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The tunable electrochemical performances of carbon fluorides/manganese dioxide hybrid cathodes by their arrangements

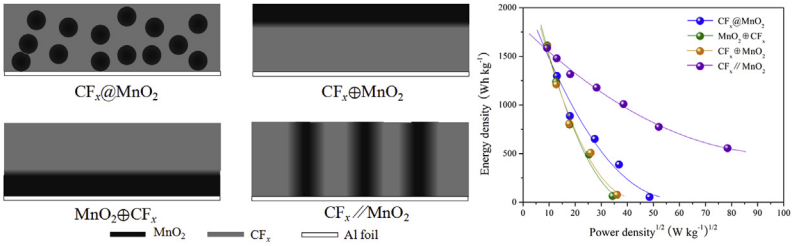
Yu Li [a, b], Wei Feng [a, b, *]

[a] School of Materials Science and Engineering, Tianjin University, Tianjin 300072, PR China
[b] Tianjin Key Laboratory of Composite and Functional Materials, Tianjin 300072, PR China

HIGHLIGHTS

- The arrangement of hybrid cathode on electrochemical performances is investigated.
- CF_x/MnO_2 hybrid cathode in parallel arrangement shows an excellent rate capability.
- The continuous MnO_2 phase in $CF_x||MnO_2$ guarantees the fast lithium ions diffusion.
- The charge transfer between MnO_2 and CF_x contributes to the rate improvements.

GRAPHICAL ABSTRACT



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ABSTRACT

The study investigates the effects of arrangements to the electrochemical performances of carbon fluorides (CF_x)/manganese dioxide (MnO_2) hybrid cathodes. When CF_x and MnO_2 are in parallel arrangement (denoted as $CF_x||MnO_2$), the hybrid cathode exhibits the best electrochemical performances than other types of arrangements, such as the mixed or stacked types. Based on the various electrochemical measurements, such as impedance spectra and galvanostatic intermittent titration technique, the charge transfer takes place at the interface of MnO_2 and CF_x particles because of the special arrangement in the $CF_x||MnO_2$ hybrid cathode, in which the continuous MnO_2 phase guarantees and facilitates the lithium ions transfer from electrolyte to current collector due to the lower charge transfer resistance. Therefore, $CF_x||MnO_2$ exhibits the best rate capability, and the maximum delivered power density is up to 6599 W kg^{-1} at 5C, associated with the energy density of 1814 Wh kg^{-1}.

1. Introduction

Although the mainly current interests in lithium ion technology focus on the secondary battery, lithium primary battery with optimal energy and power densities still remains an eminent need in electronics, medical implants, army applications, etc. Among the various cathodes, carbon fluorides (CF_x, $0 < x < 1.3$) present several unique advantages, such as flat discharge potential, high energy density, wide temperature range of use, etc [1,2]. Traditional CF_x are formed by high temperature intercalation of fluorine gas into graphite power and the utilization of CF_x as the cathode in primary lithium battery has been commercially realized in 1970s by the Matsushita Co.

However, the electrical conductivity of CF_x is very low due to the covalence of C–F bond, which leads to a serious initial voltage delay after discharge and the low rate capability, inhibiting the utilization of CF_x in high power devices. The preparation of sub-fluorinated graphite is an effective approach to improve the rate capability of

* Corresponding author. School of Materials Science and Engineering, Tianjin University, Tianjin 300072, PR China.
E-mail address: weifeng@tju.edu.cn (W. Feng).

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CF_x because of the presence of unfluorinated domains, facilitating electrons transport within CF_x, though the specific capacity of CF_x is decreased due to the lowered fluorine content [3,4]. According to the same mechanism, the thermal treatment of CF_x also improve the electrochemical performances due to the formation of sub-fluorinated carbons by the partial decomposition of CF_x during the carbothermal treatment [5,6]. The surface coating by conductive materials is another method to improve the electrochemical performances of CF_x because the coating layers enhance the electronic conductivity of CF_x particles [7,8]. Similarly, the optimization of conductive network in CF_x cathodes by adding some highly conductive additives, such as carbon nanotubes or graphene, has also been demonstrated to improve the rate capability of CF_x [9,10]. Recently, it was found that using nanostructured carbons to replace conventional natural graphite as the starting materials of CF_x improved its electrochemical performances significantly thanks to the special nanostructures [4,11–15].

Besides the methods mentioned above, the combination with other cathode materials with good rate capability, such as MnO_2 [16] or $Ag_2V_4O_{11}$ (SVO) [10,17,18], to form hybrid cathodes was considered to improve the rate capability of CF_x, but the progress is limited without significant improvements. Generally, the hybrid cathode is manufactured by mixing individual components with the help of ball milling. However, to the best of our knowledge, there have been few reports concerning the effects of components arrangements on electrochemical performances of hybrid cathode. By the consideration that MnO_2 is one of the cathode materials for lithium primary battery exhibiting a good rate capability [19], CF_x and MnO_2 hybrid cathodes with various arrangements were manufactured and the influence of components arrangements on the electrochemical performances was also investigated. In this study, four types of arrangements of hybrid cathodes are designed and the schematic diagram is shown in Fig. 1, in which CF_x and MnO_2 were mixed, stacked, and paralleled respectively. The results illustrates the electrochemical performances are significantly influenced by the arrangements of hybrid cathodes and the hybrid cathode exhibits the best electrochemical performances when CF_x and MnO_2 are parallel to each other. In addition, the mass ratio of CF_x and MnO_2 as well as the interval distance between scrapped CF_x lines in the parallel type hybrid cathode are investigated further. The mechanism of the improved electrochemical performances by the adjustment of arrangements is also discussed in this study.

