

CF_x-Cu Composites with Excellent High Rate Performances as Cathode Materials for Lithium Primary Batteries

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Abstract: CF_x-Cu cathode materials for primary lithium battery were prepared by a simple and novel in-situ chemical modification method with high-temperature calcination process. The structure, morphology, reaction mechanism and electrochemical performance of cathode materials were characterized by X-ray powder diffraction, high-resolution transmission electron microscopy, scanning electron microscope, energy dispersive X-ray spectroscopic, thermo gravimetric analysis, cyclic voltammetry and galvanostatic discharge. It can be inferred that copper oxide reacts with inert groups on the surface of CF_x to produce nano-copper particles, which increases the electronic conductivity and diffusion performance of lithium-ion in the CF_x-Cu cathode materials. Therefore, the composite exhibits excellent specific capacity, rate performance and power density. Specifically, the CF_x-Cu composites shows a high discharge specific capacity of 546 mAh/g, and a maximum power density of 8393 W/kg, with a discharge voltage platform of 2.0 V at 5 C.

Key words: CF_x-Cu cathode materials; lithium battery; high rate performance

Lithium primary batteries have entered the field of vision since the 1970s and show broad market prospects after more than 50 years of development. Lithium primary batteries have been widely used in military, aerospace and advanced medical equipment because of their advantages of high voltage, high specific energy, long storage life and high power density. As one of cathode materials in lithium primary batteries, fluorinated carbon (CF_x) materials have attracted many scholars' attention. The methods of synthesizing CF_x were mainly divided into fluorination and exfoliation^[1]. Fluorination is mainly divided into direct gas fluorination, plasma fluorination, hydrothermal fluorination and photochemical/electrochemical synthesis. Different carbon sources, such as graphite, carbon nanotubes, carbon fibers, carbon 60 and mesoporous carbon, were used to fluorinate to get CF_x materials^[2-8]. Exfoliation mainly includes sonochemical exfoliation, thermal exfoliation and modified Hummer's exfoliation. Nowadays, CF_x materials have dominated the primary battery market and poured into our daily life owing to their high specific energy (2180 (Wh)/kg), wide operational temperature range (-40 °C ~170 °C) and long storage life^[9-13]. However, the low electronic conductivity of CF_x cathode material

has led to a strong polarization, low voltage platform and poor high rate performance of Li/CF_x batteries, which has driven researchers to overcome the above mentioned problems by different strategies^[14-18]. For instance, conductive polymer, conductive carbon or oxides or using subfluorinated carbon materials are added to improve electronic conductivity of CF_x, but the disadvantage of this method is that the preparation process is complicated and the conditions are relatively rigorous. In addition, although subfluorinated carbon materials have better power density, they have lost capacity at the cost.

Herein, we present a simple in-situ chemical modification to prepare CF_x-Cu composites. Copper has long been considered as a metal with good conductivity, environmentally friendly and cost-effectiveness, which is widely used in electrical, light industry, machinery manufacturing, construction industry, national defense industry and other fields. Moreover, metal Cu supported on carbon-based materials, such as ordered mesoporous carbon, starch-derived carbon, graphene and hollow carbon spheres, have been widely investigated^[19-22]. However, few studies have been done to improve the conductivity of CF_x as cathode material for

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lithium primary batteries by Cu modification. In this paper, we have synthesized CF_x -Cu composites by a simple and novel method and the CF_x -Cu composites show a discharge capacity of 546 mAh/g at a rate of 5 C with a maximum power density of 8393 W/kg. We infer that the introduction of Cu and the decrement of electrochemically inactive CF_2 after the reaction of CuO and CF_x are the most critical factors to achieve high rate performance, high power densities with high energy densities according to the TGA results. In addition, our method of synthesizing CF_x -Cu materials with superior performance is simple and easy for scale-up, exhibiting a good application prospect.

1 Experiment

CF_x -Cu composites were prepared by in-situ modification method at room temperature. First, CF_x (Hubei, graphite precursor) was placed into mixture of water/ethanol (20 mL) and stirred for 30 min to obtain homogeneous solution. $CuSO_4 \cdot 5H_2O$ (purchased from the Beijing Changping Jingxiang Chemical Factory, China) was dispersed into the above solution and continuously stirred for 10 min in a water bath. Then, 0.1 mol/L NaOH (purchased from the Tianjin Fuchen Chemical Reagents Factory, China) was dropped into the solution to keep the pH value at 8–9 followed by continuous stirring for 6 h. After that, the precipitates were washed with deionized water and alcohol several times, and freeze-dried overnight. Finally, the mixture was annealed at 450 °C for 3 h under N_2 atmosphere to get the CF_x -Cu composites. For comparison, the pure CuO was synthesized by the same method while without CF_x adding. The material preparation process is shown in Fig.1.

