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Innovative materials

Graphene Batteries

PLASCARB
Innovative plasma based transformation of food waste
into high value graphitic carbon and renewable hydrogen

Test Report: Application of Renewable PlasCarbon in Batteries	July 5 2016

Two samples of the PlasCarb product, Renewable PlasCarbon, purified by Katerina Kampioti were tested as additive to LFP-cathodes for Li-ion batteries by Abalonyx. The work was performed by Sameer Fotedar, Ahmet Oguz Tezel and Katerina Kampioti at Abalonyx' lab in Oslo. The cathodes were prepared both with NMP and water as solvents for PVDF and CMC as glues, respectively. Different amounts of PlasCarb material were added and tested with respect to electrode performance.

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Introduction

Novel clean energy resources and related energy conversion and storage materials and devices are in high demand. Among the diverse energy storage devices, lithium-ion batteries (LIBs) have been studied overwhelmingly (Figure 1). Lithium iron phosphate (LiFePO$_4$, LFP) with olivine structure is one of the most promising cathode materials for LIBs, owing to its relatively high theoretical capacity (170 mAh/g), moderate operating voltage (3.4 V vs.Li$^+$/Li), good cycling stability, low toxicity, good thermal stability, and low cost. Unfortunately, LFP shows intrinsically poor electrical conductivity and low Li transport capability (approximately 10-14 cm^2/s), which constrains its electrochemical performance, especially the rate capability. Various attempts have been made to improve the electronic conductivity. These include doping the LFP with other metal ions and aliovalent and coating conductive carbon layer.
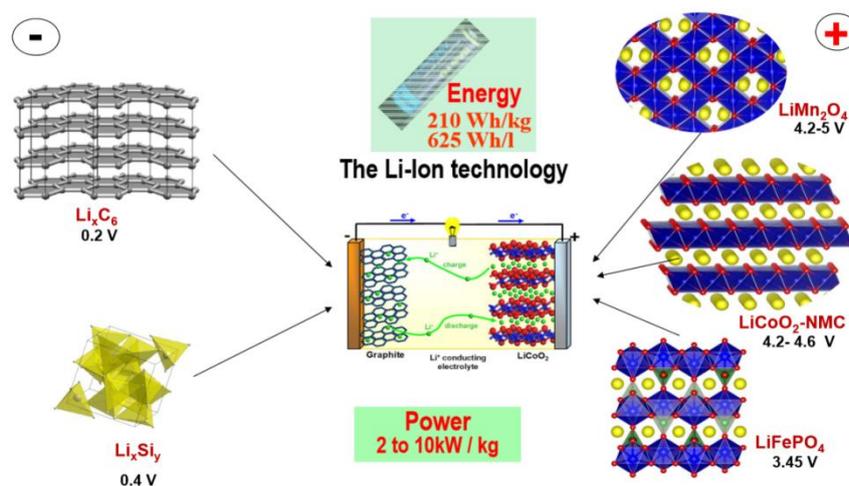

Figure 1. A schematic overview of Li-ion batteries

Carbon coating has been successfully used to improve the electrical conductivity of LFP crystals, though it may lower the energy density of the LIBs. Additionally, carbon coating can be easily accomplished through an in situ pyrolysis of organic carbon precursors, such as sucrose, glucose, starch and a range of other on the LFP. However, the composition, graphitization extent, thickness, surface functionality, and uniformity of the carbon coating layer is hard to control in practice, which, on the other hand, significantly affect the electrochemical performance of LIBs.

Carbon materials, in principle, must meet the following requirements in order to be considered as battery electrode additive;

- ➢ High purity
- ➢ Easy processing
- ➢ High electrical conductivity
- ➢ High compressibility

