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FROM PITCH TO POWER: HARNESSING DOMESTIC MESOPHASE PITCH FOR SYNTHETIC GRAPHITE ANODES IN LITHIUM-ION BATTERIES

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ABSTRACT

Synthetic graphite is a key component in the production of lithium ion (Li-Ion) battery anodes. This paper describes how domestically produced mesophase pitch is synthesized, graphitized, spheronized and made into battery anodes. Results will show that batteries have been made having high specific capacities, record breaking tap densities and surface areas, and low Irreversible Capacity Losses (ICL). Additionally, we will also show the performance advantages of using an isotropic pitch coating as the Solid Electrolyte Interface (SEI) and provide an example where doping synthetic graphite with silicon nanoparticles boosted the specific capacity above the theoretical value for graphite alone.

1. INTRODUCTION

The ever-growing demand for high-performance energy storage solutions has propelled extensive research and development in the field of lithium-ion batteries (LIBs). LIBs have become the backbone of portable electronics, electric vehicles (EVs), and grid-scale energy storage due to their high energy density, long cycle life, and environmental friendliness. Among the critical components of LIBs, the anode plays a pivotal role in determining the battery's overall performance, particularly in terms of energy density, cycling stability, and rate capability.

Conventionally, natural graphite has been the material of choice for a number of LIBs due to its exceptional electrochemical properties, including a high theoretical specific capacity (372 mAh/g) [1] [2]. Other forms of LIB tend to rely on needle-coke-derived synthetic graphite anodes which have excellent cycling stability [1]. However, the growing demand for higher energy density and faster charging capabilities has spurred the exploration of advanced anode materials with enhanced properties.

In recent years, non-needle-coke-based synthetic graphite has emerged as a

promising alternative to natural graphite for LIB anodes. Synthetic graphite offers several advantages over its natural counterpart including higher purity, and tunable morphology, leading to improved electrochemical performance. This has resulted in a surge in research aimed at understanding the synthesis, characterization, and electrochemical behavior of synthetic graphite in LIBs.

This paper describes some recent advancements in the production of non-needle-coke synthetic graphite anodes for LIBs. These synthetic graphite's are produced from domestically sourced mesophase pitch and are mechanically milled into microspheres. The microspheres are further coated with a domestically sourced isotropic pitch which functions as the SEI formation layer.

The paper will delve into the synthesis methods employed to fabricate synthetic graphite anode materials with tailored properties, including particle size, surface area, and tap density. It will also discuss the inclusion of silicon nanoparticles to further improve the specific capacity of the battery. Furthermore, the paper will explore the impact of these synthetic graphite characteristics on the electrochemical performance of LIBs, focusing on parameters such as specific capacity, cycling stability, rate capability, and efficiency.

2. BACKGROUND

ACP Technologies, LLC has developed continuous, patented processes for converting low-cost petroleum oils to high quality isotropic and mesophase pitches and is currently scaling up capacity to meet future demands. Both isotropic and mesophase pitches are being produced in large scale pilot plants. Isotropic pitch consists of large hydrocarbon molecules containing a high aromatic content. Mesophase pitch is the semi-crystalline form of the isotropic pitch molecules. These pitch materials can be used as precursors for making synthetic graphite for LIBs, carbon fiber, carbon-carbon composites, graphitic or carbon foams, electrodes for the steel industry, anodes for the aluminum industry and many other applications.

ACP Technologies can produce isotropic pitch with softening points between 100-200+°C with negligible mosaic or crystalline mesophase content. As illustrated by Figure 1, when converting isotropic pitch to mesophase pitch, droplets of mesophase form and grow in the isotropic pitch continuous phase. When the mesophase content reaches about 50-60 vol%, the continuous phase switches to the mesophase pitch. Then, the remaining isotropic pitch droplets now in the mesophase pitch continuous phase gradually shrink in size, almost disappearing as the mesophase content hits 95-99 vol%. As the mesophase content increases, so does the

