A Novel Low-Temperature Fluorination Roasting Mechanism Investigation of Regenerated Spent Anode Graphite via TG-IR Analysis and Kinetic Modeling

Xiangdong Zhu, Qiuyun Mao, Qifan Zhong,* Zhenhua Zhang, Gang Wang, Lei Tang, and Jin Xiao*

ABSTRACT: Spent anode graphite, a hazardous solid waste discarded from the recovery of spent lithium-ion batteries (LIBs), had created social and environmental issues but has been scarcely investigated. Thus, a feasible, environmentally friendly, and economical process of low-temperature fluorination roasting and water leaching technology was proposed to regenerate spent graphite anodes. The results showed that the physical and chemical properties of regenerated graphite with a purity of 99.98% reached the graphite anode standard of LIBs and exhibited a stable specific capacity (340.9 mAh/g), capacity retention (68.92% after 470th cycles), and high initial Coulombic efficiency (92.13%), much better than that of waste carbon residue and similar to that of commercial graphite. Then the reaction mechanism and kinetic modeling of fluorination roasting of spent anode material was mainly explored by differential thermogravimetry and nonisothermal analysis methods. The results showed that the complication and phase-transformation process of non-carbon valuable components in spent anode graphite occurred through three consecutive reactions in the 80−211 °C temperature intervals. The reaction mechanism of the whole process can be kinetically characterized by three successive reactions: third-order chemical reaction, Z-L-T eq, and second-order chemical reaction. Moreover, the thermodynamic functions of the fluorination roasting were calculated by the activated complex theory (transition state), which indicated the process was nonspontaneous. The mechanistic information was in good agreement with thermogravimetric-infrared spectroscopy (TG-IR), electron probe microanalysis, scanning electron microscopy, energy-dispersive spectrometry, and simulation experiments results.

1. INTRODUCTION

Lithium-ion batteries (LIBs) have extensive consumer applications, such as in new energy vehicles, energy storage, and smart medical devices, owing to their various advantages, namely, high voltage, high energy density, good cycling performance, and large charge−discharge rate.1−5 In recent years, new-energy vehicles have rapidly developed with the scale-up support of national policy and have also promoted the rapid growth of the LIB industry.6−8 According to reliable estimates, the consumption of LIBs will reach $221 billion in 2045.7,8 In general, LIBs are eventually scrapped after 5−10 years of operation owing to capacity fading and voltage decay, even after echelon utilization.9,10 The scrap amount is expected to reach about 400 million tons in 2020. Unfortunately, less than 5 wt % of them have been recycled today.11,12

Currently, the recycling system for spent LIBs primarily focuses on recovering cathode material while ignoring the regeneration of spent anode material.13−15 Owing to the complex composition of spent anode graphite, no effective technical solution for harmless resource utilization is presently available.16−18 Some researchers have focused on repreparing it into multifunctional materials. For example, Natarajan et al. successfully produced reduced graphene oxide using spent graphite anode, which could store gas efficiently.19 Zhao et al. successfully prepared a novel adsorbent by grafting MnO₂ particles onto graphite recovered from spent LIBs to treat lead-, cadmium-, and silver-contaminated water.20 Chen et al. exploited the reduced interlayer force after repeated charge−discharge cycles. They performed direct exfoliation of used anode graphite into high-quality, few-layer graphene sheets. The sonication-assisted exfoliation efficiency of the used anode graphite can be 3−11 times that of natural graphite, with the highest mass yield of dispersed graphene sheets reaching 40 wt %21. Ruan et al. successfully synthesized high-quality graphene from spent anode graphite and further applied functionalization in carbon-based redox ORR electrocatalyst, which has better methanol resistance and stability.22

However, if spent graphite anode is directly used as the regeneration anode material of LIBs, which inevitably causes...
metal impurities to react with the electrolyte and generate fluoride salts, specific problems such as the reduction of the first-cycle coulomb efficiency and excessive consumption of the electrolyte are bound to arise.\textsuperscript{23–25} Therefore, purification must be conducted before regeneration.\textsuperscript{26} Traditionally, chemical and physical purification methods are the main techniques for graphite production. Chemical purification methods include alkali, hydrofluoruric acid, and chlorinated roasting.\textsuperscript{27–29} The physical method usually adopts the high-temperature graphitization process above 2400 °C.\textsuperscript{30} These processes have the disadvantages of high carbon consumption, considerable environmental pollution, and extremely high equipment requirements, limiting applications in large-scale industrialization.

Here, fluorination roasting using ammonium fluoride as a complexing agent to convert valuable components in spent anode graphite into water-soluble complex ions is developed. In order to not destroy the layered structure of graphite, the non-carbon impurity elements are removed to the greatest extent, and the regeneration of anode graphite is realized. No publication has been published about the regeneration of spent anode graphite by fluorination roasting. We further investigated the gas-release behavior, phase-transformation principle in the roasting process, and the control steps of each stage based on our achievements. The findings can provide further theoretical support for industries to realize the regeneration of spent anode graphite.

