High-Performance Coal-Derived Pitches for Advanced Applications

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ABSTRACT

A CPCPC member bituminous coal (PSOC 3001) was hydrogenated and then solvent extracted in N-methyl pyrrolidone (NMP) to remove mineral matter and other solids. Following this purification procedure, the coal extract was thermally treated to raise its softening point temperature, re-dissolved in NMP, and pressure filtered through a 0.2μm filter to remove the finer particulate material. Enough coal extract was made to demonstrate that spinning multi-tow isotropic carbon fibers from a coal-derived pitch could be possible. Careful heat-treating of the same coal extract further resulted in a pitch consisting primarily of fluid mesophase. This mesophase-containing pitch was used to demonstrate the utility of employing coal-derived extracts as matrix binders and for fabrication into electrodes in lithium battery applications. The fibers and carbon-carbon composites produced showed acceptable properties and performance. Larger quantities of pitch are needed, however, for further detailed testing in applications such as electrodes for lithium-ion batteries.

TABLE OF CONTENTS

LIST OF TABLES

Page

LIST OF FIGURES

1.0 EXECUTIVE SUMMARY

The primary focus of the present work was the conversion of coal into pitch-like materials for spinning into carbon fibers and for utilization as a matrix binder in a carbon-carbon composite and a lithium-ion battery. The procedure entails hydrogenation of coal followed by solvent extraction in N-methyl pyrrolidone (NMP) to remove mineral matter and other solids. This raw-coal product had a Mettler softening point temperature of 138.8°C, which was increased to 205°C by thermal processing into a coal-derived isotropic pitch. The softening point temperature of the coal-derived isotropic pitch was within the range of isotropic pitches developed in prior CPCPC projects, but these previous isotropic pitches were all successfully spun using only a single-hole spinneret. It was discovered that the softening point temperature should be increased to above 225°C for proper spinning with a forty-hole spinneret. The softening point temperature could be increased by additional heat soaking in a closed reaction vessel with stirring under an inert atmosphere of nitrogen. Heat treatment at 400°C for 10 hours raised the softening point temperature to 224°C. Carbon fibers with this pitch were spun through the multi-hole spinneret at 240°C, which after stabilization and carbonization exhibited strengths between 280 and 1200MPa. Further heat treatment at 420°C for 24 hours increased the softening point temperature to 252°C. This pitch was then spun at 270°C to result in carbonized fibers with strengths between 312-2045MPa. All of the coal-derived fibers had fiber diameters between 15-17μm, which is slightly larger than petroleum-based pitches of similar softening points.

The coal-derived isotropic pitch was heat treated in a stirred 1L autoclave under vacuum until it contained approximately 50vol% mesophase. Optical microscopy of the annealed sample of the coal-derived mesophase indicates general fluidity. This anisotropic pitch was used as a binder in a PAN-based carbon-carbon composite. X-ray diffraction (XRD) patterns of intermediately heated samples showed graphite peaks beginning as low as 1800°C. Based on XRD patterns, the composite appeared to be fully graphitized at 2250°C. Composite flexural strength of 300 MPa was achieved in the one-step composite fabrication that is quite adequate for many commercial applications.

The WVU anisotropic pitch was also utilized to produce a carbon-carbon composite for a lithium battery with a petroleum-pitch-based graphite fiber (P30X). Heat treatments up to 2790°C were performed. At this temperature, the composite was completely graphitized, as evidenced by XRD. The density after only the one-step processing and heat treatment to 2790°C was 1.67g/cc, which is excellent for many commercial applications. The strength of the composite was 350 MPa, which also is excellent for many commercial applications. In the Li-ion battery, the capacity was 320 mAhr/g with an irreversible capacity of slightly less than 10%, which remained constant in cyclability. This performance is at least equivalent to an expensive mesophase carbon microbeads (MCMB).

