Low Cost, Long Cycle Life, Li-ion Batteries for Stationary Applications

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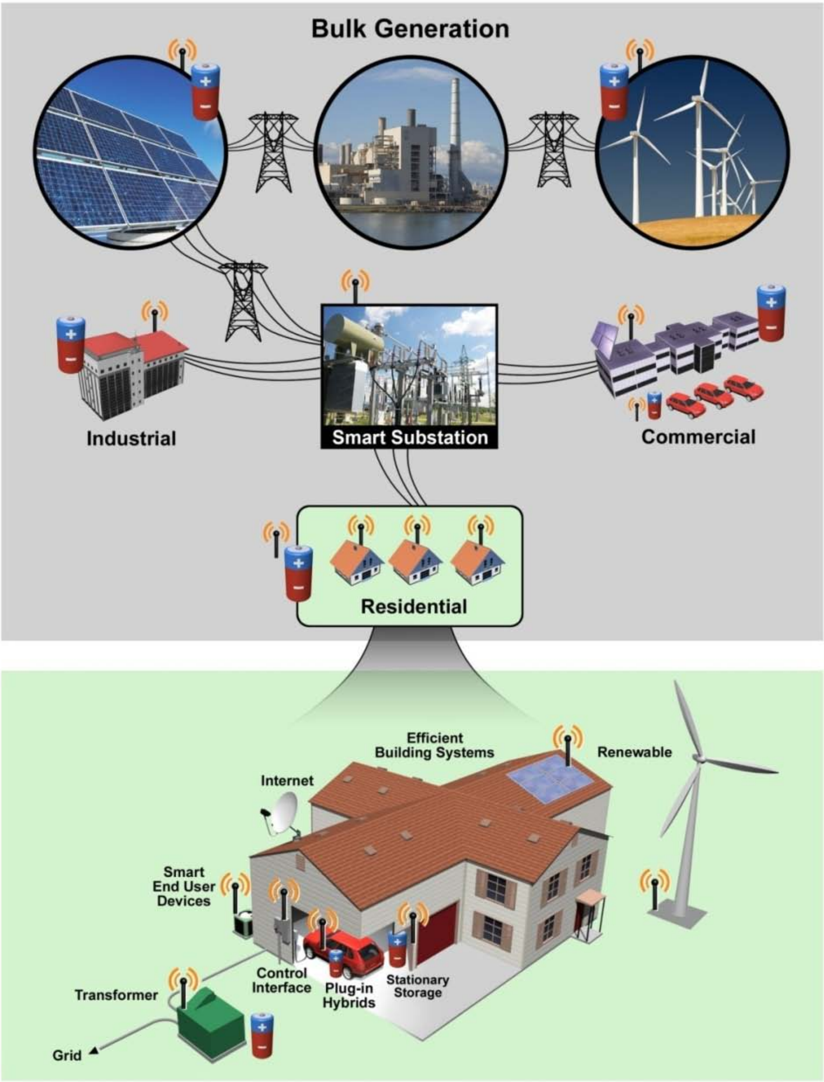
Introduction



- ❑ Investigate the Li-ion battery for stationary energy storage to compliment the renewable energy resources such as solar/ wind power and load leveling for grid integration.
- ❑ Energy storage unit for possible community application ~kWh level.
- ❑ Li-ion battery energy storage with effective thermal management to improve its cycle and calendar life.
- ❑ Design Li-ion battery pack suitable for large scale energy storage system.

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Objectives

- Screen possible electrode materials and its combinations suitable for large scale Li-ion battery.
- Characterization of inherent heat generation of possible electrode candidates and its combinations.
- Cost analyses of the full cell battery per energy density.
- Improve the cycle life of Li-ion battery >1000cycles at 1C rate in coin cell configuration.

