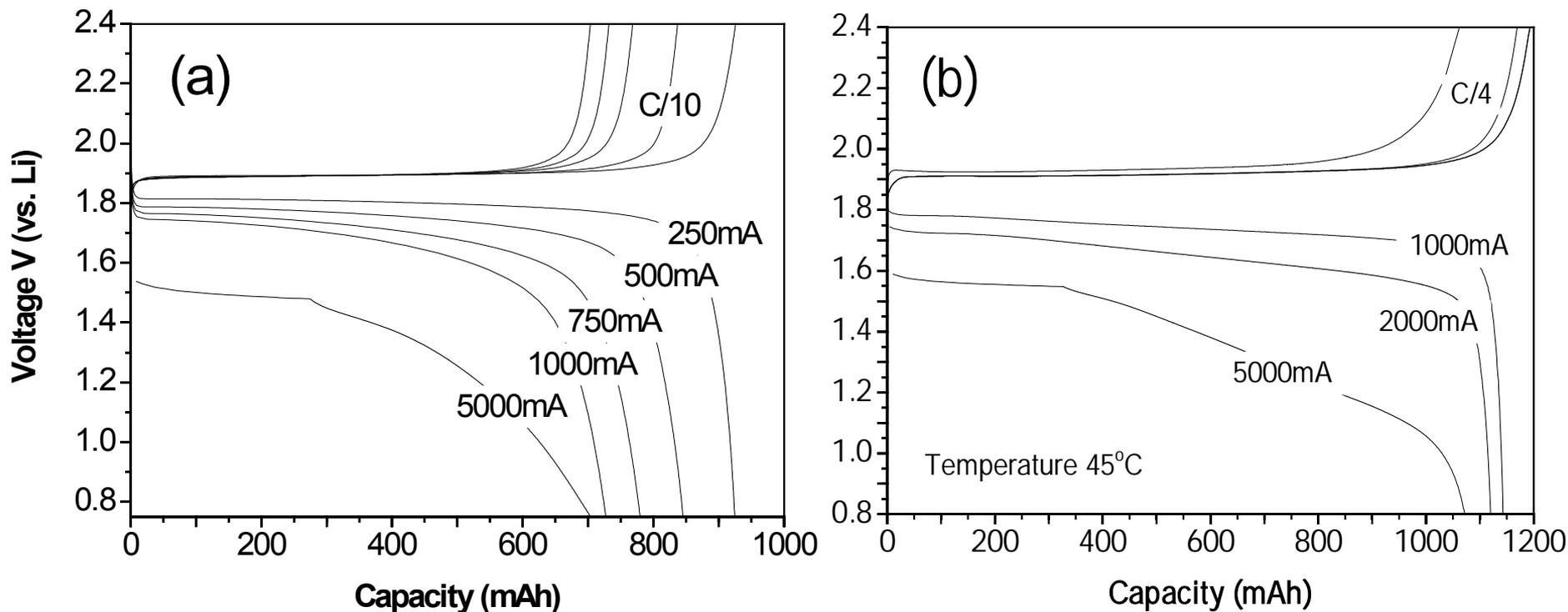
# $\text{LiFePO}_4 / \text{Li}_4\text{Ti}_5\text{O}_{12}$ 18650 Full Cell



**Figure 1.** (a) first batch  $\text{LiFePO}_4/\text{Li}_4\text{Ti}_5\text{O}_{12}$  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%.