2.0 INTRODUCTION

Carbon fibers and carbonaceous binders in carbon-carbon composites are finding ever-increasing use in a variety of materials because of their unique combination of mechanical, electrical, and engineering properties [1]. Currently there are two main types of carbon fibers produced commercially in which one type is based on thermally treating polyacrylonitrile (PAN) yarn [2]. Although PAN fibers generally exhibit high strength, they are dependent on costly precursors and suffer from low yields. Moreover, PAN fibers do not develop the long-range molecular arrangement of graphitic structures that are possible with some or mesophase-based fibers [3,4]. Thus, PAN-based fibers do not achieve high thermal and electrical conductivity possible with pitch fibers.

The other main type of carbon fiber is derived from pitch. Pitch-based carbon fibers offer the potential advantage over PAN fibers in that they can be made from inexpensive precursors, can have a higher modulus, and can be either isotropic or anisotropic in properties. Depending on the application, isotropic pitch-based fibers are used for general purposes where high strength and stiffness are not required while anisotropic or mesophase pitch-based carbon fibers yield high-performance materials.

Starting materials for pitch-based fibers are composed of complex aromatic hydrocarbons from polymerized model compounds or are obtained from the byproducts of pyrolysis, distillation, or heat treatment of petroleum or coal tar feedstocks [4-5]. Byproducts including vacuum residua, catalytic cracker bottoms, decant oils, and coal-tar pitches are some of the candidates for pitch fiber precursors. Unfortunately, since these materials are industrial byproducts, they are subject to vagaries in quality and consistency. Fluctuations in the nature of the feedstocks influence the quality and behavior of carbon fibers obtained from them.

Carbon fibers and pitches derived from coal extracts offer several advantages over conventional sources. Coal extracts are obtained in high yield and are produced as the primary product, not the byproduct. More importantly, coal extracts are tailorable in terms of reactivity, softening point, rheology, and degree of anisotropy. The ability to alter and target coal-derived pitches with particular properties offers the potential to develop carbon fibers with unique and desirable characteristics.

In prior CPCPC sponsored research projects, solvent extraction and thermal treatment were used to convert a bituminous coal into an isotropic pitch suitable for fabricating carbon-carbon composites [7,8]. Enough isotropic pitch was produced such that specimens of continuous filaments could be spun for testing of their mechanical properties and for incorporation into a carbon-carbon composite. The coal-derived pitch underwent spinning and stabilization without any unusual difficulty. Individual filaments carbonized at 1100°C typically had diameters of 10-15μm, exhibited tensile strengths up to 1.36GPa, and displayed resistivities near 4mΩ-cm. These characteristics exceed those made from other corresponding isotropic pitches. Later, a larger quantity of pitch was also successfully produced for a more extensive and systematic evaluation of the fiber spinning and stabilization parameters.

The current project builds on these previous successes by developing two coal-derived pitches with quite different attributes. Similar to earlier work, one pitch is isotropic in nature and produced using processes previously established. However, for the current work, the pitch was melt spun into fiber tows rather than single filaments to reflect more closely commercial practices. The fiber tows were stabilized, carbonized, and tested for mechanical properties.

The other pitch consists predominantly of coal-derived mesophase. It should be emphasized that we are not aware of any other reports or publications that purport the development of flowable or spinning mesophase pitch from coal extracts, as described herein. Thus, the work completed in the current project must be considered a milestone in the possible use of coal extracts in advanced technologies.

As was stated in this year's proposal, it was the intent of the current project to test the coal-derived mesophase pitch only in lithium battery applications. However, to demonstrate another potential application of the technology, a portion of the mesophase-containing pitch was investigated both as a binder for PAN-based fibers in a carbon-carbon composite and as binder for pitch-based graphite fibers for lithium-ion battery anodes.

3.0 EXPERIMENTAL

3.1 Development of coal extract

Arch Coal (PSOC 3001) was ground to less than 60 Tyler mesh, dried, and stored in sealed glass jars under refrigerated conditions until ready for use. Properties of the coal are provided in Table 1.