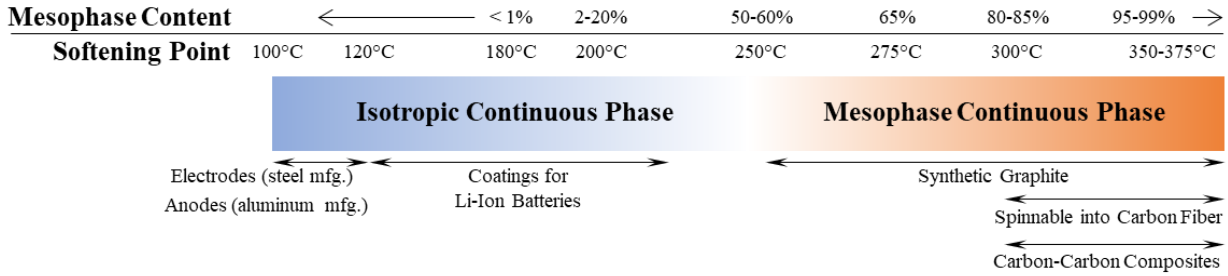

Figure 1: Diagram showing the softening points and mesophase content of isotropic and mesophase pitch, and some applications of each.

softening point and micro-carbon content of the pitch. Isotropic pitch with softening points of 100-120°C are typically used for making electrodes for the steel industry and anodes for the aluminum industry. Isotropic pitch with softening points of 140-200°C with nil mesophase pitch are preferred for the coating of microbeads for LIBs. Isotropic pitch with different softening points have been used in carbon-carbon composites. Mesophase pitch with 80-95+ vol% mesophase are preferred for carbon fiber spinning. Mesophase pitch with 95-99 vol% mesophase is preferred when producing carbon-carbon composites or graphite for LIBs to maximize carbon content.

3. METHODS

Production of Li-Ion anodes from pitch is a complex process involving many steps. The first is the conversion of low-cost petroleum oils to isotropic pitch and then to mesophase pitch as previously described.

The next step is to convert the mesophase pitch into synthetic graphite microspheres. This is accomplished by crushing/grinding the mesophase pitch to ~ 100 mesh and then calcining it at temperatures up to 1,000°C in the flow of inert gas. This converts the pitch from a thermoplastic to a thermoset. The calcined material is then classified to remove fines and large particles and are (optionally) milled with ~ 10 wt% natural graphite to enhance the roundness of the calcined mesophase pitch. The particles are then converted to spheres in a rotor/stator mill operating at 4,000+ rpm. The time inside the mill and the gap between the rotor and stator determine the final particle shape and size distribution. A schematic of the mill and SEM images of the resulting particles are shown in Figure 2. These microspheres are then graphitized at temperatures up to 3,000°C. Once the synthetic graphite microspheres are cooled, they are then coated

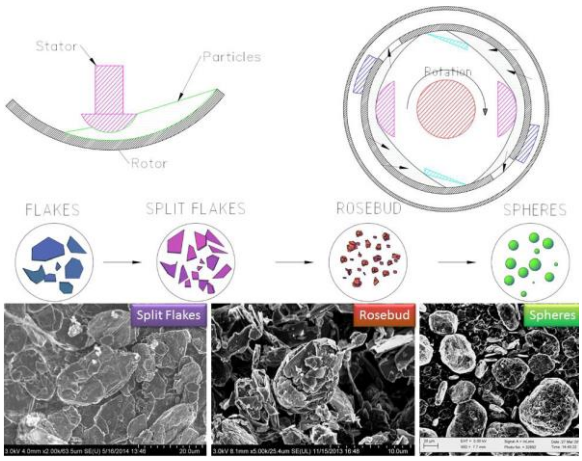

Figure 2: Schematic of the milling process used, and SEM images of the resulting particles.

with ~ 10 wt% isotropic pitch. Alternatively, the microspheres can be milled with nano silicon particles before being coated with the isotropic pitch to boost the specific capacity of the anode material. This pitch layer functions as the SEI formation facilitation layer, reduces ICL and helps prevent thermal runaway. The current process for coating the microspheres is to dissolve the isotropic pitch in a compatible solvent system. The solution is atomized into a mist aerosol and sprayed onto the spheroidized graphite while inside a mixer. The samples are dried at 90°C to remove the solvent, and then calcined at 1,000-1,400°C for ~ 1 hour. This produces coatings with thicknesses in the range of 20-70 nm. A schematic of the coating process and a SEM image showing the surface coating layer are shown in Figure 3.

