Article

Electrochemical Behavior of NH_4F -Pretreated $\text{Li}_{1.25}\text{Ni}_{0.20}\text{Fe}_{0.13}\text{Co}_{0.33}\text{Mn}_{0.33}\text{O}_2$ Cathodes for Lithium-ion Batteries

Yonglei Zheng ¹, Yikai Li ², He Wang ¹, Siheng Chen ¹, Xiangxin Guo ¹, Sheng Xu ^{1,*} and Zhongyu Cai ^{3,4,5,*}

¹ College of Physics Science, Qingdao University, Qingdao 266071, China; zhenglei940203@163.com (Y.Z.); xzss68@163.com (H.W.); supremecsh@163.com (S.C.); xxguo@qdu.edu.cn (X.G.)

² Qingdao No 58 High School, Qingdao 266071, China; liyikai1986@163.com

³ Research Institute for Frontier Science, Beihang University, Beijing 100191, China

⁴ Beijing Advanced Innovation Center for Biomedical Engineering, Beihang University, Beijing 100191, China

⁵ School of Space and Environment, Beihang University, Beijing 100191, China

* Correspondence: shengxu@qdu.edu.cn (S.X.); caizy@buaa.edu.cn (Z.C.)

Received: 23 December 2019; Accepted: 27 January 2020; Published: 4 February 2020

Abstract: We report a novel method to fabricate lithium-ion batteries cathodes with the NH_4F pretreatment. In this study, NH_4F -pretreated $\text{Li}_{1.25}\text{Ni}_{0.20}\text{Fe}_{0.13}\text{Co}_{0.33}\text{Mn}_{0.33}\text{O}_2$ hollow nano-micro hierarchical microspheres were synthesized for use as cathode materials. The X-ray diffraction patterns of NH_4F -pretreated $\text{Li}_{1.25}\text{Ni}_{0.20}\text{Co}_{0.33}\text{Fe}_{0.13}\text{Mn}_{0.33}\text{O}_2$ were analyzed with the RIETAN-FP software program, and the results showed that the samples possess a layered $\alpha\text{-NaFeO}_2$ structure. The effects of pretreatment with NH_4F on the electrochemical performance of the pristine material were evaluated through charge/discharge cycling, the rate performance, and electrochemical impedance spectroscopy (EIS). Pretreatment with NH_4F significantly improved the discharge capacities and coulombic efficiencies of $\text{Li}_{1.25}\text{Ni}_{0.20}\text{Co}_{0.33}\text{Fe}_{0.13}\text{Mn}_{0.33}\text{O}_2$ in the first cycle and during subsequent electrochemical cycling. The sample pretreated with an appropriate amount of NH_4F (NFCM 90) showed the highest discharge capacity ($209.1 \text{ mA h g}^{-1}$) and capacity retention (85.2% for 50 cycles at 0.1 C). The EIS results showed that the resistance of the NFCM 90 sample (76.32Ω) is lower than that of the pristine one (206.2Ω).

Keywords: lithium-ion batteries; cathode material; microspheres; NH_4F pretreatment; spinel phase; electrochemical performance

1. Introduction

Economic development has led to increased research on electrochemical energy storage techniques for new energy sources, such as lithium-ion [1–3], lithium–sulfur [4], and sodium-ion batteries [5], of which lithium-ion batteries are the most promising and widely investigated [6–10]. The development of lithium-ion batteries has been restricted because the capacities of anode materials are much better than those of cathode materials. $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (NCM111) which has been widely investigated is a better cathode material choice than LiCoO_2 in terms of reversible capacity, thermal and structural stability, and cost. However, the rapid capacity fading and inferior rate capability of NCM limit its sustainability and prevent its wide use in high-power applications.

Many different methods have been used to solve the above problems, e.g., formation of special morphologies, bulk doping, surface coating, and pretreatment. There are already relevant experiments on the above that constructing electrode materials with different microstructures, coating the surfaces of lithium-ion battery cathodes with materials, such as carbon and CoAl_2O_4 , and doping positive

