



Investigations on cellulose-based high voltage composite cathodes for lithium ion batteries

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ABSTRACT

Carboxymethyl cellulose (CMC), a green and low-cost binder, is used to make lithium-ion battery composite electrodes containing the high voltage cathode material $\text{Li}_2\text{MnO}_3\text{-LiMO}_2$. This combination of materials results in a homogeneous electrode, which is proved by electron microscopy. The results of the electrochemical investigation indicate that CMC operates well at very high voltages (4.8 V). Compared to the PVDF binder, the CMC-based electrode shows an improved cycling stability as well as a very promising rate capability.

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1. Introduction

Recently, the identification of cheaper, higher capacity and safer cathode materials has attracted much attention in the field of lithium ion battery research. In this regard, the solid solutions of layered Li_2MnO_3 and LiMO_2 ($M = \text{Mn, Co, Ni, etc.}$) have proved to be promising candidates for cathode materials because of their relatively high capacity, low cost and improved safety [1–6]. So far, to the best of our knowledge, most research work on this material class has been conducted using fluorine-based binders. Poly(vinylidene fluoride) (PVDF) is the most widely used binder in the lithium ion battery technology. However, PVDF is relatively costly, about 15–18 € kg^{-1} , and requires the use of volatile and toxic organic solvents such as N-methyl pyrrolidone (NMP). This, obviously results in additional processing costs to avoid (or minimize) the release of such a solvent during the electrode slurry preparation, coating and drying processes [7]. Furthermore, due to the presence of fluorine, the stability of PVDF binder towards reducing agents is also not satisfactory, sometime causing safety problems upon cycling [8,9].

In order to develop environmentally friendly, low-cost and safe lithium ion batteries, the quest for an alternative binder system has also become an interesting topic recently. With regard to this, the sodium salt of carboxymethyl cellulose (CMC) was introduced as an

alternative binder for composite electrodes in Li-ion battery technology. As CMC is a water-soluble material, water is the only solvent used in the process thus making the electrode production a safer and environmentally more benign process [8,10]. As a fluorine-free material, its disposal at the end of battery life becomes unproblematic. Last but not the least, it has a much lower price (1–2 € kg^{-1}) than PVDF [7].

Up to now, much work has been carried out on the application of CMC-based binders in anode materials, such as graphite [11], Fe_2O_3 [12], SnO_2 [12,13], $\text{Li}_4\text{Ti}_5\text{O}_{12}$ [14], and, in particular, Si-based anodes. It is proven that the chemical bonding between the CMC binder and the Si-particles enhances the capacity retention and improves the cycle life of the battery [15,16]. However, its application on the cathode side has been reported only for the production of LiFePO_4 (LFP) and LFP/C based electrodes [7,10,14,17–19]. Those reports proved that CMC can be used as a binder for cathode materials, and that LFP can be processed via an aqueous slurry preparation. In doing so, the long-term cycling performance of the battery could even be improved [7]. Yet, it was still unknown whether CMC may be used in combination with high voltage cathode, i.e., under high cut-off voltage conditions, since LFP needs to be charged up to only 4.2 V vs. Li/Li^+ .

In order to exploit this possibility, the CMC binder was combined with the self-synthesized high voltage cathode material $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.56}\text{Ni}_{0.16}\text{Co}_{0.08}]\text{O}_2$. The morphology and electrochemical performance of such electrodes were investigated. For comparison, studies on similar electrodes based on PVDF as the binder were also carried out.

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2. Experimental

$\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.56}\text{Ni}_{0.16}\text{Co}_{0.08}]\text{O}_2$ was synthesized by a solid-state reaction method from lithium hydroxide hydrate ($\text{LiOH}\cdot\text{H}_2\text{O}$ Aldrich >98%) and manganese–nickel–cobalt hydroxide precursors following a previously published method [5].

