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Toward Greener Lithium-Ion Batteries: Aqueous Binder-Based LiNi_{0.4}Co_{0.2}Mn_{0.4}O₂ Cathode Material with Superior Electrochemical Performance

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Abstract

This work reports a strategy towards greener lithium-ion batteries, by employing the aqueous sodium carboxymethyl cellulose-based LiNi_{0.4}Co_{0.2}Mn_{0.4}O₂ (CMC/NCM) as cathode electrode. Compared with conventional organic PVDF-based electrodes, the CMC/NCM electrodes display very uniform distribution of NCM and carbon particles together with strong adhesion among the particles and with the current collector, leading to significantly mitigated crack formation and delamination of the electrode upon repeated delithiation/lithiation processes. As a result, CMC/NCM electrodes show good structural integrity. Additionally, these electrodes offer enhanced Li⁺ diffusion kinetics, reduced polarization, therefore, excellent high C-rate capability,

and extremely stable cycling performance even at elevated temperature (60 °C). Moreover, benefiting from the features of low cost, environmentally friendliness, and easy disposability-recyclability, the water-soluble CMC is expected to be a promising binder for practical applicant in energy storage systems.

Keywords: sodium carboxymethyl cellulose; aqueous binder; $\text{LiNi}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.4}\text{O}_2$; lithium-ion batteries

1. Introduction

Currently, a global goal in battery technology is the exploration of greener and safer batteries with lower cost[1-3]. In the past decades, intensive efforts have been devoted to the development of lithium-ion batteries, which have dominated the current consumable portable electronics and telecommunications market[4-7]. Most of the studies focused on searching for alternatives of new active materials, new separators, new additives, modification of electrolytes, however, the investigation of binders for cathodes is apparently less investigated[8]. Even though the binder is electrochemically inert, it plays an important role in the electrode formulation and has a great influence on the electrode processing and performance.

In commercial lithium-ion batteries, poly vinylidene difluoride (PVDF) is the conventional binder for the cathode materials (but it is much less used for the anode materials), owing to its good electrochemical stability as well as the good adhesion

ability to bond the electrode materials and current collectors. However, PVDF has some serious drawbacks: 1) It is quite expensive, around 15-18 EUR kg⁻¹, considering industrial multiton scale[1, 9]; 2) It makes use of the volatile, toxic and expensive organic N-methyl pyrrolidone (NMP), resulting in safety concerns during the manufacturing process[10]; 3) Its disposal at the end of battery life is not easy; 4) It has a tendency to swell, gelify or dissolve into the organic carbonate based electrolyte, sometimes even forming gel-like polymer electrolyte with high viscosity, leading to desquamation of electrode particles and thus poor electrochemical performance[11, 12]. Therefore, new binders, which are environmentally friendly, cheap, easy for electrode processing and disposal, are searched.

Recently, the sodium salt of CarboxyMethylCellulose (CMC), which is produced by the insertion of carboxymethyl groups into natural cellulose, has emerged as a promising alternative binder. The water-soluble property of CMC undoubtedly is the biggest advantage over PVDF in which it allows the use of water as the solvent instead of the expensive and toxic NMP. Regarding the industrial cost, that of CMC (1-2 EUR kg⁻¹) is only about tenth of PVDF, making CMC even more attractive[13]. In addition, the disposability of CMC based electrode at the end of battery life is much easier, with respect to PVDF-based electrodes. The active material can be easily recovered by pyrolysis or, even better, dissolution (in water) of CMC binder, after the electrode material is removed from the current collector. Given these advantages, CMC has been widely investigated as a replacement of conventional PVDF binder for lithium-ion batteries. However, more attentions of employing CMC as a binder have