The final step is to produce a Li-ion battery using the anode material. Batteries can be assembled using conventional processes as known by those in the art. Electrochemical data was measured in this research by assembling CR2016 coin cells with Li/Li+ counter-electrode and LP30 electrolyte. Cells were cycled at C/19 charge/discharge rate.

Tap density was measured using a Quantachrome Instruments Autotap machine

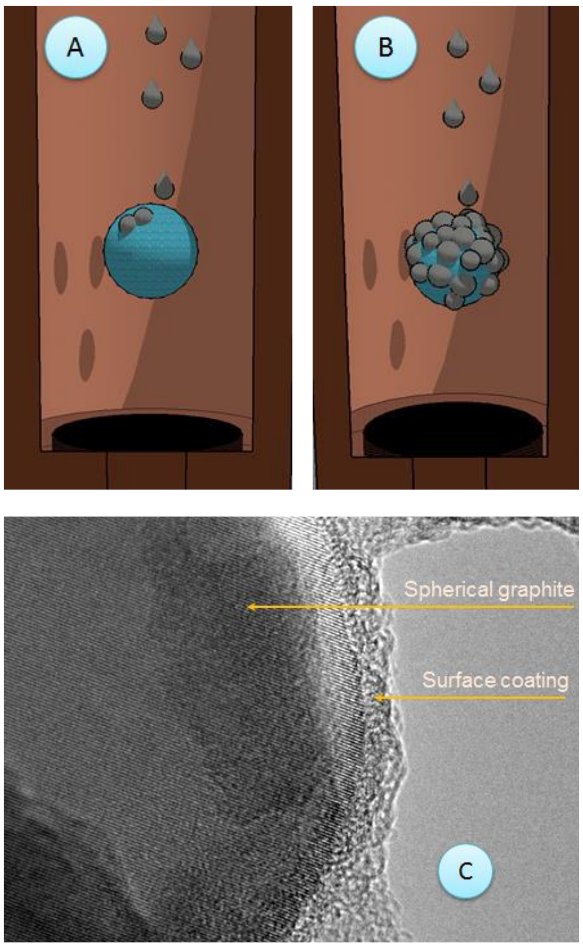

Figure 3: Illustrative representation of the isotropic pitch coating process (A and B) and C) SEM image of a typical cross section of a coated graphite microsphere.

according to ASTM standards D4781, D4164, and B527. Particles are gently poured into a graduated cylinder; in an unrestricted free flow, filling to the 110 mL mark. The graduated cylinder is then secured on the tapping platform of the instrument. An experimentally determined number of 1,500 taps was used to compress the sample, which was completed within ~ 4 minutes. The tap density is determined as the ratio of mass to compacted sample volume.

Apparent (bulk) density was measured according to the Scott Volume method of ASTM B329. Dry powdered graphite was passed through the ASTM-standardized Scott volumeter tester via a stainless-steel funnel equipped with a 14-mesh screen, three inclined glass plates, which are precisely positioned in an outer vertical rectangular column of the volumeter, a conical bottom discharge hopper, and into a stainless-steel cube whose interior volume is precisely 1 cubic inch (16.38 cm^3). Particles are then gently brushed through the top screen to facilitate a free-flowing descent into the collection cube. The powder is allowed to flow freely, eventually filling the collection cube at the bottom three times. After the third time, the cube is filled to the very top and any excess powder is leveled off by a flat-headed spatula. The weight of the graphite powder in the cube is determined to the accuracy level of ±0.1 mg. The apparent (Scott) density is determined as the ratio of the mass and collection cube volume.

Particle size and distribution was measured by laser diffraction using a Microtrac S3500 Series Light Scattering Particle Size analyzer in accordance with the ISO 13320-1 standardized test method. Particles are dispersed in a mixture of deionized water and appropriate surfactant. The values of d10 (10% particles passing a particular micron value), d50 (50% particles passing a defined micron value), d90 (90% particles passing a particular micron value), and MV (population mean value) are reported.

