Artificial Cathode–Electrolyte Interphases on Ni–Rich LiNi_{0.8}Co_{0.1}Mn_{0.1}O_{2} by Carbon Nanotubes Modified LiF for Enhanced Cycleability

Ruoyu QIU and Zhuangchun WU

*Corresponding author: zwu@dhu.edu.cn

© The Author(s) 2021. Published by ECSJ. This is an open access article distributed under the terms of the Creative Commons Attribution 4.0 License (CC BY, http://creativecommons.org/licenses/by/4.0/), which permits unrestricted reuse of the work in any medium provided the original work is properly cited. [DOI: 10.5796/electrochemistry.21-00022].

This is the final version of an authors’ manuscript, submitted by the author(s) and accepted for publication after peer review and technical editing by the Editorial Board of The Electrochemical Society of Japan. This manuscript may contain minor errors or incomplete designs that do not affect the judgment for publication. It is the responsibility of the authors to correct any errors in the Just Accepted manuscript during galley proof review.
Artificial Cathode–Electrolyte Interphases on Ni–Rich LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2 by Carbon Nanotubes Modified LiF for Enhanced Cycleability

Ruoyu Qiu, a and Zhuangchun Wu b,*,

a College of Science, Donghua University, Room 635, Science and Technology Innovation Building, 2999 Renmin North Road, Songjiang District, Shanghai, 201620 China

b Institute of Functional Materials, Donghua University, Room 628, Science and Technology Innovation Building, 2999 Renmin North Road, Songjiang District, Shanghai, 201620 China

*Corresponding Author: zwu@dhu.edu.cn

ORCID ID:
Ruoyu Qiu: 0000–0002–5289–8823
Zhuangchun Wu: 0000–0003–3362–0882
Abstract

The high energy density of nickel–rich LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2 (NCM811) was hindered by the lack of interface stability which will reduce its long cycle electrochemical performance. In this paper, lithium fluoride nanoparticles were used as artificial cathode–electrolyte interphase to protect the NCM811 from vigorous SEI formation. Since the conductivity of lithium fluoride will reduce the electrode’s electron mobility, 1 wt% multi–wall carbon nanotubes were added to mitigate this issue. Scanning electron microscope and energy disperse spectroscopy represent that the lithium fluoride and multi–wall carbon nanotubes were both evenly dispersed throughout the electrode. After cycled at the same higher c–rates, the specific capacity retention at C/5–rate of the Pristine NCM811 decreased from 92.76 % to 86.55 % (158.7 mAh g$^{-1}$) while the LiF 5 wt% + MWCNTs 1 wt% modified NCM811 decreased from 96.04% to 91.77 % (182.6 mAh g$^{-1}$). The outstanding electrochemical performance is mainly attribute to the artificial cathode–electrolyte interphase, which protects the cathode from side reactions and the consumption of electrolyte. The pulse measurements were also carried out after 50th cycle of 1C–rate, and the total voltage change of the Pristine sample was up to 1.5336V at maximum current rate of 10C, while that of LiF 5 wt% + MWCNTs 1 wt% modified sample was only 0.3408V, revealing that the artificial cathode–electrolyte interphase could reduce the polarization generated during cycles and the good conductivity by adding MWCNTs.

