

Development of high performance artificial graphite anode manufacturing process design for a lithium ion battery application

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リチウム電池用高性能人造黒鉛負極材の製造
プロセスデザインに関する研究

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2025年 3月

九州大学大学院 総合理工学府

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指導教員： 尹 聖昊

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Abstract

As demand for electric vehicles (EVs) and mobile devices (MDs) have increased, and lithium-ion secondary battery (LIB) is a possible energy source as of today. It is proven to exhibit high energy density and operating potential, long cycle life, and low self-discharge rate that it established its firm place as the most successfully commercialized and widely used battery solution.

The role of an anodic material, which is responsible for storing lithium ions during charging, now must facilitate a rapid charging. Among anodic materials, the artificial graphite has been generally. It has the advantage of having a lifespan that is longer than natural graphite. Therefore, in consideration of the lifespan characteristics and output characteristics, artificial graphite has a solid positioning in anode making of LIBs.

The manufacturing of anodic artificial graphite demands both long processing time and high production cost, thus, making China the best manufacturer with more than 95% global market share which requires raw material independence for the fierce competition. The sweet spot for that cost reduction is mainly in the process of kneading where primary particles are accumulated via a binder to form a bigger secondary particle. The conventional process usually involves a series of stages: the pulverization of cokes, the granulation of pitch and coke premix called “kneading,” carbonation, graphitization, and surface treatment, which must be time-consuming and costly. It is the focus of the thesis to design a more cost efficient and less labor-intensive kneading process. To gain raw material independence, we selected coal tar derived needle cokes provided from POSCO MC Materials Co.Ltd. which is a joint venture company between Mitsubishi Chemical and POSCO Future Materials Co. Ltd. of Korea. The attempts to streamline the kneading process are as follows.

(1) The 1st chapter of introduction gives a brief description of the background and objective of this research.

(2) The 2nd chapter explains the basic properties of Coal-tar (CT) and needle cokes (NC), the main ingredients in this research. CT as a coating material, was put into decanting for removal of Quinoline insoluble (QI), therefore, to achieve QI-free (less than 1% in content). Specifically, a centrifugal decanter was used to transform the CT into having a fixed carbon

content of $26.33 \pm 0.52\%$, QI of 0.79 ± 0.20 and TI of 2.62 ± 0.28 with innate moisture maintained at 25.19 ± 0.88 . The CT derived pitch (CTP) was manufactured via several steps of predetermined distillation conditions. The CTP that has a softening point of above 100°C presents QI (4~8%), TI (22~28%) and fixed carbon content (more than 54%), of which the QI is higher than that of petroleum derived pitch (PP) (e. g. ZL250 by Rain carbon Co. Ltd. of Germany). The PP for anodic artificial graphite has usually less than 0.5% QI contents and 30.2% TI content which translates into more beta-resin content that compared to CT derived counterpart while having more than 68% fixed carbon content. The PP has a softening point of 250°C , that is, the gluing dynamics inside has different workings in them. Accordingly, a significant difference in the internal design of these pitches are well put into plant operation catering to respective branches of various product manufactures in Japan and China. The present study also focuses on these solid pitches as well as the liquefied-state coal tar to make the best of its wide coverage property.

(3) In the 3rd chapter, a continuous kneading was studied through two types of extruding equipment comparison to obtain a proper design. After a series of tests with two types of extruders, it was confirmed a longer barrel with faster rpm of extruder was more effective in producing a more compact secondary particle. And the two barrels overlapped structure design was conceived and assembled. The novel continuous kneading showed 47% secondary particle size expansion and an electrochemical performance of the anode material, it was confirmed to have a discharge capacity of 350 mAh/g or higher and an initial coulombic efficiency of 91% or higher. The process was limited to only the use of calcined cokes and went through frequent clogging that led an author to focus on the classic batch type kneading.

(4) In the 4th chapter, instead of solid PP, liquefied CT was employed. The CT has a lower softening point than an average PP that is at least higher than 200°C . Uniform control of raw materials was made possible by the adoption of henschel type mixer which enables flash kneading at a room temperature so that a single carbonization step would finalize the anode manufacture. Apart from the cost-effectiveness of the process, it has enhanced the properties of artificial graphite by a uniform coating using less than 50% amount of soft carbon. In addition, the whole manufacturing time and cost was reduced by 12h and 20% due to the skipped manufacturing step, respectively. The improved powder properties was confirmed

with the density of 0.90 g/cc and conductivity of 120 S/cm at 1.6 g/cc, and an improvement in electrochemical performance having a discharging capacity of 357mAh/g.

(5) The 5th chapter described the conclusion of this thesis that it is highly possible to optimize the current kneading process with the proposed approaches. To guarantee the performance of commercial scaling up, more ideas are needed to better the machine. Furthermore the new design should accommodate a wider range of raw materials.

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Chapter 1.

1.1 Lithium ion battery

It is seen everywhere that lithium ion batteries (hereinafter referred to as LIBs) are playing a key part in expanding electric vehicles, smartphones and even stationary energy storage systems with the best mix of high discharge capacity and energy densities and long life span at an affordable costs [1–10]. Lithium-ion batteries (LIBs) have been on the market for more than thirty years and still they have been the only capable technology for the aforementioned applications, and are expected to continuously drive the market in the future [11]. LIB working mechanisms is so called a “rocking chair”, where lithium ions play as “rock” going between electrodes to electrodes during charge/discharge cycles. The concept of a “rocking chair” battery system goes a long way from its inception in the late 1970s [12,13]. The inception has been outside the factory for a long time until big bang innovation happened in Japan. Sony company was the pioneer in putting the idea into an actual product in 1991 [14]. The introduction of the first commercial LIB by Sony would not have been made possible without a perfect marriage of electrode active materials, especially the use of graphite anode as the “lithium sink ” and lithium cobalt oxide cathode as the “lithium source ”.

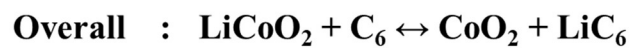
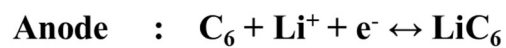
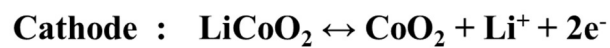
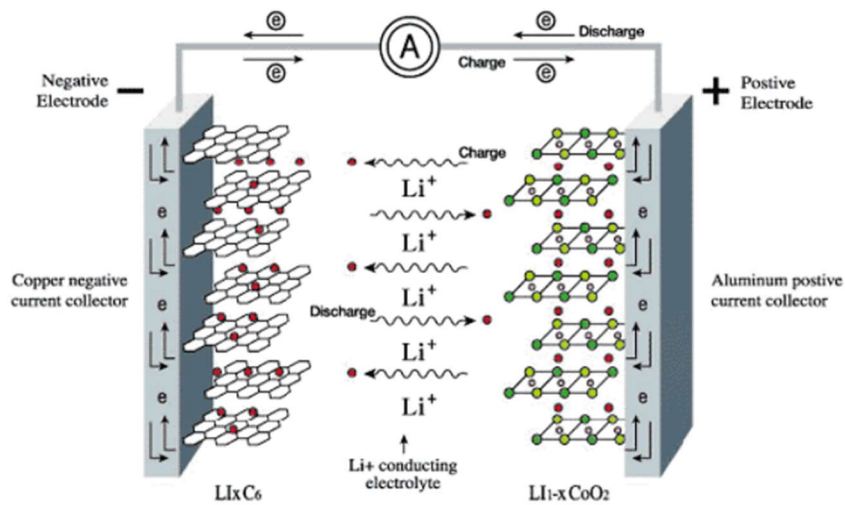
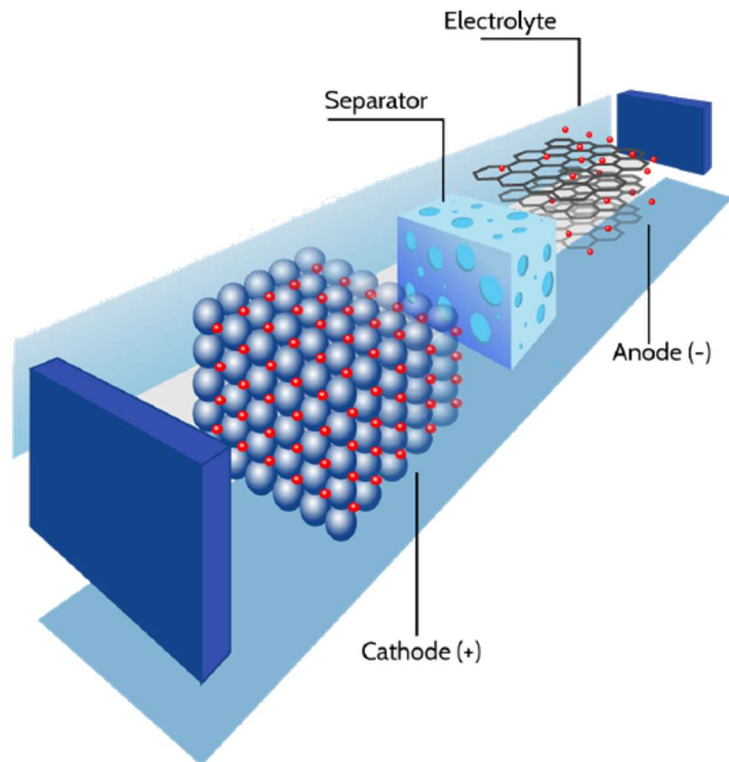


Fig. 1. Lithium ion battery charging/discharging mechanism

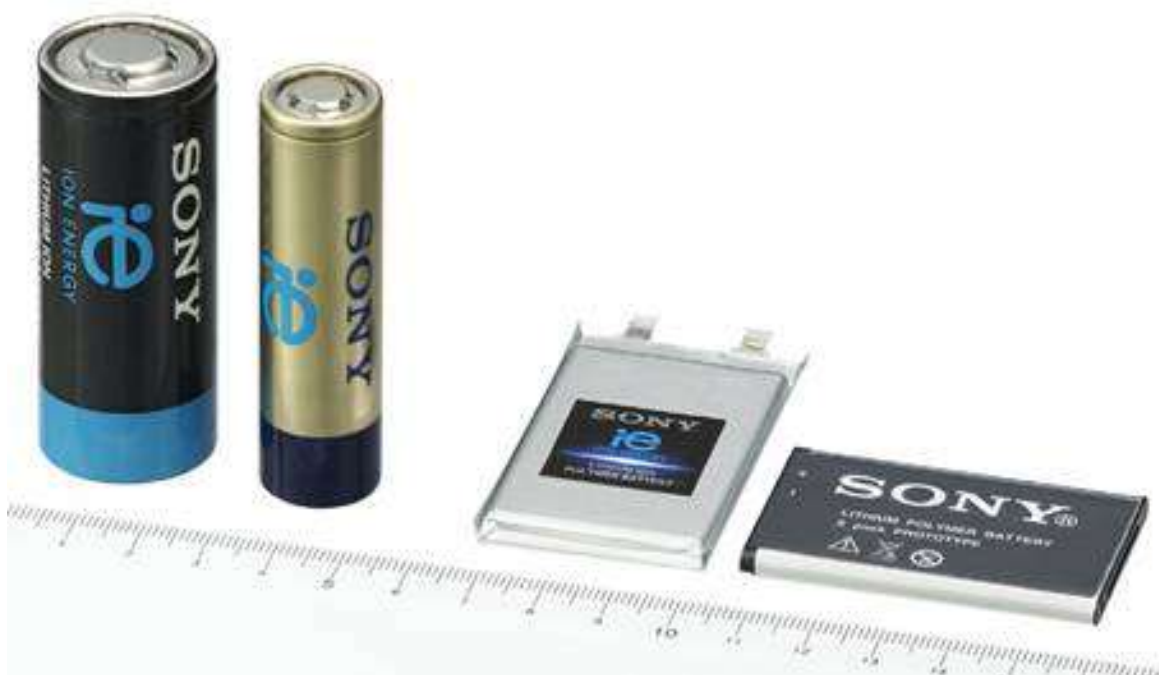


Fig. 2. Lithium ion battery product types

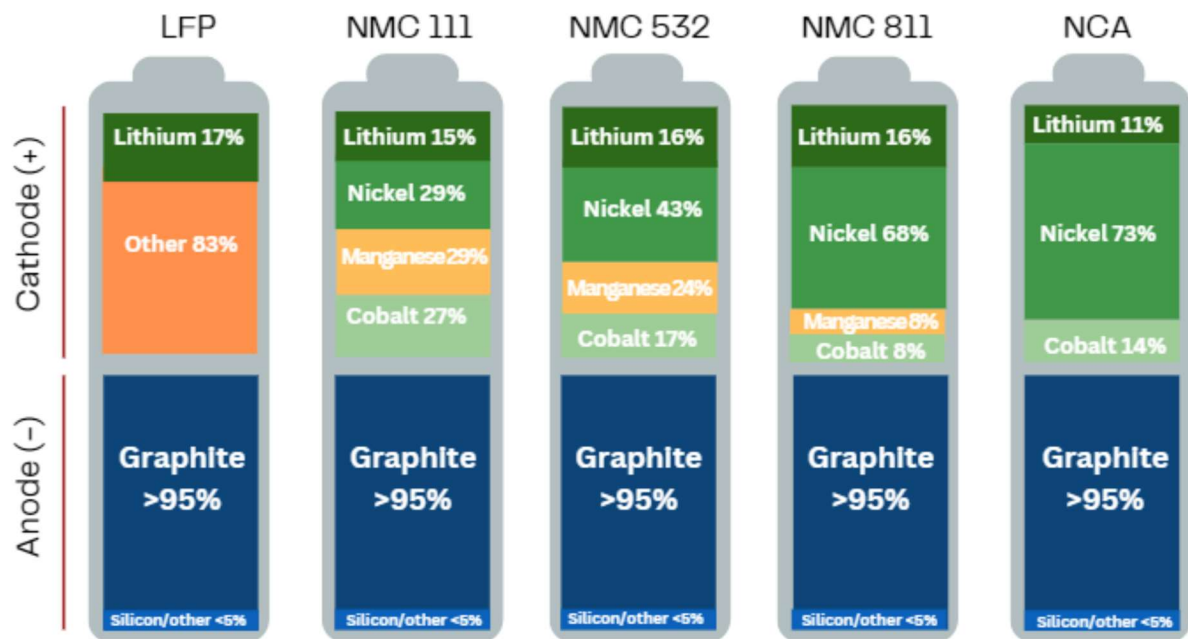


Fig. 3. Lithium ion battery composition by cathode types

No matter what type of cathodes are selected: LiCoO_2 (LCO), LiFePO_4 (LFP), LiMn_2O_4 (LMO), $\text{LiNi}_{1-y-z}\text{Co}_y\text{Mn}_z\text{O}_2$ (NCM), and $\text{LiNi}_{1-y-z}\text{Co}_y\text{Al}_z\text{O}_2$ (NCA), the LIB then and now is sticking to graphite-based anode all the way. It is perhaps due to its unmatched electrochemical performances, graphite was the perfect match. Fig. 4 presents the history and market share of various mainstream LIB cathode and anode materials, with the year of their application in LIB [15]. It is evident that there has been many changes in the selection of cathode. The origin LCO [16], cheaper LMO to reduce Cobalt [17], stable LFP [18], high-capacity NCM [19] and NCA [20] which later hybridized as NCMA were subsequently invented in 1980, 1983, 1996, 1999, and 2001, 2022 and ruled the market 5~35% respectively in years [21]. Meanwhile, graphite has a firm position with a dominating market share of 98% [22], leaving only 2% market share for $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) anode nowadays [23].

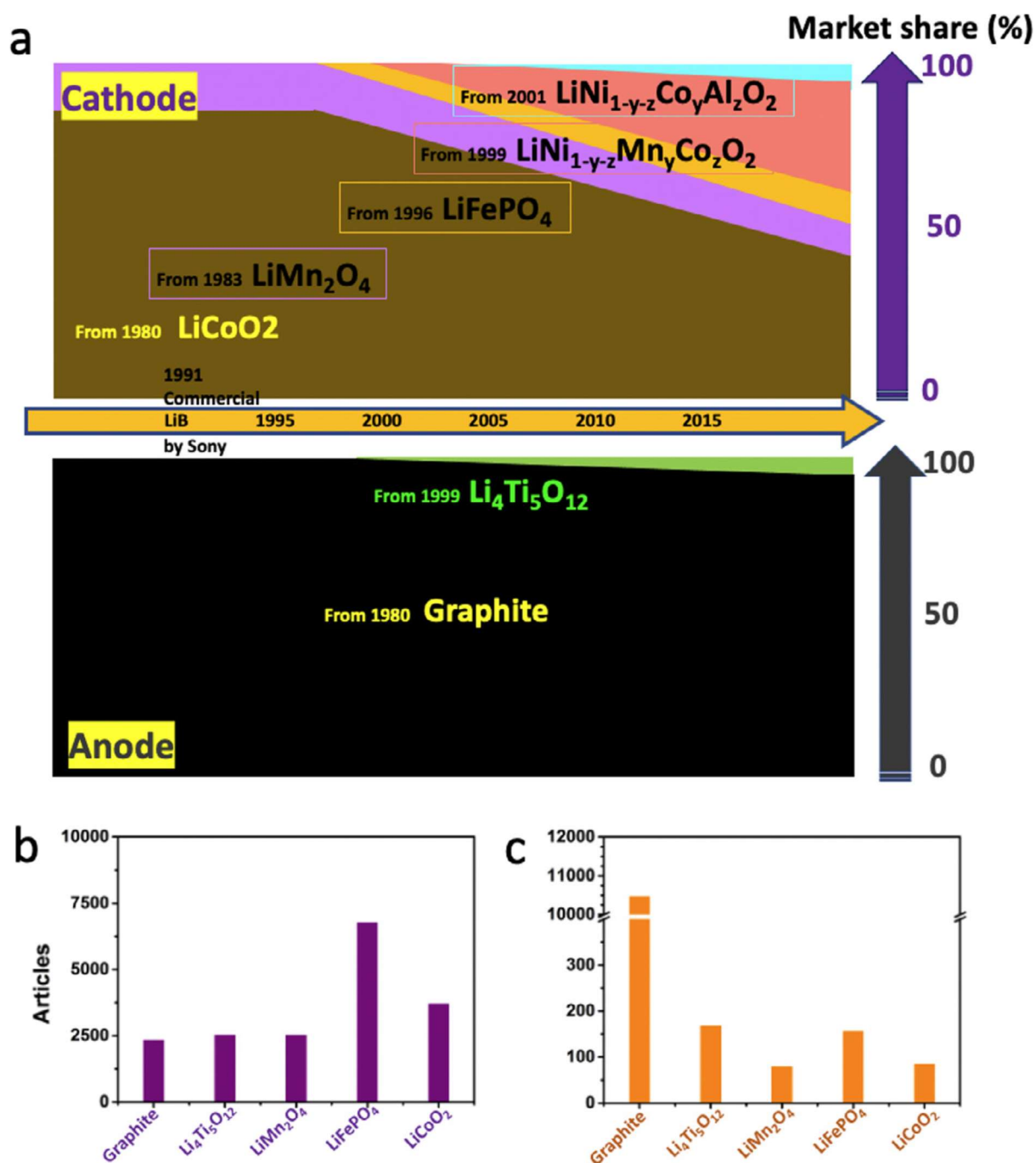


Fig. 4. (a) Schematic of history and market share of mainstream cathode and anode materials for lithium ion batteries. (b) Articles and (c) patents published during 2010 ~2020 on various electrode materials, including graphite, Li₄Ti₅O₁₂ , LiMn₂O₄ , LiFePO₄ , and LiCoO₂ .

