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

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Abstract

Lithium-ion batteries have witnessed significant advancement the last two decades. However, despite their tremendous commercial success as power source for consumer electronic devices, in recent years, there is increasing interest in developing high energy and power rechargeable lithium-ion system for large scale electrochemical energy storage for intermittent renewable power sources, such as solar cell and wind mill plant [1,2]. Unlike portable and vehicle applications, cycling stability and cost, along with safety, are more of importance for stationary energy storage as the requirement of weight and space is less stringent [1,2]. Recently, different combinations of positive and negative materials have been investigated for full cell performance, such as TiO_2, $Li_4Ti_5O_{12}$ [2-4]. In our study, olivine type $LiMPO_4$ (M: Fe or Mn) cathode will be paired with titanium oxide based anode using some of the commercially available materials with and without surface modification and carbon mixing.

Keywords: Olivine, Li-ion battery, electrochemical energy storage, renewable power sources, stationary energy storage

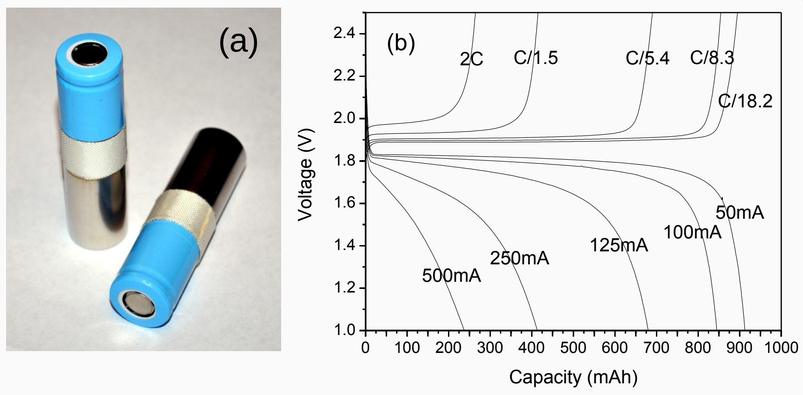


FIGURE 1 (a) $LiFePO_4/Li_4Ti_5O_{12}$ 18650 cell made in collaboration with K2 Energy Solutions+ and (b) voltage-capacity profile at various rates of the battery..

- First batch 18650 cell fabricate with commercially available cathode and anode materials
- Theoretical capacity: 1,150mAh

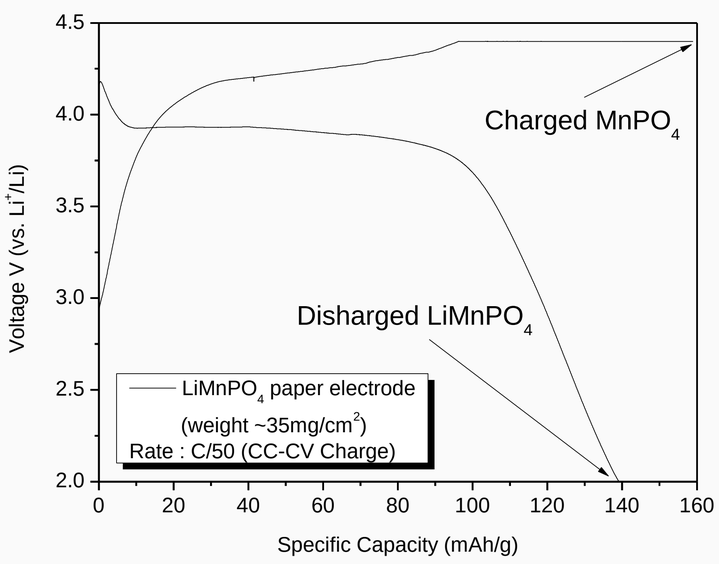


FIGURE 2. Charge/discharge voltage profiles of $LiMnPO_4$ nanoplate paper electrode at room temperature.

- Paper $LiMnPO_4$ electrodes were used for thermal stability study.

