

VSPC High-Power Nano-Phosphate Material with Improved Adhesion

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Abstract

Nano-architecture is crucial for the high rate intercalation of lithium ions in Li_xFePO_4 particles. VSPC produces truly nano-scale primary particles in a low cost production process that is amenable to scale up. Adherence of positive electrode loadings composed of such particles to aluminium current collectors is challenging. A simple and extremely effective adhesion additive has been recently developed by VSPC. The results demonstrate that the adhesion additive coupled with an optimised drying routine lead to excellent adhesion. Furthermore, the adhesion additive has been proven to be compatible with conductive graphite in positive electrode loadings. Finally, cycle life testing in rocking-chair format coin cells demonstrated that the adhesion additive is compatible with commercial graphite negative electrode material. VSPC LFP material has excellent rate capability at low carbon loadings.

Introduction

The high energy and power density requirements of the new generation of HEV, PHEV and EV vehicles for the mass market need lithium-ion batteries that are inexpensive to manufacture and have low cost raw materials. Materials with the requisite nano-architecture¹ for high rate intercalation of lithium ions are normally only available in the laboratory at great expense using processes that are not amenable to scale-up, and although there are industrial 'nano-materials' available they are really only just sub-micron in character and lack the performance characteristics.

VSPC produces truly nano-scale primary particles agglomerated into processable micron sized positive electrode powders on the industrial scale (see Figure 1). The chemistry of choice is Lithium Iron Phosphate, LiFePO_4 (LFP), which has inexpensive pre-cursors, is safe, environmentally benign, and easily manufactured using VSPC's patented² low cost production process.

In working with battery manufacturers to improve processability, VSPC has developed and patented³ a simple and

extremely effective adhesion additive that can be extended to other chemistries beyond the LFP family. The impact and effectiveness of this additive is investigated in this article.

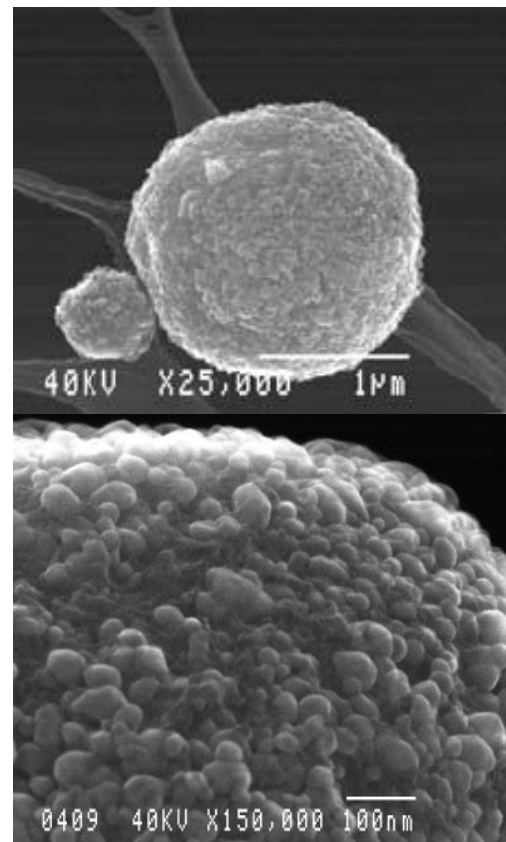


Figure 1 SEM images of VSPC process-adjustable agglomerates (1 - 20µm) and primary particle size (10 - 400nm)

Experimental

Preparation of positive electrode foils

Positive electrode foils were prepared by following the VSPC standard operating procedure. Two sets of foils, with or without the addition of 5 wt.% conductive graphite (Timcal), were prepared by mixing LFP powder (85 or 90 wt.%; VSPC; d_{50} 5.7 μ m, 36.4m²/g) with PVDF (5 wt.%; Kynar HSV 900), Super P-Li conductive carbon black (5 wt.%; Timcal) and NMP solvent (99.5% Merck). To test the effectiveness of the adhesion additive, a small volume (1.74 wt.% of the total slurry mix) of the VSPC patented solution was added to half of the prepared slurries. The electrodes were prepared by casting (doctor blade) the mixture onto an aluminium foil (current collector) and dried in a temperature-controlled oven with continuous ventilation. Previous internal testing has shown that the method for drying the cast foils, in particular the initial evaporation rate of NMP, is critical for obtaining good adhesion. The temperature was ramped from 40°C to 120°C over a period of 40 minutes, followed by another 60 minutes at 120°C. The total drying time was 100 minutes. Following drying, the foils were calendered down to the target thickness, porosity and loading density (see Table 1). Positive electrodes (ϕ 16mm) and separators (ϕ 20mm; Celgard 2325) were cut out (Hohsen). The positive electrodes and coin cell components (2032; Hohsen) were vacuum dried for 12hrs at 120°C prior to cell assembly inside a glove box (MBraun).