The structure and morphology of the samples were investigated by an X-ray powder diffraction (XRD, Cu $K\alpha$ radiation

$\lambda=0.15406$ nm in a 2θ range from 10° to 80°), high-resolution transmission electron microscopy (HRTEM), scanning electron microscope (SEM) and energy dispersive X-ray spectroscopic (EDS). Thermo gravimetric analysis (TGA) was performed by a TG/DTA6300 thermal analyzer from 40 °C to 800 °C under N_2 atmosphere with a rate of 5 °C/min.

The working cathodes consisting of active material, carbon black and PVDF as a binder (80:10:10, mass ratio) were mixed in N-methyl-2-pyrrolidinone (NMP) to form a uniform slurry. The slurry was coated on Al foil and then transferred to an oven at 80 °C for 6 h. After that, electrode foil was cut into 14 mm disks and dried in a vacuum oven at 120 °C for 24 h. The coin-type cells (CR2032) were assembled using the metallic lithium disc as the anode, 1 mol/L LiPF₆ in ethylene carbonate (EC) and dimethyl carbonate (DMC) ($v/v=1:1$) as electrolyte and a polypropylene (pp) membrane as a separator in a MBRAUN glove box ($H_2O < 0.5 \mu L/L$, $O_2 < 0.5 \mu L/L$). Finally, the batteries were tested at various current rates with a cut-off voltage of 1.5 V. The Cyclic Voltammetry (CV) test and the electrochemical impedance spectroscopy (EIS) test were conducted on an electrochemical workstation (VMP3, Bio-Logic SA).

2 Results and Discussion

The XRD patterns of pristine CF_x and CF_x -Cu are shown in Fig.2a. All samples have three typical wide peaks at $2\theta=13.4^\circ$, 25.7° and 41.2° assigned to the diffraction from (001), (002) and (100) planes, respectively, which indicate that no structural change occurs in the pristine CF_x during the process of Cu modification. The peaks around 13.4° and 41.2° could be associated with a hexagonal system and C–C in-plane length in the reticular system^[23-25]. The less sharper peak around 25.7° corresponded to the characteristic graph-

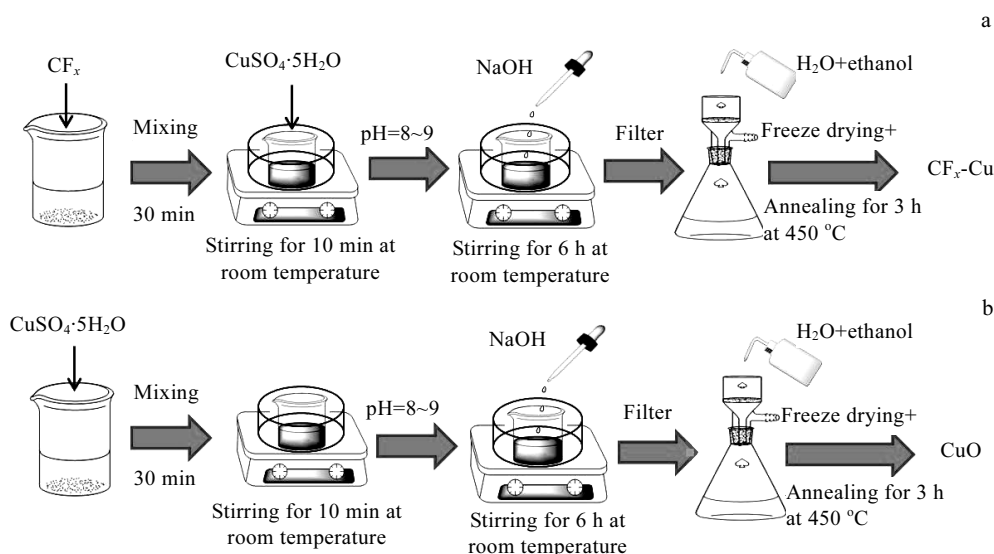


Fig.1 Schematic illustration for preparation of CF_x -Cu (a) and CuO (b) samples

itic peak, which was attributed to a poor regularity along the stacking direction^[26, 27]. From the XRD pattern of CF_x-Cu, three diffraction peaks located at 44.3°, 50.4° and 74.1° perfectly match with the Cu (111), (200) and (220) planes, respectively (JCPDS: 04-0836). As a comparison, we also measured the samples prepared under the same experimental conditions without adding CF_x. All the diffraction peaks in Fig.2b could be perfectly indexed as the CuO (JCPDS: 48-1548) and thus we infer that CF_x reacts with the modified materials to form metallic Cu and the reaction mechanism will be further discussed.

