Advanced Phosphate Cathodes at SAFT

Jacob Nykaza, Xilin Chen, Thomas A. Greszler
Saft America, Space and Defense Division
107 Beaver Court, Cockeysville, MD 21030
Jacob.Nykaza@saft.com / 1-410-568-0057

Abstract

Saft has successfully applied Li-ion electrochemistry to defense, space, and commercial applications which require very high power and safety. By optimizing both the electrochemical and electro-mechanical cell design, Saft has developed a range of Li-ion products that can deliver over 50 kW/kg of power for a fraction of a second for joint strike fighter or racing application or >250 Wh/kg for applications requiring high energy content. This paper presents research and development efforts of advanced Li-ion electrochemistry at Saft. In particular, advanced phosphates cathodes such as LMFP are developed for PHEV2 and military BB-2590s with high safety and improved electrochemical performance. Furthermore, tavorite structure LVPF chemistries to further improved energy density are under development.

Keywords

High Energy; High Safety; LMFP, LVPF, Solid-State Battery

Introduction

Saft has been manufacturing Li-ion batteries for more than 30 years and is a world leader in providing state-of-the-art Li-ion systems for demanding applications in commercial, defense and space markets. Our products have evolved to match the requirements of the market with a focus on high performance over a wide temperature range, long life, high quality and reliability, and rugged systems that can operate in uncontrolled and abusive environments. Saft continues to improve current Li-ion batteries and develop next-generation energy storage devices. Here, we highlight the results and status of Saft's research and development efforts on safe Li-ion based on phosphate LMFP and LVPF cathodes and beyond Li-ion batteries.

LMFP Cathode Chemistry

Saft has investigated the use of advanced-phosphates such as high voltage olivine structured Lithium Manganese Iron Phosphate ($LiMnFePO_4$; LMFP) as a replacement to traditional Lithium Nickel Manganese Cobalt Oxide ($LiNiMnCoO_2$; NMC) and the lower voltage olivine structured Lithium Iron Phosphate ($LiFePO_4$; LFP) for over 10 years. The higher operating voltage of LMFP, shown in Figure 1, increases the energy density significantly (15-20%) compared to existing LFP chemistry while maintaining LFP's excellent safety, performance, and cost. [1-2]. Along with dramatically improved safety, these advanced phosphate chemistries also have additional benefits compared to NMC materials including constant power throughout discharge, reduced cost and easier supply chain due to no cobalt or nickel as shown in the spider chart in Figure 2.

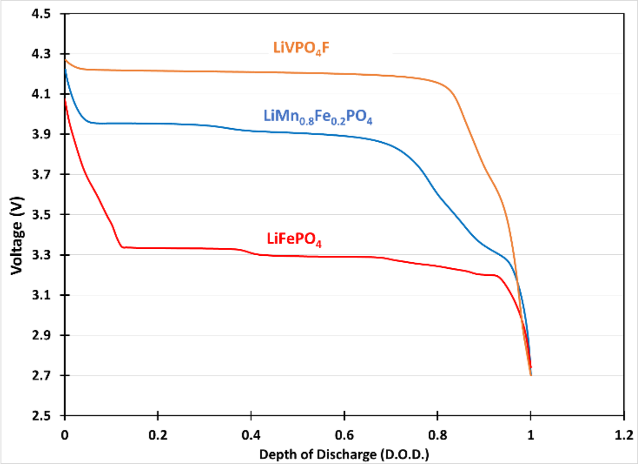

Figure 1. Voltage Profiles of LFP, LMFP, and LVPF

The increased energy and safety make LMFP chemistry attractive to various defense, aerospace, and industrial applications. Examples include military batteries like BB-2590 and CWB or 28V aviation batteries. Drawbacks to commercialize LMFP technology lies in i) poor ionic/electronic conductivity, ii) poor cycle life due in part to distortion of Jahn-Teller active Mn^{3+} ion and transition metal dissolution. Saft has improved the electrochemistry especially in rate capability, cycle life and manufacturing/process quality by optimization of electrode formulation and choice of suitable anode materials. Cells with different form factors (cylindrical, hard case prismatic, and pouch) were assembled and evaluated for different applications. [3]

