Insights into the thermochemical evolution of maleic anhydride-initiated esterified starch to construct hard carbon microspheres for lithium-ion batteries

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\textbf{A B S T R A C T}

Starch, as a typical polysaccharide with natural spherical morphology, is not only a preferred precursor for preparing carbon materials but also a model polymer for investigating thermochemical evolution mechanisms. However, starch usually suffers from severe foaming and low carbon yield during direct pyrolysis. Herein, we report a simple and eco-friendly dry strategy, by maleic anhydride initiating the esterification of starch, to design carbon microspheres against the starch foaming. Moreover, the influence of ester grafting on the pyrolytic behavior of starch is also focused. The formation of ester groups in precursor guarantees the structural stability of starch-based intermediate because it can promote the accumulation of unsaturated species and accelerate the water elimination during pyrolysis. Meanwhile, the esterification and dehydration reactions greatly deplete the primary hydroxyl groups in the starch molecules and thus the rapid levoglucosan release is inhibited, which well keeps the spherical morphology of starch and ensures the high carbon yield. In further exploration as anode materials for Lithium-ion batteries, the obtained carbon microspheres exhibit good cyclability and rate performance with a reversible capacity of 444 mAh g\textsuperscript{-1} at 50 mA g\textsuperscript{-1}. This work provides theoretical fundamentals for the controllable thermal transformation of biomass towards wide applications.

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\textbf{1. Introduction}

Biomass, as a low-cost, eco-friendly, and sustainable resource, has drawn extensive interest in recent years [1–4]. Attracted by the diversity of morphology and structure, massive biomass precursors have been used to fabricate carbon materials which have been applied in many fields, such as alkali metal ion batteries [5–7], supercapacitors [8–10], oil/water separation [11], and catalysis [12,13]. To receive carbon materials with the expected structure and properties, it is essential to achieve a controllable transformation during the pyrolysis of biomass. However, due to the complex compositions of biomass, it remains a challenge to understand and elucidate the thermochemical evolution mechanism in pyrolysis process.

Starch, one of the richest renewable biomaterials on the planet, is widespread in a variety of plants [14]. It is a typical polysaccharide with a simple composition and high carbon content, which makes it a desirable carbon precursor to investigate thermochemical transformation mechanism. In addition, compared with other biomass precursors, such as cellulose [15], lignin [16], sucrose [17], and so on, starch shows an attractive natural spherical morphology, making it a highly competitive candidate for the preparation of spherical carbon materials [18]. However, the molecular chain of starch linked by glycosidic bonds exhibits poor thermal stability [19]. During pyrolysis, the thermal scission of the glycosidic bonds allows reactions to take place in an intramolecular pathway, resulting in the formation of a large amount of volatile...
product, especially levogulcan [19,20]. Simultaneously, the rapid escape of volatiles can destroy the spherical morphology, leading to the melting and foaming of the structure with a low carbon yield [5,21].

To address these issues, intensive efforts have been made to enhance the thermal stability of starch. For example, preheating treatment strategies of starch in inert [18] or air [22] atmosphere could effectively prevent starch from melting and foaming in the following carbonization process. But these methods usually take a very long time without a clear evolution mechanism at the molecular level. In addition, cross-linking [23] and solvothermal [5] are also effective methods that could stabilize the structure of starch and improve carbon yield. Recently, our previous work reported corn starch cross-linked by (NH₄)₂HPO₄, which efficiently prevented the destruction of the original spherical morphology during pyrolysis. The cross-linking reaction mechanism and the carbonization process were deeply studied [21]. However, due to the easy pasting properties of starch, the liquid phase operating conditions still face the problem of the complicated synthesis process and high cost. Besides, the introduction of nitrogen and phosphorus heteroatoms into the carbon skeleton to some extent makes it hard to elucidate whether the chemical components or the structures of carbon skeleton is the crucial part in practical applications. Therefore, simple stabilization strategies and the involved thermochemical evolution mechanisms need further development and elaboration.

In order to investigate on these topics, modification on starch molecules is considered as an effective strategy. Maleic anhydride, as a simple organic small molecule, has been widely used for starch modification [14–27]. As previous reported, maleic anhydride was used to cross-link the corn starch binder during the fabrication of silicon anode, which enhances the cycle-life performance of Lithium-ion batteries (LIBs). Compared to pure starch, the cross-linked starch exhibits higher adhesion and thermal stability [28]. Moreover, researchers have modified the physicochemical properties of starch through the esterification reaction of maleic anhydride under dry conditions [25,26]. The hydrophobicity, affinity, thermal stability, and mechanical properties of the starch are dramatically altered even at low substitution levels. However, the pyrolytic behavior of maleic anhydride esterified starch is still unclear, and the thermochemical evolution mechanism from esterified starch to carbon materials has not been studied.

