参赛队员姓名： 陆鹏蓉

中学： 大连育明高级中学

省份： 辽宁

国家/地区： 中国

指导教师姓名： 李先锋研究员

论文题目： 咖啡渣基硬炭的制备及其作为钠离子电池负极材料的性能研究

Coffee Grounds Derived Hard Carbon towards Enhanced Performance Anode Material for Sodium-ions Battery

Group Member: Pengrong Lu

Supervisor: Xianfeng Li

大连育明高中

Dalian Yuming Senior High School

Dalian, China

September 12, 2019

Abstract

Sodium ion battery (SIB) has emerged as a proper alternative for energy storage application because of abundant sodium resource, similar working principle, and electrochemical performance as lithium ion battery. Up to date, producing high-performance anode materials is still one of the bottleneck problems. Hard carbon represents the most promising anode material due to its high storage capacity, low working potential, good cycling life as well as easy availability. However, imperfect initial Coulombic efficiency (ICE) and low rate capacity of hard carbon anode require continuous innovation for superior anode materials.

Coffee is an extensively consuming beverage, whose production inevitably generates a large amount of coffee grounds that engenders serious environmental problems. The transformation of this waste to high-value products definitely fits the concept of sustainable development. Herein, coffee grounds were first used to prepare hard carbon by carbonization associated with pre- or post-treatment. Due to specific structures and compositions, coffee grounds were found to be good candidates to synthesize hard carbon materials. Through optimization of synthesis process, the obtained carbon as anode material for SIB shows satisfactory sodium storage performance. The key factors that determined the performance were investigated.

The direct heat treatment of coffee grounds at 1000 °C under argon atmosphere can produce hard carbon with negligible surface area. The primary electrochemical test shows low discharge capacity and ICE because the metallic impurities in coffee grounds were transferred into carbon materials. Therefore, deash pre-treatment with acid solution towards the coffee grounds was carried out, which almost completely removed the metallic impurities.

Choosing a proper carbonization temperature is crucial for controlling surface area and degree of graphitization, which closely relate to the capacity and ICE of SIB. Therefore, according to the result of the thermogravimetric analysis, the deashed coffee grounds were treated at 1000 °C, 1200 °C and 1400 °C respectively for 2 h to produce hard carbons. High initial capacity of 292.5 mA h g^{-1} and high ICE of 77% were achieved at 0.02 A g^{-1} for the sample carbonized at 1200 °C,which are almost close to the top of the observed values in the literatures.

In order to improve the discharge capacity at large current, ball milling treatment was utilized to reduce materials' particle sizes. One sample was prepared by first milling of raw coffee grounds then followed by deash and carbonization; another was obtained by first deash and carbonization then followed by milling. Both of their reversible discharge capacity at large current of 1 A g^{-1} reached approximately 150 mA h g^{-1}, roughly a triple increase compared to the sample without ball milling treatment. Furthermore, the previously-carbonized sample displayed a fairly high ICE of 80%, better than another sample.

To decrease the acid solution dosage and handling amount of coffee grounds in deash and carbonization steps, and, a pre-carbonization step at a relatively low temperature of 400 °C was conducted to remove the most volatiles. The obtained carbon materials' electrochemical performance wasn't negatively affected by pre-carbonization.

The highlight of this research is to develop novel coffee grounds derived carbon anode materials, which deliver a high reversible capacity, superior rate capability and high initial Coulombic efficiency for SIB. I expect this achievement can not only provide an efficient way to solve environmental problems caused by coffee grounds, but also potentially supply extra sources of profit from an ignored bio-waste.

Key words: coffee grounds, hard carbon, anode material, sodium-ion battery, carbonization

Table of Contents

Introduction

1. Brief Introduction of Sodium-Ion Battery

The rapid growth of the economy has engendered the sharply increasing global demand for energy resources recently. Consequently, it is literally indispensable to address the serious problem of the excessive utilization of fossil fuels, which has already caused environmental deterioration and resource shortage. Aiming to tackle these crises, researchers have attached great importance to high-efficiency energy storages and conversion technologies[1-2]. Rechargeable lithium-ion battery (LIB) has been extensively applied in various electronic devices and could further be implemented to power electrical vehicles. Nevertheless, in the long run, the scarcity and the high price of lithium sources could limit the large-scale application of LIB in stationary electricity storages and electrical vehicles.

Sodium-ion battery (SIB) has been regarded as a possible alternative to LIB because of low price and abundant sources of sodium (approximately one thousand times more than that of lithium sources on the earth). Importantly, since lithium and sodium both belong to the first principal family in the periodic table, they share many similar physicochemical and electrochemical characteristics. And the SIB follows similar rocking chair working principle of LIB, therefore resulting in the rapid knowledge-development and the easy transition to manufacture from LIB to SIB[3-4]. Moreover, since sodium does not alloy with aluminium, it is quite feasible to employ much cheaper and lighter aluminium foils instead of copper ones as anode current collectors. Therefore, SIB is expected to be economical substitutes to LIB for electrochemical energy storage.

1.1 Working Principle of Sodium-Ion Battery

SIB works similarly as LIB by reversibly shuttling charged ions between cathode and anode using electrolyte as transportation medium (Fig.1). In the charging process, Na^+ ions extract from lattice sites at the cathode and embed in anode while electrons transfer from cathode to anode via an external circuit to maintain charge balance. During the discharge, it is vice versa[2].

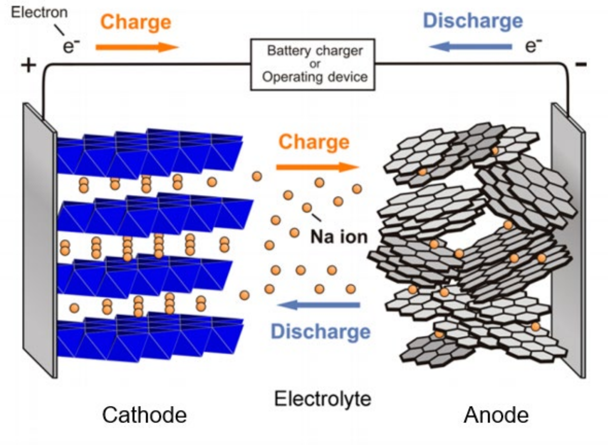

Fig.1 Working principle of sodium-ion battery.

1.2 Key Components of Sodium-Ion Battery

SIB, same as LIB, is mainly composed of anode, cathode, separator, electrolyte and external package as well. Two electrodes with different chemical potentials would generate a working voltage; the electrolyte connects anode and cathode by supplying conductive ions; the role of separator is to avoid short circuit and allow the charged ions to pass. The output electrical energy density of SIB is proportional to the capacity and the square of cell voltage, which are greatly dependent on the chemical nature and structure character of electrode materials.

Compared with lithium, sodium has larger ionic radius (1.02 Å /0.76 Å) and higher standard electrode potential (-2.71 V/-3.02 V vs standard hydrogen electrode), thus SIB always suffer from low energy density. In this case, the material choice for electrode in SIB is much more difficult and crucial.

The currently reported cathode materials basically include oxides, polyanionic compounds, Prussian blue and so on, which all have shown relatively high potential and satisfactory cycle capacity[5]. However, when it comes to anode materials, some essential problems such as volume expansion, cycle stability, and initial Coulombic efficiency are still challenging and required to broaden a variety of the anode materials.

1.3 Scientific Challenges in the Development of Anode materials

Owing to the relatively large radius of Na^+, the commercialized anode material of graphite for LIB is no longer suited to SIB. Hereinto, SIB always suffer from a slow Na^+

diffusion kinetics and the large volume expansion, which further affect the rate capability and cycling stability[6]. To address this problem, it is literally urgent to explore new anode materials that possess large interstitial space in crystallographic structures for free shuttle of Na^+ and low electrode potential (better close to zero) which guarantees greater capacity of SIB. Nowadays, researchers are continuing to explore optimal anode materials that meet all needs of superior SIB.

2. Types of Anode Materials and Their Characteristics

Anode materials that based on electrochemical reaction mechanisms are mainly grouped into three categories: intercalation, alloying and conversion ones[7].

2.1 Hard carbon

Hard carbon, consisting of randomly stacked small graphitic layers has a low Na^+ storage voltage (0.15 V vs Na/Na^+) and is suitable as anode materials for SIB. The amorphous structure and relatively large interlayer distance (0.36-0.4 nm) could facilitate both extraction and migration of sodium ions, which contribute to a high reversible discharging capacity. However, the first-cycle irreversible capacity loss (low ICE) and low rate performance of hard carbons need to be addressed.