been focused on anode materials, such as graphite[14, 15], Si[3, 16], $\text{LiTi}_4\text{O}_{12}$ [17], SnO_2 [18, 19], Fe_2O_3 [20, 21], NiO [23], MoS_2 [24] *etc.* To date, only few studies have reported CMC based cathode materials for lithium-ion batteries. Guyomard's group firstly employed CMC as aqueous binder for LiFePO_4 , with homogeneous electrode morphology and identical performance with respect to the standard PVDF-based LFP[25]. Lux *et al.* studied LiFePO_4 -based electrode using CMC as the binder, providing a possibility of developing greener and cost-effective lithium-ion batteries[1]. Both high C-rate capability and long-term cycling stability of CMC-based electrodes were superior to those of PVDF-based electrodes. Based on this result, Kim *et al.* proposed full cell configuration of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ // LiFePO_4 (both were CMC-based) using ionic liquid $\text{PYR}_{14}\text{FSI}$ as electrolyte with very stable electrochemical performance, even at elevated temperature (40 °C, 60 °C)[13]. CMC was also applied as a binder for high voltage $\text{LiNi}_{0.4}\text{Mn}_{1.6}\text{O}_4$ (5 V) cathodes, as reported in Wang's work[26]. The delivered capacity of CMC-based electrode was considerably higher than that of PVDF-based electrode due to more efficient electronic conductivity as well as more homogenous distribution of active material, conductive agent and binder. However, the PVDF system showed better cycling stability with 95% (vs 89% of CMC-based system) of capacity retention after 100 cycles at 1 C. In a more recent work, De Giorgio *et al.*[27], however, demonstrated as full graphite/LNMO cells in which both electrodes were CMC-based outperformed those based on PVDF, especially at elevated temperature. The improved performance was found to be associated with the much thinner SEI forming on the CMC-based

cathode by XPS and SEI measurements. Besides the olivine and spinel types of cathodes, CMC is also employed in layer cathodes. For example, Xu *et al.* compared the electrochemical performance of CMC, PVDF and alginate-based $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode material[28]. The CMC-based NCM electrodes displayed the highest rate capability and cycling performance, even though the capacity at low current density was lower than that of PVDF and alginate based NCM. The superior electrochemical performance was mainly attributed to the lower activation energy of CMC-based electrode, which could facilitate the lithium-ions diffusion kinetics, yielding higher ionic conductivity.

To the best of our knowledge, there has been no report of the use of CMC as binder for $\text{LiNi}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.4}\text{O}_2$. Therefore, herein, we report the CMC-based nanobar-like $\text{LiNi}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.4}\text{O}_2$ electrode, which exhibits greener and cheaper characteristics, and lower processing cost and easier disposability-recyclability, together with good high C-rate capability, remarkable cycling stability and thermal stability.

2. Experimental

2.1 Material synthesis

The cathode material is prepared based on our previous report[29]. In detail, firstly, 1.399 g of CH_3COOLi , 1.991 g of $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, 0.996 g of $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ and 1.961 g of $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ were dissolved in 200 mL of de-ionized water (DIW) and ethanol (DIW: ethanol = 1:4 v/v) under continuous

stirring until a transparent solution (A) was obtained. Meanwhile, 3.880 g of $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ were dissolved in 200 mL of DIW and ethanol (same volume ratio as above) under continuous stirring until the transparent solution (B) was obtained. Solution B was poured into solution A under stirring for 6 h. The mixture suspension was then dried at 60 °C to form the $\text{MC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ precursor with 1D nanobar-like morphology revealed by SEM. The as-prepared nanobar-like $\text{MC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ was firstly pre-heated at 450 °C for 10 h. This material was then calcined at 850 °C for 20 h in a muffle furnace (air atmosphere) to obtain the final product.

2.2 Electrode Making

For the preparation of $\text{LiNi}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.4}\text{O}_2$ with aqueous CMC binder (CMC/NCM): CMC (Dow Wolff Cellulosics, Walocel CRT 2000 PPA 12) was firstly dissolved into deionized water (DIW) under magnetic stirring for 30 min to form homogeneous solution. The required amount of Super C45 (IMERIS) was added under rigorous stirring for 2 h. Afterwards, the active material was added, together with one drop of phosphoric acid, and mixed for another 2 h. The obtained slurries were casted on alumina foils by doctor-blade technique. The wet coating was dried at 80 °C, before being vacuum dried at 170 °C for 12 h for use. The dry electrode composition was 80 wt.% active material, 15 wt.% conductive agent, and 5 wt.% binder. For the sake of comparison, the PVDF cathode electrodes were prepared with the same active material/super carbon/binder ratio. Firstly, the active materials, C-ENERGY Super C65 (IMERYS) and poly-vinylidene fluoride (PVDF6020, Solvay) were dispersed/dissolved in an appropriate amount of N-methyl-2-pyrrolidone (NMP,

Aldrich) under intimate stirring for 6 h to form homogeneous dispersion. The paste was then casted on Al foils by doctor-blade technique, followed by immediately drying step at 60 °C in an oven. Afterwards, disc electrodes (12 mm in diameter) were punched and further dried under vacuum at 100 °C for 12 h.