As variant as cathodes are while graphite has been standing firm and on its own, there has been a series of changes until reaching that position, the current graphite-based anode holds. Let alone the history of graphite/carbon and PC additives and so on. The author mainly focuses on the manufacturing of graphite. The graphite anodes generally come from cokes precursors, that is, green/calcined, needle/pitch precursors born from either petroleum residues or coal-tars. Depending on the primary size of precursors, micronization using jaw crushers, Air classifier mills (ACMs) and spheronizers comes as the first step to size and spheronize the “so-called” primary particle. The primary particles are to be attached by thermoplastic pitch binders born from the same mentioned above to form a secondary particle. There were ancient times in the 90s that graphitized primary particles would do the trick and expectation in the market was as low as its 330mAh/g discharging capacity and initial coulombic efficiency of around 90%. The formation of secondary particle became important to control the expansion of the particle during charging/discharging so as to reduce the irreversible capacity along with the market voice screaming for 350mAh/g and higher ICE. What happened between was the adoption of natural graphite based anodes that ensured high discharging capacity of up to 360mAh/g. The natural graphite has its place in the anode market for sure and it is still a vital ingredient today. However, with Tesla motor’s commercial success, lithium ion battery’s biggest application has shifted to electric vehicles which requires fast charging and longer life span. That’s a job for artificial graphite and that hurdle requires an even lower expansion rate during longer charge/discharge cycles. That was the point many Japanese companies lost their grip on their block forming artificial graphite products due to their high specific surface area that leave anodes open to more expansion and unnecessary reactions. Chinese players took their place setting a new standard for a low expansion artificial graphite product that is deemed a “the most possible” choice for EV manufacturers due to its low specific surface area, that is low

expansion rate leading to better longevity (Figure 5).

The key to the new manufacturing process of for a low expansion artificial graphite mainly lies in the kneading step. Unlike Japanese predecessors, instead of forming a block, they employed a powder based kneading concept using mainly air flows that is very close to the soft-coating of materials. Other processes of premixing, baking and graphitization are just the same as before and hard to change that they have no room for further innovations. In other words, they are not variables (Figure. 6). On the contrary, this new concept of kneader is a variable that needs more innovations. The current process step requires a large kneader that can only use around 30% of total volume, requires more labor and more energy and above all clean environment. It is important to notice that the translation of labor, energy and environment can be different according to each country and region. And it is clear, that countries like Japan, the U.S.A and Korea have to be super sensitive to these issues. As specified in that table 1, Japan needs to spend more resources on labor and cost. The objective of this thesis is to provide a strong countermeasure, a better way of kneading to give an answer to EV makers.

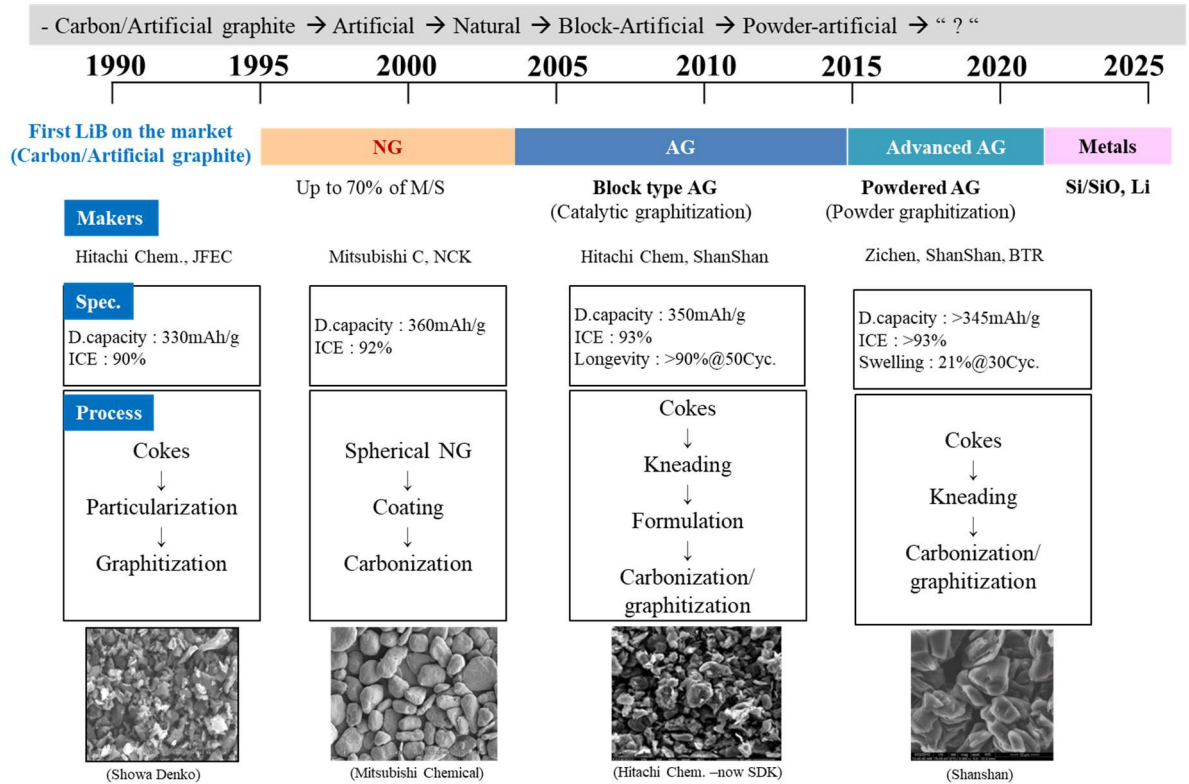


Fig. 5 Graphite anodes development history (Dr. Sei-min, Park of RIST)

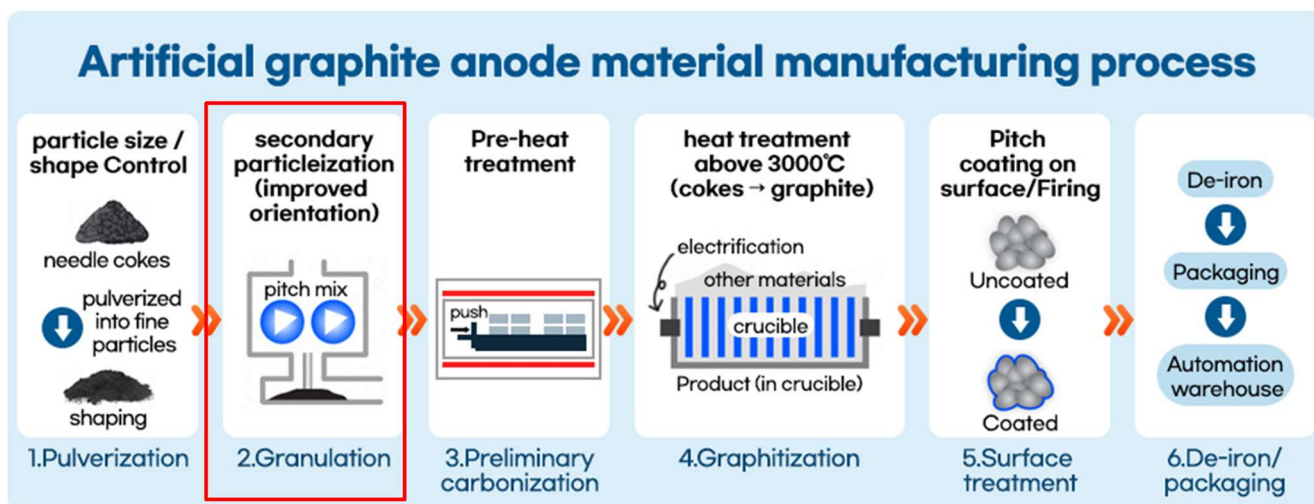
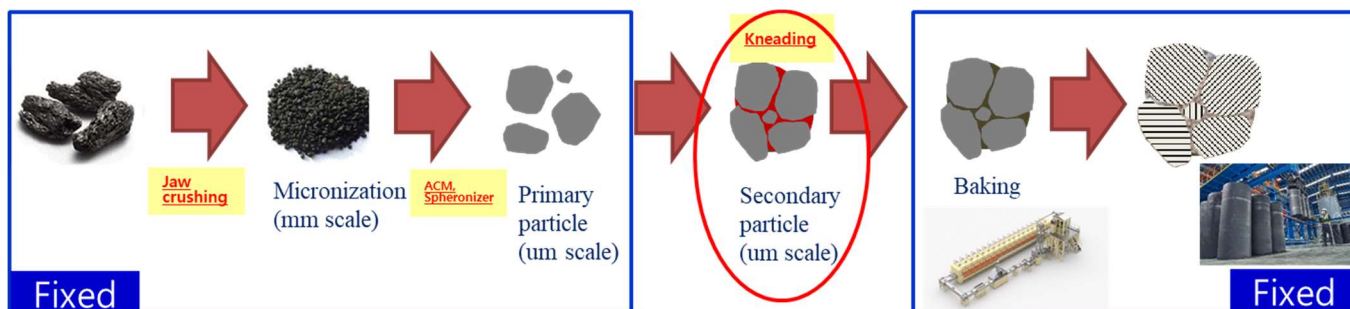


Fig. 6 Kneading (marked in red) in anode manufacturing process

Spendings	China	Japan
Labor cost (USD/month)	300	1,200
Labor cost of 3 workers a month	900	3,600
Electricity (USD/kWh)	0.08	0.21
Environmental cost (per 10 kneaders)	None	75,000
Other costs-medical, insurance,etc	None	?????

Table 1. Cost comparison (kneading) between China and Japan

1.2 Lithium ion battery anodes materials

Graphite has also successfully replaced the look-alikes, that is, soft and hard carbons, by boosting enhanced fullcell energy densities thanks to its low delithiation potential and high gravimetric discharging capacity of 372 mAh/g which is theoretically capable. Graphite has made its way slowly and steadily with several milestones, which are summarized illustratively in Fig. 5 [24]. The possibility to form a lithium intercalation compounds in combination with graphite up to a maximum lithium content of LiC_6 using a molten lithium or a compressed lithium powder has been known, in fact, since 1975.Sep.–Nov. [25-27] . 1970s marks an important tryout that reversibly intercalate and deintercalate lithium in and out of graphite electrochemically that has been a big challenge due to the presence of e.g., propylene carbonate (PC) and the graphite exfoliation was inevitable in liquid organic electrolytes [28,29]. Several breakthroughs were attempted from 1983 by Yazami and Touzain [30] introducing a stable solid polymer electrolyte. In 1990, Dahn and coworkers [31] reported that the reversible electrochemical lithium intercalation is possible also for liquid electrolyte when using ethylene carbonate (EC) as electrolyte co-solvent due to the formation of a stable solid electrolyte interphase (SEI), the well-known term coined and proposed by Peled [32]. Finally there came the first lithium-ion battery commercialized market product was rolled out by Sony in 1991; at that time, though, still incorporating PC as electrolyte solvent and a coke as anode. The quest for suitable electrolyte compositions continued based on EC, which were compatible also with 4 V-cathodes, while providing suitable conductivity and electrode wettability, led to the development of mixtures comprising EC and dimethyl carbonate (DMC), as reported by Guyomard and Tarascon in 1993 [33]. As

a result, starting from 1994, almost all commercial LIBs were (and still are) based on graphite as active material for the negative electrode [34]

Since then, the initial coulombic efficiency of graphite-based anodes and the reversible capacity and cycling stability saw a series of enhancements and it was possible by identification of stable forming of an electrolyte additive and subsequent coating layers.

Further enhancements in the 2000s saw the development of aqueous and sustainable electrode processing, replacing the obsolete, toxic and harmful polyvinylidene fluoride (PVdF) and N-methyl-2-pyrrolidone (NMP) as binder and solvent simultaneously. The

Latest research and development was definitely concentrated on the increase in EV mileage, that is, higher energy and power density. It was made possible by incorporating silicon (oxide) as additive active material. Among other alternative anode materials [35–41], graphite is still remains dominant in anode material selection in commercial LIBs.

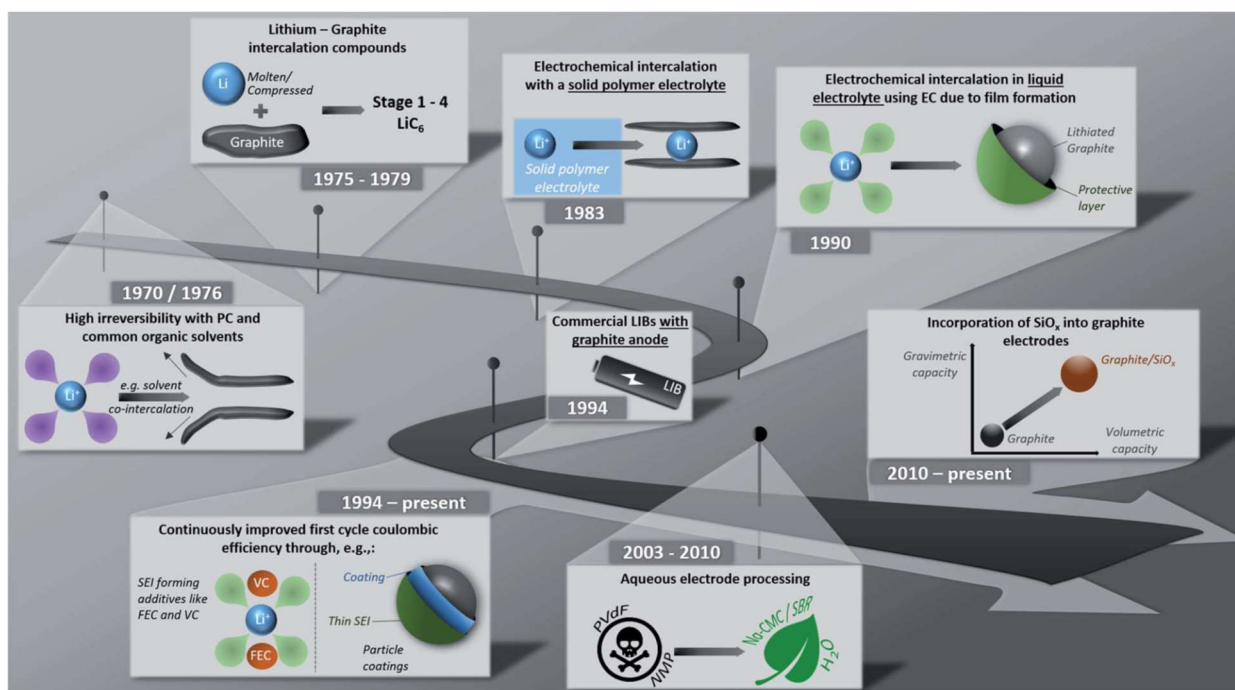


Fig. 7 Illustrative summary of major milestones towards and upon the development of graphite negative electrodes for lithium-ion batteries

1.3 Graphite anodes material

Mysteriousness of inner-workings inside LIB have been unraveled in several literatures that describe Lithium ion intercalation in graphite [42–50]. Daumas–Hérolld mechanism describes the lithiation of graphite as comprising four stages [26]. The number of stage equals the number of graphite layers between the Lithium ions [25]. For example, as can be seen in Fig. 6, stage 1 denotes LiC_6 , comprising alternating layers of Li^+ ions and graphite layers. Stages formed above 0.076 V versus Li/Li^+ are called “dilute” as only partial occupancy of Li sites between the graphite layers is found, while those formed below that potential are called “dense” (2 and 1, corresponding to LiC_{12} and LiC_6 , respectively), with the occupied Lithium layers being fully filled maximum by Lithium ions. After this simplified mechanism, subsequent work by Dahn [44] revealed the presence of additional dilute stages at low states of charge ($0.04 < x < 0.3$ in Li_xC_6), and work by Ohzuku et al.[49] revealed the existence of a “liquid” (or dilute) stage 1 (1L) prior to stage 4 and an additional stage 2L between stages 3 and 2. In these “liquid-like” stages, there is no visible Lithium ion ordering in the a–b planes [48].

These results were later confirmed using in situ Lithium [50] nuclear magnetic resonance (NMR) [16]. More recently, operando neutron diffraction by Didier and co-workers [48] confirmed the presence of a hysteresis between lithiation and delithiation of graphite in the dilute stage region. The physical and electrochemical properties of graphite have been thoroughly characterized [48–53].