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Cost Analyses

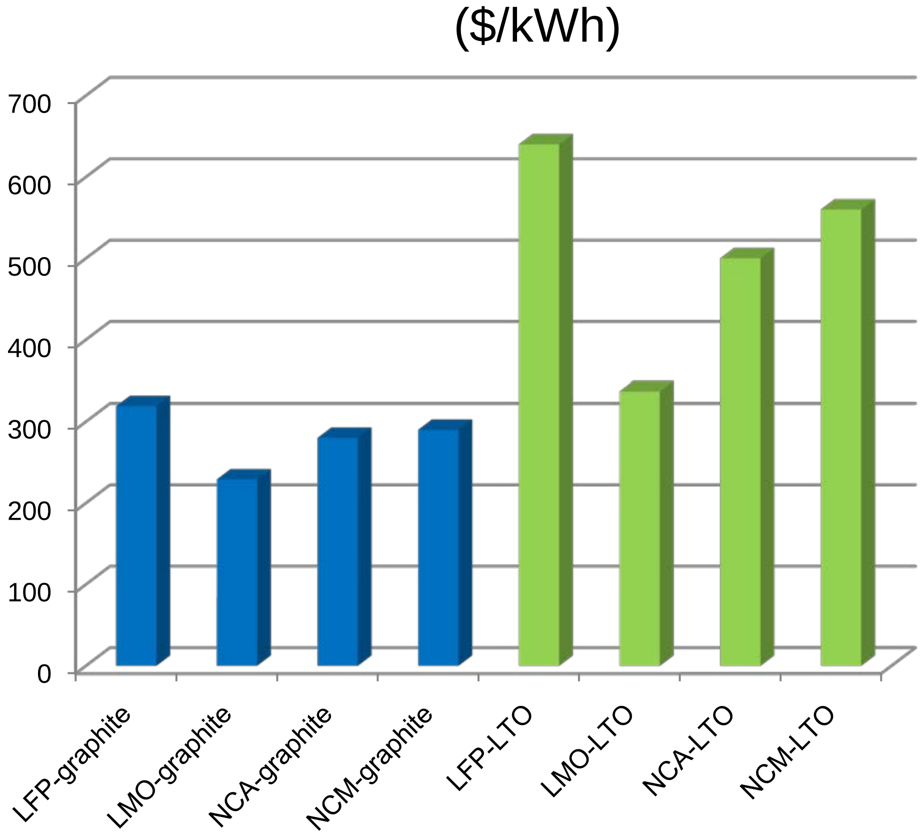

Figure 1. Cost per kWh on various cathode / anode combination Li-ion battery (40kWh).[1-3]

Ref) [1] Entek projected cost
[2] TIAX estimate
[3] Estimate based on numbers provided by Andrew Jansen at ANL

- Based on EV battery configuration.
- $Li_4Ti_5O_{12}$ anode is more expensive due to lower specific capacity 175mAh/g over graphite (372mAh/g).
- $LiFePO_4$ cathode in full cell is slightly expensive due to lower potential 3.45V vs. Li^+/Li.
- Overall cost analyses depends on safety and cycle life of the full cell battery.

- LFP : $LiFePO_4$
- LMO: $LiMn_2O_4$
- NCA: $LiNi_xCo_yAl_zO_2$
- NCM: $LiNi_xCo_yMn_zO_2$
- LTO : $Li_4Ti_5O_{12}$

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Entropy vs. State of Charge (SOC)

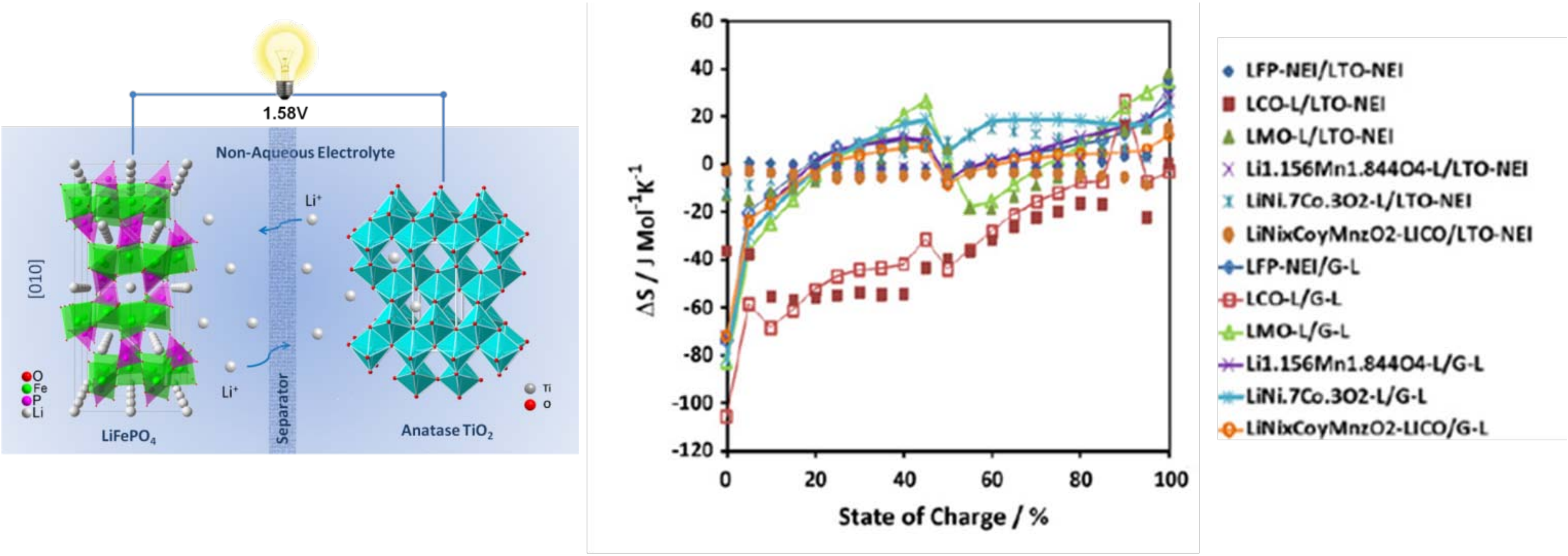

Figure 2. Entropy measurements on various electrode materials vs. state-of-charge (SOC).[1]

- ❑ Entropy changes at various state of charge (SOC) have been screened for selection of various electrode combinations with effective heat management and safety (thermal runaway).