Electrodes were prepared by casting a slurry with a composition of 85 wt% active material, 10 wt% Super P (TIMCAL), and 5 wt% binder onto an aluminum current collector foil. The slurries were prepared by ball milling the mixture for 3 h. NMP was used as the solvent for the PVDF binder (Kynar® FLEX 2801, Arkema Group), while pure deionized water was used to dissolve the sodium CMC binder (Walocel CRT 2000 PPA 12). The electrode tapes were dried in air at 80 °C for about 2 h, then punched to \varnothing 12 mm discs. These discs were dried at 120 °C (PVDF binder) or 180 °C (CMC binder) under vacuum for 24 h and then pressed at 3–4 Ton cm^2 . The active material mass loading of the electrodes was about 2 mg cm^{-2} . The two kinds of electrodes were assembled into Swagelok®-type cells with the 1 M LiPF_6 in 1:1 EC:DMC solution as electrolyte. Metallic lithium was used as the counter and reference electrodes.

The morphologies of the prepared electrodes were characterized by the high resolution scanning electron microscopy (SEM, AURIGA®, Zeiss). The composition, in terms of lithium and transition metal content, was determined by the inductively coupled plasma optical emission spectrometry (ICP-OES, SPECTRO ARCOS, Ametek, Germany). The C-rate tests were carried out by cycling the cells galvanostatically at different current rates (nominal capacity = 200 mAh g^{-1} , 1C = 200 mA g^{-1}). The power test was executed by applying charge and discharge currents corresponding to 0.2C, 0.5C, 1C and 5C. Both electrode (CMC and PVDF) were tested at 20 °C between 4.8 V and 2.5 V cut-off voltages using a Maccor series 4000 battery tester. All potentials reported in this work refer to the Li/Li⁺ couple.

3. Results and discussion

The prepared powder showed the typical layered phase of LiMO_2 (M = Mn, Ni, Co) compounds with the super lattice structure originating from the monoclinic Li_2MnO_3 . The powder was composed of homogeneous primary particles, which size ranged from 100 nm to 300 nm. In Fig. 1 SEM images of the $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.56}\text{Ni}_{0.16}\text{Co}_{0.08}]\text{O}_2$ particles as synthesized (a) and incorporated in a CMC-based composite electrode (b) are shown. The comparison of the SEM images proves that the active material particles are not substantially changed during the aqueous slurry mixing and coating processes. The particle shape and size (100–300 nm) are fully maintained. The low magnification SEM image of the electrode in Fig. 1(c) displays the very uniform electrode surface over a larger area.

The electrochemical behavior of CMC- and PVDF-based electrodes was investigated by cycling tests at low (0.2C) and moderate (1C) rates. The results of these tests are shown in Fig. 2 and summarized in Table 1. The CMC-based electrodes delivered an initial discharge capacity of 255.4 mAh g^{-1} at 0.2C and 205.0 mAh g^{-1} at 1C, while the PVDF-based electrodes achieved 266.8 mAh g^{-1} at 0.2C and 246.9 mAh g^{-1} at 1C. That is to say, the capacities delivered by CMC-based electrodes are relatively low in the initial cycles, especially at the higher rate. The reason for this decrease is not fully understood, but it might relate with a surface reaction of the active material with water discussed later. However, the long-term cycling performance (Fig. 2) exhibited by the CMC-based electrodes is outperforming that exhibited by PVDF-based electrodes at both high and low rates. For example, the PVDF-based electrode delivered 149.1 mAh g^{-1} after 200 cycles, which showed a capacity fading of 0.20% per cycle according to the initial capac-