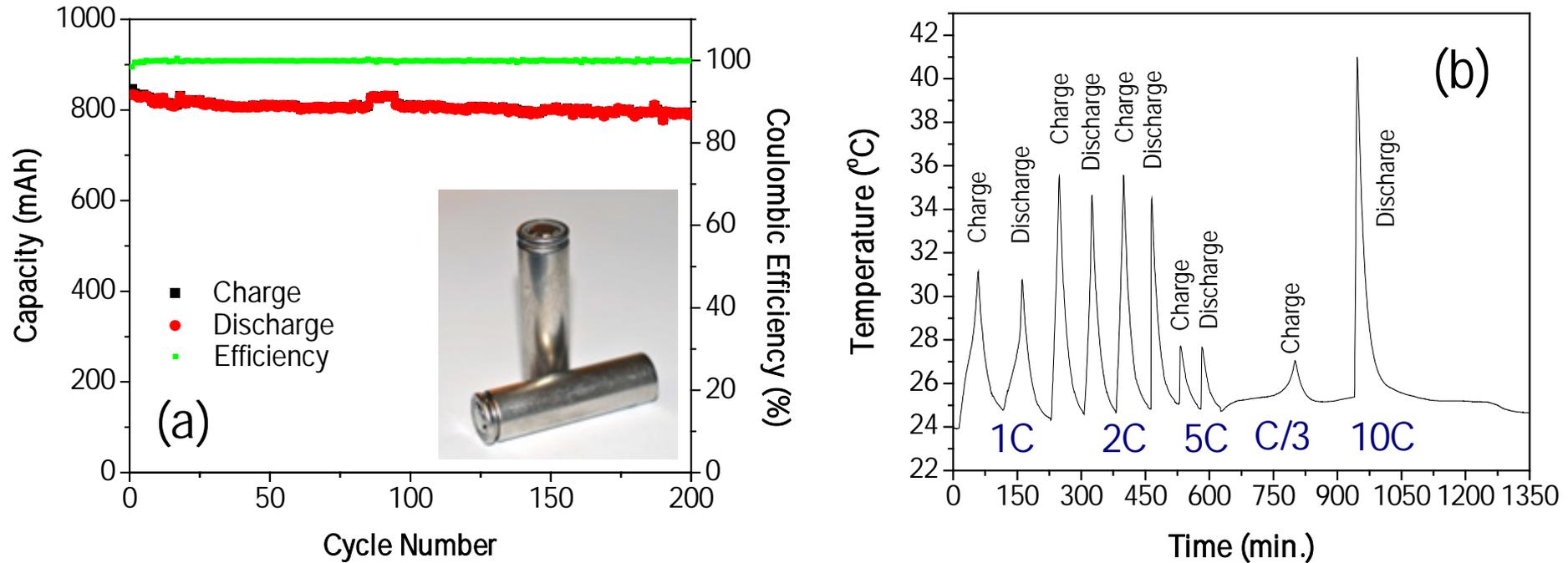
# $\text{LiFePO}_4 / \text{Li}_4\text{Ti}_5\text{O}_{12}$ 18650 Full Cell



**Figure 2.** Second batch  $\text{LiFePO}_4 / \text{Li}_4\text{Ti}_5\text{O}_{12}$  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.

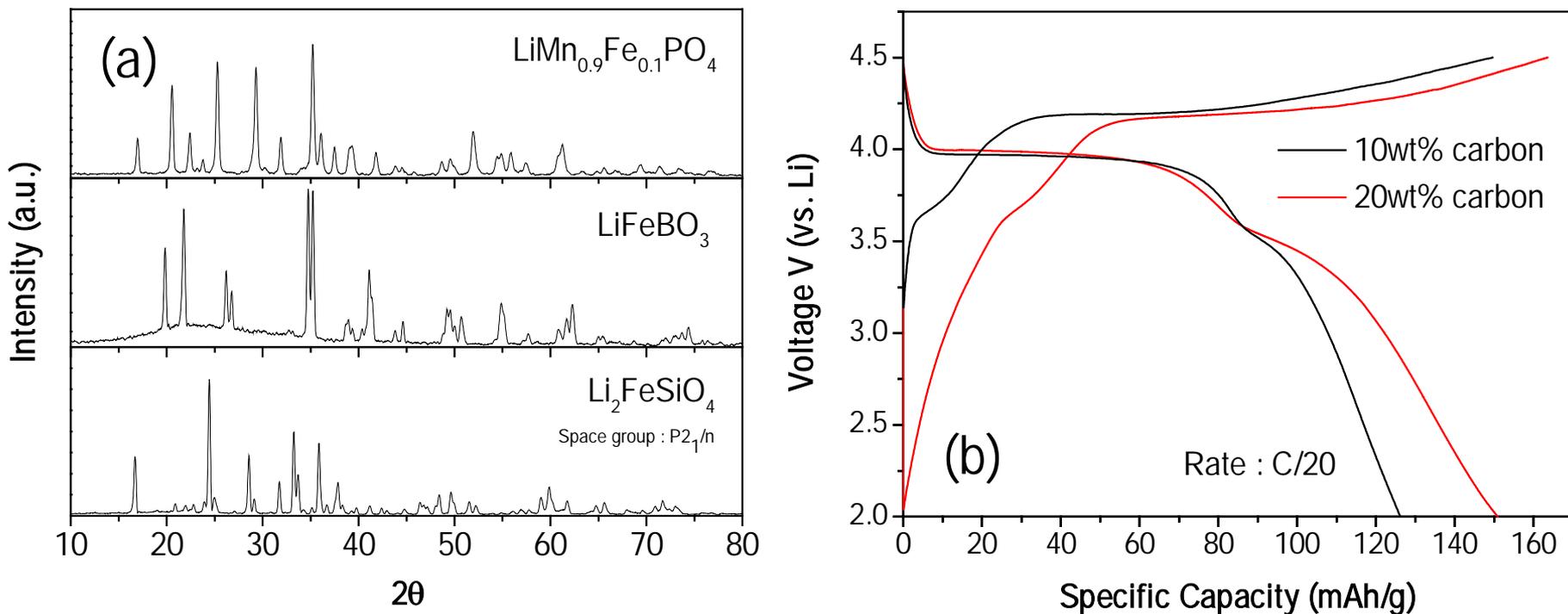
# $\text{LiFePO}_4 / \text{Li}_4\text{Ti}_5\text{O}_{12}$ 18650 Full Cell