Table 1. Properties of Arch Coal (PSOC 3001)

Moisture, wt % as received	Ash, wt % dry	Volatile Matter, wt % dry
1.79	7.36	31.57

Carbon wt % dry	Hydrogen wt % dry	Nitrogen wt % dry	Sulfur wt % dry	Oxygen by difference
80.31	4.56	1.41	0.71	5.65

Vitrinite vol % mf	Liptinite vol % mf	Inertinite Vol % mf	Mineral Matter vol % mf
57.2	8.3	30.3	4.2

Hydrogenation was accomplished by placing 600g of coal along with 1.5L of tetralin into a 1gal bolted-closure autoclave. The reactor was purged of air with hydrogen gas and then pressurized to 400psig with molecular hydrogen at room temperature. The reactor contents were stirred while heating and brought to 450°C for 1 hour. Following reaction, the reactor was cooled to room temperature and vented. The products were transferred to a 10L flask and the tetralin removed by rotary evaporation. Three liters of N-methyl pyrrolidone (NMP) were added to the flask and agitated for 2 hours at 110°C. Afterward, the mixture was transferred to 750mL centrifuge bottles and centrifuged for 1 hour at 2000 times the force of gravity (2000G) to separate unconverted coal and other insoluble material. The supernatant liquid was decanted and placed in a rotary evaporator device to remove the NMP. Finally, the coal-derived pitch was vacuum dried at about 150°C overnight before weighing. Hydrogenations were repeated until 8kg of the coal extract product were made.

3.2 Conversion of coal extract into isotropic and anisotropic pitches

The softening point of the coal extract was raised using the method developed previously. The process entails careful thermal treatment and removal of low-boiling components to increase the average molecular weight of the pitch. Following this step, the pitch was dissolved in NMP and pressured filtered through a 0.2μm Teflon filter to remove finely dispersed solids. The NMP was removed by rotary evaporation and the isotropic pitch vacuum dried for about 24 hours at 180°C under a slow purge of nitrogen. About 1.8kg of isotropic pitch were prepared.

The isotropic pitch was transformed into an anisotropic pitch by placing about 300g of the isotropic pitch into a 1-L stirred autoclave reactor. The autoclave was attached to a vacuum source and provision was made for a concurrent slow purge of nitrogen gas. The reactor contents were brought to about 400°C and about 20-30wt% distillate material removed. The reactor was cooled slightly to prevent solidification of the pitch, opened, and the product removed. A sample of pitch was annealed before being mounted in epoxy for examination by polarized microscopy [9]. It was judged that the pitch consisted of at least 50vol%mesophase. Test methods used to characterize the coal extract, isotropic pitch, and anisotropic pitch are shown in Table 2.

Table 2. Methods for measuring pitch properties.

Characterization	Method
Softening Point, °C	ASTM D 3104
Conradson Carbon, wt%	ASTM D 2416
Density, g/cm^3	ASTM D 4892
Ash Content, wt%	ASTM D 2415
Viscosity, cP	ASTM D 5018
C, H, S, N Content, wt%	CE Elemental Analyzer
Mesophase Content	Optical Microscopy

4.0 RESULTS AND DISCUSSION

4.1 Characterization of coal-derived pitches

Some of the characteristics of the coal-derived extract prior to conversion into either the isotropic or anisotropic pitch are provided in Table 1.

Table 3. Characteristics of hydrogenated and NPM-extracted PSOC 3001.

Yield[1], wt%	Mettler Softening Point, °C	Density, g/cm^3	Ash Content, wt%
64	138.8	1.244	0.13

$\text{Yield} = \frac{(\text{wt dry coal} - \text{wt dry residue})}{\text{wt dry coal}} \times 100$

Figure 1 shows the viscosity of the extract material as a function of temperature as well as that for a petroleum pitch. The petroleum pitch (Ashland) has been used as a precursor by other researchers to spin isotropic carbon fibers. As expected, because the softening point of the coal extract is comparatively low, its viscosity is lower compared to the petroleum material.

