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Published in: Journal of Power Sources

DOI: 10.1016/j.jpowsour.2024.234549

Published: 15/07/2024

Document Version Publisher's PDF, also known as Version of record

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Please cite the original version:

Hamed, S., Obrezkov, F., Huotari, S., Colalongo, M., Mousavihashemi, S., & Kallio, T. (2024). Optimized NMC622 electrodes with a high content of the active material: A comprehensive study. *Journal of Power Sources*, *608*, Article 234549. https://doi.org/10.1016/j.jpowsour.2024.234549

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Contents lists available at ScienceDirect





Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Optimized NMC622 electrodes with a high content of the active material: A comprehensive study



Sara Hamed^a, Filipp Obrezkov^a, Simo Huotari^b, Mattia Colalongo^{a,c}, Seyedabolfazl Mousavihashemi^{a,1}, Tanja Kallio^{a,*}

^a Department of Chemistry and Materials Science, School of Chemical Engineering, Aalto University, 02150, Espoo, Finland

^b European Synchrotron Radiation Facility, 71 Avenue des Martyrs, Grenoble, 38000, France

^c Department of Physics, University of Helsinki, 00100, Helsinki, Finland

HIGHLIGHTS

G R A P H I C A L A B S T R A C T

- Optimal balance of inactive materials enhances electrode performance.
- 3D conductive network improves electrical and mechanical electrode properties.
- Operando dilatometry shows 3D network suppresses volume changes.
- Operando XRD shows 3D conductive network improves lattice parameter stability.



ARTICLE INFO

Keywords: Lithium-ion battery LiNi_{0.6}Mn_{0.2}Co_{0.2}O₂ (NMC622) Carbon nanotube 3D conductive network Operando dilatometry Operand X-ray diffraction

ABSTRACT

The composition of lithium-ion battery positive electrodes, incorporating an active material, conductive carbon additives, and a binder, fundamentally influences the electrode physical and electrochemical characteristics. In this study, the properties of positive electrodes with a high amount of an active material (LiNi_{0.6}Mn_{0.2}Co_{0.2}O₂ 98 wt-%), were tested with different ratios of carbon nanotubes (CNTs) and carbon black (CB) additives, along with varying amounts of a PVDF binder. Consequently, the electrode rate capability improves with the increase of CNTs up to 30 wt-% in the total conductive carbon share and increasing the binder amount to 1 wt-%, attributed to the optimal balance of inactive material amount. The optimal composition is determined to be 98 wt-% NMC622, 1 wt-% PVDF, and 1 wt-% total conductive carbons, out of which CNT shares accounting for 30 wt-%. Furthermore, this study continues by comparing the optimal composition with the reference electrode (CNT-free)

* Corresponding author.

- E-mail address: tanja.kallio@aalto.fi (T. Kallio).
- ¹ Current address: VTT Technical research centre of Finland, 02150 Espoo, Finland.

https://doi.org/10.1016/j.jpowsour.2024.234549

Received 16 February 2024; Received in revised form 26 March 2024; Accepted 13 April 2024 Available online 4 May 2024

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to assess the impact of CNTs on electrochemical performance. With CNTs present, the electrode attains higher energy density and specific capacity owing to uniform conductive network. Operando XRD and dilatometry experiments also reveal that CNTs reduce irreversible height change during cycling and minimize anisotropic lattice changes, thus enhancing capacity retention.

1. Introduction

Lithium-ion batteries (LIBs) are widely regarded as the preferred energy storage system for small portable electronic devices [1] while they are also increasingly utilized in electric vehicles [2]. Therefore, with the increasing demand for LIBs, improving energy density, power density, capacity retention, and efficiency is essential and indisputable [3]. Ni-rich layered oxides (LiNi_xMn_vCo_zO₂, abbreviated as NMC) have been widely adopted in the past decade due to their attractive electrochemical properties and reversible performance [4]. However, despite their advantages, NMC materials still suffer from such issues as low electronic conductivity and poor cycle life due to structural instability upon long-term cycling [5]. It is well-established that the structure of active materials within lithium-ion batteries can undergo significant changes with repeated charge-discharge cycles [6]. This can lead to strain and volume fluctuations within the electrodes, increasing impedance and ultimately deteriorating the capacity of individual commercial LIBs. Over time, these changes can cause a serious imbalance in the electrochemical properties of the battery, including its discharge capacity, open circuit voltage, and cell impedance [7].

These issues significantly impact the battery performance and create practical challenges for the market application of Li-ion batteries [8]. Yet, these drawbacks can be mitigated by various methods, including modification of electrode composites by adding highly efficient conducting agents [9].