2. Experimental

CF_x ($x = 1.0$) was purchased from Shanghai CarFluor Chemicals Co., Ltd. MnO_2 was purchase from Tianjin Kewei Reagent Co. and it was heated at 350 °C for 10 h before using. The morphology was observed by hitachi S-4800 field-emission scanning electron microscopy (SEM). The quantitative analysis of the elements was carried out by Genesis XM@ energy dispersive spectrometry (EDS). X-ray diffraction (XRD) measurements were performed on a Philips diffractometer, which was composed of a quartz monochromator, a Cu Kα radiation source at a scan rate of $10^\circ min^{-1}$ and a goniometric plate.

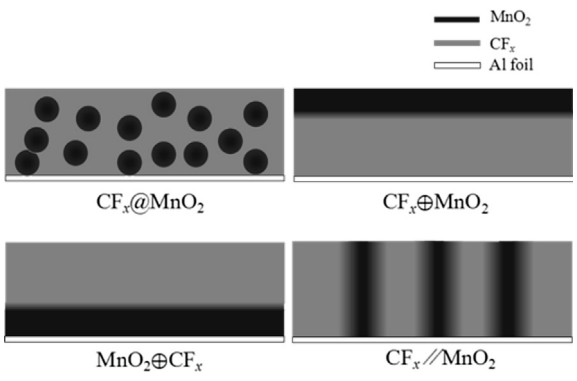

Fig. 1. The schematic arrangement diagrams of CF_x@MnO_2, $CF_x \oplus MnO_2$, $MnO_2 \oplus CF_x$ and $CF_x||MnO_2$.

Active material (80 wt%) (CF_x or MnO_2), polyvinylidene difluoride (PVDF, 10 wt%) and acetylene black (10 wt%) were stirred vigorously in the presence of N-methyl-2-pyrrolidinone to form a uniform slurry. In the case of mixed hybrid cathode (CF_x@MnO_2), the active material is the mixture of CF_x and MnO_2 (3:1, w/w). In the case of stacked hybrid cathode ($CF_x \oplus MnO_2$ or $MnO_2 \oplus CF_x$), the slurry of CF_x (or MnO_2) was cast on the aluminum foil at first and then the slurry of MnO_2 (or CF_x) was cast on the surface of the dried bottom layer subsequently. The mass ratio of CF_x to MnO_2 for $CF_x \oplus MnO_2$ and $MnO_2 \oplus CF_x$ was 2.97 and 3.08 measured by weighting, respectively. In the case of paralleled hybrid cathode ($CF_x||MnO_2$), the slurry of CF_x was cast on the aluminum foil at first and then some parts of dried CF_x film was scraped by lines carefully with the interval of 5.0 mm, with the help of a doctor blade. The slurry of MnO_2 was cast on the scraped out lines consequently and the mass ratio of CF_x to MnO_2 was 3.03 measured by weighting. The $CF_x||MnO_2$ hybrid cathodes with different mass ratio and interval distance were manufactured through the similar process. The mass ratio of CF_x and MnO_2 was chosen as 2:1, 3:1 5:1 and 10:1, respectively; the interval distance between scrapped CF_x was selected as 10.0, 7.5, 5.0 and 2.5 mm, respectively.

The manufactured films were then punched into required sizes and dried at 80 °C in a vacuum for 8 h. The prepared disks were then transferred into a glove-box filled with argon (Mikrouna Co., Advanced 2440/750) for the cell assembly. A metallic lithium disc and a microporous polypropylene/polyethylene/polypropylene film were used as the anode and the separator, respectively. The solution of 1 M $LiPF_6$ in EC:DMC (1:1, vol.) was utilized as the electrolyte. The button cells were discharged under constant current densities (Land CT2001A, Wu Han Jin Nuo Electronics Co., China) at room temperature. Electrochemical impedance spectroscopy (EIS) of a three-electrode electrochemical cell was measured in the frequency range from 0.01 Hz to 10 kHz using Advanced Electrochemical System Parstat 2263. Galvanostatic intermittent titration technique (GITT) was employed at a pulse of 0.05C for 20 min and with 4 h interruption between each pulse.

3. Results and discussion

The SEM images of these two kinds of cathode materials are shown in Fig. S1. The commercial CF_x particles exhibit the typical layer stacking structure, indicating it was made from graphite-like precursor, and the particle size is 10–15 μm. The irregular MnO_2 particles, with the particle size ranged from 50 to 200 nm, are obtained after the heat treatment. The crystal structures of these two kinds of cathode materials are characterized by XRD and the corresponding patterns are shown in Fig. S2. CF_x exhibits typical broad peaks centered at 13°, 26° and 41°, corresponding to the fluorinated phases. The XRD results clearly show that the phase identity of the received MnO_2 powder is γ-MnO_2 (ICDD-JCDPS No. 14–0644). Based on the XRD pattern, after the heat treatment, γ-MnO_2 is converted towards γ/β-MnO_2, which is in agreement with previous reports and γ/β-MnO_2 is proposed as the favorable type for Li/MnO_2 primary battery [20,21].

The galvanostatic discharge curves of pristine CF_x, MnO_2 and the hybrid cathodes are presented in Fig. 2, and the discharge current at different rates is calculated by the theoretical values (CF_x: