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Gaseous electrolyte additive BF_3 for high-power Li/CF_x primary batteries

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ABSTRACT

Lithium/graphite fluoride (Li/CF_x) batteries have attracted great attention because of the highest energy density among all commercially available lithium primary batteries. However, the inferior electrochemical performances at high discharge current densities impede their applications in high-power devices. Herein, we have found a novel and low-cost gaseous electrolyte additive BF_3 that can remarkably improve the rate capability of the Li/CF_x batteries. The CF_x (x=1.15) cathode in the carbonate electrolyte with 0.01M BF_3 additive can deliver a maximum power density of 23040 W kg^{-1} with a high gravimetric energy density of 722.8 Wh kg^{-1}. By contrast, the CF_x cathodes in the electrolyte without additive can barely provide capacity at discharge rates above 5C. Such significant enhancement can be attributed to the ability of the BF_3 additive to dissolve the insulating discharge product LiF without passivating the cathode surface and impeding the intercalation of lithium ions. This work provides a way that enables Li/CF_x batteries to have an ultrahigh power density comparable to that of supercapacitors while maintaining high energy densities.

1. Introduction

Lithium primary batteries (LPBs) have widely been used as a power source in various application fields such as medical electronics, electronic equipment, and military installations [1,2]. These applications have put forward ever-growing requirements on the performances of batteries, among which higher energy density, higher power density, and reliable safety are of the greatest concern [3-5]. As one of the commercially available LPBs, lithium/graphite fluoride (Li/CF_x) batteries have been generating considerable research interest because they possess the highest theoretical energy density (2189 Wh kg^{-1} for CF) [6,7]. The concept of using graphite fluoride (CF_x) as cathode material in LPBs was firstly proposed by N. Watanabe and co-workers [8]. Despite having the core advantage on energy density, Li/CF_x batteries face great challenges, including initial potential delay, limited rate capability, and heat generation during operation, hindering the wide adoption of Li/CF_x batteries in high-power devices [9-11]. These problems arise from the insulating feature of the pristine CF_x and the reaction product LiF. It is well-known that the CF_x has intrinsic inferior electronic conductivity. While the increase of the carbon content can bring higher electronic conductivity of the CF_x, it will simultaneously lower the specific capacity [12,13]. The discharge product LiF is also highly insulated, which will be deposited into the surface pores of the cathode electrode and prevent the subsequent migration of lithium ions into the bulk of the cathode, significantly increasing the cell resistance [14].

To solve these problems and enable Li/CF_x batteries competent in high-power application scenarios, several strategies have been attempted. Conducting additives, including carbon, [15] polythiophene, [16] and polypyrrole, [17] were coated on the surface of CF_x particles. These conductive coating layers improve the exterior electronic conductivity between particles, thus better rate capabilities could be achieved. Sub-fluorinated CF_x (x<1) were synthesized by a direct fluorination method from natural graphite [18] and carbon nanofibers [19]. The reduced fluorine contents indicate the presence of unreacted carbon inside the particles, which can serve as an intrinsic facile electron transport path and thereby ameliorate the rate performance of CF_x cathodes. Another approach is to synthesize nano-sized CF_x materials by using different precursors such as carbon nanotubes, [20] carbon nano-flakes, [21] and graphene [22]. The nanoparticle provides a large specific surface area and shortens the diffusion distance of lithium ions, leading to much enhanced electrochemical performances. While these aforementioned approaches demonstrate the great effectiveness of the materials engineering on promoting the fast discharge properties of Li/CF_x batteries, the pre-treatments on the CF_x materials could be complicated and increase the production cost. By contrast, the use of electrolyte additives is easier to operate. Nagasubramanian et al. used anion-binding-agents (ABAs, e.g., Tris(1,1,1,3,3,3-hexafluoroisopropyl) borate) as electrolyte

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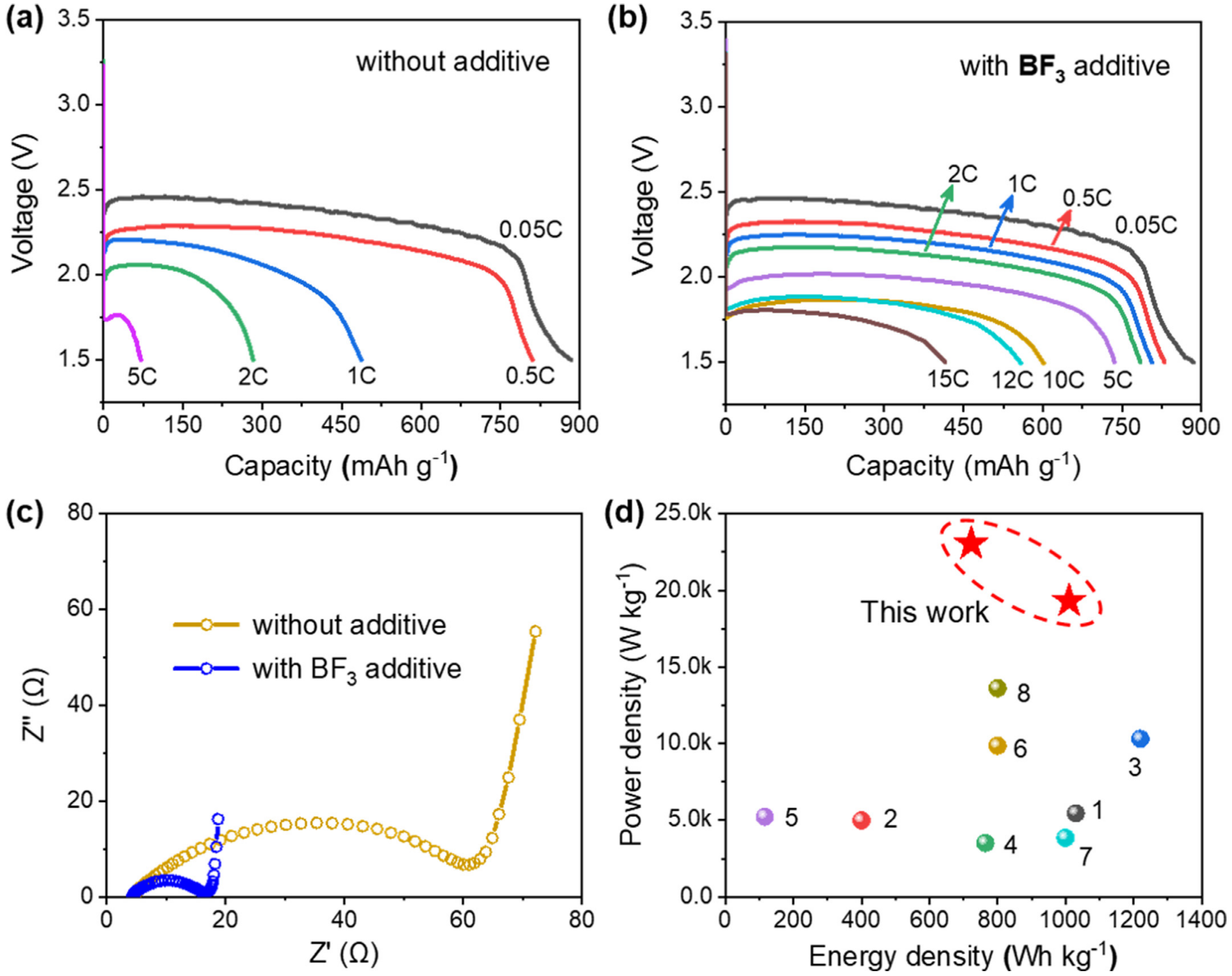