2. EXPERIMENTAL SECTION

2.1. Materials. The waste carbon residue (WCR) sample was the leaching residue obtained after sulfuric acid and \(\text{H}_2\text{O}_2\) leaching, which was provided by the Hunan Jinchi Environmental Protection Resource Regeneration Technology Co., Ltd. In order to ensure the uniformity of the WCR sample, the company currently only recycles spent ternary (NCM) lithium-ion batteries and has very strict quality control technology. Thus, the content of valuable components in the WCR will remain at a low level and will not fluctuate too much. The WCR sample was completely dissolved in aqua regia (HCl/HNO\(_3\) = 3:1, \(\text{v/v}\)) to determine the chemical compositions through ICP-OES. The results are shown in Table 1.

| element | Ni | Co | Mn | C | F | Al | Si |
|---------|----|----|----|---|---|----|---|
| wt %    | 1.22 | 0.28 | 0.41 | 94.77 | 1.03 | 0.21 | 0.56 |

As shown in Table 1, the non-carbon impurity elements in WCR samples were primarily valuable components such as nickel, cobalt, manganese, aluminum, and silicon remaining in the leaching process. The composition of impurity elements was complex with low content. To further explore the phase and crystalline structure of valuable components in WCR raw materials, X-ray diffraction (XRD) was analyzed, and the result is shown in Figure 1.

Figure 1a shows that the main element of WCR was carbon, which still retained the lamellar crystal structure of graphite. Because of the high carbon content in WCR, the composition and phase structure of elements could not be accurately analyzed via XRD. Thus, the WCR was burned to ashes at 800 °C for 4 h. The result shown in Figure 1b substantiated that the main non-carbon impurity elements in WCR were nickel, cobalt, manganese, aluminum, and silicon.

2.2. Experiment and Procedures. A near-closed-loop combined process, including fluorination roasting, water leaching, ammonia precipitation, and evaporative crystallization, were used to regenerate spent graphite anode, recovery of valuable components, and regenerated ammonium fluoride roasting agent. The specific operation steps are described in Figure 2.

2.3. Characterization. After mixing WCR raw material with 20% ammonium fluoride, an STA449FS thermal analyzer was used to perform differential thermogravimetry (TG) analyses in argon. The heating rate was 5 °C/min, and the temperature range was 28–800 °C. The phase and crystalline structure were analyzed by X-ray diffraction (XRD; Empyrean 2) with CuK\(\alpha\) radiation in the 2\(\theta\) range of 10°–90° and a scanning rate of 2°/min. The elements of the sample were analyzed by ICP-OES (CAP7400Radial). The morphology of the samples was characterized by field-emission scanning electron microscopy (SEM; JSM-7900F) and energy-dispersive X-ray spectroscopy (EDS; EDAX Octane X). The elements and morphology in small areas were qualitatively and quantitatively analyzed by electron microprobe analysis (EPMA; JXA-8230). The relationship between physicochemical properties and temperature of the samples was characterized by thermogravimetric analysis (Evolution 16/18, SETARAM)—infrared spectroscopy (TENSOR 27, Bruker).

2.4. Nonisothermal Kinetics Methods. The fluorination roasting of non-carbon valuable components in thermal-analysis research was a nonisothermal reaction process, and the reaction temperature was a function of time. For kinetic data-processing methods of nonisothermal reaction processes, the Kissinger, Flynn–Wall–Ozawa (FWO), Kissinger–Akahira–Sunose (KAS), and Šatava–Šesták methods were frequently used.\textsuperscript{31–33} The activation energy (\(E_a\)) and pre-exponential factor \(A_0\) in the nonisothermal process can be determined. Finally, through \(E_a\) and \(A_0\), the thermodynamic parameters in fluorination roasting can be calculated.

2.4.1. Kissinger Method. The Kissinger method usually did not require an accurate understanding of the reaction mechanism to obtain the apparent activation energy (\(E_a\)) of solid-state reaction by plotting the reciprocal of the logarithm of heating rate versus temperature at the maximum reaction rate of constant-heating-rate experiment. The derivation formula of the Kissinger method is listed as follows\textsuperscript{34,35}

\[
\ln \left( \frac{\beta}{T_{\text{max}}} \right) = \ln \left( \frac{A R}{E_a} \right) + \ln(n(1 - \alpha_{\text{max}})^{n-1}) - \frac{E_a}{RT_{\text{max}}} \tag{1}
\]

where \(\beta\) is the heating rate and \(T_{\text{max}}\) and \(\alpha_{\text{max}}\) are the temperature and conversion at the maximum mass loss rate \(\left(\frac{\Delta m}{\Delta t}\right)\) of the differential TG curve (DTG), respectively, \(A_0\) is the pre-exponential factor, \(R\) is the gas constant, and \(n\) is the reaction order. When \(n = 1\) and \(n(1 - \alpha_{\text{max}})^{n-1} \approx 1\), the Kissinger method can be simplified to the following equation:

\[
\ln \left( \frac{\beta}{T_{\text{max}}} \right) = \ln \left( \frac{A R}{E_a} \right) - \frac{E_a}{RT_{\text{max}}} \tag{2}
\]
By fitting the linear relationship between \( \ln \left( \frac{\beta}{T_{\text{max}}^2} \right) \) and \( \frac{1}{T_{\text{max}}} \) by the least-squares method, the pre-exponential factor \( A \) and the apparent activation energy \( E_a \) can be calculated by intercept and slope, respectively.