- ❑ $LiFePO_4$ cathode and $Li_4Ti_5O_{12}$ or TiO_2 anode combination show the low internal heat generation, due to minimum crystal structural changes “zero strain” during the Li insertion/extraction.

- ❑ $LiFePO_4$, $Li_4Ti_5O_{12}$ and TiO_2 redox potentials lie within stable window of conventional electrolyte where SEI layer formation is prevented.

Ref) [1] V.V. Viswanathan, D. Choi, D. Wang, W. Xu, S.Towne, R.E. Williford, J.-G. Zhang, J. Liu, Z. Yang, *Journal of Power Sources,*195 (2010) 3720–3729

Entropy Measurements

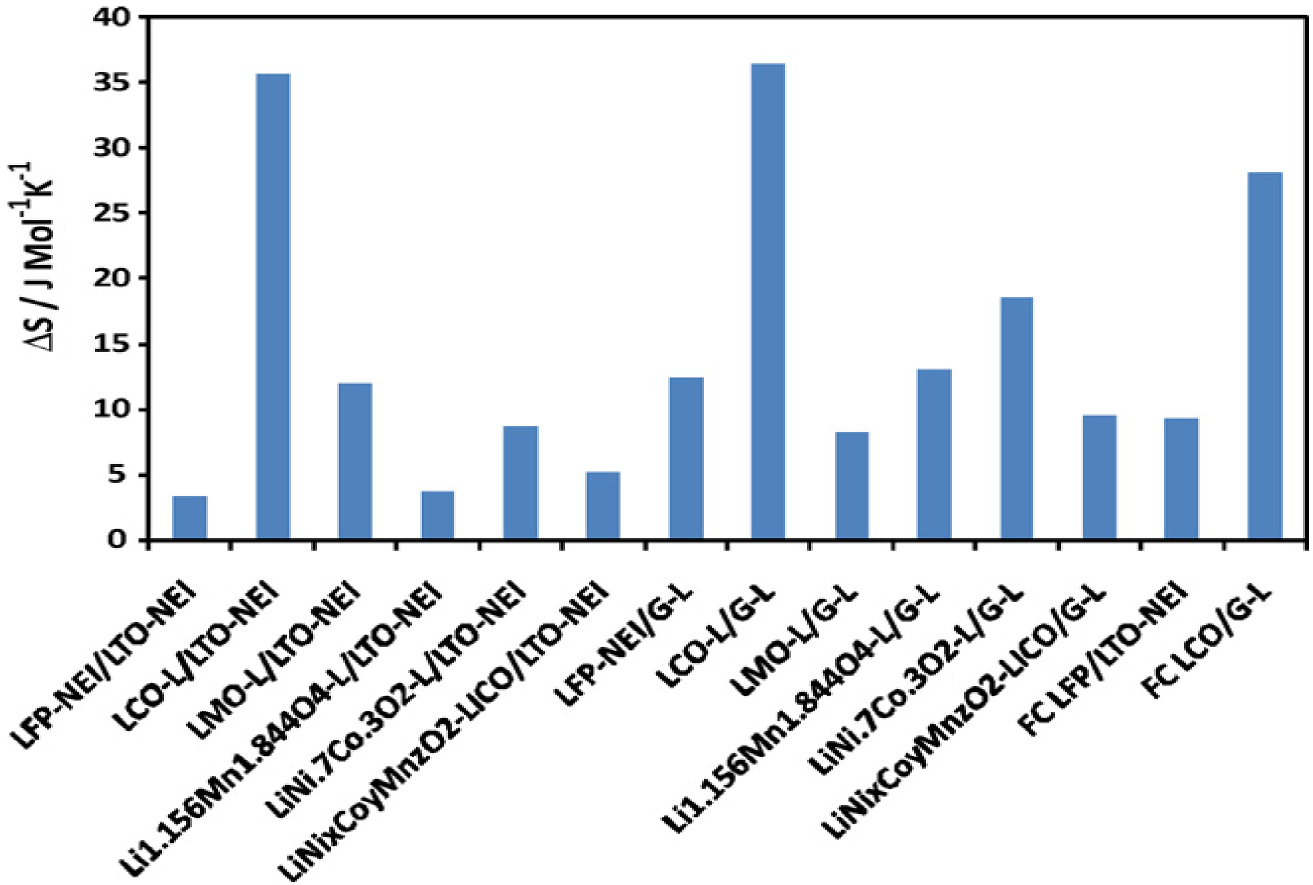

Figure 3. Average of absolute value of computed full cell entropy change over the 0~100% SOC range. FC LFP/LTO-NEI and FC LCO/G-L (last 2 columns) correspond to average of measured entropy change for full cells.