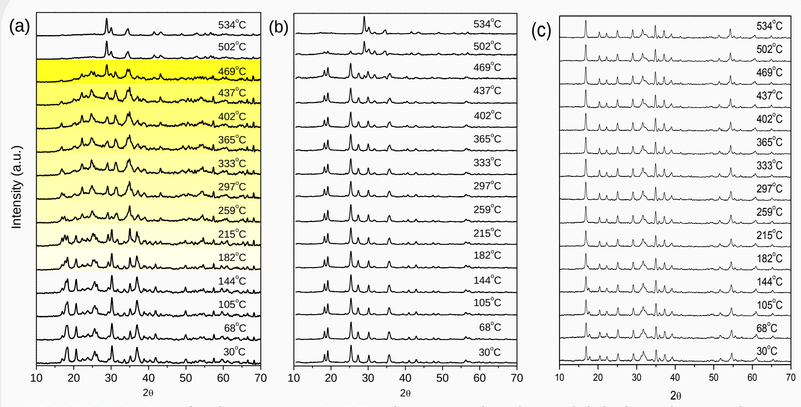


FIGURE 3. *In-situ* hot-stage XRD characterization of (a) the charged $MnPO_4$ electrode, (b) the $MnPO_4 \cdot H_2O$ powder and (c) discharged $LiMnPO_4$ under UHP-Ar atmosphere (degree of deformation, heating rate : 5°C/min).

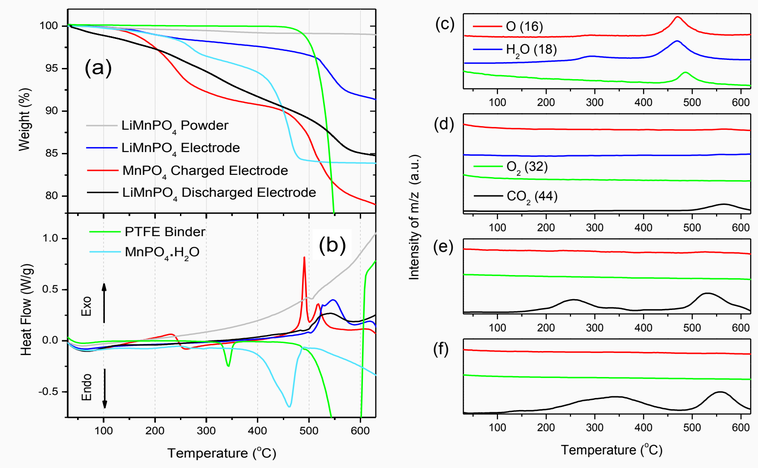
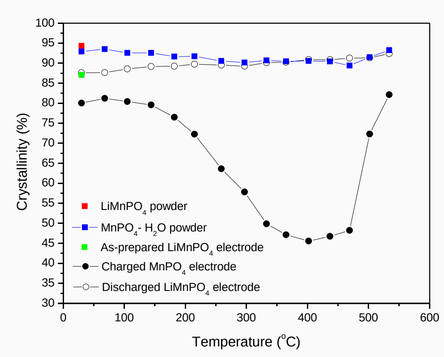


FIGURE 4. (a,b) TGA-DSC analyses and mass spectrometer signal of m/z versus temperature (c) $MnPO_4 \cdot H_2O$, (d) as-prepared $LiMnPO_4$ electrode, (e) charged $MnPO_4$ electrode and (f) discharged $LiMnPO_4$ electrode under UHP-Ar atmosphere (heating rate: 5°C/min).



- Crystallinity of the charged $MnPO_4$ start to decrease above 150°C but increased when reduced to $Mn_2P_2O_7$ above 490°C
- Overall reaction as follows:

FIGURE 5. Crystallinity of the samples calculation based on *in-situ* hot-stage XRD patterns.

$$MnPO_4 \cdot H_2O \xrightarrow{\sim 300^oC} MnPO_4 \cdot \frac{2}{3}H_2O + \frac{1}{3}H_2O\uparrow \xrightarrow{470\sim490^oC} \frac{1}{2}Mn_2P_2O_7 + \frac{2}{3}H_2O\uparrow + \frac{1}{4}O_2\uparrow$$

$$MnPO_4 \xrightarrow{150\sim180^oC} MnPO_4 \xrightarrow{490^oC} \frac{1}{2}Mn_2P_2O_7 + \frac{1}{4}O_2\uparrow$$

