Diffusion coefficient analysis of aluminum electrolysis spent cathode as anode material for lithium-ion battery

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Abstract
The aluminum electrolysis spent cathode (SC) was treated by hydrothermal method and used as anode material for lithium-ion battery. The purified SC material shows excellent electrochemical performance. In order to understand the diffusion behavior of Li⁺ in the SC electrode, the diffusion coefficient of Li⁺ in the SC electrode was systematically analyzed by galvanostatic intermittent titration technique (GITT), cyclic voltammetry (CV), and electrochemical impedance spectroscopy (EIS). The results show that the diffusion coefficient ($D_{Li^+}$) of Li⁺ in SC electrode is calculated by CV is $2.2292 \times 10^{-11}$ cm² s⁻¹, and the ranges calculated by GITT and EIS are $4.2286 \times 10^{-13} - 2.9667 \times 10^{-10}$ cm² s⁻¹, $4.05 \times 10^{-13} - 3.87 \times 10^{-12}$ cm² s⁻¹, respectively. SC electrode exhibits better Li⁺ diffusion kinetics compared to commercial graphite (CG). In addition, the full cell of LiNi₀.₅Co₀.₂Mn₀.₃O₂/SC also shows excellent cycle performance. After 80 cycles at 1 °C (1 °C = 172 mA g⁻¹), the specific discharge capacity of LiNi₀.₅Co₀.₂Mn₀.₃O₂/SC full-cell can reach 94.7 mAh g⁻¹, and the capacity retention can reach 98.13%. The fast lithium-ion diffusion rate and high discharge capacity provide a feasible direction for the high value utilization of aluminum electrolysis spent cathode.

Keywords Lithium-ion battery · Aluminum electrolysis spent cathode · Diffusion coefficient · GITT · EIS

Introduction
In aluminum electrolysis industry of China, the main components of cathode are carbon materials. The constant penetration of electrolyte in the process of electrolysis makes the impurity content in the cathode graphite carbon block increase, which causes the cathode structure to be damaged and the electrolysis efficiency is reduced [1]. Therefore, it is necessary to replace the aluminum electrolysis cathode regularly. According to statistics, China produces about 500,000 tons of spent cathode carbon blocks from aluminum electrolysis every year [2], and there is no effective treatment method. At present, most aluminum smelters use open stacking. Due to the spent cathode contains fluoride, cyanide, and other toxic substances, which is a dangerous waste and has caused great security risks to the environment [3]. Therefore, how to deal with it innocently and make secondary high-value utilization has become a current research hotspot. Yuan W et al. analyzed the composition of aluminum electrolysis spent cathode in detail and found that the ratio of graphite to amorphous carbon was about 1.5:1, which indicated that it still had a high degree of graphitization [4]. Chen B et al. realized the closed recycling of the products by burning the spent cathode carbon block of aluminum electrolysis and adsored the fluoride in the combustion flue gas, which reduced the secondary pollution and reached the national allowable emission concentration [5]. Wang J et al. used flotation chemical method to recover fluoride and carbon from spent cathode of aluminum electrolysis. The recovery rates of fluorine and carbon were up to 90.10% and 95.90% respectively, realizing zero discharge and harmless treatment of spent water [6]. At present, most of the research on aluminum electrolysis spent cathode is harmless treatment, but how to make high-value utilization of them still needs further research.

