

Fluorination of Carbon Molecular Sieve as Cathode Material for Lithium Primary Batteries and its Characteristics

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Abstract. Fluorinated carbon (CF_x) is a new material with good lubricity and resistance to high temperature and corrosion. Meanwhile, CF_x has excellent electrochemical properties when used as the cathode of the lithium primary batteries. Here, a series of carbon molecular sieve (CMS) is fluorinated via gas-phase fluorination. The CMS treated at 1550 °C has better electrochemical properties after fluorination. The fluorinated products named CMSF deliver specific capacity reaching 796 mAh g⁻¹, associated with discharge potentials exceeding 3.1 V (vs. Li/Li⁺). The discharge voltage of CMSF is about 0.4 V ~ 0.6 V higher than that of fluorinated graphite (GF), and its energy density is about 8% ~ 13% higher than that of GF. The CMSF with the better electrochemical performances than GF as well as its low cost and scalable product demonstrated its great potential practicability in the field of lithium primary batteries.

1 Introduction

Due to the advantages of large theoretical energy densities, wide temperature range, good stability, high security and long life, lithium/fluorinated carbon (Li/CF_x) batteries, which have been developed since 1970s, are widely used in portable electronic equipment, electronic instruments, chip memory power supply, embedded medical devices, etc. [1]. Because of its non-conductivity, fluorinated carbon material can only work under low current, thus limiting its application in power supplies. In order to improve the discharge performance of fluorinated carbon, man efforts have been made to improve the electrical conductivity and the power density of the material including controlled fluorination, surface coating and thermal cracking technology [4-6]. Another direction of research on fluorinated carbon used in chemical power sources is to find a suitable carbon material for fluorination in order to obtain fluorinated materials with better performance [3]. The results show that the electrochemical properties of fluorinated carbon materials are related not only to the fluorination conditions [2], but also to the physical properties of carbon materials [3]. For example, the discharge voltage of fluorinated graphite is lower than that of fluorinated activated carbon; however, the discharge voltage of fluorinated graphite keeps better than that of fluorinated activated carbon during continuous discharge. The carbon molecular sieve (CMS) is a carbon adsorbent with uniform pore structure developed in the late 20th century. It has rich microporous structure which is favourable for fluorination. In addition, its low price is also an advantage as a carbon source of fluorinated carbon materials. Because the CMS contains lots of impurities, it needs to be processed before fluorination in order to obtain

a carbon source with high purity. In this study, a simple method of thermal decomposition was used to treat the carbon molecular sieves, and the structure and electrochemical properties of the products obtained from the fluorination of these carbon sources were analysed.

2 Experimental

2.1 Material synthesis

Carbon molecular sieves were obtained from Huzhou New Orley Adsorption Material Co., Ltd. Before fluorination, the carbon molecular sieves were dried at 200 °C for 2 hours in vacuum. After drying, the carbon molecular sieves were fluorinated in a pure nickel reactor using pure NF₃ gas at temperature of 550 °C ~ 590 °C by 2~3 hours. The fluorinated products named as fluorinated carbon molecular sieve (CMSF). Fluorinated graphite (GF) was purchased from Japan Daikin Industries, Ltd.

2.2 Material characterization

FT-IR spectra were performed using an infrared spectrometer (a PerkinElmer Frontier FT-IR). XRD was studied by conventional powder X-ray diffraction (Bruker-AXS D8 Advance X-Ray Diffractometer) with CuK α radiation.

2.3 Electrochemical measurements

The cathode was papered by fluorinated compounds (CMSF or GF), acetylene black and polyvinylidene fluoride (PVDF) in a weight ratio of 8:1:1. Each cathode comprised the active materials loading as 5 mg cm⁻². Li

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metal disks were the anodes of Coin cells (CR2032), Celgard 2400 membrane was used as a separator and 1.0 M LiBF₄ in propylene carbonate/dimethoxy ethane (PC/DME, 1:1 vol) was used as the electrolyte. Discharge tests at various currents were measured with a LAND CT2001A. The battery was tested at 25 °C, and the cut-off voltage was 1.5 V.

3 Results and discussions

3.1 Carbon source treatment

Carbon molecular sieves (CMS) obtained by carbonization and activation of coal, wood, fruit shell, petroleum coke and carbon fiber, contain some impurities. These impurities will reduce the content of electroactive substances in fluorinated carbon molecular sieves (CMSF). For this reason, it is necessary to pre-treat CMS before fluorination. Some volatile and pyrolysis impurities can be removed by a simple pyrolysis method. Under argon protection, CMS was treated at high temperature of 1150 °C and 1550 °C for 3 hours. The products were CMS1150 and CMS 1550 respectively. After heat treatment, it was found that the weightlessness of carbon molecular sieve was 9% at 1150 °C and 13% at 1550 °C.