electrode materials with metal ions, such as Fe and Zn and so on. Spinel-phase LiM_2O_4 with oxygen vacancies can be formed on the surfaces of cathode materials through pretreatment. The formed spinel phase improves the diffusion of lithium ions and the escape of O_2 gas from the cathode surface during the cycle, which helps improve electrochemical performance [11]. The most common electrolyte component, namely LiPF_6 , produces a small amount of HF via reaction with water and corrodes the oxide electrode material during charging and discharging [12]. Electrode corrosion by a highly active organic electrolyte can be resolved by the addition of fluorides, such as CeF [13], Mg_2F [14], ZrF_x [15,16], AlF_3 [17], FeF_3 [18], CaF_2 [19], and LiF [20,21]. The $\text{LiFe}_x\text{Ni}_{1/3-x}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ hollow micro-spheres as cathodes for LIBs have been shown to have the best electrochemical performance at $x = 0.133$ [22], although hollow microspherical structure enhances performance, the iron substitution increases microspheres aggregation, and also reduces electrochemical properties as decreasing lithium ion diffusion.

In this study, we adopt a simple and reliable method for electrochemical performance improvement. The method involves NH_4F pretreatment of $\text{Li}_{1.25}\text{Ni}_{0.2}\text{Fe}_{0.13}\text{Co}_{0.33}\text{Mn}_{0.33}\text{O}_2$ cathodes, which were obtained by using MnO_2 microspheres as self-templates. X-ray diffraction (XRD), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), and electrochemical tests showed that the structure, morphology, and electrochemical properties of $\text{Li}_{1.25}\text{Ni}_{0.2}\text{Fe}_{0.13}\text{Co}_{0.33}\text{Mn}_{0.33}\text{O}_2$ after NH_4F pretreatment need to be considered.

2. Experimental

2.1. Materials Synthesis

MnO_2 microspheres were prepared via a previously reported method [23]. The prepared MnO_2 , $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (AR, 98%, Aladdin, Shanghai, China), $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (AR, 99%, Aladdin, China), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (AR, Aladdin, China), and $\text{LiOH} \cdot \text{H}_2\text{O}$ (AR, 98%, Aladdin, China) were added to ethanol in specific proportions (metal-ion molar ratios $\text{Li}:\text{Fe}:\text{Ni}:\text{Co}:\text{Mn} = 1.25:0.13:0.2:0.33:0.33$) to form a suspension. The suspension was stirred at 60°C until the ethanol evaporated. The mixture was calcined at 850°C for 15 h in air to give rise to $\text{Li}_{1.25}\text{Ni}_{0.2}\text{Fe}_{0.13}\text{Co}_{0.33}\text{Mn}_{0.33}\text{O}_2$ [24,25].

The NH_4F -pretreated $\text{Li}_{1.25}\text{Ni}_{0.2}\text{Fe}_{0.13}\text{Co}_{0.33}\text{Mn}_{0.33}\text{O}_2$ materials were prepared as follows. NH_4F was dissolved in deionized water. The obtained $\text{Li}_{1.25}\text{Ni}_{0.2}\text{Fe}_{0.13}\text{Co}_{0.33}\text{Mn}_{0.33}\text{O}_2$ powder was homogeneously dispersed in the NH_4F solution under stirring. Samples with $\text{Li}_{1.25}\text{Ni}_{0.2}\text{Fe}_{0.13}\text{Co}_{0.33}\text{Mn}_{0.33}\text{O}_2$ and NH_4F molar percentages of 95% and 5% (NFCM 95), 90% and 10% (NFCM 90), 85% and 15% (NFCM 85), and 80% and 20% (NFCM 80) were prepared. The mixed solutions were dried until the solvent completely evaporated and the resulting materials were calcined at 400°C for 5 h in air.

2.2. Characterization

XRD (Rigaku SmArtlab-3KW, Tokyo, Japan, $\text{Cu K}\alpha$ radiation) was performed in the range 15° to 70° to determine the crystal structures of the pristine and NH_4F -pretreated materials. The XRD results were analyzed with the RIETAN-FP program. The elemental compositions of the samples were determined by EDS (Oxford INCA, Oxfordshire, UK). The particle morphology was examined by scanning electronic microscopy (SEM, STEM Sigma500, Carl Zeiss, Oberkochen, Germany) and high-resolution transmission electron microscopy (HRTEM, JEOL JEM-2100F, Tokyo, Japan).