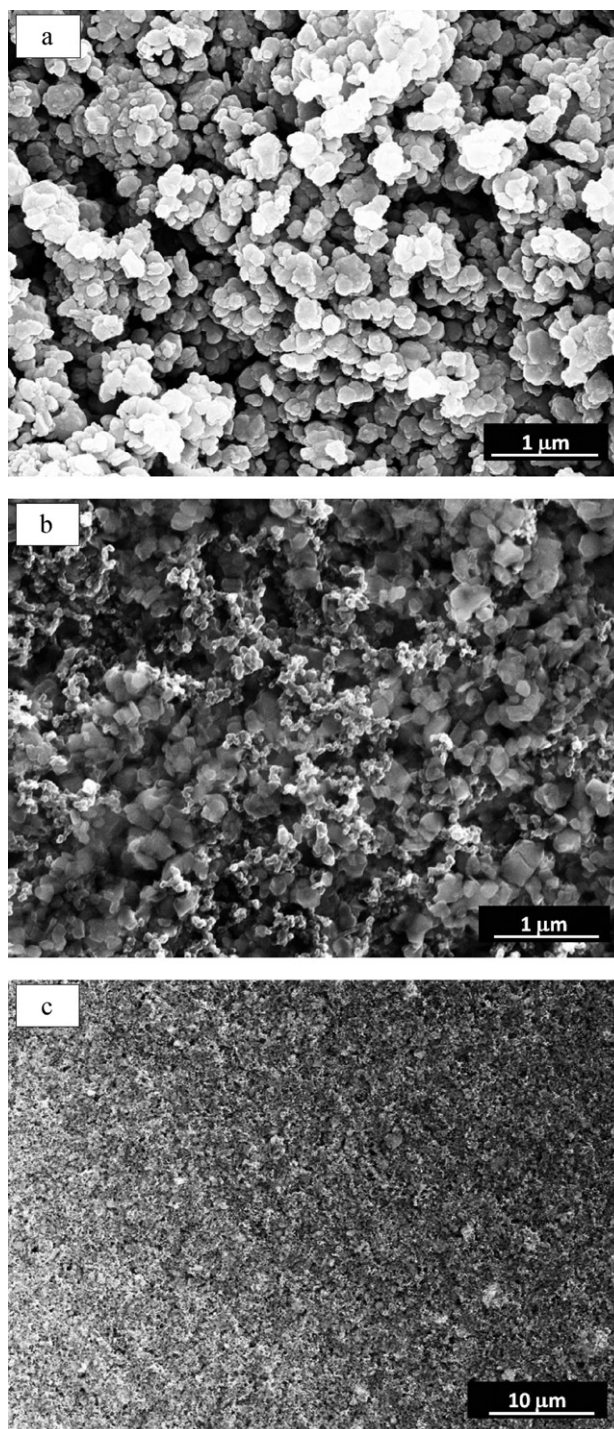


Fig. 1. SEM images of the $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.56}\text{Ni}_{0.16}\text{Co}_{0.08}]\text{O}_2$ powder at magnification of 50k \times (a), prepared electrode with CMC binder at magnification of 50k \times (b) and 5k \times (c).

ity of 246.9 mAh g^{-1} . On the other hand, the CMC-based electrode delivered only 205.0 mAh g^{-1} in the first cycle, but it maintained 169.5 mAh g^{-1} after 200 cycles. The average capacity fading for this electrode was 0.09% per cycle, thus clearly demonstrating a much better cycling stability than the PVDF-based electrode. Considering that the same performance is shown also at lower rate (0.2C), it appears that CMC is a very promising binder for high voltage cathode materials such as $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.56}\text{Ni}_{0.16}\text{Co}_{0.08}]\text{O}_2$, and that the aqueous slurry preparing process will not negatively affect the material's long-term performance. As a matter of fact, the electrode