The crystal phase structure of CMS before and after heat treatment was analysed by X-ray diffraction. Fig. 1 is XRD diagram of CMS, CMS1150 and CMS1550. All these carbons have typical amorphous carbon structure, and the main peak of carbon diffraction is dispersive. The peak near the diffraction angle of 25 ° corresponds to the (002) crystal surface of the layered carbon material. As the heat treatment temperature increases, the central position of the diffraction peak shifts slightly to the right. The average layer spacing of the carbon material is calculated by Bragg equation. The results are shown in Table 1. The average lamellar spacing of CMS decreased from 0.382 nm to 0.367 nm, but it was larger than that of pure graphite. The large-layer spacing can improve the discharge voltage and the discharge power [3], so the fluorination of these CMS will have higher discharge voltage and better discharge power.

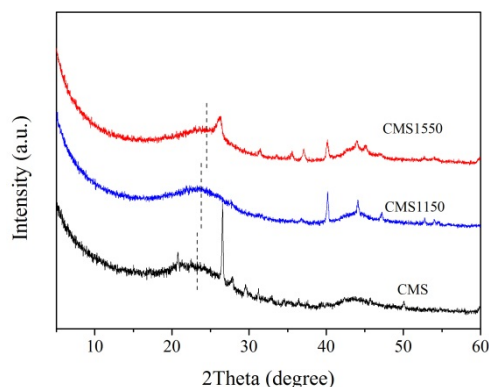


Fig. 1. XRD patterns of CMS, CMS1150 and CMS1550

In addition to the two diffraction wide peaks of amorphous carbon, some smaller but sharper peaks can be seen on the graph, which represent impurities in carbon

materials. The original carbon molecular sieve has a sharp diffraction peak at 26.6 °, which is similar to the characteristic diffraction peak of graphite. However, the diffraction peak disappeared through heat treatment, which shows that this diffraction peak is not the diffraction peak of graphite structure carbon, but the diffraction peak of some kind of impurity easily decomposed at high temperature. The impurity diffraction peaks of CMS1150 and CMS1550 are similar, and these peaks and strength distributions are similar to those of SiO₂. It can be concluded that the impurity in CMS is mainly SiO₂.

Table 1. The average lamellar spacing of CMS, CMS1150, CMS1550 and graphite

| Carbon source | 2Theta (degree) | Average lamellar spacing |
|---------------|-----------------|--------------------------|
| CMS | 23.3 | 0.382 |
| CMS1150 | 23.6 | 0.377 |
| CMS1550 | 24.3 | 0.367 |
| Graphite | 26.4 | 0.337 ^[3] |

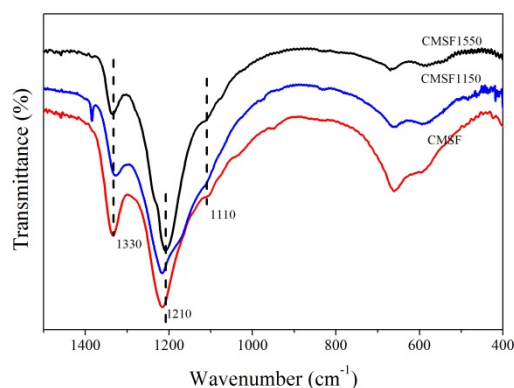
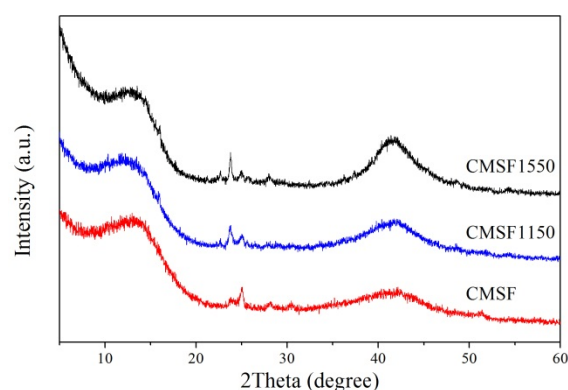
3.2 Structural characterization of fluorinated carbon molecular sieves

The three CMS were fluorinated with NF₃ at high temperature. The fluorinated products are named CMSF, CMSF1150 and CMSF1550 respectively. Table 2 shows the production conditions of these fluorinated products, in which P_{NF₃} is the air pressure in the reactor after being filled with NF₃ at normal temperature, which represents the amount of NF₃ in the reactor, T_F is the setting temperature of the furnace during the fluorination reaction, and t_F is set at T_F temperature holding time. The weight gain rate of CMS after fluorination is 62% to 104%, which increased with the increase of heat treatment temperature. In the process of fluorination, the volatile impurity will decompose into gas under the action of strong oxidizing NF₃, and the weak carbon chain on the surface of carbon will break under the action of NF₃ to form fluorinated gaseous of small molecule. Both of these conditions lead to a low weight gain rate in the fluorination reaction. Compared with untreated CMS, the fluorination gain rate of CMS1150 and CMS1550 increase greatly because of many volatile impurities removed during pyrolysis. Although the CMS treated 1550 °C has higher gain rate than untreated CMS, there is still a big gap between the theoretical value of 158%. This is mainly because although the number of impurities in the CMS is greatly reduced, the inorganic impurities cannot be removed completely, which is an important reason why the weight gain rate does not reach the theoretical value.