**Figure 3.** (a) cycling stability at C/4 charge/discharge rate and (b) cell temperature measured during various rates at room temperature using accelerating rate calorimeter (ARC).

- ❑ 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.

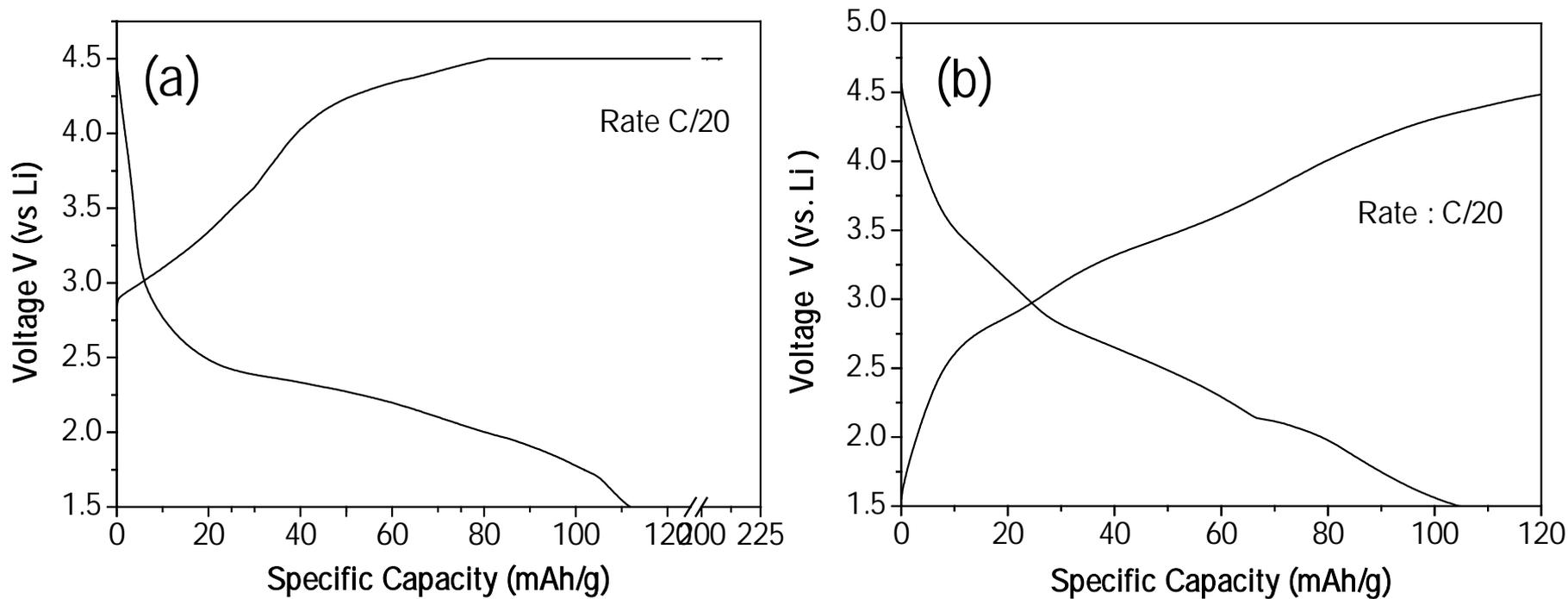
# Polyanion Type Cathode



**Figure 4.** (a) XRD patterns of the synthesized  $\text{LiMn}_{0.9}\text{Fe}_{0.1}\text{PO}_4$ ,  $\text{LiFeBO}_3$ , and  $\text{Li}_2\text{FeSiO}_4$  and (b) electrochemical voltage profile of  $\text{LiMn}_{0.9}\text{Fe}_{0.1}\text{PO}_4$  electrode.