2.2 Alloy-type anode materials

Some elements, such as tin, antimony and red phosphorus can be alloyed with sodium to from binary alloys, which are capable of delivering high specific capacities through [8-9]. However, in the cycling process, these materials mainly undergo visable volume expansion, even up to 400%, which will cause electrode pulverization, particle disconnections, capacity fade and poor cyclability eventually[10-11]. Moreover, these pure elements have a high excavation and production cost, further hindering their applications.

2.3 Conversion-type anode materials

Conversion-type materials, referring to transition metal compounds like oxides, sulphides, nitrides and phosphides, can react with Na^+ by multi-electron reactions, thus potentially resulting in a high theoretical capacity. However, structural rearrangement during the charge/discharge process, could give rise to a large volume change and pulverization of anode materials, thus leading to fast capacity fading and low rate capacity [12]. Furthermore, most reported materials, such as Fe_7Se_8[13], working through a conversion reaction, require high voltage (vs Na^+/Na) for the deintercalation, which will lead to a fairly low voltage full-cell[14].

By comprehensive comparison, hard carbon is supposed to be the promising anode material for SIB due to the good electrical conductivity, low cost, abundant resources and easy availability.

3. Precursors of Hard Carbons and Their Structure Features

3.1 Biomass

Biomass is receiving enhanced attention because of cheap prices, abundance and sustainability. The carbonization of biomass or bio-waste to produce carbon materials is an easy industrial scale-up route. Based on the diversity of sources, different kinds of biomass often present various and flexible morphology and microstructure, which have an important impact on microstructures and porosity of the carbonized products.

3.2 Coal and Petroleum Coke

Fossil fuel includes coal, natural gas and petroleum, which are dominate energy sources of human life. Coal and its derivate pitch and petroleum coke (by-product of petroleum industry) are good natural carbon sources with high carbon content, which are usually fabricated into high-graphitic-degree carbon. However, these carbon precursors always contain high content impurity, especially metallic species that could damage the electrochemical performance of anode.

3.3 Polymer

Various polymers, such as phenolic resin and polyacrylonitrile (PAN) are good candidates for carbon precursors. Since the chemical structures and properties of the polymer can be designed in the preparation stage, it offers an exciting possibility for a precise control of the nanostructure of carbons with required properties.

By considering the easy accessibility and rich diversity of biomass, the biomass and biomass waste have been most widely studied as hard carbon source in recent years.

4. Motivation and Research Content of This Study

4.1 Coffee grounds

Coffee is favorite drinks in all over the world. Surprisingly, coffee also is the second largest trading goods beside petroleum[15]. As a consequence, the production of coffee inevitably generates a large amount of coffee grounds that actually gives rise of a large environmental burden. Coffee grounds, the residue of the coffee bean in the soluble coffee industry, weight surprisingly 50% of the total input mass of coffee feedstock. Therefore, the reuse of a fairly great amount of coffee-industry residue is essential for environmental protection and economical profits. As reported, this bio-waste has many possibilities to be transformed into high value added products, like biodiesel, bioethanol or construction materials.

4.2 Compositions of coffee grounds

Coffee grounds have high organic contents, including lignin, cellulose, hemicellulose, protein, fiber, caffeine, etc. In addition, the trace amount of ashes could inevitably present in the form of metallic species. Cellulose, hemicellulose and lignin are most abundant compounds with a content exceeding 75%. Therefore, coffee grounds are considered to contain sufficient carbon, which may promise a direct reuse as hard carbon sources[12].

4.3 Research Content

Keeping in mind the challenge in the development of optimal anode materials, and taking into account the compositions and reuse of a huge amount of coffee-industry residue, in this study, I focus on the preparation of the best-performance SIB anode materials based on coffee grounds, together exploring the promotion and the regulation of electrochemical performances.

The inorganic impurities found in coffee grounds could left over in the corresponding carbon materials in the form of metallic compounds in the carbonization process, which will weaken the electrical conductivity. Therefore, coffee grounds are first deashed by acid solution and then carbonized at different temperatures to prepare pure hard carbons. Ball milling treatment is also conducted to reduce the particle size of coffee grounds with the purpose of enhancing the specific capacity and rate performance of the derived carbon anodes. Finally, by considering that coffee grounds contain a mass of light volatiles, which do not produce carbon residue, a pre-carbonization treatment is explored to decrease the volume and mass of raw coffee grounds. On this basis, the dosage of acid in deash step and handling amount in carbonization step will be reduced, which is environment- friendly and energy-saving.

This study will provide useful explosion for the rational design of hard carbon anode material with high rate capability and initial Coulombic efficiency (ICE) from coffee grounds. Successful completion of the study will potentially not only result in improved anode material for SIB from an undervalued bio-waste, but the general, could reduce the environmental burden and economic costs of disposal of massive amount of coffee ground as well.

Experimental Section

1. Synthesis of Hard Carbons from Coffee grounds

1.1 Direct Carbonization of Coffee grounds

The coffee grounds were directly carbonized at 1000 °C for 2 h under Ar atmosphere and the obtained carbon was denoted as CGC-1000 (A).

Fig.2 Tubular carbonization furnace.

1.2 Deash of Coffee grounds and Carbonization Temperature Investigation

The coffee grounds were first crushed into powders with particle sizes smaller than 100 mesh and then mixed with 10% (V/V) HF solution. After holding for 12 h at room temperature, the sample was washed by deionized water until neutral pH, and oven dried at 50 °C. Finally, the samples were treated at 1000 °C, 1200 °C and 1400 °C respectively for 2 h under Ar atmosphere to produce the hard carbons. The obtained carbons were labelled as CGC-1000, CGC-1200 and CGC-1400.

1.3 Ball-milling Treatment

Ball-milling treatment was chosen to reduce the particle size of the carbon materials. An appropriate amount of coffee grounds was first ball milled at 800 rpm for 12 min. Then the as-milled coffee grounds were deashed and carbonized at 1200 °C for 2 h to obtain carbon sample MCGC-1200. For comparison, the sample denoted as CGCM-1200 was prepared by ball milling of CGC-1200 as the method mentioned above.

Fig.3 Planetary ball mill.

1.4 Pre-carbonization Treatment

The pre-carbonization process was conducted in order to remove light volatiles. The coffee grounds were first heated to 400 °C and maintained for 1 h under an Ar atmosphere, and then subjected to deash treatment by following the above-mentioned process. After that, a second carbonization was carried out at 1200 °C, and the obtained sample was denoted as PCGC-1200.

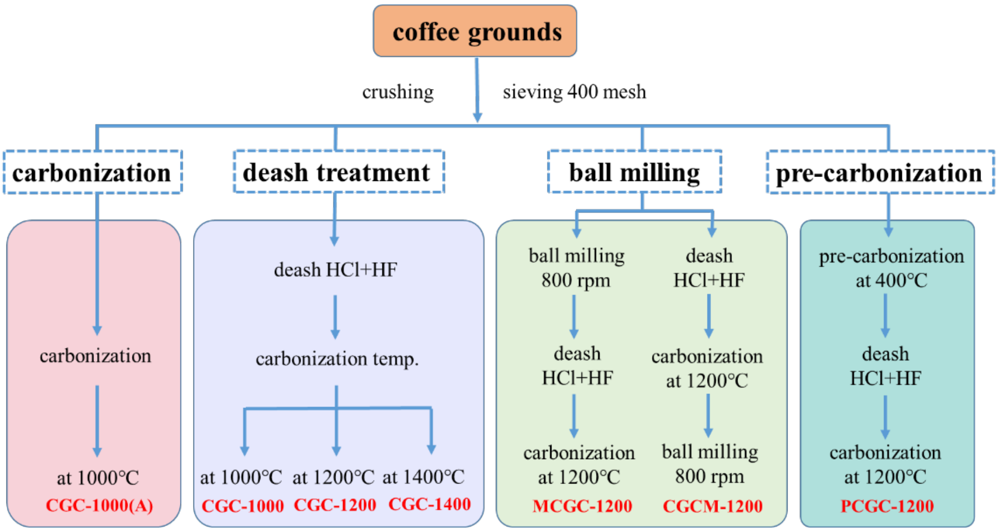

Fig.4 Preparation study of coffee grounds-based carbon materials.

2. Electrochemical Performance of Hard Carbon Anode in Half Cell System

In half cell system, the carbon anodes were prepared from the slurry containing coffee grounds derived carbons (80 wt%), conductive additive (10 wt%) and binder

(10 wt%), which was spread onto Cu foil followed by dried in a vacuum oven at 100 °C for 12 h. The coin cell was configured with a home-made Na disk as the counter electrode and a Celgard 2400 microporous membrane used the separator, respectively. The electrolyte comprises a solution of 1.3 M $NaPF_6$ in diethyl carbonate (DEC) and ethylene carbonate (EC) and (70:30, v/v). The electrochemical performances were performed on an electrochemical workstation (CHI660D, ChenHua Instruments Co., China). Cycling behaviours of the coin cells were estimated on a battery test system (Land CT2001A).