2.3 Material characterizations

The morphology of both CMC and PVDF based electrodes as made and after cycling were investigated by scanning electron microscopy (SEM, ZEISS EVO MA 10 microscope). After 100 cycles at 0.1 C, the CMC/NCM and PVDF/NCM cells were disassembled and washed before performing scanning electron microscopy and high-resolution transmission microscopy (HRTEM, JEOL JEM-2100F, 200 kV) to investigate the morphology and structure changes. For the peel test, 3M adhesive tapes were attached to fresh CMC/NCM and PVDF/NCM electrodes, with half covered, half remained pristine state. After pressed under same load for 1 min, the tapes were removed for later SEM measurement.

2.4 Electrochemical measurements

All the electrochemical measurements were carried out using CR2032 coin cells assembled in an argon-filled glove box (with O₂ and H₂O lower than 0.1 ppm). Lithium metal (Albemarle) was used as anode part. Cells were assembled using 1M LiPF₆ dissolved in ethyl carbonate–dimethyl carbonate (EC–DMC) (1:1 v/v) with 1wt.% of vinylene carbonate (VC, additive) as the electrolyte, single layer polyethylene membrane (ASAHI KASEI, Hipore SV718) as separator. The average areal loading of the electrodes was $\sim 2.0 \pm 0.2 \text{ mg cm}^{-2}$. The electrochemical

performance of the cells was tested using a Maccor series 4000 battery tester (U.S.A). The cells were cycled at different C-rates (from 0.1 C to 10 C) in the range of 3.0-4.3 V vs Li^+/Li to test the rate capability. For cycling stability test, the cells were cycled in galvanostatic conditions for 3 initial cycles at 0.1 C rate (activation of electrodes) followed by cycling at constant C-rates (0.1 C, 2 C and 10 C) for 100 cycles. Cyclic voltammetry (CV) measurements were performed using a multi-channel potentiostat (VMP Biologic-Science Instruments) within the voltage range between 2.5 and 4.5 V (vs Li^+/Li) at controlled temperature at 20 °C. Three CV cycles were performed at a scan rate of 0.1 mV s^{-1} followed by other cycles at different scan rates (from 0.1 to 1.5 mV s^{-1}). For the evaluation of cycling performance at elevated temperature, CMC/NCM and PVDF/NCM electrodes were initially activated at 0.1 C for three cycles, followed by 100 cycles at 10 C at 60 °C.

3. Results and discussion

Fig. 1 compares the electrochemical performance of CMC-based and PVDF-based NCM electrodes. Undoubtedly, CMC-based $\text{LiNi}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.4}\text{O}_2$ (marked as CMC/NCM hereafter) showed considerably superior electrochemical performance over PVDF-based $\text{LiNi}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.4}\text{O}_2$ (denoted as PVDF/NCM hereafter). The rate capability test was performed via galvanostatic cycling at various C-rates, ranging from 0.1 C to 10 C, with five consecutive cycles for each step. As it can be seen from Fig. 1(a), PVDF/NCM delivered an initial discharge capacity of 166.2 mAh g^{-1} , *i.e.*,

slightly higher than that of CMC/NCM (161.1 mAh g⁻¹). This may be attributed to the moderate leaching of Li and the transition metals (Ni, Co and Mn) occurring in aqueous slurries[30]. However, although PVDF/NCM displayed higher capacity at low to medium rates (from 0.1 C to 2 C), the capacity delivered at 10 C of CMC/NCM exceeded PVDF/NCM (78.4 vs 70.5 mAh g⁻¹). Interestingly, after high C-rate test, the capacity of the CMC/NCM electrode recovered to 133.8 mAh g⁻¹ at 1 C, *i.e.*, a capacity retention approaching 100.6%. In contrast, only a 97.6% capacity retention was achieved by the PVDF/NCM electrode. In order to examine the capacity retention ability, both CMC/NCM and PVDF/NCM electrodes were subsequently subjected to 100 cycles at 1 C after rate-capability test. Through the comparison, CMC/NCM displayed considerably more stable cycling performance with only 1% capacity fading, which is much lower than that of PVDF/NCM (19.4% of capacity fade).