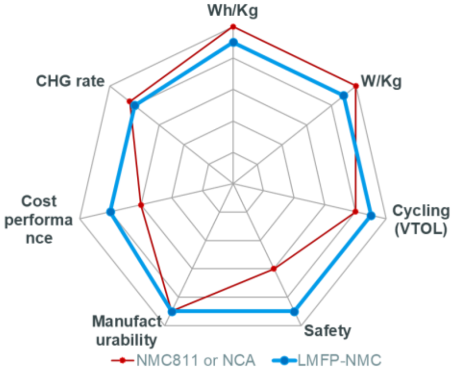

Figure 2. Spider chart comparing NMC811 to LMFP

Figure 3 summaries progress made in a 35 Ah PHEV2 size cell with LMFP cathode for both cycle life and rate capacity. The cells cycle over 3000 cycles at C/2 rate to greater than 80% capacity. The cells also have exceptional rate capability with less than 5% loss at 2C.

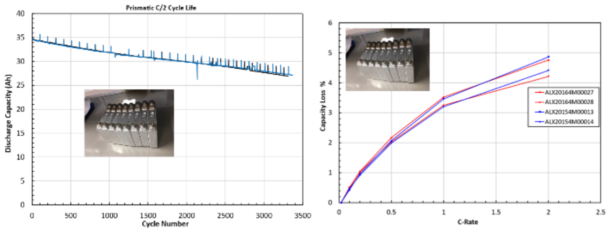

Figure 3. Cycle life and rate capability of 35 Ah PHEV2 cells with LMFP cathode.

As mentioned, the safety of LMFP cathodes is one of the main benefits due to its olivine-structure. Figure 4 reports the nail penetration of two 35 Ah PHEV2 cells. The cells meet the target of no fire, no explosion, and T < 450 °C with a EUCAR 3 and no propagation to neighboring cell in the battery pack.

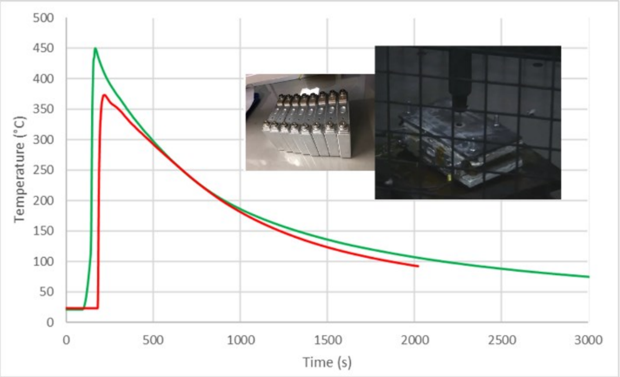

Figure 4. Nail penetration of a 35 Ah PHEV2 cell with LMFP cathode.

Saft has started to use LMFP cathodes for military batteries (i.e., BB-2590s, x6Ts, ect) along with our commercial applications. An ongoing funded program is development of a Solid-State polymer battery for BB-2590 for the Defense Logistic Agency. The program initially focused on high Ni content cathodes but these were determined, even with semi-solid-state electrolyte, to be too reactive in abuse conditions. Saft is committed to the safety of our warfighters and switched to advanced-phosphates in 2022. The program replaced the 24x 18650 commercial cells with 8x custom Saft designed pouch cells as shown in Figure 5.

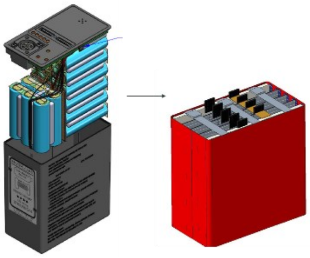

Figure 5. Example of replacing 18650s with pouch cells for a BB-2590

To further increase safety, Saft's in-situ polymerized gel polymer electrolyte was incorporated as shown in Figure 6. This process allows Saft to use traditional Li-ion cell fabrication processes but enables polymer gelation throughout the cell.

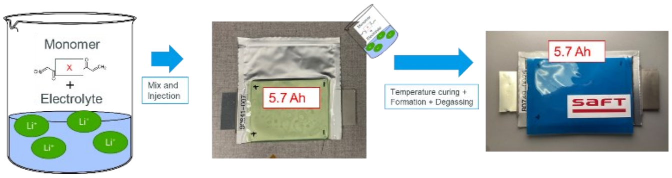

Figure 6. Example of Saft's semi-solid state chemistry design.