2.3. Electrochemical Measurements

The electrochemical performances were investigated at 25°C with the LAND CT2001A battery tester (LANHE, Guangzhou, China), which using CR2025-type coin cell including cathode and lithium metal anode separated by the Celgard 2400 film. The cathode consisted of stoichiometric amounts of the active materials, conductive carbon, and poly (vinylidene fluoride) (mass ratios 8:1:1). *N*-Methy-2-pyrrolidinone (>99.5%, Aladdin, China) was added to the mixture to obtain a slurry, which

was spread on an aluminum foil current collector and then dried in a vacuum at 100 °C for 12 h. Then use the tableting mechanism to produce a round electrode with a surface area of about 1.1 square centimeters. Use of an argon-filled glove box (water < 1 ppm, O₂ < 1 ppm) is essential for assembly of the coin cells. The electrolyte was 1 M LiPF₆ in a 1:1 v/v mixture of ethylene carbonate and diethyl carbonate (Kejing Group, Hefei, China). The NEWARE test system was used to investigate the charge/discharge performances of the cells in the voltage range 2.5–4.5 V at 25 °C. Electrochemical impedance spectroscopy (EIS) was performed with an electrochemical workstation (PARSTAT 2273, AMETEK, Berwyn, PA, USA) in the range 0.1 Hz to 100 kHz. Cyclic voltammetry (CV) was performed at a scanning rate of 0.1 mV s^{−1} in the range 2–5 V.

3. Results and Discussion

Figure 1a shows the XRD patterns of pristine and NH₄F-pretreated samples. The patterns show that all samples were layered α -NaFeO₂ structure (rhombohedral lattice with the R-3m space group). The clear separations of the (006) from the (012) peak and the (108) from the (110) peak confirm the formation of a highly ordered hexagonal layered structure.

Figure 1. (a) The XRD patterns of pristine and NH₄F-pretreated Li_{1.25}Ni_{0.2}Fe_{0.13}Co_{0.33}Mn_{0.33}O₂ samples; (b) the refined XRD pattern of the NFCM 90 sample.

The RIETAN-FP program was used to analyze XRD patterns of pristine and NH₄F-pretreated samples, the calculated structural parameters are listed in Table 1. The values of

$$\left(\equiv \sqrt{\sum_{i=1}^N \omega_i [y_i - f_i(x)]^2 / \sum_{i=1}^N \omega_i y_i^2} \right) \quad (1)$$

$$R_e \left(\equiv \sqrt{(N - n) / \sum_{i=1}^N \omega_i y_i^2} \right) \quad (2)$$

and $S (\equiv R_{wp}/R_e)$ are sufficiently small, which confirms that the final refinements are reliable. The c/a values are 4.986 and 4.982 (both greater than 4.90, Table 1) and the intensity ratios [I(003)/I(104)] are 1.54 and 1.41 (both greater than 1.2, Figure 1a) in the XRD patterns of pristine and NFCM 90 samples. This shows that NFCM 90 sample has stable layered structure and low degree of cation mixing. Figure 1b shows the XRD powder pattern (crosses) of the NFCM 90 sample together with the Rietveld refinement (solid curve); the green line corresponds to the recorded curve, the blue sticks correspond to the peak positions, the purple line corresponds to the fitted curve, and the red line corresponds to the error curve.

Table 1. The lattice parameters of all samples refined by the RIETAN-FP.

x	a (Å)	c (Å)	V (Å ³)	R_{wp} (%)	R_e (%)	S
NFCM 80	2.861(5)	14.25(1)	101.06(6)	4.309	4.054	1.0630
NFCM 85	2.861(4)	14.24(9)	101.03(5)	4.227	3.998	1.0574
NFCM 90	2.861(4)	14.25(7)	101.10(0)	4.183	4.161	1.0054
NFCM 95	2.861(7)	14.25(4)	101.09(5)	4.303	4.221	1.0194
Pristine	2.861(4)	14.26(7)	101.17(1)	4.353	4.048	1.0754

The morphologies and microstructures of the obtained electrode materials are shown in Figure 2. The submicron MnO_2 spheres, which were used for self-templating, affected the morphologies and particle sizes of the obtained materials. The materials clearly consist of sub-micron spheres of particle size 1–2 μm . There are no obvious differences among the spherical shapes and particle sizes of the pristine and NH_4F -pretreated samples. This shows that treatment with NH_4F did not significantly change the morphology of pristine material.

Figure 2. The FE-SEM images of (a,b) pristine, (c,d) NFCM 95, (e,f) NFCM 90, (g,h) NFCM 85, and (i,j) NFCM 80.