To further compare the cycling performance, several cells of both CMC/NCM and PVDF/NCM samples were assembled and cycled at 0.1 C, 2 C and 10 C for 100 cycles (at each rate). It is noticeable that CMC/NCM showed extremely stable cycling performance (Fig. 1(b)) with capacity retentions as high as 96.4% (0.1 C), 102.9% (2 C) and 111.8% (10 C). At higher current densities, *ca.* 2 C, 10 C, the capacity retention ratios exceeded 100% after 100 cycles, which is the result of slower electrode wetting process due to the high compactness of CMC-based electrodes. On the contrary, PVDF/NCM only maintained 89.7%, 78.2% and 79.4% of initial capacities at 0.1 C, 2 C and 10 C (Fig. 1(c)), respectively. For the investigation of the

cycling stability at elevated temperature (60 °C), both systems were tested at 10 C for 100 cycles. Figs. 1(d) and 1(e) display the selected charge/discharge profiles of CMC/NCM and PVDF/NCM, respectively. It is understandable that the thermal stability decreases with increased temperature due to the high activity of transition metal elements with electrolyte, which will cause more side reactions and lead to stronger capacity fading [31]. Therefore, as expected, there was a capacity decay in CMC/NCM. However, still 96.7% of initial capacity was delivered after 100 cycles. In addition, the charge/discharge voltage profiles of CMC/NCM upon the 100 cycles almost overlapped (Fig. 1(d)), suggesting excellent reversibility. On the other hand, severe capacity and voltage decay were observed for PVDF/NCM (Fig. 1(e)), indicating growing polarization upon cycling. Interestingly, the cycling performance of PVDF/NCM was abnormally more stable at 60 °C than 20 °C. This may be ascribed to accelerated Li^+ transport kinetics with increased operation temperature, leading to improved electrochemical performance. The cycling stability at higher mass loadings ($\sim 4 \text{ mg cm}^{-2}$) were also compared as shown in Figs. 1(f) and S1. Being subjected to 200 consecutive cycles at 2 C, still, CMC/NCM was able to retain 91.6% of initial capacity (Fig. (1f)). At higher mass loadings, the initial three cycles showed a slightly capacity decay of around 3 mAh g^{-1} . Afterwards, due to the slower electrode wetting, a slightly capacity increase was evidenced and stabilized at around 104.7 mAh g^{-1} . For comparison, PVDF/NCM electrode with mass loading of ($\sim 4 \text{ mg cm}^{-2}$) was test under the same condition. Albeit a higher capacity was achieved, the capacity fading upon cycling was very severe (Fig. S1). Therefore, after 200 cycles, a

substantially lower capacity retention ratio was obtained, *ca.* 70.0%, delivering an even lower capacity of 90.6mAh g⁻¹ (vs. 98.2 mAh g⁻¹ of CMC/NCM).

Fig. 1. Comparison of the electrochemical performance of CMC/NCM and PVDF/NCM electrodes. (a) Rate capability test; (b) and (c) cycling performance; (d) and (e) cycling performance at elevated temperature (60 °C); (f) cycling performance of CMC/NCM with higher mass loadings.