Herein, a facile and eco-friendly dry strategy was proposed to fabricate monodispersed hard carbon microspheres using corn starch as the raw material and maleic anhydride as the esterifying agent. Based on thermogravimetric-mass spectrometry (TG-MS), in-situ Fourier transform infrared spectra (in-situ FT-IR), and nuclear magnetic resonance (NMR) tests, the influence of ester group grafting on the pyrolytic behavior of starch was systematically investigated, and a possible thermochemical evolution mechanism of esterified starch was proposed. Moreover, since the significant differences in the pyrolytic behavior of the modified and unmodified starch, the obtained carbon microspheres from esterified starch show suitable microstructure and high conductivity, making them exhibit good cyclability and rate performance in Lithium-ion batteries. These insights into the thermochemical evolution of esterified starch pave a way for the controllable transformation from biomass precursors to desired carbon materials, towards future wide applications.

2. Experimental section

2.1. Materials and reagents

Corn starch was provided by Linqing De Neng Golden Corn Biotechnology Co., Ltd. in China and dried in a vacuum oven at 55 °C for 48 h to remove moisture before use. Maleic anhydride with AR grade was purchased from Sigma-Aladdin, Shanghai, China. Acetone (AR grade, Shanghai National Chemical Reagent Ltd.) was used to wash the samples.

2.2. Sample preparation

Corn starch (20 g) and maleic anhydride (4 g) were added into a hydrothermal reactor and mixed evenly. Then, the reactor was sealed and placed in an oven at 80 °C for 3 h to get the maleic anhydride esterified starch (MES). The resultant MES was washed in acetone to remove the residual maleic anhydride and then dried in a 55 °C vacuum condition. At last, the dried MES was carbonized at 600 °C under argon atmosphere for 2 h with a heating rate of 1 °C min⁻¹, and the obtained sample was labeled as MESS00. For comparison, pristine starch (PS) without esterification modification was heated in the same conditions to get the contrast product (PS600).

2.3. Sample characterization

The morphologies were performed on a desktop scanning electron microscope (SEM, Sphenomenon Prox, Netherland). The pyrolysis behaviors were carried out on a thermogravimetric analysis combined with a mass spectrometer (TG-MS, Rigaku, Thermo plus EV2/Thermo mass photo, Japan). The substitution degree of esterified starch was titrated by Automatic Potentiometric Titrator (Mettler Toledo, T70). The evolution of functional groups was analyzed by in-situ Fourier transform infrared spectra (in-situ FT-IR, Bruker tensor 27, Germany). The high-resolution solid-state Nuclear Magnetic Resonance (solid-state NMR, Bruker AVANCE-600, Germany) was used to study the carbon skeleton variation. The surface chemical species and elemental composition were performed by X-ray photoelectron spectra (XPS, K-alpha, Thermo Scientific) and elemental analyzer (EA, Elementar, Germany), respectively. The microstructure of carbon samples was observed by high-resolution transmission electron microscopy (HRTEM, JEM-2010F, Japan), X-ray diffraction (XRD, D8 Advance, Bruker, Germany) with Cu-Kα radiation (λ = 1.54 Å) and Raman microscopy (Horiba HR800, a laser wavelength of 532 nm, Japan) was used to analyze the hard carbon layer spacing and graphitization degree. The porous structures were analyzed with a nitrogen adsorption–desorption analyzer (Belsorp Max, Japan).

2.4. Electrochemical measurements

The electrode was prepared by a homogeneous mixture of 80 wt.% active materials, 10 wt.% Super P, and 10 wt.% Polyvinylidene fluoride (PVDF) binder, which was then pasted on the copper current collector and dried at 100 °C in vacuum for 12 h. The loading mass of each working electrode was ca. 2.5 mg cm⁻². The CR2032 coin-type cells were assembled with the above working electrode, a reference and counter electrode of lithium foil, an electrolyte solution of 1 M LiPF₆ in ethylene carbonate (EC)/diethyl carbonate (DEC) (1:1 by volume) and a separator of polypropylene (PP, Cegland2500) in a glove box where the content of both H₂O and O₂ is lower than 1 ppm, respectively. A LAND CT2001A battery tester (LAND, Wuhan, China) was employed for the charging/discharging tests (in a voltage range of 0.01–3.0 V). A VASP electrochemical workstation was used for the cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS, a frequency ranges from 100 kHz to 0.01 Hz with an amplitude of 5.0 mV).
3. Results and discussion