Figure 1. Galvanostatic discharge curves of Li/CF$_x$ batteries in the electrolytes (a) without and (b) with BF$_3$ additive at different current densities. (c) Nyquist plots of electrochemical impedance spectra (EIS were measured for Li/CF$_x$ batteries after discharge at 5C) and (d) Summary of the highest power density and corresponding energy density of Li/CF$_x$ batteries achieved in literature by various approaches, as shown in Table S2.

additives, which can lower the interfacial resistance and improves the electrochemical performances of Li/CF$_x$ batteries at high discharge rates [23]. Nevertheless, the cost-effectiveness of electrolyte additives is always an issue that should be considered for practical applications [24].

Here, we present a facile and low-cost approach to improve the rate capabilities of Li/CF$_x$ batteries by using a novel gaseous electrolyte additive BF$_3$. At the additive concentration of 0.01 M, the CF$_x$ (x=1.15) cathode delivers a discharge capacity of 415.5 mAh g^{-1} with an outstanding power density of 23040 W kg^{-1} (at a discharge rate of 15C). By contrast, without BF$_3$ additive, the cathode material is not able to provide capacity at current densities higher than 5C. The extraordinary enhancement in the electrochemical performances of Li/CF$_x$ batteries can be attributed to the ability of the BF$_3$ additive to dissolve the LiF, which is generated through the discharge reaction and can block the cathode pores, and thus reducing the diffusion resistance of lithium ions into the bulk of the cathode material. This work proposes a low-cost BF$_3$ electrolyte additive, which can effectively improve the rate performance of CF$_x$ material with high fluorine contents (x>1), exhibiting a promising application prospect.

2. Experimental methods

2.1. Materials

Graphite fluoride powder was purchased from XFNANO Materials Tech Co., Ltd, China. LiBF$_4$ was purchased from Beijing Innochem Science & Technology Co., Ltd. Graphite fluorides powder, PVdF binder and carbon black (8:1:1, mass ratio) were mixed into NMP solution with the planetary centrifugal mixer (Shashin Kagaku Co., Ltd, Japan) at 2000 rpm for 30 min. The obtained slurry was cast on a carbon-coated aluminium foil using a tape casting method, with the active material loading of 1.5~1.6 mg/cm^2. The produced cathodes were dried in a vacuum oven at 393 K for 8 h. The solution of 1.0 M LiBF$_4$ in ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1, in volume) was used as the control electrolyte. The BF$_3$ gas (Wuhan Newradar Co., Ltd, China) was then blown into the electrolyte under Ar atmosphere in a glove box. The concentration of BF$_3$ additive in electrolytes can be controlled by adjusting the ventilation time. Lithium foils (China Energy Lithium Co., Ltd.) with a thickness of 200 μm were used. In this work, all the chemicals were used as received without further purification.

