Unique Li-ion Batteries for Utility Applications

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

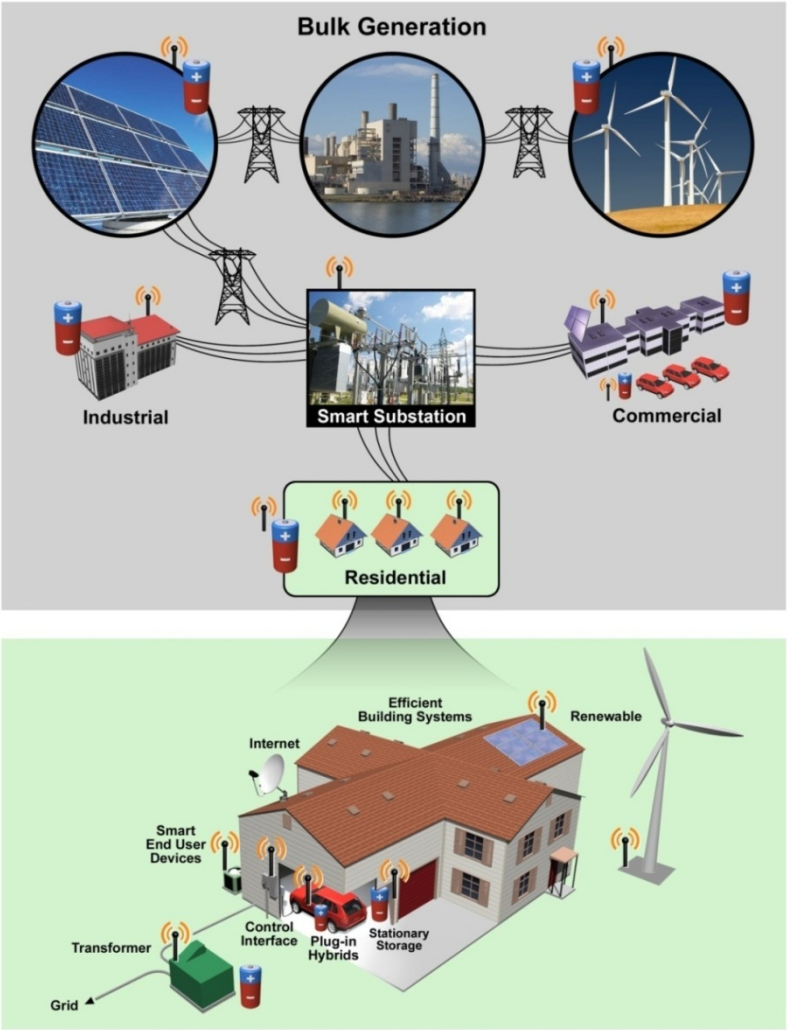
Pacific Northwest National Laboratory
902 Battelle Blvd., P. O. Box 999, Richland, WA 99352, USA

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

Pacific Northwest
NATIONAL LABORATORY

Objectives



- Investigate the Li-ion battery for stationary energy storage unit in ~kWh level.
- Fabrication and optimization of $LiFePO_4$/ $Li_4Ti_5O_{12}$ 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.

Ref) Z. Yang *et al.* ***Chem. Rev.***, 111(5), p. 3577-3613 (2011)