### 2.4.2 Flynn–Wall–Ozawa (FWO) and Kissinger–Aka-hira–Sunose (KAS) method.

The FWO and KAS methods are two different integration methods with equal conversion. Their derivation formulas are as follows:

\[
\beta = -\alpha AE_R \left( \frac{R}{E} \right) T \ln \left( \frac{\alpha}{T_{\text{max}}} \right) \left( 5.331 - 1.052 \right)
\]

where \( g(\alpha) \) is a formula of integral expression about all reaction models; when \( \alpha \) was a constant, \( g(\alpha) \) had a fixed value. Therefore, by fitting the linear relationship between \( \ln \beta \) and \( \frac{1}{T_{\text{max}}} \), \( \ln \left( \frac{\beta}{T_{\text{max}}^2} \right) \) and \( \frac{1}{T_{\text{max}}} \), the apparent activation energy \( E_a \) can be calculated with the slope.

### 2.4.3 Šatava–Šesták Method.

The expression from the Šatava–Šesták method was given by the following formula:

\[
\ln g(\alpha) = \ln \left( \frac{A}{R} \right) - 5.330 - 1.5016 \frac{E_a}{RT}
\]

Different forms of mechanism functions \( [g(\alpha)] \) were linearly fitted with \( \frac{1}{T} \) and the reaction-mechanism function most in line with the experiment was determined according to the fitting results. Meanwhile, according to the optimal mechanism
function, the activation energy \( E_s \) and pre-exponential factor \( A_s \) can be obtained. The reaction model can be identified as \( 0 < E_s < 400 \text{ kJ/mol} \). Then \( E_s \) must be compared with \( E_p \) which is the average activation energy calculated by the FWO and KAS methods. When \( E_s \) meets the conditions of \( \frac{(E_p - E_s)}{E_p} \leq 0.1 \), \( E_s \) was acceptable. Similarly, the logarithm of pre-exponential factor \( \ln A_s \) should be compared with \( \ln A_p \) calculated by the Kissinger method. If \( \ln A_s \) meets the condition of \( \frac{(\ln A_s - \ln A_p)}{\ln A_p} \leq 0.46 \), \( \ln A_s \) is acceptable. If \( g(a) \) met the above-mentioned requirements, then it would be an integral form of the most probable mechanism function of reaction.

### 2.4.4. Calculation of Parameters of Thermodynamic Functions

According to the Arrhenius equation

\[
\kappa = A_s e^{-E_s/RT_p}
\]

where \( E_s \) and \( A_s \) were the activation energy \( (E_s) \) and pre-exponential factor \( A_s \) obtained from the nonisothermal process of the Šatava–Šesták method, respectively. \( R \) was the rate constant, \( k \) was the molar gas constant \( [8.314 \text{ J/(mol·K)}] \), and \( T_p \) was the DTG peak absolute temperature at the corresponding stage.

From the activated complex theory (transition state) of Eyring, the following equation can be deduced

\[
\kappa = \frac{k_B T_p}{h} \frac{Q_{\text{AB}}}{Q_{\text{B}}} e^{-E_s/RT_p}
\]

where \( k_B \) is the Boltzmann constant \( (1.3807 \times 10^{-23}) \) and \( h \) is the Planck constant \( (6.625 \times 10^{-34} \text{ J/s}) \).

Then

\[
K = \frac{Q_{\text{AB}}}{Q_{\text{B}}} e^{-E_s/RT_p}
\]

where \( K \) is the activation equilibrium constant, which approximately has the characteristics of the general equilibrium constant.

According to transition-state theory, the Eyring formula can be abbreviated as

\[
\kappa = \frac{k_B T_p}{h} K
\]

According to the thermodynamic formula

\[
\Delta G^* = -RT_p \ln K
\]

By substituting eq 10 into eq 9, the change in the Gibbs free energy may be calculated according to the following formula:

\[
\kappa = \frac{k_B T_p}{h} \exp \left( \frac{-\Delta G^*}{RT_p} \right)
\]

After eq 11 is substituted into the Arrhenius equation (eq 6), the following equation can be obtained:

\[
\Delta H^* = E_s - RT_p \ln \left( \frac{k_B T_p}{h} \right) + E_p - RT_p \ln A_p
\]

This expression was the thermodynamic form of the transition-state theory, which was applicable to any elementary reaction. Moreover, the change in enthalpy can be calculated by the following equation:

\[
\Delta H^* = E_s - RT_p
\]

Changes in the entropy \( \Delta S^* \) can be calculated using the well-known thermodynamic equation:

\[
\Delta S^* = \frac{\Delta H^* - \Delta G^*}{T_p}
\]

The values of the change in Gibbs free energy \( \Delta G^* \), enthalpy change \( \Delta H^* \), and entropy change \( \Delta S^* \) were calculated at \( T = T_p \) (\( T_p \) is the DTG peak temperature at the corresponding stage) because this temperature characterizes the highest rate of the process and is thus an important parameter.