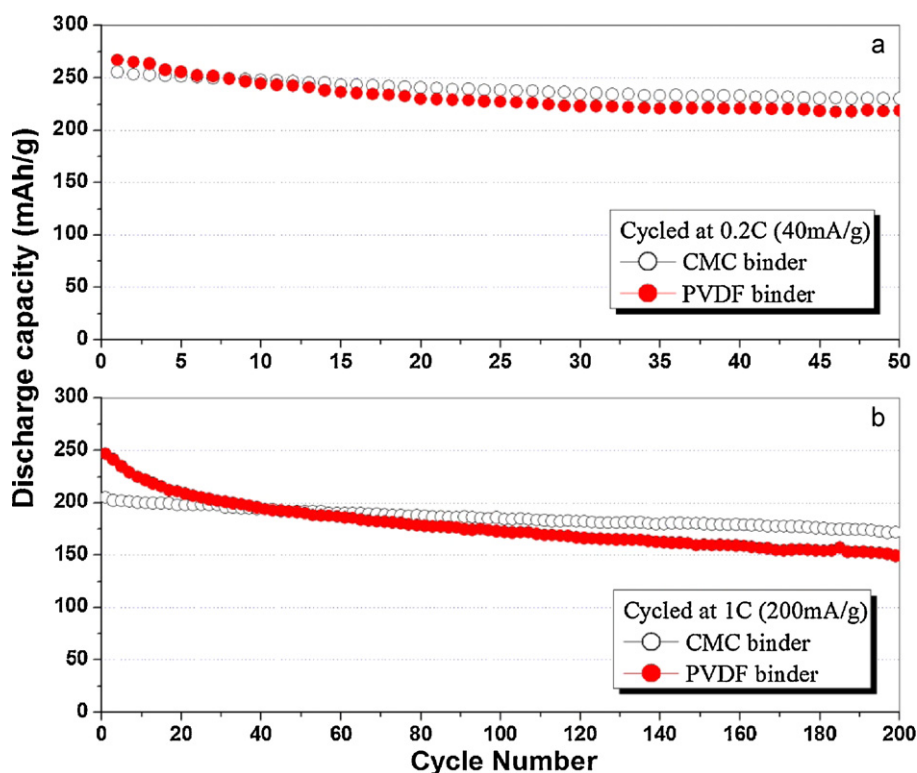


Fig. 2. Comparison of cycling performance between the $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.56}\text{Ni}_{0.16}\text{Co}_{0.08}]\text{O}_2$ electrodes with CMC and PVDF binder. The cells cycled at 0.2C (a) and 1C (b).

with CMC binder even shows better cycling performance than that with PVDF.

Fig. 3 shows the power tests result for the CMC-based $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.56}\text{Ni}_{0.16}\text{Co}_{0.08}]\text{O}_2$ electrode. The charge and discharge rates were varied between 0.2C and 5C. The electrode shows a good rate capability with CMC binder, even at very high rates. The electrode delivered a capacity of 207 mAh g^{-1} when tested at 5C/0.2D (the 5th cycle) and 174 mAh g^{-1} at 5D/0.2C (the 11th cycle). Even more, when the charge and discharge rates were set to 5C and 5D (the 17th cycle), the electrode was still able to deliver a capacity of 147 mAh g^{-1} . This is a very promising performance for the application in hybrid electric vehicles (HEV). It is also worth mentioning that, after operating at high rate for several cycles, the electrode still delivered high capacities at a lower rate (0.2C/0.2D), such as 240 mAh g^{-1} in the 7th cycle and 235 mAh g^{-1} (the 13th cycle). This indicates that increasing the rate from 0.2C to 5C does not lead to any apparent morphological or electrochemical degradation of CMC-based electrodes. In other words, CMC binder can be used in a lithium ion battery system operating under very flexible current conditions.

To clarify the improved long-term cycling performance of CMC-based electrodes against PVDF-based ones, the possible effect of the aqueous slurry preparation procedure must be considered. It has been already reported [4,6,20] that a preliminary acid treatment of Li_2MnO_3 cathode material, which leads to a $\text{Li}^+ - \text{H}^+$ ion exchange process, increases the first-cycle efficiency of $\text{Li}/\text{Li}_2\text{MnO}_3$ and the

long-term cycle performance. This is because the ion exchange process corresponds to the leaching of Li_2O and the formation of MnO_2 . On this basis, it is very reasonable to propose that during the aqueous slurry processing used to prepare the CMC-based electrodes, the $\text{Li}^+ - \text{H}^+$ exchange takes place as well, especially considering the extreme conditions experienced by the active material particles during the high-energy ball milling. To verify this hypothesis, two additional experiments were performed. First, the material was ball milled in presence of water under the same conditions (time and speed) used for the slurry preparation. After drying at 180°C over night, the lithium content of the water treated material was checked by ICP-OES. The result showed that the Li content in the water treated material was 3% lower than in the pristine material.