The final deliverable cells have an energy density ~205 Wh/kg and meet or exceed all safety requirements of MIL-PRF-32383/3 including overcharge, short circuit, forced discharge, nail penetration, and crush. Specifically, for nail penetration, cells were tested at 4.2 V, 100% state of charge, where a nail was inserted into the cell. The maximum temperature was < 170 °C with no fire/flame upon abuse and <1wt% weight loss resulting on Hazard Level 3. Figure 7 shows the setup and BB-2590 pouch cell after nail penetration tests. A metal oxide-based pouch cell is also shown with a very energetic results.

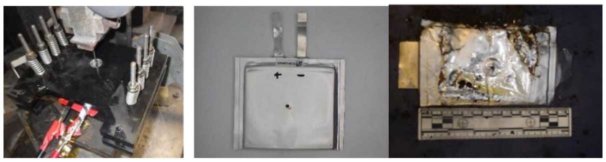

Figure 7. Nail penetration results of SAFT BB-2590 LMFP cell with semi-solid state gel polymer electrolyte (left) compared to an NMC based cell (right)

The cells with the semi-solid state gel polymer electrolyte are on pace to meet or exceed the MIL-PRF specification for cycle life and initial results show an improvement over pure liquid electrolyte as shown in Figure 8.

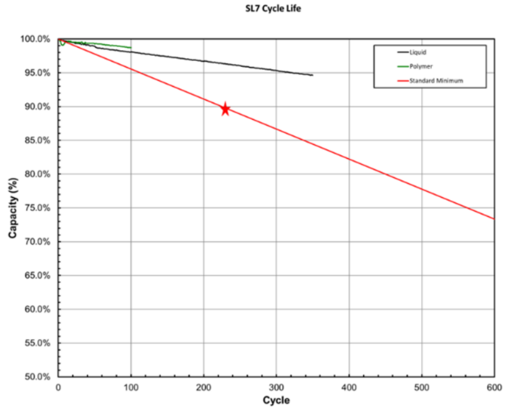

Figure 8. BB-2590 cells on cycle life.

While the program was a success at providing a very safe cell for the BB-2590, there are still areas that need improvement in future work including low temperature performance and increasing the energy density while maintaining the safety.

LVPF Cathode Chemistry

LiVPO$_4$F is expected to be an intrinsically safer cathode material than other available cathodes such as Lithium Cobalt Oxide (LCO), Nickel Cobalt Aluminum Oxide (NCA), and Nickel Manganese Cobalt Oxide (NMC) because of the presence of PO$_4$ group (as show in Figure 9) in its tavorite structure, which is similar to lithium iron phosphate. In addition, LiVPO$_4$F has a higher energy density than LiFePO$_4$ due to the higher lithiation/delithiation potential (4.2V) than that of (3.4V) LiFePO$_4$ as shown in Figure 1. LiVPO$_4$F is expected to have excellent cycle life like other phosphate cathodes, which may lead to overall lower battery lifetime cost, compared to other chemistries with much shorter life.

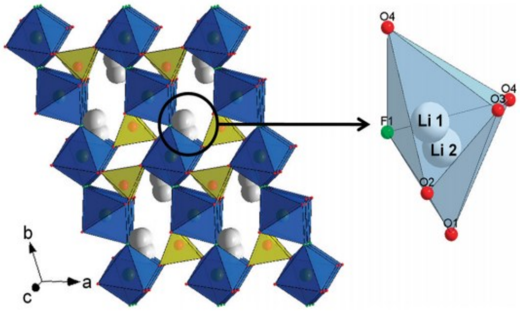

Figure 9. Pictorial representation of the structures of LiVPO$_4$F with a close-up view of the split lithium position. The vanadium octahedra are shown in blue, phosphate tetrahedra are shown in yellow, and the Li atoms are shown in white.[4]

Saft's preliminary results of LiVPO$_4$F/Graphite cells demonstrated that the cells can deliver comparable energy density, better safety and rate performance than that of NMC/graphite cells. The safety of LiVPO$_4$F/Graphite cells is comparable to lithium iron phosphate chemistry. LiVPO$_4$F delivers 142mAh/g, 91% of theoretical capacity (155 mAh/g) [5] at 4.2V, corresponding to an energy density of 596Wh/kg (theoretical energy density 651Wh/kg). The achieved energy density of LiVPO$_4$F/Graphite cells is comparable to 608 Wh/kg for LCO and is higher than 577 Wh/kg for NMC111, 574 Wh/kg for NCA, and much higher than 531 Wh/kg for LFP. In addition, the tavorite structure of LVPF overcomes the 1D ion conductivity challenge in other phosphates (i.e. lithium ion phosphate) with olivine structures and thus exhibits high ionic conductivity. [3]