In order to understand the effects of the binder on electrochemical performance, cyclic voltammetry tests were performed to examine the electrochemical behaviour of

CMC/NCM and PVDF/NCM systems. When swept at 0.1 mV s^{-1} in the voltage range of 2.5-4.5 V, one pair of redox peaks occurred in both systems. The initial three CV cycles of CMC/NCM showed higher peak current densities, reproducibility and reversibility (Fig. 2(a)) than those of PVDF/NCM (Fig. 2(d)). As it can be seen from Table 1, the initial anodic/cathodic peaks of CMC/NCM were located at 3.817 V and 3.700 V, respectively, with a redox peak separation of 0.117 V. After three cycles, the redox peak separation reduced to 0.056 V, suggesting very small polarization in the CMC/NCM electrode. With the PVDF/NCM electrode, however, a relatively larger redox peak separation, *ca.* 0.155 V, was observed in the first delithiation/lithiation process. Even after three cycles, the peak separation was about 0.1 V, *i.e.*, almost twice that of CMC/NCM electrode, indicating that higher polarization existed in the PVDF/NCM electrode. For the investigation of apparent lithium ions diffusion kinetics, CV curves at various scanning rates ($0.1\text{-}1.5 \text{ mV s}^{-1}$) were also conducted (Figs. 2(b) and 2(e)). Both systems showed a linear relationship of peak current intensity versus square root of scanning rate. Based on the Randles-Sevcik equation[32], the apparent lithium ion diffusion coefficients of CMC/NCM were to be $4.50 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ and $9.52 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$ for the delithiation and lithiation processes, respectively. These values are over two folds those of PVDF/NCM ($1.85 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$, $4.85 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$). The faster lithium ion transfer kinetics clearly explain the better high C-rate capability of CMC/NCM, comparing to PVDF/NCM.

Fig. 2. Comparison of the electrochemical behaviour of CMC/NCM and PVDF/NCM electrodes. (a) and (d) Initial three cyclic voltammetry (CV) curves (0.1 mV s⁻¹); (b) and (e) CV curves at various scanning rates (see legend); (c) and (f) plots of current peak intensity versus the square root of the scan rate.

Table 1 Detailed information from CV results.

	1 st cycle		3 rd cycle	
	anodic/ cathodic (V)	peak separation (V)	anodic/ cathodic (V)	peak separation (V)
CMC/NCM	3.817/3.700	0.117	3.756/3.699	0.057
PVDF/NCM	3.877/3.722	0.155	3.822/3.722	0.100

The voltage profiles of the two electrodes upon galvanostatic charge/discharge cycles at different current densities are shown in Fig. 3. During the initial three activation cycles at 0.1 C, the voltage profiles of systems exhibited almost ideal symmetry. As it can be seen from the last ten galvanostatic cycles when tested at 2 C

in Fig. 3(a), CMC/NCM still showed nice symmetric voltage profiles, suggesting very low polarization and high reversibility. When testing at 10 C (Fig. 3(b)), an increased voltage gap between the charge and discharge profiles is observed due to limited electrode kinetics. This problem, however, is already serious at 2 C for the PVDF/NCM electrode (Fig. 3(c)), resulting from the sluggish Li^+ kinetics, which is in consistent with the CV results. At 10 C, the severe asymmetry of the voltage profiles is well evidenced in Fig. 3(d), implying that a very severe polarization existed, especially during discharge. This results in much less Li^+ to be re-inserted into the NCM host during discharging process. As a consequence, severe capacity fading upon cycling occurred. Figs. 3(e-g) compare the corresponding differential capacity plots (last five cycles) of CMC/NCM and PVDF/NCM. The CMC/NCM electrode well maintained its profiles even at 10 C. In contrast, the intensity of the PVDF/NCM cathodic peak decreased substantially upon increasing rates. Also, at 2 C and 10 C very distorted profiles are presented. As expected, the redox peak separation showed a tendency to increase at higher current densities. Table 2 lists the detailed information obtained from the differential capacity plots. The separation increased from 0.015 V (0.1 C) to 0.049 V (2 C), and to 0.167 V (10 C) for the CMC/NCM electrode. However, much larger separations were observed in PVDF/NCM system, *ca.* 0.043 V (0.1 C), 0.158 V (2 C), 0.243 V (10 C). These values provide quantitative proofs of the much severe polarizations occurring with the PVDF/NCM electrode, which justifies its inferior high rate capability and long-term cycling stability with respect to the CMC/NCM electrode.

Fig. 3. Comparison of the voltage profiles versus time of (a) and (b) CMC/NCM; (c) and (d) PVDF/NCM galvanostatically cycled at 0.1 C and then either 2 C or 10 C; (e-g) differential capacity plots of CMC/NCM (red) and PVDF NCM (black).

