Purification mechanism of microcrystalline graphite and lithium storage properties of purified graphite

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Abstract
In order to improve the application value of natural microcrystalline graphite with carbon content of 49.5%, high-purity microcrystalline graphite was prepared by emulsifying kerosene flotation firstly, and then purifying hydrofluoric acid and hexafluorosilicic acid. Then the purified microcrystalline graphite was prepared for the lithium-ion battery anode material, its microstructure and electro-chemical properties were analyzed, the purification mechanism and lithium storage mechanism were discussed. The research results show that carbon content of microcrystalline graphite after emulsified kerosene flotation and mixed acid purification are 93.5% and 99.0% respectively. After pickling, high-purity microcrystalline graphite shows the largest layer spacing, which is 0.351 5 nm and is 0.001 4 nm higher than that of natural microcrystalline graphite. Size disparity of acid washing sample is larger, layered structure is more obvious, cycle performance and magnification performance are better than those of floatation sample. The pickled sample has the highest initial reversible specific capacity of 477.4 mAh/g, and the first Coulomb efficiency is 61.3%. Charge transfer impedance, interface impedance and SEI membrane impedance, and lithium ion diffusion impedance in electrode material are significantly lower than those of microcrystalline graphite after flotation.

1. Introduction

Lithium-ion batteries have the advantages of high energy density, long cycle life, no memory effect and environmental protection, which are widely used in small electronic devices, energy storage systems, electric vehicles and other fields [1–3]. Natural graphite is one of the high quality raw materials for making negative electrode of lithium ion battery. Compared with lamellar graphite, microcrystalline graphite has smaller grain size and higher disorder degree, and the particles are isotropic, so the lithium ion diffusion performance of microcrystalline graphite is higher in theory [4, 5]. It is an ideal raw material for anode materials for lithium-ion batteries. However, there are many impurities in natural microcrystalline graphite, and it is relatively difficult to purify. So preparing high purity microcrystalline graphite for application in lithium-ion battery anodes and improving the microstructure and electrical properties of lithium-ion batteries are urgent problems [6–8].

The purification methods of microcrystalline graphite are divided into physical method and chemical method; physical method includes flotation method [9–11] and high temperature method [12]. Chemical method includes alkali-acid method [13, 14], hydrofluoric acid method [15, 16] and chloride roasting method [17]. In the microcrystalline graphite concentrate purified by flotation, some impurities are impregnated in the graphite in the form of very fine particles, which cannot be completely dissociated, so only the most high-carbon products can be obtained. However, flotation process does not corrode the equipment and has a low cost. The microcrystalline ink purified by high temperature method has the highest carbon mass fraction, but the equipment is expensive and the investment is huge. The alkali-acid method has an unfriendly environment and is easy to corrode the equipment; the chloride roasting method has poor controllability, chlorine gas is toxic, and there are hidden dangers in safety.
To solve the above problems, the emulsified kerosene flotation method \[18, 19\] is used for flotation, which is noncorrosive and low cost, is used for flotation. This method can reduce the corrosion of equipment caused by excessive pickling, and it is easier to capture microcrystalline graphite than ordinary flotation method. Then, the high-carbon graphite after flotation was further purified by using low concentration hydrofluoric acid (HF) reagent. As HF reacts with mineral impurities and produce some insoluble salts, which cannot be separated from the microcrystalline graphite. Finally, hexafluorosilicic acid (H\(_2\)SiF\(_6\)) was used to dissolve the precipitation generated after HF washing to generate soluble salt. After water washing, high-purity microcrystalline graphite is obtained with carbon mass fraction of \(\geq 99.0\%\). The purification mechanism was analyzed. Then the high purity microcrystalline graphite was used as the anode material of lithium-ion battery to prepare lithium-ion battery. The changes of microstructure and electrical properties before and after purification were compared, and the lithium storage mechanism was analyzed, which provides a new idea for the deep processing of microcrystalline graphite, and provides some reference for broadening the application field of microcrystalline graphite.

