

Fluorinated Ketjen-black as Cathode Material for Lithium Primary Batteries

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Abstract. Lithium/fluorinated carbon (Li/CF_x) batteries are the highest-energy-density primary batteries which are widely used in various field. Herein, the novel fluorinated carbon (CF_x) with superior performance are made of fluorination of ketjen-black. The fluorinated ketjen-black (F-KB) as the cathode material of Li/CF_x delivered a high specific capacity over 880 mAh g⁻¹ with a discharge plateau ~ 3.1 V (vs. Li⁺/Li). The energy density over 2400 Wh kg⁻¹ for F-KB is higher than the theoretical energy density (2180 Wh kg⁻¹) of fluorinated graphite. F-KB can be discharged at high rate of 5C delivering a high-power density of 9710 W kg⁻¹ with the energy density of 1610 Wh kg⁻¹, showing good performance of rate capability.

1 Introduction

As is known to all, the solid-state lithium primary batteries have the highest specific energy. Fluorinated carbons (CF_x) used as the cathode of the lithium primary batteries have a very high theoretical energy densities (2180 Wh kg⁻¹ with x=1 for fluorinated graphite)[1] comparing with other primary lithium batteries such as Li/SOCl₂ (1470 Wh kg⁻¹) batteries and Li/MnO₂ (1005 Wh kg⁻¹) batteries[2]. Due to the advantage of theoretical energy densities, a wide operating temperature, long storage life, reliability, and so on[3], lithium/fluorinated carbon (Li/CF_x) batteries have been widely used in many civil and military applications[4]. Despite the intriguing merits of Li/CF_x batteries, the weak intrinsic conductivity of CF_x and high polarizability of Li/CF_x cell impeded the practical application[5]. Been considered to be one of the most important factors for poor rate performance of Li/CF_x batteries, the poor conductivity makes the actual capacity lower than the theoretical for Li/CF_x batteries and the initial voltage delay[6]. Consequently, various efforts have been used to enhance the conductivity of CF_x compounds for improving the electrochemical performance of Li/CF_x batteries.

In this study, a fluorinated ketjen-black(F-KB) was prepared by a direct gas fluorination of ketjen-black. As the cathode material in Li/CF_x batteries, the F-KB has a high energy density over 2400 Wh kg⁻¹ higher than the theoretical value (2180 Wh kg⁻¹) of fluorinated graphite. The maximum power density for Li/CF_x could be as high as 9710 W kg⁻¹ (F-KB) with the energy density of 1610 Wh kg⁻¹ showing good performance of rate capability.

2 Experimental

2.1 Material synthesis

Ketjen-black was directly purchased from Japan Lion Specialty Chemicals Co., Ltd. Before the fluorination, the ketjen-black was dried at 200 °C for 2 hours in vacuum. After the drying, the ketjen-black was fluorinated in a pure nickel reactor using pure NF₃ gas at temperature of 510 °C by 5 hours. The fluorinated products named as F-KB. Fluorinated graphite (FG) was purchased from Japan Daikin Industries, Ltd.

2.2 Material characterization

FT-IR spectra was 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 CuKα radiation. XPS analysis was measured with a spectrometer (PERKINELMZRPHI 3056) with an Al anode source operated at 15 kV. TG-DSC of materials was performed on SDT Q600 V8.0 Build 95 heated to 800 °C in N₂ at a rate of 10 °C min⁻¹. The N₂ adsorption/desorption isotherms and Brunauer-Emmett-Teller (BET) surface area was measured using an Autosorb-iQ instrument.

2.3 Electrochemical measurements

The cathode was papered by fluorinated compounds, acetylene black, polyvinylidene fluoride (PVDF) in a weight ratio of 8:1:1. The fluorinated compounds were F-KB and graphite fluorides (GF; Daikin. Japan) respectively. Each cathode comprises the active materials loading as between 1.5 and 2 mg cm⁻². Li 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

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battery test system at 25°C, and the cut-off voltage was 1.5 V.