- ❑ Single phase  $\text{LiMn}_{0.9}\text{Fe}_{0.1}\text{PO}_4$ ,  $\text{LiFeBO}_3$ , and  $\text{Li}_2\text{FeSiO}_4$  was synthesized by solid-state reaction.
- ❑ Lowering carbon content is important to be competitive with other cathodes.
- ❑ Charge rate is limiting  $\text{LiMnPO}_4$  cathode for power application.

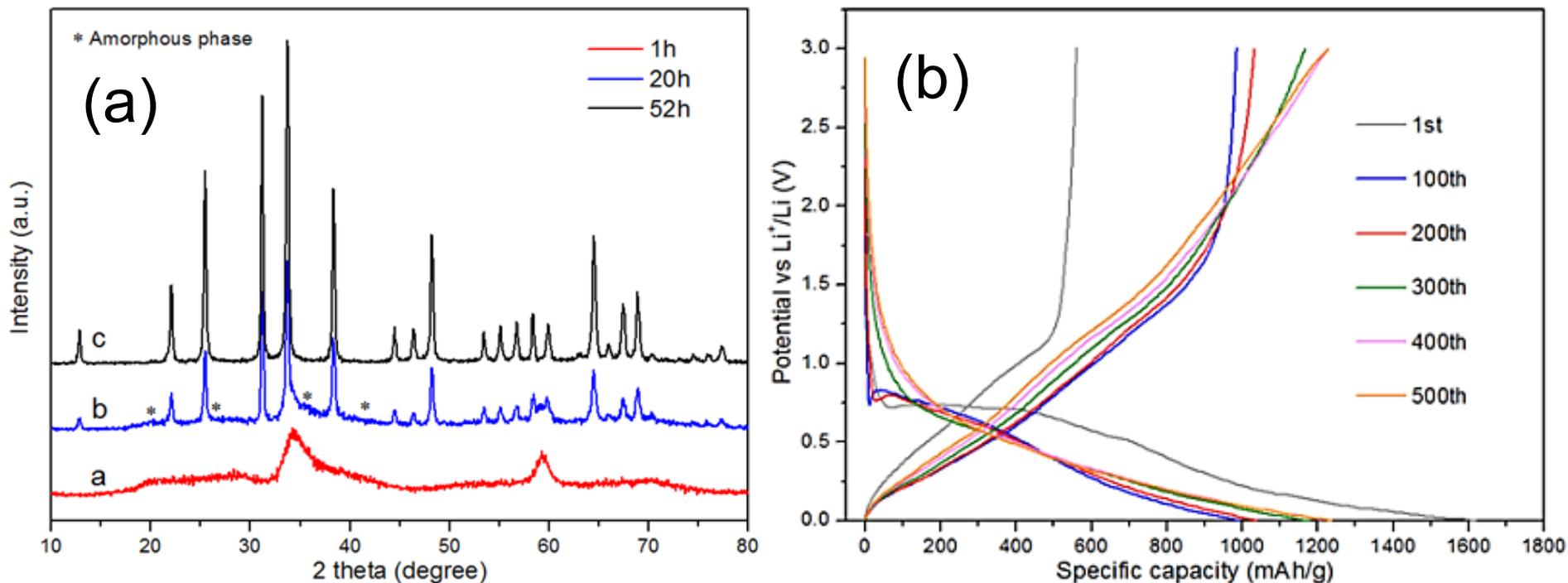
# Polyanion Type Cathode



**Figure 5.** Electrochemical voltage profile of (a)  $\text{LiFeBO}_3$  and (b)  $\text{Li}_2\text{FeSiO}_4$  cathode electrode.

- ❑ Single phase  $\text{LiFeBO}_3$  has been synthesized at  $650^\circ\text{C}$  but obtained half of the theoretical capacity of  $220\text{mAh/g}$ .
- ❑ Single phase  $\text{Li}_2\text{FeSiO}_4$  has been synthesized at  $700^\circ\text{C}$  but obtained 63% of the theoretical capacity of  $166\text{mAh/g}$  (single Li).
- ❑ More work is required to fully understand  $\text{LiFeBO}_3$  and  $\text{Li}_2\text{FeSiO}_4$  cathode.