To confirm that the lithium loss took place during the contact with water and not, for example, during the drying process, the pristine material was dispersed in water (1 mol of material per liter of water) by magnetic stirring for one day. The pH value of the dispersion was seen to increase after one day to values from around 9 to 11. This is a clear indication that Li^+ ions are exchanged by H^+ already in water.

The $\text{Li}^+ - \text{H}^+$ exchange would also explain the lower capacity initially delivered by the CMC-based electrodes with respect to the PVDF-based ones. The voltage profiles showed by CMC- and PVDF-based electrodes in the first charge/discharge cycle (Fig. 4) also support the mechanism described above. During the first charge plateau (below 4.5 V), which is associated to the delithiation of

Table 1
Electrochemical data collected at 0.2C and 1C of $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.56}\text{Ni}_{0.16}\text{Co}_{0.08}]\text{O}_2$ electrodes with CMC and PVDF binder.

	0.2C			1C		
	1st discharge capacity (mAh g^{-1})	50th discharge capacity (mAh g^{-1})	Capacity fading per cycle (%)	1st discharge capacity (mAh g^{-1})	200th discharge capacity (mAh g^{-1})	Capacity fading per cycle (%)
CMC binder	255.4	230.0	0.20	205.0	169.5	0.09
PVDF binder	266.8	218.8	0.36	246.9	149.1	0.20

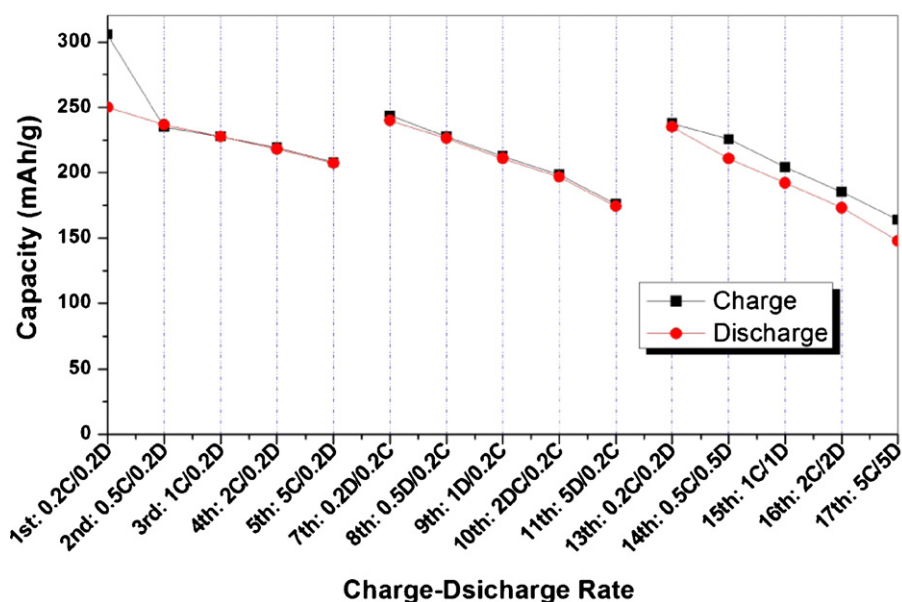


Fig. 3. Power test of $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.56}\text{Ni}_{0.16}\text{Co}_{0.08}]\text{O}_2$ electrodes with CMC binder.

the LiMnO_2 -like regions [21], the profiles for both CMC-based and PVDF-based electrodes are perfectly overlapping. However, the second plateau (located above 4.5 V during charging), which is widely accepted to originate from the oxygen loss from the layered Li_2MnO_3 lattice [22] shows a large capacity difference. At this plateau, the capacity involved for the CMC-based electrode is about 30 mAh g^{-1} lower than that of the PVDF-based electrode. This indicates that part of the material in the Li_2MnO_3 -like regions was chemically transformed to MnO_2 during the aqueous slurry processing with a resulting positive effect on the first cycle Coulombic efficiency and the long-term cycling performance.