Fig.3 shows the thermogravimetric (TG) curves of the pristine CF_x and CF_x-Cu composites. It can be seen that the two samples show significant mass loss, especially at 450 °C. The mass loss rate of the pristine CF_x material is about 11.31%, which is mainly due to the thermal decomposition of CF_x material surface to form volatile fluorocarbons^[28]. The mass loss rate of CF_x-Cu composite is about 14.17%, which is significantly higher than that of the pristine CF_x material. According to the literature^[29-31], Cu complexes could be effective defluorination reagents with unique ability to react with C-F bonds. Therefore, we believe that the mass loss of CF_x-Cu composites comes not only from the thermal decomposition of CF_x surface, but also from the reaction of CuO with inert groups such as CF₂ on the surface of CF_x.

Fig.4 shows the SEM images of the pristine CF_x material and the CF_x-Cu composite prepared by in-situ composite. It can be seen from Fig.4a that the appearance of the CF_x material is irregularly layered particles and the

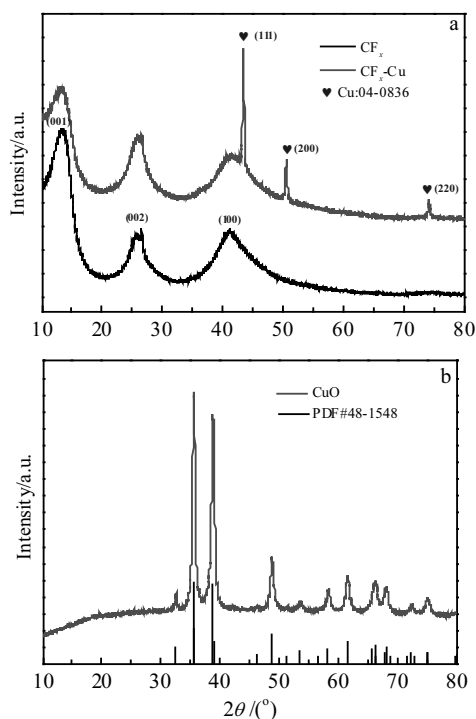


Fig.2 XRD patterns of CF_x, CF_x-Cu (a) and CuO (b)

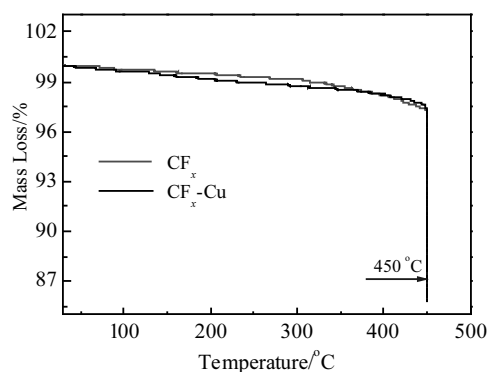


Fig.3 TG curves of CF_x and CF_x-Cu

particle size is about 10 μm. In addition, the pristine CF_x material has a smooth appearance, which indicates that the conductivity of the material itself is poor. From Fig.4b, we can find that CF_x-Cu composites still retain the layered structure of the material before modification, but the surface of the material is rough, the edges and corners are clearly visible, and many cracks appear. The broken surface of modified CF_x material is conducive to the formation of more active sites and the shortening of lithium ion migration path.

It is difficult to observe the presence of Cu in the SEM images of CF_x-Cu composites, so we tested the prepared materials by the elemental distribution map and the results are shown in Fig.5. From Fig.5, we can find the existence of copper, but the distribution is not uniform. In order to further observe the morphology of Cu and the distribution of copper on CF_x, TEM tests were carried out on CF_x-Cu composites. It can be clearly seen from Fig.6 that the Cu particles have a large size and agglomeration after high-temperature heat treatment.

Fig.7 shows HRTEM images of CF_x-Cu. From Fig.7, we can clearly observe the diffraction image of the black area in the red frame region by Fourier transform. The lattice spacing measured by inverse Fourier transform is about 0.208 nm, which corresponds to the (111) crystal plane of metal Cu. This is consistent with the data measured by XRD. The analysis of EDS, XRD and HRTEM shows that CF_x materials modified by metal Cu are successfully prepared.

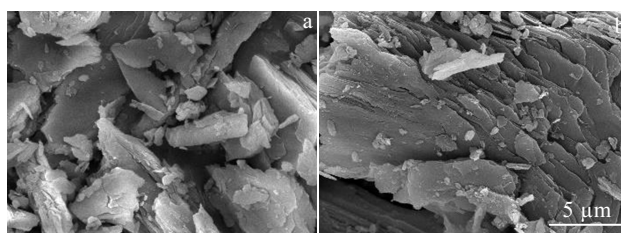


Fig.4 SEM images of the samples: (a) pristine CF_x and (b) CF_x-Cu

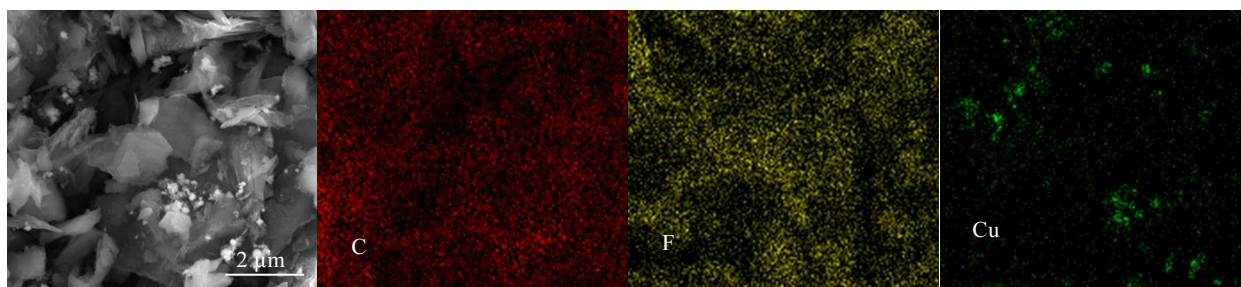


Fig.5 EDS element mapping of the modified sample CF_x -Cu

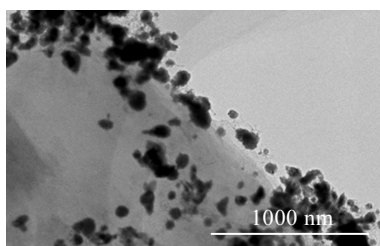


Fig.6 TEM image of the modified sample CF_x -Cu

Fig.8a~8b display the galvanostatic discharge curves of pristine CF_x and CF_x -Cu composites at different rates from 0.5 C to 5 C. Electrochemical performance of CF_x and CF_x -Cu cathodes are listed in Table 1. As shown in Fig.8a, the pristine CF_x exhibits specific discharge capacities of 665, 611, 603, 495 and 217 mAh/g at 0.05, 0.5, 1, 2 and 5 C, with plateau of 2.4, 2.2, 2.1, 1.8 and 1.7 V, respectively. Obviously, with the increase of current density, the discharge capacity and voltage decrease sharply, which is due to the poor intrinsic conductivity of CF_x materials. However, the CF_x -Cu composites exhibit high specific discharge capacities of 697, 656, 646, 618 and 546 mAh/g at 0.05, 0.5, 1, 2 and 5 C, with plateau of 2.5, 2.4, 2.2, 2.1 and 2.0 V, respectively. The superior electrochemical performance of CF_x -Cu may be attributed

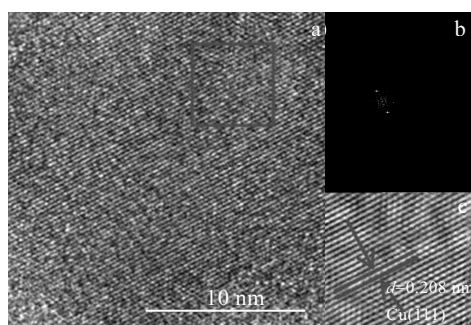


Fig.7 HRTEM images of CF_x -Cu (a); Fourier transformed (FT) pattern (b); inverse fast Fourier-filtered FT (IFFT) image (c) of the red box regions in Fig.7a

to the formation of copper with excellent conductivity and the consumption of inert groups on the surface of CF_x by in-situ composite. As shown in Fig.8c and Fig.8d, a Ragone plot and the Gravimetric energy densities are given to compare the performance of the pristine CF_x and CF_x -Cu at different discharge rates. The Ragone plot shown in Fig.8c demonstrates that the energy density and power density of CF_x -Cu are significantly higher than those of pristine CF_x . Meanwhile, with the increase of power density, the energy density of pristine CF_x decreases faster than that of CF_x -Cu. It is clearly observed that CF_x -Cu exhibits greater energy density than CF_x at all rates. At 5 C, the energy density of the former is almost three times that of the latter.