**Keywords**: Ni–rich cathode material; Artificial cathode electrolyte interface; LiF;
Multiwalled carbon nanotube

1. Introduction

With the lithium–ion batteries (LIBs) becoming more and more integrated into our daily lives, including portable electronic products and electric vehicles (EV), the energy density of traditional cathode materials, i.e., LiCoO$_2$ and LiFeO$_4$ etc. are unable to meet their demands gradually.\textsuperscript{1,2} In recent years, high nickel content LiNi$_x$Co$_y$Mn$_{1-x-y}$O$_2$ (NCM, with $x$ greater than 0.6) materials cathode materials have engaged enormous attention, especially for the Ni–rich ones ($x\geq0.8$).\textsuperscript{3} Among them, LiNi$_{0.8}$Co$_{0.1}$Mn$_{0.1}$O$_2$ (NCM811) is one of the most popular cathode materials and is widely used in industrial applications. Higher nickel content leads to a huge advantage in energy density and lithium storage capacity, but also brings some serious issues which would influence the electrochemical performance. When the limited charge voltage is above 4.3V vs. Li$^+$/Li, the oxidation capability of Ni$^{3+/4+}$ redox couple is increased which brings high reactivity.\textsuperscript{4} As a result, the interfacial stability of Ni–rich materials is under greater stress, leading to intensification of the side reactions between the electrolyte and the electrodes, which would further cause decomposition of electrolyte. Those decomposed adducts continuously accumulate on the electrode surfaces and increase the interface impedance as the adducts severely obstruct Li$^+$ migration through the interface. Moreover, the structure of Ni–rich materials also tends to decay from layer structure to spinel structure and even unordered rock salt structure after several charge–discharge cycles.\textsuperscript{5}

To solve the above problems, especially the interface stability, surface coating
has been proved to be a simple and effective modification method, which can improve the structural stability and electrochemical Cycleability of cathode materials. The coating on the electrodes can also act as artificial solid electrolyte interface (α–SEI), and the one on the cathode is called the artificial cathode electrolyte interphase (α–CEI). The coating materials include metal oxides (Al₂O₃, TiO₂, ZrO₂), fluorides (AlF₃, MgF₂), phosphates (AlPO₄, Co₃(PO₄)₂), conducting polymers. The α–CEI is not only chemically stable which protects the cathode from harmful side reactions by insulating the cathode from contact with the electrolyte, but also optimizes the electrochemical performance by reducing electrolyte consumption caused by side reactions.¹³

In this paper, we chose lithium fluoride (LiF) as an α–CEI material. As one of the by–products of the naturally formed SEI, LiF is often used as α–SEI material for the anode materials especially for the lithium metal anode, and sometimes used for cathode modification as well. Xiong et al. prepared the LiF coated NCM811 material in situ using the excess Li remaining on the surface during the preparation of NCM, which improved the electrochemical performance. However, the Li⁺ conductivity of LiF is not so good for lithium ion transmission. As a solution, nano–carbon materials were also added during the formation of LiF to improve its conductivity.¹⁷,¹⁸ We prepared Ni–rich NCM811 materials modified by LiF with and without multiwalled carbon nanotubes (MWCNTs) as conductive additives. To illustrate the improvement of electrochemical performance of α–CEI, charge–discharge cycles with different C–rates, XRD, SEM, EDS were used to characterize the modified particles.
as well as cathode electrodes. The experimental conclusion was that LiF as α–CEI could effectively improve the cycleability of NCM811 materials, and the influence of the MWCNTs on the polarization of the battery was characterized by pulse measurement.

2. Experimental

2.1 Material Preparation

LiF nanoparticles were synthesized via a liquid phase reaction. Lithium hydroxide and ammonium fluoride were weight at the molar ratio of 1:1.1. First, the lithium hydroxide was added to ethyl alcohol and stirred vigorously by magnetic stirrer in a teflon container. The ammonium fluoride was then added into gradually per twenty minutes. The magnetic stirring lasted for 3 hours in total to react sufficiently. Then suspension was centrifuged and the sediment was dried in a vacuum oven at 60 °C overnight to obtain the precursor. The precursor was heated at 150 °C in a tube furnace for 10 hours in high purity Ar. The temperature was then risen to 300 °C and kept for 6 hours. At the same time, flowing high purity Ar is used as carrier gas to remove impurities. After cooling to room temperature, white LiF nanoparticles were obtained.