With the demand for energy storage devices in electric vehicles, computers, mobile phones, and large-scale energy storage equipment, lithium-ion batteries have become a
Research hotspot in recent years. In order to improve the performance of battery, the research of cathode and anode materials has become the mainstream direction. At present, LiFePO$_4$ [7] and NCM [8] are the main cathode materials of lithium-ion batteries, and carbon materials and silicon-based materials are the main cathode materials. In recent years, some oxide anodes, such as ZnCo$_2$O$_4$ [9], ZnMn$_2$O$_4$ [10], MoNb$_{12}$O$_{33}$ [11], and V$_2$Nb$_{17}$O$_{50}$ [12], have also attracted much attention due to their high discharge specific capacity. Graphite is one of the main anode materials for Li-ion batteries by the reason of high specific discharge capacity, high compaction density, non-toxicity, stable cycling performance, and better safety compared with lithium metal [13, 14]. Zhang P et al. took the LiFePO$_4$||Graphite system as the research object and studied the effects of different current densities on the failure of graphite negative electrode. It is found that at a current intensity of 1 °C, the initial discharge specific capacity is 125 mAh g$^{-1}$. After 100 cycles, lithium metal begins to deposit on the surface of graphite cathode, resulting in rapid attenuation of capacity. When the current intensity is small (0.2 °C), the initial discharge capacity can reach 158 mAh g$^{-1}$, and the capacity retention rate is 87.0% after 100 cycles [15]. During the battery cycle, a passive film (SEI) is formed on the surface of graphite negative electrode, and proper SEI is beneficial to improve the stability of the electrode. Additives are usually added to the electrolyte to induce the formation of stable SEI. Ding Z et al. added 1% ethyl sulfate (DTD) to the electrolyte to induce the formation of uniform and smooth SEI. The cycle retention rate was increased from 85.3 to 105.3%, and the cycle stability of the battery was significantly improved [13]. The spent cathode of aluminum electrolysis is graphite carbon block, which contains 60–70% carbon [1]. Therefore, it is an effective way to use it as anode of lithium-ion battery after impurity removal. Yang K et al. used the materials obtained by graphitization after impurity removal of aluminum electrolysis spent cathodes as anode materials for Li-ion battery [16]. The purified graphite exhibited excellent reversible discharge capacity and cycle retention. The deintercalation/intercalation mechanism of lithium ion in aluminum electrolysis spent cathodes was explained by graphite/graphene co-intercalation. In order to improve the graphitization degree of SCC and improve the discharge specific capacity of SCC, Yang K et al. realized 100% graphitization by high-temperature calcination of aluminum electrolysis spent cathodes. The purely graphitized SCC showed a higher discharge specific capacity (455.2 mAh g$^{-1}$, while the non-graphitized SCC was only 319 mAh g$^{-1}$), and, it still had 460.1 mAh g$^{-1}$ after 50 cycles at 0.1 °C [16].

As a kind of secondary battery, lithium-ion battery mainly depends on the movement of lithium ions between the cathode and anode electrodes. During the charging process, Li$^+$ comes out from the cathode material and embeds into the anode material through the electrolyte. In contrast, Li$^+$ comes out from the anode material and embeds into the cathode material during the discharge process. Therefore, the cathode and anode materials of Li-ion battery are required to have excellent Li$^+$ deintercalation/intercalation performance. The diffusion rate of Li$^+$ in the electrode direct influence on the charge and discharge rate of Li-ion battery. In the field of battery, the chemical diffusion coefficient is usually used to characterize the transfer characteristics of Li$^+$, so it is very important to calculate the diffusion coefficient of Li$^+$ in the electrode for understanding the kinetics of electrode materials. The methods commonly used to calculate the diffusion coefficient of Li$^+$ are galvanostatic intermittent titration technique (GITT), potentiostatic intermittent titration technique (PITT), electrochemical impedance spectroscopy (EIS), and cyclic voltammetry (CV) [17–21]. These methods have been widely used in the kinetics of electrode materials during charging and discharging of the battery.

In this paper, the aluminum electrolysis spent cathode carbon block was simply treated by hydrothermal method, and then it was used as electrode material to assemble the battery, and its cycle performance and rate performance were studied. The diffusion rate of Li$^+$ in SC electrode was studied by EIS, GITT, and CV curves, and compared with CG electrode. This research aims to study the high-value utilization of aluminum electrolytic spent cathodes carbon, analyze the feasibility of SCC as electrode material, and explain the high capacity and high rate through different calculation methods. It is found that the diffusion coefficient of Li$^+$ and specific discharge capacity in the SC electrode are higher than those of CG electrode. This may be due to the intercalation of Al$^{3+}$ and Na$^+$ during the aluminum electrolysis process, which expands the graphite layer spacing, provides a wider diffusion path for the diffusion of Li$^+$, and provides more sites for the intercalation of Li$^+$ (as shown in Fig. 1). All these results confirm the feasibility of aluminum electrolysis spent cathodes as anode materials for Li-ion batteries.

