Enhanced electrochemical performance of fluorinated carbon nanotube as cathode for Li–O₂ primary batteries

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The electrochemical performance of fluorinated carbon nanotube (CF x, x = 0.31) is investigated as oxygen electrode for Li–O₂ battery. When compared with conventional carbon nanotube (CNT)-based electrode in Li–O₂ battery, the battery with CF0.31-based oxygen electrode exhibits significantly enhanced specific capacities and high-rate capability. For CF0.31-based Li–O₂ battery, two electrochemical reactions (oxygen reduction reaction and CF0.31 conversion reaction) occur during discharge process. The defects on the carbon nanotube after fluorination improves electrocatalytic activity of oxygen reduction on the material, and the loosely discharge products coated on the cathode due to the conversion of CF0.31 and reduction of oxygen occurred simultaneously provide further reactive sites on CF0.31 for oxygen reduction, is one of the main reasons for the enhanced electrochemical performance of fluorinated CNT. CF0.31 is shown as one promising material as oxygen electrode which can exhibit a good rate performance and a high specific energy density.

1. Introduction

Development of energy-storage systems with high energy density will prove extremely useful in a myriad of applications ranging from electric power driven vehicles to storing energy generated from renewable sources, e.g., wind energy and solar energy. Among rechargeable battery systems, lithium air battery has attracted much attention due to its highest theoretical energy density (11,140 Wh kg−1) [1]. However, designing batteries to actualize this estimated performance has been challenging [1–5]. Studies on the first polymer electrolyte-based rechargeable lithium/oxygen battery indicated that the discharge process mainly involves the reaction of oxygen with lithium to form the insoluble oxides of Li₂O₂ [1]. Another insoluble discharge product Li₂O in non-aqueous electrolyte was also reported by Read [2]. From these observations, the author suggested that the formation of a passivation layer at cathode limits discharge capacity by sealing off the reaction interface and preventing further oxygen reduction.

To eliminate the limitation of organic solvent on the cathode side, Wang and Zhou developed a novel Li–air battery with aqueous solution at the air–cathode side, non-aqueous electrolyte at

the Li-anode side and a super-ionic conductor glass film (LISICON) as a separator [6]. It delivers a discharge capacity as high as 50,000 mAh g⁻¹ as there is not any clogging of the porous cathode and the reaction between lithium and water is avoided. But the LISICON is the key factor affecting the cell performance because of its instability in alkaline solution. In addition, in non-aqueous electrolyte system, the interior structure, morphology, pore volume and particle size of carbon materials affect their catalytic performance for oxygen reduction and the discharge capacity [5,7,8]. It is found that high discharge capacity can be achieved by choosing superior carbon with high active area as oxygen diffusion electrode. It indicates that cathodes with large catalytically active area and high mesoporous volume facilitate oxygen diffusion and could provide much volume to store the discharge products, thus delivers high capacity. Furthermore, it was reported that doping of carbon with nitrogen could improve both the electrocatalytic performance for oxygen reduction and the discharge capacity of Li–O₂ battery [9,10]. Kichambare et al. [9] found that nitrogen doped KB600JD activated carbon exhibits two times higher capacity than that of the undoped one, which can be attributed to the higher surface area, porosity and catalytic activity toward oxygen reduction. In the other case, nitrogen-doped carbon nanotubes (CNTs) were proved to improve the reversibility of Li–O₂ battery due to its better electrocatalytic activity for Li₂O₂ decomposition compared to CNTs [10]. Carbon fluoride, i.e., fluorinated graphite, fluorinated nanotube, etc., as cathode for Li/CFx primary battery has been widely studied recently due to its highest theoretical capacity (865 mAh g−¹...
for \( x = 1.0 \) of all the cathode material for lithium primary battery [11]. As the theoretical discharge plateau of \( \text{Li/CF}_x \) battery is similar to \( \text{Li–O}_2 \) battery, the use of \( \text{CF}_x \) as cathode of \( \text{Li–O}_2 \) battery may combine two discharge reactions, thus achieve higher discharge capacity. Based on this, Xiao et al. developed a hybrid oxygen cathode of \( \text{CF}_x/\text{Ketjen black composite (weight ratio of 30:55) for Li–O}_2 \) battery, which delivers a high capacity of \( 935 \text{ mAh g}^{-1} \) at 0.1 mA cm\(^{-2} \) (about 5 mA g\(^{-1} \)) [12]. It would be very interesting to further study the detail electrochemical reaction mechanism on \( \text{CF}_x \) cathode during discharge process.