2. Test method and characterization

2.1. Purification process
Carbon mass fraction of natural microcrystalline graphite (MG) is 49.5\%. MG was broken by two stages of jaw breaking and one stage of counteraction hammering, and the ultra-fine powder of \(-10 \, \mu m\) was prepared by horizontal stirring mill-dry cyclone classification. As flotation feed, the concentrate was collected by self-made emulsified kerosene as collector and marked as PMG\(_1\) after one rough separation and five times fine washing in the flotation cell. Carbon mass fraction of PMG\(_1\) is 93.5\%. Through the pre-test, it is determined that the impurity removal effect is the best when the volume ratio of hydrofluoric acid to hexafluorosilicic acid is 1:1, the mass ratio of mixed acid to microcrystalline graphite is 2:1, the reaction temperature is 70 °C and the reaction time is 3 h. The prepared high purity microcrystalline graphite is named PMG\(_2\), whitch carbon mass fraction is 99.0\%.

2.2. Battery preparation
The carbon mass fraction of natural microcrystalline graphite is low, so it is of little significance to prepare lithium-ion batteries. Therefore this paper only assembles the microcrystalline graphite samples before and after pickling. PMG\(_1\) and PMG\(_2\) were mixed with binder and conductive agent according to the mass ratio of 8: 1: 1, respectively. The solvent was added to form a sticky paste, which was uniformly coated on the copper foil with a thickness of 25 \(\mu m\). After drying in a vacuum drying oven at 120 °C for 24 h, it was pressed into a working electrode. After drying, it was put into a vacuum glove box equipped with high purity Ar. The lithium sheet was used as the counter electrode, the electrolyte was EC/ PC/ DMC with a volume concentration of 1 mol l\(^{-1}\). The separator was a porous polypropylene membrane (Celgard2400 type). The button battery was assembled.
2.3. Structural characterization and electrical performance test

The phase of the samples was analyzed by XRD-6100 x-ray diffractometer; the structure and crystallinity of the samples were analyzed by using Thermo Fischer DXR Raman spectrometer; the functional groups of the materials were analyzed by using Fourier transform Infrared spectrometer (IR Prestige-21); the morphology of the samples was observed by JSM-7500 field emission scanning electron microscope, and the charge-discharge, cycle and rate performance of the battery were tested by BTS-5V/2.2A battery performance tester. The cyclic voltammetry curve and AC impedance curve of the battery were measured by electrochemical workstation (CHI-660E) to analyze the conductivity and electrode reaction mechanism of the battery.

3. Results and discussion

3.1. Physical phase

The x-ray diffraction (XRD) spectrum of MG, PMG1 and PMG2 is shown in figure 1. Before purification, there are many impurities in MG sample, mainly containing quartz, mica and pyrite. The main chemical composition of quartz is SiO$_2$, the chemical formula of mica is KAl$_2$(AlSi$_3$O$_{10}$(OH)$_2$, and the chemical formula of pyrite is FeS$_2$. After emulsified kerosene flotation, the impurity contents of PMG1 sample, mica and quartz in PMG1 sample decrease, and the characteristic peaks of graphite 26° (002) crystal face and 43° (100) crystal face are broadened. After HF-H$_2$SiF$_6$ pickling, there may be a small amount of mica in PMG2 sample. Steamed bread peaks appear in microcrystalline graphite before and after pickling, indicating that the graphite peak before flotation is relatively low, so the content of impurities is relatively high. The peak position change of each sample in the (002) crystal face is shown in table 1. The calculation by Bragg equation shows that the layer spacing of sample does not change before and after flotation. However, after pickling, the layer spacing slightly increases, which may be caused by the acid oxidation. The layer space of PMG2 sample is the largest, which is 0.001 4 nm higher than that of natural microcrystalline graphite.

| Samples | $\theta$ (°) | $d_{002}$ (nm$^{-1}$) |
|---------|-------------|-----------------------|
| MG      | 25.42       | 0.350 1               |
| PMG1    | 25.42       | 0.350 1               |
| PMG2    | 25.32       | 0.351 5               |

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3.2. Crystallization

The Raman spectra of MG, PMG1 and PMG2 are shown in figure 2. The characteristic peak D loated at the wavenumber of 1 360 cm$^{-1}$ is corresponding to the disordered carbon structure of graphite and the
characteristic peak G appeared at the wavenumber of 1580 cm$^{-1}$ is corresponding to the E$_{2g}$ vibrational mode. The single crystal of graphite contains order, but the raman spectrum contains only a sharp G peak. The microcrystalline graphite appears D peak due to the decrease of crystal size and long-range period. And the intensity is enhanced. The $R$ values of the above samples [20] ($R = I_D/I_G$, $I_D$ and $I_G$ denote the intensity of D peak and G peak of raman spectrum, respectively) are 0.919, 0.826 and 0.824, respectively, indicating that the disorder degree of microcrystalline graphite before flotation is higher due to the high content of mineral impurities, which destroys the periodic structure of microcrystalline graphite. The crystallinity of PMG1 sample after flotation is increased, which is similar to the microcrystalline graphite PMG2 sample after pickling.
may be due to the small difference in impurity content, which has little effect on the arrangement of lattice structure.