Pacific Northwest
NATIONAL LABORATORY

$LiFePO_4$ / $Li_4Ti_5O_{12}$ 18650 Full Cell

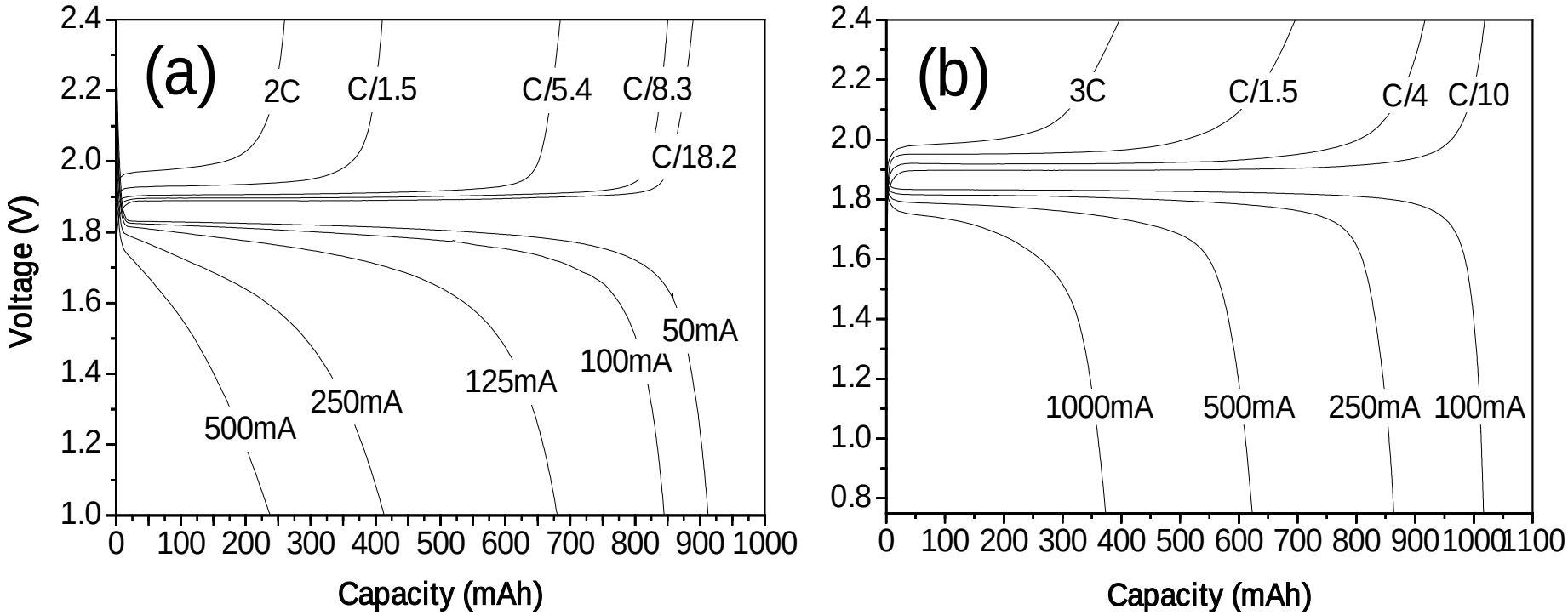


Figure 1. (a) first batch $LiFePO_4/Li_4Ti_5O_{12}$ 18650 cell, (b) second batch with various charge/discharge rates at room temperature (measured C-rate).

- 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%.