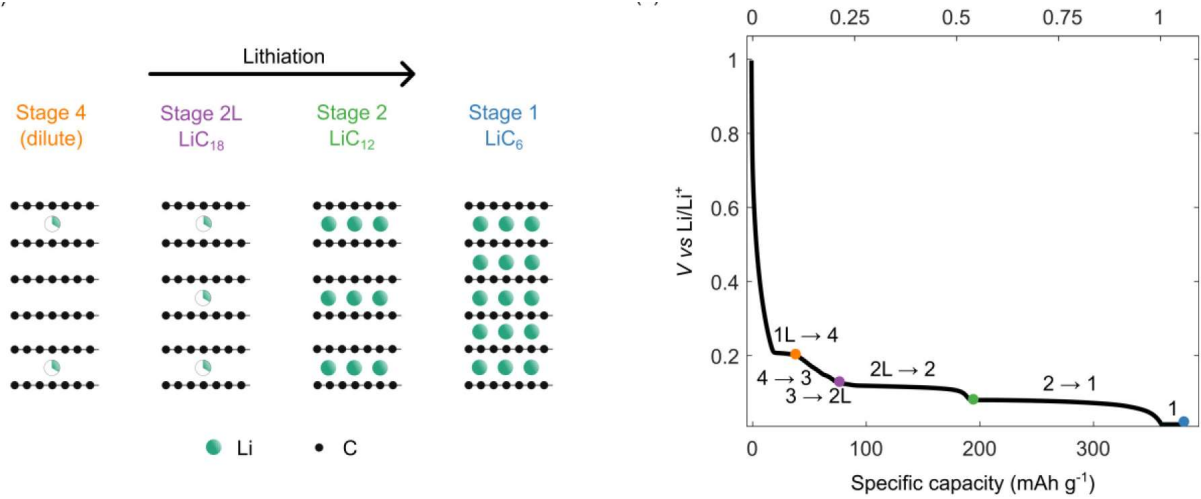


Fig. 8. (Left) Li intercalation stages. The dilute stages are formed first (1L, followed by stages 4 and 3, the last two distinguished by the number of graphite sheets between the Li layers) up to a 25% state of charge (where “charge” is used, because graphite is typically charged vs a positive electrode material (cathode)). After this, the dilute stage 2 (2L) and the dense stages 2 and 1 form. The interlayer spacing was kept constant for the sake of clarity in this figure, but as the concentration of Li⁺ ions increases, the *c* lattice parameter, and thus interlayer spacing, increases by $\leq 10\%$ (see the text). (Right) Typical voltage profile for constant-current cycling of a Li: graphite half-cell.

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Chapter 2.

Materials and Methodology

2.1 Raw materials

2.1.1 Petroleum derived cokes

Petroleum cokes are a by-product carbon rich solid material with some other heavy, sulfur, and hydrogen, the resultant of the oil refining. It is also referred to as coke, pet coke or petcoke and it that can be used for various industrial and commercial applications, not to mention as an old energy source. Given the importance of these uses, petroleum cokes is an essential part of the global energy supply.

The petcokes is structurally close to the so-called cokes family and is generally used in manufacturing processes such as aluminium smelting, carbon black manufacture, and other industrial processes that require high temperature heat treatment and activation. Petroleum cokes also can be obtained from some unconventional sources other than oil residues. One of these sources is the manufacture and processing of Bitumen (Asphalt) extracted from oil sands in refineries majorly in the U.S.A.

The production of petroleum cokes has a long history, starting in the late 1800s. After that, the areas of its use began to spread globally. It was used primarily as an industrial fuel source for boilers and furnaces. Its use has expanded to include a variety of other applications, ranging from industrial to consumer-oriented applications. Today, it is a main fuel source for power plants and boilers due in large part to its high energy content. It can also be used in cement production as an additive or binder. In addition, Petroleum cokes is used to produce graphite via high heat treatment “graphitization”, which can be used in more luxurious and

various products, such as specialty graphite or graphite electrode and recently anodes for lithium ion batteries which is the main theme of this thesis. Today in the field of anodes manufacture, the petroleum cokes-derived graphites are the main drivers for lithium ion batteries that majorly shines in China.

As mentioned above, the production of petroleum cokes starts from the oil refining process. The first stage is the extraction of crude oil from the ground, simply put, drilling an oil well. The second stage involves the transporting the pumped liquid to the oil refinery. Oil refineries literally refine these mixtures of raw hydrocarbons into useful products for the market, for example, petroleum oils, gasoline, diesel, kerosene, and other derivatives. Refining petroleum hydrocarbons includes equipment, stages, techniques, and resulting chemical reactions to obtain the final product. At this stage, raw materials are heated to high temperatures in distillation towers and pressed to high pressures. Then, each hydrocarbon compound separates at a predetermined pressure and temperature.

The residues of these derivatives remain in the form of liquids. These liquids are transported to next units called "coking units" to complete the filtering process. Then, these liquids are processed at a predetermined temperature and pressure to produce petroleum cokes in the form of solids after purging them of all gases and volatile matters. Finally, all remaining light and heavy oils are separated. The resulting petroleum cokes at this stage is called "Green cokes". The green petroleum cokes can be used as it is, but other applications require more heat treatment processes to produce "Calcined cokes". This process usually involves transferring petroleum cokes to a rotary kiln to remove the remaining volatile hydrocarbon residues. The calcined petroleum coke can be further processed to be used mainly in manufacturing steel or aluminium smelting. For storage and transportation, such as

coal, petroleum cokes can be stored in large piles in bags or silos. Conveyors, hopper belts, and trolleys can easily transport in large quantity.

Because petroleum cokes is carbon-rich, it is important that it must be stored in a dry environment. Under a humid condition, it will easily transform into a hard solid called "damp cokes". It can also be fragile to be easily broken or removed through the use of a ripper, which is a high-pressure water hose.

The physical and chemical specifications of petroleum cokes depends on the production methodology and the resulting final product. Some of the most common properties for petroleum cokes are as follows.

- Chemistry: Most petcoke has an average carbon content of 85~99%, and hydrogen in concentrations between 3.0- 4.0%. Raw (or green) coke contains 0.5-1% nitrogen and 0.2- 6.0% sulfur, which become emissions when cokes is calcined.
- Heating Value: Petroleum cokes is highly combustible and has a high heating value, often between 8,000 and 10,000 BTU/lb.
- Size: The particle sizes of petcoke are typically in the range of 1-50 mm.
- Ash: Depending on the origin of petroleum cokes, it may range from 0.5~1%.

- Moisture: The moisture content within the petroleum cokes particles varies with the mining place; it may range from under 1% to over 10%.

- Volatile Matter Content: The concentration of volatile matter in petroleum cokes varies depending on the place of mining, which is usually found in proportions of less than 10%.

- Hardness: There are two distinct varieties of petroleum cokes: calcined and green. Calcined petcoke is more complex and denser than green petcokes due to its increased carbon concentration.

- Sulfur Content: Sulfur content can vary from 0.2% to 6%, depending on the type of petcokes and the refining process used.

- Metal Content: The total metal content is typically less than 0.5%. The metals in Petcokes are aluminium, cobalt, iron, chromium, calcium, and others.

- Fixed Carbon: Petcoke's selected carbon content is typically more than 85% and can be as high as 99%.

- Absolute Density typically ranges from 0.8 to 1.0 g/cm³ and real density around 2.0g/cc

There are several types of petroleum coke, which differ according to the processing and refining conditions.

- Sponge Coke

It is a petroleum cokes produced from heavy residue feedstocks by pyrolysis in a fluidised bed. Why it is called a sponge is due to its high porosity and low bulk density.

Sponge cokes is mainly used to produce electrodes for the aluminium smelting industry. Sponge cokes is ideal for anodes due to its high purity, low sulfur content, and good electrical conductivity. It is also highly resistant to thermal shock and has a low coefficient of thermal expansion.

Sponge cokes is also used as fuel in industrial boilers and cement kilns. Its low sulfur content causes it to produce less sulfur dioxide emissions when burned.

- Shot Cokes

This type of cokes is from the delayed coking process. When cokes particles undergoes rapid quenching, irregularities are accompanied in the structure. Accordingly, it becomes difficult to handle and unacceptable for special cokes applications. For example, aluminium anode production requires high purity low porosity coke. It can be used as a fuel in various industrial processes, including cement kilns and power plants. Its high porosity makes it

possesses a good combustion property and also reduces emissions.

- Needle Cokes

It is produced exclusively from fluid catalytic cracking decant oil (FCC-DO) or coal tar pitch. Its unique structure and high purity make it ideal for producing high-quality graphite electrodes, essential for manufacturing anodes for lithium ion batteries for electric vehicles (EVs), smartphones and other energy storage systems. Next to graphite electrodes, lithium ion battery is the key consumer of the petroleum needle cokes.

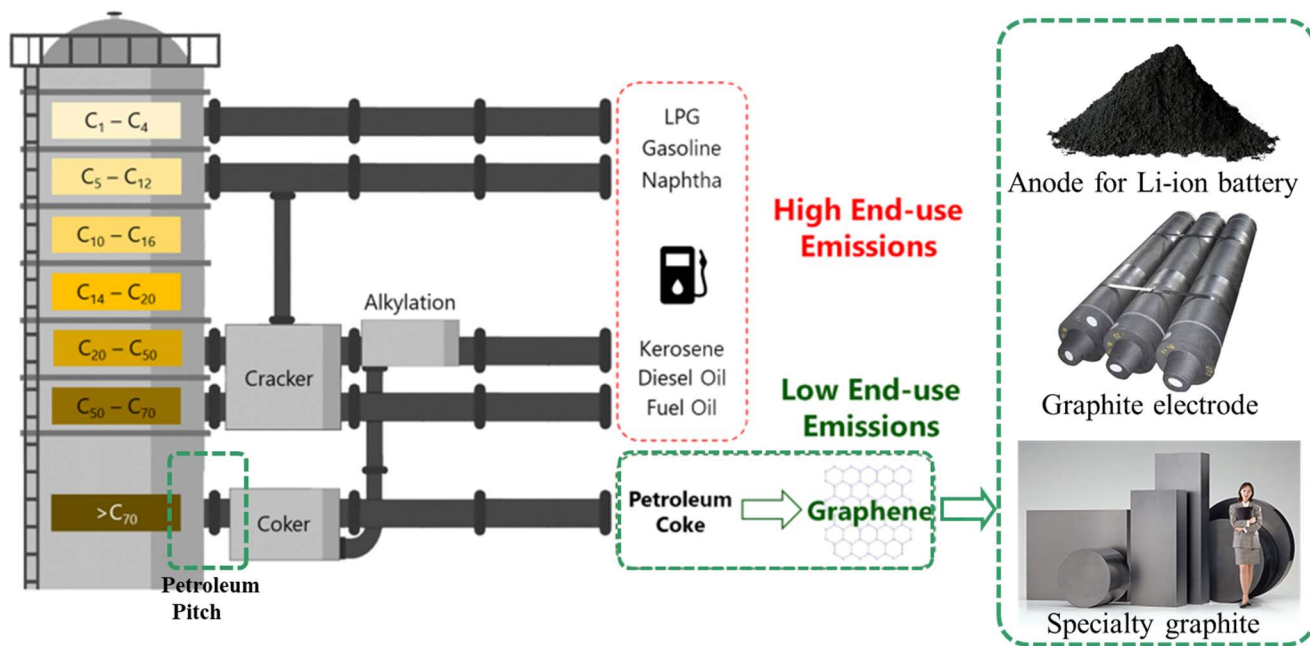


Fig. 1 Schematic of Oil refinery products

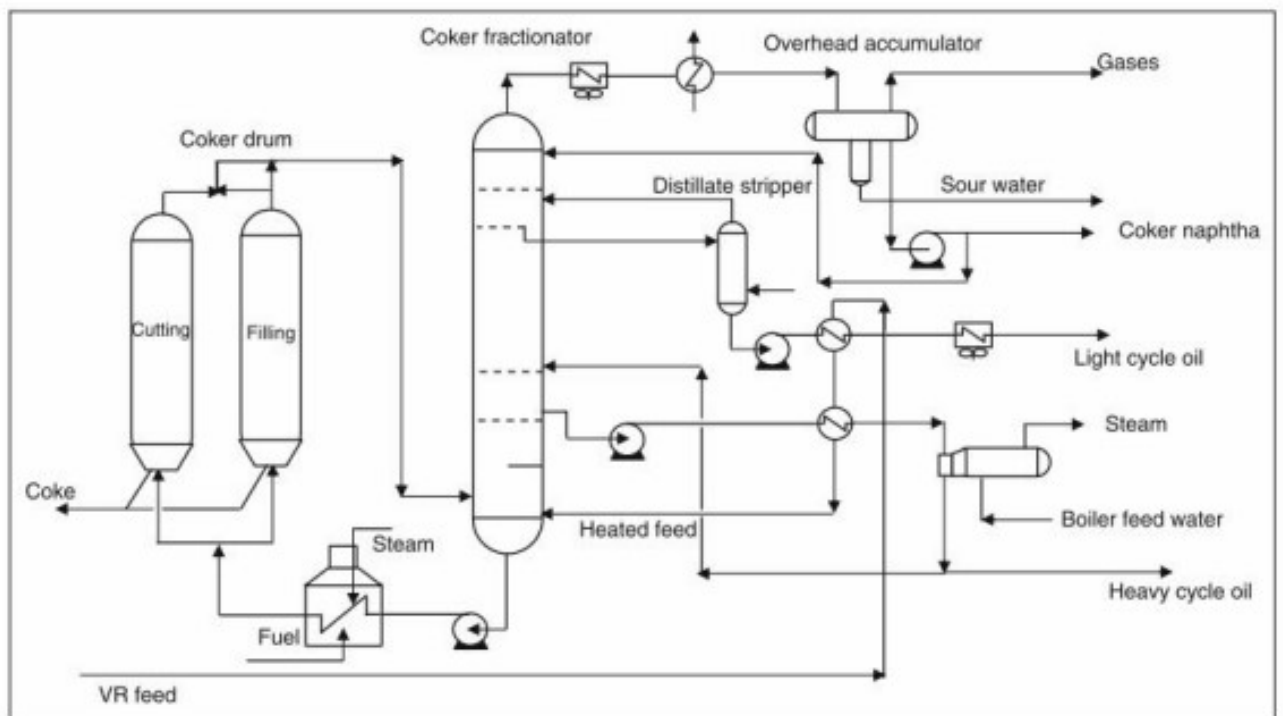


Fig. 2 Schematic of Delayed coking process



Fig. 3 Calcined petroleum needle cokes for graphite electrodes and anodes for lithium ion battery manufacture

2.1.2 Coal-tar derived cokes

With a fluctuating oil price, many countries without a well are exposed to higher degree of risk in cokes supply. Such a reality has sparked the development of coaltar-based needle/pitch(isotropic) cokes production technology, it was first successfully commercialized by Mitsubishi Chemical company of Japan (Figure 4).

Coal-derived needle/pitch cokes is born from the raw coal material coking which produces firstly metallurgical cokes that cater to the steel making and secondly a coal-tar which is the cradle for the needle/pitch cokes as illustrated in Figure 5. From raw material pretreatment, series of processes follows: centrifugal decanting, distillation, extraction, delayed coking and calcination as presented in Figure 6. The coal-tar and its pitch's main component is a polycyclic aromatic compound, wherein contain a certain amount of quinoline insolubles (QI). It is a definite factor to control the quality and quantity of needle/pitch cokes production.

As stated above, coal-tar treatment process comprises of: pretreatment, distillation, extraction, coking and finally calcination. POSCO MC Materials, established on November 5, 2012, is a joint adventure between Mitsubishi Chemical company of Japan which provides needle/pitch cokes technology and POSCO Future M company of Korea which provides the infrastructure. From the Korea's first coal-derived needle/pitch cokes company, above process are explained in detail as follows.

- Pretreatment : Utilizing a centrifuge separator facility, refined tar is produced by removing moisture and sludge in Coal-tar.

- Distillation Process : Heating Coal Tar, raw material, separating it into Oil Fraction and Soft Pitch, leveraging the differences in their boiling points. The resultant Oil Fraction includes Light Oil (BTX), Naphthalene Oil, Absorption Oil, and Creosote Oil.
- Extraction Process : This process involves the removal of elements from the Soft Pitch obtained from distillation, hindering anisotropy, and segregating it into soft pitch for needle and pitch. The factor that disrupts anisotropy is used in soft pitch for pitch coke for an isotropic structure.
- Coking Process : Soft Pitch undergoes a Polycondensation reaction to generate semi-finished Green Coke for Needle and pitch applications. Cracking Gas and Creosote Oil are by-products of Green Coke manufacture.
- Calcination Process : Rotary Kiln to enhance the crystallinity of the coke under high-temperature conditions, ultimately yielding Needle and Pitch Coke. At present, the production equipment operation solvent method that has only normal and that produce the high-quality coal-based needle coke has been realized suitability for industrialized production in Japan.

It is important that delayed coking process is the most critical process of producing needle cokes, originally the technology was first introduced from that of producing petroleum needle cokes. And be it petroleum or coal, the formation of mesophase pitch is the defining phenomenon inside the coker that a phase inversion process (transformed from isotropic to

anisotropic) occurs. It is a result in which the pitch precursor undergoes thermal decomposition and thermal polycondensation to a certain extent. Nowadays, either thermal polycondensation of commercial coal-tar pitch and petroleum pitch (or even their certain soluble fractions) or catalytic polymerization of some aromatic substances is commonly used to prepare the carbonaceous mesophase as can be illustrated in Figure 7.