**Experimental**

**Impurity removal of aluminum electrolysis spent cathode**

After crushing the aluminum electrolysis spent cathode carbon block with a crusher, 3 g was taken to put it into a 200-mL autoclave. Sixty milliliters of 4 M HCl was added into the autoclave and was stirred thoroughly, and then reacted at 180 °C for 12 h. The product was filtered, dried it in an oven at 100 °C for 24 h. After ground, the spent cathode material after impurity removal can be obtained.
Material characterization

X-ray diffraction (XRD, D8 ADVANCE A25) was used to compare the lattice structure of spent cathode and commercial graphite under a scan speed of 5°/min in the range of 2θ = 10°–80°. The graphitization was analyzed by Raman spectroscopy (HORIBA Scientific LabRAM HR Evolution). The morphology was analyzed by field emission scanning electron microscopy (FE-SEM, Gemini SEM 300) for commercial graphite and spent cathode. The microstructure of the material was observed by Transmission electron microscope (TEM, FEI Tecnai G2 F20).

Electrochemical measurements

Preparation of graphite anode

Both SC and CG electrodes were prepared by mixing the active materials, acetylene black and polyvinylidene fluoride (PVDF, Canrd) were fully grinded at a mass ratio of 8:1:1, and then N-methyl pyrrolidinone (NMP, AR, Canrd) solution was added dropwise to obtain the slurry. The slurry was evenly coated on the copper foil and then dried in the oven at 60 °C to remove NMP, and then it was cut into 14 mm pole pieces by the punching machine (Load 2.34 mg cm⁻²).

Preparation of LiNi₀.₅Co₀.₂Mn₀.₃O₂ (NCM523) cathode

The commercial NCM523 material was mixed with acetylene black and PVDF at a mass ratio of 8:1:1. NMP solution was added to the above mixture, then it was coated on the aluminum foil after full grinding. Finally, it was dried and cut into pole pieces with a diameter of 14 mm for standby.

Assembly of half-cell

The battery was assembled in a glove box filled with argon by using the graphite electrode as the cathode electrode, 1 M LiPF₆ in ethylene carbonate (EC): dimethyl carbonate (DMC): ethyl methyl carbonate (EMC) (1:1:1, v/v/v, DoDoChem) as the electrolyte, Celgard 2500 polypropylene diaphragm as the separator and lithium as the anode electrode.

Assembly of full-cell

NCM523 electrode, 1 M LiPF₆ in EC: DMC: EMC (1:1:1, v/v/v, DoDoChem), Celgard 2500 polypropylene diaphragm and graphite electrode were used as cathode electrode, electrolyte, separator, and anode electrode, respectively. The battery was assembled in a glove box.

All the batteries were tested with LANHE-CT2001A (LANHE Product Series battery testing system) at 25 °C and activated by a small current of 0.1 °C (1 °C = 372 mA g⁻¹) for 2 cycles before the test. The cycle performance of the battery was tested at 0.2, 1.0, and 2.0 °C (the full-cell test was calculated based on the theoretical specific capacity of cathode active material). The current intensity of 0.1, 0.2, 0.5, 1.0, 2.0, 5.0, and 10 °C was used for 5 cycles to test the rate performance, and then the charge–discharge test was continued with 0.1 °C. The CV (0.005–2 V, 0.1, 0.2, 0.5, 0.8, 10 mV s⁻¹, respectively) curve and EIS (1 MHz–0.01 Hz) were measured with Electrical Workstation (Parstat 4000 A).

Result and discussion

Figure 2a shows the XRD pattern of the aluminum electrolysis spent cathode material after impurity removal. It can be seen that the diffraction peak of the material is good agreement with that of Graphite-2 h and no impurity peaks are found in the diffraction peak, which indicates that the impurities (such as Al₂O₃, CaF₂, Na₂AlF₆, Na₅Al₃F₁₄, and NaF [3, 22]) in the spent cathode carbon block of aluminum electrolysis are basically removed. The XRD results were processed by Jade software to obtain the lattice constants, the results are shown in Table 1. Compared with commercial graphite, the increase of c and c/a value indicates that SC material has larger interlayer spacing, which provides a larger path for Li⁺
diffusion between graphite layers. Through the calculation formula of graphitization degree \( P = 1 - \left( \frac{d_{002} - 0.3354}{0.344 - 0.3354} \right) \) [23], it can be obtained the graphitization degree of SC material is 89.91%.