The Nyquist plots of the cells with CF_x -Cu and pristine CF_x as cathodes at discharge states are shown in Fig.9. All plots show semicircle portion at high frequency region and slanted straight portion at low frequency region. It is well known that the semicircle portion is related to charge transfer resistance at the electrolyte/electrode interface. Obviously, the modification of copper reduces the charge transfer impedance, making it drop to about half of that of the original CF_x . This result indicates that the introduction of metallic Cu improves the conductivity of the material, thus leading to a lower polarization, a higher discharge capacity and rate capability.

To further evaluate the samples' electrochemical performance, the CV measurement of pristine CF_x and CF_x -Cu electrodes were performed at a scan rate of 0.05 mV/s. As shown in Fig.10, the reduction peaks of the original CF_x and CF_x -Cu electrodes are about 2.06 and 2.25 V, respectively, which can be attributed to the reaction between CF_x and lithium-ion. Comparing the CV curves of all samples, it can be seen that the reduction peak area of CF_x -Cu material is larger than that of pristine CF_x material, which indicates that the CF_x -Cu materials have a higher discharge capacity and rate capability. Meanwhile, the peak position of CF_x -Cu shifted significantly to the positive potential, indicating that its polarization decreased. This result is consistent with impedance analysis.

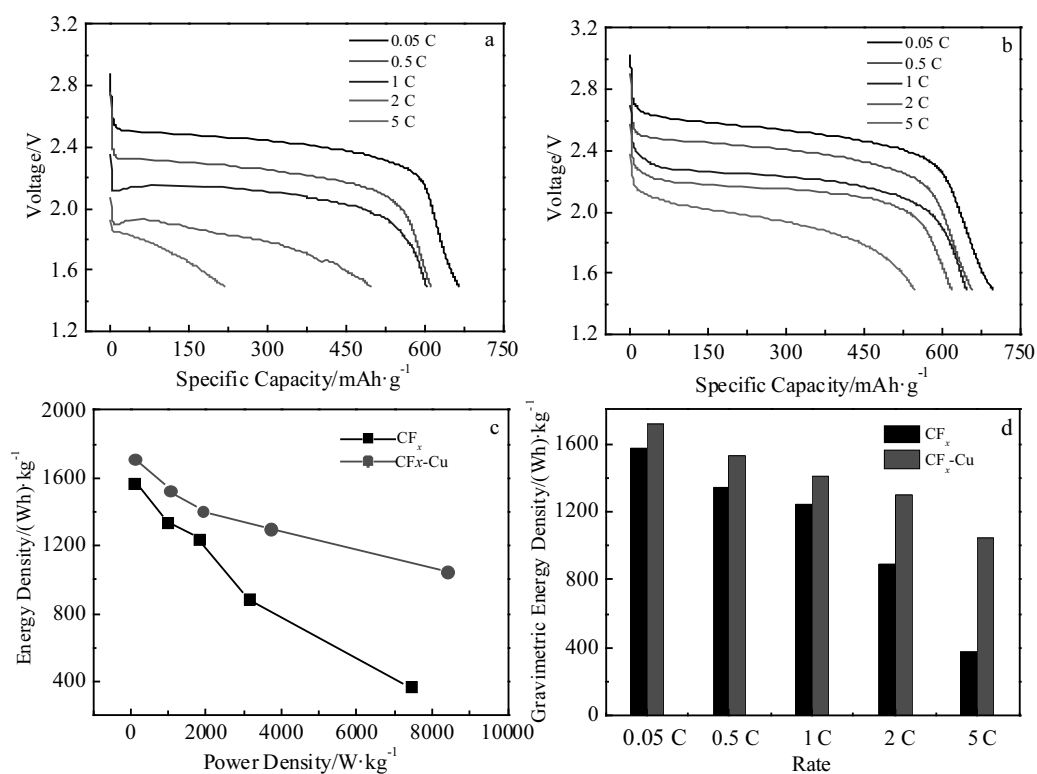


Fig.8 Galvanostatic discharge curves of CF_x (a), $\text{CF}_x\text{-Cu}$ (b); variation of energy density and power density (c), and gravimetric energy densities (d) of CF_x , $\text{CF}_x\text{-Cu}$ samples at different C-rates