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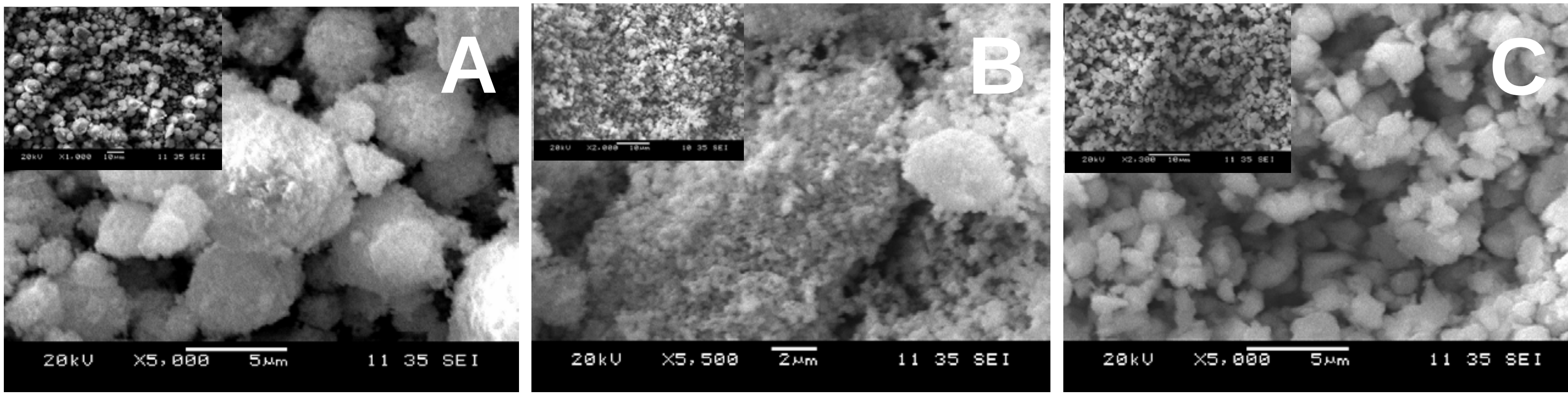
Microstructures of $LiFePO_4$ & $Li_4Ti_5O_{12}$

$Li_4Ti_5O_{12}$



$LiFePO_4$

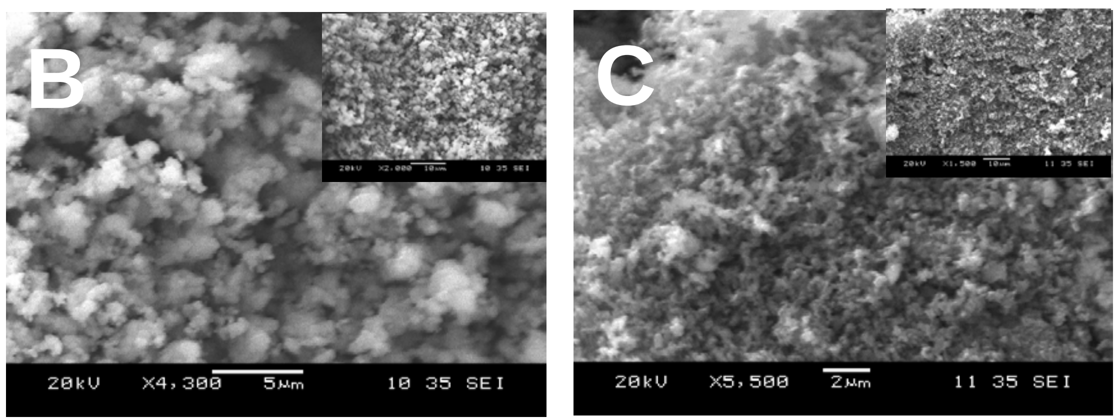


Figure 4. SEM micrographs of $LiFePO_4$ and $Li_4Ti_5O_{12}$ electrode materials from different commercial sources (Company A, B, and C).

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Cathode & Anode Half-Cell Rate Analyses