### 3. RESULTS AND DISCUSSION

#### 3.1. Analysis of the Rthermogravimetry (TG) Curve

Figure 3 shows the TG-DTG curve of fluorination roasting after mixing WCR raw material with 20% ammonium fluoride solid at heating rates of 5, 10, 15, and 20 °C/min argon. During heating, the mass loss of the sample included the evaporation of water. The non-carbon elements in graphite underwent phase transformation under the ammonium fluoride system, thereby forming metal amine complexes such as \([\text{CoF}_3]^-\), \([\text{NiF}_3]^-\), \([\text{MnF}_3]^-\), \([\text{AlF}_3]^{3-}\), and \([\text{SiF}_6]^{2-}\). Meanwhile, \( \text{NH}_3, \text{HF}, \text{H}_2\text{O}, \text{and SO}_2 \) gases were released. The high-valence metallic oxide can be reduced to low-valence metallic ions by carbon to produce \( \text{CO}, \text{CO}_2 \), and other gases. When the temperature exceeded 200 °C, the unreacted ammonium fluoride decomposed to form HF and \( \text{NH}_3 \).
Moreover, the organic substances such as binder in the WCR were pyrolyzed into NO\textsubscript{x}, H\textsubscript{2}, F\textsubscript{2}, and other hydrocarbon gases. This result revealed that fluorination roasting had three stages, and the TG curve indicated that the total mass loss was about 22.34\textendash 29.61 wt %. The main reactions were as follows:

\begin{align}
3\text{NH}_4\text{F} + \text{MSO}_4 &= (\text{NH}_4)\text{SO}_4 + \text{NH}_4\text{MF}_3 \\
3\text{NH}_4\text{F} + \text{MSO}_3 &= 2\text{NH}_3(g) + \text{H}_2\text{O}(g) + \text{SO}_2(g) + \text{NH}_4\text{MF}_3 \\
\text{MS}_2 + 3\text{O}_2(g) &= \text{MO}_2 + 2\text{SO}_2(g) \\
\text{MO} + 2\text{NH}_3\text{F} &= \text{MF}_2 + 2\text{NH}_3(g) + \text{H}_2\text{O}(g) \\
\text{MO}_2 + 3\text{NH}_3\text{F} + \text{C} &= 2\text{NH}_3(g) + \text{H}_2\text{O}(g) + \text{NH}_4\text{MF}_3 + \text{CO}(g) \\
6\text{NH}_3\text{F} + \text{SiO}_2 &= 4\text{NH}_3(g) + (\text{NH}_4)_2\text{SiF}_6 + 2\text{H}_2\text{O}(g) \\
12\text{NH}_3\text{F} + \text{Al}_2\text{O}_3 &= 6\text{NH}_3(g) + 2(\text{NH}_4)_3\text{AlF}_6 + 3\text{H}_2\text{O}(g) \\
\text{NH}_3\text{F} &= \text{NH}_3(g) + \text{HF}(g)
\end{align}

where M was Co, Mn, Ni, or other metal ions.

The kinetics of such solid-state reactions was described by various equations taking into account the special features of their mechanisms.

Considering the solid-state reaction mechanism, such types of kinetics were described by various equations. Accordingly, the reaction rate needed to be converted into the degree of conversion rate $\alpha$ to adapt to various equations, and the specific formula was as follows:

$$\alpha = \frac{m_i - m_f}{m_i - m_0}$$

where $m_0$, $m_i$, and $m_f$ were the initial mass, current sample mass, and final mass, respectively. Generally, the following general kinetic-reaction equation can be used:

$$\frac{d\alpha}{dt} = k(T)\tilde{f}(\alpha)$$

The results are shown in Figure 4.

As shown in Figure 4, fluorination roasting was primarily reacted at a low temperature of 70\textendash 300 °C, which had completed about 90% within the temperature range. Meanwhile, taking the heating rate $\beta$ of 5 °C/min as an example, the temperature corresponding to the conversion at 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, and 0.9 was approximately 58, 68.8, 80, 127.8, 148.8, 177.8, 214.3, and 250 °C, respectively. Thus, the fluorination-roasting system was completed at 250 °C at this heating rate. Then the activation energy and pre-exponential factor at each conversion can be calculated by the non-isothermal kinetic method. The best mechanism function and thermodynamic parameters of fluorination reaction can be selected.

### 3.2. Calculation of Thermal-Kinetic Parameters and Kinetic Modeling

To investigate the thermal-kinetic behavior of each stage, the methods of Kissinger, FWO, and KAS were used to calculate the value of activation energy ($E_a$) and pre-exponential factor $A_s$, respectively. Meanwhile, the Štava–Šesták method was used to optimize the mechanism equation of each process of heat-loss mass and calculate the thermodynamic parameters in fluorination roasting.

#### 3.2.1. Kissinger Model Analysis

According to Figure 4b, fluorination roasting can be divided into three stages, namely ST@1, ST@2, and ST@3. The absolute temperature at the maximum reaction rate is shown in Table 2 at different heating rates.