Fig. 4 Coal-derived needle/pitch cokes from Mitsubishi Chemical company



Fig. 5 Schematic of Coal /Coal-tar treatment process

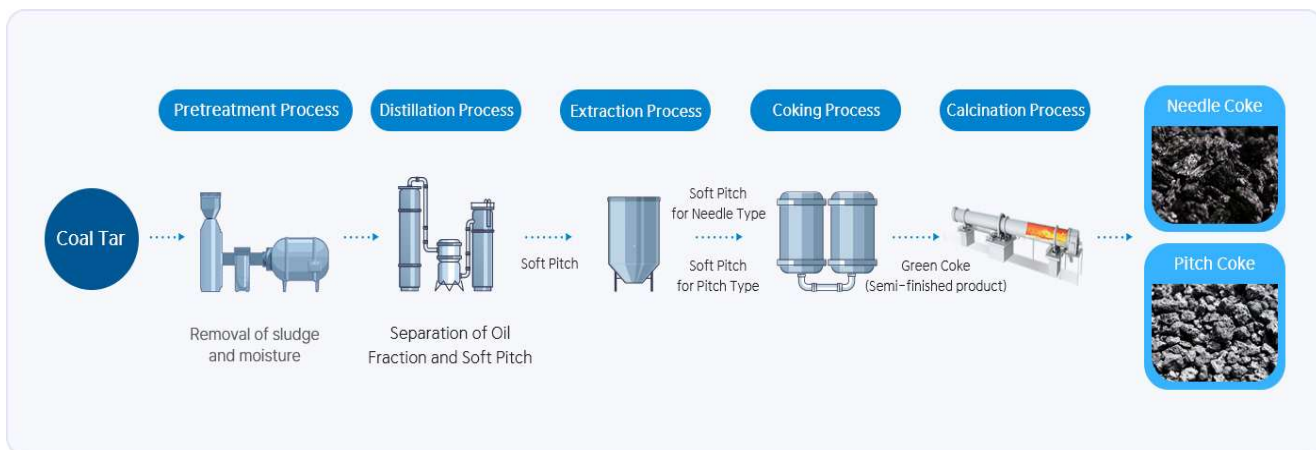


Fig. 6 Schematic of Coal-tar originated treatment process (POSCO MC Materials)

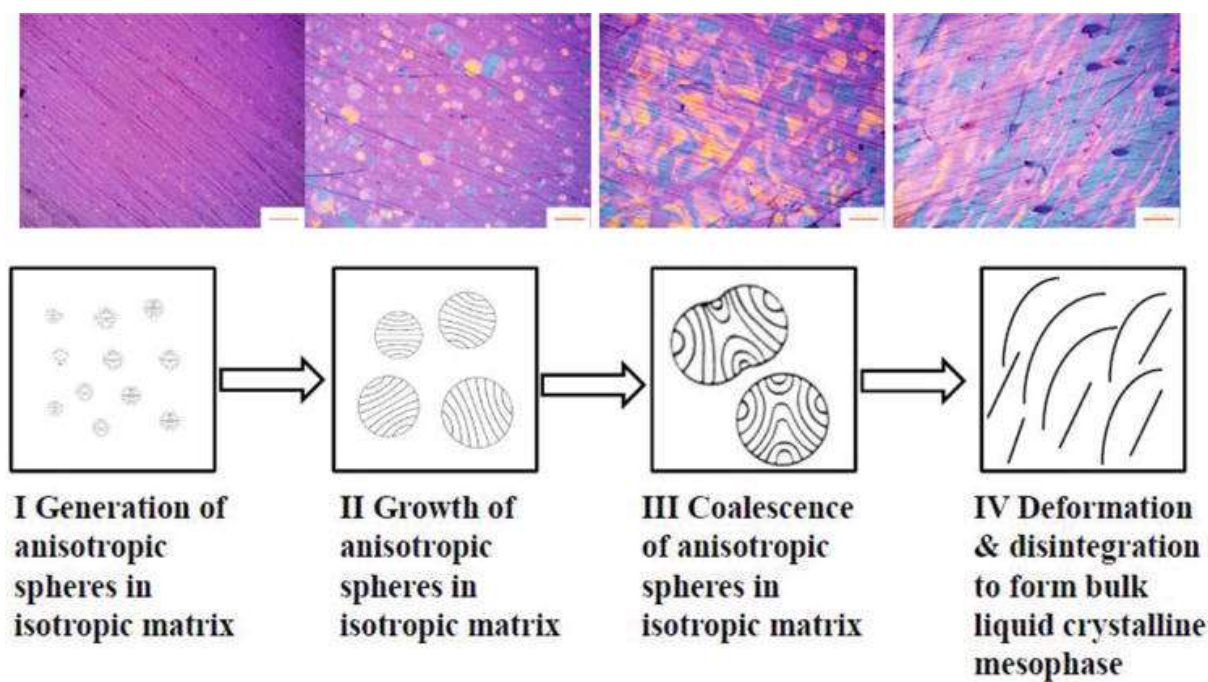


Fig 7. Schematic illustration of the formation and development process of bulk liquid-crystalline mesophase (scale bar in PLM micrographs is 100 μm), G. Yuan and Z. Cui DOI: 10.5772/intechopen.88860.

2.1.3 Graphite anodes from coal-derived needle/pitch cokes

Coal-tar based needle/pitch cokes were selected from POSCO MC Materials company and cokes were sized to a predetermined target D50 and span via air classifier mill (ACM) and spheronizer. It was Hosokawa Micron which first introduced the concept of both of these machineries to the world. And China has arduously and continuously incorporated the design into their manufacturing environment in that, it has evolved into a bigger capacity even though more labor and parts change were required. By using Jingxin fenti of China's ACMs and Tianyuan fenti of China's spheronizer, we have successfully acquired the target D50 of 6um and 10um, respectively as described in Table 1.

Conventional process of anode making starts from the same procedure of sizing cokes for a high-temperature kneading with binder material (Table 2) which is then followed by steps of calcination, graphitization, coating and secondary calcination as described in Figure 8. Other than graphitization that is likely a fixed but definite process, the whole flow takes several days to finish and the most sweet spot for reducing these time and money lies in the process of kneading which is the beef of this thesis.

As raw materials, cokes and pitch were selected and prepared according to respective novel process design by the author. Green and calcined cokes (Table 3) were pulverized and spheronized (Figure 9) to fit the experimental purpose and journeys starts in the following chapters.

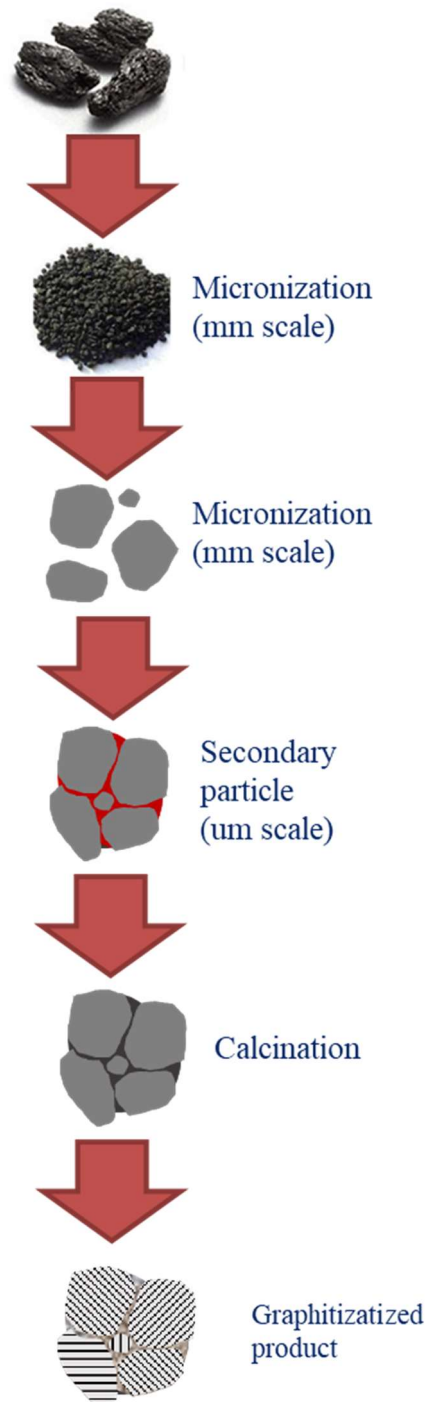


Fig. 8 Conventional (current) manufacturing process of graphite anodes

Pitch	Type	Real Density (g/cc)	CTE ($\times 10^{-7} / ^\circ\text{C}$)	Fixed Carbon (%)	Ash(%)	Sulphur (%)	VM(%)
Needle cokes	Green	2	-	95			5
Needle cokes	Calcined	2		99	0.00	0.3	0.4
Isotropic cokes	Green	2	22	95	0.3	0.3	5
Isotropic cokes	Calcined	2	35	99	0.3	0.3	0.4

Table.1 Characteristic of needle/isotropic cokes (POSCO MC Materials)

Pitch	Source	Softening point(%)	QI(%)	TI(%)	Beta-resin(%)	Fixed Carbon (%)	Ash(%)	Sulphur (%)
ZL250	Petroleum	250	0.5	30.2	29.7	68	0.02	0.01
BX95KS	Coal tar	110	4~8	22~28	16~24	>54	0.3	0.7
Coaltar	POSCO	- (Moisture: : 25.19)	0.79	2.62	1.83	26	-	-

Table. 2 Characteristic of pitch binding materials

Typical Properties	Green	Calcined
Moisture (%)	0.1	0.1
Ash (%)	0.02	0.02
VM (%)	5.0	0.9
Sulfur (%)	0.3	0.3
Nitrogen (%)	0.6	0.6
RD (Real density, g/cc)	2.14	2.13
CTE (x 10 ⁻⁷ /°C)	3.5	5

Table.3 Coal-tar derived cokes properties

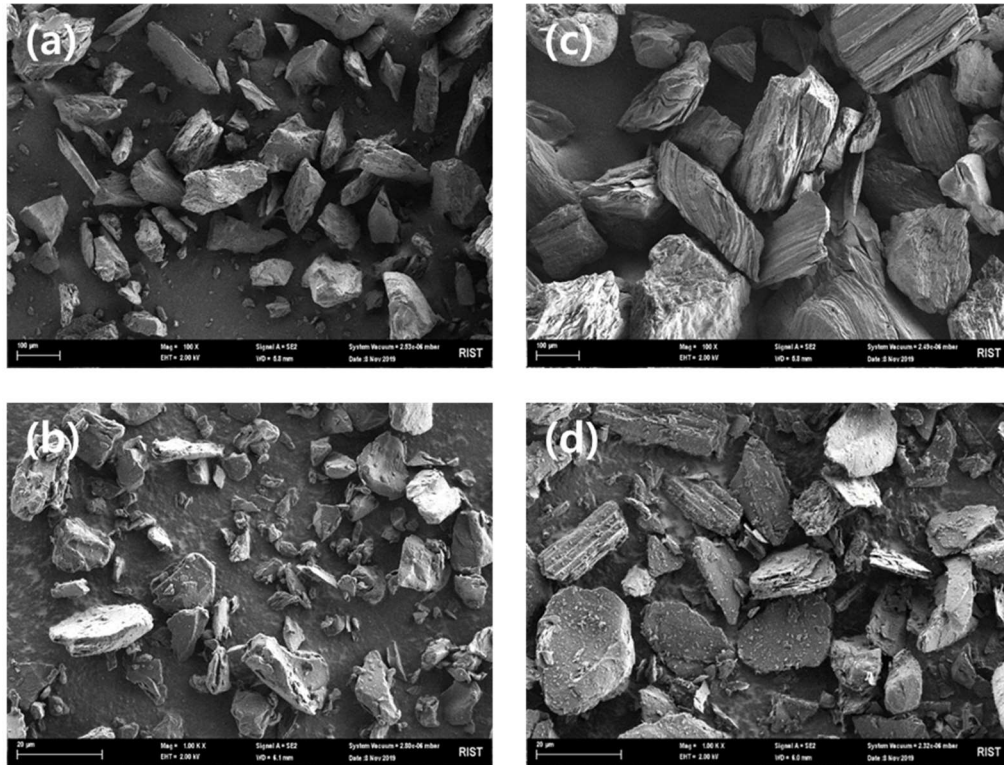


Fig. 9 Scanning electron microscope images of coal-derived cokes particles

(a) Green needle cokes-pristine (b) Green needle cokes-spheronized

(c) Calcined needle cokes-pristine (d) Calcine needle cokes-spheronized

2.2 Property analysis

- Quinoline Insoluble (QI) / Toluene Insoluble(TI) measurement

Based on the ASTM D2318-20 standard test method, QI & TI were determined. This method is useful for evaluating and characterizing tar and pitch, and for establishing the uniformity of shipments and sources of supply. Simply explained as below (Beta resin was calculated by TI-QI)

1. Digesting the sample in hot quinolone→2. Filtering the sample→3. Washing the insoluble material→4. Drying the insoluble material→5. Weighing the insoluble material

- Coefficient of Thermal Expansion (CTE) measurement

Based on Nippon steel protocol, After pulverizing a coke, the particle size is adjusted (16 to 60 mesh: 20%, 60 to 200 mesh: 45%, and 200 mesh or less: 35%), → pulverized coke is blended with a binder pitch at 160° C. for 20 min. → An addition amount of the binder pitch is selected so that molded Bulk Density is maximized→Extrusion-molded into a size of 20 mm Ø x100 mm. → Baked at 900 C. & graphitized at 2500 °C → Determining the CTE. An average CTE at Room Temperature to 500°C.

- Softening point measurement

Based on Nippon steel protocol, An outer cylinder of a device for determining a glass viscosity by a rotating cylinder method is stopped in a position where the cylinder is rotated

by some angle, and the time spent for causing an inner cylinder rotated accordingly to return to the initial position is determined, wherein the Softening point is defined by a temperature at which the reduced viscosity is 107.6 poise (“Glass Engineering” written by S. Naruse, published by Kyoritsu Shuppan Co., Ltd.).

For more other references, ASTM D 1525, ASTM D 648, ASTM E 2347

2.2.1 X-Ray diffraction measurement

The graphitization degree of a sample showing the lowest surface area was selected for X-ray diffraction measurement (RIGAKU RINT Ultima+) at a narrow scan rate of 0.5 o/min (Cu K α) in ranges 24-30° based on Gakushin method using Si as a reference.

2.2.2 Field-Emission Scanning electron microscope

FE-SEM (JEM-ARM200F, W cold FEG, equipped with Double Cs-Correctors by Jeol, Japan) images the electronic signals of secondary electrons and backscattered electrons emitted from the surface of a sample when the surface of the sample is irradiated with an electron beam.

2.2.3 Powder Conductivity Measurement

The bulk density and powder conductivity was measured by a powder electrical characteristics evaluation system (HPRM-FA2, Hantech) with a 200 to 1200 kgf loading range.

2.2.4 Surface properties

For surface properties, 3 Flex type surface analyzer (Micromeritics. USA) was used to characterize surface area and pore size distribution characteristics.

2.2.5 Elemental analysis

Elemental analysis was performed based on 1 g of each sample up to 750°C with a heating rate of 5°C/min.

2.2.6 Particle size analysis

Particle size analyzer (Cilas 1090), using a laser diffraction to measure the particle size, and size distribution was used for anode material characterization

2.2.7 Tap density measurement

Tap density measurement was performed based on 20 g of each sample with tapping direction of up and down for 3000 counts.

2.3 Electrochemical evaluation

The anode material was produced with the carboxyl methyl cellulose and styrene butadiene rubber as the binder and the conductive material (Super-P), that were uniformly mixed in distilled water to turn into slurry, so that the weight ratio thereof became 97:2:1

(described in the order of anode active material/binder/conductive material). The slurry was coated with a copper (Cu) current collector, compressed by a roll press, and dried under vacuum conditions for 12 h at 100 °C. During this step, the electrode density was set to 1.6 g/cc. 1 M solution of LiPF₆ in a mixture of ethylene carbonate (EC), and dimethyl carbonate (DMC) with 1:1 ratio by volume was used as an electrolyte solution. A CR 2032 coin type cell was produced with lithium foil as a counter electrode, according to a common half-cell assembly method. The coin cell test was driven under the condition of 0.2 C, 5 mV, 0.005 C cut-off charging and 1.5 V cut-off discharging, and the rate performance and retention rate were measured in 0.2, 1, 2, 3 and 5 C rate condition.

Chapter 3.

Design of continuous kneading system for active anode material fabrication using retrofitted assembly of co-rotating screw extruder

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Processes 2023, 11, 2660. <https://doi.org/10.3390/pr11092660>

3.1 Introduction

Recently, twin screw extruder is widely used in various industrial uses such as foods[1-5], ceramics[6-9], polymers[10-13] and so on. However, research on the twin-screw extruder optimized for manufacturing artificial graphite has not been conducted, and so far, artificial graphite has been simply pulverized and sold as extruded graphite. Therefore, it is necessary to suggest the optimal extruder for artificial graphite manufacturing process. In addition, the kneading process is often considered the most costly step. For instance, the current kneading process takes more than 12 hours when it includes processing time as well as cooling/cleansing steps. It becomes a great labor challenge wherever kneading process operates in current system. It is also of a significant concern because government agency in the environmental safety awareness may take severe measures. It is inevitable that the current technology emits a certain amount of un-healthy fumes during charging and discharging of feeds.

One of exemplary cases is motivated to build new design of kneading assembly. The case

employed the continuous operation of co-rotating twin-screw extruders in anode and cathode manufacture and the result was effective[14]. In advance, two distinctive types of parallel co-rotating twin-screw extruders, KRC-S2 model (Kurimoto., LTD, Japan) and CHT-20 model (Nanjing Cowin Extrusion Machinery Co., LTD, China), were selected and evaluated. The KRC-2S model has the axis dimension ratio of 44 : 5 (440 mm in length and 50 mm in diameter) with 30 rpm (Figure 1 (a)). The system is equipped with reverse heli-cal shaped screw paddle at the end so that the feed can apply to the additional compact-ness before discharging. The sample discharging outlet is placed downside of the barrel where sliding gate adjusts the opening time. In comparison, CHT-20 model was built-in with axis dimension ratio of 44 : 1 (968 mm in length and 22 mm in diameter) (Figure 1 (b)). CHT-20 model has more than twice the length of KRC-S2 model. In addition, CHT-20 model is set to 300 rpm thereby advantageous for avoiding feed clogging. In order to compare KRS-S2 and CHT-20, the kneading performances were evaluated at the same residence time of 20 min at 250°C. CHT-20 showed the superiority to secondary particle expansion of D50. Subsequently, the retrofit design was realized by installing a certain portion into CHT-20 (Figure 2). Here, two twin-screw extruders are placed and connected by another single screw feeder so that outlet of the 1st extruder and inlet of the 2nd extruder are overlapped to prevent fume discharge. With maintaining the same axis diameter of 22 mm, the length to diameter ratio was lengthened from 44 : 1 to 64 : 1 (1408 mm in length and 22 mm in diameter). The conveying, mixing and engaging elements are made of W6Mo5Cr4V2 with core material selected from 40CrNiMo. And each barrel comprises 8 sections with heating capability that can raise up to 400°C. And each heating unit length is 160 mm which translates to 1280 mm in total. As given the smooth running of powder mix of cokes and pitch under high pressure, single screw vertical feeder (0.18 kW, Output speed : Up to 50 rpm) was placed so that the premix could go directly to the

rotating axis by force. This is in response to anti-clogging under lower 20 rpm (a fifteenth of the previous setting).

The objective of this work is to design the continuous kneading process with minimize of harmful volatile material. It is well known that the various volatile materials and dusts are generated in artificial graphite manufacturing process. In actual industry, purifier and dust collector was utilized to remove them. As eco-friendly technology development is required world-widely, the demand of volatile material and dust generation minimized process of artificial graphite is also increasing. In present work, based on the demand of suppressing of dust and volatile material, we would like to suggest optimal continuous process using twin-screw extruder for artificial graphite manufacturing process. Consequently, we evaluated LIB anode performance for obtained artificial graphite.