In order to attain stable cycling characteristics and enhance electrical conductivity of a positive electrode, it is necessary to integrate an external electron transfer network into the electrode [10,11]. This involves utilizing carbon materials as a conductive additive in the electrode. Examples of such carbon materials include carbon black [9] (CB), carbon nanotubes [12] (CNTs), graphene [13], and carbon nanofibers [14], which have high electrical conductivity and relatively low cost.

Carbon black is a form of non-crystalline carbon featuring graphitelike crystalline structures with stable electrochemical properties. However, CB is a 0-dimensional material [15] with a low aspect ratio and relatively lower intrinsic electrical conductivity $(0.1-10^2 \text{ S cm}^{-1})$ [16]. This hinders its suitability for high-power density batteries, as electron mobility poses a limitation, especially at higher C-rates [17].

CNTs are an attractive alternative as they have a high intrinsic electrical conductivity (from 10^6 to 10^7 S cm⁻¹) [18], large specific surface area (commonly from 200 to 500 m² g⁻¹) [19], excellent mechanical properties (270–950 GPa) and tensile strength in the range of 11–63 GPa [20]. The primary challenge arises from the robust van der Waals interactions and the substantial specific surface area of CNTs,

making it difficult to uniformly disperse them in an electrode fabrication slurry containing active materials and binders in an organic solvent [21]. This difficulty can result in clustering of CNTs into bundles, leading to localized electrical disconnections within the electrode [22]. On the other hand, the OD carbon black nanoparticles adhere to the surface of NMC particles, while the 1D carbon nanotubes wrap around the particles and bridge the NMC particles and the carbon black nanoparticles [15]. Due to the limitations that arise from using each of these carbon conductive solely, it is better to incorporate them together in an appropriate proportion. This helps to avoid the exclusive use of CNTs and also enables the benefits from the synergistic effect of 1D CNTs and OD CBs, efficiently building a three-dimensional (3D) conductive framework in the electrode (Fig. 1) [23].

In this study, the effect of the amount of a binder, total amount of conductive agents and the ratio between conductive agents were studied to find out their effect on a NMC622 electrode performance for highpower applications. To find the optimum composition, the CNT to CB ratio was studied in the range of, 15:85, 20:80, 25:75, 30:70, and 35:65 for different amounts of PVDF, in the range of 0.8-1.4 wt-%, while fixing the active material (NMC622) amount at constant high value, to 98 wt-%. Morphology observations show that CNTs are uniformly distributed throughout the electrode, and they are evenly spread on the entire surface of the individual NMC particles. By increasing the CNTs share in the conductive carbon mix up to 30 %, higher rate capability, and capacity retention are achieved. However, reaching 35 % share of CNTs, the electrode shows poor performance, which is ascribed to forming CNT aggregates and non-uniform distribution that can result in a weak conductive network. The achieved positive effect of the CNTs on the electrode performance is investigated through operando XRD and dilatometry. Compared to the reference electrode, the presence of CNTs reduces irreversible height change that occurs during a formation cycle and reduces overall electrode height change. Interestingly, the electrode with CNT exhibits reduced anisotropic lattice changes in comparison to the reference electrode. Song et al. [24] study reported how the aspect ratio of the conductive agent can affect the kinetic properties of lithium ion batteries, while they measured longterm cycling, rate capability and EIS. They did not perform neiter postmrtem analysis, nor operando measurements. Liu et al. [21] study reported the dual effect of graphene sheets and CNTs together by measuring longterm cycling, rate capability and EIS. They also did not perform any operando or postmortem analvsis. To compelement understanding on CNT containig electrodes, our study offers significant insights into the mechanisms underlying particle disintegration and capacity degradation in NMC622 and CNT-based Li-ion batteries. These insights can promote the design of NMC



Fig. 1. Schematic structure of the electrical pathway formed by (a) 0D network formed by carbon black and (b) 3D network formed by a mixture of carbon black and carbon nanotubes.

electrodes that offer both higher capacity and capacity retention.

2. Materials and methods

2.1. Electrode preparation

First, an 8 wt-% PVDF (Kynar HSV 1810, Arkema) solution in Nmethyl-2-pyrrolidone (NMP, BASF, Life Science) was made for fabricating positive electrodes. It was mixed by a magnetic stirrer (Stuart UC152 Hot Stirrer) for 4 h and allowed to rest overnight. Subsequently, a mixture of 5 wt-% carbon black (PRINTEX® kappa 100, Orion Engineered Carbons) in NMP was made by using a dispergator (Dispermat^RCV) using the following mixing protocol:

I. 1 min 1000 rpm.

- II. 5 min 2000 rpm.
- III. 25 min 4000 rpm.