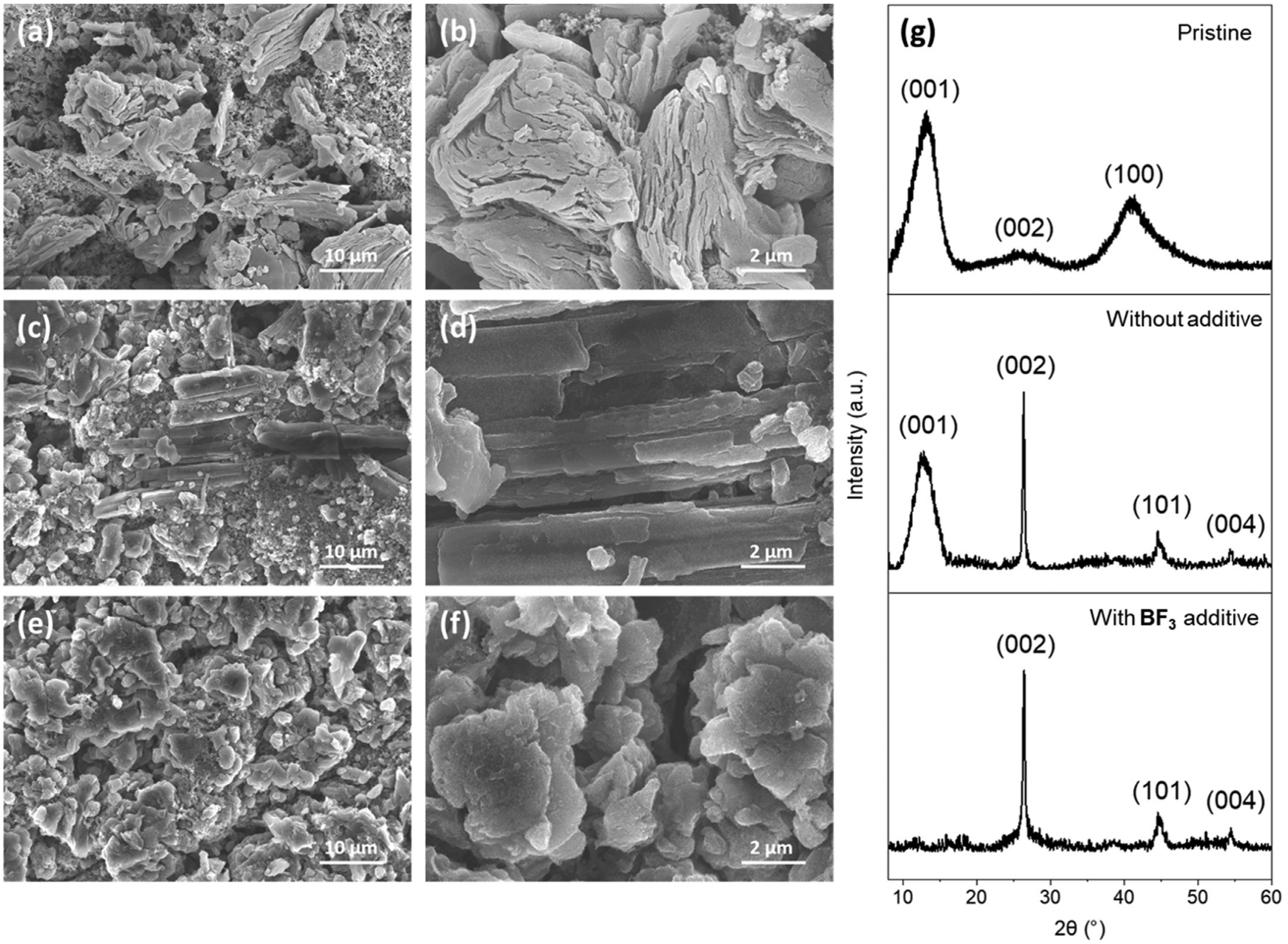

Figure 2. The morphology of (a) pristine CF_x cathode and discharged CF_x cathodes in electrolytes (c) without additive and (e) with BF_3 additive. (b, d, f) The corresponding SEM images at a higher magnification. (g) The XRD patterns of pristine CF_x cathode and discharged CF_x cathodes in electrolytes without additive and with BF_3 additive. The discharge rate is 5C.

2.2. Electrochemical Tests

The Li/CF_x coin cells were assembled in an argon-filled glovebox (H_2O < 0.1 ppm, O_2 < 0.1 ppm) with 100 µL electrolytes with and without BF_3 additive. The coin cells were discharged under different current densities from 0.05C to 15C (based on the active material of cathodes) on Land BA2100A Battery Test System (Wuhan LAND Electronic Co., Ltd, China) with a termination discharging voltage of 1.5 V. The electrochemical impedance spectroscopy (EIS) measurements were carried out on an electrochemical workstation (Zahner-Zennium, Germany) in a frequency range between 10 kHz and 200 mHz with a voltage amplitude of 5 mV. Cyclic voltammetry (CV) measurements were conducted using a CHI1000C instrument (Chenhua, China) from 4.0 V to 1.5 V at a scanning rate of 0.1 mV s^{-1}.

2.3. Characterizations

The discharged Li/CF_x coin cells were dissembled in the glove box to obtain CF_x cathodes. The discharged CF_x cathodes were washed three times by DMC solvent to remove the residual electrolyte before further analysis. The morphologies of the pristine and discharged cathodes were characterized by scanning electron microscopy (SEM, S-8100, Hitachi) with an accelerating voltage of 10.0 kV. The valence states and elemental composition of CF_x powder and CF_x cathodes were obtained from X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi, Thermo Scientific). The Ar^+ sputtering rate for the XPS depth-profiling calibration on SiO_2 surface was 10 nm min^{-1}. XRD patterns were recorded by a D8 advance X-ray diffractometer (Bruker).

3. Results and discussion

To determine the elemental composition of the graphite fluorides powder utilized in this research, X-ray photoelectron spectroscopy (XPS) measurement was carried out, and the results are shown in Figure S1 and Table S1. The fluorine content of the CF_x (or the F/C ratio) is a key parameter that determines the theoretical specific capacity (Q_c) of CF_x material by the following equation, [25]

$$Q_c\ \left(\mathrm{mAh\ g^{-1}}\right) = \frac{xF}{3.6\ \times\ (12 + 19x)} \tag{1}$$

where F is the Faraday's constant (96485 C mol^{-1}) and 3.6 is a unit conversion constant. The XPS results indicate that the employed CF_x powder possesses a high F/C ratio of 1.15 (Table S1), which can theoretically deliver an exceedingly large specific capacity of 910.5 mAh g^{-1}. However, the high fluorine content can simultaneously reduce the electronic conductivity of CF_x particles [26]. Moreover, the situation will get aggravated during the discharge process when the formed reaction product LiF plugs the void space of the cathode electrode at the surface and blocks the lithium intercalation into the CF_x particles [27]. Inferior electronic and lithium-ion conductivities are anticipated to severely impede