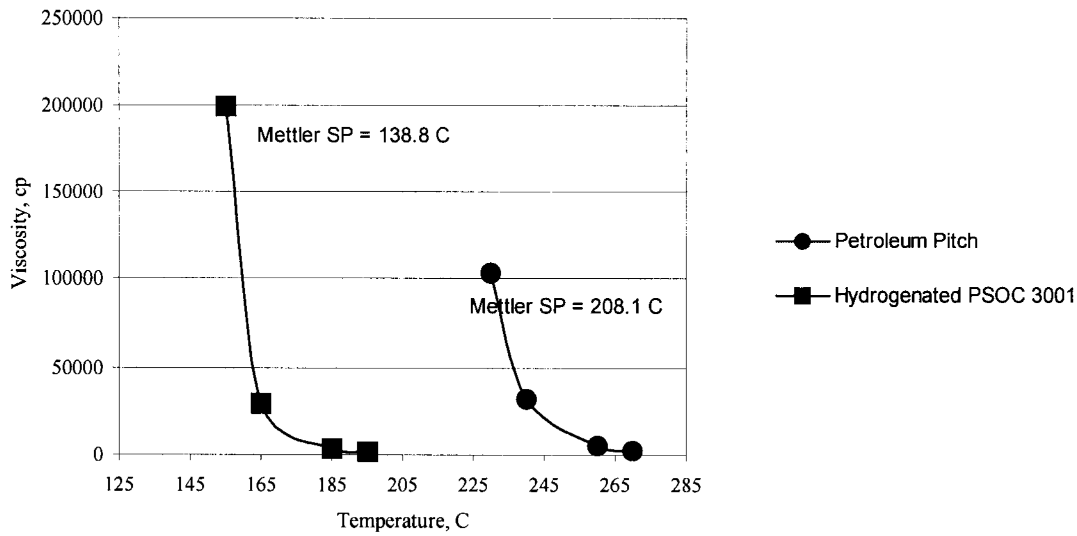

Figure 1. Viscosity vs. temperature for coal extract and petroleum pitch.

Some properties of the isotropic pitch precursor are shown in Tables 4 and 5. The Mettler softening point temperature and the other properties are within the range of pitches produced in prior CPCPC projects. Note that the elemental analysis indicates the pitch is relatively aromatic, C/H atomic ratio equal to 1.34, and relatively low in sulfur content. However, the nitrogen content above 2wt% is not unusual for coal-derived pitches and liquids [10].

Table 4. Properties of coal-derived isotropic carbon fiber precursor pitch.

Metter Softening Point, °C	Density, g/cm^3	Conradson Carbon, wt%	Ash Content, wt%
205	1.290	72	0.03

Table 5. Elemental analysis of coal-derived isotropic carbon fiber precursor pitch.

Carbon	Hydrogen	Nitrogen	Sulfur	C/H Atomic Ratio
91.06	5.67	2.69	<0.1	1.34

Figure 2 shows the viscosity vs. temperature of the coal-derived isotropic pitch compared to a petroleum pitch with similar softening point temperature. Although the Mettler softening point temperature of the coal-derived material is only 3°C less than the petroleum pitch, the viscosity of the coal-derived pitch is significantly less.