Table 1 Electrochemical performance of batteries with CF_x and $\text{CF}_x\text{-Cu}$ cathodes

Samples	Rate	Average potential, E/V	Specific capacity/ $\text{mAh}\cdot\text{g}^{-1}$	Energy density/ $(\text{Wh})\cdot\text{kg}^{-1}$	Average power density/ $\text{W}\cdot\text{kg}^{-1}$
CF_x	0.05 C	2.4	665	1575	104
	0.5 C	2.2	611	1345	967
	1 C	2.1	603	1242	1816
	2 C	1.8	495	888	3121
	5 C	1.7	217	372	7418
$\text{CF}_x\text{-Cu}$	0.05 C	2.5	697	1715	109
	0.5 C	2.4	656	1529	1032
	1 C	2.2	646	1407	1915
	2 C	2.1	618	1302	3698
	5 C	2.0	546	1050	8393

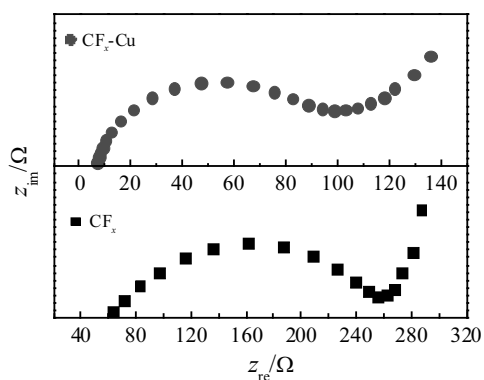


Fig.9 EIS spectra of CF_x and $\text{CF}_x\text{-Cu}$ cathodes

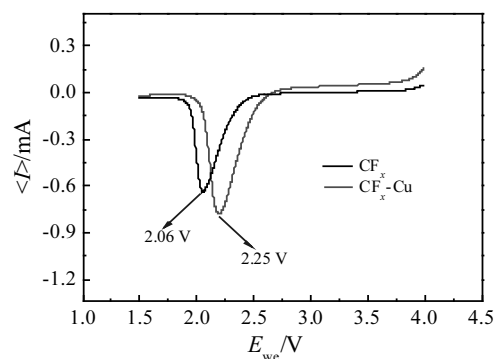


Fig.10 CV profiles of CF_x and $\text{CF}_x\text{-Cu}$ electrodes at a scanning rate of 0.05 mV/s

3 Conclusions

1) A novel cathode of $\text{CF}_x\text{-Cu}$ composite with nano/micro hierarchical structure was synthesized by a simple in-situ chemical modification method.

2) Compared to pristine CF_x , the $\text{CF}_x\text{-Cu}$ composites show higher discharge capacity, higher discharge voltage and higher rate capability. The $\text{CF}_x\text{-Cu}$ composites display a discharge capacity of $546 \text{ mAh}\cdot\text{g}^{-1}$, with a plateau of 2.0 V at a current density of 5 C, which is much higher than that of pristine CF_x .

3) The $\text{CF}_x\text{-Cu}$ composites achieve maximum power density of $8393 \text{ W}\cdot\text{kg}^{-1}$ and energy density of $1050 \text{ (Wh)}\cdot\text{kg}^{-1}$. The excellent electrochemical properties of $\text{CF}_x\text{-Cu}$ composites are attributed to the reduction of charge transfer resistance due to the interaction between CuO and CF_2 on the surface of CF_x .

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锂一次电池正极材料 $\text{CF}_x\text{-Cu}$ 的高倍率性能研究

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摘要: 采用一种简单新颖的原位化学改性方法制备了锂电池用 $\text{CF}_x\text{-Cu}$ 复合正极材料。采用 XRD、SEM、EDS、TGA、EIS、CV 和恒电流放电对正极材料的结构、形貌、反应机理和电化学性能进行了表征。 CuO 与分布在 CF_x 边缘或表面的非活性基团反应原位生成纳米铜, 有效地提高了材料的电子导电性和锂离子扩散率, 从而使改性材料显示出优异的比容量、倍率性能及功率密度。 $\text{CF}_x\text{-Cu}$ 复合材料在 5 C 的高倍率下, 其放电比容量高达 546 mAh/g , 最大功率密度为 8393 W/kg , 放电电压平台为 2.0 V。

关键词: $\text{CF}_x\text{-Cu}$ 正极材料; 锂电池; 高倍率性能

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