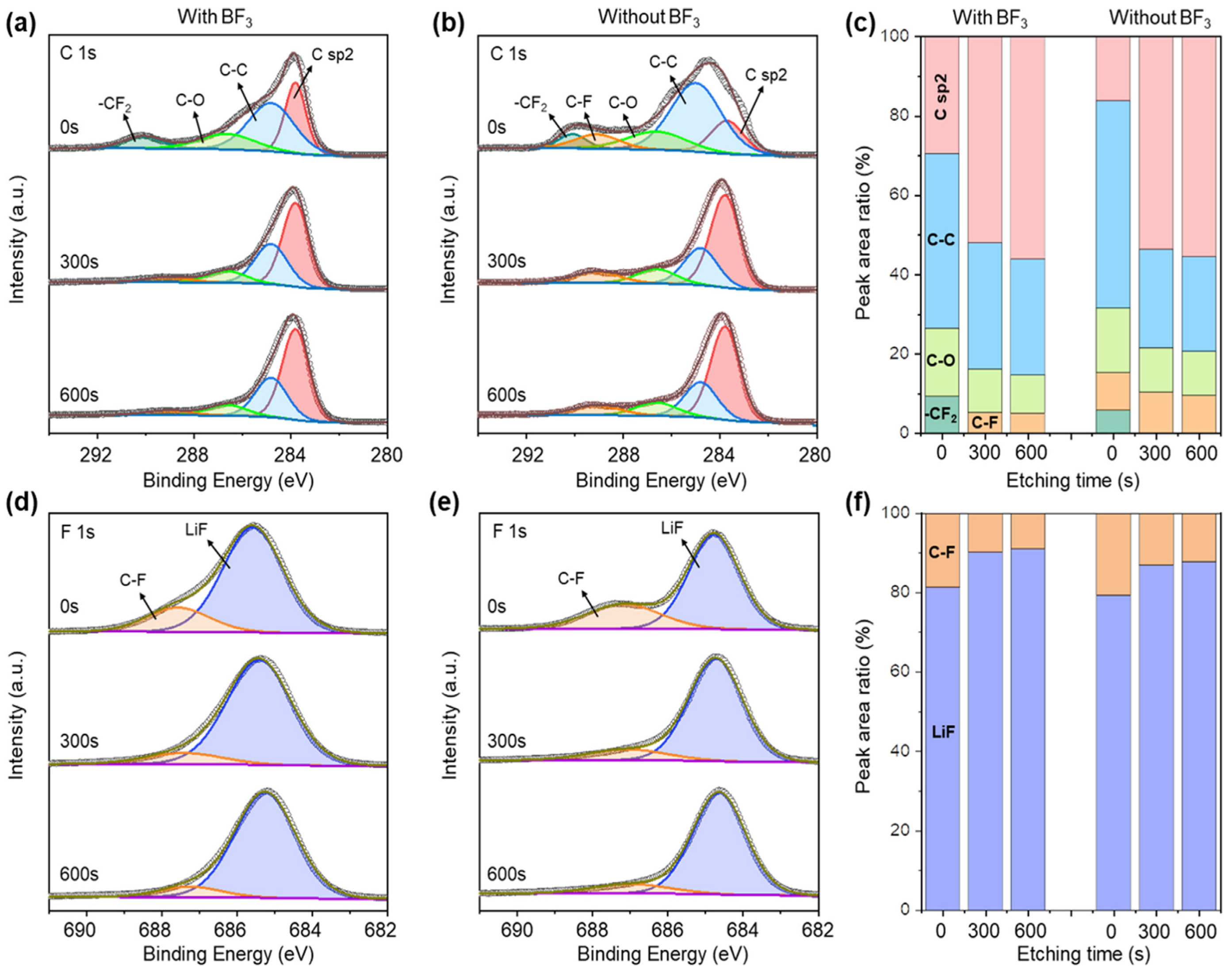

Figure 3. XPS depth profiling results of C 1s and F 1s spectra for discharged CF_x cathdes (a, d) with and (b, e) without BF_3 additive (the discharge rate is 5C). The relative contents of different compositions from C 1s and F 1s are given in (c) and (f), respectively.

the discharge performance of CF_x at high current densities in conventional electrolytes.

The discharge performances of CF_x were evaluated in Li/CF_x batteries. The solutions of 1.0 M $LiBF_4$ in ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1, in volume) with and without BF_3 additive (0.01M) were used as electrolytes, respectively. The discharge capacities of the Li/CF_x batteries with and without BF_3 additive are comparable at low current densities, exhibiting 884.9 mAh g^{-1} and 883.6 mAh g^{-1} respectively at 0.05C rate (Figure 1), which are close to the theoretical specific capacity of the CF_x cathode. However, the performances of CF_x batteries without BF_3 additive degrade significantly at high rates, with their discharge voltages and specific capacities fade rapidly (Figure 1a). At a discharge rate of 1C, the CF_x can merely give out a specific capacity of 486.9 mAh g^{-1}, which is around 55% of that at 0.05C. Meanwhile, the CF_x can hardly provide capacity due to serious voltage polarization at discharge rates above 5C. The inferior discharge performances and severe polarization of CF_x at fast discharge rates, which are consistent with previous reports, [28,29] can be ascribed to the poor electronic conductivity and sluggish lithium-ion transport kinetics of CF_x. In contrast, the CF_x cathodes working in the electrolyte containing BF_3 additive exhibit remarkably improved discharge performance at high current densities (Figure 1b). The specific capacity of the CF_x cathode at 5C is 735.7 mAh g^{-1}, which is about 83% of that at 0.05C. Besides, even at a high discharge rate of 15C, the CF_x cathode can still provide a high capacity of 415.5 mAh g^{-1}, accompanied by an ultrahigh power density of 23040 W kg^{-1}. The effect of additive concentration on the rate capabilities was investigated (**Figure S2**), and we found that the electrolyte with 0.01 M BF_3 additive can yield the best performance. The effects of BF_3 additive in a different electrolyte (1 M $LiPF_6$ EC/DMC (1:1 in volume)) and on higher loading CF_x cathodes have also been studied (**Figure S3** and **S4**). It is clear that after adding the BF_3 additive (0.01 M) in electrolytes, the discharge performance of CF_x cathodes has been greatly enhanced, indicating that the BF_3 additive can work in various conditions. It is noteworthy that the CF_x powder adopted in this work was used as received without any pretreatments, thereby the electronic conductivity of the cathode should be very low (can be verified by the poor-quality of the SEM image caused by charging effect, **Figure S5**). Thus, the superior electrochemical performance in terms of power density and energy density (Figure 1d and **Table S2**) is reasonably assumed to be related to the enhanced ionic transport kinetics of CF_x cathodes, which is facilitated by the BF_3 additive in the electrolyte.