The preparation processes of both carbon microspheres and foamed carbon from starch were depicted in Fig. 1(a). First, MES was synthesized by dry method in a closed hydrothermal reactor. In this process, the molten maleic anhydride undergoes a nucleophilic substitution reaction with the starch molecules to form ester groups. The introduced ester groups could act as a bridge connecting different molecular chains or adjacent pyranose rings [29]. To verify the grafting of ester groups, FT-IR analysis was performed on PS and MES (Fig. S1). Besides the characteristic absorption peaks of the PS, a new peak near 1720 cm\(^{-1}\) is detected in MES, corresponding to the stretching vibration peak of the ester bond [24]. As described in the experimental section, MES has been thoroughly washed with acetone before characterization. The residual maleic anhydride has been completely removed, and thus it can be determined that C = O comes from MES. In addition, the characteristic absorption peak of the butyl ester appears at 820 cm\(^{-1}\), which is formed by ring-opening esterification of maleic anhydride in starch [25]. The identification of the characteristic peaks demonstrates that the starch is successfully esterified by dry method. Moreover, in order to quantify the extent of the reaction, the acid-alkali solution titration method was used to calculate the substitution degree (DS) of maleic anhydride and the esterification reaction efficiency (RE). After parallel experiments, the DS of maleic anhydride and the RE are determined to be 0.2325% and 66%, respectively. The low DS is due to the natural polycrystalline structure of starch, which makes it difficult for the reaction to proceed inside the starch granules. The detailed calculation steps are shown in the Supporting information.

![Fig. 1.](image-url)
3.1. Pyrolytic analysis of unmodified and modified starch

3.1.1. Pyrolytic process

The natural supramolecular structure of starch is modified by the grafting of ester groups. As shown in Fig. 1(b and c), there is no obvious change in the morphology of the MES compared to that of the PS, both exhibiting a spherical morphology with around 15 μm in diameter. During the pyrolysis process, MES maintains the spherical morphology of starch granules and eventually transforms into monodisperse carbon microspheres (Fig. 1d and h). As expected, PS melts and foams during direct pyrolysis, leading to the formation of three-dimensional foamed carbon whose microscopic morphology exhibits irregular fragments (Fig. 1e and Fig. S2). It indicates that the esterification modification facilitates the preservation of the spherical morphology.

To explore the influence of ester grafting on the pyrolytic behavior of starch, TG-MS was conducted from room temperature to 600 °C in Argon atmosphere. As observed in Fig. 2(a), the thermal decomposition temperature of MES (200 °C) is significantly ahead of PS (280 °C), indicating that their structures have undergone different evolutions at the same temperature. Interestingly, despite the early decomposition, the weight loss rate of MES is much lower than that of PS, and the carbon yield of MES (29%) shows a significant improvement compared to PS (13%). This demonstrates that not only the morphology is inherited during pyrolysis but also more carbon species are immobilized at the same time. As can be seen from the mass spectrometry (Fig. 2b and c), the small molecules released are mainly H2O, CO, and CO2, which attributes to the dehydration, decarburization, and decarboxylation reactions, respectively [30]. In contrast to PS, MES exhibits a two-stage continuous pyrolysis process. It can be speculated that the stepwise pyrolysis process promotes the fixation of more carbon species. The variation in the composition of the samples was investigated by elemental analysis (Fig. S3). No significant change in the C/O atomic ratio of PS until 250 °C (Fig. S3a). In comparison, the C/O atom ratio rises from 0.92 in MES160 to 1.08 in MES250 (Fig. S3b), which demonstrates the premature dehydration of MES at a lower temperature. The color change of PS and MES samples treated at different temperatures is shown in Fig. S4. At room temperature, both PS and MES are white powders. When the temperature rises to 250 °C, the MES shows a more pronounced color change (sun orange) compared to the PS (light yellow), indicating an advance dehydration of MES, which is consistent with the results of TG-MS and EA.
cussed above, it can be concluded that the grafting of ester groups not only promotes the pyrolysis of MES but also plays an important role in stabilizing the carbon skeleton. The following section will be combined with more in-depth analytical studies to elucidate the thermochemical evolution mechanisms of MES.