Table 2. Fluorination reaction condition of CMS, CMS1150 and CMS1550

| Products | Carbon source | P_{NF_3} (atm) | T_F ($^{\circ}C$) | t_F (min) | Weight gain rate (%) |
|----------|---------------|------------------|-----------------------|-------------|----------------------|
| CMSF | CMS | 1.72 | 550 | 120 | 62 |
| CMSF1150 | CMS1150 | 1.72 | 575 | 180 | 84 |
| CMSF1550 | CMS1550 | 1.71 | 590 | 180 | 104 |

Fig. 2 is an infrared spectrum of three kinds of fluorinated products. The absorption peaks of between 1100 cm^{-1} and 1400 cm^{-1} represent C-F bonds, and the absorption peaks of inorganic impurities and fluorinated impurities are below 800 cm^{-1} [2]. There are obvious impurity peaks in the infrared spectrum, that is, there are more impurities in the products. The largest absorption peak in the spectrum is at the 1210 cm^{-1} , which is the vibration peak of the C-F covalent bond. From its shape, it is not formed by the covalent bond with single energy, but is composed of a series of vibrational peaks of covalent bonds with close but slightly different energy. The relationship between the absorption peak width and the number of C-F bond types is monotonic. With the increase of the temperature of the carbon source pyrolysis treatment, the absorption peak of the product is narrowed at the 1210 cm^{-1} , which indicates that the structure of the carbon is regular by heat treatment, and the type of C-F bond of different bond energy in the fluorinated product is reduced. The vibration absorption peak around 1100 cm^{-1} belongs to the semi-ionic C-F bond, and the vibration absorption peak around 1330 cm^{-1} belongs to the $-CF_2$ group. These two absorption peaks strength of CMS is stronger than these of CMSF1550. The results show that there are more- CF_2 groups and semi-ion C-F bonds in CMSF. Previous studies have shown that semi-ionic C-F bonds could effectively improve discharge voltage of Li/ CF_x batteries, and $-CF_2$ with no electrochemical activity could reduce the discharge specific capacity [3]. Therefore, CMSF should have higher discharge voltage and lower discharge capacity than that of CMSF1550 respectively. Fig. 3 is X-ray diffraction diagrams of the three fluorinated products. The two widest peaks are corresponding to the crystal structure of fluorinated carbons, and the small diffraction peaks around 25° represent the crystal structure of the impurity in the fluorinated products. With the increase of pyrolysis temperature of CMS, the half peak width of the characteristic diffraction peak of fluorinated carbon becomes narrower, which indicates that CMSF1550 has a more regular structure.

**Fig. 2.** FTIR spectra of CMSF, CMSF1150 and CMSF1550**Fig. 3.** XRD patterns of CMSF, CMSF1150 and CMSF1550

3.3 Electrochemical performance of fluorinated carbon molecular sieves

Fig. 4 shows the discharge curve of 0.01 C for three fluorinated products, and the cut-off voltage is 1.5 V . With the increase of heat treatment temperature of CMS, the discharge voltage of fluorinated product decreases slightly. The median voltage decreases from 3.1 V to 3.0 V . The specific capacity of CMSF, CMSF1150 and CMSF1550 is $700, 702, 796\text{ mAh g}^{-1}$ with the energy density $1835, 1854$ and 2090 Wh kg^{-1} at 0.01 C , respectively. The results show that CMSF1550 is relatively good for comprehensive electrochemical properties. Compared with the other two kinds of fluorinated products, the discharge curve of CMSF1550 has two discharge platforms. The main discharge platform is about 3.0 V , and the other small discharge platform is about 2.4 V . The presence of two discharge platforms with a difference of about 0.6 V means that CMSF1550 contains two different types of fluorinated carbon fluoride materials. This phenomenon shows that some carbon structure in the CMS has changed in crystal shape through high temperature treatment at $1550^{\circ}C$.