Electrochemical impedance spectroscopy (EIS) and cyclic voltammetry (CV) were used to study the electrochemical kinetics of the CF_x cathodes in the electrolytes with and without BF_3 additive. The impedance

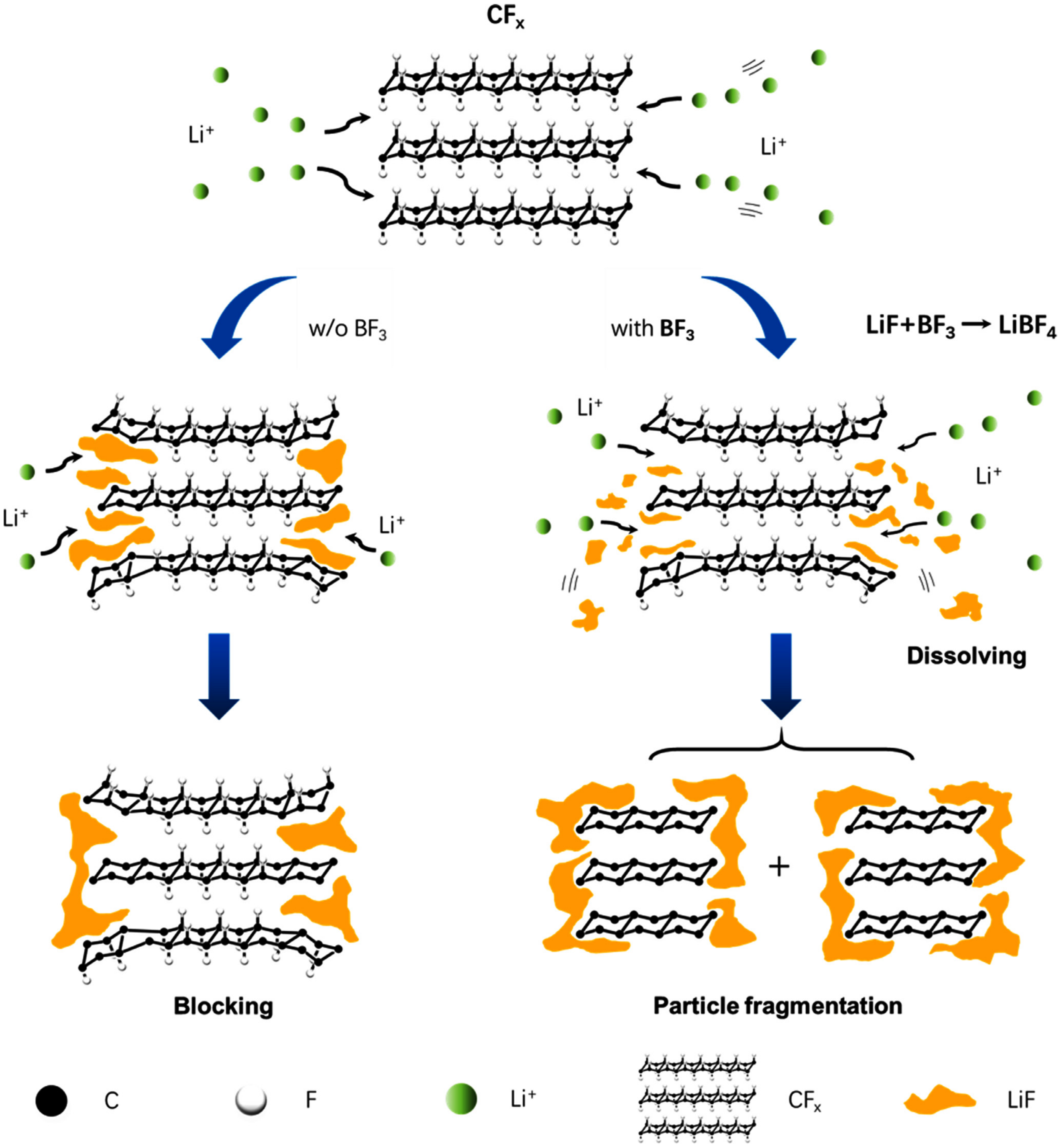

Figure 4. The schematic of the action mechanism of BF_3 additive on CF_x cathodes. The deposited LiF in the surface pores of CF_x particles can be dissolved by BF_3, facilitating the transport of lithium ions into the bulk of the cathode material and thus significantly enhancing the electrochemical performance of Li/CF_x batteries at fast discharge rates.

spectra were recorded at a fully discharged state and shown in Figure 1c and **S6**. The semicircle in the high and middle-frequency region is designated to the bulk resistance (R_b) and charge transfer resistance (R_{ct}) [30]. It is obvious that the R_{ct} of the Li/CF_x battery with BF_3 additive (11.9 ohm) is much lower than that without additive (58.6 ohm), indicating a faster reaction kinetics when BF_3 additive is introduced. Meanwhile, the slope of the straight line in the low-frequency region reflects the diffusion coefficient of lithium ions in the bulk of the CF_x electrode, [31] thus the greater slope of a straight line in the electrolyte with BF_3 additive than that without additive indicates an enhanced lithium ionic conductivity of CF_x particles. The CV profiles exhibit a much higher reaction current in the electrolyte with BF_3 additive than that without additive, which suggests the same conclusion as revealed in the EIS measurements (**Figure S7**).