Surface area was measured using a Quantachrome NOVA 2200e surface area and pore size analyzer using a 2-station, multi-gas (i.e. N2 / Ar / CO2 / CH4 / C4H10) surface area analyzer model. This instrument is outfitted with a built-in microprocessor guided calibration feature, which adheres to the ISO-9000 requirements. The NOVA 2200e performed fully automated single and multi-point Brunauer-Emmett-Teller (BET) analysis of graphite samples developed and tested as part of this project.

Scanning Electron Microscopy (SEM) was performed using a JEOL JCM-7000 system with EDS to produce images of selected samples mounted on aluminum substrate using double sided carbon tape with aluminized backing. An electron beam in the range of 1-10 keV was used for imaging. The Secondary Electron Imaging mode (SEI) was predominantly employed for samples used in this study. Certain samples presented in this report were additionally analyzed using the Energy Dispersive Scan (EDS) and Back Scattering (BS) mode via SEM available on the same instrument.

4. RESULTS AND DISCUSSION

To further enhance the sphericity/roundness and tap density of the particles, small amounts of natural graphite were added to the synthetic graphite during the milling process. It was determined that adding ~ 10 wt% natural graphite provided an advantage. For example, synthetic graphite made of 95% mesophase was milled without any natural graphite, and this sample had a tap density of 0.99 g/cm^3, a d50 of 17.6 µm, and a Scott volume of 0.60 g/cm^3. When 10 wt% natural graphite was added, the tap density increased to 1.28 g/cm^3 (potentially a world record), a d50 of 20.8 µm, and a Scott volume of 0.83 g/cm^3. SEM images of these microspheres are shown in Figure 4. Higher tap density materials facilitate increased loading of active materials in the anode and are an effective means to improve specific capacity.

To further boost the specific capacity of the anode material, silicon can be added to the microspheres before being coated by the isotropic pitch SEI layer as described in the Methods section, above. The theoretical specific capacity of graphite is 372 mAh/g [1] [3]. Silicon, however, has a theoretical specific capacity of 3,579 mAh/g [3].

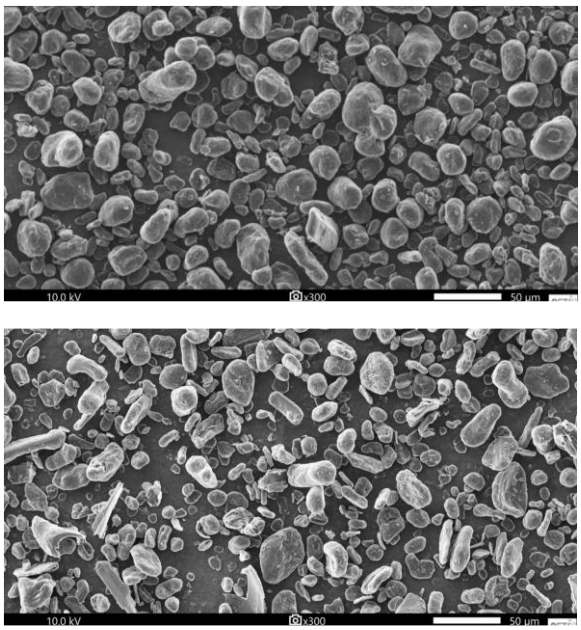

Figure 4: SEM image of synthetic graphite microspheres milled (top) without any natural graphite, and (bottom) with 10% natural graphite.

Therefore, blending small amounts of silicon into the graphite has been a common approach employed to avoid many of the pitfalls associated with making 100% silicon anodes, primarily the 300-400% volumetric expansion of the silicon during lithiation [1] [3]. A schematic representation of a silicon-enhanced synthetic graphite microsphere is shown in ***Figure 5***.

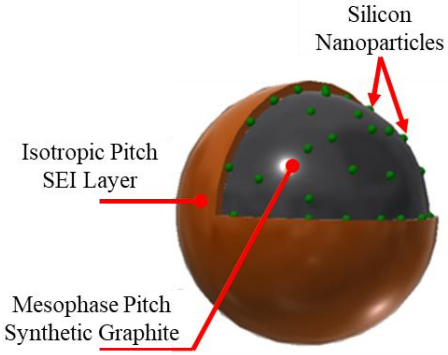

Figure 5: Schematic representation of a Si-enhanced composite microsphere.