The selected amount of the CNT dispersion (CNT dispersion at 8 wt% in NMP, Graphistrength® C M19-5 HP, Arkema) and PVDF solution were added to the carbon black dispersion and mixed for 2 min at 2000 rpm. Finally, NMC 622 (commercial material) and NMP to reach 70 % of solid mass content were added to the mixture and let them mix for 10 min at 4000 rpm.

The resulting slurry was allowed to rest for 1 h after which it was spread on 20 μm aluminum foil (MTI) using the doctor blade technique to achieve the aspired loading of 2 mAh cm $^{-2}$. After the coating, electrodes were transferred to an oven (Memmert UNB 100 Oven) for drying at 80 °C for 4 h and calendared with a pressure of 3 ton cm $^{-2}$ at room temperature to improve the contact. For preparing the sample without CNT, only the CNT addition step is omitted; otherwise, the procedure is entirely the same. The prepared electrodes had loading of 10.5–11 mg cm $^{-2}$ with a thickness of 50 μm . Table 1 lists the compositions of the electrodes prepared for this study.

2.2. Material characterization

Table 1

The electrodes morphology was investigated using a scanning electron microscope (SEM, Tescan Mira3, in-beam secondary electrons). The crystalline structures of the electrodes were measured using X-ray diffraction (XRD, PANalytical X'Pert Pro-MPD, CuK_{\alpha1}-radiation); the Bragg angle was tested over a range of 10°–80°. The lattice parameters were obtained by fitting the XRD pattern using GSAS-II software. To gain a more profound insight into the impact of the CNTs on the crystal lattices and phase changes of the cathodes, operando XRD measurements

Compositions of the reference and CNT containing NM622 electrodes.

were done using $CuK_{\alpha 1}$ -radiation and a transmission wide-angle x-ray scattering setup with a MAR345 image plate detector. The beam size on the samples was reduced by slits to 400 \times 400 μ m and the distance between the sample and the detector was 115 mm. Powder diffraction rings up to about $2\Theta = 50^{\circ}$ could be captured by the setup. The cycling was done by a home-built constant-current charger, whose control was integrated into the diffractometer control software SPEC [25].

2.3. Electrochemical evaluation

To evaluate the electrochemical properties of the samples, the electrodes were assembled into half-cells and full-cells (Hohsen 2016). The prepared electrodes (active material loading ~ 2 mAh cm⁻²) were cut into 14 mm diameter discs, and after being pressed with 3 ton cm⁻² pressure, were dried in a vacuum oven (~ 0.05 mbar, 80 °C) for 12 h and transferred to a glove box (Jacomex GP Campus) without exposure to air. Regarding the test, a proper cell was assembled in the glovebox, then rested for 24 h and finally analyzed at room temperature (20 °C).

For half-cell assemblies, a Li foil (Alfa Aesar, 0.5 mm thick, 19 mm diameter) with 100.15 mAh cm⁻² areal capacity, the prepared electrode with 10.5–11.5 mg cm⁻² active material areal density, 200 μ L of a lithium hexafluorophosphate (LiPF₆) solution (BASF, LP30, 1:1 EC/DMC solution), and a glass fiber paper (Whatman GF/A, 19 mm diameter, 0.26 mm thick) were used as a counter electrode, working electrode, electrolyte, and separator, respectively. The prepared coin cells were analyzed by galvanostatic rate capability tests (Neware battery test system, TC53) in the voltage range of 3.0–4.3 V. The discharge current density for rate capability tests varied from 0.1 to 10 C while the charge current density was kept constant at 0.2C, followed by a constant voltage charge at 4.3 V with a 0.03C rate cut-off. The C-rates were calculated based on a theoretical capacity of 185 mAh g⁻¹ for NMC622. Three repeats of each sample were prepared to confirm the results. The reported values in Fig. S3, are the average \pm the standard deviation.

In a full-cell assembly (with an N:P ratio of 1.2), a graphite electrode (commercial material), the prepared electrode, 200 μ L of a 13 wt % LiPF₆ in 20:25:40 wt % EC/DMC/EMC (ethyl methyl carbonate) with a 2 wt % vinylene carbonate (VC) solution, and Celgard 2500 (Asahi Kasei, 25 μ m) were used as a counter electrode, working electrode, electrolyte, and separator, respectively.