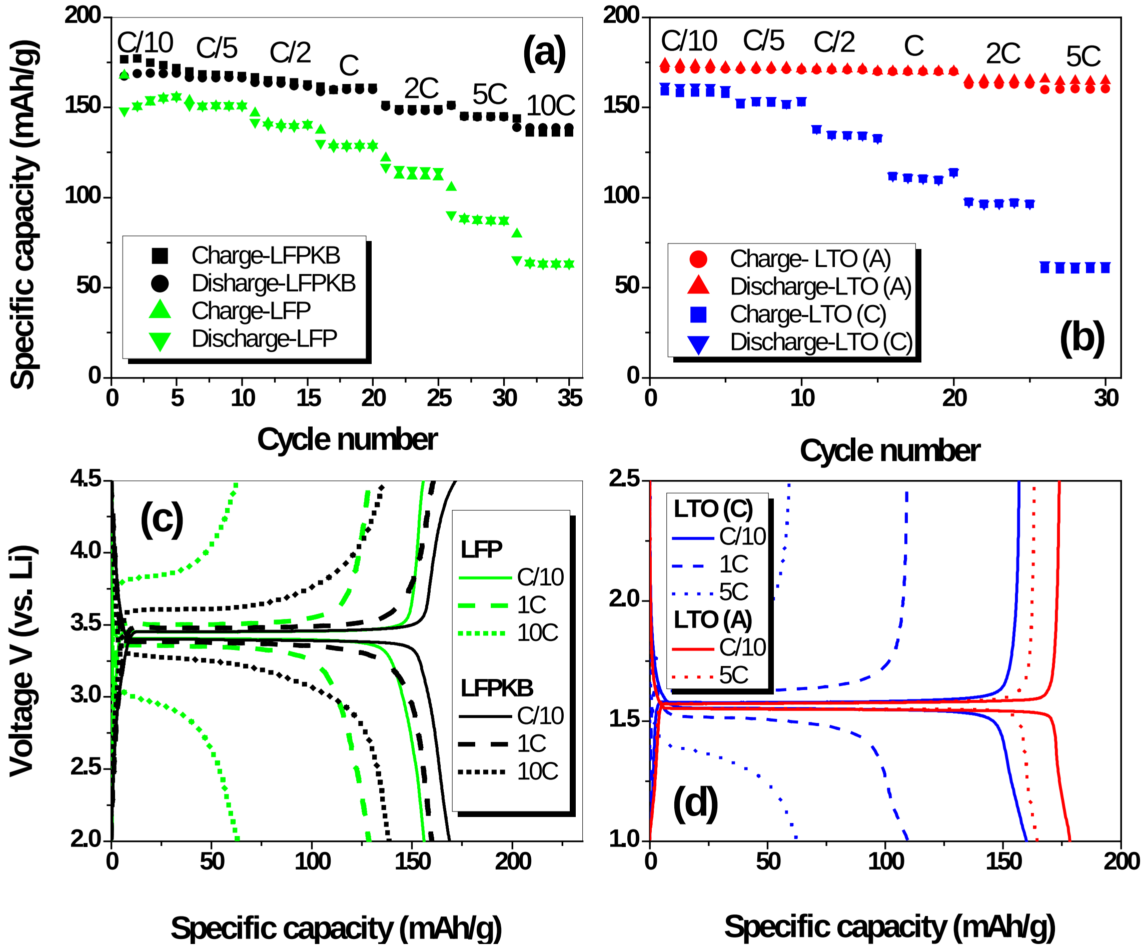

Figure 5. Electrochemical cycling at various C rates (a) $LiFePO_4$ and Ketjen black modified $LiFePO_4$, (b) $Li_4Ti_5O_{12}$ (company A and C) and voltage profiles of charge/discharge at various C rates (c) $LiFePO_4$ and Ketjen black modified $LiFePO_4$, (d) $Li_4Ti_5O_{12}$ (company A and C).

- $LiFePO_4$ from company B and C was similar. $Li_4Ti_5O_{12}$ from company C was not as good as those from company A and B.
- Ketjen Black modified $LiFePO_4$ by milling shows much improved rate performance.
- Effective carbon mixing with electrode material and preparation step is critical for achieving the high rate and cycling stability

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$LiFePO_4$-$Li_4Ti_5O_{12}$ Full Cell Evaluation