Table 1 Positive electrode morphologies for tests with (85:5:5:5) and without (90:5:5) conductive graphite

	loading [mg/cm ²]	loading density [g/cm ³]	loading thickness [μ m]
1*	7.9	1.8	44
2**	7.8	1.7	45

*90:5:5 slurry mix; **85:5:5:5 slurry mix

Coin cell measurements vs. lithium foil

Coin cells were constructed with lithium foil as the negative electrode (ϕ 16mm) and 1M LiPF₆ EC:DEC (1:1 by vol.) liquid electrolyte (Novolyte; 3.8ppm H₂O, 8.7ppm HF). Coin cells were crimped (Hohsen) and secured in a cell holder prior to electrochemical measurements with a Solartron 1480E Multichannel potentiostat (controlled by a MultiStat computer program) at room temperature. The cell cycling protocol was CC charge (4.2V cut off) / CV (4.2V, 1h) / OCP (1h) / CC discharge (2.5V cut off) / OCP (1h). This protocol was performed at nine current levels [C/10(x1), C/5(x1), C/2(x1), C(x2), 2C(x2), 3C(x2), 5C(x2), 10C (x2), 15C (x2)].

Coin cell measurements vs. graphite negative electrode

Porous negative electrodes were prepared with a power-optimised commercial graphite cast onto a copper foil (current collector). The positive and negative electrode morphologies can be found in Table 2.

Table 2 Electrode morphologies for rocking-chair cells

	loading [mg/cm ²]	loading density [g/cm ³]	loading thickness [μ m]
1*	8.4	1.7	49
2**	5.4	1.4	40

*VSPC LFP; **commercial graphite

Coin cells were constructed following the previous procedure and cycled with the same equipment. The cell was cycled twice with the formation protocol of a C/10 CC charge (3.6V cut off) / CV (3.6V, 1h) / OCP (1h) / CC discharge (2V cut off) / OCP (1h). Cells that passed the beginning-of-life (BOL) criteria were cycled with a continuous 1C charge (3.8V cut off) / 6C discharge (1.8V cut off) profile [see Figure 5(a)]. The end-of-life (EOL) criterion was the reduction of the 6C discharge capacity by 20%.

Results and Discussion

Improved adhesion

The impact of the combination of the adhesion additive and optimised drying routine on the compressibility of the casted positive foils is shown in Figure 2. It can be clearly seen that this approach to electrode manufacturing with nano-scale LFP leads to enhanced adhesion and higher press densities (see Table 1).

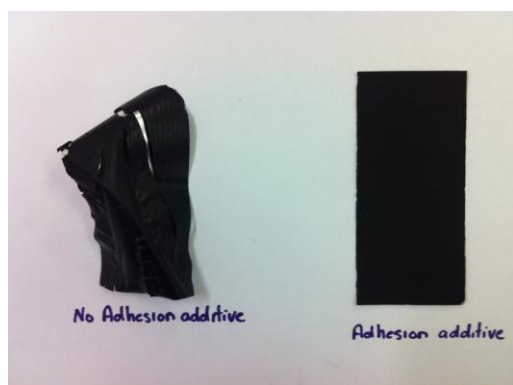


Figure 2 Impact of using adhesion additive and optimised drying routine. Left foil after pressing (no adhesion additive, but using optimised drying routine). Right foil after pressing (adhesion additive plus optimised drying routine)

The electrochemical performance of the positive electrodes manufactured with this approach (no graphite additive) is shown in Figure 3(a). The electrodes had very good high-power performance, with greater than 75% of the theoretical electrode capacity accessible at high rates and very small loss of performance in the voltage plateau region. The electrodes exhibited 100% first cycle efficiency, not shown.

Performance vs. lithium foil with 5 wt.% conductive graphite

The compatibility of the adhesion additive with a common positive electrode conductive graphite is shown in Figure 3(b). The addition of the graphite led to an improvement in both the attainable capacities and power performance at high rates. These results clearly demonstrate that the

adhesion additive did not have an adverse effect on the graphite in the positive electrode.