### Table 2. Influence of Heating Rate on the Characteristic Absolute Temperatures of Fluorination Roasting

| $\beta$ (°C/min) | TP-1 (K) | TP-2 (K) | TP-3 (K) |
|-----------------|---------|---------|---------|
| 5               | 344.988 | 424.988 | 484.488 |
| 10              | 345.89  | 431.89  | 498.89  |
| 15              | 355.387 | 450.887 | 510.387 |
| 20              | 361.532 | 451.032 | 520.032 |

On the basis of Table 2, with the increased of heating rate ($\beta$), the reaction rate curve tended to move to a high-temperature area. According to the kinetic analytical formula 2, the reaction activation energy at the extreme rate value can be directly solved under the conditions of different heating rates, also called the free-model method.

Figure 5 shows the linear relationship between $\ln\left(\frac{\beta}{\tilde{T}_{\text{max}}}\right)$ and $\frac{1}{\tilde{T}_{\text{max}}}$ at different heating rates by fitting the four points linearly.
to obtain a straight line whose slope can represent the apparent activation energy $E_a$ and whose intercept can represent the pre-exponential factor $A_o$.

The results in Figure 5 indicated that the activation energy $E_a$ in the first stage (ST@1) was 43.01 kJ/mol and $\ln A_o = 14.06$ min$^{-1}$, and the linear regression ($R^2$) was 0.99683. Similarly, $E_a = 60.99$ kJ/mol, $\ln A = 15.83$ min$^{-1}$, $E_a = 73.48$ kJ/mol, and $\ln A = 16.62$ min$^{-1}$ in ST@2 and ST@3, respectively, and the linear regression ($R^2$) was 0.8675 and 0.98999, respectively. This finding proved that a greater activation energy was required for the reaction with increased temperature, which meant a more difficult reaction.

### 3.2.2. FWO and KAS Model Analysis

For each heating rate ($\beta = 5,10,15,20$ °C/min), a point of $\alpha$ every 0.1 was selected within the range of 0.1−0.8 for $\alpha$. The reason for selecting this range was that most reactions, especially solid-state ones, are unstable at the beginning and ending periods. Then, the activation energy $E_a$ was calculated by formulas 3 and 4, which were calculated by the FWO and KAS methods, respectively. The results are shown in Figure 6. The FWO and KAS methods all had a good linear relationship. Thus, according to the FWO and KAS kinetic model, the activation energy of fluorination roasting can be calculated by the slope of formulas 3 and 4, and the results are shown in Table 3.

### Table 3. Activation Energy Calculated by FWO and KAS Methods

| kinetic model | $\alpha = 0.1$ | $\alpha = 0.2$ | $\alpha = 0.3$ | $\alpha = 0.4$ | $\alpha = 0.5$ | $\alpha = 0.6$ | $\alpha = 0.7$ | $\alpha = 0.8$ | avg |
|---------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|-----|
| FWO           |                |                |                |                |                |                |                |                |     |
| slope         | 7483.68        | 7225.54        | 6925.69        | 6032.91        | 5289.49        | 6018.85        | 4876.91        | 8137.49        | 6248.82 |
| regression    | 0.96036        | 0.97595        | 0.98993        | 0.96963        | 0.9576         | 0.97453        | 0.90722        | 0.94307        | 0.95979 |
| $E_a$(kJ/mol) | 41.42431       | 39.99543       | 38.33568       | 29.27884       | 22.32331       | 33.31606       | 26.99509       | 45.04334       | 34.589  |
| KAS           |                |                |                |                |                |                |                |                |     |
| slope         | 6833.89        | 6541.81        | 6218.36        | 5133.99        | 3921.79        | 5133.99        | 3921.79        | 7123.64        | 5435.68 |
| regression    | 0.95271        | 0.97066        | 0.98746        | 0.95581        | 0.94204        | 0.96583        | 0.86458        | 0.92733        | 0.94580 |
| $E_a$(kJ/mol) | 56.81696       | 54.38861       | 51.69945       | 36.9751        | 24.68399       | 24.68399       | 32.60576       | 39.22594       | 45.192  |

This result indicated that the activation energy initially decreased and then increased throughout the entire reaction.
process. The activation energy values calculated by FWO and KAS were also surprisingly consistent.

3.2.3. Šatava–Šesták Model Analysis. The mechanism function of fluorination roasting was determined by the linear-fitting degree after fitting the common mechanism function (Table S1) with the Šatava–Šesták method. The related coefficients of different kinetic mechanism functions for the three stages of fluorination roasting are shown in Tables S2–S4, respectively. According to the correlation coefficient of linear regression $R^2$ fitted by each mechanism function from Tables S2–S4, the most probable mechanism function $g(\alpha)$ was determined as $F_D$ for $D_1$ and $D_2$ at ST@1, ST@2, and ST@3, respectively. The correlation coefficient of $D_8(0.95924)$ was slightly higher than that of $D_5(0.95761)$, but the activation energy of $D_8(16.43 \text{ kJ/mol})$ was too low. According to the principle of $\frac{E_1 - E_2}{E_2} \leq 0.1$, D8 was unacceptable and D5 model was superior to D8.