3.3. Functional group
The Infrared spectra (FTIR) of MG, PMG1 and PMG2 are shown in figure 3. The corresponding characteristic peaks of ferrosilicate are found at the wavenumber of 473 cm$^{-1}$, calcium-containing aluminosilicate can be found near the wavenumber of 540 cm$^{-1}$, characteristic absorption peaks of corresponding Si–O–Si stretching vibration are found near the wavenumber of 800 cm$^{-1}$, characteristic absorption peaks of O–H bending vibration are found near the wavenumber of 880 cm$^{-1}$ and 1 050 cm$^{-1}$, and characteristic absorption peaks of C–O stretching vibration and O–H stretching vibration are observed at the wavenumber of 1 086 cm$^{-1}$ and 3 387 cm$^{-1}$. The characteristic absorption peaks of alkene C=C or carbonyl C=O stretching vibration are found near the wavenumber of 1 650 cm$^{-1}$, and the characteristic absorption peaks of C–H stretching vibration are found near the wavenumber of 2 882 cm$^{-1}$ and 2 975 cm$^{-1}$. There are many kinds of MG absorption peaks of microcrystalline graphite before flotation, indicating that there are many mineral impurities. The ferrosilicate and calcium aluminosilicate minerals of microcrystalline graphite PMG1 disappear after flotation. Combined with XRD analysis, the content of mica decreases and the characteristic peak of Si–O–Si disappears, indicating that quartz is removed. PMG2 sample purified by pickling method weakens at the wavenumber of 2 882 cm$^{-1}$, indicating that the impurity content is further reduced.

3.4. Micromorphology
The surface morphology of the samples was observed by scanning electron microscope (SEM). As shown in figure 4, the morphology of microcrystalline graphite has little difference before and after purification, indicating separately distributed earth-like particles with irregular shape, and there are many fine particles on the surface or interstitial of microcrystalline graphite. The MG particles of natural microcrystalline graphite are relatively fine and uniform. After purification, the size difference gets more obvious, and the layered structure is more obvious, and some fine particles are distributed on the surface.

3.5. Purification mechanism
Figure 5 shows the purification mechanism of microcrystalline graphite. Natural microcrystalline (figure 5(a)) contains a large number of impurities between crystals and lamellae, mainly quartz (SiO$_2$), containing a small amount of magnesium oxide, calcium oxide and alumina. The chemical formula of mica is KAl$_2$(AlSi$_3$O$_{10}$)(OH)$_2$, mainly contains silica, alumina and a small amount of calcium, magnesium and iron, and the main composition of impurity pyrite is FeS$_2$. During flotation, the inhibitor sodium silicate and sodium carboxymethyl cellulose are added firstly, mainly to increase the viscosity of the system and restrain the flotation of mineral oxide impurities, and then the kerosene is strongly stirred into an emulsion in order to more evenly collect fine particles of microcrystalline graphite. Then add 2$\%$ oil, which graphite flotation foam is on the liquid surface of the flotation cell, and scrape the foam. Microcrystalline graphite and a small part of interlayer impurities are collected together with the foam under the dual action of inhibitor and flotation agent. When the...
cleaning process is repeated for 5 times, the mass fraction of fixed carbon has no change, and the flotation test is over. The flotation test is shown in figure 5(b).

In order to further improve the purity of microcrystalline graphite, the microcrystalline graphite after flotation was reacted with HF. The reaction principle can be seen in the chemical reaction formula (1)–(6).