This paper describes the investigation of electrochemical reaction process of a lithium oxygen battery with fluorinated carbon nanotubes (\( \text{CF}_0.31 \)) as cathode material. XPS technique is also used to analyze the reaction products on carbon fluoride \( \text{CF}_x \) and understand the electrochemical process during discharge process. Raman and BET results also clarify the higher electrochemical catalytic activity of \( \text{CF}_x \) than that of pure CNTs.

2. Experimental

2.1. Chemicals

Multiwall carbon nanotubes (MWCNTs) were kindly provided by Prof. Hongzhang Zhang (Department of Chemistry, Xiamen University) [13]. Fluorinated CNTs were synthesized with 0.3 g CNTs at a temperature of 350 °C in a fluorinating gas atmosphere for 12 h. The fluorination level of the products were determined to be 31 mol% (ca. \( \text{CF}_x, x=0.31 \)) by quantitative \(^{1} \text{C} \) Solid State Nuclear Magnetic Resonance (ssNMR) [14]. PUROLYTE® 80000 electrolyte (1 M LiClO\(_4\)/Propylene Carbonate (PC)/1, 2-Dimethoxyethane (DME)/1, 3-Dioxolane/Ethyl Methyl Carbonate (EMC) (volume ratios of 3:5:10:2), \( \text{H}_2\text{O} < 20 \text{ ppm} \)) was bought from NOVOLOYTE Technologies.

2.2. Characterization of \( \text{CF}_0.31 \) and MWCNTs

Powder X-ray diffraction (XRD) was carried out using PANalytical X’Pert diffractometer with Cu Kα radiation from 5° to 80° at a scanning rate of 0.0167° per 10 s.

The disorder of the carbon-based samples was analyzed by Raman spectroscopy (LabRam I, Dilor, France), and the surface area was measured by Brunauer–Emmett–Teller (BET) (JW-BK112).

2.3. Assembly and electrochemical measurements

\( \text{CF}_x \) based cathode was prepared with a composition of 80 wt% \( \text{CF}_x \), 10 wt% CNTs conductive additive and 10 wt% polyvinylidene fluoride (PVDF) binder by mixing calculated amounts of \( \text{CF}_x \), CNTs and PVDF in 1-methyl-2-pyrrolidone (NMP) solvent and then casting onto the nickel foam current collector, followed by drying at 120 °C for one night. Then the home-made cells for electrochemical test were assembled in small glass U tubes (inner diameter = 12 mm) with the prepared electrode as cathode, metallic lithium foil as the counter electrode and PUROLYTE® 80000 as the electrolyte. The assembly process was carried out in argon-filled glove box (\( \text{H}_2\text{O} < 5 \text{ ppm} \)). Carbon nanotube-based oxygen electrodes were prepared with a composition of 90 wt% CNTs and 10 wt% PVDF binder. The loading amount of CNTs or CNTs+\( \text{CF}_0.31 \) is about 9 mg cm\(^{-2} \). The batteries were operated in a gastight vessel continuously saturated with 1 atm of oxygen, the schematic diagram of the assembled Li–O\(_2\) battery is shown in Fig. 1. Electrochemical measurements were carried out galvanostatically at room temperature using Arbin BT-2043 battery test system. Electrochemical impedance spectra (EIS) were carried out using VersaSTAT MC Potentiostat/Galvanostat in the frequency range from 100 kHz to 0.1 Hz with ac oscillation of 5 mV. The spectra were obtained at open circuit potential (OCP) for cells before discharge and after discharge to various depths at different rates. All tests were performed at room temperature and all potential values were reported against Li/Li\(^+\).

2.4. XPS

The discharge products on oxygen electrodes were characterized using Quantum 2000 Scanning ESCA Microprobe with monochromatic Al Kα radiation (1486.6 eV). The batteries discharged to different voltages were disassembled in the Ar-filled glovebox, rinsed with dimethyl carbonate (DMC) twice to remove any electrolyte salts remaining on the electrodes surface and dried to eliminate the residual DMC and maintained dry under Ar to prevent reaction with air using a desiccator. The XPS analysis was performed under high vacuum conditions (less than 1 × 10\(^{-7} \) Pa). The binding energy of each peak in the XPS spectra was calibrated using contaminative C (284.8 eV). The analysis and peak-fitting of the XPS spectra were carried out by XPSPeak software.