Table 2 Detailed information obtained from differential capacity plots.

	0.1 C	2 C	10 C
	anodic/cathodic (V)	anodic/cathodic (V)	anodic/cathodic (V)
CMC/NCM	3.771/3.756	3.795/3.747	3.881/3.713
PVDF/NCM	3.786/3.744	3.877/3.719	3.938/3.695

In order to better understand the binder effect on the electrode performance, the morphology of the electrodes was examined by scanning electron microscope (SEM).

Both systems were calendared under the same conditions. Figs. 4(a) and (b) display the morphology of a CMC/NCM electrode at different magnifications, showing as the NCM nanobars were homogeneously distributed among the active carbon particles and binders. The surface of the electrode is very flat, indicating even thickness of the electrode layer. However, a particle agglomeration phenomenon is seen in case of PVDF/NCM electrode (Figs. 4(c) and (d)). Plenty of NCM particles were connected with very few or even without any conductive agent, which would cause poor electronic conductivity and thus seriously affect the electrochemical performance, particularly at higher current densities. The difference in electrode morphology of CMC/NCM and PVDF/NCM could be due to the thermoplastic characteristics of the PVDF binder favouring for the NCM particles to align parallel to the surface, while the compression of the CMC/NCM electrode does not affect the original morphology, leaving a more uniform but open morphology.

Fig. 4. SEM images (at different magnifications) comparing the morphology of (a) and (b) CMC/NCM and (c) and (d) PVDF/NCM pristine electrodes.

The adhesion property of the binder plays an important role on the electrochemical performance. Therefore, peel tests were conducted to compare the adhesion of CMC/NCM and PVDF/NCM. As shown in Fig. S2(b), almost all of the PVDF/NCM coating in the right side of the electrode (*i.e.*, the part subjected to peel test) was peeled off, with only some spots of active material left. In contrast, the difference between the pristine and tested areas of the CMC/NCM electrode is not obvious (Fig. S2(a)). The colour of the peeled side appears darker, implying that some material was removed making the surface rougher, however, to a much lesser extent than the PVDF/NCM electrode. SEM images were taken to give a more direct view for comparison. Panel S2(c) displays the front view of the CMC/NCM electrode, confirming as almost no difference is observed between the peeled and pristine halves of the CMC/NCM electrode. Only the very surface layer of the coated electrode is removed. On the other hand, the coating of the PVDF/NCM electrode (Fig. S2(d) and insert) was almost completely removed after peeling, leaving only tiny and isolated islands. These results indicate the better adhesion property of the CMC binder, which is expected to greatly alleviate the electrode exfoliation over repeated charge/discharge cycles.

Fig. 5. SEM images comparing the electrode morphology of cycled electrodes (after 100 cycles at 0.1 C). Front views of (a) and (b) CMC/NCM and (d) and (e) PVDF/NCM electrodes at different magnifications; cross-sectional views of (c) CMC/NCM and (f) PVDF/NCM electrodes.

To validate our assumption, we also performed SEM characterization of electrodes after 100 cycles at 0.1 C (Fig. 5). The front views of the CMC/NCM electrode show intact surface and uniformly distributed NCM and super C45 particles (Figs. 5(a) and (b)). This leads to uneven (de)lithiation due to non-uniform current distribution occurring in different electrode areas, resulting in uneven strain in the coating. As a result, a striking gap between the PVDF/NCM electrode layer and the aluminum current collector is seen in Fig. 5(f). This exfoliation of the active material from the current collector. According to the cross sectional view, the electrode layer is tightly adherent to the aluminum current collector. For the PVDF/NCM electrode, however, obvious cracks are observed on the surface (Fig. 5(e)), possibly due to the particles agglomeration and conductive additive distribution, leading to some certainly results in the increased polarization severely deteriorating the

electrochemical performance, even at low current densities. Therefore, to a large extent, the high adhesion property of CMC binder as well as the highly homogeneous distribution of all the electrode materials are the reasons for the excellent high rate and long-term cycling performance of CMC/NCM.