Pacific Northwest
NATIONAL LABORATORY

$LiFePO_4$ / $Li_4Ti_5O_{12}$ 18650 Full Cell

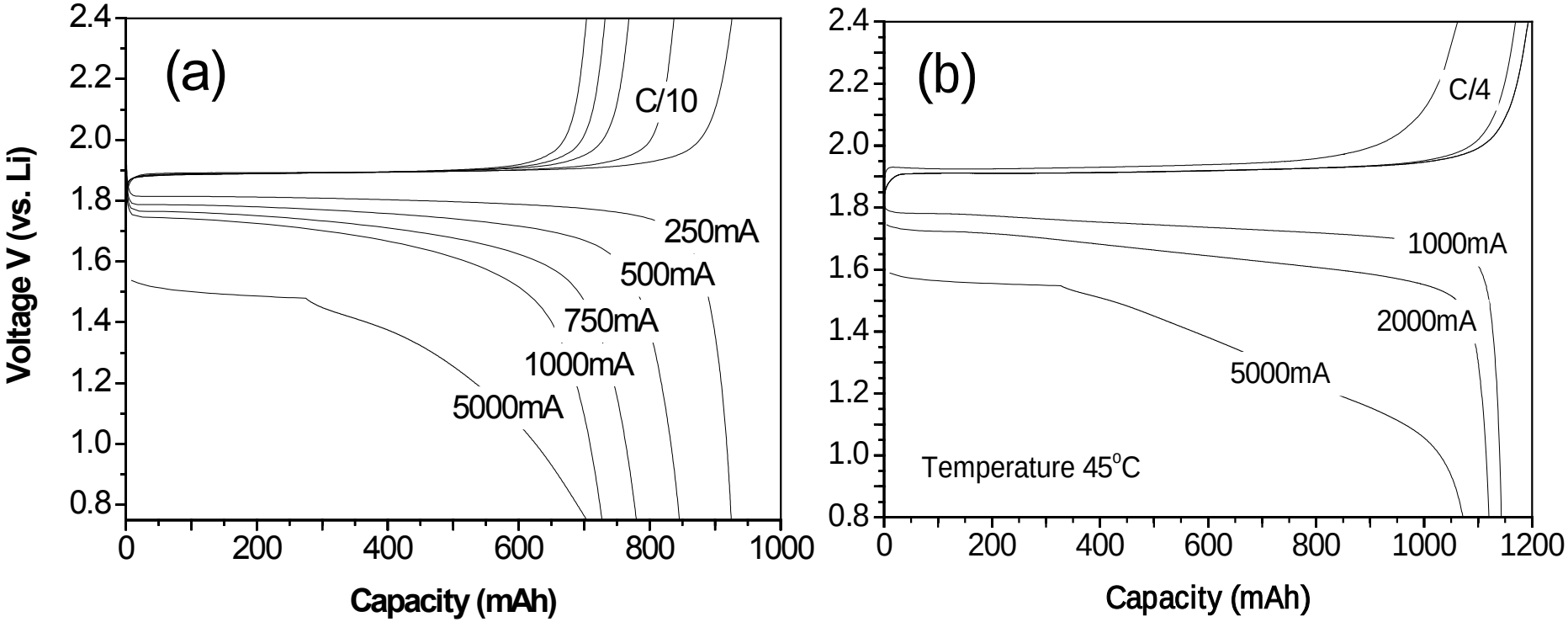


Figure 2. Second batch $LiFePO_4/Li_4Ti_5O_{12}$ 18650 cell under full charge followed by various discharge rates at (a) room temperature of 25°C and (b) 45°C.

- 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.