3 Results and discussions

3.1 structural characterization

The chemical structures of kejeten-black, fluorinated graphite (FG,) and fluorinated kejeten-black (F-KB) were studied by the Fourier-transform infrared (FT-IR) spectra, and the spectra are showing in Fig.1. There were no obvious absorption peaks for KB in the FT-IR spectra, indicating no oxygen-containing organic groups in KB. The FG and F-KB exhibit intense band at the wavenumber of 1196 cm^{-1} , which is the stretching vibration of covalent C-F bond. The FT-IR spectra shows that the strength of C-F bond of FG is stronger than C-F bond of F-KB. The band existed at around the wavenumber of 1330 cm^{-1} indicated the existence of $-\text{CF}_2$ groups. There are no obvious absorption peaks for FG in the FT-IR spectra at about wavenumber of 1100 cm^{-1} because of the low content of semi-ionic C-F bands. But, the semi-ionic C-F bonds are existed in the chemical structure of F-KB duo to the absorption peaks for F-KB in the FT-IR spectra at about 1100 cm^{-1} . The $-\text{CF}_3$ groups are still found because of the absorption peaks for FG and F-KB in the FT-IR spectra at about 670 cm^{-1} .

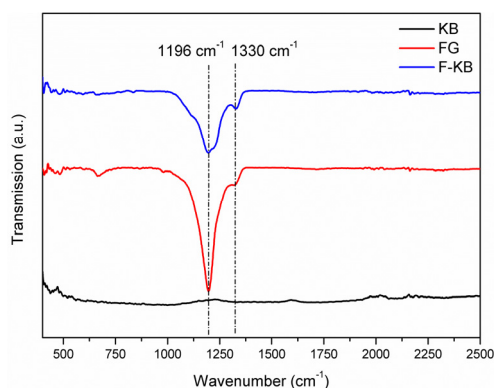


Fig1. FT-IR images of KB, FG and F-KB

The XRD patterns of KB, FG and F-KB are showing in the Fig.2. The tow diffraction peaks of KB located at

nearly 24° and 43°, responding to (002) and (100) reflection of graphite structure. This signified that there are some graphic domains stacking in the pristine KB. Using the Bragg equation, the (002) layer spacing of KB is calculated to be 0.370nm which is bigger than the theoretical value of graphite (0.335 nm).After fluorination, the new phase of F-KB appears according to the diffraction peaks at 12.6°and 41°attributed to the diffraction of (001) and (100) lattice plane of fluorinated graphite, which means the graphic structure in pristine KB were destroyed by NF_3 molecules at high temperature.

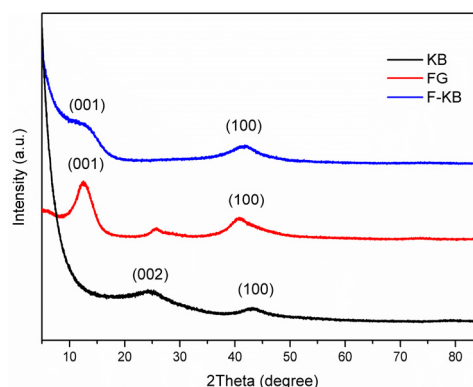
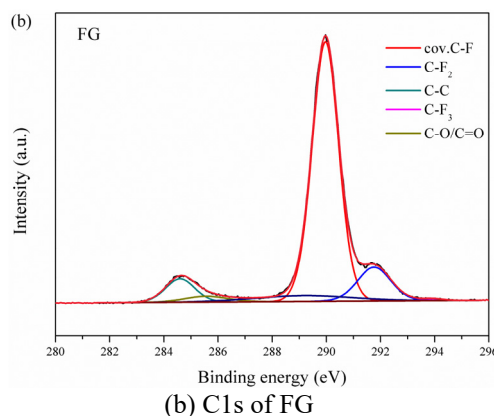
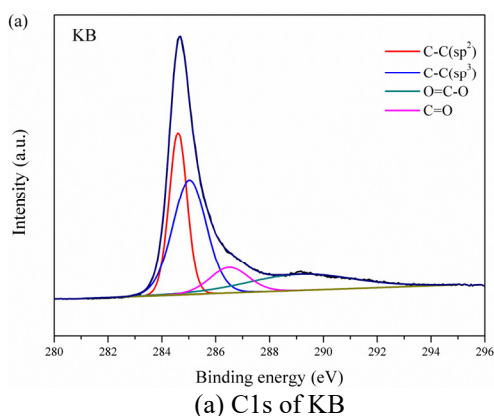


Fig2. XRD images of KB, FG and F-KB

The chemical states of C elements for KB, FG and F-KB are analysed by high resolution XPS (shown in Fig.3). There are four different states of carbon species fitting to the C1s spectrum of KB at binding energy of ~ 284.6 eV for sp^2 -type C-C, ~ 285.02 eV for sp^3 -type C-C, ~ 286.5 eV for C=O and ~ 289.1 eV for O=C-O[7]. After the fluorination, the O=C=O disappears and many C=C bands changes to C-F bonds. The C=C bond still exist in the XPS spectra of F-KB means that the carbon atoms are not completely fluorinated. The big difference between the XPS spectra of FG and F-KB is that there are semi-ionic C-F bond peaks for F-KB located at binding energy of ~ 286.8 eV, which is consistent with the FT-IR analysis. Previous studies have shown that semi-ionic C-F bonds could effectively improve electron transport and the rate capability of Li/CF_x batteries[8].