3.1.2. The evolution of functional groups and structure

In-situ FT-IR test was carried out to qualitatively analyze the evolution of oxygen-containing functional groups in the pyrolysis process. The IR spectra of PS and MES collected at different temperatures are shown in Fig. 2(d–f) and Fig. 2(g–i), respectively. In accordance with the previous report, PS exhibits a typical polysaccharide structure with several characteristic absorption peaks at ambient temperature [31]. The peak centered at 3310 cm$^{-1}$ corresponds to O–H stretching and vibration of the hydrogen bond association, 2930 cm$^{-1}$ arises from C–H asymmetrical stretching and vibration, 1635 cm$^{-1}$ belongs to O–H bending vibration, 1152 cm$^{-1}$ is from C–O–C asymmetrical stretching and vibration, 1080 cm$^{-1}$ corresponds to D-glucopyranose and hydroxyl-linked C–O stretching and vibration, and 925 cm$^{-1}$ is due to glycosidic bond vibration [24,26]. As discussed in Fig. S1, in addition to all the above absorption peaks, MES also adds the ester group and butyl ester absorption peaks at 1720 and 820 cm$^{-1}$, respectively [25]. As can be observed in Fig. 2(g), there is no obvious change among the IR spectra of MES at low temperatures. Elevating the pyrolysis temperature up to 200 °C, the decreased intensity of the absorption peak at 1720 cm$^{-1}$ demonstrates the thermal cleavage of the ester group due to its thermolabile properties, and this signal has a frequency shift, proving the formation of different carbonyl species [23]. Moreover, the key information worth noting is that the adsorption peak of C = C unsaturated species at 1600 cm$^{-1}$ appears and becomes stronger as the temperature increases. This is attributed to that the breakage of ester bond can allow the extraction of a hydrogen atom from pyranose ring, resulting in the formation of unsaturated species. The accumulated unsaturated species can act as precursors for the construction of aromatic structures [20]. In addition, the acidic species produced by ester pyrolysis could catalyze the dehydration of glucose units and lead to the formation of more cyclic structures [32]. In comparison, the structure of PS remains unchanged in this temperature range, which further supports the result of TG-MS. Briefly, the grafting of ester group could enhance the structural stability of starch-based intermediate, facilitating the retention of morphology during the pyrolysis process. Followed by further temperature increases, there is sufficient heat to break the glycosidic bonds. As shown in Fig. 2(e and h), the glycosidic bonds in MES and PS begin to break at approximately 260 and 280 °C, respectively. After that, the starch molecules undergo rapid depolymerization, decomposition, and complex free radical reactions, releasing volatile substances and producing residual char [19]. In the temperature range of 360 to 600 °C, the characteristic structure of starch is completely lost and the transformation to carbon materials takes place. As observed in Fig. 2(f and i), the appearance of three obvious absorption peaks in the range between 1170 and 1600 cm$^{-1}$ is indicative of the formation of aromatic rings [30].

XPS was employed to further analyze the content and configuration of C and O in the MES products (Fig. 3a–c). With pyrolysis temperatures increasing, the carbon content increases, while the oxygen content declines continuously, in line with the EA results. The C 1s spectra can be divided into six peaks with binding energies (B.E.) of approximately 284.2, 284.8, 286.07, 287.3, 289.1, and 291 eV in Fig. 35(a–d), which can be attributed to C = C, C–C, C–O, C = O, C(O)O, and π–π*, respectively [26,33]. The C configuration has been further quantitatively evaluated as illustrated in Fig. 3(b and c) and Table 1. It is worth noting that the proportion of C(O)O slightly decreases from 5.1% to 3.59% as the temperature increases from 160 to 250 °C, while that of C = O increases from 12.03% to 13.92%. The reason for this may be that the temperature reaches 200 °C, some of the ester groups are broken off and transform into unsaturated species such as aldehydes, ketones, and carboxylic acids, as described in in-situ FT-IR results. As the pyrolysis reaction temperature rises further (340 °C), both C(O)O and C = O gradually decrease, which is attributed to the decarboxylation and decarboxylation reactions. Moreover, the shakeup transition of aromatic carbon (π–π* transition, at 291 eV) appears, demonstrating the occurrence of aromatization reactions and the initial formation of the carbon skeleton [34]. The O 1 s spectra can be divided into four peaks with B.E. at about 531.3, 532.1, 533.2, and 534.8 eV, corresponding to the C(O)C, C = O, C–O, and O–H bonds, respectively (Fig. S5h–j) [35,36]. Table 1 displayed the fitting results. The proportion of C(O)O decreases from 4.19% (MES160) to 3.45% (MES250), while that of C = O increases from 12.18% (MES160) to 12.72% (MES250), which is consistent with the C 1s results. The oxygen-containing species are gradually removed as the temperature increases, demonstrating the formation of a carbon skeleton.