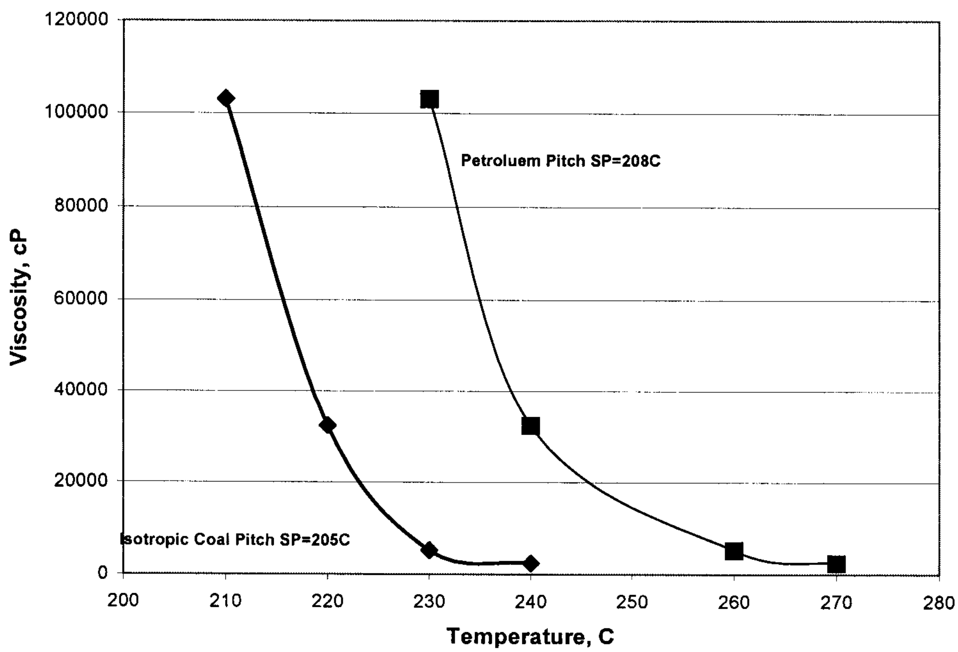

Figure 2. Viscosity vs. temperature of coal-derived and petroleum isotropic pitches.

Tables 6 and 7 provide some characteristics of the coal-derived anisotropic pitch. As expected, the anisotropic pitch is more aromatic (C/H atomic ratio of 1.60) than its isotropic precursor because of the additional heat treatment. Also, the nitrogen and sulfur containing organic molecules in the anisotropic pitch appear to be enriched.

Table 6. Properties of coal-derived anisotropic pitch.

Metter Softening Point, °C	Density, g/cm^3	Conradson Carbon, wt%	Ash Content, wt%
Approximately 310	1.307	75.1	0.09

Table 7. Elemental composition of coal-derived anisotropic pitch, wt%.

Carbon	Hydrogen	Nitrogen	Sulfur	C/H Atomic Ratio
91.60	4.78	3.18	1.28	1.60

Figure 3 is a photomicrograph of a sample of the coal-derived anisotropic pitch as it came out of the reactor and before annealing. Note the spheres of mesophase, which indicate a highly deformable and plastic state. Though it is well known that coal liquids and coal extracts can undergo a mesophase transformation, usually this mesophase is viscous or reactive. Figure 4 is a photomicrograph of the same anisotropic pitch after annealing. It is apparent from the figure that annealing promoted extensive mesophase coalescence.

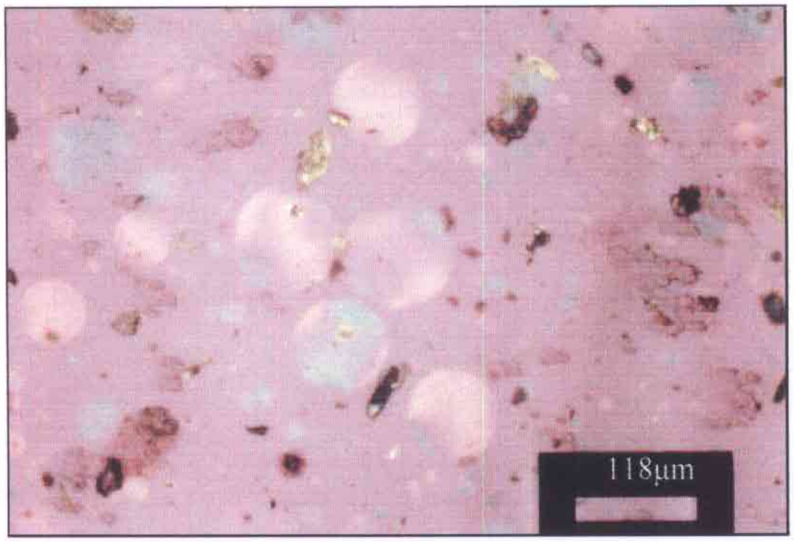

Figure 3. Coal-derived anisotropic pitch before annealing.