In order to study the order of SC structure, the Raman spectra of SC were measured and compared with CG. The results are shown in Fig. 2b. The D peak near 1360 cm\(^{-1}\) represents the lattice defects of carbon atoms, and the G peak near 1580 cm\(^{-1}\) corresponds to the in-plane stretching vibration of sp\(^2\) hybrid carbon atoms. The intensity ratio of D peak to G peak is commonly used to characterize the graphitization degree of carbon materials. It can be seen that CG sample has no diffraction peak near 1300 cm\(^{-1}\), which indicates that CG has no lattice defects and is an ordered pure graphite structure. However, SC has obvious diffraction peak at D, which may be due to the destruction of cathode structure during aluminum electrolysis, resulting in the defects of carbon lattice. Comparing the intensity ratio of D peak and G peak, \( I_D/I_G = 0.41 \), which also shows that the material still has a high degree of graphitization, similar to XRD results. The pore structure of SC material has been further studied by N\(_2\) adsorption–desorption isotherm test, and the results are shown in Fig. 2c, d. SC exhibits a type IV adsorption–desorption curve, and the pore size is mainly distributed around 2.4 nm, which indicates that there are mesopores in SC materials [24]. The Braeuer-Emmett-Teller (BET) results show that the specific surface area and pore volume of SC material are expected to be 12.6547 m\(^2\) g\(^{-1}\) and 0.030916 cm\(^3\) g\(^{-1}\), respectively. The low specific surface area and pore volume can be attributed to the inherent repeated stacking tendency of SC materials [25].

Figure 3 shows the morphology of spent cathode material after purification. It can be seen from Fig. 3a that the SC material is a porous structure formed by agglomeration of small particles, which makes the material have a larger specific surface area, ensures that the electrolyte can fully contact with the electrode material, and shortens the diffusion path of Li\(^+\). At a larger magnification (as shown in Fig. 3b), it is observed that these small particles still have the flake-like structure of graphite with a size of 2–4 μm. Figure 3c, d shows the TEM and HRTEM of SC material, respectively. It can be seen that SC has a typical layered structure and obvious lattice fringes can be observed from Fig. 3d. Through line scanning of different regions (Fig. 3d1–d3), it can be observed that the lattice spacing of d1, d2, and d3 regions are 0.341, 0.353, 0.341, 2.461, 2.461, 6.708, 35.2, 2.72572 – 0.3976

| Sample            | a (Å) | b (Å) | c (Å) | V (Å\(^3\)) | c/a     | Error (%) |
|-------------------|-------|-------|-------|-------------|---------|-----------|
| Commercial graphite | 2.461 | 2.461 | 6.708 | 35.2        | 2.72572 | –         |
| Spent cathode     | 2.46391 | 2.46391 | 6.72536 | 35.36       | 2.72955 | 0.3976    |

Fig. 2 a XRD patterns and b Raman diagram of SC and CG materials. c Nitrogen adsorption–desorption isotherms and d pore size distribution curves of SC materials.
and 0.343 nm respectively, which correspond to the (002) plane of graphite [26, 27]. The result shows that the inter-layer spacing is larger than that of commercial graphite (0.3354 nm), which is consistent with the results of XRD.

Figure 4 shows the cycle performance and rate performance of the half-cell assembled by SC and CG, respectively. The cycle performance of SC and CG electrodes at 0.2 °C (1 °C = 372 mA g⁻¹) is shown in Fig. 4a. The first 2 cycles were activated with 0.1 °C, and the specific

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**Fig. 3** a–d SEM and TEM of SC materials. d1–d3 Corresponding lattice spacing scanned by the line scan

**Fig. 4** a, d Cycle performance diagrams of the SC electrode and CG electrode at 0.2 °C and 2 °C, respectively. b, c First 3 cycles of the SC electrode and CG electrode at 0.2 °C current cycle Discharge curve.