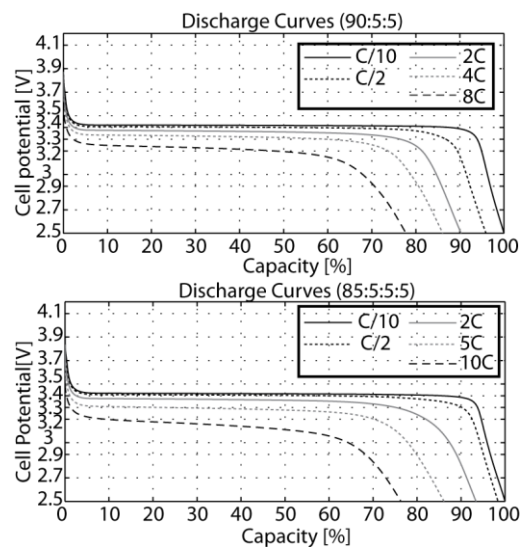


Figure 3 Discharge performance of positive electrode vs. lithium foil in 2032 coin cell (2.5 – 4.2V): (a) without graphite (90:5:5), (b) with graphite (85:5:5)

Formation cycling vs. graphite negative electrode

The performance of a VSPC LFP electrode in a rocking-chair format was tested. The porous negative electrode powder has been optimised for both high-power performance and coupling with a LFP positive electrode. The formation cycling results for one cell are shown in Figure 4.

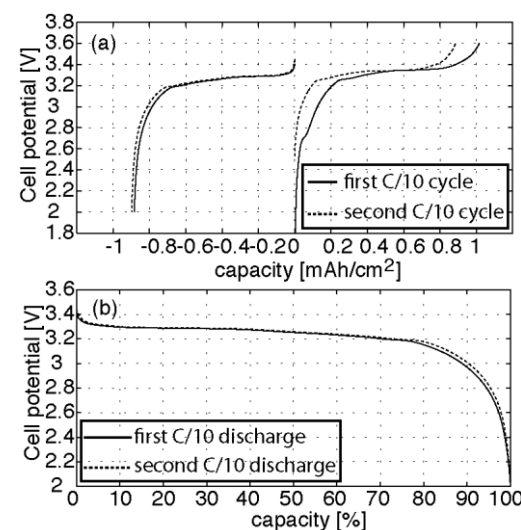


Figure 4 Formation cycling: (a) C/10 cycling (2–3.6V), (b) focus on discharge curves

The coin cell formation cycling results are consistent with typical LFP battery results, with a first cycle irreversible lithium ion loss of approximately 10% and reproducible discharge curves. The results demonstrate that the positive electrode adhesion additive did not adversely impact on formation cycling.

Preliminary high-power cycle life performance

The impact of the adhesion additive on cycle life performance was investigated with a 1C / 6C high-power constant current cycle [see Figure 5(a)]. The results are shown in Figure 5(b).

The first C charge demonstrates the high-power capability of the LFP material in rocking chair format. The 1C / 6C capacities obtained during the continuous cycling are slightly less due to the lack of potentiostatic or OCP periods.

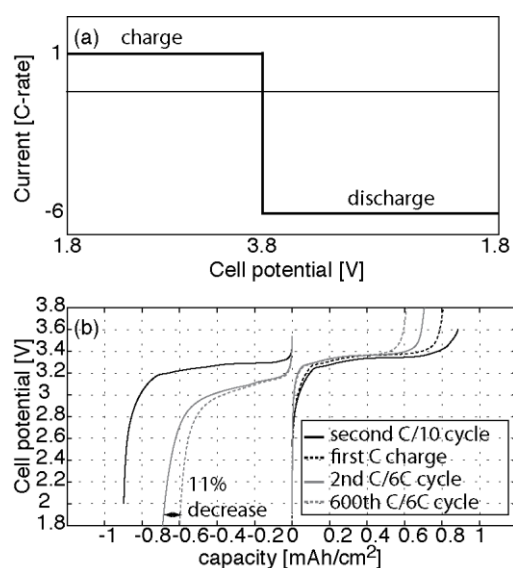


Figure 5 Preliminary cycle life data: (a) current profile, continuous 1C charge / 6C discharge, (b) C/10 formation cycling, first C charge and 1C / 6C cycling data after the 2nd and 600th cycle

A comparison of the 1C charge and 6C discharge curves after 2 and 600 cycles shows an approximately 11% decrease in capacity. The cause of this decrease (genuine capacity loss

or increase in impedance) will require further work. However, this preliminary data obtained in the accelerating environment of a coin cell (with no life-enhancing additives) is very positive, given that the commercial target with such a cycle is no more than 20% loss after 1500 cycles.

Conclusions

The results illustrate that VSPC nanophosphate positive electrode material has excellent rate capability at low carbon loadings. The patented adhesion additive has been shown to lead to excellent adhesion of the active electrode material to the aluminium current collector. Furthermore, the adhesion additive has been proven to be compatible with both conductive graphite in positive electrode loadings and commercially available graphite negative electrode material.

Future work will focus on improving the design of the rocking-chair cell, optimisation of the positive electrode morphology and developing innovative formulations that could be incorporated into the existing VSPC production line. Finally, further life cycle testing has started with the acquisition of a 92 channel multi-range Series 4000 Maccor (with FRA).

Acknowledgements

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