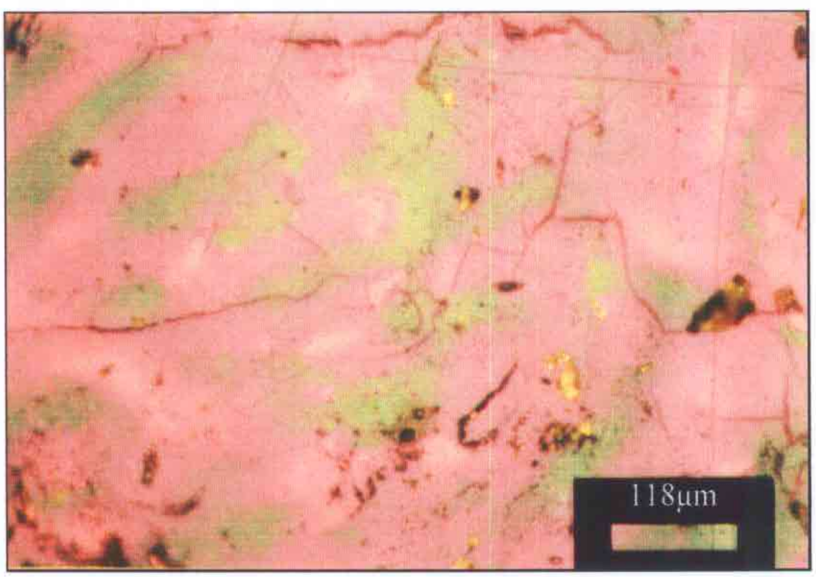

Figure 4. Coal-derived anisotropic pitch after annealing.

4.2 Evaluation of coal-derived pitches for fiber spinning and binders

4.2.1 Spinning of the coal-derived isotropic pitch into carbon fibers

The isotropic pitch was directly used for fiber spinning in a multi-head spinneret set-up. In this case, there were forty spinneret holes in the spinneret head. Because the softening point temperature was relatively low for this pitch, spinning was carried out at 220°C, which is lower than would be typical for spinning other pitch fibers. Spinning at higher temperatures would result in a viscosity too low to achieve continuous fibers without breakage. However, at 220°C it was possible to spin multi-fibers successfully without any major difficulty.

After spinning, the fibers were stabilized by oxidization in air to prevent fusion during subsequent carbonization. Typical stabilization temperatures for conventional pitch fibers are usually conducted at above 270°C for a few hours. However, because the softening point temperature of the coal-derived isotropic pitch is low, attaining temperatures above 200°C too rapidly would cause the coal-derived isotropic fibers to fuse. Thus, stabilization was carried out by heating at 0.5°C/min to 180°C and held there for 24 hours. After the 24-hour hold at 180°C, the temperature was again raised at 0.5°C/min until 270°C was reached with a 4-hour hold and then increased to 300°C. This stabilization sequence was successful and the coal-derived fibers were then carbonized to 1100°C under an inert atmosphere. These fibers had an average diameter of 15μm and the strength ranged from approximately 250 to 516 MPa. This strength is considered relatively low even for isotropic fibers.

To improve the mechanical properties of the fibers, the same pitch was heated in a closed system under nitrogen to 400°C with stirring for ten hours to effect polymerization and increase average molecular weight. This thermal treatment raised the softening point to approximately 224°C. Fibers were again spun with the multi-hole spinneret at 240°C. After stabilization and carbonization, the strength of these fibers ranged from a low of 280 to a high of 1200 MPa.

The pitch was next heat treated as before but at 420°C under nitrogen with stirring for 24 hours, which increased the softening point to 252°C. The pitch was spun at 270°C and after stabilization and carbonization to 1200°C the strength of the filaments ranged from a low of 312 to a high of 2045 MPa.

By comparison, fiber diameters from the multi-head spinning system were slightly larger at approximately 15 - 17μm than commercially available petroleum pitch fibers at 10 - 12μm. A smaller diameter fiber would likely increase strength to some extent. It is probably possible, with additional coal-derived isotropic pitch and a few iterations with the multi-head spinning system, to produce 10 – 12μm diameter fibers.