The state of art LFP electrodes contain as high as 7-10 wt.% carbon black to attain sufficient electrical conductivity. However, the energy density of the electrode decreases with increasing carbon black content since carbon additives do not store charge and therefore are regarded as "dead" mass (Figure 2). Other carbon materials, such as graphene or other high surface area carbons may facilitate the reduction of the overall carbon content down to 2 wt.% in the composite while maintaining high electrical conductivity.
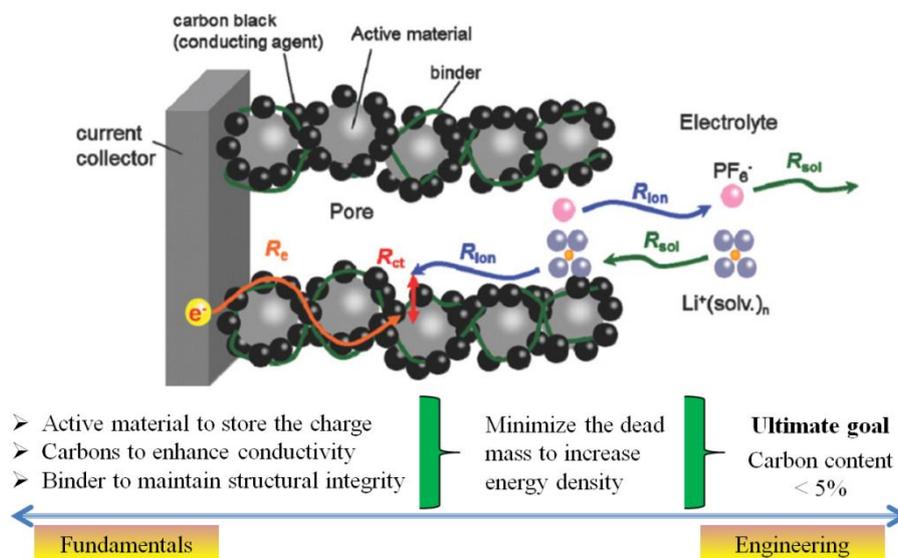
Figure 2. A schematic of a porous cathode composite consisting of active material, carbon additive and binder.

Previous attempts to prepare LFP/carbon/graphene composites, have been based on simple physical mixing of the LFP particles. For example, using LFP nanoparticles and chemically reduced GO (rGO) sheets as raw materials, a facile procedure was developed including the physical mixing of LFP and rGO suspensions to generate the slurry with certain LFP–rGO ratio, the spray-drying the slurry, and finally the thermal annealing in. It was demonstrated that in the composites the LFP nanoparticles were coated (wrapped) homogeneously with rGO sheets forming three-dimensional (3D) network, a structure for facilitating the electron transfer and Li^+ diffusion throughout the composites.

In this work the effects of the Plascarb nanocarbon (NC) on the electrical and electrochemical properties of the LFP/C composites are explored in comparison to various cathode slurries with state of art carbon black additives.

Experimental

LFP/C composite cathodes made from Plascarb NC and SuperC65 (IMERYS Graphite & Carbon) were used for all experiments, see Table 1. The composite electrode sheets were prepared by coating aluminium foil using doctor blading (Figure 3). A slurry of active material (LFP), polyvinylidene difluoride (Solef 5104)/CMC and C additives with a weight ratio of 91:7:2, 88:7:5 and 85:7:8 respectively, was prepared in N-methyl pyrrolidone (NMP; Sigma-Aldrich)/water as the solvent (Table 1). Dried electrodes were cut into 14 mm discs and pressed under 0.65 ton/cm². Li foil served as counter electrode. A monolayer polypropylene separator (CELGARD 3401) soaked with a commercial electrolyte, LP30 [1 M $LiPF_6$ in EC/DMC (1:1 weight ratio), BASF] was placed between working and counter electrode to prevent short circuit. The cells were assembled in an argon-filled dry box with a water and oxygen level of <1 ppm. Electrochemical measurements were conducted using a computer controlled cell capture system (Arbin). Galvanostatic lithiation/delithiation was performed in a potential range of 2.4 – 4.2 V. (vs. Li^+/Li). All cells were subjected to 10 mA/g (~C/17) and 170 mA/g (C) and 340 mA/g (2C) specific currents, respectively. (*It should be noted that a C rate of xC means that the battery is charged or discharged in 1/x hours. Therefore when a cathode is charged at 1C rate, the specific current is equal to 170 mA/g.*)

Table 1. The set of electrode slurry compositions prepared.