The cathode slurry consisted of cathode materials, carbon black (Super P) and polyvinylidene fluoride (PVDF) at a ratio of 80:10:10 (mass ratio). To make the comparison about the content of LiF, different weight percentage of LiF nano particle modified samples, i.e. 2.5 wt%, 5 wt% and 9 wt%) were prepared and marked as LiF–
2.5, LiF–5, LiF–9 respectively. To improve the conductivity of the cathode, 1 wt% of MWNTs were added to the 5 wt% LiF modified sample, which contains 74 wt% of NCM811, without change the percentage of the carbon black and PVDF percentage, were marked as LiF–5/MWCNTs–1. At the same time, the samples modified only by MWCNTs were also prepared for comparison and marked as MWCNTs–1. The commercial NCM811 cathode powder was supplied from ZhiChuan tec Co., ltd. It should be noted that since MWCNTs are prone to agglomeration due to van der Waals forces and are not easily dispersed in N–methyl–2pyrrolidone (NMP), the commercial dispersion solution of MWCNTs in NMP was directly used in this paper. The MWCNTs dispersion is provided by Jiangsu Cnano Technology Co., Ltd. Those materials were dispersed in NMP at room temperature through magnetic stirring for 12 hours. The homogeneous slurry was then coated on aluminum foil with Doctor Blade method and dried at 120 °C for 10 h in vacuum. The cathode electrode was cut into 14mm diameter discs for later use.

The coin–type cell (CR2025) LIBs were assembled in the glove box which water and oxygen content were all under 1 ppm in room temperature. Li–metal was used as anode (China Energy Lithium Co., Ltd). Polypropylene microporous film was used as separator and the electrolyte was consisted of 1M LiPF6 and EC/DMC/EMC(1:1:1 in volume).

2.2 Material Characterizations
The structures of the Pristine and modified NCM811 were examined by the X-ray diffraction (D/max–2550VB+/PC, Rigaku, Japan) with Cu Ka radiation (40kV,150mA), and the diffraction angle 2θ ranges from 10° to 80°. The morphology features were characterized with Scanning Electron Microscope (SEM, TESCAN MAIA 3, Czech republic). Energy Disperse Spectroscopy (EDS) on the field emission scanning electron microscope (FESEM, JSM–7500F, JEOL, Japan) was also used to observe the morphological as well as the element component features.

2.3 Electrochemical Measurements

The electrochemical tests were executed using the half-cell batteries after standing for 24h to make the electrolyte infiltrate adequately. The cycle performance and rate behaviors of the batteries were characterized by charge–discharge test in the voltage range from 3 to 4.4V. First the battery was activated at a low rate of C/10–rate for 2 cycles. The cycle was composed of constant current charging, constant voltage charging and constant current discharge. Among them, the constant currents of charge and discharge vary from the corresponding rate, while the constant voltage charge is carried out at the voltage limit of 4.4V to reduce the polarization. All charging and discharging cycle tests were completed on LAND test platform (CT3001A, Wuhan China). Pulse measurements were performed by an electrochemical workstation (CHI600E, Shanghai China). All electrochemical tests were performed at room temperature.
3. Results and Discussion

3.1 Structural Characterization

The XRD pattern of LiF is shown in Fig.1a. All peaks of the prepared LiF can be indexed on the space group of Fm–3m without any impurity peaks being found, which was in good agreement with PDF#70–1934 showing a great crystallinity. Figure 1b shows the XRD patterns of Pristine and 5 wt% and 1 wt% MWCNTs modified NCM811 (LiF–5/MWCNTs–1) electrodes. It is obvious that the addition of LiF and MWCNTs did not affect the structure of NCM811, both samples exhibit hexagonal $\alpha$–NaFeO$_2$ structure with R$\bar{3}$m space group, while no distinct LiF or CNTs peaks are found due to low content.\textsuperscript{20}

Figure 2a shows the SEM image of LiF particles with average particle size less than 1 μm. Figure 2b shows the bare NCM811 particles which consist of secondary particles with 5–20 μm in diameter. Compare to the LiF–5/MWCNTs–1 modified particles showing in Fig.2c, they represent similar particle morphologies which agrees well with the XRD patterns. Figure 2d magnified LiF–5/MWCNTs–1 further, and the dispersed multi–wall carbon nanotubes were observed clearly in the electrode without agglomeration and can improve the conductivity of the electrode.