The high-resolution solid-state NMR test was employed to further investigate the effect of ester grafting on the structural evolution of starch during pyrolysis. As shown in Fig. 3(d), the chemical shift signal from 28 to 80 ppm is the overlap region of C$_2$, C$_3$, and C$_4$, while the peaks at 100, 80–84, and 61 ppm are assigned to C$_7$, C$_8$, and C$_9$ of the ordered starch polysaccharides, respectively [37,38]. After esterification, the peaks of the starch are still present in MES25. Moreover, two new peaks at 168 and 134 ppm that are attributed to the carbonyl carbon and the alkyl carbon, respectively, appeared (Fig. 3e), which further confirms the formation of the ester linkage [28]. Compared with PS25, the broadness of C$_6$ resonances in MES25 indicates the esterification reaction between maleic anhydride and starch chains/units that generated a complex chemical shift distribution [37]. This is due to the lower spatial resistance and the higher reactivity of the C$_6$ site, which makes it easier to react with maleic anhydride [39,40]. When the treatment temperature reaches 250 °C, the peak of the C$_6$ in MES250 is of weaker intensity and shifts to downfield by 1 ppm. This change is caused by the dehydration condensation reaction of primary hydroxyl groups at low temperatures, making large alterations in the chemical environment of the C$_6$ site. In contrast, there are no obvious changes in the spectrum of PS25 as is compared to PS25. As displayed in the in-situ FT-IR results (Fig. 2h), the glycosidic bond in MES starts to break at 260 °C. Profited by the significant depletion of the primary hydroxyl group at the C$_6$ site by esterification and dehydration reaction, the direct formation of levoglucosan by transglycosylation is inhibited, allowing the pyrolysis reaction to proceed towards the production of residual char [19,41]. Therefore, the grafting of the ester group leads to a favorable structural evolution of the MES, which could keep the spherical morphology of starch and ensure the high carbon yield during pyrolysis. At higher temperatures, the skeleton features of starch largely disappear, and the characteristic peak of the aromatic ring at around 128 ppm is detected [21]. In addition, two peaks at 30 and 13 ppm represent the aliphatic structure with CH$_2$. Besides, the shoulder at 152 ppm corresponds to C$_1$ and C$_4$ of the furan ring [30]. These analyses provide solid evidences for the structural transformation process of esterified starch to carbon materials.

Ex-situ XRD patterns of the MES and PS samples at different temperatures were shown in Fig. 3(f) and Fig. 5, respectively. The peaks centered at ca. 15.3°, 17.1°, 18.2°, and 23.5° for PS attributed to the A-type starch crystalline structure [42]. After the esterification reaction, the crystalline structure of MES25 did not change significantly, which indicates that the esterification reaction occurs mainly in the amorphous region of starch [26]. When the temper-
Table 1

The content of the C 1s peaks in deconvoluted MES samples.

<table>
<thead>
<tr>
<th>B.E. (eV)</th>
<th>C1 (284.2)</th>
<th>C2 (284.8)</th>
<th>C3 (286.07)</th>
<th>C4 (287.3)</th>
<th>C5 (289.02)</th>
<th>C6 (291.0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Assignment</td>
<td>C = C</td>
<td>C - C</td>
<td>C - O</td>
<td>C = O</td>
<td>C(O)O</td>
<td>π-π*</td>
</tr>
<tr>
<td>MES160</td>
<td>3.12</td>
<td>9.76</td>
<td>30.43</td>
<td>12.03</td>
<td>5.10</td>
<td>0.00</td>
</tr>
<tr>
<td>MES250</td>
<td>2.68</td>
<td>11.73</td>
<td>28.82</td>
<td>13.92</td>
<td>3.59</td>
<td>0.00</td>
</tr>
<tr>
<td>MES340</td>
<td>0.00</td>
<td>49.72</td>
<td>15.29</td>
<td>9.10</td>
<td>2.37</td>
<td>4.45</td>
</tr>
<tr>
<td>MES460</td>
<td>0.00</td>
<td>60.27</td>
<td>14.26</td>
<td>6.17</td>
<td>1.09</td>
<td>5.97</td>
</tr>
</tbody>
</table>