Figure 3 shows TEM and HRTEM images of pristine and NFCM 90 samples. The TEM images show that treatment with NH_4F changed the electrode material surface. Figure 3b shows a lattice spacing of 0.47 nm corresponding to the (003) plane of the layered phase, and Figure 3d shows lattice spacings of 0.24 and 0.20 nm corresponding to the (222) and (004) planes, respectively, of the spinel phase. The above results prove the presence of the spinel phase on the pretreated material surfaces.

The chemical composition of the NFCM 90 sample was determined by EDS. The elemental mappings (Figure 4) show the distributions of Ni, Co, Mn, Fe, and F elements, in the ratios Fe:Ni:Mn:Co = 4.27:6.03:11.34:10.96, which are close to the theoretical molar ratios. The weight percentage of fluorine in the positive electrode material is close to the expected value, which indicates successful preparation of the positive electrode material.

Figure 3. The TEM and HRTEM images of (a,b) pristine and (c,d) NFCM 90.

Figure 4. The EDS spectra and element mapping analysis spectra of the NFCM 90 sample.

The electrochemical performances of pristine and NFCM 90 samples were investigated. Figure 5a shows the discharge curves of samples at 0.1 C ($1\text{ C} = 278\text{ mA h g}^{-1}$). After 50 cycles, the discharge capacities of pristine and NFCM 90 samples are 129.4 mA h g^{-1} and 178.2 mA h g^{-1} , respectively. The capacity retention rates for pristine and NFCM 90 samples are 76.3% (169.4 mA h g^{-1}) and 85.2% (209.1 mA h g^{-1}), respectively. Figure 5b shows the charge/discharge curves of the initial cycle for pristine and NFCM 90 samples at 0.1 C. The continuity of the voltage curve during the charge-discharge cycles confirms the stability of electrode material. The charge capacities of pristine and sample NFCM 90 are 195.1 mA h g^{-1} and 250 mA h g^{-1} , and the discharge capacities are 169.4 mA h g^{-1} and 209.1 mA h g^{-1} , respectively. The NFCM 90 sample has a higher capacity retention, higher than those of pristine samples after 15 cycles ($92.3\% > 90.4\%$) and 30 cycles ($87.5\% > 82.8\%$). Pretreatment with an appropriate amount of NH_4F can prevent the cathode surface from reacting with the electrolyte. Partial substitution of oxygen in the crystal by fluorine improves the cycling stability of the NH_4F -pretreated samples. The performances of lithium batteries can be degraded by treatment with an excessive amount of NH_4F . Electrolyte corrosion by NH_4F therefore needs to be considered.

Figure 5. (a) Comparative cycling performances and coulombic efficiencies at 0.1 C; (b) galvanostatic charge—discharge curves at 0.1 C over a potential window of 2.5–4.5 V; (c) comparative rate capabilities of pristine and NFCM 90 samples; (d) the cyclic voltammetry (CV) curves of pristine and NFCM 90 samples.

Figure 5c shows the discharge curves of pristine and NFCM 90 samples at various rates from 0.1 to 2 C. The voltage charge must be kept constant for 30 min to reach the predetermined voltage when the constant current charge at rates higher than 0.5 C. The discharge capacities of the NFCM 90 sample at 0.1, 0.5, 1, and 2 C are 206.4 , 161 , 106 , and 47.5 mA h g^{-1} , respectively. The capacity of the NFCM 90 sample returns to 182.8 mA h g^{-1} (88.6%) when the current rate finally returns to 0.1 C, whereas the pristine sample capacity returns to 141.6 mA h g^{-1} (85.7%). This suggests that the NFCM 90 sample has better reversibility. Formation of spinel phase after NH_4F pretreatment can improve the lithium ion diffusion rate, form oxygen vacancies to limit the release of O_2 from the cathode surface,

and improves the structure of the solid electrolyte interphase (SEI) film on the cathode surface. These factors may be responsible for the better rate capacity of the NFCM 90 sample.

Figure 5d shows the cycle voltammetry results for the pristine and NFCM 90 samples. Lithium ion extraction ability is related to oxidation peak, and lithium ion insertion ability is related to reduction peak. The specific capacity of the electrode material is related to the redox peak area. The potential interval between the anode peak and the cathode peak represents the electrode polarization capacity, which indicates the reversibility of lithium ion insertion and extraction. The potential interval for the NFCM 90 sample is 0.39 V, which is smaller than the pristine one (0.44 V), indicating a smaller electrode polarization. The redox peak for the NFCM 90 sample is larger than that for the pristine sample, which indicates a higher specific capacity.