e Rate performance graph of SC electrode and CG electrode. f First cycle charge and discharge curve at different rates
discharge capacities of SC and CG electrodes are as high as 482.5 mAh g\(^{-1}\) and 408.3 mAh g\(^{-1}\), respectively. When the current is increased to 0.2 °C, the discharge specific capacities are 324.4 mAh g\(^{-1}\) and 262 mAh g\(^{-1}\), respectively. However, the ungraphitized SC electrode after removal of impurities by Yang K et al. has a capacity of only 319 mAh g\(^{-1}\) at 0.1 °C [16]. The performance improvement is due to the insoluble impurities in the SC are dissolved by HCl and the remaining porous structure can be made by the electrolyte better permeate. After 120 cycles, the capacities are 307.8 mAh g\(^{-1}\) and 257.1 mAh g\(^{-1}\), and the capacity retention rates are 94.88% and 98.13%, respectively. Compared with the failure mechanism reported by Zhang P et al., the capacity of graphite anode will rapidly decay below 87% due to the precipitation of metallic lithium on the surface of the graphite negative electrode after 100 cycles [15], but the cycle performance of the micro-expanded SC has been significantly improved. This can be attributed to the porous structure and larger specific surface area of SC, which increase the insertion site of lithium and alleviates the deposition of lithium metal. Figure 4b, c shows the charge discharge curves of the first 3 cycles of SC and CG electrodes respectively. Although the degree of graphitization of SC is less than that of CG, the main lattice structure of SC still maintains the typical graphite structure. The discharge platform is kept below 0.5 V and has the same discharge curve as that of CG electrode. During the first cycle of activation, a voltage plateau appeared at 0.7 V, which corresponding to the decomposition of electrolyte and the formation of SEI film [28, 29]. The platform disappeared in the second circle and did not appear in the subsequent cycles. This is due to the SEI film was formed during the first circle, which inhibited the decomposition of the electrolyte [27]. There are three discharge platforms in the range of 0.005–0.2 V, indicating that the deintercalation/intercalation behavior of Li\(^{+}\) in the graphite electrode has obvious segmentation, which is consistent with that reported in the literature [30, 31]. Figure 4d is the cycle performance graph of SC and CG electrodes at 2 °C. It can be observed that SC electrode still has higher specific discharge capacity than CG electrode under high current. The coulomb efficiency of SC electrode is about 100%, which indicates that the irreversible capacity of SC electrode is low during the cycle. Compared with CG electrode, the coulomb efficiency fluctuates significantly, so its irreversible capacity is higher, which leads to poor capacity retention. Figure 4e, f are the rate performance of SC and CG electrodes and the first charge discharge curves under different discharge intensities respectively. At the initial low current of 0.1 °C, there is little difference between the discharge specific capacities of SC and CG electrodes, but with the increase of current intensity, SC electrode shows higher discharge specific capacity. It can be seen from the charge discharge curve that the initial voltage of the charge discharge curve shifts with the increase of current intensity (as shown in the red dotted line box in Fig. 4f). This phenomenon is more intense, especially when the current intensity reaches 5.0 °C and 10 °C, which indicates that there is a large polarization phenomenon on the electrode surface. Compared with CG electrode, SC electrode shows smaller polarization phenomenon and higher discharge capacity.

Since the surface of the graphite electrode is prone to generate uneven and thick SEI film, it increases the time for Li\(^{+}\) to diffuse. Moreover, graphite has high orientation, and Li\(^{+}\) can only be inserted in the c-axis direction, so its high current discharge performance is not ideal. Compared with commercial graphite materials, SC materials have smaller lamellar size and larger interlayer spacing (c value), which can provide more insertion sites for Li\(^{+}\), thus improving the diffusion rate of Li\(^{+}\). In order to confirm the high diffusion rate of SC material, the diffusion coefficient of Li\(^{+}\) in SC electrode is calculated by different methods and compared with CG material.