Fig.5 Battery test system.

Results and discussion

1.1 Electrochemical Performance of Coffee Grounds Derived Carbon

Coffee grounds consist of cellulose, hemicellulose, lignin, protein, caffeine and ash etc. In order to determine the optimal carbonization temperature, the thermogravimetric analysis (TGA) of the coffee grounds was performed at temperature up to 1350 °C with a heating rate of 10 °C min^{-1} under Ar atmosphere.

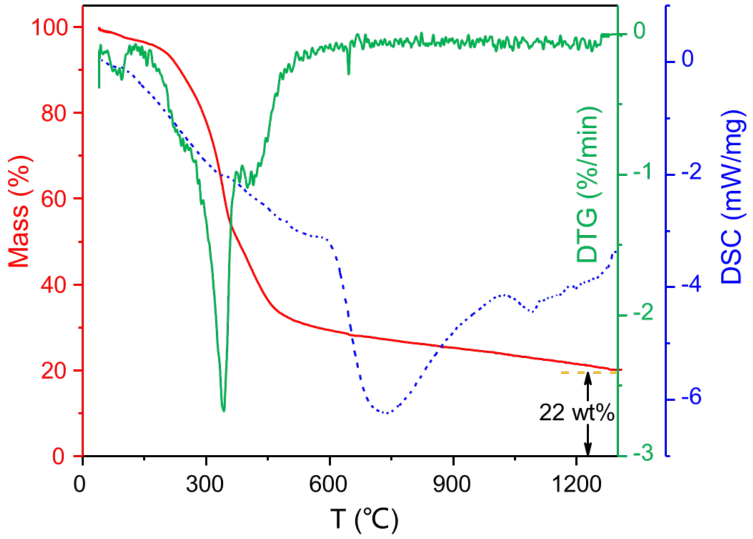

Fig.6 Thermogravimetric analysis curves of the coffee grounds.

As seen in Fig.6, the thermal decomposition behaviour of coffee grounds appears to undergo three stages. At the first stage (25-150 °C), a slight weight loss of 3 wt% caused by water desorption was found . The second stage is in the range of 150-600 °C, and a significant weight loss of 72wt% could be attributed to the elimination of volatile small molecules such as H_2, CH_4, CO, CO_2 and so on. The third stage between temperature 600°C and 1350°C, the weight loss becomes very small, an obvious exothermal peak in Differential Scanning Calorimeter (DSC) curve at this stage suggests the recombination of structure and formation of fundamental carbon skeleton. The inorganic residue of the carbon product at 1350 °C is about 22 wt%.

According to the Thermogravimetric analysis analysis, the coffee grounds were subject to a direct carbonization at 1000 °C for 2 h in Ar atmosphere. The obtained carbon sample CGC-1000(A) was first characterized by XRD analysis. As displayed in Fig.7, XRD spectra has two broad featured peaks referring to (002) and (100) reflections of carbon materials, respectively. The peak (002) at 24.5° is commonly related to the degree of carbon interlayer-stacking and (100) at 44.0° to the reflection of the degree of ordered hexagonal carbon structure. The interlayer spacing of CGC-1000 (A) is estimated to be 0.380 nm, larger than the interlayer spacing of graphite (0.335 nm). Besides, some small peaks are also visible, which would relate to the impurity existence in the coffee grounds derived carbon. The surface area of CGC-1000(A) determined by N_2 sorption measurement is 22.3 m^2 g^{-1}, which may benefit a high ICE.

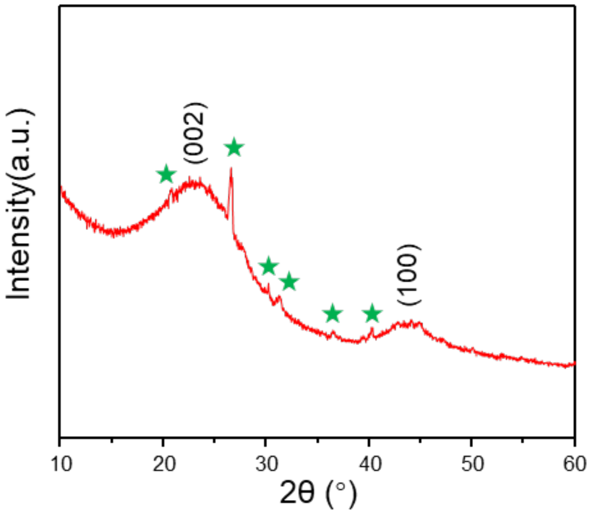

Fig.7 XRD pattern of CGC-1000(A).

The electrochemical performance of CGC-1000(A) was tested in half cells system. The initial discharge/charge profiles in Fig.8a confirm that a capacity of 202.5 mA h g^{-1} with an ICE of 50.3% can be achieved for CGC-1000(A) electrode. According to the rate performance of the samples at current density up to 1 A g^{-1} in Fig.8b, the capacity of CGC-1000(A) electrode gradually decreases with the increase of current density. The capacity of the sample can recover to 198.6 mA h g^{-1} at 0.02 A g^{-1} after cycling at higher current density, indicating the carbon anode is stable for a wide range of current densities.

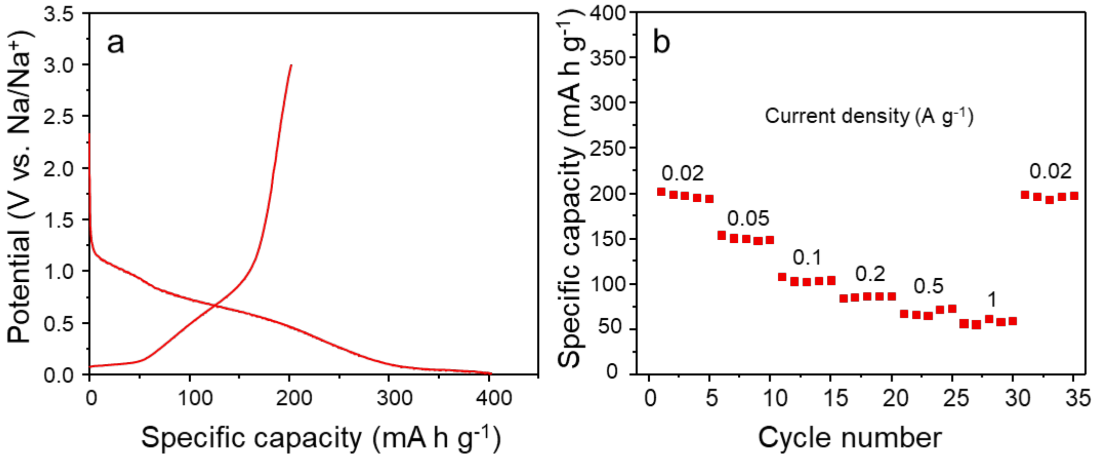

Fig.8 (a) Discharge/charges profile at 0.02 A g^{-1} at the initial cycle. (b) Rate capability of CGC-1000(A) from 0.02 A g^{-1} to 1 A g^{-1}.

Both the low discharge capacity and ICE of CGC-1000(A) anode may be correlated with the impurity effects. The impurities contained in the materials not only significantly affect the electronic conductivity, but also impact on the initial irreversible capacity due to the occurring of the side reaction between the impurities and Na^+. Therefore, deash treatment of the coffee grounds becomes important with a purpose of improving more reversible capacity.

1.2 Effect of Impurities and Carbonization Temperature on Charge Performance

The total ash content and its chemical composition in the coffee grounds were analyzed by using XRF. An approximate 4% ash exists in the coffee grounds calculated in form of oxides. The detailed composition is listed in Table 1, and the majority of the ash consists of SiO_2, SO_3, Al_2O_3, Fe_2O_3 *etc*. Considering the SiO_2-dominant ash components in the coffee grounds, HF acid solution was used to remove the impurities. Afterwards, less than 1% total impurity was left and metallic species were essentially removed.