For a pouch cell assembly (with an N:P ratio of 1.2 and 12 \pm 0.5 mAh capacity), the prepared positive electrode (27 \times 17 mm) and graphite electrode (28 \times 18 mm) were pressed with 3 ton cm⁻², and connected to the positive (4 mm width aluminum tab, MTI) and negative terminal (4

Sample name	wt- % NMC 622	wt- % PVDFs	wt- % total conductive carbon	% CNT/C _{total}
NMC-0.8B-20CNT	98	0.8	1.2	20
NMC-0.8B-25CNT	98	0.8	1.2	25
NMC-0.8B-30CNT	98	0.8	1.2	30
NMC-1B-15CNT	98	1	1	15
NMC-1B-20CNT	98	1	1	20
NMC-1B-25CNT	98	1	1	25
NMC-1B-30CNT	98	1	1	30
NMC-1B-35CNT	98	1	1	35
NMC-1.2B-20CNT	98	1.2	0.8	20
NMC-1.2B-25CNT	98	1.2	0.8	25
NMC-1.2B-30CNT	98	1.2	0.8	30
NMC-1.4B-20CNT	98	1.4	0.6	20
NMC-1.4B-25CNT	98	1.4	0.6	25
NMC-1.4B-30CNT	98	1.4	0.6	30
NMC-0.8B-0CNT	98	0.8	1.2	0
NMC-1B-0CNT	98	1	1	0
NMC-1.2B-0CNT	98	1.2	0.8	0
NMC-1.4B-0CNT	98	1.4	0.6	0

mm width nickel tab, MTI), respectively, using a welding machine (TMAX-VS-40A, TMAXCN). Then, the cell was manually stacked and laminated while Celgard 2500 (Asahi Kasei, 25 μm thickness, non-coated and polyolefin-based) was used as a separator. Afterwards, the sides were sealed (MSK-115-III, MTI), and the cell was filled with 600 μl of a 13 wt % LiPF₆ in 20:25:40 wt % EC/DMC/EMC (ethyl methyl carbonate) with a 2 wt % vinylene carbonate (VC) solution and the final side sealed under vacuum.

To conduct electrochemical impedance spectroscopy (EIS), a three-

electrode assembly using EL-CELL®, the ECC-Ref model was prepared. An Autolab potentiostat (PGSTAT302 N, Nova 2.1 software) was used to perform the EIS measurements, applying an alternating potential amplitude of 5 mV in the frequency range of 200 kHz-15 mHz. The cells were cycled up to 100 cycles in constant current mode, and EIS was measured at SOC 50 % after every 50 cycles.

Regarding the operando dilatometry measurement, an ECD-3-nano electrochemical dilatometer from El-Cell GmbH which uses a capacitive displacement sensor was utilized. The electrochemical cell, which is



Fig. 2. (a)–(d) rate capability of the NMC 622 samples in the 3.0–4.3 V voltage range in half cell setup. (e) Specific capacity at 10 C vs. the share of CNTs (in wt-%) of the total conductive carbon mixture for 1 wt-% PVDF and, (f) specific capacity at 10 C vs. the PVDF content in wt-% (different series) for 30 wt-% CNT share in the conductive carbon mixture.

completely sealed against the ambient atmosphere, forms the core of the ECD-3-nano. Two electrodes are situated within the cell and separated by a stiff glass frit that is fixed in position. The upper (working) electrode is sealed employing a thin metal membrane through which any charge-induced height change is transmitted toward the sensor/load unit above. The dilatometer was placed inside a climate chamber (VC3 4018), and a constant temperature of 20 °C was maintained throughout the entire measurement period.

3. Results and discussion

3.1. Optimizing the electrode composition regarding the CNT/C_{total} ratio and binder amount

To investigate the effect of different amounts of CNT addition on the electrochemical properties of all the fabricated NMC622 electrodes (see Table 1), half cells were assembled and the electrodes were cycled within the voltage range of 3.0-4.3 V. Fig. 2 shows the rate capability plots of the samples at various C-rates (0.1-10C). As described above, the samples have different amounts of PVDF (0.8 wt-%, 1.0 wt-%, 1.2 wt-%, and 1.4 wt-%). Also, the CNT share in the conductive carbon mixture varies (15, 20, 25, 30, 35 wt-%). In Fig. S1, the electrodes galvanostatic charge-discharge profiles during the formation cycle (0.03C) in the potential range of 3.0-4.3 V for all the studied compositions are depicted. All the electrodes show smooth and stable charge/discharge profiles which suggest that there is no phase transformation from cubic to spinel. The initial discharge capacities of all compositions at 0.03C rate are approximately the same (3 \pm 0.2 mAh), leading to initial coulombic efficiencies of 85 % \pm 2 % (Fig. S2) in the formation cycle. With increasing the amount of the CNT share to 30 wt-% and maintaining the PVDF amount at 1 wt-%, the discharge capacity reaches 3.2 mAh. Since the compositions are slightly different, the significant differences emerge at high current densities (5 and 10C) while performances are similar at lower C-rates, as shown in Fig. 2.