Pacific Northwest
NATIONAL LABORATORY

$LiFePO_4$ / $Li_4Ti_5O_{12}$ 18650 Full Cell

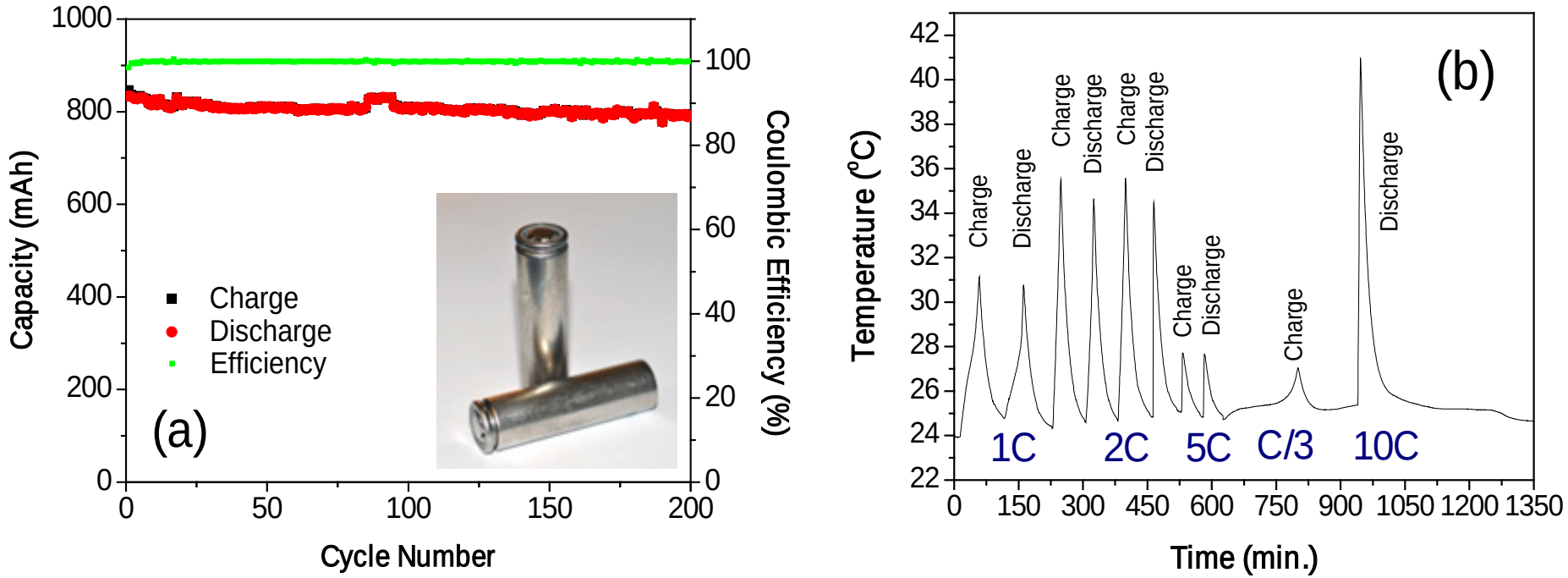


Figure 3. (a) cycling stability at C/4 charge/discharge rate and (b) cell temperature measured during various rates at room temperature using accelerating rate calorimeter (ARC).

- 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.