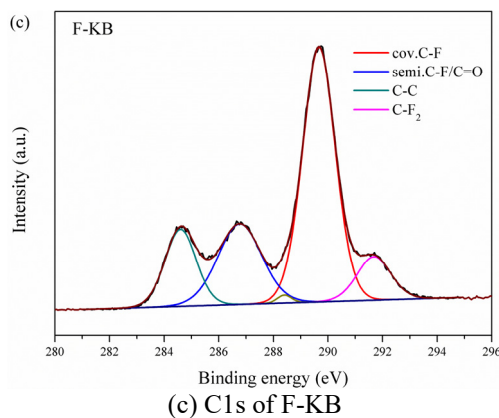


Fig3. High resolution C1s spectra of KB, FG and F-KB

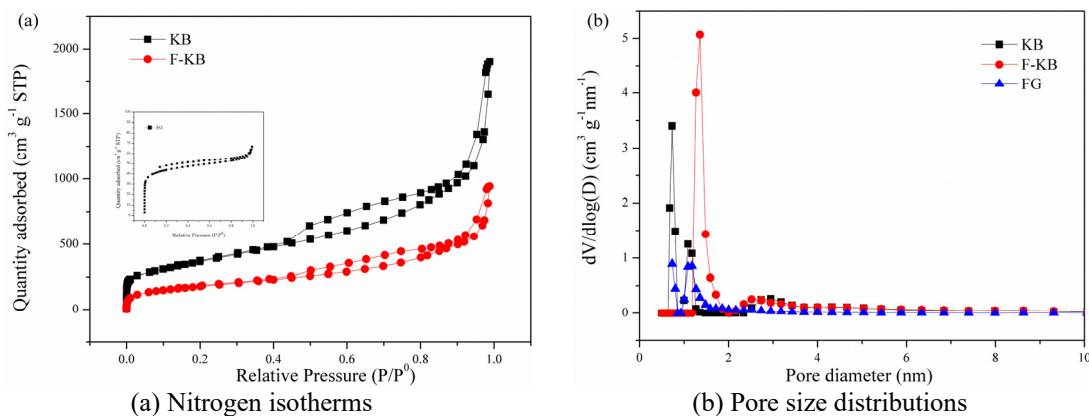


Fig4. Nitrogen isotherms and pore size distributions of KB, FG and F-KB

The surface characterizations of KB and F-KB as shown in Fig.4 were measured using Brunauer-Emmett-Teller (BET) method. The N₂ adsorption-desorption isotherm of KB and F-KB could be classified as type IV, which means that the structures have large amount of micropores and mesopores. The specific surface areas for KB, F-KB and FG were measured to be 1321.4 m²g⁻¹, 651.7 cm² g⁻¹ and 144.8 cm² g⁻¹ respectively. The pore sizes of the KB, FKB and FG are analysed based on

nonlocalized density functional theory (NLDFT). The micropores were enlarged and the mesopores still existed by fluorination which might promote lithium ion transfer.

As showing in Fig.5, the TG-DSC were used to test the thermal stabilities of KB, FG and F-KB under N₂ atmosphere. The decomposition of F-KB starts at 570.0 °C, which is lower than 618.9 °C for FG. The result suggests that the C-F bond of F-KB is much weaker than that of FG, which is agree with the results obtained by FT-IR.