A third very important effect resulting from the chemical leaching of Li_2O appears when the application of this electrode in a full Li-ion battery is considered. In fact, the lower decrease of capacity upon the initial cycles showed by the CMC-based cathodes (Fig. 2) results in a much easier balancing of the negative electrode in the lithium-ion battery.

Last of all, it is worthwhile to comment on the different changes taking place in the active cathode material upon cycling with the two different binders. Since the voltage profiles cannot

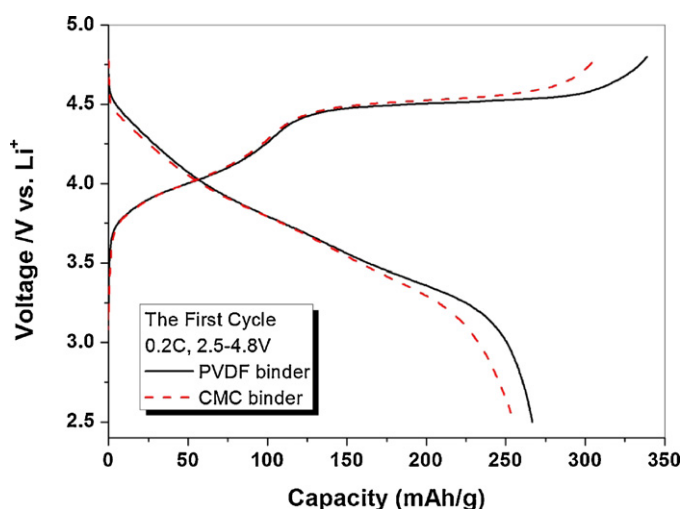


Fig. 4. Initial charge and discharge profiles of $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.56}\text{Ni}_{0.16}\text{Co}_{0.08}]\text{O}_2$ electrodes with CMC and PVDF binder.