3. Results and discussion

3.1. Characterization of MWCNTs and \( \text{CF}_0.31 \)

The structure of fluorinated MWCNT was characterized by XRD and Raman spectra. Fig. 2 shows the XRD patterns of pristine MWCNT and fluorinated MWCNT. Pristine MWCNTs shows a strong (0 0 2) graphite peak at 26° position of 26.0°, which indicates a highly crystalline graphite structure. After fluorination, the intensity of the (0 0 2) diffraction peak of \( \text{CF}_0.31 \) is significantly reduced indicating a reduction in graphitized structure with the formation of fluorinated CNT.

The most prominent features in the Raman spectra of carbon-based material are the so-called D band at 1360 cm\(^{-1} \) and G band at 1580 cm\(^{-1} \). The Raman spectra of pristine MWCNT and fluorinated
MWCNT are shown in Fig. 3. R value obtained from the intensity ratio of D-band peak and G-band peak ($R = I_D/I_G$) gives a degree of surface disorder [15]. The R value is 0.19 for MWCNTs, While nearly 1.67 for CF$_{0.31}$, indicating that the defects on MWCNT are increased after fluorination.

The surface area of CNTs is 81 m$^2$ g$^{-1}$ determined by BET measurements. While CF$_{0.31}$ shows an increased surface area of 195 m$^2$ g$^{-1}$, which may be due to the increased defects of CF$_{0.31}$ after fluorination.

3.2. Discharge characteristic

3.2.1. Discharge characteristic of the pure Li/CF$_{0.31}$ battery

The fluorinated carbon nanotube such as CF$_{0.31}$ can be used as cathode operating under Ar atmosphere (Fig. 4), it is just considered as Li/CF$_{0.31}$ primary battery. It shows a specific capacity of 387 mAh g$^{-1}$ at 30 mA g$^{-1}$ and sloping discharge profile when discharged to 1.5 V vs. Li/Li$^+$. According to literature, lithium intercalation into CNT mainly takes place at the potentials below 0.3 V vs. Li/Li$^+$ [16], thus there is no capacity contribution from CNT conductive additive in these cells at the potential region studied (OCP – 1.5 V). It is generally accepted that the conversion reaction during CF$_x$ discharge process can be described as Eq. (1):

$$\text{CF}_x + x\text{Li}^+ + xe^- \rightarrow \text{C} + x\text{LiF}$$

(1)

3.2.2. Discharge characteristic of the Li–O$_2$ battery with CNTs and CF$_{0.31}$ cathode

Fig. 5a–c show the discharge curves of the Li–O$_2$ battery with CF$_{0.31}$ and CNT based oxygen electrode at 30, 70 and 100 mA g$^{-1}$ at 1 atm O$_2$ pressure, the discharge curves of Li/CF$_{0.31}$ primary battery with CF$_{0.31}$ based cathode in Ar are also given for comparison. It shows that remarkably higher discharge capacity can be obtained from the battery with CF$_{0.31}$ based cathode than CNTs based cathode, especially at high current density. At a current density of 30 mA g$^{-1}$, CF$_{0.31}$ shows a capacity of 1007 mAh g$^{-1}$ which is higher than that of CNTs (682 mAh g$^{-1}$). When the current density increases to 100 mA g$^{-1}$, CF$_{0.31}$ still delivers a high capacity of 676 mAh g$^{-1}$, while the discharge capacity of CNTs dramatically decreases to only 188 mAh g$^{-1}$. It can be also seen that the capacity of the battery with CF$_{0.31}$ cathode discharged in O$_2$ is significantly higher than that of the battery with CF$_{0.31}$ cathode discharged in Ar.
Apparently, the discharge process only involves the conversion reaction of CF0.31 for pure Li/CF0.31 primary battery (Fig. 4) or reduction of O2 for CNT based Li–O2 battery. However, CF0.31 based Li–O2 battery combines two electrochemical reactions, i.e., oxygen reduction reaction and CF0.31 conversion reaction. Therefore, the discharge capacity of CF0.31 based Li–O2 battery is a sum of the capacities of these two reactions theoretically. By subtracting the capacity contribution of CF0.31 conversion reaction from the total capacity, the specific capacity of oxygen reduction reaction for the Li–O2 battery with CF0.31-based cathode is given by:

$$c_0 = \frac{C_1 - C_2 W_1 \times 80\%}{W_1 \times 90\%}$$  \hspace{1cm} (2)

where $C_1$ and $W_1$ are the capacity and the total amount of loading of CF0.31-based cathodes in Li–O2 battery, respectively; $C_2$ is the specific capacity of the Li/CF0.31 primary battery, given by:

$$C_2 = \frac{C_2}{W_2 \times 80\%}$$  \hspace{1cm} (3)

where 80% and 90% are the mass fraction of CF0.31 and CNTs + CF0.31 in CF0.31-based cathode, respectively. In addition, the specific capacity of oxygen reduction reaction for the Li–O2 battery with CNTs-based cathode is given by:

$$c_3 = \frac{C_3}{W_3 \times 90\%}$$  \hspace{1cm} (4)

where $C_2$, $C_3$ are the capacities of the Li/CF0.31 primary battery and the Li–O2 battery with CNTs-based cathode, respectively; $W_2$, $W_3$ are the total amount of loading of CF0.31-based cathodes in Li/CF0.31 primary battery and CNTs-based cathode in Li–O2 battery, respectively; 90% is the mass fraction of CNTs in CNTs-based cathode in Li–O2 battery.

Fig. 6 shows the capacities of oxygen reduction reaction for CF0.31 based Li–O2 battery and CNTs based Li–O2 battery. The difference observed in the capacities from the oxygen reduction reaction between CF0.31 and CNTs-based cathode is very small at low current density, e.g., at the current density of 30 mA g$^{-1}$, the capacity of the oxygen reduction reaction for CF0.31 based Li–O2 battery is 663 mA h g$^{-1}$, which is close to that of CNTs based Li–O2 battery (682 mA h g$^{-1}$). However, with current density increasing, the capacity from oxygen reduction reaction of CNTs based cathode decreases more dramatically than CF0.31-based cathode. For example, the capacity of the oxygen reduction for CF0.31-based cathode is 367 mA h g$^{-1}$ at 120 mA g$^{-1}$, which is 2.9 times as high as that for CNTs-based cathode (125 mA h g$^{-1}$). It indicates that CF0.31-based electrode facilitates the reduction of oxygen, especially at high rate conditions. These results suggest clearly that there is a synergy effect on the oxygen reduction reaction and CF0.31 conversion reaction for CF0.31-based cathode, particularly at a high current density.
Fig. 7a–c shows the differential capacity curves (dQ/dV versus potential) derived from the discharge curves for Li/CF0.31 battery and Li–O2 battery with CNTs and CF0.31 cathode at different current densities. At a current density of 30 mA g⁻¹, dQ/dV of Li–O2 battery with CNTs cathode shows a sharp oxygen reduction peak in the voltage range of 2.8–2.5 V (Fig. 7b). As the discharge current density increases, the kinetics of oxygen reduction decreases. Thus the peak in dQ/dV becomes broader and shifts toward lower potential with increasing discharge current density. The dQ/dV curve of Li/CF0.31 battery shows a broad peak in the voltage range of 2.8–1.5 V at a current density of 30 mA g⁻¹ (Fig. 7a). The differential capacity mainly comes from the voltage range below 2.5 V, which is lower than that of pure oxygen reduction on carbon shown in Fig. 7b. However, at a higher current density, i.e., 100 mA g⁻¹, a broad peak appears nearly in the same voltage range where oxygen reduction occurs (Fig. 7a and b). The differential capacity curves derived from the discharge curves of Li–O2 battery with CF0.31 cathode (Fig. 7c) also shows a broad peak in the voltage range of 3.0–1.5 V at 30 mA g⁻¹, indicating a complicated discharge process. The differential capacity in the voltage range of 3.0–2.5 V mainly comes from the oxygen reduction based on the analysis of Fig. 7b. The higher onset potential of oxygen reduction for Li–O2 battery with CF0.31 cathode than CNT cathode also implies that the defects on the carbon nanotube after fluorination improve the electrocatalytic activity of oxygen reduction on the material. With the increase of current density, the peak shifts negatively due to the increased polarization for discharge process, especially for oxygen reduction process.