GITT is a new and effective method to calculate the diffusion coefficient of Li\(^{+}\) by electrochemical titration. The calculation method is as follows [32].

\[
D_{\text{GITT}} = \frac{4}{\pi} \left( \frac{I_0 V_m}{FS} \right)^2 \left( \frac{dE/dt}{dE/dt^{1/2}} \right)^2
\]

(1)

where \(D_{\text{GITT}}\) (cm\(^2\) s\(^{-1}\)) is the chemical diffusion coefficient, \(I_0\) (A) is the applied current, \(V_m\) (cm\(^3\) mol\(^{-1}\)) is the molar volume, \(F\) (96,500 C mol\(^{-1}\)) is the Faraday constant, \(S\) (cm\(^2\)) is the electrode/electrolyte contact area, \(dE/dt\) is the slope of coulometric titration curve, \(dE/dt^{1/2}\) is the relationship between potential and time. When the applied current \((I_0)\) is very small and the discharge time \((t)\) is very short, the relationship of \(dE/dt^{1/2}\) is linear, and the above formula can be simplified as (2) [33].

\[
D_{\text{GITT}} = \frac{4}{\pi \tau} \left( \frac{n_b V_m}{S} \right)^2 \left( \frac{\Delta E_s}{\Delta E_t} \right)^2
\]

(2)

where \(\tau\) is the relaxation time, \(n_b\) (mol) is the number of moles, \(\Delta E_s\) (V) is the voltage change caused by the pulse, \(\Delta E_t\) (V) is the voltage change of constant current charge and discharge. The GITT curves of SC and CG electrodes during discharge are shown in Fig. 5a, b.

First, discharge with 0.1 °C current intensity for 10 min \((t)\) and then stand for 50 min \((\tau)\), repeat this process until the battery voltage drops to 0.005 V. After substituting each unit \(\Delta E_s\) and \(\Delta E_t\), the diffusion coefficient of each unit can be calculated and the results are shown in Fig. 5c, d. The results show that the diffusion coefficient ranges of SC electrode and CG electrode are 4.2286 × 10\(^{-13}\)–2.9667 × 10\(^{-10}\) cm\(^2\) s\(^{-1}\), 1.6346 × 10\(^{-14}\)–2.8138 × 10\(^{-10}\) cm\(^2\) s\(^{-1}\), respectively. It can be seen that the diffusion coefficient of Li\(^{+}\) in SC
electrode is higher than that in CG electrode. This result can be attributed to the fact that ions with a larger radius (such as Al\(^{3+}\) and Na\(^+\)) are constantly deintercalation/intercalation in the cathode during aluminum electrolysis, which widens the graphite layer spacing and provides a wider diffusion path for Li\(^{+}\) diffusion. On the other hand, SC has small particles and large specific surface area, so there are more sites and shorter paths for Li\(^{+}\) to enter the graphite. The SC and CG electrodes both have high Li\(^{+}\) diffusion coefficients at the beginning of the discharge. As Li\(^{+}\) is embedded in the graphite layer to generate Li\(_x\)C\(_6\), the diffusion coefficient gradually decreases and fluctuates greatly at the discharge platform. It can be seen that there are three valleys in the range of 0–0.2 V, corresponding to the three discharge platforms on the discharge curve. In this stage, a large number of Li\(^{+}\) floods into the graphite layer, leading to the phase transformation of graphite structure and reducing the diffusion rate [32].

The SC and CG electrodes were activated at 0.1 °C for 2 cycles and discharged at 0.2 °C current for every 30 min. The EIS was tested after sufficient standing, and then continue discharged until the voltage was less than 0.005 V. The impedance of SC and CG electrodes under different amount of lithium insertion are shown in Fig. 6a, b. It can be seen that the EIS impedance of the two samples is composed of SEI film impedance (R\(_{sf}\)) corresponding to semicircle in high frequency region, charge transfer impedance (R\(_{ct}\)) corresponding to semicircle in medium frequency region and Warburg impedance corresponding to oblique line in low frequency region [34]. The resistance values of each part are fitted by ZSimpWin software. The fitting circuit diagram is shown in Fig. 6e and the fitting results are shown in Table 2 [31]. It can be seen from the results that R\(_{sf}\) increased with the increase of discharge degree, which corresponds the gradual formation of SEI film. As a by-product of electrode reaction, SEI film is an electronic insulator but an excellent conductor of lithium ion. Therefore, a uniform, stable and appropriate thickness SEI film is conducive to improve the performance of the battery. With the increase of discharge degree, the SEI film on the electrode surface gradually thickens, resulting in the increase of R\(_{sf}\). By comparison, SC electrode has smaller R\(_{sf}\) than CG electrode and remains basically stable in the later stage of the discharge, indicating that a stable SEI film is formed on the surface of the SC electrode, which is due to the smaller size of SC particles, rough surface, and larger specific surface area. Uniform SEI film is formed during the charging and discharging process to prevent the continuous decomposition of electrolyte and the occurrence of side reactions. This means that the service life of the battery is closely related to the SEI film, and a more stable SEI film can effectively improve the service life of the battery. Therefore, SC electrode can achieve better discharge specific capacity and cycle stability [35, 36].
$R_{ct}$ can reflect the reaction rate of the electrode, which is related to the morphology and structure of the electrode material [37, 38]. It can be seen that the $R_{ct}$ fluctuation of SC electrode is small, which ensures a stable charge transfer rate. The lower $R_{ct}$ is because SC materials can be better attached to copper collecting fluid, reduce the contact impedance between electrode materials and collecting fluid, which provide effective channels for charge transfer between graphite layer and collecting fluid.