Fig. 2 displays the specific discharge capacity for all the studied compositions. Significant differences emerged at high current densities (5 and 10C). When focusing on those values, the results demonstrate that the samples with the lowest specific capacity vary across the series. Yet, the electrodes with the 30 wt-% CNT share of the total conductive carbon mixture exhibit the highest specific capacity consistently. Notably, the specific discharge capacity at 10C varies significantly among the samples with the 30 wt-% CNT share (Fig. 2f), with the different amounts of PVDF of 0.8, 1, 1.2, and 1.4 wt-% exhibiting 60, 84, 46, and 30 mAh g⁻¹, respectively.

The sample series with 1.0 wt-% of PVDF appears to have the highest specific capacity at the higher C-rates compared to the other series with different amounts of PVDF. Based on these results, the sample with 1.0 wt-% of PVDF, 98 wt-% of NMC622, and the total conductive carbon loading of 1.0 wt-%, out of which 30 wt-% share CNTs, is selected as the optimum composition. These results are summarized in Fig. 2e and f, where the effects of the CNT/C ratio for the 1.0 wt-% of PVDF samples, and the PVDF content in different series for the 30 wt-% CNT share of the total conductive carbon mixture are clearly observable, respectively. With a constant binder content, increasing the amount of CNTs increases the specific capacity (Fig. 2e) suggesting that a higher concentration of CNTs improves the conductive network, leading to a greater specific discharge capacity [26]. It is worth noting that the NMC-1B-30CNT sample also demonstrates a higher specific capacity than the sample with a higher CNT content (NMC-1B-35CNT), indicating that the CNT concentration of 30 wt-% is sufficient for creating conductive pathways in the electrode. However, increasing the CNT amount by reducing the amount of carbon black affects the rheological properties of the slurry. This leads to an increase in the viscosity of the electrode slurry, which in turn entangles the dispersion process of CNTs within a solvent. Consequently, it is preferable to have a well-balanced mixture to benefit from both conducting materials as creating even electrodes becomes difficult when replacing all the carbon black with carbon nanotubes [27].

A sufficient binder amount promotes close contact between the carbon conductive agents and active materials while preventing CNTs agglomeration, which enables efficient local electronic charge injection. As depicted in Fig. 2f, an increase in the binder amount initially leads to a higher specific discharge capacity, which suggests improved mechanical contact between CNT/CB conductive pathways and the active material particles. Also, considering the long-term cycling performance, it is not recommended to use a very low content of inactive materials, as this may result in a mechanical integrity issue for the electrode. However, further increasing the amount of binder can lead to ineffective charge transport kinetics, resulting in a lower specific discharge capacity [28].

The interplay between the active material, PVDF binder, and conductive carbon is crucial in determining electrode physiochemical properties and electrochemical performance. Therefore, finding an appropriate balance between the constituent materials of the electrode is crucial in designing high-performance electrodes. This requires careful consideration of the composition and morphology of an electrode, with a focus on optimizing the interfacial interactions between the electrode components. Achieving this balance can lead to electrodes with enhanced physiochemical properties and electrochemical performance, which are critical for various applications [29].

3.2. Optimizing the reference sample composition

In Fig. 3a, the binder contribution is also investigated at the same range (0.8, 1, 1.2, and 1.4 wt-%) for the reference sample with 0 wt-% CNT. The rate capability results indicate that the same binder amount results in the highest discharge capacity for the reference electrode (NMC-1B-0CNT). Hence, this electrode is selected as the CNT free reference for further investigations.

3.3. Comparing the electrochemical performance of the optimum sample to the reference sample

To find the effect of CNTs on the positive electrode electrochemical performance, rate capability tests were conducted in half cells with the LiPF₆ electrolyte. Results are shown in Fig. 3b. The reference electrode (NMC-1B-0CNT) has solely 1 wt-% of carbon black as a conductive agent while for the optimum sample (NMC-1B-30CNT) the total conductive carbon amount is likewise fixed to 1 wt-% and out of that the CNT share is 30 wt-%. NMC-1B-30CNT exhibits specific discharge capacity of 84 mAh g^{-1} at 10C. Upon returning to the current density of 0.2C, the discharge capacity reverts to the initial level of 168 mAh g⁻¹. On the other hand, the reference NMC-1B-0CNT electrode displays poorer kinetic properties with a specific discharge capacity of only 47 mAh g^{-1} at a high current density at 10C. These results suggest that a proper amount of CNTs is required to build a uniform and effective conductive network along with CB that fully covers the surfaces of NMC622 secondary particles. This contributes to improved kinetics, resulting in a higher specific capacity, especially at higher C-rates.