Combining the results from differential capacity analysis with the discharge curves suggests that at low current density, the oxygen reduction reaction and CF0.31 conversion reaction may take place separately. At high voltage region, the oxygen reduction reaction predominates due to the higher electrochemical potential of oxygen reduction. However, at high current density, the difference between discharge potential of oxygen reduction and CF0.31 conversion becomes very small due to the higher polarization of oxygen reduction than that of CF0.31 conversion, thus oxygen reduction reaction and CF0.31 conversion reaction will take place simultaneously during discharge process. When these two reactions take place at the same time, it induces a synergy effect which facilitates the oxygen reduction reaction and retards the formation of dense insulating products that occlude the cathode surface during the discharge process. This phenomenon significantly improves the electrochemical performance of CF0.31 based cathode at high current density.

Electrochemical impedance spectra (EIS) are used to further clarify the electrochemical behavior of cathode in the Li–O2 battery. Fig. 8 shows the Nyquist plots for Li–O2 battery with CNT (Fig. 8A and B) and CF0.31 (Fig. 8C and D) based cathode obtained before discharge and after discharge to various depths at 30 and 100 mA g⁻¹. As Wan et al. [17] reported, Li anode has only a weak contribution to the whole impedance of the battery system, the major source of cell impedance in a Li–O2 battery comes from the cathode. The Nyquist plot for Li–O2 battery with CNT cathode before discharge shows two depressed semicircles at high and medium frequency range, followed by a sloping line at low frequency range (see inset, Fig. 8A). The high frequency intercept at the real axis is mainly attributed to the electrolyte bulk resistance [18]. The first large semicircle (approximately form 100 kHz to 100 Hz) is related to the impedance of surface film on carbon support [19]. The second small semicircle (approximately form 100 Hz to 10 Hz) is related to the charge-transfer kinetic resistance of the oxygen electrode [19–21]. The linear tail at very low frequency region below 10 Hz shows a mass transport process [17,22,23]. The shape of the Nyquist plot for Li–O2 battery with CF0.31 cathode (see inset, Fig. 8C) is similar to that of CNT except for the diameter of the first semicircle at high frequency, which means that the
electrode/electrolyte interface for CF0.31 cathode is different from that for CNT. The first semicircle becomes larger for CNT cathode as the discharge proceeds at 30 mA g\(^{-1}\) (plot b in Fig. 8A), indicating the increase of interfacial impedance. This is due to the formation of discharge products on the oxygen electrode/electrolyte interface with poor conductivity, which indicates that the initial discharge process is mainly affected by the electrochemical interface. In contrast, the Nyquist plot for CF0.31 does not change much indicating the superior performance of CF0.31 (plot b in Fig. 8C). The unchanged interfacial impedance mainly results from the looser discharge products deposited on CF0.31 than that on CNT. The phase angle of the low frequency line decreases for both the cathodes, especially for CNT-based cathode discharged to 1.5 V at 30 mA g\(^{-1}\) (plot c in Fig. 8A), suggesting the largely reduced mass transport process across the surface film/carbon interface [19].

In addition, the high frequency semicircle in the Nyquist plot for CNT-based cathode after discharge to 1.5 V at 100 mA g\(^{-1}\) increases greatly (plot c in Fig. 8B), which is due to the formation of a dense film at cathode as the discharge proceeds at high current density. This dense film greatly suppresses the oxygen reduction at the cathode. Therefore, the Li–O\(_2\) battery with CNT-based cathode shows a significantly decrease in discharge capacity at high current density. However, for CF0.31-based cathode discharged to 1.5 V at 100 mA g\(^{-1}\), the high frequency semicircle in the Nyquist plot changes not so much (plot c in Fig. 8D). This may be because that the discharge products on CF0.31 are not so dense as that on CNT, which explains the better electrochemical performance of CF0.31-based cathode operating at high current than that of CNT-based cathode.

The EIS results correlate very well with the electrochemical characterization, indicating that the film formed at the cathode at high current density (such as 100 mA g\(^{-1}\)) limits the oxygen diffusion, which suppresses the oxygen reduction reaction in Li–O\(_2\) battery with pure carbon cathode. The high hydrophobicity of CF\(_x\) is believed to promote the oxygen diffusion in the cathode and alleviate air-electrode blocking problem during the discharge process [12], this may also contribute to the high discharge capacity of CF0.31 based cathode at high current density.