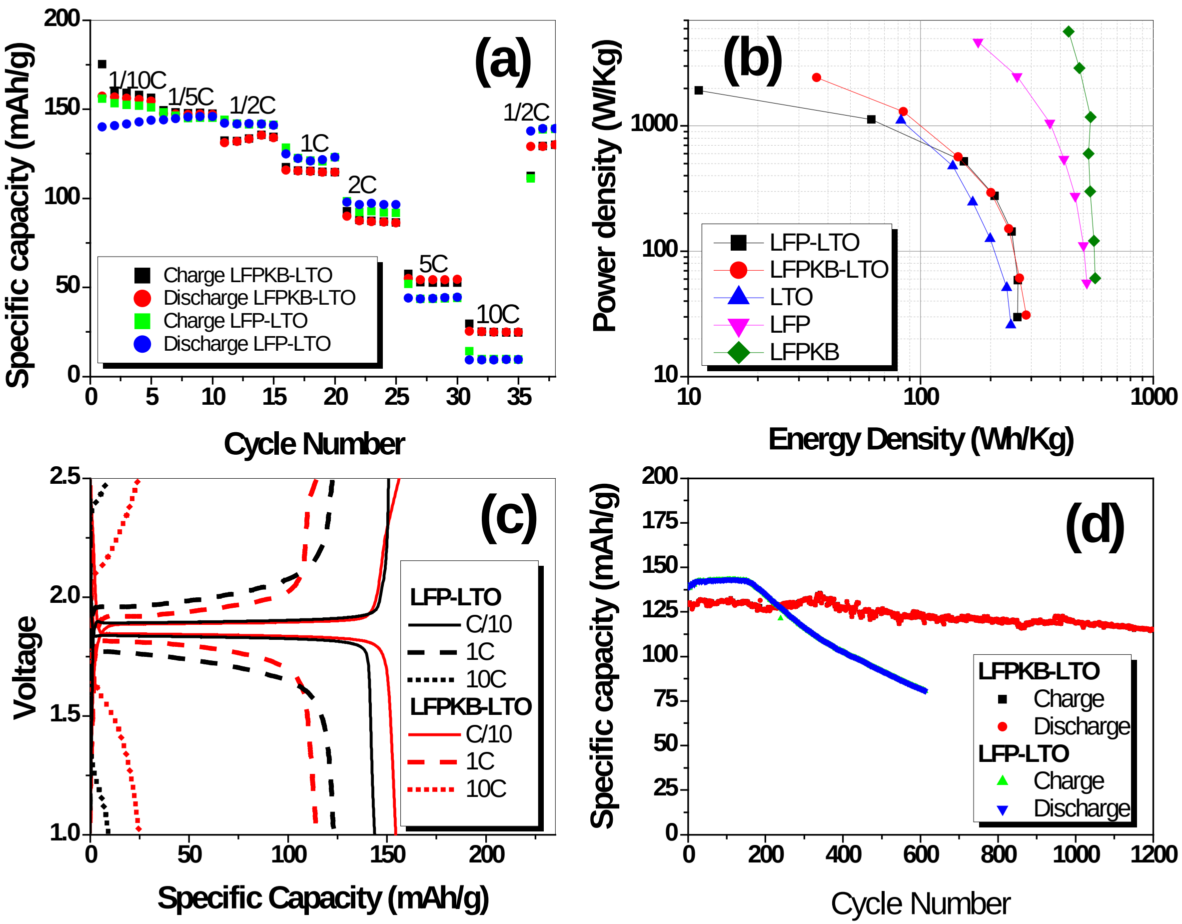

Figure 6. Electrochemical cycling at various C rates of (a) $LiFePO_4$-$Li_4Ti_5O_{12}$ full cell with and without Ketjen black modified $LiFePO_4$, (b) Ragone plot of full cell and half cell, (c) voltage profiles of charge/discharge at various C rates and (d) long term cycling of $LiFePO_4$-$Li_4Ti_5O_{12}$ full cell with and without Ketjen black modification.

- Ketjen Black modified $LiFePO_4$ by milling shows improvement in rate performance.
- Effective carbon mixing with electrode material and electrode preparation is critical for achieving the high rate and cycling stability.
- $LiFePO_4$ cathode plays important role in cycling stability.

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Full Cell Cycling Evaluation

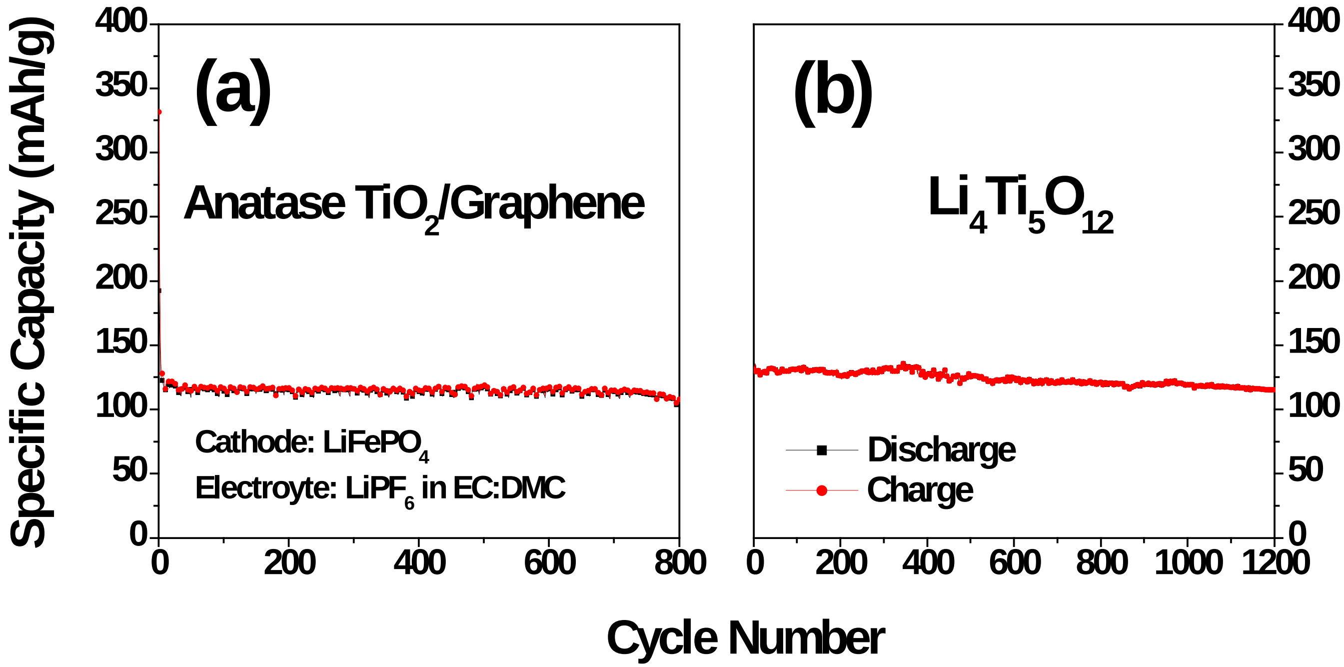

Figure 7. Cycling performance of Li-ion batteries made from $LiFePO_4$ cathode and (a) self-assembled anatase TiO_2/graphene (5wt%) composite anode and (b) $Li_4Ti_5O_{12}$ anode.[1]

- Over 1000cycles without negligible capacity fade have been achieved in coin cell.
- Full cell cycling stability depends on $LiFePO_4$ cathode stability.
- Effective carbon coating on $LiFePO_4$ cathode improves rate and cycle life.