To explore why the BF_3 additive renders superior rate capabilities, the morphologies and crystal structures of the pristine and the discharged CF_x cathode electrodes were characterized by scanning electron microscopy (SEM) and X-ray diffraction (XRD) (Figure 2). In the pristine cathode, the CF_x particles show an integrated and typical layered stacking structure, with a relatively large particle size ranged from several to tens of microns (Figure 2a and 2b). The large particle size is not beneficial for the lithium ionic conduction as a longer diffusion distance is required [32]. After discharge at 5C, the discharged cathodes display notable morphologic changes but with different degrees of particle fracture with and without BF_3 additive (Figure 2c and 2e).

The destruction of the CF_x structure can be attributed to the fact that the reaction product LiF will deposit into CF_x interlayers during discharge and induce a significant amount of internal stress, leading to the creation of cracks and even breakage of CF_x particles [33]. It is generally accepted that the collapse of the cathode structure is detrimental to the cycling performance of rechargeable batteries [34,35]. However, as to lithium primary batteries, the exfoliation of the CF_x can effectively reduce the particle size and expose more active materials from the interior of the sample particles, which is favorable for fast lithium intercalation kinetics. As shown in Figure 2c, 2d and **S8**, although a large number of broken particles can be observed in the discharged cathode without BF_3 additive, there are still unbroken, sheet or column-shaped particles. The surface of these unbroken particles is completely covered by reaction products (**Figure S9**), which may impede further discharge reaction from occurring at the bulk of CF_x cathode and thus integrated particle structures are maintained. By contrast, the discharged cathode with BF_3 additive shows greater degrees of fragmentation (Figure 2e and 2f), with no large-size CF_x particles observed. The utter destruction of particle structure reflects a more complete usage of CF_x capacity and facilitates a faster diffusion rate of lithium ions. In addition, no characteristic diffraction peaks of LiF were detected in the discharged cathodes (Figure 2g), suggesting the crystalline nature of the discharge product LiF is amorphous. The structure of pristine CF_x is mainly in an amorphous state, while after discharge more ordered graphite structure is observed, which is in good agreement with previous report [36]. The (001) plane with an interlayer distance of 0.67 nm corresponds to the unreacted CF_x and its absence in the discharged cathode with BF_3 additive indicates that almost all CF_x has participated in the discharge reaction.

To further understand the working mechanism of the BF_3 additive, X-ray photoelectron spectroscopy (XPS) depth profiling was performed to investigate the chemical compositions of discharged cathodes in depth. The C=C sp2 bonds (283.8 eV) in Figure 3a and 3b correspond to amorphous carbon, which is generated by the discharge reaction: $xLi + CF_x \rightarrow xLiF + C$ [37]. Two peaks at 290.1 eV and 286.6 eV in C1s spectra are attributed to $-CF_2$ and C-O bonds, [38] which stem from PVdF binder and decomposition products of electrolyte solvents, respectively. In comparison to the CF_x cathode without additive, the CF_x cathode with BF_3 additive possesses lower C-F bond (289.1 eV) contents both on the surface and after 5, 10 min etching by Ar^+ ions (Figure 3c), which indicates that more CF_x material has participated in the discharge reaction (especially the material in the bulk) with the assistance of BF_3 additive. A similar conclusion can be obtained from F 1s spectra (Figure 3d, 3e and 3f). More LiF and less C-F bond are detected in the bulk of the cathode with BF_3 additive than that without additive, indicating that lithium ions can diffuse into the bulk of the cathode more easily in the presence of BF_3 additive. The action mechanism of BF_3 was further studied by analysing the B 1s spectra of discharged cathodes. In order to eliminate the interference of $LiBF_4$ salt on detection, another lithium salt $LiPF_6$ was used in electrolytes. The discharged cathodes were not washed before dried in vacuum to maintain the solutes on the electrode surface. As shown in **Figure S10**, there is no signal of elemental B in the cathode without additive. In contrast, the peak for BF_4^- anion can be observed in the cathode with BF_3 additive. This indicates that the BF_3 additive can react with LiF to form soluble species BF_4^-, thereby improving the discharge performance of CF_x cathodes.

Based on the above results and analysis, a mechanism proposed for the effectively upgraded rate capability of CF_x cathodes facilitated by BF_3 additive is illustrated in Figure 4. Through the discharge reaction, the produced LiF can generate large internal stress in the CF_x structure, which leads to the breakage of CF_x particles and exposes more active material from the bulk. However, as the reaction progresses, the surface pores of some CF_x particles will be completely blocked by LiF and the diffusion of lithium ions into the bulk of cathodes is retarded. These CF_x particles could maintain relatively integrated structures, but give rise to fairly high interfacial resistances and limited rate capabilities. By contrast, when the electrolyte contains BF_3 additive, the stuck LiF will be dissolved through the reaction: $LiF + BF_3 \rightarrow LiBF_4$, which keeps the bulk of CF_x particles accessible for further discharge reaction. Consequently, adding BF_3 into the electrolyte can reduce the diffusion resistance of lithium ions and make full use of CF_x capacity, leading to significantly enhanced electrochemical performance of Li/CF_x batteries especially at fast discharge rates. Meanwhile, it is noteworthy that the lithium salt ($LiBF_4$) concentration of the BF_3-added electrolyte can increase during discharge, but to a fairly limited extent owing to the low concentration of BF_3 additive (0.01M). Therefore, this minor change in lithium salt concentration may not be the main reason for the enhanced electrochemical performance of Li/CF_x batteries.

4. Conclusion

In summary, considerably improved rate capability of Li/CF_x primary batteries have been realized by adding gaseous BF_3 electrolyte additive. The CF_x cathode in the electrolyte without additive can hardly deliver capacity at discharge rates above 5C. In contrast, the CF_x cathode in the electrolyte with BF_3 additive can provide an ultrahigh power density of 23040 W kg^{-1} at 15C, associated with a high energy density of 722.8 Wh kg^{-1}. Faster lithium-ion transport kinetics and more complete utilization of CF_x capacity have been achieved with the assistance of BF_3 additive because the additive can dissolve the plugged reaction product LiF and facilitate the lithium-ions diffusion into the bulk of cathodes. This work provides a facile and low-cost approach to enhance the electrochemical performance of Li/CF_x primary batteries at high discharge rates, which will promote the practical application of Li/CF_x batteries in high-power devices.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Quan Li: Investigation, Visualization, Formal analysis, Writing – original draft. **Weiran Xue:** Investigation, Formal analysis, Writing – original draft. **Xiaorui Sun:** Data curtion, Resources, Formal analysis. **Xiqian Yu:** Project administration, Supervision, Funding acquisition, Writing – review & editing. **Hong Li:** Conceptualization, Project administration, Funding acquisition, Supervision, Writing – review & editing. **Liquan Chen:** Methodology, Resources, Writing – review & editing.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.ensm.2021.03.024.