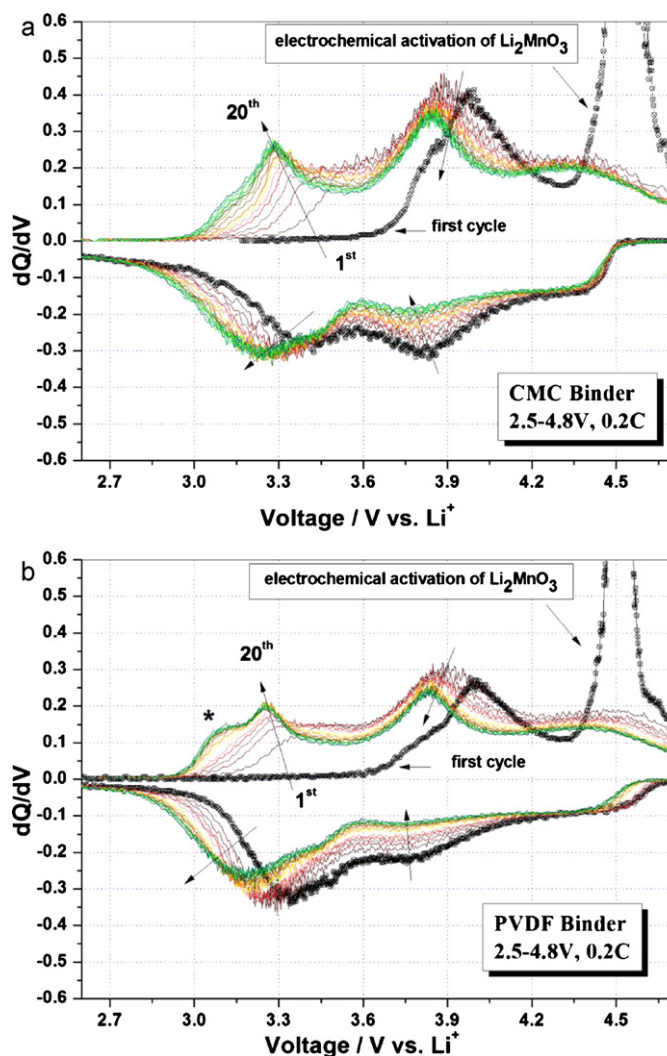


Fig. 5. dQ/dV derivative plot of the voltage profile for $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.56}\text{Ni}_{0.16}\text{Co}_{0.08}]\text{O}_2$ electrode with CMC (a) and PVDF (b) binder.

very clearly show the redox features occurring during cycling, derivative capacity vs. voltage (dQ/dV) plots for both CMC- and PVDF-based $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.56}\text{Ni}_{0.16}\text{Co}_{0.08}]\text{O}_2$ electrodes were elaborated and graphed in Fig. 5. During the first charge process, both graphs show a strong peak above 4.5 V, which arises from the electrochemical activation of the Li_2MnO_3 component accompanied by oxygen loss. Since the reaction is highly irreversible, no corresponding reduction peak is observed in the 1st discharge profile.

Comparing the evolution of the profiles in the following cycles (Fig. 5(a) and (b)), however, three main differences can be observed. First, the redox peaks at about 3.3 V and 3.9 V, which correspond to the lithium insertion/extraction reactions from the octahedral sites [6,23], show much less variation for the CMC-based electrode, thus indicating a better reversibility of this electrode with respect to the PVDF-based one.

The higher peak reproducibility of the CMC-based electrode upon cycling can also be observed for the redox features above 4.2 V as it is shown in Fig. 5(a) where the high voltage features are practically overlapping from the 2nd cycle to the 20th cycle. Since this redox features correspond to the lithium insertion/extraction from the tetrahedral sites [24], it can be concluded that this reaction is more reversible in CMC-based electrodes.

Finally, an oxidation peak at about 3.1 V (marked with an asterisk in Fig. 5(b)) emerges more sharply during the cycling of the PVDF-based electrode, which might be caused by the growth of a new crystalline phase. Although this feature also appears for the CMC-based electrode, its growth on cycling is much less pronounced. This, once more confirms the higher stability of the CMC-based electrode upon cycling.

These three observations all prove that the active material in CMC-based electrodes has a better structural stability during the electrochemical processes than in the PVDF-based electrodes, which may also be the reason for its better cycling stability.

4. Conclusion

The introduction of CMC as a binder for Li_2MnO_3 – LiMO_2 high voltage cathode materials appears to be a very promising approach. In fact it has been proved, that CMC can be used at high voltage conditions, at least to 4.8 V vs. Li/Li^+ . Besides, the advantages of the lower price of CMC itself and the environmental friendliness of the aqueous slurry preparation procedure, CMC-based electrodes also show superior cycling stability by showing less than 0.1% capacity fading per cycle. Under the same conditions, PVDF-based electrodes showed a two-fold higher capacity fading (0.2% per cycle). In addition, $\text{Li}[\text{Li}_{0.2}\text{Mn}_{0.56}\text{Ni}_{0.16}\text{Co}_{0.08}]\text{O}_2/\text{CMC}$ electrodes delivered 174 mAh g^{-1} of discharge capacity at 5C and may be used in batteries operating under very flexible current conditions.

All these improvements are attributed to the aqueous slurry preparation that, most likely, induces the Li^+ – H^+ ion exchange and favors the Li_2O leaching out from the Li_2MnO_3 phase, a phenomenon which is known to reduce the initial irreversible capacity and improves the cycling performance of the Li-insertion process in Li_2MnO_3 .

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