EDS was performed to check the uniformity of $\alpha$–CEI coating layer on the surface of modified particles. The images are shown in Fig.3. The F element of LiF was selected to identify the existence of $\alpha$–CEI. The bright dots assigned to F element are almost uniformly dispersed on the NCM surface although there was a partial agglomeration.
3.2 Electrochemical Characteristics

Firstly, the theoretical content of LiF was estimated by utilizing the size of the NCM811 particles as well as that of LiF. According to this very simple model calculation, by adding 5.6 wt% of LiF nano particles, it will roughly cover the full surface of NCM811 particles. We then assembled 2.5 wt%, 5 wt% and 9 wt% of LiF modified NCM811. The constant current charge–discharge cycle with different C–rate were performed, as shown in Fig.4. At smaller current, i.e., C/5–rate, especially after 25 cycles of different (higher) C–rate, 2.5 wt% showed better capacity than the rest. But, at higher rate (C/2–rate, 1C–rate and 2C–rate), the battery performs best with 5 wt% LiF modification. Because we are keener to higher C–rate (fast charging/discharging) performance in electric vehicles applications, we then by adding 1 wt% MWNTs into this 5 wt% LiF modification sample and tested the electrochemical properties. According to our previous experiences, 1 wt% MWCNTs was choose to enhance the conductivity of the cathodes throughout this study.

The initial charge–discharge rates at C/10–rate (1C–rate = 180 mAh g$^{-1}$) between 3 and 4.4V is shown in Fig.5. The charging and discharging platforms were similar, indicating that the α–CEI did not participate in electrochemical reaction during lithiation or delithiation. In contrast to the Pristine one, those modified NCM811 samples perform better initial discharge capacity. Compared with 185.5 mAh g$^{-1}$ of Pristine NCM811, the materials modified only by MWCNTs and LiF showed specific
discharge capacities of 189.6 mAh g$^{-1}$ and 193.5 mAh g$^{-1}$ respectively. While the samples modified by both of them reached 195.9 mAh g$^{-1}$, showing a significant improvement.

Rate performance of the Pristine and modified NCM811 are shown in Fig.6. In Fig.6a and 6b, it is obvious that the gaps of specific discharge capacities between Pristine and modified NCM811 widen with the increase of the discharge rates. When the cycles of 2C-rate were finished, the discharge capacity of Pristine NCM811 decreased to 138.6 mAh g$^{-1}$ with the specific capacity retention of 75.59 %, while the LiF–5/MWCNTs–1 performs the best rate capacity at 163 mAh g$^{-1}$ and the specific capacity retention of 81.92 %. After the high rate test, a C/5–rate cycle is followed to test the battery's recovery performance by comparing the data of the 10th and 26th cycles with the same current density of C/5–rate. The specific capacity retention of Pristine NCM811 decreases from 92.76 % to 86.55 %, while the LiF–5/MWCNTs–1 decreases from 96.04 % to 91.77 % which showed better cyclic recovery performance and reduced the irreversible capacity loss. At the same time, it can also be found that the specific discharge capacity and capacity retention have been greatly improved when MWCNTs were added. Although LiF does not improve much, it shows good capacity recovery in the followed C/5–rate cycles, indicating that α–CEI does play a certain role in protecting the electrode at high current and effectively reducing the irreversible cycle caused by side reactions.

Differentiation of the charge–discharge curves can amplify the relationship between voltage and capacity making it easy to observe and interpret. Figure 7 shows
the $dQ/dV$ profiles of Pristine and LiF–5/MWCNTs–1 on the 5th, 10th and 25th cycles at C/10 rate between 3V and 4.4V. The position of the peaks and the shift through cycles reflect the reaction process of the electrode material interface. The curve has three different pairs of reduction and oxidation peaks corresponding to the phase transitions from H1 to M to H2 and H3, respectively. As the charging and discharging cycle proceeds, the H1 to M peak of the Pristine NCM811(Fig.7a) shift more than the one of LiF–5/MWCNTs–1(Fig.7a). The shift demonstrates that in the process of charging and discharging cycles the rising resistance of the electrode material leading to the increased polarization, so that lithium ions need to overcome a higher barrier in the process of extraction and insertion. Those peak shifts prove that the LiF and MWCNTs modification can partly protect the nickel–rich NCM811 material, inhibiting the increase of material resistance, and stabilize the electrochemical performance of LiF–5/MWCNTs–1.