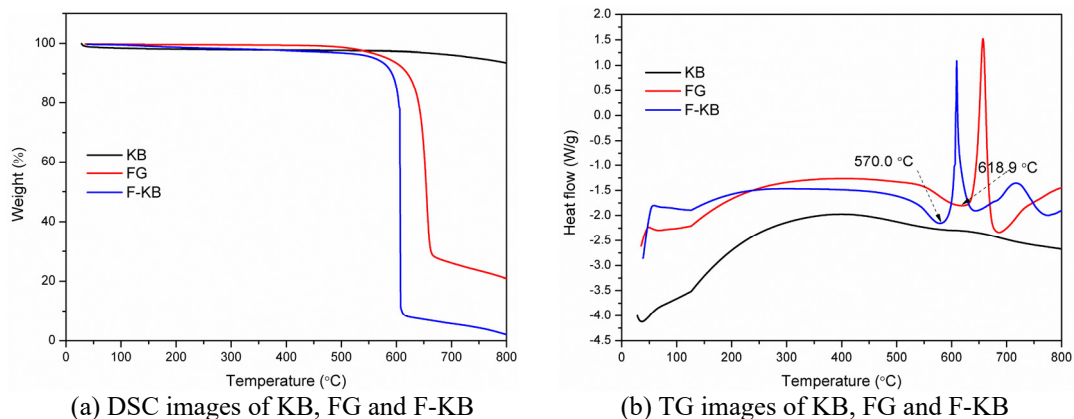


Fig5. Thermal analysis of KB, FG and F-KB

3.2 Electrochemical performance

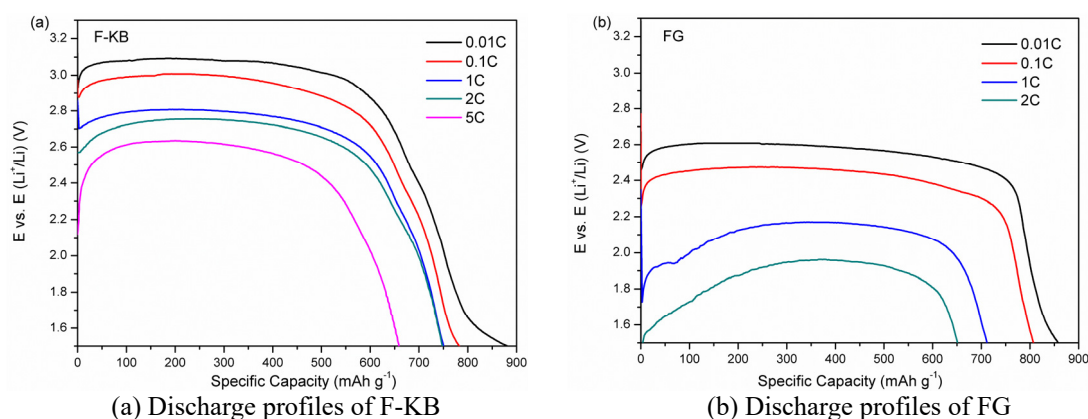


Fig6. Galvanostatic discharge profiles of F-KB and FG at different current densities

The electrochemical performance of F-KB and FG as cathode materials of Li/CF_x batteries investigated at different discharge rate with a potential cut-off of 1.5 V are showing in Fig.6. The F-KB material delivers a specific capacity of 880 mAh g⁻¹ with a discharge plateau ~ 3.1 V at 0.01C, which is better than 850 mAh g⁻¹ with a discharge plateau ~ 2.6 V for FG. The specific capacity of F-KB was higher than its theoretical values probably because of the side reactions of intermediates with electrolyte components. The energy density for F-KB up to 2400 Wh kg⁻¹ is much better than 2130 Wh kg⁻¹ for FG at 0.01C. With the discharge rate increases, the voltage hysteresis for F-KB is superior to that for FG. When the discharge rate is over 2C, FG as the cathode materials of Li/CF_x cannot give off electricity. But the F-KB still maintain very good electrochemical performance. Due to the part of the carbon atoms with fluorine atoms in the form of sp² hybridization combination and the non-fluorinated carbon atoms which maintain the original porous structure, enhanced the conductivity of fluoride products and improved the lithium ion diffusion rate, the rate capability of F-KB as the cathode of Li/CF_x batteries have been greatly improved. Comparable to fluorinated nanotubes and nanofibers, F-KB as the cathode material has a specific capacity of 650 mAh g⁻¹ with a discharge plateau ~ 2.6 V, and the maximum power density is up to 9710 W kg⁻¹ at 5C.

4 Conclusions

The fluorinated ketjen-black (F-KB) has been papered through direct fluorination with NF₃ gas and ketjen-black at 510 °C. The structural feature of F-KB displays that large layer spacing, the certain amount of semi-ionic C-F and huge number of micropores and mesopores facilitated electron and lithium ion transfer. The F-KB as cathode material of Li/CF_x batteries has excellent electrochemical performance. The F-KB possesses the maximum energy density over 2400 Wh kg⁻¹ at discharge rate of 0.01C. The maximum power density for Li/CF_x could be as high as 9710 W kg⁻¹ (F-KB) with the energy density of 1610 Wh kg⁻¹ at discharge rate of 5C. The high specific capacity and excellent power density make the F-KB material has the potential to become a cathode material for Li/CF_x batteries.

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