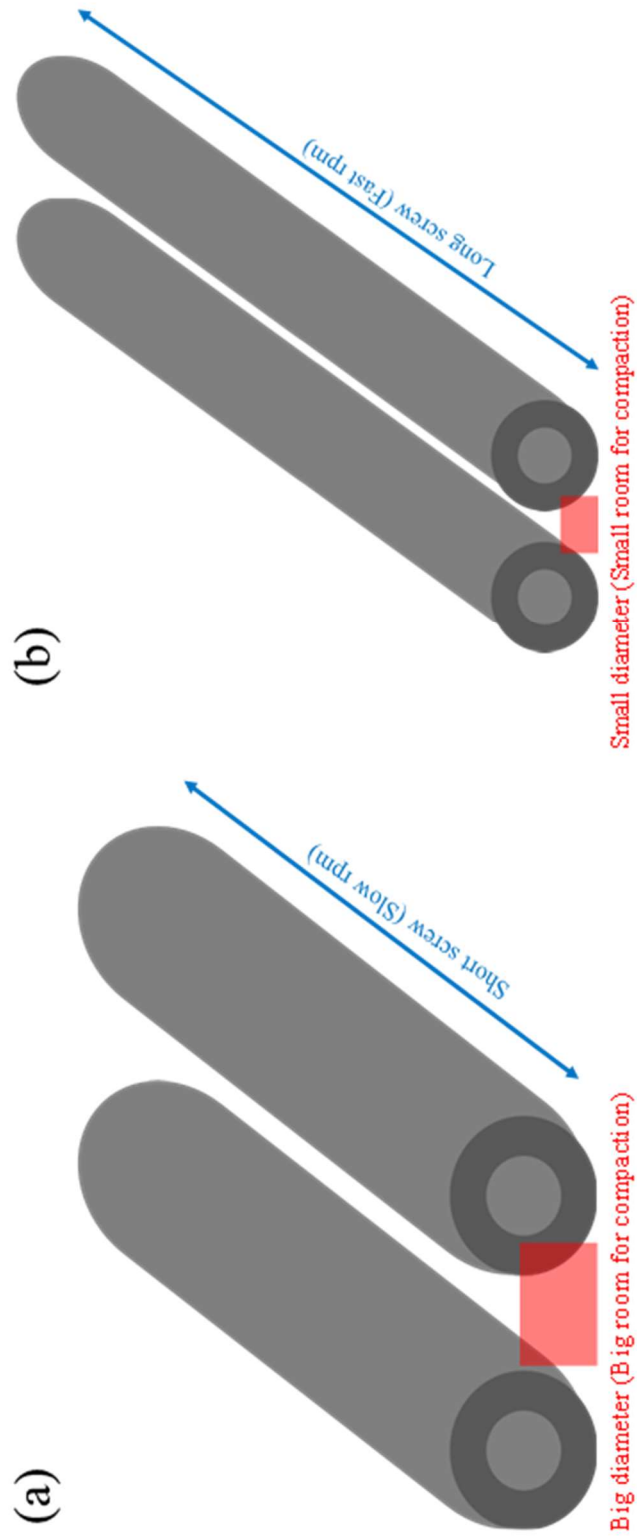


Figure 1. (a) KRC-S2 (In the courtesy of Kurimoto.,Ltd) and (b) HCT-20 (In the courtesy of Nan-jing Cowin.,Co.Ltd) kneader screw paddle composition.

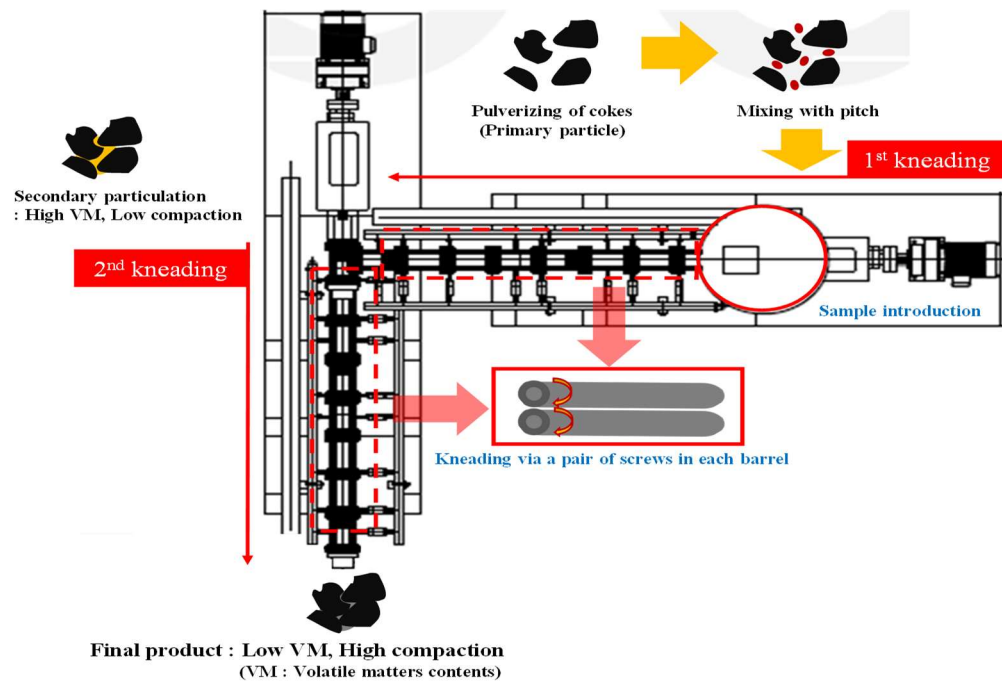


Figure 2. Retrofitted design of double twin-extruder type continuous kneader

3.2 Experimental

3.2.1 Needle cokes and binding pitch composition

Two types of coal-derived needle cokes, green and calcined, were prepared by POSCO MC Materials, Co. Ltd. (Republic of Korea). The cokes were pulverized to have a particle size distribution of D50 set to approximately 10 μm . The petroleum-derived binding pitch (ZL250, RÜTGERS GmbH in Germany) was premixed at room temperature with needle cokes for 30 min at 30 rpm by KRC-S2 sigma blade type mixer. The weight ratio of cokes to binding pitch is set to 1 : 0.12. The pitch has the softening point of 250°C.

Pitch binder	Source	QI(%)	Fixed Carbon(%)	Ash(%)	Sulphur(%)
ZL250	Petroleum	0.5	68	0.02	0.01

Table 1. Characteristic of pitch binder, ZL250.

3.2.2 Continuous kneading effect comparison

The premix samples of cokes and pitch were inserted into respective co-parallel rotating extruders when the barrel temperature reached up to 250°C and residence time passed 20 minutes. In order to maintain the same residence time, and given the different internal structure mechanism of respective machineries, rotating speed were controlled to 30 rpm for KRC-S2 and 300 rpm for CHT-20 to prevent the machineries from clogging. The feeds were retrieved upon discharge, which were later heat-treated at 1200°C for 2 hours. The measurement of samples' particle size distribution was also determined regularly.

3.2.3 Continuous kneading effect by a retrofitted double co-rotating parallel extruding system kneading process

Carbon/graphite precursor (1 kg) is mixed with pitch binder (10~13.5 % by extrapolation) at room temperature (25°C) for 30 min. That is, pitch binding material (10 % by weight) is applied to cokes while graphitized primary cokes are based on both 13.5 % and 10 % of the same for comparison in regards to hydrophobic surface deriving from graphitization at 3200°C. Specifically, KRC-S2 sigma-blade type kneader (2 liter) was employed so that twin rotors with opposite direction of rotation can enhance more uniform distribution of the feed. After the room temperature mixing, the mixture was introduced into a double barrel extruding type continuous kneader (Retrofitted CHT-20 model). Each screw's rotating speed was set to 20 rpm with a connecting single screw feeder at 7 Hz so that residence time was maintained to 20 minutes. The temperature was set to increase 90~100°C over the softening point temperature of the binding pitch mixed feed, that is, 350°C for a pitch with 250°C softening point and 200°C for a pitch with 110°C.

3.2.4 Surface properties

For surface properties, 3 Flex type surface analyzer (Micromeritics. USA) was used to characterize surface area and pore size distribution characteristics.

3.2.5 Particle size analysis

Particle size analyzer (Cilas 1090) was used to find particle size distributions and spans.

3.2.6 Tap density measurement

Tap density measurement was performed based on 20 g of each sample with tapping direction of up and down for 3000 counts.

3.2.7 Elemental analysis

Elemental analysis was performed based on 1 g of each sample up to 750°C with a heating rate of 5°C/min.

3.2.8 X-Ray diffraction measurement

The graphitization degree of a sample showing the lowest surface area was selected for X-ray diffraction measurement (RIGAKU RINT Ultima+) at a narrow scan rate of 0.5 °/min (Cu K α) in ranges 2 θ 24-30° based on Gakushin method using Si as a reference.

3.2.9 Topological characterization

Scanning electron microscope (JEM-ARM200F, JEOL, Japan), W cold FEG, equipped with Double Cs-Correctors was used for topological characterization of anode materials.

3.2.10.1 Electrochemical performance- Cell preparation

The negative electrode active material was produced with the binder (carboxy methyl cellulose and styrene butadiene rubber) and the conductive material (Super P) that are uniformly mixed by distilled water so that the weight ratio thereof becomes 97:2:1 (described in the order of the anode active material: the binder: the conductive material). The mixture was applied to a copper (Cu) current collector, compressed by a roll press, and dried under vacuum condition for twelve hours at 100°C. In this case, the electrode density is set to be 1.5 to 1.6 g/cc. Lithium metal was used as a counter electrode, and 1 mol. solution of LiPF₆ in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) by 1:1 ratio by volume is used as an electrolyte solution. The respective constituent elements are used, and a CR2032 half coin cell is produced with lithium as a counter electrode according to a conventional production method.

3.2.10.2 Electrochemical performance- Electrochemical testing

Coin cell test is driven under the condition of 0.1 C, 5 mV, 0.005 C cut-off charging and 0.1 C, 1.5 V cut-off discharging, and initial discharging capacity and efficiency are measured.

3.3 Results and discussion

3.3.1 Comparison of KRC-S2 and CHT-20 for continuous kneading effects

The coal-derived needle cokes and petroleum-derived binder pitch were inserted into two distinctive models of co-parallel rotating type extruders, KRC-S2 and CHT-20. The compounding effects were evaluated, respectively. While green needle cokes showed clear signs of secondary particle size expansion by both models. Here, the secondary particle size was categorized and evaluated as 10, 50, 90 μm . Each particle was named as D10, D50 and D90 respectively. The expansion rate results are increased for D10, D50 and D90 (Figure 3 (a)). In specific, CHT-20 showed the superior effect in the range of D50 and D90 outperforming. In Figure 3 (b), calcined needle cokes showed the inferior expansion data in D10 and D50 ranges in CHT-20, but the higher expansion was shown in D90. Given the low wettability of calcined cokes in the bigger particle range, CHT-20 showed more effective result. It is probably due in large part to longer barrel with higher rotation speed of paddle movement and smaller paddle depth which leads to less residues inside the barrel. Therefore, the relatively small diameter rotating axis with a longer dimension operating at a faster rpm. would be more effective in kneading as well as compounding primary particles. And it also generates bigger and desirable secondary particles. It can be predictable that bigger axis could translate into more redundant leftover particles that could result in additional unnecessary reaction with a newly-fed particles after introduced.

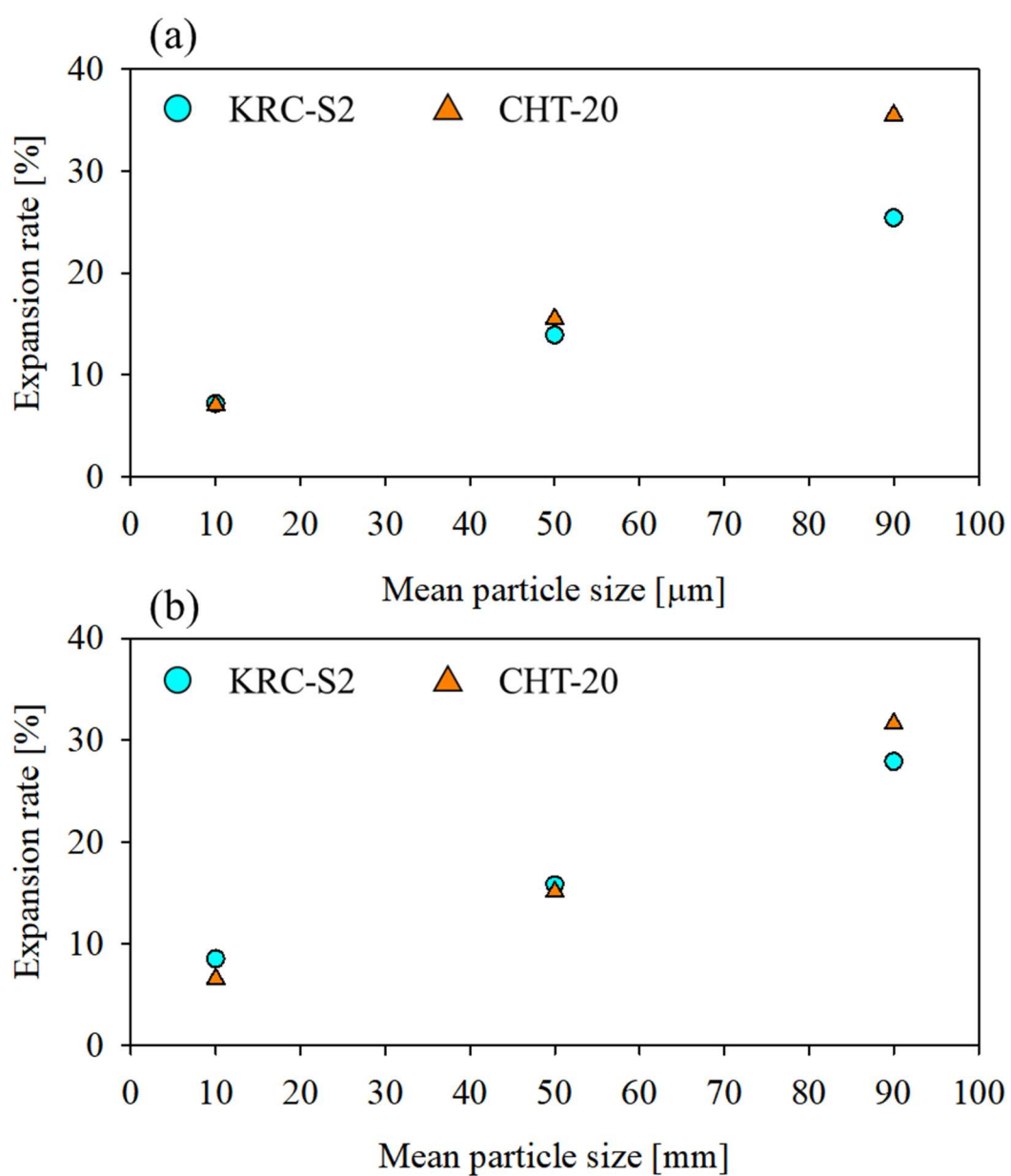


Figure 3. Secondary particle size expansion results of (a) green needle cokes and (b) calcined needle cokes composition.

3.3.2 Continuous kneading effects by a consecutive dual co-rotating parallel extruding system

After continuous kneading and compounding of samples, elemental analysis was examined. The result implied that the mixtures with petroleum derived pitch with higher softening point of 250°C contains higher volatile matters. Unfavorably, it is notable in green cokes with pitch mixture regardless of being isotropic or needle cokes. The calcined cokes also showed the same tendency in even smaller scale. It was expected that volatile material contents of cokes are inevitable whether isotropic or needle cokes were used (Figure 4). Petroleum-derived pitch showed the uniform tendency of higher residual rate when combined with either coke mixture even though pitches were treated at temperatures of 90~100°C higher than the softening point. In the end, it needs the elimination of volatile matters generated from either cokes or pitches. The newly retrofitted system may provide the solution to prevent the volatiles emission. More pitch derived binding materials would be affordable as well if the high-speed and limited internal dimension of the barrel structure was attempted in retrofitted system.

Primary particle size (D50, μm)	Pitch	Secondary particle size (D50, μm)	After graphitization			
			Span	Tap density (g/cc)	d ₍₀₀₂₎ (nm)	Surface area (m ² /g)
10	Pet.	15.24	1.40	0.82	0.3358	1.48
6	Pet.	8.90	1.48	0.63	0.3358	2.94
10	Coal	14.76	1.25	0.72	0.3358	1.96
6	Coal	10.91	1.34	0.62	0.3360	2.70

Table 2. Physical properties of calcined needle coke based samples.

In relation to volatile matter contents, particle size distribution measurement based on D50 volumetric analysis suggested that the parallel direction may provide the solution to minimize volatile emission where the sample with a smaller amount of volatile matters has a bigger particle size distribution. Therefore, it is assumed that the reduced amount of volatile matters have been transformed and formed a stronger bonding with other particles. Thereby a comparatively larger secondary particles would be generated. Coal-derived pitch samples evidently present higher rate of compounding effect and this is mainly attributed to its innate higher beta-resin content over its petroleum-derived counterpart. Regardless of calcination, this tendency firmly maintains on both needle coke and isotropic coke. In terms of wettability, it can be concluded that coal-derived cokes agree with the flows created by melting the same origin, coal-derived pitch binding material.

Regarding the perspective of volatile matters contents connected to secondary particle expansion, the specific details on the physical properties of the samples were further analyzed in combination with various primary particle size and pitch binding material types. Calcined cokes were selected to exclude the possible surface chemistry with binding pitch material deriving from coke structure.

In Figure 5, coal-tar based pitch binding samples showed apparently narrower span rates, that is $(D_{90}-D_{10})/D_{50}$, less than 1.35, meanwhile, petroleum-based pitch binding material samples showed higher values in tap density over their counterparts. The primary particle size of supporting cokes can be translated to better electrode processability. Such a phenomenon can be interpreted by severe centralization of D50 particle size of petroleum-based pitch groups. Meanwhile, coal-tar based pitch groups is expected to have a comparatively uniform distribution in all particle size distribution ranges. It is confirmed that all the samples have a

fair value of graphitization degree of less than or equal to 0.3360 nm as can be measured by X-ray diffraction. The surface area suggests that it is enormously affected by secondary particle size in reciprocal proportion.