Fig. 6. Comparative HRTEM images of (a) and (b) CMC/NCM and (d) and (e) PVDF/NCM electrodes. The corresponding FFT patterns are also shown in (c) and (f), respectively.

For the investigation of structural integrity of the CMC/NCM and PVDF/NCM electrodes after cycling, high-resolution transmission electron microscopy (HRTEM) was performed. From the low magnification TEM images (Figs. 6(a) and (d)), the CMC/NCM particle exhibits a more smooth and clean surface while the PVDF/NCM particle displays a rough and porous surface. At higher magnification, the CMC/NCM particle presents a crystalline structure with clear lattice fringes (Fig. 6(b)), further validated by the corresponding FFT pattern (Fig. 6(c)) showing the hexagonal

structure. However, the FFT pattern of PVDF/NCM is highly disordered and is more like polycrystalline structure (Fig. 6(f)), which maybe due to severe transition metal dissolution, as reported by Zhang *et. al*[33]. Thus, simply substituting the conventional binder, PVDF, with CMC results in the improved structural integrity of NCM upon cycling. These results are in line with a previously published study comparing the performance of LNMO electrodes made with CMC and PVDF binders, which showed that the former binder can actually protect the active material particles[27].

4. Conclusions

This work reports the use of CMC as aqueous binder for 1D nanobar-like $\text{LiNi}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.4}\text{O}_2$, which exhibited superior high C-rate capability, long-term cycling stability and thermal stability over the conventional electrodes based on PVDF. The excellent electrochemical performance of CMC/NCM is attributed to faster lithium ion diffusion kinetics (two times faster than that of PVDF/NCM) and lower electrode polarization increase during cycling. These improvements are bound to the high adhesive property of CMC binder, which greatly mitigated the formation of cracks and exfoliation of electrode materials from Al current collector, ensuring good electronic conductivity networks, as well as to the already reported protective effect of CMC on the active material particles upon cycling. Additionally, CMC has many prominent advantages over PVDF, such as low cost, environmentally friendliness and

easy disposability-recyclability due to its water-soluble characteristics. No flammable, costly and toxic solvents need to be used during the electrode-making as well as active material recycling at the end of the battery life. Therefore, the employment of CMC, as well as other water-soluble, natural polymers, as a binder for NCM highlights a promising direction for the development of greener lithium ion batteries with excellent electrochemical performance.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at

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References

- [1] S.F. Lux, F. Schappacher, A. Balducci, S. Passerini, M. Winter, J. Electrochem. Soc. 157 (2010), A320-A325.
- [2] J.Y. Luo, Y.Y. Xia, Adv. Funct. Mater. 17 (2007) 3877-3884.
- [3] B. Lestriez, S. Bahri, I. Sandu, L. Roué, D. Guyomard, Electrochem. Commun. 9 (2007) 2801-2806.
- [4] G. Amatucci, J.M. Tarascon, J. Electrochem. Soc. 149 (2002) K31.
- [5] Z. Wang, Y. Sun, L. Chen, X. Huang, J. Electrochem. Soc. 151 (2004) A914.
- [6] Y.-S. He, Z.-F. Ma, X.-Z. Liao, Y. Jiang, J. Power Sources 163 (2007) 1053-1058.
- [7] Z. Chen, D. Chao, J. Lin, Z. Xiang, Mater. Res. Bull, (2017) In press.
- [8] H. Buqa, M. Holzapfel, F. Krumeich, C. Veit, P. Novák, J. Power Sources 161 (2006) 617-622.
- [9] N. Loeffler, J. von Zamory, N. Laszczynski, I. Doberdo, G.-T. Kim, S. Passerini, J. Power Sources 248 (2014) 915-922.
- [10] I. Doberdò, N. Löffler, N. Laszczynski, D. Cericola, N. Penazzi, S. Bodoardo, G.-T. Kim, S. Passerini, J. Power Sources 248 (2014) 1000-1006.
- [11] Z. Zhang, T. Zeng, Y. Lai, M. Jia, J. Li, J. Power Sources 247 (2014) 1-8.
- [12] S.S. Zhang, T.R. Jow, J. Power Sources 109 (2002) 422-426.
- [13] G.T. Kim, S.S. Jeong, M. Joost, E. Rocca, M. Winter, S. Passerini, A. Balducci, J. Power Sources 196 (2011) 2187-2194.
- [14] J.-H. Lee, S. Lee, U. Paik, Y.-M. Choi, J. Power Sources 147 (2005) 249-255.