3.3. Characterization of the discharge products by XPS

The discharge process for Li–O\(_2\) battery with CF0.31 based cathode is complex since at least two electrochemical reactions: oxygen reduction and CF0.31 conversion occurs simultaneously. By analyzing the reaction products, we hoped to get more direct indications of the complexity of the reactions during the discharge process. CF0.31-based oxygen electrodes discharged to different voltages were analyzed by XPS. Figs. 9–11 show the C 1s, Li 1s and F 1s spectra of CF0.31-based oxygen electrodes discharged to different voltages, respectively. The C 1s of the CF0.31-based oxygen electrode before discharge consists of two peaks at 284.8 eV and 289.8 eV (Fig. 9a). The peak at 284.8 eV can be assigned to hydrocarbon contamination and carbon atoms bound to carbon, which mainly come from CF0.31 and carbon conductive additives. The peak at 289.8 eV can be assigned to carbon atoms bound to fluorine, which exists in CF0.31 [24]. The peak at 688.2 eV in F 1s spectrum (Fig. 11) can be assigned to CF0.31.

After discharge to 2.5 V, obvious changes can be observed in C 1s spectrum (Fig. 9b). Two new peaks appear at 286.5 eV and 288.2 eV, which reveals the generation of new carbon containing species. These two peaks have been assigned to C–O and O=C–O by Tarascon and Dudney, respectively [25, 26]. Considering our battery system, we assigned them to ROCOOLi and RCOO\(_2\)Li, which are thought to be the main components of the O\(_2\)\(^{-}\) intermediate reaction with PC solvent during discharge process [27]. Moreover, Li\(_2\)CO\(_3\) is also thought to exist on the surface of oxygen electrode after discharge [27, 28]. The corresponding reactions are [27]:

\[
\begin{align*}
\text{O}_2 + e^- & \rightarrow \text{O}_2^- \quad (5) \\
\text{PC} + \text{O}_2^- + 2\text{Li}^+ + \text{O}_2 + e^- & \rightarrow \text{H}_2\text{O} + \text{CO}_2 + \text{HCOOOLi} \\
& \quad + \text{CH}_3\text{COOOLi} \quad (6) \\
2\text{O}_2^- + 2\text{CO}_2 & \rightarrow \text{C}_2\text{O}_6^{2-} + \text{O}_2 \quad (7) \\
2\text{O}_2^- + \text{C}_2\text{O}_6^{2-} + 4\text{Li}^+ & \rightarrow 2\text{Li}_2\text{CO}_3 + 2\text{O}_2 \quad (8)
\end{align*}
\]

Besides the appearance of two new peaks, the relative intensity of the two peaks at 284.8 eV and 289.8 eV changes obviously. The intensity ratio of the peak at 284.8 eV to that of the peak at 289.8 eV in pristine oxygen electrode is larger than 1 (Fig. 9a), while it decreases to lower than 1 in the oxygen electrode after discharge to 2.5 V (Fig. 9b). This can be explained by the formation of Li\(_2\)CO\(_3\) product from oxygen reduction (C 1s binding energy (BE) of Li\(_2\)CO\(_3\) at ~289.8 eV, which is overlapped with the BE of C–F) which covers on the surface of cathode, thus results in the increase in relative intensity of the peak at 289.8 eV. The formation of Li\(_2\)CO\(_3\) product also can be confirmed from the appearance of a new peak at 55.4 eV at Li 1s spectrum (Fig. 10b) which can be assigned to Li\(_2\)CO\(_3\). These indicate it mainly occurs the reaction of oxygen reduction on CF0.31-based cathode in the voltage range of open circuit potential (OCP) to 2.5 V. From XPS analysis results, we can conclude that the layer formed at the cathode mainly consists of products of Li\(_2\)CO\(_3\), RCOO\(_2\)Li and RCOOOLi.