Pacific Northwest NATIONAL LABORATORY

Polyanion Type Cathode

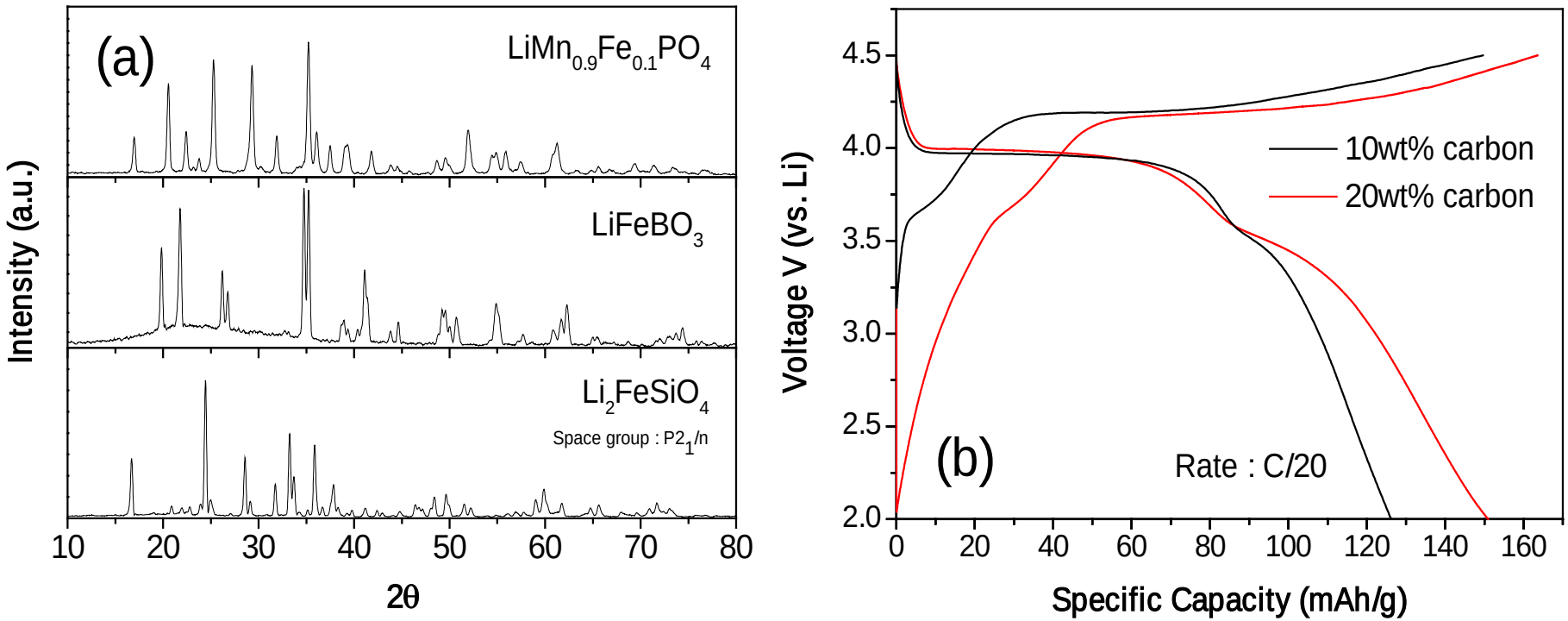


Figure 4. (a) XRD patterns of the synthesized $LiMn_{0.9}Fe_{0.1}PO_4$, $LiFeBO_3$, and Li_2FeSiO_4 and (b) electrochemical voltage profile of $LiMn_{0.9}Fe_{0.1}PO_4$ electrode.

- Single phase $LiMn_{0.9}Fe_{0.1}PO_4$, $LiFeBO_3$, and Li_2FeSiO_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.

Pacific Northwest
NATIONAL LABORATORY

Polyanion Type Cathode

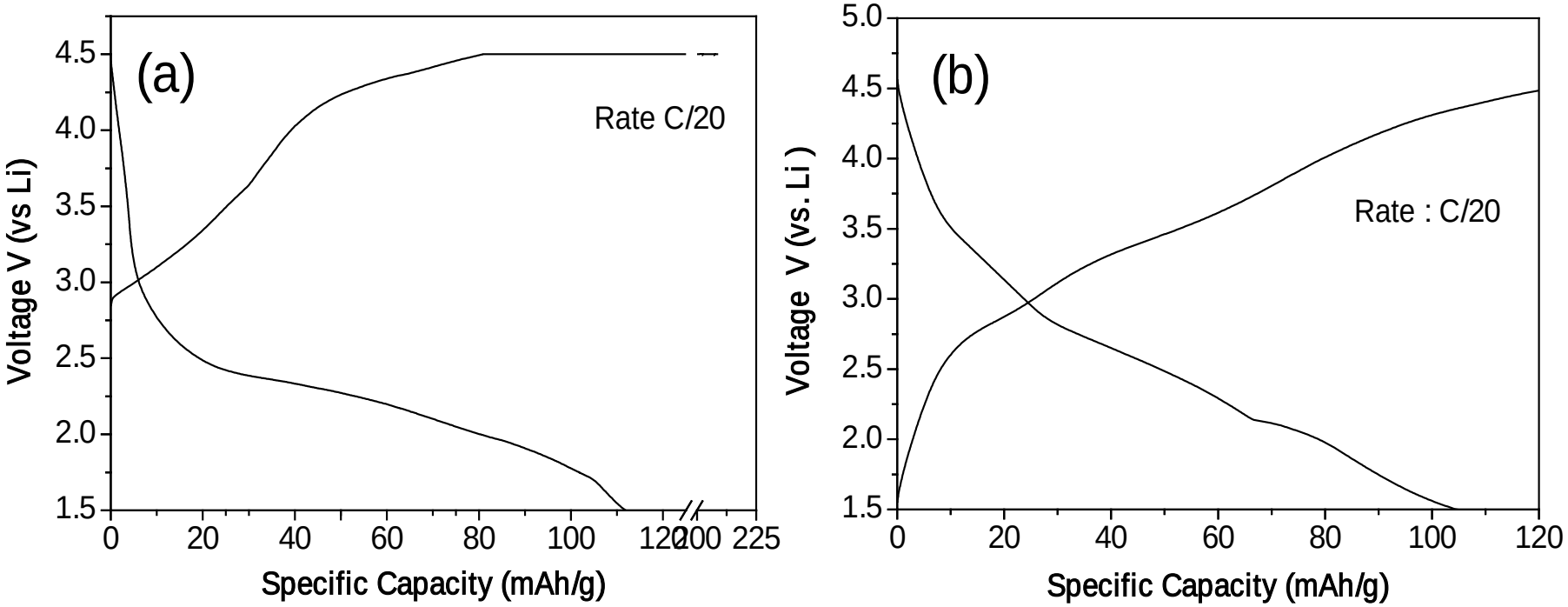


Figure 5. Electrochemical voltage profile of (a) $LiFeBO_3$ and (b) Li_2FeSiO_4 cathode electrode.

- Single phase $LiFeBO_3$ has been synthesized at 650°C but obtained half of the theoretical capacity of 220mAh/g.
- Single phase Li_2FeSiO_4 has been synthesized at 700°C but obtained 63% of the theoretical capacity of 166mAh/g (single Li).
- More work is required to fully understand $LiFeBO_3$ and Li_2FeSiO_4 cathode.

Pacific Northwest
NATIONAL LABORATORY

Novel High Capacity Anode

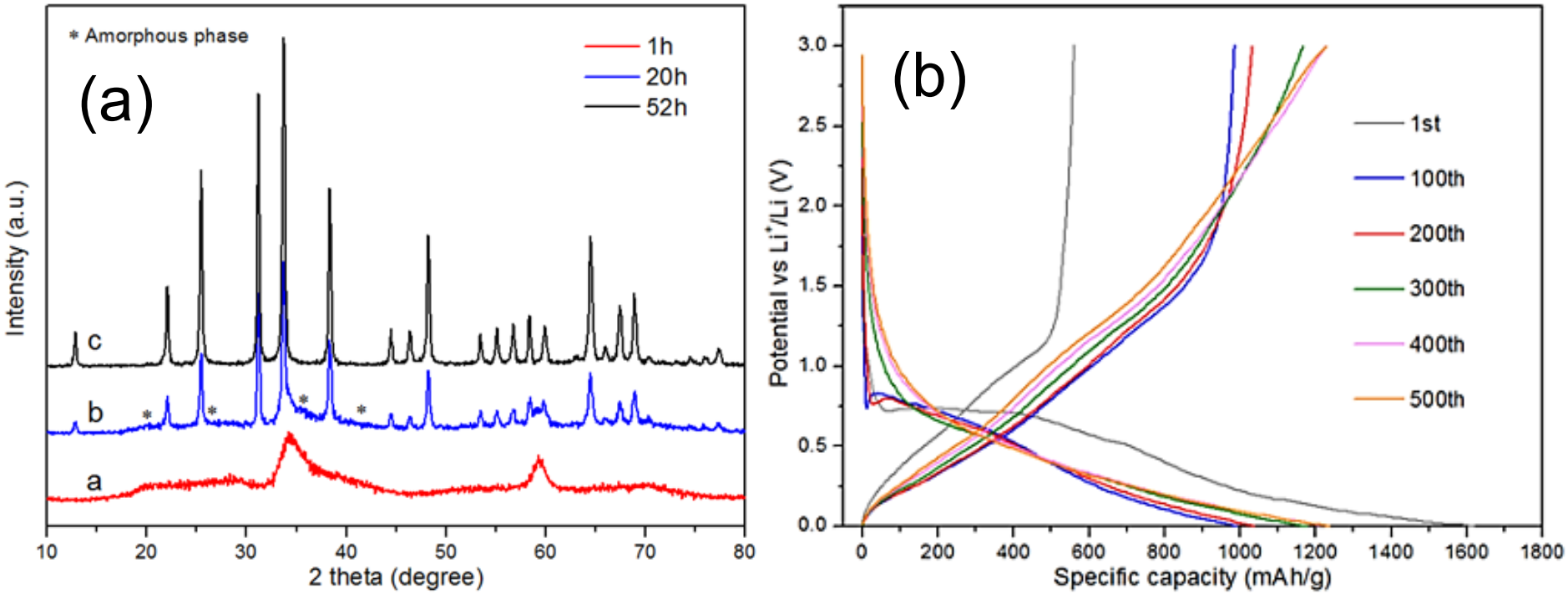


Figure 6. (a) XRD patterns Zn_2GeO_4 with different heat-treatment time and (b) electrochemical voltage profile of Zn_2GeO_4 anode heat-treated for 1h.

- Zn_2GeO_4 heat-treated for 1h show amorphous structure compared to extended heat-treatment.
- Zn_2GeO_4 (heat-treated 1h) show specific capacity >1,000mAh/g close to theoretical capacity of 1,416mAh/g.

Pacific Northwest
NATIONAL LABORATORY

Novel High Capacity Anode

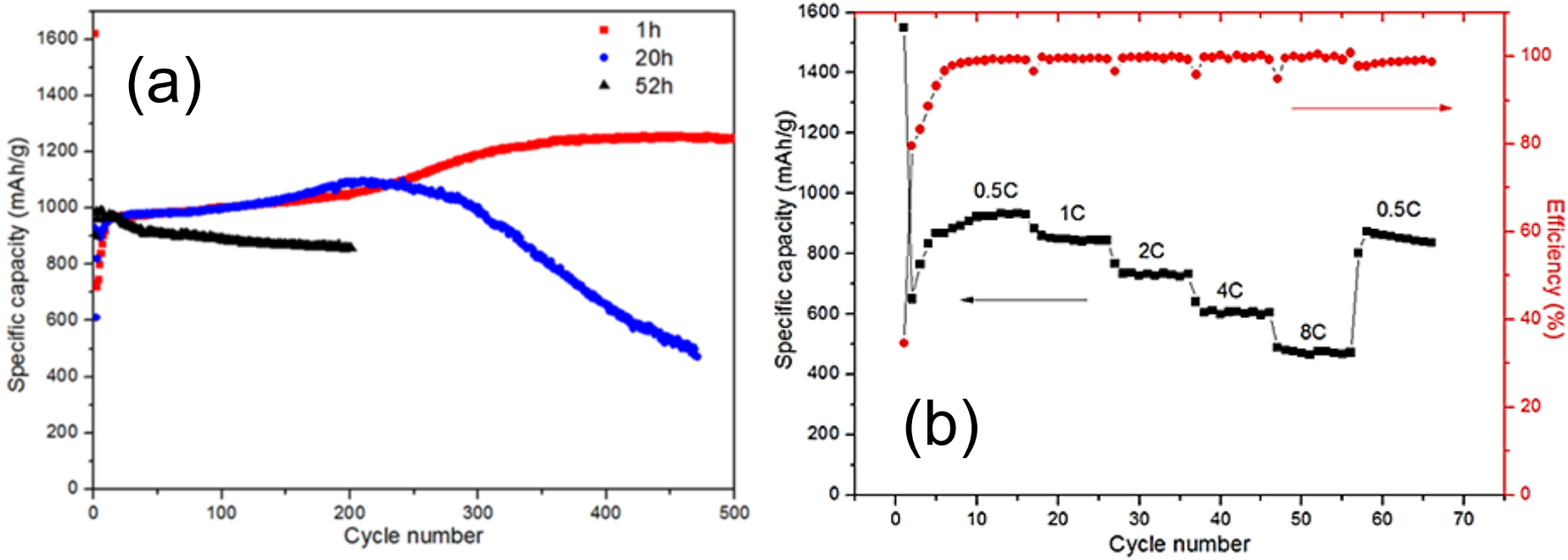


Figure 7. (a) cycling stability and (b) rate performance of Zn_2GeO_4 anode electrode heat-treated for 1h.

- Zn_2GeO_4 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.

Pacific Northwest
NATIONAL LABORATORY

Summary

- Second batch $LiFePO_4/Li_4Ti_5O_{12}$ 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_2FeSiO_4 was synthesized and electrochemically characterized.
- Zn_2GeO_4 anode with specific capacity of ~1,000mAh/g was developed where both the rate and the cycling stability showed promising results.

Pacific Northwest
NATIONAL LABORATORY

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 $LiFePO_4/Li_4Ti_5O_{12}$ chemistry.
- Modify synthesis of $LiMn_{1-x}Fe_xPO_4$, $LiFeBO_3$, and Li_2FeSiO_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.

Pacific Northwest
NATIONAL LABORATORY

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

Pacific Northwest
NATIONAL LABORATORY