Fig. 3. (a) XPS surveys, (b and c) high-resolution C 1s spectrum results, (d and e) 13C NMR spectrum, and (f) ex-situ XRD patterns of starch samples treated at different temperatures.
ature reaches 250 °C, the crystallinity of MES drops greatly. Combined with the conclusion from the in-situ FT-IR and TG-MS, it can be known that the breakage of ester group takes away the hydrogen atom and is accompanied by the dehydration of the active hydroxyl group. The hydrogen bonds in MES are broken, which destroys the polycrystalline structure of starch (Fig. 3f). In comparison, PS has no obvious structural changes in this temperature range, and PS250 still shows obvious starch polycrystalline structure (Fig. S6). The removal of water and the formation of cross-linked structure make the microcrystalline structures of MES difficult to melt, leading to the preservation of spherical morphology during the subsequent pyrolysis [22]. From 340 to 460 °C, the characteristic structure of starch completely disappeared. The (002) and (100) peaks representing the graphitic carbon begin to appear when the thermal treatment temperature reaches 460 °C. This proves that MES460 undergoes aromatization and condensation reactions at this temperature, in agreement with the result of the $^{13}$C NMR spectrum [43].

3.1.3. Thermochemical evolution mechanism of MES

The above analysis results provide sufficient evidence that the grafting of ester groups changes the pyrolytic behavior of starch, which can maintain the spherical morphology of starch during the pyrolysis process and increase the carbon yield. A possible thermochemical evolution mechanism of MES has been proposed as shown in Fig. 4. According to the temperature at which the starch structure changes, the whole process can be divided into four stages. At lower temperatures, MES only removes the physically absorbed water without obvious structural changes. Stage I: as demonstrated in the in-situ FT-IR spectrum, the ester groups start to break at 200 °C due to their weak thermal stability. The cleavage of the ester group allows the extraction of a hydrogen atom from the pyranose ring, giving rise to unsaturated species containing C = C double bond that facilitate the formation of aromatic structures. Moreover, the acidic species generated by the cleavage of the ester group can accelerate the water elimination during pyrolysis, which can be confirmed by the TG-MS results. Therefore, the starch intermediate acquires a stable structure in the primary stage of pyrolysis, facilitating the inhibition of structural melting in the subsequent high-temperature treatment. Stage II: when the temperature rises to 260 °C, the glycosidic bonds in MES begin to break and the molecular chain of starch undergoes depolymerization to form oligomers and small molecules including levoglucosan (LG), glycolaldehyde (HAA), and 5-hydroxymethylfuran (5-HMF), and so on [44]. These carbon-containing species undergo a complex and violent pyrolysis process, including primary and secondary reactions [45]. Benefiting from the significant depletion of the primary hydroxyl group by the esterification and dehydration reactions, the side reaction of intramolecular dehydration to produce volatile products, especially LG, is inhibited. In this process, the weight loss rate is significantly reduced, which further ensures the retention of spherical morphology and high carbon yield. Stage III: As the pyrolysis reaction proceeds, the structural characteristics of starch disappear (340 °C). The carbon-containing species are fixed by cross-linking and polycondensation reactions, and the aromatic structure is initially formed. Stage IV: When the temperature is heated to 460 °C, aromatization and carbonization reactions occur. The organic skeleton of starch granules is transformed into inorganic carbon materials, forming monodisperse carbon microspheres.

3.2. Characterization of carbon materials

To better understand the effects of esterification modification on the microstructure of carbon materials, HRTEM, XRD, Raman spectroscopy, and N$_2$ adsorption–desorption techniques were employed to investigate the structural properties of PS600 and MES600. Table 2 shows the physical parameters of both products.

![Fig. 4. Possible scheme of chemical evolution during thermal treatment for MES.](image-url)
Table 2
Physical parameters of both samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>2-Theta (°)</th>
<th>d_{002} (Å)</th>
<th>I_{D}/I_{G}</th>
<th>L_{a} (nm)</th>
<th>S_{BET} (m² g⁻¹)</th>
<th>V_{tot} (cm³ g⁻¹)</th>
<th>D_{ave} (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS600</td>
<td>22.53</td>
<td>3.94</td>
<td>1.82</td>
<td>10.56</td>
<td>500</td>
<td>0.17</td>
<td>1.35</td>
</tr>
<tr>
<td>MES600</td>
<td>21.82</td>
<td>4.07</td>
<td>1.89</td>
<td>10.17</td>
<td>441</td>
<td>0.19</td>
<td>1.69</td>
</tr>
</tbody>
</table>

* The average interlayer d-spacing is conducted by the Bragg’s equation.