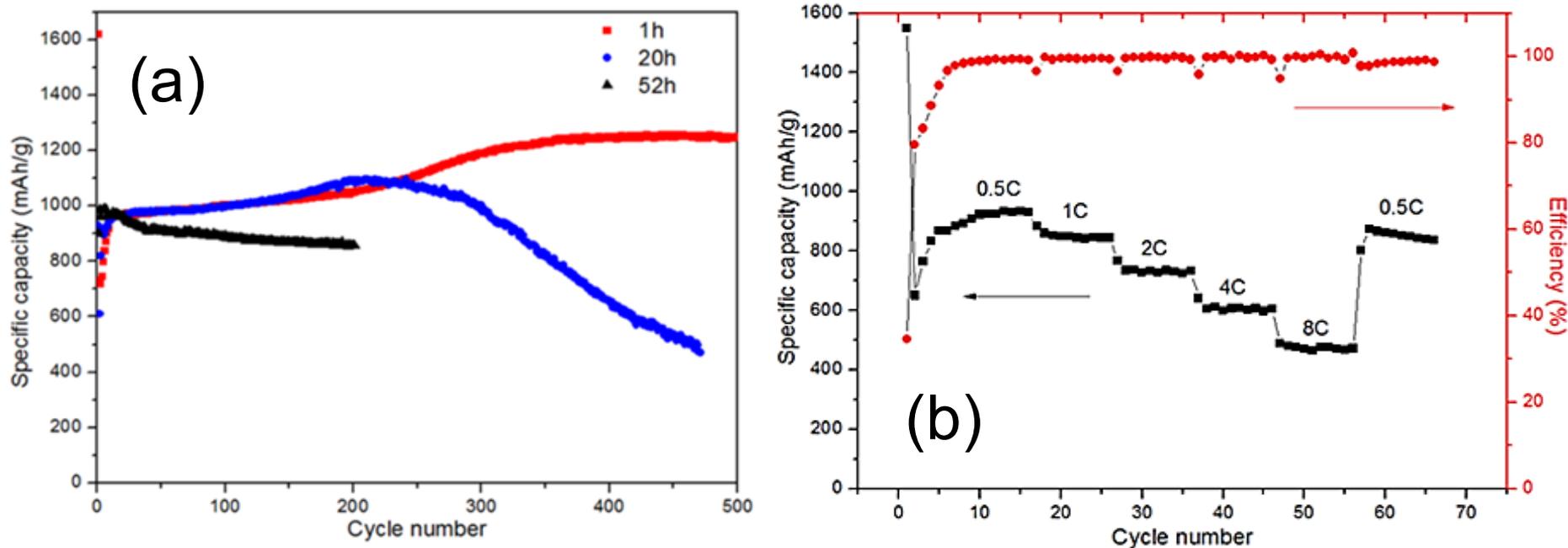
# Novel High Capacity Anode



**Figure 6.** (a) XRD patterns Zn<sub>2</sub>GeO<sub>4</sub> with different heat-treatment time and (b) electrochemical voltage profile of Zn<sub>2</sub>GeO<sub>4</sub> anode heat-treated for 1h.

- ❑ Zn<sub>2</sub>GeO<sub>4</sub> heat-treated for 1h show amorphous structure compared to extended heat-treatment.
- ❑ Zn<sub>2</sub>GeO<sub>4</sub> (heat-treated 1h) show specific capacity >1,000mAh/g close to theoretical capacity of 1,416mAh/g.

# Novel High Capacity Anode



**Figure 7.** (a) cycling stability and (b) rate performance of Zn<sub>2</sub>GeO<sub>4</sub> anode electrode heat-treated for 1h.

- Zn<sub>2</sub>GeO<sub>4</sub> heat-treated for 1h delivers stable cycling up to 500cycles with over 1,000mAh/g.
- Along with stable cycling, specific capacity of > 400mAh/g was delivered at 8C rate.

# Summary

- ❑ Second batch  $\text{LiFePO}_4/\text{Li}_4\text{Ti}_5\text{O}_{12}$  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.
- ❑  $\text{LiMn}_{0.9}\text{Fe}_{0.1}\text{PO}_4$ ,  $\text{LiFeBO}_3$ , and  $\text{Li}_2\text{FeSiO}_4$  was synthesized and electrochemically characterized.
- ❑  $\text{Zn}_2\text{GeO}_4$  anode with specific capacity of  $\sim 1,000\text{mAh/g}$  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  $\text{LiFePO}_4/\text{Li}_4\text{Ti}_5\text{O}_{12}$  chemistry.
- ❑ Modify synthesis of  $\text{LiMn}_{1-x}\text{Fe}_x\text{PO}_4$ ,  $\text{LiFeBO}_3$ , and  $\text{Li}_2\text{FeSiO}_4$  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