Figure 6a shows the EIS results for pristine and NFCM 90 samples. Figure 6b shows the fitted experimental results and equivalent circuits (inset). At the interface between the electrode material and electrolyte, the capacitance double-layer and Li-ions form a semicircle from high frequency to intermediate frequency in the AC impedance spectrum under the action of the interfacial exchange resistance. The exchange resistance of Li-ions at the interface between electrode material and electrolyte corresponds to the intercept of the semicircle on the x-axis, which represents the charge-transfer resistance (R_{ct}) in the analog circuit. The detailed fitted results are listed in Table 2. The R_{ct} (76.3 Ω) of the NFCM 90 sample electrode is smaller than the pristine one (206.2 Ω), which indicates that the R_{ct} of the NFCM 90 sample in the lithium-ion battery is smaller, and this confirms that NH_4F pretreatment can effectively inhibit the reaction between $\text{Li}_{1.25}\text{Ni}_{0.2}\text{Fe}_{0.13}\text{Co}_{0.33}\text{Mn}_{0.33}\text{O}_2$ particles and the electrolyte, as well as retard thickening of the SEI film. The NFCM 90 sample is suitable as lithium-ion anode material because it has better conductivity, in addition to electrolyte oxidation and electrolyte/electrode interface degradation being effectively alleviated through NH_4F pretreatment.

Figure 6. (a) The electrochemical impedance spectra of pristine (Init E (V) = 3.127) and NFCM 90 samples (Init E (V) = 3.7, High Freq (Hz) = 1×10^5 , Low Freq (Hz) = 0.01); (b) the used equivalent circuit.

Table 2. Parameters obtained from simulation of elements in an equivalent circuit model.

Sample	R_e (Ω)	R_{ct} (Ω)
Pristine	4.491	206.2
NFCM 90	8.753	76.32

4. Conclusions

Pretreatment with NH_4F and self-templating with MnO_2 microspheres enabled successful synthesis of $\text{Li}_{1.25}\text{Ni}_{0.2}\text{Fe}_{0.13}\text{Co}_{0.33}\text{Mn}_{0.33}\text{O}_2$. The XRD and SEM results show that pretreatment did not obviously affect the crystal structures, morphologies, nor particle sizes of the obtained $\text{Li}_{1.25}\text{Ni}_{0.2}\text{Fe}_{0.13}\text{Co}_{0.33}\text{Mn}_{0.33}\text{O}_2$ samples. NH_4F pretreatment improved initial coulombic efficiency and stability in subsequent electrochemical cycling, as well as rate capability. The NFCM 90 sample

had a rate capacity of 209.1 mA h g⁻¹ at 0.1 C and a capacity retention of 85.2% (178.2 mA h g⁻¹) after 50 cycles at 0.1 C. These values are better than the pristine ones. We developed a feasible method for synthesizing NH₄F-pretreated lithium-rich layered oxides, which contributes to promote electrochemical performances of Li-ion batteries.