HF fully reacts with oxide impurities in minerals to form KF soluble fluoride, SiF₄ gas and fluoride precipitation of Ca, Mg, Al and Fe. Because the microcrystalline graphite after pickling needs to be neutralized by using deionized water, these fluoride precipitates need to be converted into soluble substances and filtered together, and the H₂SiF₆ happens to react with these fluoride precipitates, such as the reaction expression (7)–(10), to form soluble fluoroosilicates, which can be separated from microcrystalline graphite by washing, thus achieving the purpose of removing impurities [21]. The sample after pickling is shown in figure 5(c), and the purity of microcrystalline graphite is 99.0%. Most of the fine impurities in the crystal are removed. Combined with the structural characterization of this sample, the proposed method shows a high impurity removal efficiency.

\[
\begin{align*}
K_2O + 2HF & \rightarrow 2KF + H_2O \quad (1) \\
SiO_2 + 4HF & \rightarrow SiF_4 \uparrow + 2H_2O \quad (2) \\
CaO + 2HF & \rightarrow CaF_2 \downarrow + H_2O \quad (3) \\
MgO + 2HF & \rightarrow MgF_2 \downarrow + H_2O \quad (4) \\
Al_2O_3 + 6HF & \rightarrow 2AlF_3 \downarrow + 3H_2O \quad (5) \\
Fe_2O_3 + 6HF & \rightarrow 2FeF_3 \downarrow + 3H_2O \quad (6) \\
CaF_2 + H_2SiF_6 & \rightarrow CaSiF_6 + 2HF \quad (7) \\
MgF_2 + H_2SiF_6 & \rightarrow MgSiF_6 + 2HF \quad (8) \\
2FeF_3 + H_2SiF_6 & \rightarrow Fe_2SiF_{10} + 2HF \quad (9) \\
2AlF_3 + H_2SiF_6 & \rightarrow Al_2SiF_{10} + 2HF \quad (10)
\end{align*}
\]

3.6. Initial charge-discharge performance

The current density is 50 mA g⁻¹, and the first charge and discharge curves of microcrystalline graphite before and after pickling are shown in figure 6. With the increase of lithium intercalation capacity, voltage of PMG1 sample decreases rapidly to 0.7 V after flotation, slows down in the diagonal region of 0.2 V to 0.7 V, and slows down to 0.2 V. With the increase of lithium intercalation capacity, the voltage of PMG2 sample decreases rapidly to 1.0 V, and decreases slowly at 0.2 V to 1.0 V. The voltage tends to be flat at 0.2 V. The voltage of microcrystalline graphite before purification is lower than that of microcrystalline graphite after purification, which shows that after purification, the lithium intercalation capacity of purified microcrystalline graphite increases, the formed SEI membrane is less likely to fall off, the solvent is also not easy to decompose during subsequent lithium embedding, the impurity content of microcrystalline graphite decreases, the contact between electrolyte and microcrystalline graphite is more sufficient, and the concentration polarization of the electrode decreases. The first lithium removal voltage before and after purification is about 1.3 V, mainly due to

![Figure 6. First charge and discharge of samples after purification.](image-url)
the formation of SEI film during lithium intercalation. Some lithium ions are consumed and cannot produce reversible capacity in the lithium removal process. The first charge-discharge and charge specific capacity of PMG2 sample is the highest. The experimental results show that the specific capacity of the microcrystalline graphite battery purified by hydrofluoric acid and fluorosilicic acid is the highest, the first reversible specific capacity is 477.4 mAh g⁻¹, and the first coulomb efficiency is the highest, which is 61.3%. This may be due to the largest interlayer spacing of microcrystalline graphite.

3.7. Cycle performance
Figure 7 shows the cycle performance curve of PMG1 sample after flotation and PMG2 sample after pickling with HF-H₂SiF₆ at a current density of 50 mAh g⁻¹ and 400 mAh g⁻¹. The specific capacity of PMG2 is higher than that of PMG1. After 100 cycles, the reversible specific capacity retention of PMG1 and PMG2 is 78.4% and 96.2% at 50 mAh g⁻¹ and 400 mAh g⁻¹, respectively, and the reversible specific capacity retention of PMG1 and PMG2 is 80.2% and 87.2% at 400 mAh g⁻¹, indicating that the cycle performance of the sample is improved after pickling.
3.8. Rate performance

Rate performance of the PMG1 and PMG2 is shown in Figure 8. The specific rate performance of the batteries was tested at the current densities of 50 mAh g\(^{-1}\), 100 mAh g\(^{-1}\), 200 mAh g\(^{-1}\), 400 mAh g\(^{-1}\), 800 mA g\(^{-1}\) and 50 mA g\(^{-1}\), respectively. The average specific capacity of the battery at different current densities is calculated. PMG2 sample attenuates more slowly than PMG1 sample at a high current density, and the specific capacity is higher. When the current density is 800 mA g\(^{-1}\), the capacity retention of PMG1 and PMG2 are 51.4% and 37.7% of those at the current density of 50 mA g\(^{-1}\), respectively. When the current density returns to 50 mA g\(^{-1}\), the capacity retention of PMG1 and PMG2 are 89.3% and 99.0%, respectively.