Ref) [1] D. Choi, D. Wang, V. V. Viswanathan, I.-T. Bae, W. Wang, Z. Nie, J.-G. Zhang, G. L. Graff, J. Liu, Z. Yang, T. Duong, *Electrochem. Commun.*12 (2010) 378–381.

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$LiFePO_4$ and $Li_4Ti_5O_{12}$ Half Cell Cycling

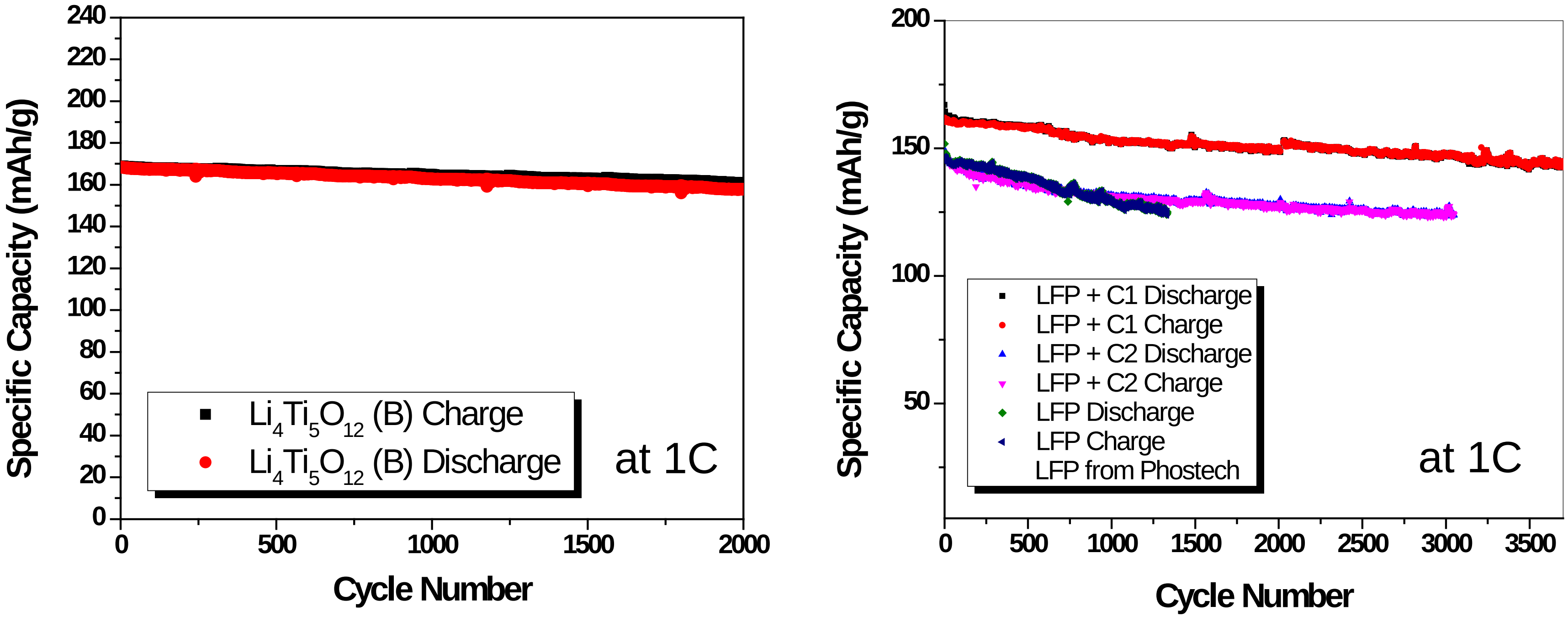

Figure 8. Electrochemical cycling of $Li_4Ti_5O_{12}$ and $LiFePO_4$ cathode with various carbon (C1, C2 and super P) additives (10wt%).

- $LiFePO_4$ cathode plays important role in cycling stability.
- Optimized cycling of $LiFePO_4$ cathode using different conductive carbon.
- On going test (>3500 cycles).