Moreover, the corresponding averages of activation energy and pre-exponential factor index were 43.44 kJ/mol and 21.52 min$^{-1}$ at ST@1, 36.58 kJ/mol and 14.44 min$^{-1}$ at ST@2, and 41.05 kJ/mol and 17.62 min$^{-1}$ at ST@3, respectively, as shown in Table 4. Compared with the average of the activation energy ($E_\alpha$) values calculated by the two methods (KAS and FWO) and the logarithm of pre-exponential factor $\ln A_\alpha$ calculated by the Kissingar method. The $\left[ \frac{(E_\alpha - E_\alpha)}{E_2} \right]$ values of ST@1, ST@2, and ST@3 were 0.089, 0.083, and 0.029, respectively, which were all less than 0.1, and the $E_\alpha$ values of ST@1, ST@2, and ST@3 were acceptable. Similarly, the logarithm of the pre-exponential factor $\ln A_\alpha$ was compared with $\ln A_\alpha$ calculated by the Kissingar method, and the $\left[ \frac{(\ln A_{\alpha} - \ln A_{\alpha})}{\ln A_{\alpha}} \right]$ values of ST@1, ST@2, and ST@3 were 0.347, 0.088, and 0.057, respectively, which were all less than 0.46. The $E_\alpha$ of ST@1, ST@2, and ST@3 were acceptable. Therefore, from the most probable mechanism function of the studied reaction, we determined that ST@2 was controlled by chemical reaction and the forms of the integral and differential equations for mechanism function $g(\alpha)$ were $\frac{1}{2}(1 - \alpha)^{1/3} - 1$, $f(\alpha) = \left( \frac{1}{2}(1 - \alpha)^{1/3} - 1 \right)^2$. Similarly, ST@3 was controlled by three-dimensional diffusion and the forms of the integral and differential equations for mechanism function $g(\alpha)$ were $\frac{3}{2}(1 - \alpha)^{1/3}[(1 - \alpha)^{1/3} - 1]^{-1}$, $f(\alpha) = \frac{3}{2}(1 - \alpha)^{1/3}[(1 - \alpha)^{1/3} - 1]^{-1}$. ST@3 was controlled by chemical reaction and the forms of the integral and differential equations for mechanism function $g(\alpha)$ were $\frac{1}{2}(1 - \alpha)^{1/3} - 1$, $f(\alpha) = (1 - \alpha)^2$.

3.3. Thermodynamic Parameters. According to the results of the activation energy $E_\alpha$ and the logarithm of pre-exponential factor $\ln A_\alpha$ calculated by Šatava–Šesták model, the thermodynamic parameters at the peak temperature ($T_p$) for the formation of the activated complex from the raw material were calculated by the above eqs 12–14 and listed in Table 5.

Table 5 shows that the calculated values of Gibbs free energy ($\Delta G^\circ$), entropy ($\Delta S^\circ$), and reaction enthalpy ($\Delta H^\circ$) in ST@1 were 67.15 kJ/mol, 40.51 kJ/mol, and $-75.69 \text{ J/mol}$; 92.90 kJ/mol, 32.92 kJ/mol, and $-136.40 \text{ J/mol}$ in ST@2; and 92.79 kJ/mol, 36.86 kJ/mol, and $-111.09 \text{ J/mol}$ in ST@3, respectively. The entropy of activation ($\Delta S^\circ$) values for the three stages were all negative, indicating a highly ordered activated complex. The degrees of freedom of rotation and vibration were less than they were in the nonactivated complex. The change in the activation enthalpy ($\Delta H^\circ$) showed the energy difference between the raw material and activated complex; i.e., a smaller value corresponded with a lower reaction potential-energy barrier and more favorable formation of the activated complex. The positive value of the enthalpy in the three stages of fluorination roasting well agreed with endothermic effects in DTA data, which was conducive to the formation of the fluorination complex. Moreover, the positive values of Gibbs free energy ($\Delta G^\circ$) indicated that fluorination roasting was a nonspontaneous reaction process. These thermodynamic functions were consistent with kinetic parameters and thermal analysis data.

3.4. Thermal Behavior and Gas-Release Analyses. TG-infrared spectrometry (TG-IR) analysis was adopted to characterize the thermal behavior and gas release of fluorination roasting at a heating rate of 5 °C/min and maintained for 1 h under an argon atmosphere. The temperature was raised from room temperature (28 °C) to 600 °C and maintained for 1 h under an argon atmosphere. The result is shown in Figure 7.

As shown in Figure 7b, the gases produced during fluorination roasting were primarily NH$_3$, HF, SO$_2$, nitrogen oxides (N$_2$O), CO, CO$_2$, and H$_2$O. The main gases in ST@1 were NH$_3$ and H$_2$O, indicating that the oxide in the raw material initially reacted with ammonium fluoride at a lower temperature (28–80 °C) to form ammonium, complex ammonium salt, and H$_2$O (reaction formulas 18, 20, and 21). ST@2 occurred within the range of 80 °C to 162.1 °C. Aside from NH$_3$ and H$_2$O, the gases in this stage were SO$_2$, CO, N$_2$O, and HF, indicating that sulfate, sulfite, and sulfide in the raw material began to react with ammonium fluoride to form ammonium, complex ammonium salt, and H$_2$O (reaction formulas 18, 20, and 21).
produce SO$_2$ and NH$_3$ gas. Meanwhile, the macromolecular organics attached to the surface and PVDF binder started decomposing to produce HF and N$_x$O. The last stage (ST@3) occurred within the range of 161.2–211 °C, in which the

Figure 7. Thermal behavior and gas release of fluorination roasting under the optimal conditions. (a) Fourier transform infrared spectrometer (FT-IR) spectra (0–4000 cm$^{-1}$) and (b) enlarged view of partial analysis of the released gas at different temperatures.