3.9. Lithium storage mechanism

Figure 9(a) shows the first and second charge-discharge curves of PMG2 sample. With the increase of lithium intercalation capacity, the voltage drops rapidly to 1.0 V, and the potential platform appears. During the second lithium intercalation, the platform basically disappears. Referring to the cyclic voltammetry curve of figure 9(b), the first irreversible reduction peak appears at 1.3 V to 1.75 V. The second irreversible reduction peak appeared between 1.0 V and 1.2 V, and there were no reduction peaks in the second and later cyclic voltammetry curves, so it can be considered that a relatively stable SEI film was formed at the second reduction peak voltage. As shown in figure 9(b), an oxidation peak appears at the voltage of 1.75 V to 1.95 V, indicating that the lithium removal process occurs at this time, and the oxidation peak disappears during the second lithium removal. Combined with figure 9(a), the voltage decreases rapidly to about 1.75 V at the first charge, then on the second charge, the
slope of the curve becomes larger and the platform is not obvious, which is consistent with the cyclic voltammetry test results.

Comparing the impedance of the samples before and after pickling, as shown in Figure 10, two curves are composed of oblique lines in low frequency region, semicircles in medium frequency region and semicircle in high frequency region [18, 20]. The semicircle diameter after purification becomes smaller, indicating that the charge transfer, interface and SEI film impedance are decreased. The stability of SEI film is improved after purification. The slope of PMG2 is larger than that of PMG1, indicating that the diffusion impedance of lithium ion in microcrystalline graphite is lower. Compared with the AC impedance curve of PMG1 and PMG2, the impedance of microcrystalline graphite after flotation is much higher than that of microcrystalline graphite after pickling, indicating that the diffusion ability of lithium ion in electrode materials decreases with the increase of the purity of microcrystalline graphite. This is because after pickling, the purity of microcrystalline graphite increases, and the active sites increase. The irreversible specific capacity decreases, and the decomposition amount of solvents on graphite surface decreases. Moreover the thickness of SEI film decreases, the interface impedance and SEI film impedance decrease. After purification, the fine microcrystalline graphite increases, and the lithium ion diffusion channels increase. Meanwhile the lithium ion diffusion rate increases, and the diffusion impedance decreases.

To sum up, microcrystalline graphite after emulsified kerosene flotation destroys the periodic arrangement of microcrystals because of its high impurity content, which not only increases the transfer resistance of lithium atom in its interior, but also makes the interlayer and in-plane structure of hexahedron unstable, resulting in the decrease of electrochemical performance. After purified by HF-H$_2$SiF$_6$, the content of impurities in microcrystalline graphite is very low, the structural stability is improved, and the volume expansion during lithium intercalation and de-lithium is reduced. Due to the oxidation of strong acid, the interlayer spacing increases, the lithium ion diffuses more easily between the layers. The formed of SEI film is more stable, the reversible specific capacity increases, and the cycle performance is improved.

4. Conclusions

(1) The carbon mass fraction of natural microcrystalline graphite with carbon mass fraction of 49.5% is 93.5% and 99.0% after emulsified kerosene flotation and mixed acid purification. Kerosene is strongly stirred to form an emulsion in order to capture fine particles of microcrystalline graphite more evenly. HF can react fully with oxide impurities in minerals to form soluble fluoride and fluoride precipitation. H$_2$SiF$_6$ can react with these fluorides to form soluble fluorosilicate, which can be separated from microcrystalline graphite by washing.

(2) The interlayer spacing of high purity microcrystalline graphite is the largest after pickling, which is 0.3515 nm. The size difference of the samples is larger, and the layered structure is more obvious. After purification, the number of functional groups of the sample decreases gradually, indicating that the content of impurities decreases.

(3) After pickling, the lithium intercalation capacity of high purity microcrystalline graphite is increased, and the SEI film is more difficult to fall off. Moreover the solvent is not easy to decompose in the subsequent lithium intercalation process, and the concentration polarization of the electrode is reduced. The first reversible specific capacity of PMG2 is 477.4 mAh g$^{-1}$. After pickling, the ratio performance and cycle performance of microcrystalline graphite are improved. Meanwhile the interface and SEI film impedance of PMG2 are decreased, and the diffusion impedance of lithium ion in the electrode material is significantly lower than that of flotation graphite.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).
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