References

[1] H Park, HD Lim, HK Lim, WM Seong, S Moon, Y Ko, B Lee, Y Bae, H Kim, K. Kang, High-efficiency and high-power rechargeable lithium–sulfur dioxide batteries exploiting conventional carbonate-based electrolytes, Nat. Commun. 8 (2017) 14989, doi:10.1038/ncomms14989.

[2] L Zeng, L Qiu, HM. Cheng, Towards the practical use of flexible lithium ion batteries, Energy Storage Mater 23 (2019) 434–438, doi:10.1016/j.ensm.2019.04.019.

[3] M Tarascon J, M Armand, Issues and challenges facing rechargeable lithium batteries, Nature 414 (2001) 359–367, doi:10.1142/9789814317665_0024.

[4] Landon Oakes, Rachel Carter, Cary L. Pint, Nanoscale defect engineering of lithium–sulfur battery composite cathodes for improved performance, Nanoscale 8 (2016) 19368–19375, doi:10.1039/c6nr06332b.

[5] X.W. Shen, Y.T. Li, T. Qian, J. Liu, J.Q. Zhou, C.L. Yan, J.B. Goodenough, Lithium anode stable in air for low-cost fabrication of a dendrite-free lithium battery, Nat. Commun. 10 (2019) 1–9, doi:10.1038/s41467-019-08767-0.

[6] P. Sun, P. Bai, Z. Chen, H. Su, J. Yang, K. Xu, Y. Xu, A Lithium-Organic Primary Battery, Small 16 (2020) 1906462, doi:10.1002/smll.201906462.

[7] C. Jiang, B.J. Wang, Z.R. Wu, J.L. Qiu, Z.P. Ding, J. Zou, S.L. Chen, P. Gao, X.B. Niu, L.P. Wang, H. Li, Electrolyte-assisted dissolution-recrystallization mechanism towards high energy density and power density CF cathodes in potassium cell, Nano Energy 70 (2020) 104552, doi:10.1016/j.nanoen.2020.104552.

[8] N. Watanabe, M. Fukuda, Primary cell for electric batteries., US, 1970.

[9] S.K. Peng, S.J. Yan, N. Wang, W.Z. Nan, J.X. Wang, X. Chen, C. Wang, X. Qi, S.L. Dai, Fluorinated graphene/sulfur hybrid cathode for high energy and high power density lithium primary batteries, RSC advances 8 (2018) 12701–12707, doi:10.1039/C8RA00226F.

[10] SW Lee, N Yabuuchi, BM Gallant, S Chen, BS Kim, PT Hammond, Y. Shao-Horn, High-power lithium batteries from functionalized carbon-nanotube electrodes, Nature nanotechnology 5 (7) (2010) 531–537, doi:10.1038/nnano.2010.116.

[11] M Agostini, S Brutti, MA Navarra, S Panero, P Reale, A Matic, B. Scrosati, A high-power and fast charging Li-ion battery with outstanding cycle-life, Scientific reports 7 (1) (2017) 1–7, doi:10.1038/s41598-017-01236-y.

[12] Y. Matsuo, J. Inamoto, H. Yamamoto, K. Matsumoto, R. Hagiwara, Discharge Characteristic of Fluorinated Graphene-like Graphite as a Cathode of Lithium Primary Battery, Electrochemistry 88 (2020) 437–440, doi:10.5796/electrochemistry.20-64068.

[13] R Fan, B Yang, Z Li, D Ma, W Yuan, J Ma, H. Ren, First-principles study of the adsorption behaviors of Li atoms and LiF on the CF x (x= 1.0, 0.9, 0.8, 0.5,∼ 0.0) surface, RSC Advances 10 (53) (2020) 31881–31888, doi:10.1039/D0RA03635H.

[14] Y. Li, Y.Y. Feng, W. Feng, Deeply fluorinated multi-wall carbon nanotubes for high energy and power densities lithium/carbon fluorides battery, Electrochimica Acta 107 (2013) 343–349, doi:10.1016/j.electacta.2013.06.086.

[15] Q. Zhang, S. d'Astorg, P. Xiao, X. Zhang, L. Lu, Carbon-coated fluorinated graphite for high energy and high power densities primary lithium batteries, J. Power Sources 195 (2010) 2914–2927, doi:10.1016/j.jpowsour.2009.10.096.

[16] X.D. Yin, Y. Li, Y.Y. Feng, W. Feng, Polythiophene/graphite fluoride composites cathode for high power and energy densities lithium primary batteries, Synthetic Metals 220 (2016) 560–566, doi:10.1016/j.synthmet.2016.07.032.

[17] H. Groult, C.M. Julien, A. Bahloul, S. Leclerc, E. Briot, A. Mauger, Improvements of the electrochemical features of graphite fluorides in primary lithium battery by electrodeposition of polypyrrole, Electrochem. commun. 13 (2011) 1074–1076, doi:10.1016/j.elecom.2011.06.038.

[18] P. Lam, R. Yazami, Physical characteristics and rate performance of (CFx)n (0.33 < x < 0.66) in lithium batteries, J. Power Sources 153 (2006) 354–359, doi:10.1016/j.jpowsour.2005.05.022.