** I_{D} and I_{G} are the integrated intensities of the D and G band.

*** L_{a}(nm) = \left(2.4 \times 10^{-10}\right) \times 4\left(\frac{I_{G}}{I_{D}}\right).

**** The resultant Brunauer-Emmett-Teller (BET) surface areas.

***** The total pore volume (V_{tot}).

****** The average pore sizes (D_{ave}).

Fig. 5. TEM images of (a) PS600 and (b) MES600 (the inserts are SAED patterns). (c) XRD patterns, (d) Raman spectra, (e) Nitrogen adsorption–desorption isotherms, and corresponding (f) pore size distributions of PS600 and MES600.
HRTEM images of both carbon samples display amorphous graphite-like microcrystal structure (Fig. 5a and b). This reveals that the carbon derived from starch is nongraphitizable, so-called hard carbon, containing small and randomly oriented domains of sp$^2$ carbon planes in the particle, as previously reported [17,46–48]. The corresponding selected area electron diffraction (SAED) patterns show dispersing diffraction rings, which is further verifying the amorphous structure [49]. The XRD patterns in Fig. 5(c) exhibit that both products appeared two broad diffraction peaks corresponding to the (002) and (100) planes of amorphous carbon, in line with the results in HRTEM image [50,51]. It should be noted that the center of (002) peak in MES600 shifts slightly to a lower diffraction angle compared to PS600, implying an enlarged increased interlayer distance. The reason is that the MES produces more cross-linking structures during the pyrolysis process, which hinder the orderly arrangement of graphene flake layers and result in a more disordered structure. Meanwhile, the A$_{1g}$ symmetry vibration mode of defects in graphene layer edges (D band) and the E$_{2g}$ symmetry vibration mode of an ideal graphitic lattice (G band) can be identified at 1345 and 1590 cm$^{-1}$ in Raman spectra, respectively [52,53]. As shown in Fig. 5(d), both the samples show a high $I_D/I_G$ ratio, indicating that low-temperature pyrolysis of biomass precursors generally yields highly defective carbon materials [17,54–56]. Moreover, the $I_D/I_G$ value of MES600 is larger than that

Fig. 6. (a) The initial galvanostatic charge/discharge profiles, (b) the first CV curves at 0.2 mV s$^{-1}$, (c) the rate capacity, (d) the cycle stability, and (e) the Nyquist plots of PS600 and MES600.
of PS600, confirming that the introduction of ester groups inhibits the graphitization process.

N₂ adsorption–desorption was carried out to characterize the specific surface area and pore structure (Fig. 5e and f). Both PS600 and MES600 exhibit the typical type I isotherm, indicating the existence of abundant micropores in the materials [57]. The pore size distribution curves also show that the prepared carbon material contains mainly micropores of less than 2 nm. As listed in Table 2, PS600 exhibits a higher specific surface area of 500 m² g⁻¹ than MES600 of 441 m² g⁻¹. This can be explained by the fact that PS releases more volatiles during pyrolysis, thereby increasing the porosity of the PS600. In addition, the pore size distribution becomes larger from 0.45 nm in PS600 to 1.39 nm in MES600 (Fig. 5f). It can be inferred that the slow release of volatile substances inhibits the formation of dense pores. These phenomena demonstrate that the change of the pyrolysis pathway could modify the characteristics of the pore structure.

3.3. Electrochemical characterization

Hard carbon, as a kind of anode materials, has been widely investigated for LIBs in recent years [58,59]. Profited by a more disordered microstructure and larger interlayer space, hard carbon can provide more storage sites and promote Li⁺ migration rather than graphite [49,60,61]. Herein, PS600 and MES600 are selected as anode materials to explore the lithium storage performance. Fig. 6(a) displays the initial galvanostatic charge/discharge curves of PS600 and MES600 at 50 mA g⁻¹ with a potential window of 0.01–3 V. As previously reported, the sloping region at high voltage corresponds to Li⁺ adsorption on the active sites surface, and the plateau region at lower voltage is related to Li⁺ intercalation into the graphite layers [35,62]. Electrode constructed with PS600 offers a first discharge and charge capacities of 882 and 358 mAh g⁻¹, respectively, and the initial Coulombic efficiency (ICE) is only 40.6%. By contrast, MES600 offers a high initial discharge capacity of 986 mAh g⁻¹ and a charge capacity of 444.2 mAh g⁻¹, respectively, with 45.05% of ICE. This is attributed to the higher surface area of PS600, leading to more decomposition of electrolyte and formation of solid electrolyte interphase (SEI) layer on the electrode surface [34,63,64]. Moreover, the smaller micropores in PS600 cannot reversibly insert/extract Li⁺, which may cause abundant “dead lithium” [65]. Thus, this phenomenon could further increase the irreversible capacity and reduce the ICE.