The electrodes galvanostatic charge-discharge profiles at 5C and 10C in the potential range of 3.0-4.3 V are depicted in Fig. 3c and d, respectively. The NMC-1B-0CNT (areal discharge capacity at 0.1C: 1.92 mAh cm⁻²) and NMC-1B-30CNT (areal discharge capacity at 0.1C: 1.79 mAh cm⁻²) cells deliver areal discharge capacities of 1.02 and 1.30 mAh cm⁻² at a rate of 5C, and 0.23 and 0.91 mAh cm⁻² at a rate of 10C, respectively. The NMC-1B-30CNT cell exhibits more than 4 times higher areal capacities at 10C than the NMC-1B-0CNT cell. Moreover, the long-term cycling stabilities in half-cell configuration of NMC-1B-30CNT and NMC-1B-30CNT (~93 %) is higher compared with that of NMC-1B-0CNT (~88 %). The Coulombic efficiency of both samples is maintained at around 98 % after 100 cycles. This result indicate that the NMC-1B-30CNT cell exhibits superior cyclability and more reversible



Fig. 3. (a) Rate capability of the reference electrode with different binder amounts in the range of 0.8 wt% to 1.4 wt%. (b) Rate capability comparison of the NMC-1B-0CNT and NMC-1B-30CNT electrodes. (c) Galvanostatic charge-discharge profile of the NMC-1B-0CNT and (d) NMC-1B-30CNT electrode. (e) Cycle performance of NMC-1B-0CNT and NMC-1B-30CNT in half cell assembly (vs. Li foil). (f) Cycle performance of NMC-1B-0CNT and NMC-1B-30CNT in full-cell assembly (vs. graphite electrode).

behavior compared to the reference cell. Due to the electrolyte decomposition, side reactions occur at interfaces and contribute to capacity fading during cycling. The formation of an unstable conductive network in the NMC-1B-0CNT electrode is known to initiate adverse side reactions at the electrode/electrolyte interfaces, which, in turn, result in a reduction in capacity. These phenomena are particularly pronounced for NMC secondary particles, especially when subject to long-term cycling. The development of microcracks within individual particles is a pivotal factor in this process, as it frequently disrupts electron conductive pathways, leading to a reduced share of active material utilization [30]. Furthermore, this allows electrolyte to penetrate into the active material particles and come into contact with the freshly exposed surfaces, further facilitating the side reactions and resulting in a severe loss of capacity over time [31]. In order to suppress the electrolyte decomposition effect during longterm cycling, vinylene carbonate (VC) was incorporated as an additive, and NMC-1B-30CNT/graphite and NMC-1B-0CNT/graphite full cells were prepared. In this study (Fig. 3f), the cells were cycled at 1C up to 4.2 V versus graphite in constant current mode. Out of the samples analyzed, NMC-1B-30CNT exhibits more stable cycling performance, retaining 86 % of its initial capacity (127 mAh g⁻¹) after 250 cycles, while NMC-1B-0CNT maintains 72 % of its initial capacity (121 mAh g⁻¹). Therefore, these findings illustrate that adding a small quantity of CNTs and combining CNTs and CB not only improves electrochemical performance but also enhances electrode structural stability, leading to a significant increase in the cell energy density after cycling (398 Wh kg⁻¹ vs. 351 Wh kg⁻¹ - calculation of energy density is derived from the data obtained from the cathode electrode).



Fig. 4. (a) A schematic view of an ECD-3 nano dilatometer. (b) Voltage and thickness change during the first cycle for both the NMC-1B-0CNT and NMC-1B-30CNT electrodes. dQ/dV analysis for the (c) NMC-1B-0CNT and (d) NMC-1B-30CNT samples.

In order to clarify the reason behind the higher capacity retention observed for the CNT containing sample, an operando dilatometry investigation was performed on both electrodes. Dilatometry is a diagnostic technique employed to quantify dimensional changes in a material undergoing controlled parameters, such as changes in potential. In the context of operando electrochemical dilatometry, the changes in the thickness of the working electrode are recorded during the electrochemical cycling process. The ECD-3 nano set-up assembly is shown in Fig. 4a. There is a sensor unit on top of the cell which includes a sensor tip in touch with a working electrode for height change recording. A metallic membrane positioned above the working electrode serves both as a seal and as a means of connecting the sensor to the working electrode. The cell components include a stiff glass frit separator which facilitates monitoring exclusively height changes in the working electrode. Adjacent to the glass frit separator, a small amount of Li metal is introduced for utilization as a reference electrode.