As confirmed by images from scanning electron microscope, all the samples showed the evidence of agglomeration to form secondary particles. Petroleum-based pitch samples tend to possess less agglomerated morphologies both in 10 μm and 6 μm compared to their counterparts (Figure 6).

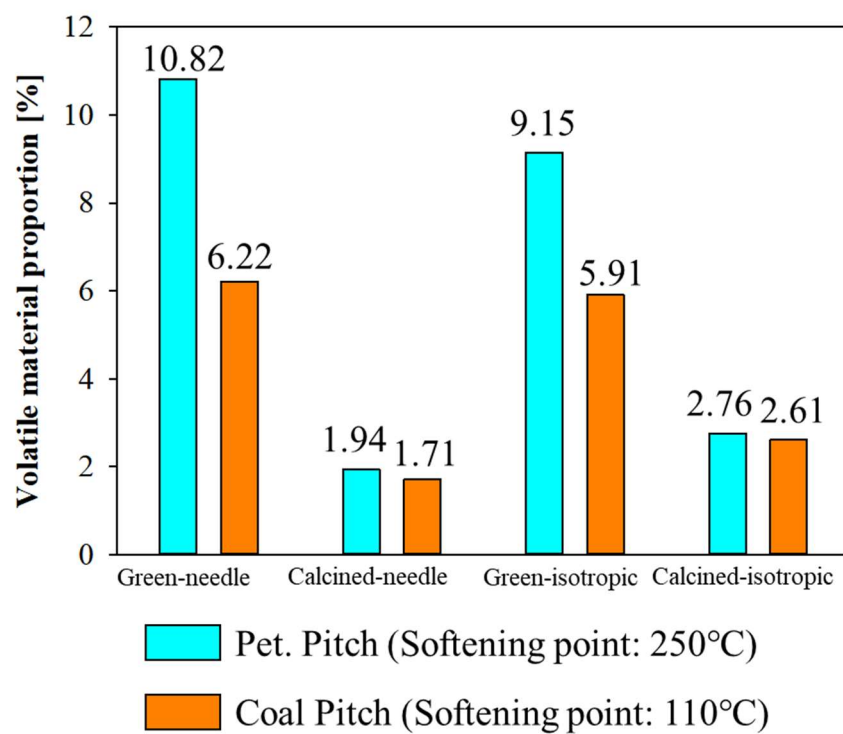
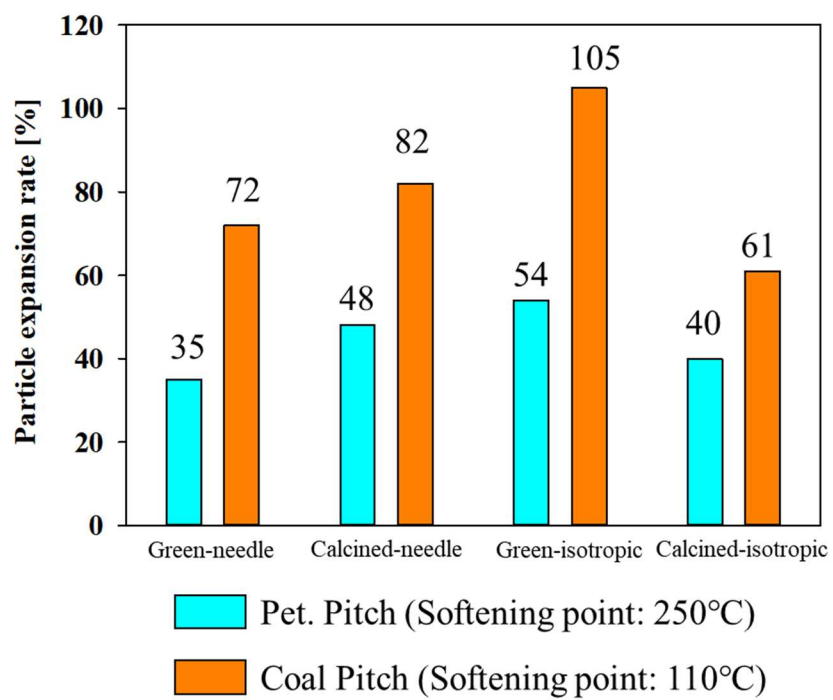


Figure 4. Volatile material proportion of after continuous kneading process.



**Figure 5 Particle size distribution expansion rate comparison in %
after continuous kneading.**

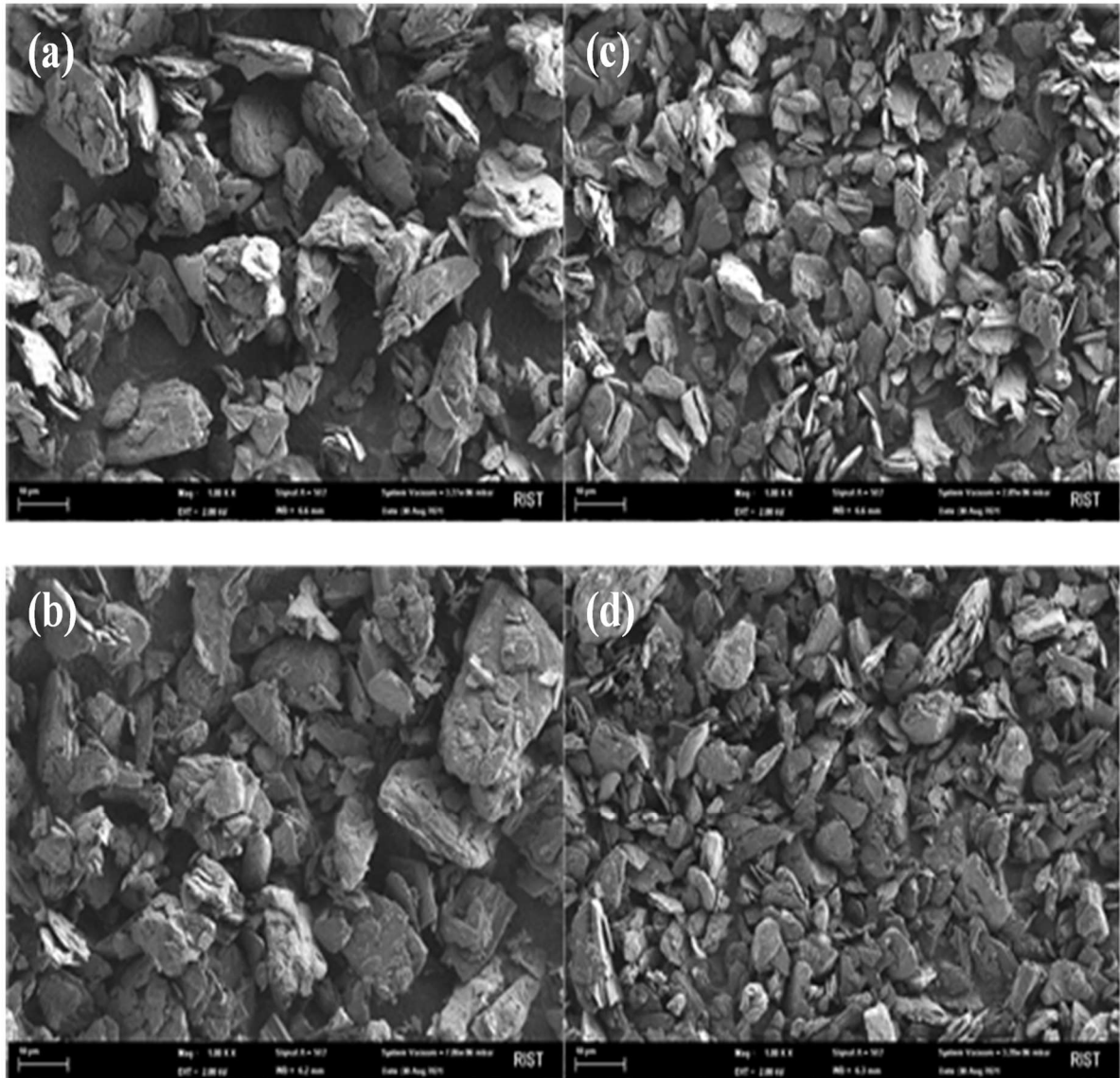


Figure 6. Scanning electron microscope photographs from graphitized active anode samples.

- (a) Calcined needle coke with D50: 10µm & petroleum based pitch binding material**
- (b) Calcined needle coke with D50: 6µm & petroleum based pitch binding material**
- (c) Calcined needle coke with D50: 10µm & coal-tar based pitch binding material**
- (d) Calcined needle coke with D50: 6µm & coal-tar based pitch binding material.**

3.3.3 Electrochemical testing result

For calcined needle coke with D50, LIB anode material test was performed. The 3rd discharging capacity of all calcined needle coke with D50 were more than 350 mAh/g (Figure 7). This showed an acceptable industrial standard by major lithium ion battery makers. Except for a calcined needle coke with D50 particle size : 6 μm & coal-tar based pitch binder sample which shows an initial Coulombic efficiency of over 90%. It is clear that petroleum pitch binding material seems to create a positive bonding with coal-derived calcined needle coke support that leads to both higher discharging capacity and initial Coulombic efficiency. This discharge capacity and Coulombic efficiency is much higher than 327 mAh/g and 81.6% of typical coal-derived artificial graphite [23]. Charging and discharging performance of the aforementioned samples all have a similar pattern of stable staging with a plateau above 20th cycle ranges in all 4 samples during charging. Uniform discharging characteristics can also be identified.

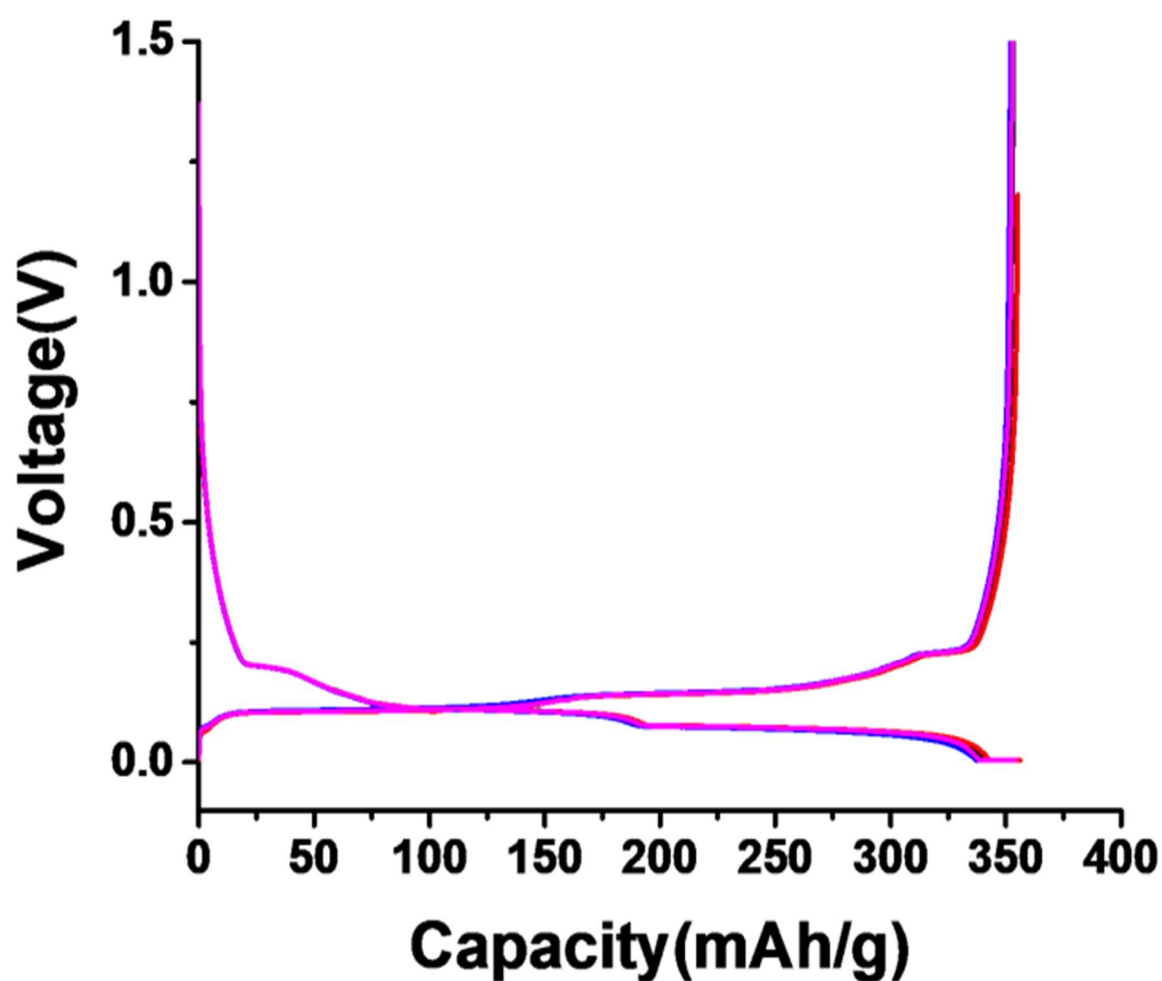


Figure 7. Charging and discharging cyclic characteristics

■-Calcined needle coke with D50: 10 μm & petroleum based pitch binding material,

■-Calcined needle coke with D50: 6 μm & petroleum based pitch binding material,

■-Calcined needle coke with D50: 10 μm & coal-tar based pitch binding material,

■-Calcined needle coke with D50: 6 μm & coal-tar based pitch binding material).

Primary particle size (D50, μm)	Pitch	Electrochemical performance	
		Discharging capacity (3 rd , mAh/g)	Initial coulombic efficiency (1 st , %)
10	Pet.	353.1	93.7
6	Pet.	355.0	92.7
10	Coal	350.3	92.4
6	Coal	352.9	91.5

Table 3. Electrochemical testing result of calcined needle coke based samples.

Calcined needle-cokes based samples have proven the proposed system's versatility by presenting better than average electrochemical performance that is, higher dis-charging capacity and initial Coulombic efficiency satisfying industrial standard. Simul-taneously it has become clear that cokes combination with various pitch binding materials amounts can be adjusted for a better production capacity. It is assumed that a limited space inside each barrel of the proposed continuous kneading system was not fully opti-mized enough to accommodate green coke based feeds treatment which exposed a great need for further study to prevent incineration of the feeds with high volatile matters con-tents since green cokes are more affordable to cater to current industry demands, that is higher discharge capacity and initial Coulombic efficiency. If they can apply to the pro-posed kneading system. Installing more discharge outlets in between heating compart-ments can be considered based on more detailed analysis on volatile matters contents dy-namics.

3.4 Conclusion

The objective of this work is suggestion of artificial graphite manufacturing process with suppression of harmful volatile material generation. In present step, two distinctive types of parallel co-rotating twin-screw extruders, KRC-S2 model (Kurimoto., LTD, Japan) and CHT-20 model (Nanjing Cowin Extrusion Machinery Co., LTD, China), were selected and evaluated. In order to compare KRC-S2 and CHT-20, the kneading performances were evaluated at the same residence time at 250°C.. CHT-20 showed the superiority to second-ary particle expansion of D50. Subsequently, the retrofit design was realized by installing a certain portion into CHT-20. With maintaining the same axis diameter of 22 mm, the length to diameter ratio was lengthened from 44 : 1 to 64 : 1 (1408 mm in length and 22 mm in diameter). It was

verified that a smaller diameter combined with longer screw facilitated kneading performance. Various premixed feeds of cokes and binding pitch were inserted into a retrofitted kneading system at 100°C, which is higher temperature than the softening pitch. Feeds were heat-treated and graphitized at 3200°C in an Acheson furnace. The retrofitted extruder assembly showed the effective control of intrinsic volatiles when kneading cokes and pitch. In a certain case, the resulting calcined cokes (D50) showed the 47% increase of their particle size distribution with no signs of smokes. In addition, the anode materials presented the highest discharging capacity over 350 mAh/g and 90% of initial Coulombic efficiency.

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Chapter 4.

Development of a shortened process for efficient manufacturing of artificial graphite for anode material in lithium-ion battery

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4.1 Introduction

In this study, we propose an efficient process for AG production. The processes are as follows: pulverization—granulation—graphitization—pitch coating—carbonization. Compared with commercial processes, the carbonization stage is eliminated. Due to our consideration of the spherical degrees of graphite particles and the void compensation within particles, coal-derived pitch was used in this work. A wet coating by coal tar was employed to ensure a uniform pitch coating [35]. In addition, we confirmed that the shortened process was realized by replacing the binder pitch with coal tar pitch, due to its lower softening point and ability to coat graphite particles. We evaluated the physical proper-ties of graphite anode materials produced by the streamlined process, and tested the LIB performance, suggesting the feasibility of the streamlined process through a comparative analysis with graphite produced by the conventional process.

4.2 Experimental

4.2.1 Sample Preparation

As the starting material, coal derived needle coke (POSCO MC MATERIALS. Co. Ltd., Republic of Korea) was adopted. The basic information of binder pitch [34] and coal tar pitch used in this research is summarized in Table 1. The entire processes of the commercial and shortened process of AG manufacturing are visualized in Figure 1.

Pitch Code	Source	⁽¹⁾SP (°C)	⁽²⁾QI (%)	⁽³⁾FC (%)	Ash (%)	Sulfur (%)
ZL250 [34]	Petroleum	250	0.5	68	0.02	0.01
BX95KS	Coal tar	110	6	63	0.32	0.70

⁽¹⁾ SP: softening point; ⁽²⁾ QI: quinoline insoluble content; ⁽³⁾ FC: fixed carbon.

Table 1. Characteristics of binder pitch and coal tar pitch.

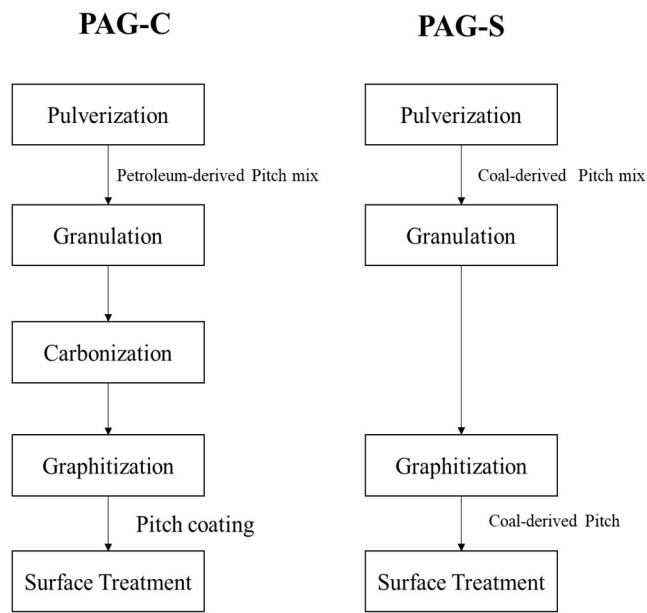


Figure 1. Flow chart comparison of AG manufacturing by Conventional(Left) and shortened process(Right).