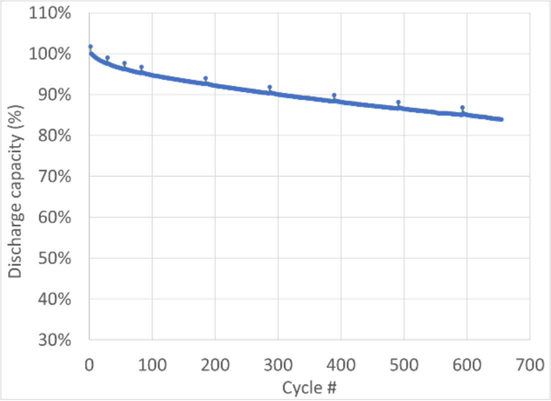

Figure 10. Cycling performance of a 4Ah LVPF/Gr cell

Figure 10 shows the preliminary cycling performance of a 4Ah LVPF/Gr pouch cell, which delivers 84% of initial capacity after 655 cycles. The rate capability of 4Ah LVPF/Graphite pouch cells is tested under different temperatures. The tests were completed for 25 °C, 0 °C and -20 °C. As shown in **Table 1**, the cells delivered a great rate capability at 25 °C, 98% capacity at 1C, 95% capacity at 2C and 74% at 5C. At 0 °C, the cell delivered 84% capacity at 1C and 61% at 2C. At negative 20 °C, the rate capability is still decent at C/2, 63% of capacity at C/10 rate.

In prelimnary abuse tests (i.e., Nail penetration, overcharge, short-circuit), the LVPF/Gr cells achieve EUCAR 2-3 ratings.

Acknowledgements

The LMFP and semi-solid state gel polymer electrolyte was sponsored by the Defense Logistic Agency under Contract Number SP-4701-20-C-0026

The LVPF Research was sponsored by the Army Research Laboratory and was accomplished under Cooperative Agreement Numbers of W911NF-20-2-0284 and W911NF-22-2-0021.

References

1. Zhao, X., An, L., Sun, J., and Liang, G., "LiNiCo0.2Mn0.3O2-LiMn0.6Fe0.4PO4 Mixture with Both Excellent Electrochemical Performance and Low Cost as Cathode Material for Power Lithium Ion Batteries," *J. Electrochem Soc*. Vol. 165(2), pp. A142-A148, 2018
2. Zhang, X., Hou, M., Tamirate, A. G., Zhu, H., Wang, C., and Xia, Y., "Carbon coated nano-sized $LiMn_{0.8}Fe_{0.2}PO_4$ porous microsphere cathode material for Li-ion batteries," *J. Power Sources*, Vol 448, no. 1, pp. 227438, 2020
3. Huang, W., Hu, J., Yang, L., Zhao, W., Wang, Z., Wang, H., Guo, Z., Li, Y., Liu, J., Yang, K., and Pan, F., "Revealing the degradation mechanism of $LiMn_xFe_{1-x}PO_4$ by single particle electrochemistry method," *ACS Applied Mat. & Int.,* vol. 11, no. 1, pp. 957-962, 2019
4. Ellis, B. L., Ramesh, T. N., Davis, L. J. M., Goward, G. and Nazar, L. F., "Structure and Electrochemistry of Two-Electron Redox Couples in Lithium Metal Fluorophosphates Based on the Tavorite Structure", *Chemistry of Materials*, vol. 23, pp. 5138-5148, 2011
5. Barker, J. Saidi, M. Y., Swoyer, J. L. "Electrochemical Insertion Properties of the Novel Lithium Vanadium Fluorophosphate, $LiVPO_4F$," *J. Electrochem. Soc.,* vol. 150, pp. A1394, 2003

Table 1. Rate capability of 4Ah LVPF /Graphite pouch cells

	25°C		0°C		– 20°C	
	Discharge Capacity (Ah)	**Discharge (% C/10)**	**Discharge Capacity (Ah)**	**Discharge (% C/10)**	**Discharge Capacity (Ah)**	**Discharge (% C/10)**
C/10	4.20	100%	3.89	93%	3.74	89%
C/2	4.16	99%	3.78	90%	2.66	63%
1C	4.10	98%	3.53	84%	1.46	35%
2C	4.00	95%	2.55	61%	0.16	4%
5C	3.11	74%	0.47	11%	N/A	N/A