Author Contributions: S.X., X.G. and Z.C. conceived and designed the experiments; Y.Z. performed the experiments; Y.Z., S.C., H.W. and Y.L. analyzed the data; S.X. supervised and contributed reagents and analysis tools; Y.Z. wrote the manuscript; S.X. and Z.C. supervised and revised the manuscript. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the National Natural Science Foundation of China (51,673,103), the joint French-Singaporean MERLION program (Grant No. R279,000,334,133), and the Taishan Scholars Program of Shandong Province.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Wang, J.; Zhang, G.; Liu, Z.; Li, H.; Liu, Y.; Wang, Z.; Li, X.; Mai, L.; Shih, K. Li₃V(MoO₄)₃, as a novel electrode material with good lithium storage properties and improved initial coulombic efficiency. *Nano Energy* **2017**, *44*, 272–278. [\[CrossRef\]](#)
2. Yan, Z.; Hu, Q.; Yan, G.; Li, H.; Shih, K.; Yang, Z.; Li, X.; Wang, Z.; Wang, J. Co₃O₄/Co nanoparticles enclosed graphitic carbon as anode material for high performance Li-ion batteries. *Chem. Eng. J.* **2017**, *321*, 495–501. [\[CrossRef\]](#)
3. Li, L.; Xu, M.; Yao, Q.; Chen, Z.; Song, L.; Zhang, Z.; Gao, C.; Wang, P.; Yu, Z.; Lai, Y. Alleviating surface degradation of nickel-rich layered oxide cathode material by encapsulating with nanoscale Li-ions/electrons superionic conductors hybrid membrane for advanced li-ion batteries. *ACS Appl. Mater. Interfaces* **2016**, *45*, 30879–30889. [\[CrossRef\]](#)
4. Tan, L.; Li, X.; Wang, Z.; Guo, H.; Wang, J. Lightweight reduced graphene oxide@MoS₂ interlayer as polysulfide barrier for high-performance lithium-sulfur batteries. *ACS Appl. Mater. Interfaces* **2018**, *10*, 3707–3713. [\[CrossRef\]](#)
5. Hou, H.; Craig, E.; Jing, M.; Zhang, Y.; Ji, X. Carbon quantum dots and their derivative 3d porous carbon frameworks for sodium-ion batteries with ultralong cycle life. *Adv. Mater.* **2015**, *27*, 7861–7866. [\[CrossRef\]](#)
6. Yang, Z.; Guo, H.; Li, X.; Wang, Z.; Wang, J.; Wang, Y.; Yan, Z.; Zhang, D. Graphitic carbon balanced between high plateau capacity and high rate capability for lithium ion capacitor. *J. Mater. Chem. A* **2017**, *5*, 15302–15309. [\[CrossRef\]](#)
7. Wang, J.; Liu, Z.; Yan, G.; Li, H.; Peng, W.; Li, X.; Song, L.; Shih, K. Improving the electrochemical performance of lithium vanadium fluorophosphate cathode material: Focus on interfacial stability. *J. Power Sources* **2016**, *329*, 553–557. [\[CrossRef\]](#)
8. Li, T.; Wang, J.; Wang, Z.; Guo, H.; Li, Y.; Li, X. A new design concept for preparing nickel-foam-supported metal oxide microspheres with superior electrochemical properties. *J. Mater. Chem. A* **2017**, *5*, 13469–13474. [\[CrossRef\]](#)
9. Li, X.; Wu, G.; Chen, J.; Li, M.; Li, W.; Wang, T.; Jiang, B.; He, Y.; Mai, L. Low-crystallinity molybdenum sulfide nanosheets assembled on carbon nanotubes for long-life lithium storage: Unusual electrochemical behaviors and ascending capacities. *Appl. Surf. Sci.* **2017**, *392*, 297–304. [\[CrossRef\]](#)
10. Zhou, Y.; Guo, H.; Yong, Y.; Wang, Z.; Li, X.; Zhou, R. Introducing reduced graphene oxide to improve the electrochemical performance of silicon-based materials encapsulated by carbonized polydopamine layer for lithium ion batteries. *Mater. Lett.* **2017**, *195*, 164–167. [\[CrossRef\]](#)
11. Hu, X.; Guo, H.; Wang, J.; Wang, Z.; Li, X.; Hu, Q.; Peng, W. Structural and electrochemical characterization of NH₄F-pretreated lithium-rich layered Li[Li_{0.2}Ni_{0.13}Co_{0.13}Mn_{0.54}]O₂ cathodes for lithium-ion batteries. *Ceram. Int.* **2018**, *44*, 14370–14376. [\[CrossRef\]](#)
12. Hou, X.; Wang, Y.; Song, J.; Gu, H.; Guo, R.; Liu, W.; Mao, Y.; Xie, J. Electrochemical behavior of Mn-based Li-rich cathode material Li_{1.15}Ni_{0.17}Co_{0.11}Mn_{0.57}O₂ fluorinated by NH₄F. *Solid State Ion.* **2018**, *325*, 1–6. [\[CrossRef\]](#)