Table 1 Ash Composition analysis via XRF (oxide based wt%)

Composition	SiO_2	SO_3	Fe_2O_3	Al_2O_3	CaO	TiO_2	Cr_2O_3	K_2O	MgO	SrO	P_2O_5
original	1.57	0.72	0.56	0.54	0.07	0.05	0.05	0.08	0.06	0.04	0.04
deashed	0.13	0.59	0.10	0.15	0.06	0.02	0.01	-	-	-	-

The deashed coffee grounds were subsequently carbonized at 1000 °C, 1200 °C and 1400 °C for 2 h in Ar atmosphere aiming for investigating the impact of high temperature on the microstructure evolution of carbon materials. As seen in the XRD patterns in Fig 6a, all three samples CGC-1000, CGC-1200 and CGC-1400 dominantly exhibit broad (002) and (100) peaks. By increasing the carbonization temperature, the (002) peak position moves to a higher angle that revealing the interlayer distance being narrower and *Lc* increasing, illustrating an improved degree of graphitization. The calculated interlayer distance of CGC-1000, CGC-1200 and CGC-1400 corresponds to 0.381 nm, 0.379 nm and 0.371nm. The average length (*La*) and thickness (*Lc*) of the graphite domains are also estimated based on the XRD results. As expected, higher carbonization temperature helps the growth of microcrystallite size with *La* and *Lc* increasing (Table 2). Besides, a significant removal of ash from the original coffee grounds is also confirmed by the disappearance of impurity peaks.

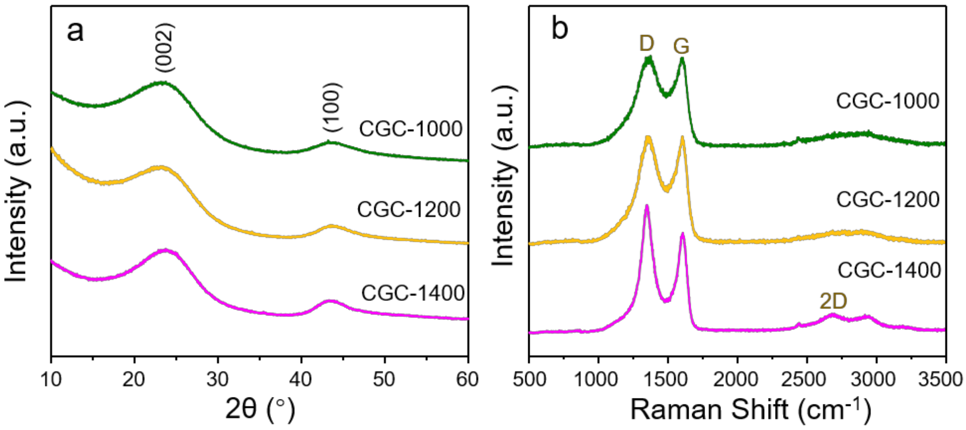

Fig.9 XRD patterns (a) and Raman spectra (b) of CGC-1000, CGC-1200 and CGC-1400.

Raman spectroscopy is a powerful method to study the degree of graphitization for carbon materials. As observed in Fig.9b, Raman spectra of CGC-1000 and CGC-1200 present typical D band peaks at around 1340 cm^{-1} and G band peaks at around 1580 cm^{-1}, while CGC-1400 has a 2D band arising, suggesting the formation of graphite crystals in carbon materials. Furthermore, the half width of G and D bands decreases slightly with increasing carbonization temperature, implying the development of an ordered hexagonal structure. The intensity ratios of G band versus D band increase from 0.38 for CGC-1000 to 1.03 for CGC-1400 (Table 2), indicating a high degree of graphitization. The calculated highest surface area is only around 20 m^2 g^{-1} (Table 2). The XPS analysis confirmed that a high carbonization temperature results in a super high carbon content exceeding 95% (Table 2).

Table 2 Physical parameters of carbon materials from deashed coffee grounds.

Samples	d_{002}(nm)	*La* (nm)	*Lc* (nm)	I_G/I_D	S_{BET} (m^2 g^{-1})	C (at%)	O (at%)	N (at%)
CGC-1000	0.383	1.39	1.75	0.38	6.4	95.75	2.26	1.99
CGC-1200	0.379	1.41	1.81	0.44	6.1	96.37	2.79	0.84
CGC-1400	0.371	1.47	1.95	1.03	21.8	96.43	2.77	0.80

The microstructures of the samples were observed by SEM and HRTEM. As observed in SEM (Fig.10a-c), the coffee grounds derived carbon materials have no regular morphology and some stacked layers are visible. From Fig.10d-f, a gradual development of long-range ordered domains can be observed with an increase of carbonization temperature. Significant graphitic structure occurs in sample CGC-1400.

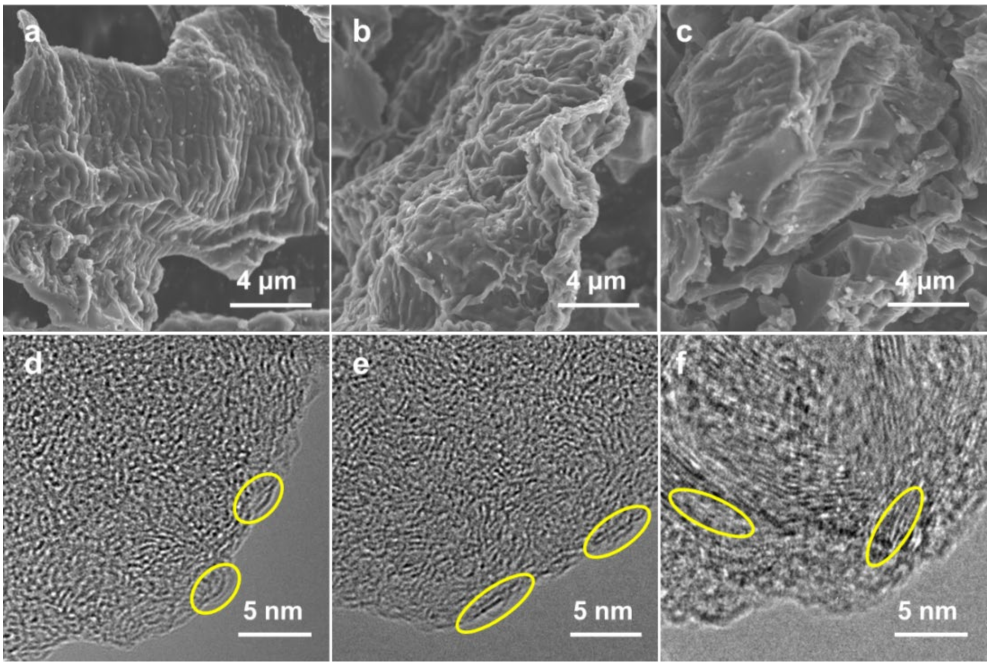

Fig.10 SEM and HRTEM images of the carbon materials: (a,d) CGC-1000, (b,e) CGC-1200 and (c,f) CGC-1400.

The charge-discharge performance of the obtained carbon materials was examined in half cell system. The first charge/discharge profiles of the samples at

0.02 A g^{-1} are presented in Fig.11. Both the initial reversible capacity and ICE of the three deashed samples are 235.2 mA h g^{-1} & 63.6% for CGC-1000, 292.5 mA h g^{-1} &77% for CGC-1200, and 242.5 mA h g^{-1} &71.7% for CGC-1400, respectively, all higher than those of sample CGC-1000(A) without deash treatment (202.5 mA h g^{-1} & 50.3%), demonstrating the indispensability of impurity removal. The high capacity and ICE of CGC-1200 could be ascribed to the larger interlayer spacing profiting a valid Na$^+$ insertion and extraction as well as good graphitization relating high electrical conductivity.

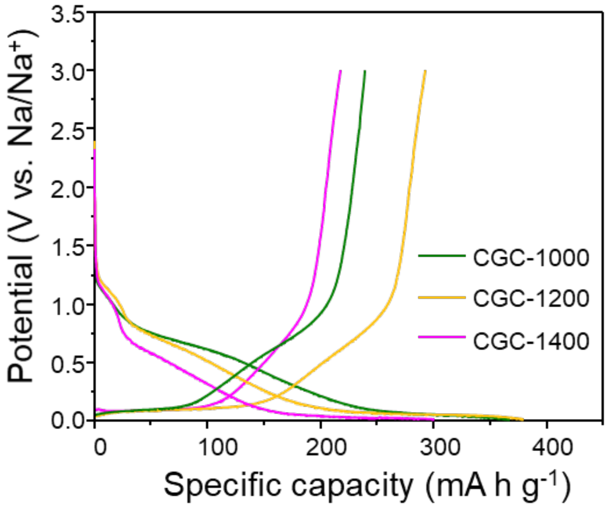

Fig.11 1st discharge/charge profiles at 0.02 A g^{-1} of three carbon samples

Furthermore, the rate performances of the carbon samples were measured by running the electrodes at current densities from 0.02 A g^{-1} to 1 A g^{-1} (Fig.12). Still, CGC-1200 electrode offers a remarkable rate capability that reversible capacities of 55 mA h g^{-1} (1 A g^{-1}) can be observed, which is still doing better than others. When the current comes back to 0.02 A g^{-1}, the capacity can still be kept at around 282.5 mA h g^{-1}, suggesting the stable electrochemical character of CGC-1200.