The CV curves display the lithium storage behavior of PS600 and MES600 apparently (Fig. 6b and Fig. S7). For the first cathodic process, an irreversible reduction peak is observed between 0.2–0.5 V for both samples and disappears in the subsequent scans (Fig. S7a and b), which is attributed to formation of the SEI layer. The peak at ca. 0.01 V indicates the intercalation process of Li⁺. In reverse anodic process, the broad oxidation peak at ca. 0.2 V is attributed to the deintercalation of Li⁺ from the carbon layer [35,66]. Moreover, a pair of reversible peaks are observed between 0.5–1 V in the subsequent cycles, which is due to the reversible absorption and desorption reaction of Li⁺ on the surface-active sites [34].

Fig. 6(c) displays the rate performance of the samples. The capacity retention of PS600 largely reduced at high current densities, while that of MES600 gradually reduced. When the current density reached even up to 2000 mA g⁻¹, MES600 can still deliver a capacity of 80 mAh g⁻¹. When slowing the current density back to 50 mA g⁻¹, the capacity of MES600 retained 324 mAh g⁻¹, while that of PS600 was only 282 mAh g⁻¹ after 10 cycling, suggesting that the MES600 has a stable cyclic process at different rates. The cycle stability of both PS600 and MES600 was tested at 500 mA g⁻¹ (Fig. 6d). The amorphous carbon products exhibit good cycle performance at high currents, but due to the large specific surface area and numerous defects, some lithium ions cannot be reversibly deintercalated, resulting in a gradual decrease in capacity [34]. After 450 cycles, a capacity of 144 mAh g⁻¹ can be retained with MES600, while the capacity of PS600 decay to 99 mAh g⁻¹. Table S2 shows the comparison of LIBs performance of MES600 with other biomass-derived-hard carbon.

To gain more insights into the advantage of the obtained hard carbon microspheres, EIS was performed. Fig. 6(e) shows the Nyquist plots and equivalent circuit of PS600 and MES600. The equivalent circuit is composed of equivalent series resistance (Rₛ, intercept on the real axis), migration resistance of Li⁺ through SEI (Rₚ, high-frequency arc), charge transfer resistance (Rₜ, medium-frequency arc), and Li⁺ diffusion resistance (low-frequency tail) [35,67]. As the fitting parameter values display (Table S3), the Rₛ and Rₜ of MES600 (12.86 and 79.26 Ω) are much lower than PS600 (15.49 and 101.1 Ω). This can be ascribed to a suitable pore size, a large layer distance and a low specific surface area, which facilitates the transmission of Li⁺ and reduces the formation of SEI films. Moreover, MES600 exhibits a higher conductivity than PS600, which is beneficial to promote the transmission of electrons and improve the capacity retention rate at high current densities (Fig. S8) [60]. Therefore, the construction of hard carbon microspheres facilitates the enhancement of electrochemical performance. At the same time, the maintenance of the spherical morphology is beneficial to increase the electrode packing density. More importantly, the ICE of the hard carbon microspheres should further improve by structure optimization or surface modification/coating, and this work is being carried out in our laboratory.

4. Conclusion

In this contribution, the monodispersed hard carbon microspheres were controllably prepared by a facile and eco-friendly dry strategy using corn starch as the raw materials and maleic anhydride as the esterifying agent. The thermochemical evolution from maleic anhydride esterified starch to carbon microspheres was systematically investigated. At the initial stages of pyrolysis, the ester groups in precursors promote the accumulation of unsaturated species and the removal of water, along with cyclization to guarantee the structural stability of starch-based intermediate. Meanwhile, the primary hydroxyl groups in starch molecules are depleted by the esterification and dehydration reactions, and thus the rapid release of levoglucosan is inhibited, which makes the MES600 well inherit the spherical morphology from starch, ensuring the high carbon yield. Based on the in-depth analysis of the pyrolysis process, a possible thermochemical evolution mechanism was proposed. Afterwards, the effect of esterification modification on the microstructure of MES600 was studied. The results show that the esterification modification leads to a more disordered structure, a larger pore size, and a higher electrical conductivity. Benefiting the desirable microstructure and spherical morphology, the MES600 exhibits a higher reversible capacity of 444 mAh g⁻¹ compared to PS600 of 358 mAh g⁻¹ at 50 mA g⁻¹. This work will provide theoretical foundations for the better preparation and design of biomass-based carbon materials towards more high-value-added applications.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.
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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jchem.2021.08.050.

References


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