Firstly, coke powder is pulverized using a jaw crusher to give an average particle size distribution under 3 mm. The coke particles are then introduced finely pulverized using an air classifier mill (hereafter referred to as ACM) to have a particle size (D50 volumetric ratio) of 9 to 15 μm . The coke powder pulverized by ACM still possesses a rough surface that could later adversely affect the formation of a SEI (solid electrolyte interface), providing unnecessary active sites derived from rough morphologies. Thus, coke powder is mixed with petroleum-derived pitch powder in pre-mixing using a V-mixer (30 rpm for at least 30 min). The granulation comes as the next step to smooth these edges to obtain a primary particle. The pre-mixed powder then goes to the next step, which is the secondary particle granulation process via kneading. The vertical kneader requires 11 h and 30 min, that includes reaching the temperature up to 700 $^{\circ}\text{C}$ for 5 h and 30 min, and then kneading at the same temperature for 3 h. Upon the completion of kneading, natural cooling down to room temperature requires around 3 h. The kneaded feed is baked at 1200 $^{\circ}\text{C}$, and then introduced to the final step of graphitization process at 3000 $^{\circ}\text{C}$. The graphitized sample goes through surface coating with the binder or coal tar pitch and is then baked at 1200 $^{\circ}\text{C}$ to obtain the finalized product. Here, the shortened process that we proposed uses coal-derived pitch, which has a lower softening point, so the granulation process is shorter and does not require the formation of secondary particles, and the intermediate carbonization process can be skipped.

4.2.2. Material Characterization

A scanning electron microscope (JSM 7600F, JEOL) equipped with double Cs-correctors was used for the topological characterization of graphite particles. A particle size analyzer (Cilas 1090, Bruben) was used to find the particle size distributions and spans. The span was calculated using the formula $(D_{0.9}-D_{0.1})/D_{0.5}$. To obtain the surface properties, a surface analyzer (3 Flex, Micromeritics) was used to characterize the specific surface area, which was calculated by the BET method. A tap density measurement was performed on 20 g of each sample, with a tapping direction of up and down for 3000 counts. Raman spectroscopy (Ram II-Senterra, Bruker) was performed based on 980 to 1980 cm^{-1} of Raman shift range to confirm the ID band (1320 to 1350 cm^{-1}) and IG band area (1620 cm^{-1}).

Raman 3D mapping is a three-dimensional observation method that expresses the ratio of ID/IG values as the intensity with respect to the sample observation plane. Therefore, in this study, Raman 3D mapping was performed as a method for evaluating surface graphitization. Here, it was performed on a $150\ \mu\text{m} \times 75\ \mu\text{m}$ area based on ID/IG ratio. The graphitization degree of each graphitized sample from the commercial or shortened process by X-ray diffraction measurement (RINT Ultima+ series, Rigaku), at a scan rate of $0.5^\circ/\text{min}$ ($\text{Cu-K}\alpha$) in $24\text{--}30^\circ$ range, was based on the Gakushin method, using standard silicon powder as a reference material.

4.2.3. Powder Conductivity Measurement

The bulk density and powder conductivity was measured by a powder electrical characteristics evaluation system (HPRM-FA2, Hantech) with a 200 to 1200 kgf loading range.

4.2.4. Cell Preparation and Evaluation

The anode material was produced with the carboxyl methyl cellulose and styrene butadiene rubber as the binder and the conductive material (Super-P), that were uniformly mixed in distilled water to turn into slurry, so that the weight ratio thereof became 97:2:1 (described in the order of anode active material/binder/conductive material). The slurry was coated with a copper (Cu) current collector, compressed by a roll press, and dried under vacuum conditions for 12 h at 100 °C. During this step, the electrode density was set to 1.6 g/cc. 1 M solution of LiPF₆ in a mixture of ethylene carbonate (EC), and dimethyl carbonate (DMC) with 1:1 ratio by volume was used as an electrolyte solution. A CR 2032 coin type cell was produced with lithium foil as a counter electrode, according to a common half-cell assembly method. The coin cell test was driven under the condition of 0.2 C, 5 mV, 0.005 C cut-off charging and 1.5 V cut-off discharging, and the rate performance and retention rate are measured in 0.2, 1, 2, 3 and 5 C rate condition.

4.3 Results and discussion

4.3.1. Physical Parameter Comparisons of the PAG-C and PAG-S Process

The physical properties, such as the mean particle size; span of particle distribution; specific surface area, d_{002} calculated from XRD; and tap density, were summarized in Table 2. Particle size control is one of the important factors in AG evaluation that should be checked for anode material application. The mean particle size of PAG-S was 13.8 μm , which was slightly lower than that of PAG-C, which was 15.6 μm . This would be favorable for conductivity improvement due to the reduction of inter-particle voids during electrode application. In addition, for the span, a lower number indicates a narrower and more uniform particle size distribution, which is important for the merchantability and reliability of particle size, and we found that PAG-S had a more uniform particle size distribution, with a value of 1.10 for PAG-C and 0.91 for PAG-S. The specific surface area, d_{002} , and tap density were all found to be similar between the conventional and shortened processes. Of all the factors, AG from the shortened process had similar physical properties, but from the mean particle size and span results, it is believed that it may be more suitable as an anode material for LIB.

Sample Code	Physical Parameters				
	Mean Particle Size (D ₅₀ , μm)	Span	Specific Surface Area (m ² /g)	d ₀₀₂ (nm)	Tap Density (g/cc)
PAG-C	15.6	1.10	1.18	0.3358	0.88
PAG-S	13.8	0.91	1.16	0.3358	0.90

Table 2. Physical parameters of AG from the commercial and shortened processes.

SEM images of AG derived from the commercial and shortened processes are shown in Figure 2. Since the shape of the AG particles after granulation is an important factor in the AG manufacturing process and electrode fabrication on LIB, we observed the granulation shape by using conventional and shortened processes. The SEM image in Figure 2 shows a comparison of the shape of the rounded graphite. From the observation of the particle morphology after granulation by the conventional process, it is clear that some cracked surfaces are visible on the sides of the particles. Furthermore, when the particles that appeared to have been granulated were observed under magnification, the layered surface was also revealed. On the other hand, the particles that were granulated by the shortened process almost did not reveal the layered surface. When comparing the particles after granulation, it was found that the artificial graphite produced by the shortened process is more granulated than in the conventional process and can be applied directly to commercial grade products. The reason for the better granulation of the artificial graphite by the shortened process seems to be due to the better impregnation of the coal tar pitch to the conventional binder pitch. From the particle observation result, we expect that the conventional process would require two or three additional granulation processes for LIB application, but the shortened process would contribute to an AG manufacturing cost reduction and better LIB performance, due to the relatively uniform spherical shape.

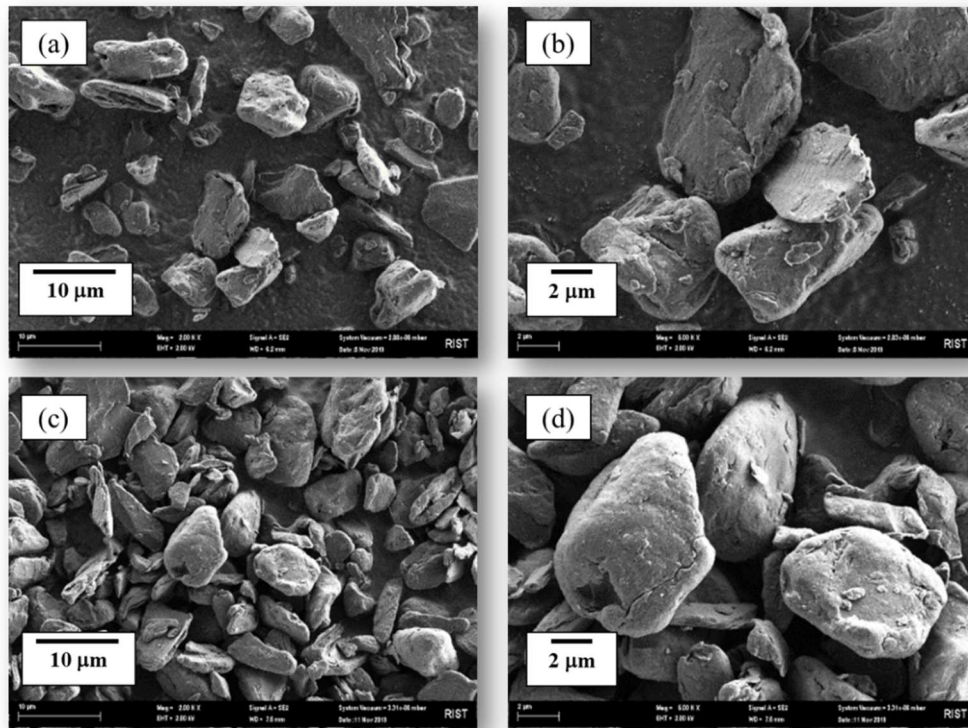


Figure 2. SEM images of AGs from the commercial process (a,b) and shortened process (c,d).

4.2. Raman Spectroscopy and 3D Mapping Results

In general, the harder the carbon derived from binder pitches in anode materials for LIBs, the fewer lithium-ion storage sites, which occur due to the adverse effects of charge and discharge capacity. This is due to the low degree of graphitization of the hard carbon. Therefore, it is necessary to minimize the hard carbon formed from the binder pitch on the sphericalized AG surface. Since the coal tar pitch used to shorten the process has a lower softening point and a lower fixed carbon content than the conventional binder pitch, it was expected that there would be a difference in the generation of hard carbon after carbonization. Therefore, the AG from the shortened process proposed in this study was analyzed for a hard carbon coating, as a difference in hard carbon content was expected compared to the AG from the commercial process. To compare the powder PAG-C and PAG-S or the electrode surface of PAG-C and PAG-S, each ID/IG mean ratio is shown in Figure 3.

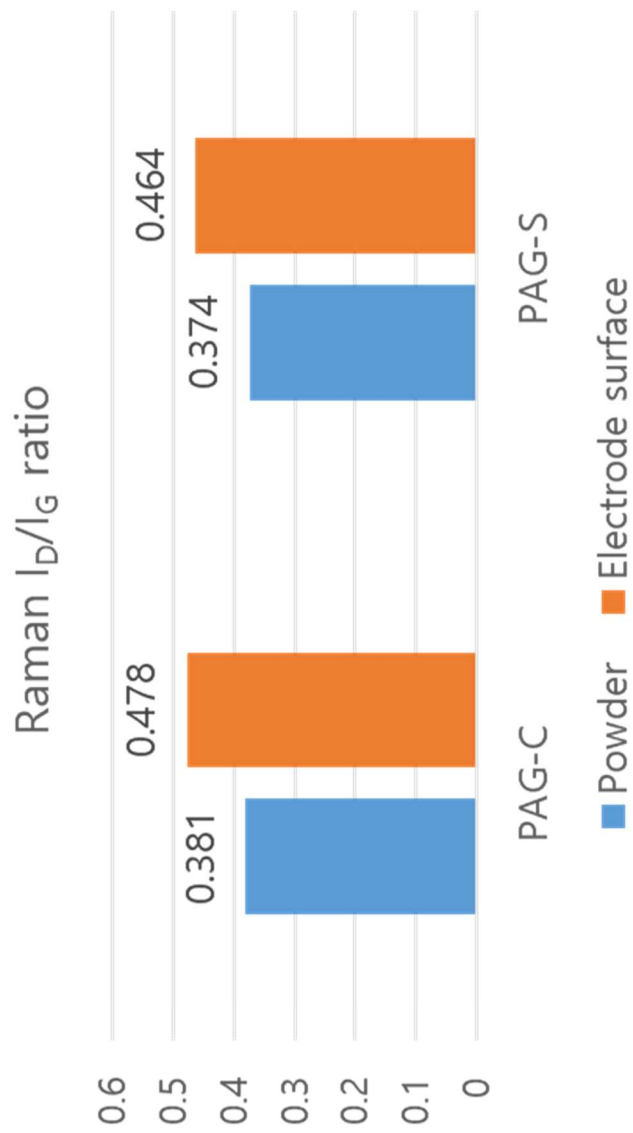
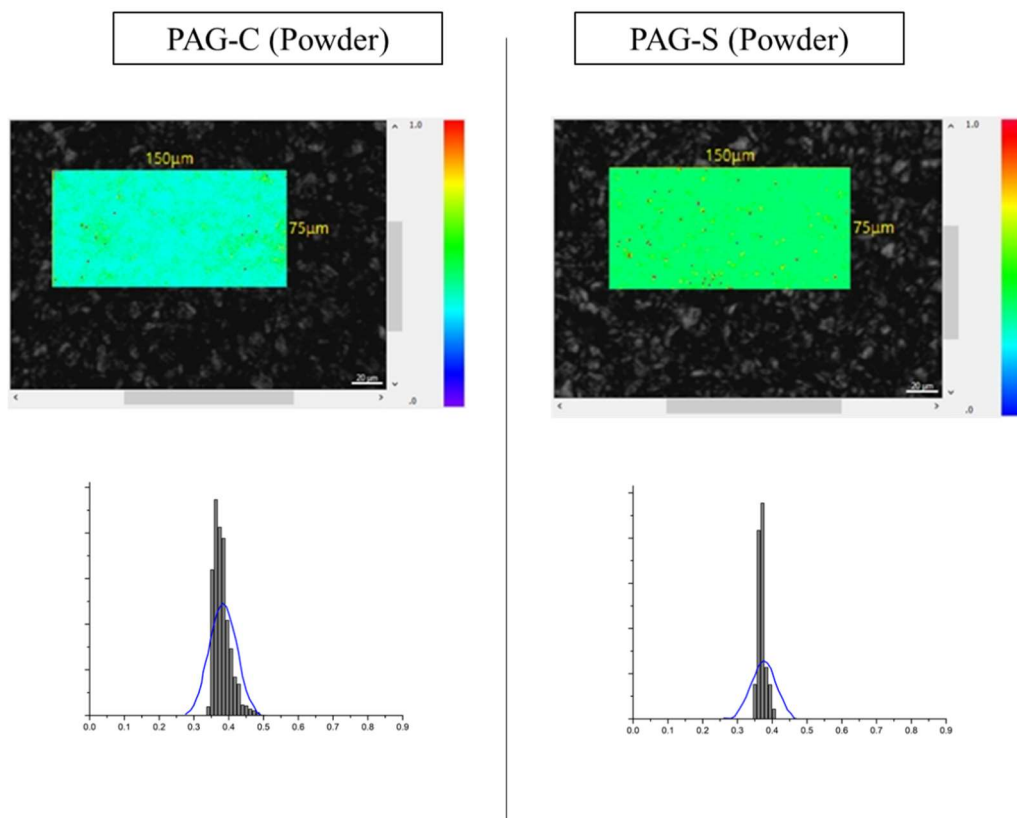


Figure 3. Powder and electrode surface mean ID/IG ratio of PAG-C and PAG-S.

By comparing the ID/IG values, it was found that the graphitization degree was lower for PAG-S compared to PAG-C for both powder and electrode surfaces, i.e., higher for PAG-C. However, the ID/IG value results only provide the averaged information on the surface of each sample, and it is not possible to quantitatively analyze and identify the distribution of hard carbon formed by binder pitches or coal tar pitches. Therefore, in this study, the distribution of ID/IG value by Raman spectroscopy was analyzed to map the distribution of ID/IG value in three dimensions [36–39]. Figure 4 shows the Raman mapping images of PAG-C and PAG-S and each distribution of ID/IG values. The color bar on the right side of the mapping image shows the height of the ID/IG distribution. The closer to blue, the lower the ID/IG, which means the closer to hard carbon having a low graphitization degree. On the other hand, from green to red, the higher the ID/IG, the higher the graphitization degree. By comparing the mapping images, we found that the AG with the shortened process has more green and red areas compared to the existing process. Also, the ID/IG distribution peak of PAG-S is sharp, indicating that a small amount of hard carbon is uniformly distributed. On the other hand, in the case of PAG-C, a relatively large amount of hard carbon was distributed over a wide range. Therefore, it is believed that the sphericalized AGs produced by the shortened process can be sphericalized with minimal hard carbon formation, contributing to the improvement of capacity and lifetime when utilized as an LIB anode material. To verify the differences when introduced into actual electrodes, Figure 5 shows the distribution of ID/IG values and the results observed by Raman mapping of the electrode surface after processing PAG-C and PAG-S into LIB electrodes. Compared to Figure 3, the ID/IG peak distribution is broadened due to the influence of the electrode binder and conductor material, but PAG-S shows a narrower distribution compared to PAG-C. From these results, it was confirmed that the difference in ID/IG distribution was visible even when applied to actual LIB electrodes.