Pulse measurements were also used to estimate the polarization occurred during the charge–discharge cycles. Starting at a specific SOC (State of charge) and the batteries were discharged in a selected constant current. The voltage changing during the limit pulse time was recorded and analyzed, reflecting charge transfer, ion mass transfer and solid–state diffusion in the cycles. The schematic diagram of pulse measurement is shown in Fig.8. $E_{\text{IR-drop}}$ is the voltage drop that occurs within a few microseconds after the start of the pulse. $\Delta E_i$ is the subsequent voltage change during the pulse time. DC–IR is the sum of $E_{\text{IR-drop}}$ and $\Delta E_i$ that represents the total polarization during the pulse discharge. In this paper, we start the pulse
measurement at 50 % SOC and the constant discharge current increases gradually from C/2–rate, 1C–rate, 2C–rate, 5C–rate and 10C–rate. The pulse discharge lasts for 30s and relaxation for 1 hour. The batteries were then charged and discharged to 50 % SOC to continue the pulse discharge of the next current.

Moreover, in order to clearly demonstrate the effect of α–CEI, the Pristine, LiF–5 and LiF–5/MWCNTs–1 samples were tested before (Fig.9a) and after 50 cycles at 1C–rate (Fig.9b), and the DC–IR, $E_{\text{IR-drop}}$ and $\Delta E_t$ of both situations are also represented respectively. $E_{\text{IR-drop}}$ mainly shows charge transfer polarization ($\eta_{\text{ct}}$), while $\Delta E_t$ is mainly controlled by solid state diffusion polarization ($\eta_{\text{diff}}$) and concentration polarization ($\eta_{\text{conc}}$). The slope of the curve represents the polarization of the sample. As the conductivity of LiF is not so good, the polarization of LiF–5 increases significantly with the increase of current before the cycle, while the addition of MWCNTs with excellent conductivity improves this situation, effectively reduces the increase of polarization. After the cycle, the polarization of the Pristine NCM811 material was significantly increased, while the situation of LiF–5 was improved, indicating that LiF, as α–CEI, had a protective effect on the electrode from side reactions in the cycle and reduced the increase of polarization caused by the decomposed adducts of electrolyte. The polarization of LiF–5/MWCNTs–1 was further reduced which was consistent with its rate performance.

Concerning about the Li$^+$ diffusion coefficient, the change of $D_{\text{Li}^+}$ values before and after 50 cycles at 1C–rate were measured by pulse measurements. $\Delta E_s$ in the previous Fig.8 is the steady–state voltage change of the battery caused by the current
applied. We suppose that the diffusion process of Li ions is one–dimensional (1D) diffusion. Furthermore, the charge transfer and phase change process during the charge–discharge process can be ignored.\textsuperscript{27} The method to calculate the $D_{Li^+}$ can be derived from Fick's second law, through the following Eq (1).

$$D_{Li^+} = \frac{4}{\pi} \left( n_m V_m \right) \left( \frac{\Delta E_S}{\Delta E_t} \right)^2 \left( \tau \ll \frac{l^2}{D_{Li^+}} \right)$$ (1)

\(\tau\) represents the relaxation time, \(n_m\) and \(V_m\) represent the mole number and molar volume of electrode material respectively, \(S\) represents the electrode/electrolyte contact area. \(\Delta E_s\) and \(\Delta E_t\) are the same with the pulse measurement. The formula can be further simplified by approximating the particle of electrode material to a sphere with diameter \(R\), that is Eq (2).\textsuperscript{28}

$$D_{Li^+} = \frac{4}{\pi} \left( \frac{R}{2} \right)^2 \left( \frac{\Delta E_S}{\Delta E_t} \right)^2 \left( \tau \ll \frac{R^2}{D_{Li^+}} \right)$$ (2)