Figure 6 shows the galvanostatic cycling of composite graphite with 1.5 wt% silicon in the graphite. This material has a reversable

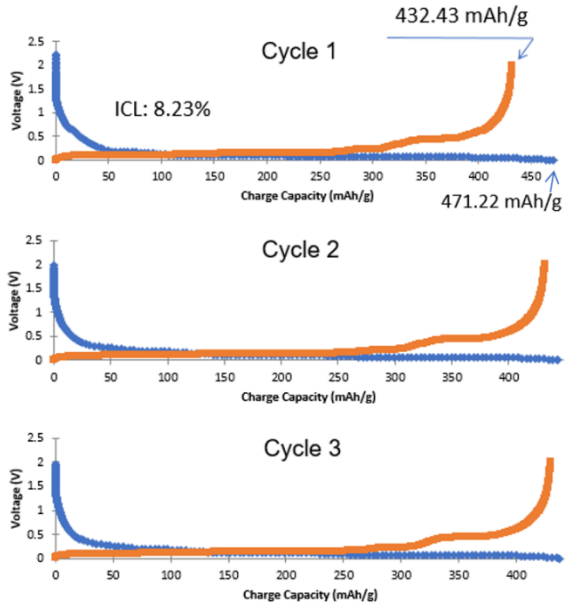

Figure 6: Electrochemical performance of 1.5 wt% Si-enhanced anodes.

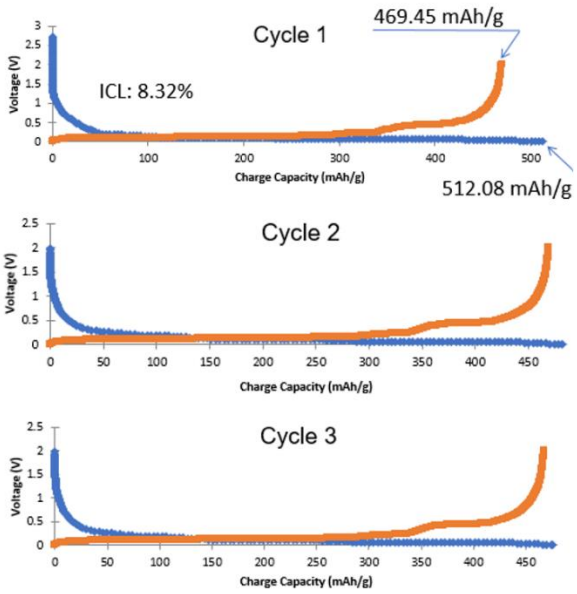

Figure 7: Electrochemical performance of 2.5 wt% Si-enhanced anodes.

capacity of 432 mAh/g with an ICL of 8.23%. By contrast, Figure 7 shows the results of galvanostatic cycling of a composite material composed of 2.5 wt% silicon with graphite. This material has an even more impressive reversible capacity of 469 mAh/g with an ICL of 8.32%. Both materials exhibit rather impressive ICL's.

In another example, a 90% mesophase content pitch was used to synthesize graphitic microspheres that were milled with 5 wt% natural graphite and then coated with 5 wt% isotropic pitch. The particles had a tap density of 1.1 g/cm^3, a Scott volume of 0.77 g/cm^3, a BET surface area of 2.7 m^2/g, and a d50 particle size of 15.9 µm. This sample was subjected to electrochemical cycling and yielded a specific capacity of 349 mAh/g with an ICL of only 3.03%. The results are shown below in Figure 8. Compared to the identical sample prepared without the isotropic pitch coating which had a specific capacity of 379 mAh/g and an ICL of 11.01%, it can be observed that the isotropic pitch provides a substantial improvement in the ICL.