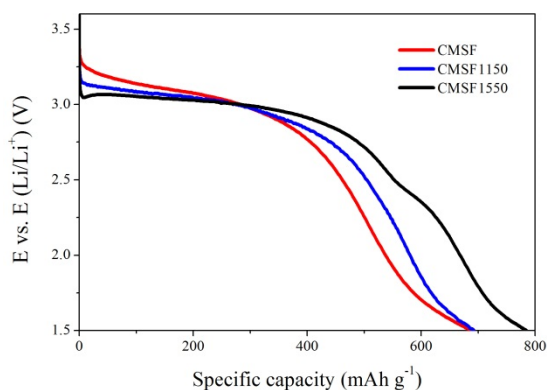


Fig. 4 Galvanostatic discharge profiles of CMF, CMF1150 and CMF1550 at 0.01C

The discharge performance of fluorinated graphite (GF, Aldrich Chemical, Inc.) and CMSF1550 at different current densities is shown in Fig. 5. The discharge voltage of GF at 0.01 C, 0.1 C and 1 C is lower than that of CMSF1550. With the discharge current increases, the difference of discharge voltage increase. The maximum difference is about 0.4 V ~ 0.5 V at 1C. The specific capacity of GF at 1.5 V cut-off voltages is similar to that of CMSF at 2.0 V cut-off voltages. The energy density of GF and CMSF1550 is shown in Table 3. It can be seen that the energy density of CMSF1550 is 8% to 13% higher than that of GF at different current densities.

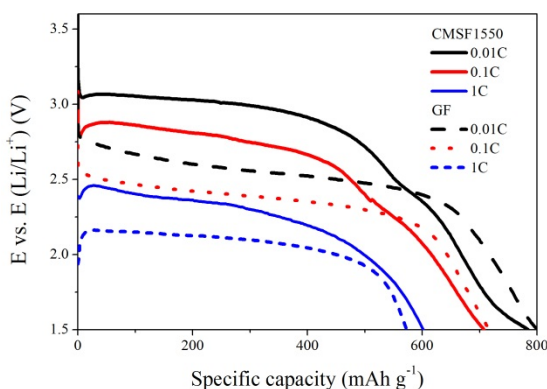


Fig. 5. Galvanostatic discharge profiles of CMF1550 and GF at different current densities

Table 3 Comparison of energy density between CMSF1550 and GF

| Current densities | Energy density (Wh kg ⁻¹) | | Ratio |
|-------------------|---------------------------------------|------|-------|
| | CMSF1550 | GF | |
| 0.01C | 2090 | 1933 | 1.08 |
| 0.1C | 1793 | 1659 | 1.08 |
| 1C | 1333 | 1175 | 1.13 |

4 Conclusions

The carbon molecular sieves (CMS) used in the experiment have a large number of impurities, which affect the discharge performance of fluorinated carbon molecular sieves (CMSF). The CMS after pyrolysis can be a good carbon source of fluorinated carbon materials and the products of fluorination have the characteristics of better discharge voltage and energy density compared with the fluorinated graphite. As the cathode of lithium primary batteries, the CMSF1550 possesses the maximum energy density about 2090 Wh kg⁻¹ at discharge rate of 0.01C, associated with discharge potentials exceeding 3.1 V (vs. Li/Li⁺). And the energy density of CMSF1550 with 1333 Wh kg⁻¹ at discharge rate of 1C is about 13% higher than that of GF. The fluorinated carbon molecular sieve with the better electrochemical performances than fluorinated graphite as well as its low cost and scalable product demonstrated its great potential practicability in the field of lithium primary batteries.

References

- Lam P, Yazami R. Physical characteristics and rate performance of (CF_x)_n (0.33 < x < 0.66) in lithium batteries [J]. Journal of Power Sources, 2006, 153:354-359.
- Jérôme Giraudet, Céline Delabarre, Katia Guérin, Marc Dubois, Francis Masin, André Hamwi, Comparative performances for primary lithium batteries of some covalent and semi-covalent graphite fluorides, [J]. Journal of Power Sources. 2013, 221: 261-265.
- Liu Z C , Preparation and Energy Storage Performance of a Novel Carbon Fluoride Material: [D]. Xi'an: Northwest Institute of Nuclear Technology, 2014.
- Yazami R, Hamwi A, et al. Fluorinated carbon nanofibres for high energy and high power densities primary lithium batteries [J]. Electrochemistry Communications, 2007, 9: 1 850-1 855.
- Peng, C., et al., Ultrahigh-energy-density fluorinated calcinated macadamia nut shell cathodes for lithium/fluorinated carbon batteries. Carbon, 2019. 153: p. 783-791.
- Zhang S S, Donald Foster, Jeffrey Read. Enhancement of discharge performance of Li/CF_x cell by thermal treatment of CF_x cathode material [J]. Journal of Power Sources. 2009, 188: 601-605.