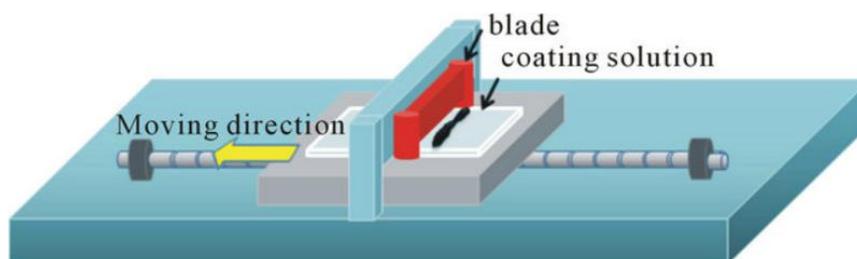|	%wt.CB			%wt.NC		
	2	5	8	2	5	8
%wt.LFP	91	88	85	91	88	85
%wt.CMC/SBR	7	7	7	7	7	7
2nd cycle rev. Capacity (C/17)	118	150	158	120	150	162
20th cycle rev. Capacity (2C)	70	110	95	0	70	108

Figure 3. Doctor blade coating of a current collector for Li-ion battery electrodes.

Results and Discussion

NB!: NMP/PVDF based electrodes are not included in this report since the cycling with this electrodes were not possible due to high electrical resistance. These slurries will be tested at increased pressure to enable better particle-to-particle and particle-to-collector contact.

Figure 4 is a plot of specific capacity for de-lithiation as a function of cycle number for the CB and NC based composites. The cells were cycled at C/17, 1C and 2C rate, respectively, for over 20 cycles after the formation cycles. At the cycling rates of C/17 and 1C, both composites demonstrate equal specific capacity. Capacity fade occurs in the 2wt.%NC composite at 2C rate, delivering almost no capacity. However, the 2wt.%CB based composite experiences much less capacity fade at 2C rate. 5 and 8wt.% NC composites perform comparable to their CB counterparts. It is known that the practical specific capacity of composite electrodes decrease with increasing charging rate due to *i) limited ionic conductivity, especially within the pores,   ii) low electronic conductivity*. It should be noted that in this work intrinsic ionic and electronic conductivity of LFP is not elaborated since both composites contain the same LFP material and therefore the discussion is carried out in terms of the bulk properties.
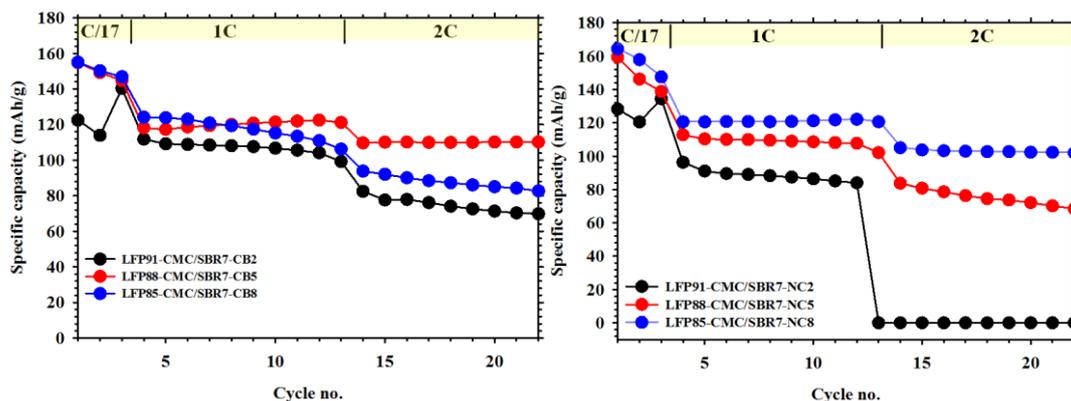
Figure 4. Specific capacity versus cycle number for coin cells cycled at C/17, C and 2C rates with LP30 electrolytes.