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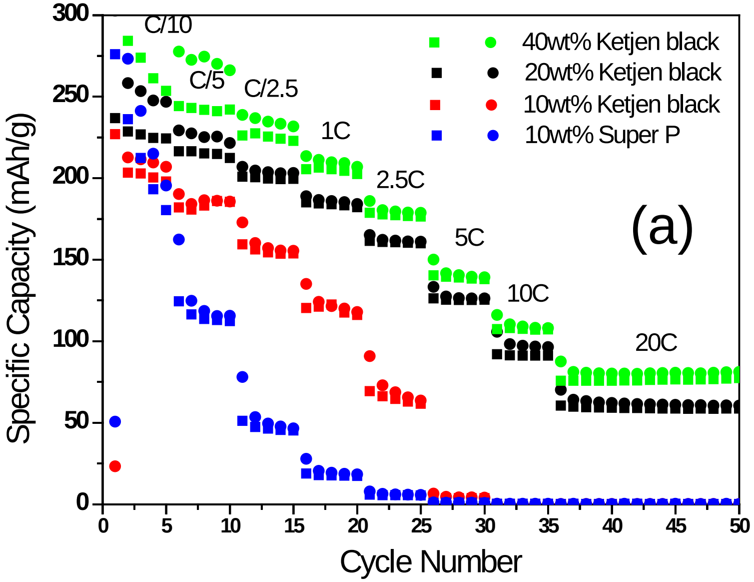
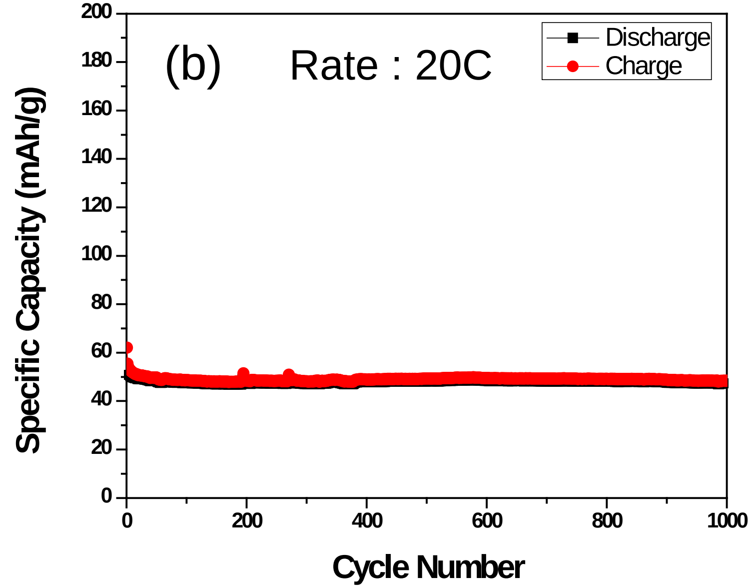
Commercial anatase TiO_2 Anode





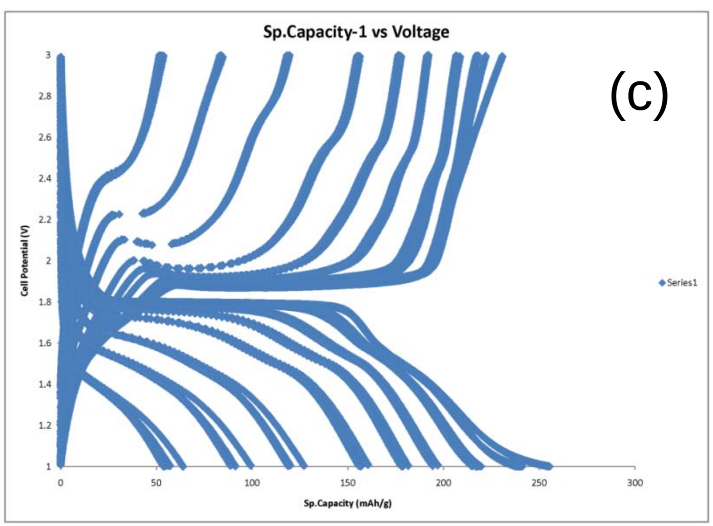


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Figure 9. Electrochemical rate test on (a) Ketjen black modified anatase TiO_2 (b) extended cycling at 20C and (c) voltage profiles at various C-rates.

- Cheapest anatase TiO_2 commercially available have been tested for anode.
- Working to improve the rate performance through effective carbon mixing.
- Cycling stability is excellent.

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Summary

- Various electrode materials have been tested for entropy (reversible heat) measurements. $LiFePO_4/Li_4Ti_5O_{12}$ cathode/anode combination is suitable Li-ion battery for stationary energy storage.

- Cost comparison on different electrode material combinations show ~$600/kWh for $LiFePO_4/Li_4Ti_5O_{12}$ but life cycle cost ($/kWh/cycle) plus safety is expected to be competitive over other combinations.

- Rate and cycling tests were performed on half and full cell and electrodes are being further optimized. Cathode using $LiFePO_4$ is critical for stable cycling.

- Cycling performance of >1000cycles at 1C rate was achieved at R.T.

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Future Tasks

- Enhance cycling stability >1000 cycles of $LiFePO_4$ using cheaper route.
- Fabrication and testing of 18650 cell using $LiFePO_4$ / $Li_4Ti_5O_{12}$ combination electrodes.
- Calorimetric analyses of 18650 cell for total heat-generation.
- Cost analysis on 18650 cell with cost per cycle will be reported.

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