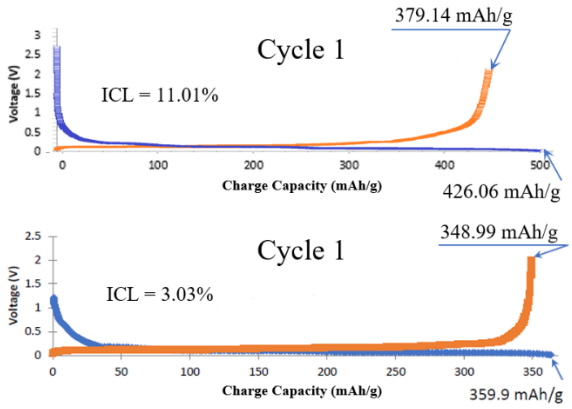

Figure 8: Electrochemical testing of anode material with 5 wt% isotropic pitch coating.

ACP Technologies recently demonstrated that the non-spheroidal graphite, which is produced as a byproduct of spheroidization of the main anode-grade mesophase graphite material, can be used as a very efficient conductive diluent into a Nickel Manganese Cobalt (NMC 8:1:1) cathode active material. This means that the graphitized mesophase pitch can now be consumed at nearly 100% yield for use in advanced lithium-ion battery applications. Another breakthrough stemming from this work is that a water-

based binder was used, and the properties were compared to a traditional solvent-based (NMP/PVDF) binder as shown below in Figures 9 and 10. Using a water-based binder will lower production costs and reduce the environmental impact of lithium-ion battery production.

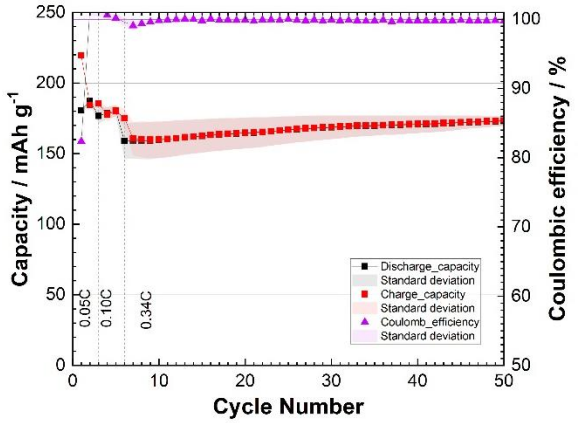

Figure 9: Capacity and coulombic efficiency of cathodes made with a solvent-based binder.

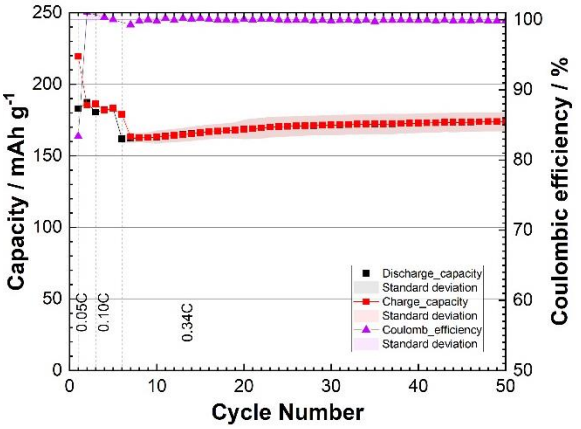

Figure 10: Capacity and coulombic efficiency of cathodes made with a water-based binder.

5. CONCLUSIONS

Domestically sourced mesophase pitch has been successfully processed into high-quality Li-Ion battery anodes. Batteries made with these anodes have been tested for their electrochemical cycling performance and several key metrics have been identified:

- Specific capacities as high as 469 mAh/g have been achieved by adding ~ 2.5 wt% silicon nanoparticles to the synthetic graphite anode materials.
- Irreversible capacity losses (ICL) as little as 3% have been achieved with synthetic graphite microspheres made with 90% mesophase when coated with ~ 10 wt% isotropic pitch.
- Tap densities are improved when synthetic graphite is milled with ~ 10 wt% natural graphite and we have demonstrated values as high as 1.28 g/cm^3.
- Further improvement to the tap density can be achieved by coating the synthetic graphite microspheres with ~ 5 wt% isotropic pitch and we have demonstrated values as high as 1.29 g/cm^3.

While great progress has been made creating high energy density batteries with the materials and methods described herein, it is believed that further improvements will be achieved through additional optimization.

6. REFERENCES

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