Fig. 4b shows the 1.53 % and 1.83 % expansion during delithiation in the first charge-discharge cycle for the NMC-1B-30CNT and the NMC-1B-0CNT, respectively; however, both electrodes show an equal degree of contraction. Moreover, as depicted in the plot presented in Fig. 4b, the NMC-1B-30CNT sample exhibits a reversible change in height, whereas the NMC-1B-0CNT sample displays an irreversible height change of 0.36 %. Hence, these findings indicate that the presence of CNTs decreases the volume changes within the electrode. Notably, given that the NMC-1B-30CNT sample comprises merely 0.003 % CNTs, it significantly reduces the extent of height changes in the electrode. This phenomenon may be attributed to the superior mechanical reinforcement brought by CNTs wrapped around the NMC622 particles (see Fig. 1 and the SEM images below in Fig. 6), which enables

the NMC622 secondary particles to withstand significant mechanical stress throughout the cycling process. This characteristic is particularly critical for high-performance applications demanding durability and reliability [15]. In Fig. 4b, increased discharge overpotential is noted in the NMC-1B-30CNT sample which is in contrast to the rate capability results exhibited in Fig. 3b. This is attributed to the special features of the dilatometry cell, which does not restrict the electrode expansion, and the NMC-1B-30CNT sample, featuring both nanotubes and PVDF binder, may hinder lithium insertion due to restricted volume changes. Conversely, the use of only PVDF as a binder in the NMC-1B-0CNT sample restricts less volume changes during lithium insertion in the dilatometry cell. Therefore, the CNT and PVDF combination results in a higher discharge overpotential for the NMC-1B-30CNT sample. Porosity of the composite electrodes also affects the volume change behavior. Yet, addition of 0.003 wt-% of CNTs does not change the porosity or volume of the electrodes notably (porosity calculations in SI). The extent of the volume change calculated based on the dilatometry result is more than twice than the estimated volume change caused by the porosity difference (0.3 % vs. ~0.12 %).

To gain a deeper understanding on how the electron transfer network impacts the charge and discharge properties of the electrodes, differential capacity (dQ/dV) curves are calculated (Fig. 4c and d) by utilizing the above long term cycling data (Fig. 3e). The dQ/dV curves for NMC622, have a single redox peak, which can be attributed to the phase transition from hexagonal (H1) to monoclinic (M) [32] which has the same potential for both of the electrodes in the first cycle (3.72 V). With an increase in the number of cycles, the H1-M oxidation peak shifts towards higher potentials for both electrodes with an associated shift of the reduction peak towards lower potential values. After 100 cycles, the

NMC-1B-0CNT sample exhibits a significant shift in the H1-M oxidation peak (0.13 V), whereas the shift is less pronounced for the NMC-1B-30CNT electrode (0.07 V). This observation suggests that the NMC-1B-30CNT electrode displays greater stability and reversibility during the H1-M phase transition during cycling, as compared to the reference sample. This may be due to the conductive and mechanically robust CNT network, which maintains contact within the active material particles and the current collector throughout the cycling process.

To investigate the difference in electrochemical kinetics between the NMC-1B-30CNT and NMC-1B-0CNT cells, EIS analysis was performed. The Nyquist plots for both electrodes were generated before and after cycling at 50 % state of charge (SOC) utilizing the frequency range from 200 kHz to 15 mHz (Fig. 5a and b). The plots reveal a semicircle at high frequencies related to the cathode-electrolyte interface resistance (R_{cei}), a semicircle at medium frequencies corresponding to charge transfer resistance (R_{ct}), and a sloping line in low frequencies attributed to Li⁺ diffusion into the bulk of NMC622 (Warburg diffusion, CPE_{CT-2}) [33]. The provided equivalent circuit (inset in Fig. 5a and b) was used to fit the Nyquist plots. The evolution of charge transfer resistance values for both cells are presented in Fig. 5c, with a considerable difference observed. The fresh NMC-1B-0CNT and NMC-1B-30CNT cells display R_{ct} values of 4.2 and 4 Ω , respectively. A reduction in the R_{ct} value of the NMC622 electrodes is noticed when adding the CNT additive, indicating that the electrode composite with 0.3 % CNT and 1 % PVDF demonstrates faster electron transfer kinetics. This suggests that the CNT, CB, and PVDF combination facilitates effective and continuous conducting pathways for electrons in the electrode. Furthermore, this outcome can be attributed to the distinctive properties of CNTs, such as their high electrical conductivity and large surface area, which can facilitate electron transfer between the electrode and the electrolyte [34].

Moreover, throughout all cycles, only the NMC-1B-0CNT sample exhibits a Warburg diffusion ($CPE_{CT\cdot2}$) at low frequencies, whereas it cannot be detected in the NMC-1B-30CNT sample. The reason is that due to the relatively higher intrinsic ionic conductivity of the CNTs compared to CB, the NMC-1B-30CNT shows higher ionic conductivity with no diffusion limit in low frequency range. Furthermore, the reference sample experiences electrode degradation during cycling due to a lack of mechanical stability provided by the CNT network [35] which is discussed in section 3.4.