- [15] J. Drofenik, M. Gaberscek, R. Dominko, F.W. Poulsen, M. Mogensen, S. Pejovnik, J. Jamnik, *Electrochim. Acta* 48 (2003) 883-889.
- [16] U.S. Vogl, P.K. Das, A.Z. Weber, M. Winter, R. Kostecki, S.F. Lux, *Langmuir* 30 (2014) 10299-10307.
- [17] S.-L. Chou, J.-Z. Wang, H.-K. Liu, S.-X. Dou, *J. Phys. Chem. C* 115 (2011) 16220-16227.
- [18] P. Gurunathan, P.M. Ette, K. Ramesha, *ACS Appl. Mat. Interfaces* 6 (2014) 16556-16564.
- [19] S.-L. Chou, J.-Z. Wang, C. Zhong, M.M. Rahman, H.-K. Liu, S.-X. Dou, *Electrochim. Acta* 54 (2009) 7519-7524.
- [20] J. Li, H.M. Dahn, L.J. Krause, D.-B. Le, J.R. Dahn, *J. Electrochem. Soc.* 155 (2008) A812.
- [21] K. Cao, L. Jiao, H. Liu, Y. Liu, Y. Wang, Z. Guo, H. Yuan, *Adv. Energy. Mater.* 5 (2015) 1401421.
- [22] Y.-M. Lin, P.R. Abel, A. Heller, C.B. Mullins, *J. Phys. Chem. Lett.* 2 (2011) 2885-2891.
- [23] C. Zhong, J.-Z. Wang, S.-L. Chou, K. Konstantinov, M. Rahman, H.-K. Liu, *J. Appl. Electrochem.* 40 (2010) 1415-1419.
- [24] U.K. Sen, S. Mitra, *ACS Appl. Mat. Interfaces* 5 (2013) 1240-1247.
- [25] W. Porcher, B. Lestriez, S. Jouanneau, D. Guyomard, *J. Electrochem. Soc* 156 (2009) A133.
- [26] Z. Wang, N. Dupré, A.-C. Gaillot, B. Lestriez, J.-F. Martin, L. Daniel, S. Patoux,

- D. Guyomard, *Electrochim. Acta* 62 (2012) 77-83.
- [27] F. De Giorgio, N. Laszczynski, J. von Zamory, M. Mastragostino, C. Arbizzani, S. Passerini, *ChemSusChem* 10 (2017) 379-386.
- [28] J. Xu, S.-L. Chou, Q.-f. Gu, H.-K. Liu, S.-X. Dou, *J. Power Sources* 225 (2013) 172-178.
- [29] Z. Chen, D. Chao, J. Liu, M. Copley, J. Lin, Z. Shen, G.-T. Kim, S. Passerini, *J. Mater. Chem. A*, 5 (2017) 15669-15675.
- [30] N. Loeffler, G.-T. Kim, F. Mueller, T. Diemant, J.-K. Kim, R. J. Behm, S. Passerini, *chemSusChem* 9 (2016) 1112.
- [31] M.-J. Lee, M. Noh, M.-H. Park, M. Jo, H. Kim, H. Nam, J. Cho, *J. Mater. Chem. A*, 3 (2015) 13453-13460.
- [32] Z. Chen, J. Wang, D. Chao, T. Baikie, L. Bai, S. Chen, Y. Zhao, T.C. Sum, J. Lin, Z. Shen, *Sci. Rep.* 6 (2016) 25771.
- [33] S. Zhang, H. Gu, H. Pan, S. Yang, W. Du, X. Li, M. Gao, Y. Liu, M. Zhu, L. Ouyang, D. Jian, F. Pan, *Adv. Energy. Mater.* (2016) 1601066.

Fig. S1. Cycling performance of PVDF/NCM with higher mass loadings.

Fig. S2. Peel test of (a) and (c) CMC/NCM; (b) and (d) PVDF/NCM electrodes.