The Warburg impedance of EIS in low frequency region is related to the diffusion rate of lithium ion in SC and CG electrodes. The calculation formula of diffusion coefficient is as follows [7, 39]:

$$D_{EIS} = \frac{R_{ct}^2 T^2}{2 A n^4 F^2 C^2 \sigma^2}$$  \hspace{1cm} (3)

where $D_{EIS}$ (cm$^2$ s$^{-1}$) is the diffusion coefficient of lithium ion calculated by EIS, $R$ (8.314 J mol$^{-1}$ K$^{-1}$) is the ideal gas constant, $T$ (K) is the absolute temperature, $A$ (cm$^2$) is the cross-sectional area of the electrode, $n$ is the electron transfer number, $F$ (96,500 °C mol$^{-1}$) is the Faraday constant, $C$ (mol cm$^{-3}$) is the concentration of lithium ion in the electrode, $\sigma$ is Warburg factor, the calculation formula is as follows [40]:

$$Z=R_s+R_{ct}+\sigma \omega^{1/2}$$  \hspace{1cm} (4)

$Z$ is proportional to the $-1/2$ power of the angular frequency ($\omega$), and the slope $\sigma$ can be obtained by fitting. Figure 6c shows the relationship diagram of $\omega^{-1/2} - Z$ when the CG electrode is discharged for 150 min. The slope is 4.26447, and the diffusion coefficient is $1.07 \times 10^{-12}$ cm$^2$ s$^{-1}$ when substituted into the formula. Figure 6d is the diffusion coefficient of Li$^+$ calculated by EIS for SC and CG electrodes at different discharge times. It can be seen that the diffusion coefficient of Li$^+$ in SC and CG materials are $4.05 \times 10^{-13} - 3.87 \times 10^{-12}$ cm$^2$ s$^{-1}$, $4.24 \times 10^{-13} - 1.47 \times 10^{-12}$ cm$^2$ s$^{-1}$, respectively, which are consistent with the results of GITT.

Figure 7a, b shows the CV curves of SC and CG samples in the voltage range of 0.005–2 V at a scan rate of 0.1 mV/s, 0.2 mV/s, 0.5 mV/s, 0.8 mV/s, and 1.0 mV/s, respectively. It can be seen that there is an obvious oxidation peak near

### Table 2  EIS impedance fitting results of SC and CG electrodes at different discharge degrees

| Time (min) | Spent cathode | Commercial graphite |
|-----------|---------------|---------------------|
|           | $R_s$ (ohms) | $R_{ct}$ (ohms) | $R_s$ (ohms) | $R_{ct}$ (ohms) |
| 30        | 38.35         | 9.691              | 41.16        | 5.969            |
| 60        | 42.78         | 13.93              | 53.20        | 1.802            |
| 90        | 47.53         | 15.4               | 49.32        | 11.47            |
| 120       | 46.07         | 23.39              | 61.24        | 35.7             |
| 150       | 58.92         | 37.36              | 180.30       | 75.07            |
| 180       | 124.30        | 15                 | 187.20       | 3.613            |
| 210       | 121.40        | 16.01              | 199.00       | 6.043            |
0.3 V, which corresponds to the insertion of Li\(^+\) in the graphite electrode [41]. With the increase of scanning rate, the oxidation peak gradually shifts to the direction of high voltage, which corresponds to the discharge platform under different current intensities. The relationship between peak current \(I_p\) and \(\nu^{1/2}\) is shown in Fig. 7c. It can be seen that the intercalation of lithium ions in graphite is obviously controlled by the diffusion rate, and the diffusion coefficient can be calculated by Randles Sevcik equation [32, 42].