Fig. 9. C1s XPS spectra for the CF0.31 composite electrode (a) before discharge, and after discharge to (b) 2.5 V, (c) 1.9 V and (d) 1.5 V.
After discharge to 1.9 V, the change of C 1s spectrum is evident in the relative intensity of the peaks (Fig. 9c). The peak intensity at 289.8 eV decreases while the peak intensity at 284.8 eV increases in comparison to Fig. 9b. This indicates the increase of the components of C or/and the decrease of CF0.31, which is consistent with the result of CF0.31 conversion reaction, which consumes CF0.31 and produces C and LiF, thus leads to the decrease of CF and the increase of C–C. In addition, a slight decrease in intensity of peaks at 286.5 eV and 288.2 eV can also be seen in comparison to Fig. 9b, which may be attributed to the formation of C and LiF products. In addition to C 1s spectra, the formation of LiF product also can be confirmed from the appearance of a new peak at 56.2 eV at Li 1s spectrum (Fig. 10c) and a new peak at 684.8 eV at F 1s spectrum (Fig. 11c). This further confirms the conversion of CF0.31 to LiF after discharge to 1.9 V. XPS analysis results show clearly that CF0.31 conversion reaction dominates the whole electrode reaction in the voltage range of 2.5 V to 1.9 V.

After further discharged to 1.5 V, the changes of C 1s spectrum (Fig. 9d) are not so obvious, a slight increase in peak intensity at 289.8 eV can be observed. This can be attributed to the formation of additional Li2CO3 on the new active sites of carbon generated by the conversion of CF0.31. C1s, Li1s and F1s binding energies of the CF0.31 composite electrode before discharge and after discharge to different voltages are summarized in Table 1.

A cyclical process of reactions involving regeneration of reactive sites can be envisaged to explain results from the XPS analysis of CF0.31 at low current density. During the early discharge process, the electrochemical reduction of oxygen dominates the discharge process; as discharge progresses, the insulating discharge products, i.e., Li2CO3, ROEOLi and ROCO2Li, accumulate and occlude the surface of CF0.31, resulting in high polarization and decrease in cell voltage. At a particular threshold of cell voltage, the electrochemical conversion of CF0.31 takes place and gradually dominates the discharge process. Then the conversion of CF0.31 produces C which

![Image](https://example.com/image.png)

**Fig. 10.** Li 1s XPS spectra for the CF0.31 composite electrode (a) before discharge, and after discharge to (b) 2.5 V, (c) 1.9 V and (d) 1.5 V.

![Image](https://example.com/image.png)

**Fig. 11.** F 1s XPS spectra for the CF0.31 composite electrode (a) before discharge, and after discharge to (b) 2.5 V, (c) 1.9 V and (d) 1.5 V.

| Table 1 | C 1s, Li 1s and F 1s binding energies of XPS spectra for the CF0.31 composite electrodes before discharge and after discharge to different voltages. |
|---------|-------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------|
| Exp. conditions | C 1s binding energy (eV) | Li 1s binding energy (eV) | F 1s binding energy (eV) | Assignment of the components |
| Before discharge | 284.8 | 289.8 | 688.2 | C–C | C–F |
| Discharged to 2.5 V | 284.8 | 286.5 | 288.2 | 289.8 | 688.2 | C–C | C–C–O | Li2CO3 |
| Discharged to 1.9 V or 1.5 V | 284.8 | 286.5 | 288.2 | 289.8 | 55.4 | 56.2 | 685.2 | Li2CO3 | Li–F |
provides new active site for oxygen reduction and the deposition of the oxygen reduction products. According to the above discharge mechanism, at low current density, the discharge capacity of CF\textsubscript{0.31} based Li–O\textsubscript{2} battery should be proportional to the capacity of oxygen reduction plus the capacity of CF\textsubscript{0.31} conversion reaction. Our electrochemical results also support this conclusion.

4. Conclusions

Cathode constructed using fluorinated CNTs significantly improves the performance of Li–O\textsubscript{2} battery in comparison to the unfluorinated CNTs, e.g., the capacity of fluorinated CNTs is 676 mAh g\textsuperscript{-1} at a current density of 100 mA g\textsuperscript{-1}, while that of CNTs is only 188 mAh g\textsuperscript{-1}. The enhanced improvement in electrochemical performance is ascribed to dual reactions at the electrode and incorporation of the defects on the fluorinated CNT, thereby increasing the surface area and number of active sites to catalyze the reduction of oxygen. The synergy effects discovered in this CF\textsubscript{0.31}–based cathode system may help us to explore some other promising systems with high-energy density.

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References

[23] F. Croce, F. Nobili, A. Deputila, W. Lada, R. Tessici, A.D. Epifanio, B. Scrosati, R. Marassi, An electrochemical impedance spectroscopic study of the transport properties of LiN\textsubscript{10}Co\textsubscript{0.2}O\textsubscript{2}, Electrochemistry Communications 1 (1999) 605.