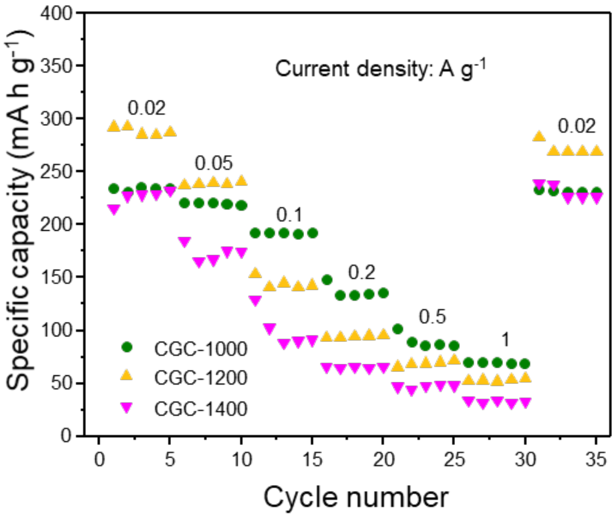

Fig.12 Rate performances at current densities increasing from 0.02 A g^{-1} to 1 A g^{-1}.

Therefore, the cycling performance of CGC-1200 was further tested. After activation at 0.2 A g^{-1} for initial five cycles, the charge/discharge tests were carried out at 1 A g^{-1} for long cycles. After 600 cycles (Fig. 13), the capacity remains 71 mA h g^{-1}, corresponding to 0.009% capacity decay per cycle. In addition, during the cycling test, CGC-1200 exhibits a high Coulombic efficiency of nearly 100%, further indicating the good stability of anode material.

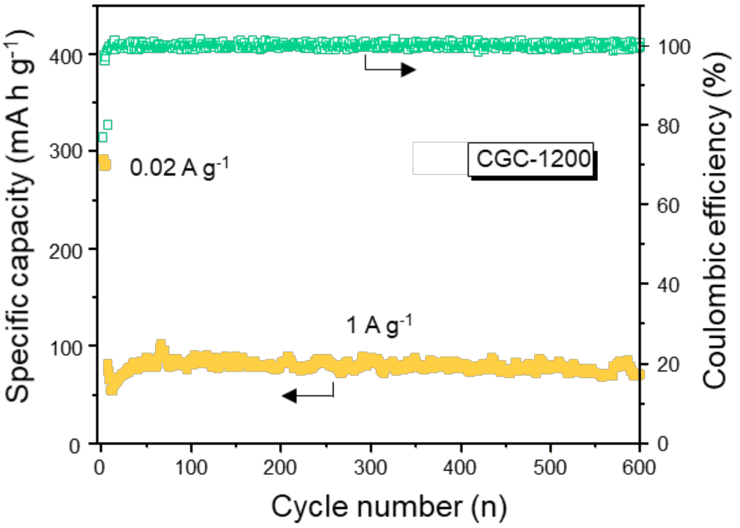

Fig.13 Cycling performance of CGC-1200 at 1 A g^{-1}.

Briefly, in this part, an essential necessity of impurity removal is experimentally confirmed, and the choice of an optimal carbonization temperature is crucial both from the points of accomplishing a high capacity and ICE. The change of the carbonization temperature will affect the interlayer distance, surface area and functional groups. The low surface area can enhance the ICE yet sacrificing the rate performance. Therefore, I will continuously make an effort to find an efficient method to strength the diffusion in the following section.

1.3 Effect of Particle Size of Carbons on the Rate Performance

In recent years, the ball-milling technique is widely utilized to reduce the particle size of the materials and create new defects. Here, one sample was prepared by first milling of raw coffee grounds then followed by deash and carbonization at 1200°C; another was obtained by direct milling of CGC-1200. The obtained carbon samples are correspondingly named as MCGC-1200 and CGCM-1200. In order to observe whether the particle sizes were reduced, a sedimentation experiment was performed. The milled carbon samples MCGC-1200 and CGCM-1200 together with one controlled sample CGC-1200 were first dispersed in alcohol solution by ultrasonic treatment for 5 min and then stood for 3 h. The left side picture in Fig.14 shows three samples disperse very well at beginning. However, after 3h, the contrast sample CGC-1200 has already set down, which preliminarily proves the existence of smaller particle sizes in MCGC-1200 and CGCM-1200.

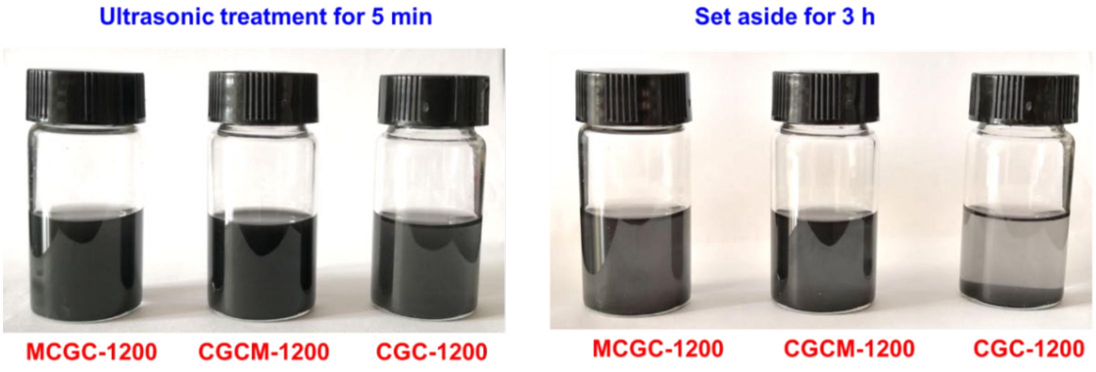

Fig.14 Optical photographs of 1 mg mL^{-1} sample-alcohol dispersion.

SEM images show that both carbon materials have smaller particle sizes (Fig.15) than that of samples without ball milling (Fig.10a-c). Moreover, ball milling towards carbonized sample results in a relatively smaller particle size compared with ball milling towards original coffee grounds.

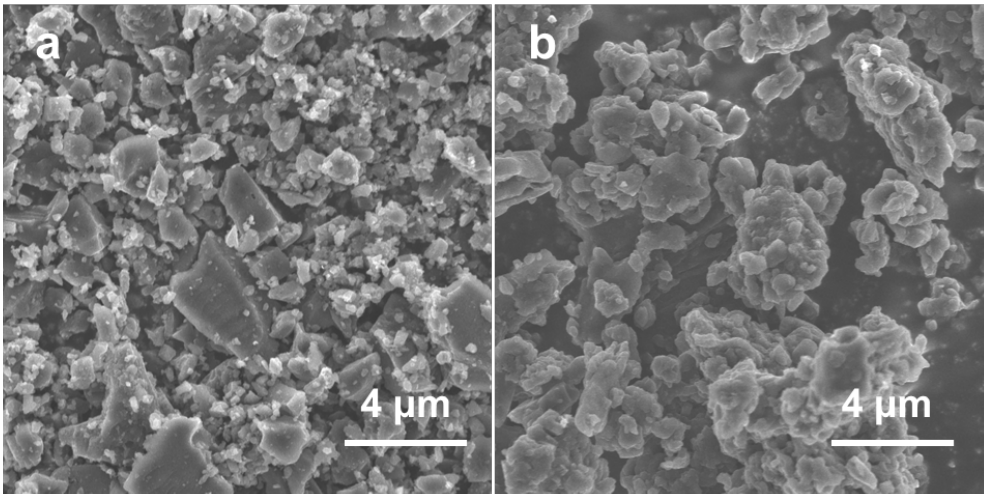

Fig.15 SEM images of (a) CGCM-1200 and (b) MCGC-1200.

XRD and Raman analyses were conducted to observe the possible microstructure change made by ball milling. XRD patterns of CGCM-1200 and MCGC-1200 (Fig.16a) display broad peaks with the similar shape as CGC-1200, and the average interlayer spacing of the graphene sheets (d_{002}) has a very slight increase (Table 3).

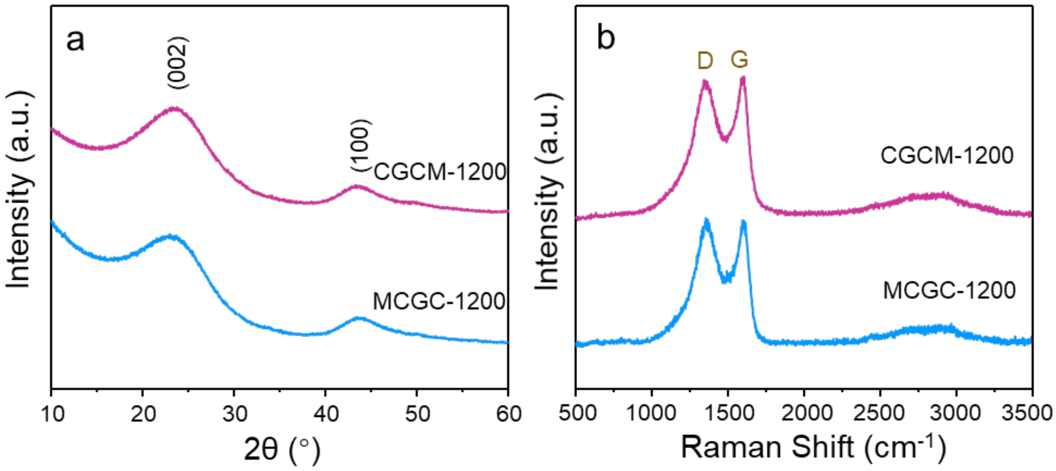

Fig.16 XRD patterns (a) and Raman spectra (b) of CGCM-1200 and MCGC-1200.

The Raman spectra of the two samples (Fig.16b) also display two characteristic peaks of D band (1350 cm^{-1}) and G band (1580 cm^{-1}). As shown in Table 3, the I_G/I_D ratios for CGCM-1200 and MCGC-1200 are almost the same, but a little bit higher than that of CGC-1200, implying that small sized particles obtained by ball milling could be easily graphitized. It is found that the ball milling towards carbon material improves the surface area to 62.3 m^2 g^{-1} (CGCM-1200).

Table 3 Physical parameters of the carbon materials.

Samples	d_{002}(nm)	*La* (nm)	*Lc* (nm)	I_G/I_D	S_{BET} (m^2 g^{-1})
CGCM-1200	0.375	1.69	1.74	0.49	62.3
MCGC-1200	0.382	1.31	1.89	0.48	7.5

In the following, electrochemical performances were conducted in half cells with metallic Na as the counter electrodes. Fig.17 shows the discharge/charge profiles of CGCM-1200 and MCGC-1200 in the first cycle at 0.02 A g^{-1}. Apparently, MCGC-1200 shows a larger irreversible capacity of 332.6 mA h g^{-1} at the first cycle delivering a relatively low ICE of 61.9%. In comparison, CGCM-1200 delivers an initial charge capacity of 304.6 mA h g^{-1} at 0.2 A g^{-1} with a high ICE of 80.7%. The ball milling treatment leads to an increased capacity for both samples. It is noted that the ICE of CGCM-1200 with high surface area is higher than that of MCGC-1200 with low surface area. Normally, a high surface area of carbon material always result in a loss of ICE, here the reduced particle size may contribute a high ICE.

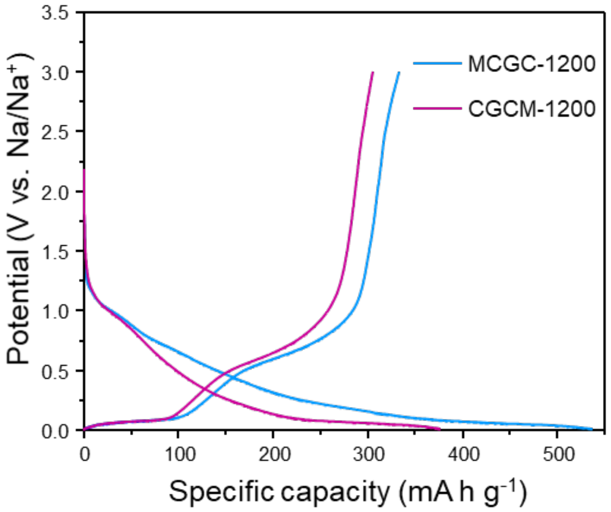

Fig.17 Galvanostatic charge-discharge profiles for the first cycles for CGCM-1200 and MCGC-1200 electrodes at 0.02 A g^{-1}.

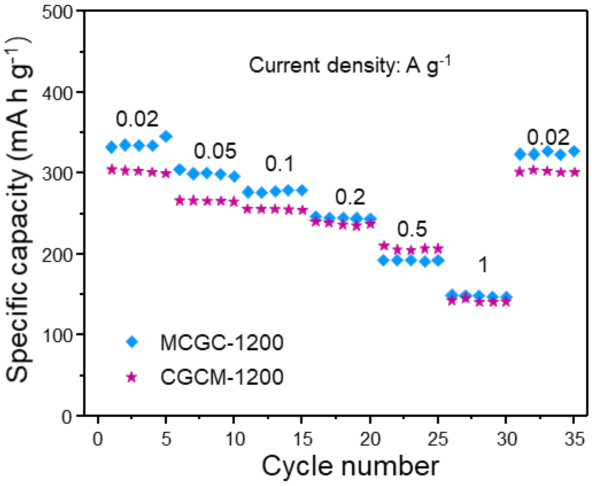

Fig.18 Rate capability for CGCM-1200 and MCGC-1200 anodes at current densities ranging from 0.02 to 1 A g^{-1}.

As depicted in Fig.18, after ball milling, the rate performance significantly improved no matter original coffee grounds or coffee grounds derived carbon was milled, and the capacities from the MCGC-1200 and CGCM-1200 are far superior to those from CGC-1200. This is because the smaller sized particles of the materials and are effective to shorten the diffusion paths of Na^+ de/insertion reaction. The reversible discharge capacities of both samples at current density up to 1 A g^{-1} reached approximately 150 mA h g^{-1}, roughly triple increase. It is worthy that after cycling at different current densities the capacities of MCGC-1200 and CGCM-1200 are both fully recovered, suggesting good stability of the electrodes.

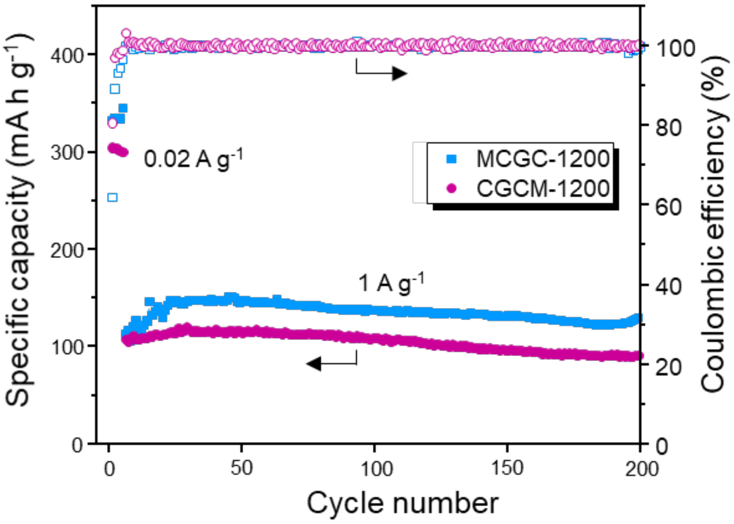

Fig.19 Cycling behaviors of CGCM-1200 and MCGC-1200 at 1 A g^{-1}.

The long cycling life of CGCM-1200 and MCGC-1200 at 1 A g^{-1} is presented in Fig.19. They deliver a similar initial capacity, but 200 cycles later MCGC-1200 maintains a higher reversible capacity (115.1%) than does CGCM-1200 (84.7%).

1.4 Process Optimization through Pre-carbonization

With continuous research and explortion, the challenges facing anode materials of SIB like low reversible capacity, low ICF and poor rate performance have been to some extent solved by choosing coffee grounds as hard carbon precursor associated with optimizing reaction conditions and process technology. The deash treatment is necessary to obtain pure hard carbons materials and ball milling is helpful to reduce the particle size of the hard carbons.

When I encouraged by the scientific innovation achievement, a brave idea is coming out. That is, taking one step further, if there will be the possibility for the scientific achievement transfer, what else should be considered? Economic and environmental issues should be the first priority.

The carbon yield of coffee grounds is roughly 20 wt%, and most light volatiles are decomposed into gas molecule without forming carbon residue. On one hand, if the original coffee grounds are directly subject to deash treatment by acid and ball milling, the handling amount and acid solution will be large and thriftless; on the other hand, if deash treatment is carried out after carbonization, it is not easy to remove most of metallic impurities because of the formation of stable metallic carbides at high carbonization temperature. After comprehensive consideration, an attempt is thus made by introducing a pre-carbonization step at relatively low temperature.

According to the DTG profile of coffee grounds (Fig.6), the volatiles decomposition starts at about 150 °C and the main mass loss is typically observed in the range 150-450 °C. Hence, the pre-carbonization temperature is tentatively set as 400°C. After pre-carbonization step, the collected sample was deashed as did before, and finally carbonized at higher temperatures of 1200 °C for 2 h to obtain sample PCGC-1200.

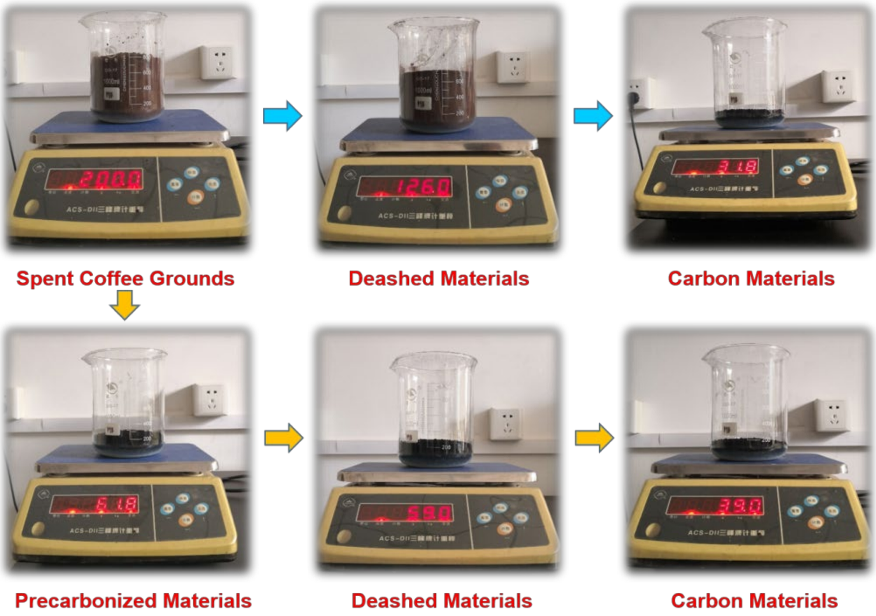

Fig.20 Associated mass changes of the products during the preparation process.

Fig.20 depicts the associated mass changes of the products during the preparation process. One can see if 200 g dried coffee grounds was directly washed with acid solution, the mass decreases to 126.0 g and the volume looks similar. Whereas, pre-carbonization step remarkably removed the large quantity of volatile and the collected sample was 61.8 g in weight with only one-fourth volume compared to original coffee grounds, indicating a significantly lower acid dosage. It is worthy pointing out that no matter which route was chosen, the carbon yield basically maintained similar.

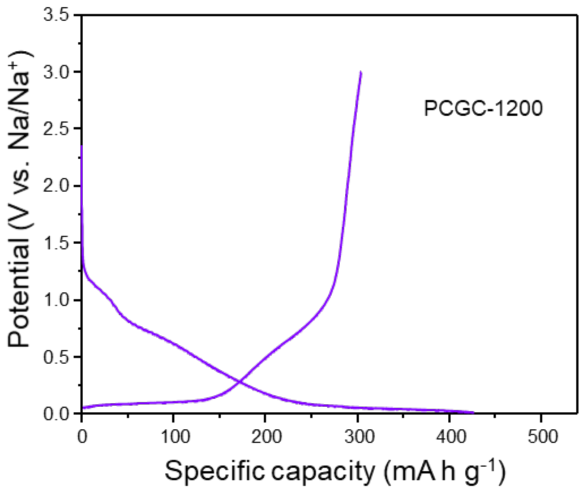

Fig.21 The initial galvanic charge/discharge curves at 0.02 A g^{-1}

The Na^+ storage behaviors of PCGC-1200 were tested with sodium metal as the counter electrode. Fig.21 shows the sodium charge-discharge curves at 0.02 A g^{-1}, the first discharge capacity is 304 mA h g^{-1} with 71.4% ICE, closing to that of CGC-1200 (77%), demonstrating that effectiveness of introduction of pre-carbonization treatment.

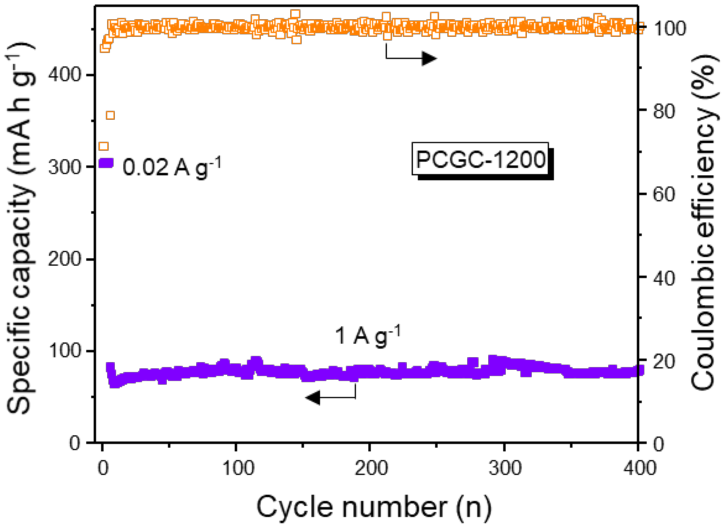

Fig.22 Cycling performance of PCGC-1200 anode.

The cycling test at a constant current rate of 1 A g^{-1} for 400 cycles was performed to test the structural stability of PCGC-1200, and the result is provided in Fig.22. After activation at 0.2 A g^{-1} for initial five cycles, PCGC-1200 exhibits a capacity of 80.6 mA h g^{-1}, which retains 97% after 400 cycles. Additionally, the Coulombic efficiency is kept at nearly 100%, further indicative of the high reversibility.

Conclusions

In this study, we demonstrated that coffee grounds were good candidates for the preparation of hard carbon materials. The obtained carbon has negligible surface area and suitable as anode material for sodium ion battery. The preparation conditions of carbon materials have been investigated. The deash with acid solution can remove the metallic impurities in the coffee grounds, which is the key step to obtain high purity hard carbons. Furthermore, an optimal carbonization temperature was determined as 1200°C, which ensure a larger interlayer distance and low surface area and subsequently an improved the capacity and ICE. Ball milling is helpful to reduce the particle size, which can enhance the kinetics of Na^+ de/insertion reaction relating good rate capacity. Finally, considering the practicability of coffee grounds derived carbon materials, a pre-carbonization step at a relatively low temperature was introduced in the preparation process to remarkably decrease the handling amount of coffee grounds and acid solution dosage. The obtained carbon materials delivered a comparative reversible capacity and ICE. Several commercial red LEDs can be powered by sodium ion full cell by using coffee grounds derived carbon as anode.

Prospect

Sodium-ion battery has been widely accepted as an ideal candidate for energy storage by considering the abundant Na resource relative to the Li counterparts. Hard carbon has dragged intense attention due to its high reversible capacity, low working potential and easy accessibility, especially from cheap and renewable biomass and even biomass waste.

Although various biomass and wastes have been purposely carbonized to prepare high performance anodes of SIB, a fundamental understanding of Na storage mechanism associated with structure-activity relationship is still unclear and even opposite, which in return limit the development of practical carbon anode materials in large scale. In this study, coffee grounds were luckily found to be a good candidate for the preparation of hard carbon after several biomass wastes were attempted. Nevertheless, why the good precursor is coffee grounds rather than others biomass, what is special in the structure of coffee grounds? Can we find other similar biomass or chemically synthesize similar structured carbon materials? We need to have a breakthrough in the cross field of biology and chemistry.

Biomass basically consists of cellulose, hemicellulose, lignin *etc*. We need to quantitatively characterize the microstructure of coffee grounds, try to realize the well-controlled preparation of its carbon product. The key issues include surface area, particle size, degree of graphitization.

At the same time, how to figure out the Na storage mechanism, how to establish universal carbon anode model will be considered in next step. Maybe compute science or big data analytics will help.

In addition, metallic impurities in biomass are always inevitable and the current removal method of impurities is environmentally unfriendly. The essential influence of impurities on the charge-discharge performance is supposed to be the next step work. A mild deash method is keenly required.