4.2.2 Coal-derived anisotropic pitch as a matrix binder

The anisotropic pitch produced was ground to minus 200 mesh, oxidized in air at 270°C for four hours, and placed in an isopropyl alcohol diluted phenolic solution to produce a slurry. The slurry was painted onto each side of a PAN (T300 five-harness satin (5HS)) weave fabric. The coated fabric pieces were air dried and stacked in a steel mold. In a heated platen press, the die was heated to 400°C under 500psi. As the pitch melts, it is squeezed into the fabric and continued heating brings the pitch to a low-temperature-char state while still under pressure. After cooling, the composite was removed from the steel die and heated in an inert atmosphere up to 2250°C. X-ray diffraction (XRD) patterns of intermediately heated samples showed graphite peaks beginning as low as 1800°C. Based on XRD patterns, the composite appeared to be fully graphitized at 2250°C. While 2250°C produces a graphite matrix in the case of PAN-base fibers, heating to higher than 1800°C is known to reduce fiber strength. Nonetheless, composite flexure strength of 300 MPa was achieved in the one step composite fabrication that is quite adequate for many commercial applications. An additional impregnation step with the coal-derived anisotropc pitch using vacuum plus pressure would substantially increase strength and, in the case of PAN fiber reinforcement, thermal treatment under 1800°C should also maximize strength. The main motivation to heat to higher temperatures is to graphitize the matrix in order to enhance electrical or thermal conductivity.

4.2.3 Evaluation of the coal-derived anisotropic pitch in a lithium battery

Petroleum-pitch based graphite fiber (P30X) also utilized to produce a carbon-carbon composite for a lithium battery utilizing the WVU anisotropic pitch. The composite was prepared using the same technique as with the PAN fabric. The P30X fabric is a plain weave, 19x19 rods from a 2K tow. With pitch-base fibers, higher heat-treatment temperature is desirable, thus heat treatments up to 2790°C were performed. At this temperature, the composite was completely graphitized, as evidenced by XRD. The density after only the one-step processing and heat treatment to 2790°C was 1.67g/cc, which is excellent for many commercial applications. The strength of the composite was 350 MPa, which also is excellent for many commercial applications. A re-impregnation under vacuum and pressure with the WVU anisotropic pitch could be expected to produce a composite density in the range of 1.9g/cc.

This composite was utilized as an electrode in a lithium-ion battery. Although the thickness of this composite was greater than desirable (less than approximately 100μm is ideal for a Li-ion battery electrode), nonetheless, its performance was considered excellent. The capacity was 320 mAhr/g with an irreversible capacity of slightly less than 10%, which remained constant in cyclability. This performance is at least equivalent to an expensive mesophase carbon microbeads (MCMB), which cost $35 - $50/kg. In other Li-ion battery work, MER has demonstrated there is a significant safety factor in overcharge-discharge with the composite anode over the MCMB. Thus, the anisotropic pitch provides an excellent binder to produce Li-ion battery composite anodes that have at least equal performance to MCMB and provides significant additional safety. Additional development with the coal-derived anisotropic pitch is required to produce thinner C-C composite electrodes. This pitch could also probably be spun into fibers to provide electrodes completely from coal.

5.0 CONCLUSIONS

Bituminous coal was successfully hydrogenated and solvent extracted to produce a pitch-like material. Thermal processing converted the raw hydrogenated product into an isotropic pitch suitable for spinning carbon fibers. Although the softening point of the isotropic pitch was within the range of the softening points of similar pitches produced in prior CPCPC projects, all of the earlier studies spun filaments through a single-hole spinneret. The work completed in the current project indicates that the softening point of the coal-derived pitch should be raised above 225°C to achieve acceptable spinning characteristics through a multi-hole spinneret and to increase the rate of stabilization temperatures.

The anisotropic pitch performed well as a binder pitch with a high-char yield that readily graphitizes. It could be readily used to produce C-C artifacts advantageously because of the excellent density and composite strength achieved in one step. If used as a binder with pitch-based fibers, its excellent graphitizability could be useful for virtually any high electrical or thermal conductivity application, such as Li-ion battery electrodes and thermal management composites. It offers significant potential to produce an all coal-based electrode (fiber and binder) for Li-ion batteries.

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