Figure 8. SEM images of WCR (a,b) and its roasted product (c,d). Changes in non-carbon impurity elements before and after roasting (e).

Figure 9. XRD patterns of pure cobalt sulfate roasted products (a), nickel sulfate roasted products (b), and manganese sulfate roasted products (c).
macromolecular organics attached onto the surface and PVDF binder further decomposed. The excess ammonium fluoride was also decomposed into NH₃ and HF gases. After ST@3, the reaction was complete, and the mass loss of the material was minimal. Therefore, fluorination roasting can be completed at 200 °C. However, the final weight of WCR material increased by 4.19%, ammonium fluoride decomposed, or the reaction was completed. The weight increase was due to the non-

Figure 10. EPMA images of PGC: (a) morphology, (b) C, (c) O, (d) Al, (e) F, (f) Si, (g) Co, (h) Mn, (i) Ni, and (j) elemental mass analysis in the red area.
carbon impurity elements complexing with F to form metal complexes, confirming fluorination roasting feasibility.

3.5. Morphological Changes in Sample and Reaction Mechanism. The morphologies and phase compositions of WCR (before treatment) and its roasted product (after treatment) at 200 °C are shown in Figure 8. As shown in Figure 8a,b, graphite in the WCR was primarily spherical with a particle size of 5−20 μm, and it had an apparent layered flake structure, consistent with the characteristics of natural flake graphite. Moreover, the WCRs’ surface was attached with many microspheres and distributed in a chain, speculated to be the pyrolysis product of the conductive carbon black or the binder PVDF. After fluorination roasting (Figure 8c,d), the surface of graphite acquired a metallic luster, and some large graphite particles broke into small graphite particles, which increased the specific surface area. This phenomenon was conducive to the complexation reaction and stripping of non-carbon impurity elements contained in graphite. As shown in Figure 8e, the nitrogen content in the roasted product increased from 0% to 35.35%, whereas the oxygen content decreased from 10.61% to 1.15%. The carbon content also decreased slightly. Given that ammonium fluoride decomposed at 250 °C, we inferred that the current form of nitrogen may have combined with valuable components to form complexes, such as [CoF₃]⁻, [NiF₃]⁻, [MnF₃]⁻, [AlF₆]₃⁻, and [SiF₆]²⁻. Excess [NH₄]⁺ combined with [SO₄]²⁻ to form water-soluble (NH₄)₂SO₄. However, because of the very high C content in the WCR, the carbon peak masked the peaks of other substances during XRD characterization. Unfortunately, the content of valuable components in WCR was very low. The characteristic peak itself was tiny, so the phase transition of the reaction process was difficult to characterize by XRD.

Furthermore, simulation experiments on the reaction of pure cobalt sulfate, nickel sulfate, and manganese sulfate with ammonium fluoride roasting were performed under the same conditions to prove this inference. The results are shown in Figure 9. It can be seen that cobalt sulfate (Figure 9a), nickel sulfate (Figure 9c), and manganese sulfate (Figure 9b) combined with ammonium fluoride to form soluble complex compounds such as NH₃CoF₃, (NH₄)₂NiF₄, and NH₄MnF₃, which was the reaction mechanism of fluorination roasting.

3.6. Characterization of PGC. As shown in Figure 8d, the graphite-layered structure of the regenerated graphite (PGC) has not been damaged. The PGC was basically natural graphite with the morphology of spherical, which could be seen in Figure 10a. Furthermore, the elements of PGC were qualitatively and quantitatively analyzed by electron microprobe analysis (EPMA). The result showed that although the purity of PGC was higher than 99.98% after purification by low-temperature fluorination roasting, and there were still traces of Al and Si in some areas (Figure 10d,f), and the valuable metals such as Ni, Co, and Mn were completely removed (Figure 10g−i). Meanwhile, combined with the distribution of O (Figure 10c) and F (Figure 10e) elements, it can be inferred that silicon and aluminum remained in the gaps between graphite particles in the form of SiO₂ and AlF₃ instead of inside the graphite. This conclusion can also be inferred from Figure 10j, which found the purity of graphite to be 100% without any other impurities by quantitative analysis on the surface of spherical graphite.

3.7. Characterization of Electrochemical Performance. The working electrode was fabricated by conventional slurry mixing and a casting method on the copper current collector. The electrode compositions were PGC (as active material), carboxymethylcellulose sodium (CMC, as thickener), styrene–butadiene rubber (SBR, as binder), and 1 wt % carbon black (as conducting agent) with a mass ratio of
95.5:1:5:2:1, which also mixed into water. Prior to cell fabrication, the electrodes were heated in a vacuum oven at 80 °C for 10 h. The areal mass loadings of the electrodes were 1.29–1.45 mg/cm². Coin type cells (2032) were fabricated inside an Ar-filled glovebox with a lithium metal as the counter electrode, Celgard 2400 as the separator, and 1 mol/L LiPF₆ in ethylene carbonate/ethyl methyl carbonate/dimethyl carbonate (EC:EMC:DMC = 1:1:1, v/v) as the electrolyte. The electrochemical performances were tested by using a LAND-CT3001A, and the results are shown in Figure 11.