13. Lu, C.; Wu, H.; Zhang, Y.; Liu, H.; Chen, B.; Wu, N.; Wang, S. Cerium fluoride coated layered oxide $\text{Li}_{1.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}\text{O}_2$ as cathode materials with improved electrochemical performance for lithium ion batteries. *J. Power Sources* **2014**, *267*, 682–691. [\[CrossRef\]](#)
14. Sun, S.; Wan, N.; Wu, Q.; Zhang, X.; Pan, D.; Bai, Y.; Lu, X. Surface-modified $\text{Li}[\text{Li}_{0.2}\text{Ni}_{0.17}\text{Co}_{0.07}\text{Mn}_{0.56}]\text{O}_2$ nanoparticles with MgF_2 as cathode for li-ion battery. *Solid State Ion.* **2015**, *278*, 85–90. [\[CrossRef\]](#)
15. Chen, H.; Hu, Q.; Huang, Z.; He, Z.; Wang, Z.; Guo, H.; Li, X. Synthesis and electrochemical study of Zr-doped $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$ as cathode material for li-ion battery. *Ceram. Int.* **2016**, *42*, 263–269. [\[CrossRef\]](#)
16. Zhang, X.; Yang, Y.; Sun, S.; Wu, Q.; Wan, N.; Pan, D.; Bai, Y. Multifunctional ZrF_4 nanocoating for improving lithium storage performances in layered $\text{Li}(\text{Li}_{0.2}\text{Ni}_{0.17}\text{Co}_{0.07}\text{Mn}_{0.56})\text{O}_2$. *Solid State Ion.* **2016**, *284*, 7–13. [\[CrossRef\]](#)
17. Kim, J.H.; Park, M.S.; Song, J.H.; Byun, D.J.; Kim, Y.J.; Kim, J.S. Effect of aluminum fluoride coating on the electrochemical and thermal properties of $0.5\text{Li}_2\text{MnO}_3 \cdot 0.5\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ composite material. *J. Alloy. Compd.* **2012**, *517*, 20–25. [\[CrossRef\]](#)
18. Li, C.D.; Xu, J.; Xia, J.S.; Liu, W.; Xiong, X.; Zheng, Z.A. Influences of FeF_3 coating layer on the electrochemical properties of $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.54}\text{Ni}_{0.13}\text{Co}_{0.13}]\text{O}_2$ cathode materials for lithium-ion batteries. *Solid State Ion.* **2016**, *292*, 75–82. [\[CrossRef\]](#)
19. Liu, X.; Huang, T.; Yu, A. Surface phase transformation and CaF_2 coating for enhanced electrochemical performance of li-rich Mn-based cathodes. *Electrochim. Acta* **2015**, *163*, 82–92. [\[CrossRef\]](#)
20. Xiong, X.; Wang, Z.; Yin, X.; Guo, H.; Li, X. A modified LiF coating process to enhance the electrochemical performance characteristics of $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ cathode materials. *Mater. Lett.* **2013**, *110*, 4–9. [\[CrossRef\]](#)
21. Du, Z.; Peng, W.; Wang, Z.; Guo, H.; Li, X.; Hu, Q. Improving the electrochemical performance of Li-rich $\text{Li}_{1.2}\text{Ni}_{0.13}\text{Co}_{0.13}\text{Mn}_{0.54}\text{O}_2$ cathode material by LiF coating. *Ionics* **2018**, *24*, 3717–3724. [\[CrossRef\]](#)
22. Chang, Q.; Zhang, H.; Wang, X.; Shao, W.; Li, H.; Yuan, F.; Xu, X.; Xu, S. Structure and electrochemical performance of hollow microspheres of $\text{LiFe}_x\text{Ni}_{1/3-x}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ ($0.000 \leq x \leq 0.267$) as cathodes for lithium-ion batteries. *RSC Adv.* **2015**, *5*, 56274–56278. [\[CrossRef\]](#)
23. Li, J.; Cao, C.; Xu, X.; Zhu, Y.; Yao, R. $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ hollow nano-micro hierarchical microspheres with enhanced performances as cathodes for lithium-ion batteries. *J. Mater. Chem. A* **2013**, *1*, 11848–11852. [\[CrossRef\]](#)
24. Reddy, M.; SubbaRao, G.; Chowdari, B. Preparation and Characterization of $\text{LiNi}_{0.5}\text{Co}_{0.5}\text{O}_2$ and $\text{LiNi}_{0.5}\text{Co}_{0.4}\text{Al}_{0.1}\text{O}_2$ by Molten Salt Synthesis for Li-ion Batteries. *J. Phys. Chem. C* **2007**, *11*, 11712–11720. [\[CrossRef\]](#)
25. Reddy, M.; SubbaRao, G.; Chowdari, B. Synthesis and electrochemical studies of the 4V cathode, $\text{Li}(\text{Ni}_{2/3}\text{Mn}_{1/3})\text{O}_2$. *J. Power Sources* **2006**, *160*, 1369–1374. [\[CrossRef\]](#)