To distinguish between the effects of ionic and electronic conductivities, Figure 5 shows the voltage profiles for the second and the 20th cycle, performed at C/17 and 2C rate, respectively. Potential plateaus (ca. 3.4V) seen on the graphs typically correspond to two phase lithiation/delithiation of LFP electrodes (eq.1). It should be stated that when the phase transformation is diffusion limited, the plateaus appear sloppy; while the system displays overvoltage when the electron transfer is rate limiting (lithiation and delithiation potentials are far apart). It is clear that the lithiation and delithiation demonstrate flat plateaus even at high charging rates. However the potential difference between lithiation and delithiation is substantial, especially with NC composites at 2C rate, thus indicating impeded electron transfer rather than diffusion.
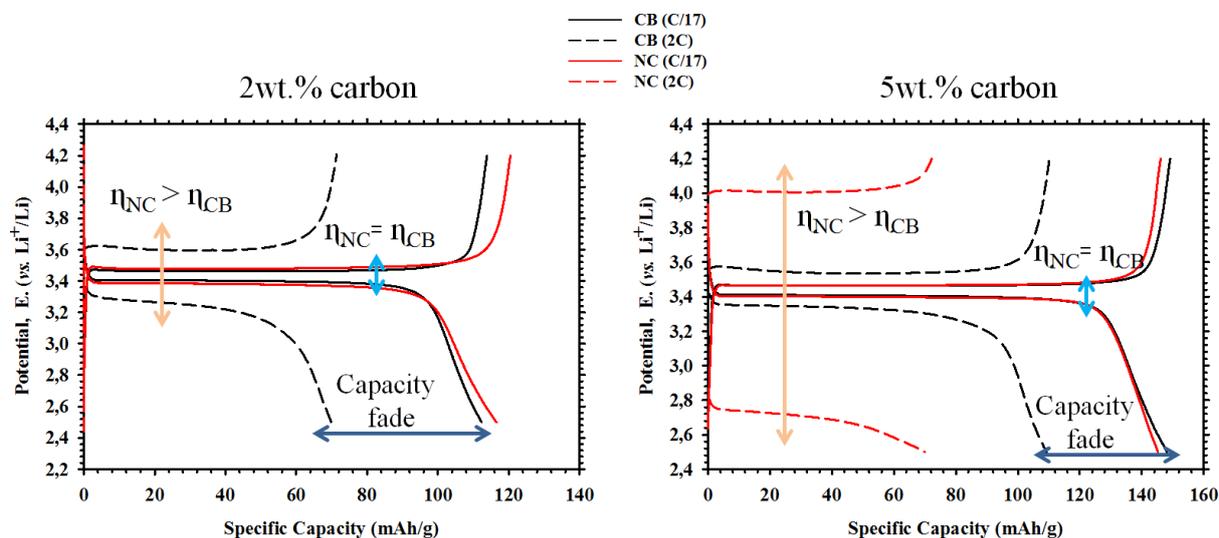
$$LiFePO_4 \leftrightarrow FePO_4 + Li^+ + e^- \quad [eq.1]$$

Figure 5. Potential versus capacity plots for coin cells cycled at C/17 and 2C rates with LP30 electrolyte.

Conclusion

Effect of NC on the LFP cathode was investigated in comparison to state of art additive, carbon black.

- ➢ None of the additives provide sufficient conductivity when added below 8% in an PVDF based electrode

- ➢ Results show that NC delivers equally high specific capacity as the CB when added in commercially relevant amounts (>5%) at moderate cycling rates (i.e. C/17 and C)* (CMC based electrode)

- ➢ Lowering the NC content down to 2% results in fail to charge at 2C rate, indicating low bulk electrode conductivity (CMC based electrode)

- ➢ *NC might be an alternative to CB for high carbon electrode formulations*.

PVDF vs. CMC comparison

- ➢ Electrodes prepared with PVDF requires at least 10% carbon additive to have sufficient electronic conductivity to charge. Below 10% it`s not possible to charge the electrodes even at very low rate (10 mA/g=C/17). Therefore results are not shown in this report.

- ➢ Electrodes prepared in CMC charges at even low carbon additives (2%) at low rates (10mA/g=C/17). Therefore NC vs. CB comparison was only possible in CMC based electrodes.

CB vs. NC comparison

- ➢ At low and moderate rates of C/17 and C, NC performs similar to CB at 2%, 5% and 8% addition. However when the rate is 2C, at least 5% NC is required to maintain reasonable capacities.

Future work suggestions

The electrochemical characterization presented here gives insight into the functionality of the NC in comparison to CB. However further work is required to fully explore the potential of the material. Electrode pressing at increasing pressures is expected to help realize the full potential both in PVDF and CMC based compositions.