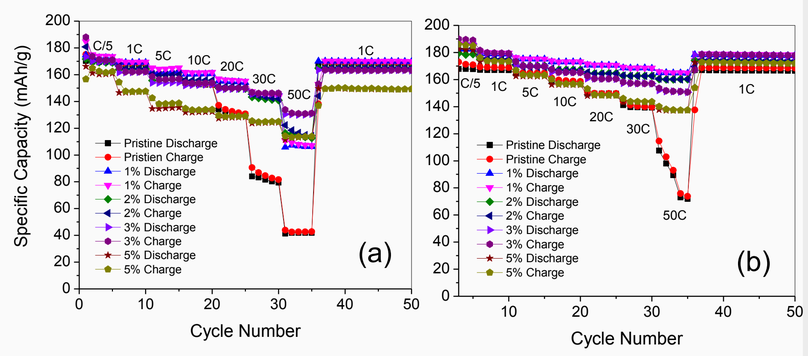
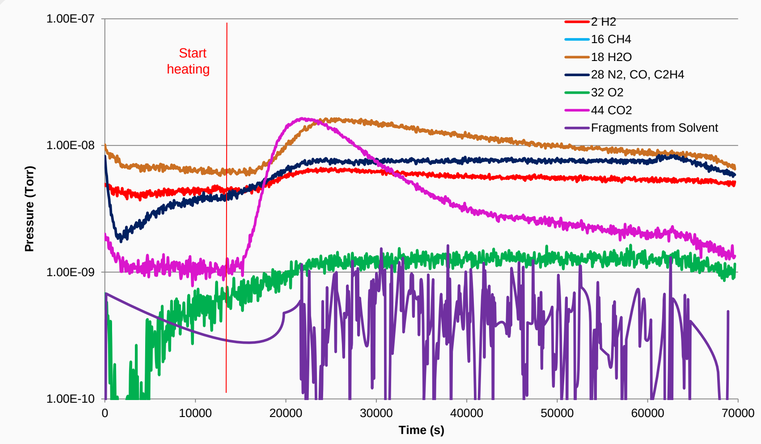


FIGURE 6. Electrochemical performance at various rates of the surface modified $Li_4Ti_5O_{12}$ anode at (a) 25°C and (b) 55°C (Super P 10wt%).

- 1~3wt% coated $Li_4Ti_5O_{12}$ shows enhanced rate performance at 25°C and 55°C



Gases (mass)	2	4	15	16	18	28	29	31	32	40	44	45	59	60	SUM
Cum mL out	0.19	0.00	0.01	0.03	0.64	0.45	0.03	0.01	0.08	-1.93	0.48	0.02	0.00	0.00	1.95
Cont. mL	0.01	0.00	0.00	0.00	0.01	0.03	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.08
Total	0.20	0.00	0.01	0.03	0.65	0.48	0.03	0.02	0.09	-2.01	0.48	0.02	0.01	0.00	2.03

Gases	Mass values	mL out
Water	18	0.65
Hydrogen	2	0.20
Carbon Dioxide	44+28+16 (see right)	0.58
$N_2/CO/C_2H_4$	28 (minus CO_2)	0.43
Oxygen	32 (see right)	0.10
Carbonates	60+59+45+31+29+15	0.09

Gas	%	Mass	mL
CO_2	78.4	44	0.48
	8.6	28	0.05
	7	16	0.04
O_2	89.4	32	0.09
	10.2	16	0.01

FIGURE 7. Mass spectroscopy analysis on the gas produced with EC electrolyte at charged $Li_4Ti_5O_{12}$ electrode.

Conclusion

- 18650 cell based on $LiFePO_4/Li_4Ti_5O_{12}$ electrodes was fabricated and tested. Further optimization and improvement in rate is underway.
- $LiMnPO_4$ cathode is thermally stable as $LiFePO_4$ with higher potential of 4.1V vs. Li/Li^+.
- Surface modified $Li_4Ti_5O_{12}$ shows much improved rate performance at 25°C and 55°C.
- Electrolyte stability and gassing with charged $Li_4Ti_5O_{12}$ anode is like due to the moisture level in the electrolyte and the electrode.

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