Finally, by considering the full cell construction, proper cathode needs to be explored to ensure a well matching with anode. Hopefully, after studying and training, we have a chance to undertake innovation and pioneering in the near future.

Attached Schedule

Summary of synthesis information, structure properties and electrochemical performance of the hard carbon samples

Samples	Synthesis information	Carbonization temperature (°C)	d_{002} (nm)	*La* (nm)	*Lc* (nm)	I_G/I_D	S_{BET} (m^2 g^{-1})	RC0.02[a] (mA h g^{-1})	RC1[b] (m A h g^{-1})	ICE[c] (%)
CGC-1000(A)	direct carbonization	1000	0.380	-	-	-	22.3	202.5	61.7	50.3
CGC-1000	deash + carbonization	1000	0.383	1.39	1.75	0.38	6.4	235.2	70.3	63.6
CGC-1200	deash + carbonization	1200	0.379	1.41	1.81	0.44	6.1	292.5	55.0	77.0
CGC-1400	deash + carbonization	1400	0.371	1.47	1.95	1.03	21.8	232.5	33.9	71.7
CGCM-1200	deash + carbonization +ball milling	1200	0.375	1.69	1.74	0.49	62.3	304.6	146.5	80.7
MCGC-1200	ball milling +deash + carbonization	1200	0.382	1.31	1.89	0.48	7.5	345.6	149.6	61.9
PCGC-1200	precarbonization (400°C)+ deash + carbonization	1200	0.378	1.50	1.81	0.48	11.3	305.8	69.7	71.4

a: The reversible capacity at 0.02 A g^{-1} (RC0.02)

b: The reversible capacity at 1 A g^{-1} (RC1)

c: The initial Coulombic efficiency (ICE)

References

1. Yun-Xiao Wang, Wei-Hong Lai, Yun-Xia Wang, Shu-Lei Chou, Xinping Ai, Hanxi Yang, and Yuliang Cao. Sulfur-Based Electrodes that Function *via* Multielectron Reactions for Room-Temperature Sodium-Ion Storage. *Angew. Chem. Int. Ed.* **2019**, DOI: 10.1002/anie.201902552.

2. 潘都，戚兴国，刘丽露，蒋礼威，陆雅翔，白莹，胡勇胜，陈立泉. 钠离子电池正负极材料研究新进展. 硅酸盐学报. 2018，46，479.

3 Li Li, Yang Zheng, Shilin Zhang, Jianping Yang, Zongping Shao and Zaiping Guo. Recent Progress on Sodium Ion Batteries: Potential High-Performance Anodes. *Energy Environ. Sci.*, **2018**, 11, 2310.

4 Huiteng Tan, Dong Chen, Xianhong Rui, and Yan Yu. Peering into Alloy Anodes for Sodium-Ion Batteries: Current Trends, Challenges, and Opportunities. *Adv. Funct. Mater.* **2019**, 29, 1808745.

5 刘双，邵涟漪，张雪静，陶占良，陈军. 水系钠离子电池电极材料研究进展. 物理化学学报. 2018，34，581.

6 Seung Ho Choi, You Na Ko, Jung-Kui Lee, and Yun Chan Kang. 3D MoS_2–Graphene Microspheres Consisting of Multiple Nanospheres with Superior Sodium Ion Storage Properties. *Adv. Funct. Mater*. **2015**, 25, 1780.

7 谢银斯，孙丁武，林维捐，何国强. 钠离子电池负极材料研究进展. 电源技术. 2019, 43, 351.

8 Xiujuan Wei, Xuanpeng Wang, Xin Tan, Qinyou An, and Liqiang Mai. Nanostructured Conversion-Type Negative Electrode Materials for Low-Cost and High-Performance Sodium-Ion Batteries. *Adv. Funct. Mater*. **2018**, 28, 1804458.

9 Qiang Bai, Lufeng Yang, Hailong Chen, and Yifei Mo. Computational Studies of Electrode Materials in Sodium-Ion Batteries. *Adv. Energy Mater*. **2018**, 8, 1702998.

10 Kudakwashe Chayambuka, Grietus Mulder, Dmitri L. Danilov, and Peter H. L. Notten. Sodium-Ion Battery Materials and Electrochemical Properties Reviewed. *Adv. Energy Mater.* **2018**, 8, 1800079.

11 Miguel Ángel Muñoz-Márquez, Damien Saurel, Juan Luis Gómez-Cámer, Montse Casas-Cabanas, Elizabeth Castillo-Martínez, and Teófilo Rojo. Na-Ion Batteries for Large Scale Applications: A Review on Anode Materials and Solid Electrolyte

Interphase Formation. *Adv. Energy Mater.* **2017**, 7, 1700463.

12 Hanna He, Dan Sun, Yougen Tang, Haiyan Wang, and Minhua Shao. Understanding and Improving the Initial Coulombic Efficiency of High-Capacity Anode Materials for Practical Sodium Ion Batteries. *Energy Storage Mater.* **2019**, DOI: 10.1016/j.ensm.2019.05.008.

13 Min Wana, Rui Zeng, Kongyao Chen, Ganxiong Liu, Weilun Chen, Lili Wang, Nan Zhang, Lihong Xue, Wuxing Zhang, and Yunhui Huang. Fe_7Se_8 Nanoparticles Encapsulated by Nitrogen-Doped Carbon with High Sodium Storage Performance and Evolving Redox Reactions. *Energy Storage Mater*. **2018**, 10, 114.

14 Claude Delmas. Sodium and Sodium-Ion Batteries: 50 Years of Research. Adv. Energy Mater. 2018, 1703137.

15 Josiah McNutt, and Quan (Sophia) He. Coffee grounds: A Review on Current Utilization. *J. Ind. Eng. Chem.* **2019**, 71, 78.

Acknowledgement

Every day we can see the Starbucks everywhere. Gradually I am getting interested in why the coffee culture is that popular nowadays. Besides reading books about coffee history, I also worked as an intern in a Café on holidays. At that time I thought it was not environmentally friendly to just throw away a large amount of coffee grounds as garbage. Since I had read some papers about batteries when I studied the Chemistry Olympiad, I learned that coffee grounds, one kind of biomass wasre, could possibly be utilized as carbon electrode materials. I contacted Prof. Li after searching online for Professors in Dalian who engaged in battery research. Prof. Li was enthusiastic about science education among teenagers. Under his guidance, I prepared carbon materials based on coffee grounds, which was suitable for the anode of sodium ion battery. For further research, we discussed and tested several key factors that probably determine the properties of this sodium ion battery. After experiments and analysis, I finished this repot in summer vacation.

I wish to express sincere gratitude to my supervisor Prof. Xianfeng Li for his advice on the experiments and writing, and the provision of research laboratory at Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

I also wish to extend my thanks to the staff in Dalian Institute of Chemical Physics for assisting me with SEM and TEM. I am also grateful for doctoral students in Prof. Li’s group for assisting me with XRD and XPS analysis.

Special thanks to Shi-Sheng Li, my chemistry teacher in Dalian Yuming Senior High School for his support and encouragement.

Resume of Team Member

Name: Pengrong Lu

Education:

Middle School: Attached School of Dalian University of Technology

High School: Dalian Yuming Senior High School

Awards

2018年9月	第32届中国化学奥林匹克竞赛辽宁省二等奖(中国化学会主办）
2018年12月	中学生英语能力大赛全国二等奖（国家基础教育实验中心外语教育研究中心主办）
2019年1月	美国数学竞赛(AMC，12级) Top 5%（美国数学学会主办）
2019年4月	美国化学奥林匹克竞赛中国赛区金奖（辽宁省唯一金奖，美国化学会主办）
2019年4月	全国中学生科技创新大赛辽宁省一等奖 （辽宁省科协主办）

Resume of the supervisor

Xianfeng Li, Full professor and head of Energy Storage Division in Dalian Institute of Chemical Physics. His research areas include the molecular design, structures and properties of functional polymer membrane materials, ion exchange membranes and ion conducting membranes for flow batteries, electrode materials for sodium-ion battery. He has obtained awards like NSFC for Distinguished Young Scientists, the National Youth Top-notch Talent Award, National Technology Invention Award (second prize), outstanding Science and Technology Achievement Prize of the CAS, *etc*.

本参赛团队声明所提交的论文是在指导老师指导下进行的研究工作和取得的研究成果。尽本团队所知，除了文中特别加以标注和致谢中所罗列的内容以外，论文中不包含其他人已经发表或撰写过的研究成果。若有不实之处，本人愿意承担一切相关责任。

参赛队员：　　　　指导老师：

2019 年　9　月　14　日