[19] R. Yazami, A. Hamwi, K. Guérin, Y. Ozawa, M. Dubois, J. Giraudet, F. Masin, Fluorinated carbon nanofibres for high energy and high power densities primary lithium batteries, Electrochem. commun. 9 (2007) 1850–1855, doi:10.1016/j.elecom.2007.04.013.

[20] Y. Li, Y. Chen, W. Feng, F. Ding, X. Liu, The improved discharge performance of Li/CFx batteries by using multi-walled carbon nanotubes as conductive additive, J. Power Sources 196 (2011) 2246–2250, doi:10.1016/j.jpowsour.2010.10.005.

[21] Y. Ahmad, M. Dubois, K. Guérin, A. Hamwi, W. Zhang, Pushing the theoretical limit of Li–CFx batteries using fluorinated nanostructured carbon nanodiscs, Carbon 94 (2015) 1061–1070, doi:10.1016/j.carbon.2015.07.073.

[22] D. Damien, P.M. Sudeep, T.N. Narayanan, M.R. Anantharaman, P.M. Ajayan, M.M. Shaijumon, Fluorinated graphene based electrodes for high performance primary lithium batteries, RSC Advances 3 (2013) 25702–25716, doi:10.1039/C3RA45377D.

[23] G. Nagasubramanian, B. Sanchez, A new chemical approach to improving discharge capacity of Li/(CFx)n cells, J. Power Sources 165 (2007) 630–634, doi:10.1016/j.jpowsour.2006.10.037.

[24] CS Rustomji, Y Yang, TK Kim, J Mac, YJ Kim, E Caldwell, H Chung, YS Meng, Liquefied gas electrolytes for electrochemical energy storage devices, Science 356 (6345) (2017), doi:10.1126/science.aal4263.

[25] E. Rangasamy, J. Li, G. Sahu, N. Dudney, C. Liang, Pushing the Theoretical Limit of Li-CFx Batteries: A Tale of Bifunctional Electrolyte, J. Am. Chem. Soc. 136 (2014) 6874–6877, doi:10.1021/ja5026358.

[26] P. Zhou, J. Weng, X. Liu, Y. Li, L. Wang, X. Wu, T. Zhou, J. Zhou, S. Zhuo, Urea-assistant ball-milled CFx as electrode material for primary lithium battery with improved energy density and power density, J. Power Sources 414 (2019) 210–217, doi:10.1016/j.jpowsour.2019.01.007.

[27] L. Wang, Y. Li, S. Wang, P. Zhou, Z. Zhao, X. Li, J. Zhou, S. Zhuo, Fluorinated Nanographite as a Cathode Material for Lithium Primary Batteries, ChemElectroChem 6 (2019) 2201–2207, doi:10.1002/celc.201900194.

[28] A. Tressaud, H. Groult, Fluorinated carbonaceous nanoparticles as active material in primary lithium battery, J. Fluor. Chem. 219 (2019) 1–9, doi:10.1016/j.jfluchem.2018.12.007.

[29] H. Groult, A. Tressaud, Use of inorganic fluorinated materials in lithium batteries and in energy conversion systems, ChemComm 54 (2018) 11375–11382, doi:10.1039/C8CC05549A.

[30] Y. Zhu, L. Zhang, H. Zhao, Y. Fu, Significantly improved electrochemical performance of CFx promoted by SiO2 modification for primary lithium batteries, J. Mater. Chem. A. 5 (2017) 796–803, doi:10.1039/C6TA07919A.

[31] J.P. Jones, S.C. Jones, F.C. Krause, J. Pasalic, M.C. Smart, R.V. Bugga, E.J. Brandon, W.C. Wes, Additive Effects on Li||CFx and Li||CFx-MnO2 Primary Cells at Low Temperature, J. Electrochem. Soc. 164 (2017) A3109, doi:10.1149/2.0831713jes.

[32] R. Tian, S.H. Park, P.J. King, G. Cunningham, J. Coelho, V. Nicolosi, J.N. Coleman, Quantifying the factors limiting rate performance in battery electrodes, Nat. Commun. 10 (2019) 1–10, doi:10.1038/s41467-019-09792-9.

[33] A. Lewandowski, P.J. Jakobczyk, Kinetics of Na|CFx and Li|CFx systems, Solid State Electrochem 20 (2016) 3367–3373, doi:10.1007/s10008-016-3305-5.

[34] E Zhao, M Zhang, X Wang, E Hu, J Liu, X Yu, M Olguin, TA Wynn, YS Meng, K Page, F. Wang, Local structure adaptability through multi cations for oxygen redox accommodation in Li-Rich layered oxides, Energy Storage Mater 24 (2020) 384–393, doi:10.1016/j.ensm.2019.07.032.

[35] E Zhao, L He, B Wang, X Li, J Zhang, Y Wu, J Chen, S Zhang, T Liang, Y Chen, X. Yu, Structural and mechanistic revelations on high capacity cation-disordered Li-rich oxides for rechargeable Li-ion batteries, Energy Storage Mater 16 (2019) 354–363, doi:10.1016/j.ensm.2018.06.016.

[36] Z Ding, C Yang, J Zou, S Chen, K Qu, X Ma, J Zhang, J Lu, W Wei, P Gao, L. Wang, Reaction Mechanism and Structural Evolution of Fluorographite Cathodes in Solid-State K/Na/Li Batteries, Adv. Mater. 33 (2021) 2006118, doi:10.1002/adma.202006118.

[37] P.M. Gomadam, D.R. Merritt, E.R. Scott, C.L. Schmidt, P.M. Skarstad, J.W. Weidner, Modeling lithium/hybrid-cathode batteries, J. Power Sources 174 (2007) 872–876, doi:10.1016/j.jpowsour.2007.06.164.

[38] A.V. Sosunov, D.A. Ziolkowska, R.S. Ponomarev, V.K. Henner, B. Karki, N. Smith, G. Sumanasekera, J.B. Jasinski, CFx primary batteries based on fluorinated carbon nanocages, New J. Chem. 43 (2019) 12892–12895, doi:10.1039/C9NJ02956G.