The $D_{Li^+}$ value of Pristine and LiF–5/MWCNTs–1 were estimated after 2nd C/10–rate charge–discharge cycle and 50th 1C–rate cycle, which summarized in Table1. The 1\textsuperscript{st} cycle, the two samples showed similar diffusion coefficient. But after 50 cycles, the $D_{Li^+}$ value of the Pristine decreased much more than that of the LiF–5/MWCNTs–1. This is attributed to the protective effect of \(\alpha\)–CEI on the structure and its own good lithium ion conductivity, while the addition of MWCNTs improves the electrical conductivity of \(\alpha\)–CEI, representing desirable Li$^+$ insertion and extraction kinetics.\textsuperscript{29}

In order to characterize the protective effect of \(\alpha\)–CEI, after 100 cycles of 1C–rate, the Pristine and LiF–5/MWCNTs–1 batteries were disassembled and the as–is (with all the by–products covered the electrodes, without washing) cathode electrodes
were directly characterized by XRD. The XRD patterns of the after cycled battery are shown in Fig.10. All the peaks of the Pristine were weakened, as well as there are more impurity peaks appeared, implying the structures being damaged and more side reactions occurred through the charge–discharge cycles. On the contrary, the modified NCM811 shows a stronger I(003)/I(104) peak than that of the Pristine one, indicating better layered structure maintained and less cation mixing which owes to the protection of α–CEI improving the structural stability.\textsuperscript{30}

4. Conclusion

In summary, LiF and MWCNTs have been used to modified the Ni–rich cathode material NCM811 as α–CEI. Due to the protection of the α–CEI and enhanced conductivity of MWCNTs, the NCM811 modified with 5 wt% LiF and 1 wt% MWCNTs results with 163 mAh g\textsuperscript{−1} after 25 cycles with 5 each of following C–rates (C/10–rate ,C/5–rate, C/2–rate, 1C–rate, 2C–rate), while that of the Pristine sample is only 138.6 mAh g\textsuperscript{−1}. Also, the Li\textsuperscript{+} diffusion coefficient was well maintained after 50 cycles with the help of α–CEI. In conclusion, the LiF 5 wt%+MWCNTs 1 wt% modification will be an effective way to improve the cyclic performance of Ni–rich NCM811 materials.

Acknowledgment(s)
This work was carried out with financial support from Donghua University with startup funding (grant no. 62416307) and Jiangsu Cnano Company with R&D funding.

References

1. N. Nitta, F. Wu, J. T. Lee, and G. Yushin, Mater. Today, 18, 252(2015).
2. S. T. Myung, F. Maglia, K. J. Park, S. Y. Chong, and Y. K. Sun, ACS Energy Lett., 2, 196(2017).
3. J. Kim, H. Lee, H. Cha, M. Yoon, M. Park, and J. Cho, Adv. Energy Mater., 8, 1702028(2017).
4. W. Liu, P. Oh, X. Liu, M. Lee, W. Cho, S. Chae, Y. Kim, and J. Cho, Angew. Chem., Int. Ed., 54, 4440(2015).
5. L. Zou, W. Zhao, Z. Liu, H. Jia, J. Zheng, G. Wang, Y. Yong, J. G. Zhang, and C. Wang, ACS Energy Lett., 3, 2433(2018).
6. M. Dong, Z. Wang, H. Li, H. Guo, X. Li, K. Shih, and J. Wang, ACS Sustainable Chem. Eng., 5, 10199(2017).