**Figure 4. Raman 3D mapping image and ID/IG distributions of powder
PAG-C and PAG-S.**

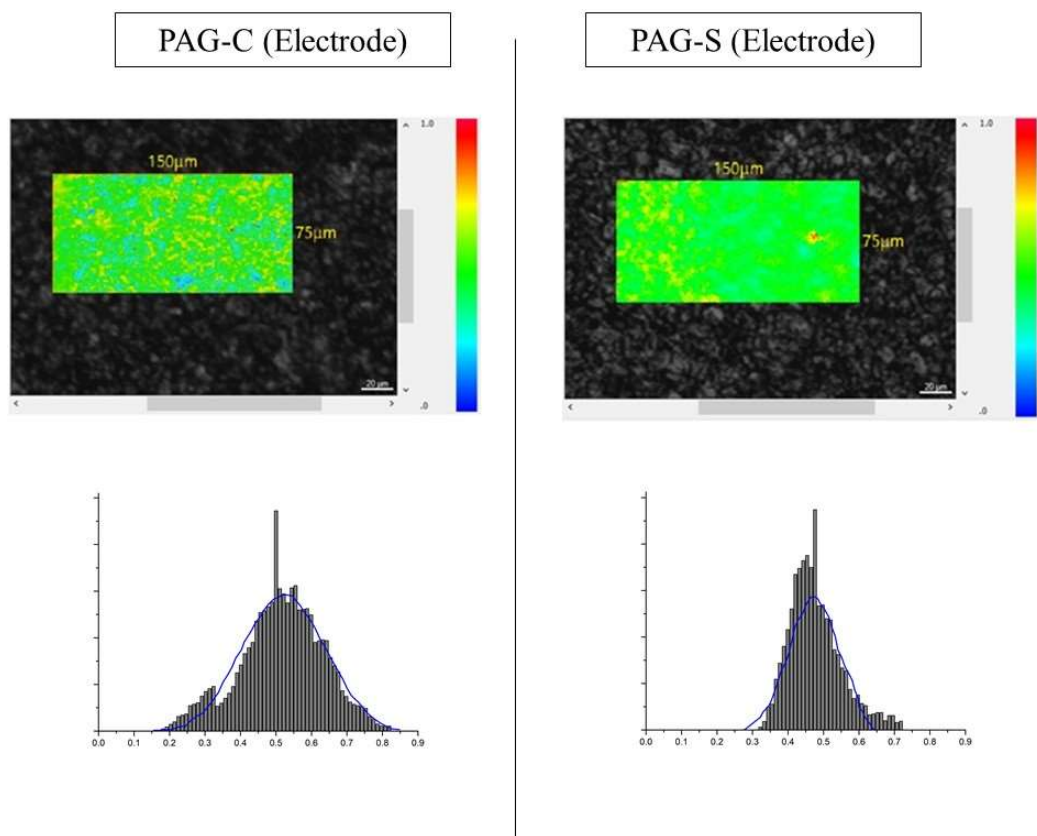


Figure 5. Raman 3D mapping image and ID/IG distributions of electrode surface of PAG-C and PAG-S.

4.3. Electrochemical Testing Result

The bulk density and powder conductivity results are summarized in Figure 5. We observed an increase in bulk density with load from 200 to 1200 kgf. The density at 200 kgf was 1.21 g/cc for PAG-C and 1.23 g/cc for PAG-S, which was not significantly different. After that, the density of PAG-C and PAG-S gradually increased with the increase in load, and it was found that the density value of PAG-C and PAG-S was 1.72 g/cc, even at the maximum load of 1200 kgf. Therefore, it was confirmed that the bulk density of AG, produced by both the conventional process and shortened process, does not show a significant difference depending on the load. However, when looking at the increase in powder conductivity with the increase in bulk density, the conductivity at the first 1.3 g/cc showed a slight difference between 20.1 S/cm and 24.6 S/cm, and at the maximum density of 1.72 g/cc, the conductivity of PAG-C and PAG-S was 104.1 S/cm and 120.5 S/cm, respectively. This is considered as a result of the small deviation from the amount of coating of hard carbon formed on the AG surface. Since the anode electrode of the LIB product is processed at about 1.6 g/cc, the conductivity at 1.6 g/cc (the red dotted line in Figure 6) is 79.3 S/cm for PAG-C and 89.5 S/cm for PAG-S, and it is also believed that the battery performance of PAG-S is superior when applied into the electrode.

The rate performance results are visualized in Figure 7. In addition, we would like to attach long-term rate performance and cycle life result on Supplemental information. After assembling CR 2032 type half-cells by processing PAG-C and PAG-S as anode electrodes, the rate performance results are shown in Figure 7. The C-rate is the discharge capacity and rate retention percentage at 0.2, 1, 2, 3, and 5 C after charging at 0.2 C, respectively. From the discharge capacity results, PAG-C is shown as having 352.4 mAh/g of discharge capacity. However, PAG-S showed 357.8 mAh/g of discharge capacity. The PAG-S shows a high

discharge capacity at 0.2 C, and even goes as high as 5 C. This is believed to be due to the granulation having minimal hard carbon, which ensures that there are sufficient effective Li-ion storage sites on the electrode. In addition, the rate retention results at each C-rate after 0.2 C charging showed little difference between the capacity of PAG-C and PAG-S, indicating that PAG-S maintains its high discharge capacity at a higher C-rate compared to PAG-C. Hard carbon is known to have a high initial capacity, but at a high C-rate, this is mainly irreversible capacity. On the other hand, reversible capacity has been reported for graphite with high graphitization degree. From these results and the references, it is concluded that the increased discharge capacity of PAG-S has a reversible discharge capacity, due to the uniformly sphericalized surface using a smaller amount of coal tar pitch-derived hard carbon compared to PAG-C. It is well known that hard carbon has good initial discharge capacity, but, at a high C-rate, hard carbon exhibits irreversible discharge capacity and low rate retention, due to the low graphitization degree [24,40–42]. From these results and the references, it is concluded that the PAG-S has an increased reversible discharge capacity that originates from being uniformly sphericalized, and using a smaller amount of coal tar pitch-derived hard carbon compared to PAG-C.

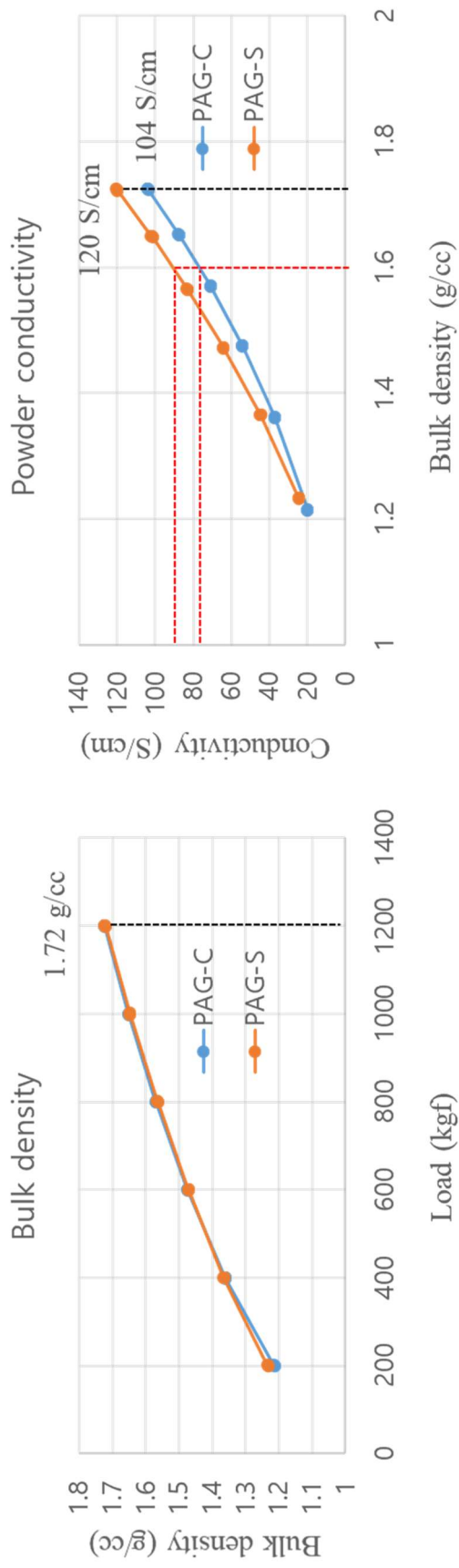


Figure 6. Bulk density and powder conductivity of graphite samples from

commercial and short-ened process.

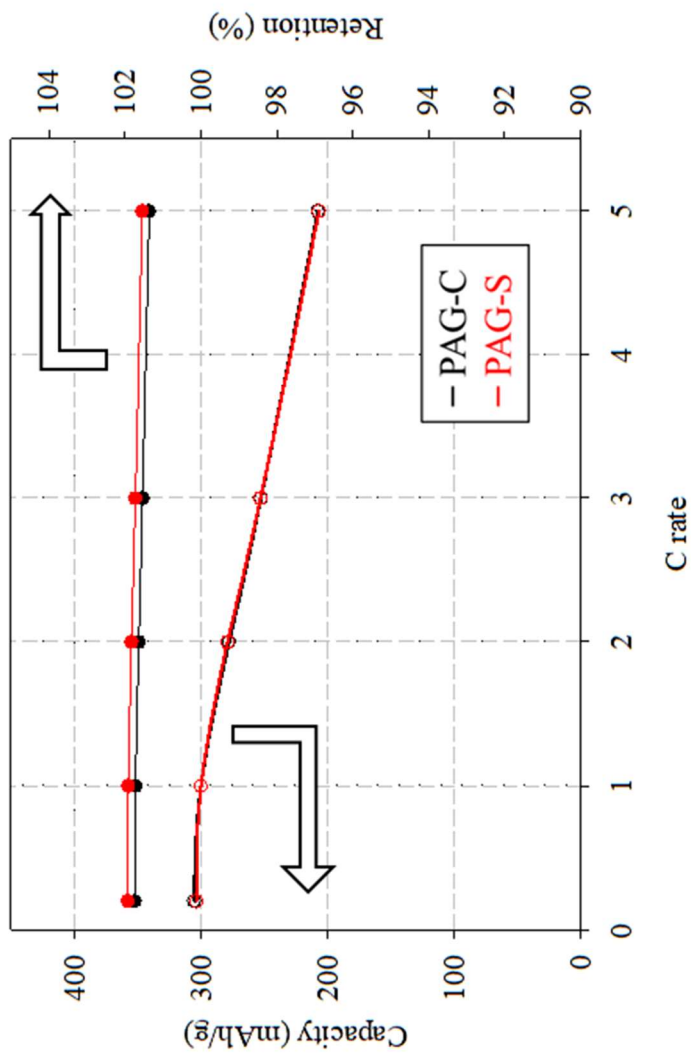


Figure 7. Rate performance and rate retention results of PAG-C and PAG-S at

various C-rates (empty circle lines: capacity, filled circle lines: rate retention)

4.4 Conclusion

In this study, we developed a shortened process of the artificial graphite manufacturing process for use in LIBs. While most of the same level of physical properties were shown between the two different AG manufacturing methods, we found that the AGs from shortened process had an advantage in particle size control. From a morphological comparison, it was found that the surface of the particles prepared by the shortened process, compared to the conventional process, was relatively well sphericalized, with no obvious layered surface. Although the comparison of the average ID/IG ratio obtained from Raman spectroscopy did not reveal any significant difference, the difference in hard carbon formation and the distribution of AG by the conventional process with binder pitch and the shortened process with coal tar pitch was clearly identified from the Raman 3D mapping results and ID/IG distributions. The AG of the shortened process was uniformly coated with a smaller amount of hard carbon, and the same trend was confirmed not only in the powder but also on the electrode surface. The same level of bulk density resulted in a higher powder conductivity, which is the effect of the minimized and uniformly coated hard carbon on the AG particle's surface. Through a comparison of the rate performance, it was found that the AG manufactured by the shortened process showed the same rate retention as the AG from the conventional process, but it was a better anode material for LIB due to its higher capacity. By comparing the AG produced by the conventional process and the shortened process based on the same raw material, we reported the production of artificial graphite with similar or superior properties. Consequently, this research can be used to skip some of the steps of the AG manufacturing process, and this is expected to help reduce the production cost of AG.

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Chapter 5.

General Conclusion

It is the conclusion of this thesis that it is highly feasible to replace the current kneading process that is probably mainly advantageous to Chinese or Chinese-like workshop environment with more convenient, faster and cost-effective alternatives. And it is clear that a glimpse of hope marks the first footprint, a humble beginning that still, more improvements are needed as can be confirmed throughout the two published papers and it is far out there but now it is no longer shrouded in darkness.

Other than China, most of the competent battery manufacturers are located in Japan and Korea where intensive labor and time are considered a luxury especially in times of worldwide “chasm” of lithium ion battery and EV, policy volatility sparked by the U.S. president-elect & his future cabinet and the downfall of the one and only European battery maker “Northvolt”. Under such uncertainties, the proposed batch-type “flash kneading” and continuous kneading by extruders overlapped structure hold a great potential as the next gen. kneading. The resulting secondary particles proved the usefulness with effective electrochemical testing results even though it needs more and more additional works on its properties to guarantee the commercial-grade production and performance, that is, scaling up to meet the capacity expectations of the battery makers.

Other than the scope of this research, it is believed the future cost down lies in the use of scraps and byproducts from graphite products such as graphite electrode, specialty graphites and so on. The proposed methods should be retrofitted to accommodate those harsh and hard-to-deal-with raw materials. To sum it up, below are the results and improvements needed.

First approach of kneading was to go continuous. It's the ultimate solution but not as easy as it sounds. The two distinct types of parallel co-rotating twin-screw extruders were compared KRC-S2 model (Kurimoto) / 2. CHT-20 model (Nanjing) and the author selected CHT-20 for its better particle expansion of D90 (31.64um over 27.92um) for calcined cokes which is deemed not so wetting-friendly with binders. The testing result led to a further retrofitting of its barrel design by longer screws and multiple barrel structure.

The new design provided a longer residence time(5→20min.), therefor offered more compaction effect that 10% less pitch binder was used so that raw-material cost-effectiveness became another merit of the continuous kneading (Table 3 & 4)

In detail, the double longer barrels structure has a smaller screw diameter, yet longer to facilitate the kneading and compacting with less binder. Separate 8 heat zones were effective for secondary particularization control with more vent outlets to discharge fumes and gases.

In its retrofitted extruder assembly, effective kneading for calcined cokes demonstrated a 47% increase in the particle size distribution and the highest discharging capacity of more than 350 mAh/g and 90% of ICE. As encouraging as the outcomes are, the proposed process however, needs more work on venting outlet design to accommodate green cokes as well as scaling up to meet the high market expectations.

The author wishes this thesis, achievements and failures would all be grinded and granulated into a single solid rock, a launch pad for more series of trials.

Conventional

Conventional	Cost	Ratio
	(\$/kg)	(%)
Coarse grinding	0.40	3.8
Fine pulverizing	0.70	6.7
Fine pulverizing -spheronization	0.85	8.1
Pre-mixing	0.70	6.7
Kneading*	1.50	14.4
Baking	1.50	14.4
Graphitizing	3.00	28.7
Coating(Dry)	0.90	8.6
2nd Baking	0.90	8.6
Total	10.45	100

* High temperature kneading up to around 700°C

Continuous

Conventional	Cost	Ratio
	(\$/kg)	(%)
Coarse grinding	0.40	4.2
Fine pulverizing	0.70	7.4
Fine pulverizing -spheronization	0.85	4.2
Pre-mixing	0.70	7.4
Kneading*	0.50	5.3
Baking	1.50	15.9
Graphitizing	3.00	31.7
Coating(Dry)	0.90	9.5
2nd Baking	0.90	9.5
Total	9.45	100

* Low temperature kneading up to around 250°C

Table 1. Manufacturing cost comparison-Anodes

Category	Topic	Conventional	Continuous
Binder	Binder type	Solid pitch	Solid pitch
	Price(USD/kg)	2	2
	Amount(%)	15	10~13
	Fixed carbon rate(%)	50	50
	Total amount of Soft carbon (%)	7.5	5.0~6.5
Process	Premixing time (min.)	30	30
	Kneading time(min.)	750	20
	Total mixing-kneading time(min.)	780	50
Production	Batch amount(kg)	600(PP)	-
	Daily amount (kg/day)	1,200	24
	Labor (Person/kneader)	3	1
	Daily amount/labor (kg/day)	400	24
	Cost (USD/kg)	1.5	0.5

Table 2. Kneading cost/time comparison

Batch-type quick kneading process “flash kneading” design was proven effective by the combination of liquefied pitch (Coal-tar) and a Henschel type mixer that can utilize the liquid to uniformly coat the filler material (cokes). More specifically, the liquefied coal tar derived binder has a wide coverage with lesser amount of soft carbon ($I_D/I_G = 0.374$) in anode compared to 0.464 of its conventional counterparts. When coated onto the Cu current collector, in electrode state, it still showed lower soft carbon content ($I_D/I_G = 0.381$) over its counterparts having 0.478 and that can be also confirmed in powder resistivity measurement. The shortened process offered higher powder conductivity of 89.5S/cm which is 10.2S/cm higher at same 1.60g/cc. Less amount of soft carbon in uniform distribution not only enables better properties but also testified its electrochemical performance having 353.8mAh/g with ICE of 92.7% with higher power of 45.4% which not only exceeds the conventional, but also meets the demand of lithium ion battery and EV industries.

Aside from better performance, a shortened batch-type process “flash kneading” needs processing time of less than 1/10 of the conventional (Table 3 & 4). Furthermore, the prior graphitization of primary particles and the following novel kneading leads to less coating and baking. Overall, author can proudly give a calculation of total manufacturing cost reduction by 29% marking under 10USD/kg. This is because the new type of mixer requires less than one worker compared to the 3 people per two kneaders for the conventional type thereby producing anodes at 0.99USD/kg compared to the conventional 1.50USD/kg.

This work is promising but needs more improvements to reach commercial scale production and it involves scaling-up of the kneader to minimize dead space as well as uniform control of the coal-tar’s viscosity which is a very tricky issue.

Conventional

Conventional	Cost	Ratio
	(\$/kg)	(%)
Coarse grinding	0.40	3.8
Fine pulverizing	0.70	6.7
Fine pulverizing -spheronization	0.85	8.1
Pre-mixing	0.70	6.7
Kneading*	1.50	14.4
Baking	1.50	14.4
Graphitizing	3.00	28.7
Coating(Dry)	0.90	8.6
2nd Baking	0.90	8.6
Total	10.45	100

* High temperature kneading up to around 700°C

Shortened

Shortened	Cost	Ratio
	(\$/kg)	(%)
Coarse grinding	0.40	5.4
Fine pulverizing	0.70	9.4
Fine pulverizing -spheronization	0.85	11.4
Graphitizing	3.00	40.3
Kneading (Wet coating)	0.99	13.3
Baking	1.50	20.2
Total	7.44	100.0

Table 3. Manufacturing cost comparison-Anodes

Category	Topic	Conventional	Shortened
Binder	Binder type	Solid pitch	Liquefied pitch
	Price(USD/kg)	2	0.5
	Amount(%)	15	10
	Fixed carbon rate(%)	50	25
	Total amount of Soft carbon (%)	7.5	2.5
Process	Premixing time (min.)	30	-
	Kneading time(min.)	750	30
	Total mixing-kneading time(min.)	780	30
Production	Batch amount(kg)	600(PP)	5(Lab)
	Daily amount (kg/day)	1,200	240
	Labor (Person/kneader)	3	0.5
	Daily amount/labor (kg/day)	400	480
	Cost (USD/kg)	1.5	0.99

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