The regenerated spent anode graphite (PGC) with a purity of 99.98% separated from non-carbon valuable components through simple water-bath leaching to purify graphite without damaging the graphite structure. As shown in Figure 11a, the particle size ($D_{50} = 16.829 \mu m$), true density (2.2408 g/cm³), tap density (0.85 g/cm³), and compacted density (2.095 g/cm³) of the PGC sample did not change and reached the graphite anode standard of LIBs after fluorination roasting and water bath leaching. Meanwhile, the specific surface area was reduced from 8.68 to 6.12 m²/g. The reduction of specific surface area was beneficial to improve the electrochemical performance of the PGC, which exhibited a stable specific capacity of 340.9 mAh/g and high ICE of 92.13%, much better than that of WCR (293.4 mAh/g, ICE = 86.52%) and similar to that of commercial graphite (353.8 mAh/g, ICE = 93.24%), as shown in Figure 11b. Meanwhile, after 100 cycles at 1C (Figure 11c), the capacity retention of PGC was higher than 96.7% with a high cycle stability, which was significantly better than that of WCR (88.07%) and commercial graphite (91.89%). Moreover, the regenerated spent anode graphite (PGC) products also had a stable long-cycle performance (Figure 11d), and the retention capacity in the 470th cycle of the PGC was 68.92% (specific capacity 109.1 mAh/g) and in the 1000th cycle was 39.35% (specific capacity 62.3 mAh/g).

In addition, the exhaust gas was absorbed in fluorine-containing leachate adjusting pH value and fluorine–ammonium ion balance to recover ammonium fluoride products by evaporation crystallization. Almost no waste liquid, exhaust gas, and waste residue were discharged during the entire purification and recovery process.

4. CONCLUSIONS

The mechanism and kinetic parameters of the fluorination roasting of WCR were investigated by different analysis methods, namely Kissinger, FWO, KAS, and Šatava–Šesták. The results showed that the fluorination roasting of non-carbon impurity elements in WCR was a complex process that can be divided into three stages. In the first stage (28–80 °C), the oxide in the raw material initially reacted with ammonium fluoride to form ammonia, complex ammonium salt, and H₂O, which was controlled by a chemical reaction. In the second stage (80–161.2 °C), the sulfate, sulfite, and sulfide began to react with ammonium fluoride to produce SO₂ and NH₃ gas, which was controlled by three-dimensional diffusion. In the last stage (161.2–211 °C), under chemical reaction control, the macromolecular organics and excess ammonium fluoride were decomposed into N₂O, NH₃, and HF gases. Meanwhile, after fitting 30 different common mechanism functions with the Šatava–Šesták method, the most probable models in each stage were F₀, Dₓ and Fₜ, respectively. The acceptable activation energy $E_a$, the logarithm of pre-exponential factor $ln A_v$ and the thermodynamic parameters at the peak temperature ($T_p$) can also be calculated. Additionally, the thermal behavior and reaction mechanism of fluorination roasting were characterized by TG-IR and SEM-EDS analyses, indicating that fluorination was a process in which valuable components underwent complexation to form soluble complex ions. The superior electrochemical performance and properties of the regenerated spent graphite anode (PGC) indicated that the process can contribute to meeting the increasingly strict environmental concerns and establishing recyclable and low-cost recycling processes suitable for regeneration of spent anode graphite from spent LIBs.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c07190.

AUTHOR INFORMATION

Corresponding Authors
Qian Zhong — School of Metallurgy and Environment, Central South University, Changsha 410083 Hunan Province, China; orcid.org/0000-0003-4963-0516; Email: 348259246@qq.com
Jin Xiao — School of Metallurgy and Environment, Central South University, Changsha 410083 Hunan Province, China; orcid.org/0000-0002-9244-7859; Email: csucarbon@126.com

Authors
Xiangdong Zhu — School of Metallurgy and Environment, Central South University, Changsha 410083 Hunan Province, China
Qiuyun Mao — Department of Educational Science, Hunan First Normal University, Changsha 410205 Hunan Province, China
Zhenhua Zhang — School of Metallurgy and Environment, Central South University, Changsha 410083 Hunan Province, China
Gang Wang — School of Metallurgy and Environment, Central South University, Changsha 410083 Hunan Province, China
Lei Tang — School of Metallurgy and Environment, Central South University, Changsha 410083 Hunan Province, China

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.1c07190

Author Contributions
X.Z. performed the conceptualization, methodology, formal analysis, writing-original draft, writing-review, and editing; Q.M. performed the supervision, formal analysis, simulation, writing-review, and editing; Q.Z. performed the validation, conceptualization, methodology, funding acquisition, writing-original draft, writing-review, and editing; Z.Z. performed the investigation, validation, data analysis, writing-review, and editing; G.W. performed the validation, methodology, simulation, writing-review, and editing; L.T. performed the validation, writing-review, and editing; J.X. performed the supervision, validation, writing-review editing, and funding.
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Notes
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