7. Y. Hao, D. Ke, G. Hu, Z. D. Peng, Y. B. Cao, K. P. Wu, et al., Electrochim. Acta, 289, 149(2018).

8. J. Z. Kong, S. S. Wang, G. A. Tai, L. Zhu, L. G. Wang, H. F. Zhai, et al., J. Alloys Compd., 657, 593(2016).

9. S. H. Lee, C. S. Yoon, K. Amine, and Y. K. Sun, J. Power Sources, 234, 201(2013).

10. K. Yang, B. Niu, Y. Liu, J. Zhong, and J. Li, Int. J. Electrochem. Sci., 14, 3139(2019).

11. R. Zhao, J. Liang, J. Huang, R. Zeng, J. Zhang, H. Chen, and G. Shi, J. Alloys Compd., 724, 1109(2017).

12. Y. R. Bak, Y. Chung, J. H. Ju, M. J. Hwang, Y. Lee, and K. S. Ryu, J. New Mater. Electrochem. Syst., 14, 203(2011).

13. K. W. Nam, S. M. Bak, E. Y. Hu, X. Q. Yu, Y. N. Zhou, X.J. Wang, et al., Adv. Funct. Mater., 23, 1047(2013).

14. J. Lang, Y. Long, J. Qu, X. Luo, H. Wei, K. Huang, et al., Energy Storage Materials, 16, 85(2019).

15. S. Ma, X. Zhang, S. Li, Y. Cui, Y. Cui, Y. Zhao, and Y. Cui, Ionics, 26, 2165(2020).

16. M. Stich, N. Pandey, and A. Bund, J. Power Sources, 364, 84(2017).

17. X. Li, X. Zhao, M. S. Wang, K. J. Zhang, Y. Huang, M. Z. Qu, et al., RSC Adv., 7, 24359(2017).
18. W. Liu, C. Li, X. Sun, X. Zhang, K. Wang, Z. Li, et al., *J. Alloys Compd.*, 758, 206(2018).

19. L. L. Wang, Y. Zeng, H Xie, S. H. Deng, X. P. Li, F. C. Yi, et al., *Chin. J. Mater. Res.*, 33, 271(2019).

20. S. J. Shi, J. P. Tu, Y. Y. Tang, Y. Q. Zhang, X. Y. Liu, X. L. Wang, and C. D. Gu, *J. Power Sources.*, 225, 338(2019).

21. C. Ban, Z. Wu, T. D. Gillaspie, L. Chen, Y. Yan, J. L. Blackburn, and A. C. Dillon, *Adv. Mater.*, 22, E145(2010).

22. F. Wu, N. Liu, L. Chen, Y. F. Su, G. Q. Tan, L. Y. Bao, et al., *Nano Energy*, 59, 50(2019).

23. F. Schipper, H. Bouzaglo, M. Dixit, E. M. Erickson, T. Weigel, M. Talianker, et al., *Adv. Energy Mater.*, 8, 1701682(2017).

24. T. DuBeshter and J. Jorne, *J. Electrochem. Soc.*, 164, E3539(2017).

25. D. W. Kim, S. M. Hwang, J. B. Yoo, and Y. J. Kim, *ChemElectroChem*, 7, 2000283(2020).

26. F. J. Mo, J. F. Ruan, S. X. Sun, Z. X. Lian, X. Y. Yue, et al. *Adv. Energy Mater.*, 9, 1902123(2019).

27. W. H. Zhang, L. W. Liang, F. Zhao, Y. Liu, L. R. Hou, and C. Z. Yuan, *Electrochim. Acta*, 340, 135871(2020).

28. S. H. Cui, Y. Wei, T. C. Liu, W. J. Deng, Z. X. Hu, Y. T. Su, et al., *Adv. Energy Mater.*, 6, 1501309(2016).
29. M. Wang, R. Zhang, Y. Q. Gong, Y. F. Su, D. B Xiang, L. Chen, et al., *Solid State Ionics*, 312, 53 (2017).

30. J. Wang, Q. Yuan, R. Wang, G. Q. Tan, Y. F. Su, D. H. Li and F. Wu, *IOP Conference Series: Materials Science and Engineering*, 735, 012007 (2020).

**Figure Captions**

**Figure 1.** XRD patterns of (a) LiF sample (b) Pristine and LiF–5/MWCNTs–1 electrodes. The LiF samples were consistent with PDF#70–1934 and had good crystallinity. With the modification of LiF and MWCNTs, the XRD pattern shows a crystal structure of $\alpha$–NaFeO$_2$ layered structure with R$\bar{3}$m space group like the Pristine one, indicating the formation of $\alpha$–CEI did not affect the structure.
**Figure 2.** SEM images of (a) LiF (b) Pristine NCM811 particles (c–d) LiF–5/MWCNTs–1 electrode. Figure 2a indicates that the LiF prepared particles are small. In Fig.2b, 2c and 2d, since the materials have been prepared into electrode, it was hard to distinguish various materials on the surface of NCM811 particles, the multi–wall carbon nanotubes dispersed in the electrode could be clearly seen after magnification, which enhanced the conductivity of the electrode.