\[
I_p = 0.4463n^{3/2}F^{3/2}C^{1/2}S^{1/2}R^{1/2}D_{CV}^{1/2}V^{1/2}
\]  
(5)

where \(I_p\) (A) is the peak current, \(n\) is the charge transfer number, \(F\) (96,500 °C mol\(^{-1}\)) is the Faraday constant, \(C\) (mol cm\(^{-3}\)) is the concentration, \(S\) (cm\(^2\)) is the electrode area, \(R\) (8.314 J mol\(^{-1}\) K\(^{-1}\)) is the gas constant, \(T\) (K) is the absolute temperature, and \(D_{CV}\) (cm\(^2\) s\(^{-1}\)) is the chemical diffusion measured by CV, \(\nu\) (V s\(^{-1}\)) is the sweep speed. After linear fitting of \(I_p - \nu^{1/2}\), the corresponding slopes of SC and CG are 0.05433 and 0.04203, respectively. The diffusion coefficient of Li\(^+\) in SC is \(2.2292 \times 10^{-11}\) cm\(^2\) s\(^{-1}\), while in CG is \(1.3341 \times 10^{-11}\) cm\(^2\) s\(^{-1}\). The results are consistent with the GITT results, which shows that all the values calculated by the three methods are in good agreement.

The above three calculation methods all show that the SC electrode has a high diffusion rate. In order to study the application of SC electrode in the full-cell, SC electrode and commercial NCM523 electrode were assembled into a full-cell. The cycle performance and rate performance are shown in Fig. 8. The initial discharge capacity is 151 mAh g\(^{-1}\) at 0.1 °C (1 °C = 172 mA g\(^{-1}\)) and the corresponding coulomb efficiency reaches 58.12% (commercial graphite is 114.5 mAh g\(^{-1}\), 38.71%). The first discharge capacity is 96.5 mAh g\(^{-1}\) at 1 °C, and the capacity retention rate is 95.23% after 100 cycles. It can be seen from the rate performance that the capacity decreases rapidly at 0.1 °C current, which may be due to the formation of SEI film on the surface of graphite anode. With the gradual uniformity of SEI film, the capacity fading is suppressed. When the current intensity continues to increase, the capacity keeps stable under the same current intensity, which indicates that uniform and stable SEI film is formed at 0.1 °C. When continuing to increase the current intensity, the SC electrode can provide specific capacity of 127.8, 108.8, 83.6, 30.1 mA h g\(^{-1}\) at 0.2, 0.5, 1.0, 2.0, and 5 °C, respectively. However, the discharge capacity of CG electrode is obviously low, and even the battery stops working at 5 °C. The discharge capacity of SC electrode can reach 116.7 mA h g\(^{-1}\) with 0.1 °C after high current charge–discharge, while that of CG electrode is only 79.7 mA h g\(^{-1}\). The cycle performance and rate performance indicate that SC electrode can provide enough insertion sites for Li\(^+\) separated from cathode material, and maintain good structural stability during long-time cycling and high current intensity.
Conclusion

In this paper, the feasibility of aluminum electrolysis spent cathode as anode material for lithium-ion battery was studied. Through the structure, morphology and electrochemical performance, it can be seen that the purified SC material has the unique charge discharge characteristics of graphite, although the degree of graphitization is insufficient. SC material has rich pore structure and larger specific surface area, which can make the electrode material fully contact with electrolyte and reduce the generation of interface impedance. Meanwhile, the large interlayer spacing shortens the diffusion path of Li$^+$ and provides more active sites for lithium-ion intercalation, therefore proving a higher discharge capacity. The diffusion coefficient of lithium ion in aluminum electrolysis spent cathode was evaluated by GITT, EIS and cyclic voltammetry, and the results were compared with commercial graphite. The results calculated by different calculation methods are in good agreement. The calculation with commercial graphite. The results calculated by different
electrode carbon blocks from aluminum smelters. Light Metals 5:31–35

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Declarations

Conflict of interest The authors declare that they have no conflict of interest.

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