**Figure 3.** (a) FESEM image of LiF–5/MWCNTs–1 electrodes, corresponding EDS (b–g) images. The distributed F element represents that α– CEI composed of LiF almost uniformly dispersed on the NCM811 surface.

**Figure 4.** Rate performance of Pristine and LiF–2.5, LiF–5, LiF–9. Among different LiF contents, LiF–5 showed the best cycleability at high rates, so LiF–5 was selected for subsequent modification.

**Figure 5.** The initial charge–discharge plots at C/10–rate between 3V and 4.4V of Pristine, MWCNTs–1, LiF–5 and LiF–5/MWCNTs electrodes. Those modified samples show good initial discharge capacity. The specific discharge capacity of LiF–5/MWCNTs–1 reached 195 mAh·g$^{-1}$ in the first circle, which was higher than 185 mAh g$^{-1}$ of the Pristine sample.

**Figure 6.** Rate performance (a–b) of Pristine and LiF–5, MWCNTs–1, LiF–
5/MWCNTs–1 electrodes from C/10–rate to 2C–rate between 3V and 4.4 V. With the increase of the charge–discharge rates, the capacity of the Pristine NCM811 material fades seriously, while the addition of LiF and multiwalled carbon nanotubes effectively improves the rate performance. In addition, LiF also improves the capacity recovery performance when the battery changes from high rate of 2C-rate to low rate of C/5-rate.

**Figure 7.** dQ/dV profiles of Pristine and LiF–5/MWCNTs–1 modified at C/10–rate between 3V and 4.4 V. The peak migration of LiF–5 /MWCNTs–1 during the cycle was smaller than that of the Pristine one. It indicates that the α–CEI kept the stability of NCM811 material from side reactions.

**Figure 8.** Schematic diagram of pulse test in a pulse time of 30s.

**Figure 9.** Scheme of the pulse measurements (a) before and (b) after 50 cycles at 1C–rate of the Pristine, LiF–5 and LiF–5/MWCNTs–1 modified NCM811 samples at current rates in the range of C/2–rate to 10C-rate resulting parameters of DC–IR, $E_{IR\,\,drop}$, and $\Delta E_i$ versus the current. Before the cycles, the LiF–5/MWCNTs–1 modified sample showed a smaller slope, indicating that the polarization problem caused by LiF addition is alleviated, reflecting the role of multiwalled carbon nanotubes. After the cycles, the α–CEI showed good electrode protection and inhibited the increase of polarization caused by side reactions during the cycles, especially in high current rates,
which is consistent with the rate capabilities data.

**Figure 10.** XRD patterns of Pristine and LiF–5/MWCNTs–1 electrodes after 100 charging and discharging cycles at 1C-rate. Compared with Pristine, LiF–5 /MWCNTs–1 maintained a good XRD peak pattern, indicating that the cathode electrode is well protected by α–CEI and there are fewer side reaction deposits.

| sample    | the 2nd $D_{Li^+}$(cm$^2$ s$^{-1}$) | the 50th $D_{Li^+}$(cm$^2$ s$^{-1}$) |
|-----------|-----------------------------------|-------------------------------------|
| Pristine  | $2.502 \times 10^{-9}$            | $1.87 \times 10^{-10}$             |

Tab.1 $D_{Li^+}$ value of Pristine and LiF-5/MWCNTs-1 samples after 2nd and 50th charge-discharge cycles. As cycles progressed, LiF-5/MWCNTs-1 maintained a higher Li$^+$ diffusion coefficient, reflecting the protection of α-CEI to the electrode.
| LiF-5/MWCNTs-1 | 3.126×10⁻⁹  | 0.647×10⁻⁹ |

Figure 1
Figure 5
Figure 7
Figure 8
Figure 9
Figure 10