3.4. Comparing the characterization of the optimum sample to the reference sample regarding the fresh and post-mortem analysis

The morphology of the NMC particles and the NMC-1B-0CNT and NMC-1B-30CNT electrodes is presented in Fig. 6a–h. The NMC secondary particles (Fig. 6a and b) exhibit a spherical shape and are composed of densely packed primary particles. The primary particles have a diameter of approximately 500 nm, while the secondary particles vary in the size range of 3–10 μ m. Fig. 6c and d shows slightly aggregated carbon black nanoparticles in the NMC-1B-0CNT electrode, whereas



Fig. 5. Nyquist plots of (a) the NMC-1B-0CNT and (b) NMC-1B-30CNT samples, different resistance elements values for (c) comparison of charge transfer resistance for both samples during cycling at 1C-rate.



Fig. 6. SEM images of the top surface of (a) and (b) the NMC powder, (c) and (d) the NMC-1B-0CNT electrode, (e) and (f) the NMC-1B-30CNT electrode. SEM images of (g) the NMC-1B-0CNT and (h) NMC-1B-30CNT electrodes after 100 cycles at 1C.

Fig. 6e and f illustrate that the electrical network, consisting of PVDF and CNT/CB in the NMC-1B-30CNT electrode, is uniformly formed around the NMC622 particle surfaces. When conductive additives/ binder networks are not evenly distributed around the active material surfaces, they fail to create a consistent electron pathway throughout the charge-discharge cycle. This leads to an unstable interface between the cathode and electrolyte, which causes the capacity of lithium-ion batteries to deteriorate over time [36,37]. The dispersion of carbon nanoparticles among the active material particles in the electrode is crucial to facilitate conductivity through point-to-point pathways. In contrast to the zero-dimensional carbon black, one-dimensional CNTs form a unique 3D network that further enhances conductivity significantly.

The surface FE-SEM images of the cycled electrodes, as shown in Fig. 6g and h, indicate that at the grain boundaries, the 3D networks between the secondary particles within the NMC-1B-0CNT electrode undergo significant collapse and fragmentation into primary particles, leading to a breakdown in the electrical networks within the electrodes. In contrast, the surface morphology of the NMC-1B-30CNT remains unchanged even after cycling, with no evident changes observed. As discussed below, in the operando XRD results (Fig. 8), during the electrochemical cycling processes, the lattice structure of NMCs experiences

periodic changes which lead to micro-strain accumulation and subsequent crack formation. Hence, this suggests that the NMC-1B-30CNT electrode maintains exceptional structural stability, attributed to the robust binding between the NMC622 particles facilitated by the CNT network, even after long cycling. All of the characterizations discussed above demonstrate a significant enhancement in electrode performance by incorporating a minimal quantity of CNTs, ascribed to the development of a conductive and mechanically strong network.

Additionally, the structural stability of the NMC-1B-30CNT and NMC-1B-0CNT electrodes is assessed through extracting changes in the unit cell volume and lattice parameters in fresh full cells and after 250 cycles at 1C between 2.9 and 4.2 V. XRD patterns were collected for the cycled electrodes after being fully discharged to 2.9 V. Fig. 7a and b displays the patterns and resultant lattice parameters, respectively. The NMC622 powder, NMC-1B-0CNT, and NMC-1B-30CNT exhibit a distinct layered structure that belongs to the R-3m space group as expected. Additionally, no noticeable impurities or secondary phases are observed. The lattice parameters of the NMC622 powder are a = 2.8677 Å, and c = 14.2308 Å, with their ratio of 4.962 and unit cell volume of 101.581 Å³. The fresh NMC-1B-0CNT and NMC-1B-30CNT electrodes have similar values to the NMC622 powder. The (003) reflection peaks



Fig. 7. (a) XRD pattern of the NMC powder, the NMC-1B-0CNT, and NMC-1B-30CNT electrodes, fresh and after 100 cycles at 1C. (b) Changes in the lattice parameters after 100 cycles at 1C.



Fig. 8. NMC-1B-0CNT electrode contour plot of the total range, the (003) peak, and the (101) peak diffraction patterns during (a) the first cycle and (b) the 50th cycle. The NMC-1B-0CNT electrode (c) c-lattice and (d) a-lattice parameter evolution during the first and 50th cycles. NMC-1B-30CNT electrode contour plot of the total range, the (003) peak, and the (101) peak diffraction patterns during (a) the first cycle and (b) the 50th cycle. The NMC-1B-30CNT electrode (c) c-lattice and (d) a-lattice parameter evolution during the first cycle and (b) the 50th cycle. The NMC-1B-30CNT electrode (c) c-lattice and (d) a-lattice parameter evolution during the first cycle and (b) the 50th cycle. The NMC-1B-30CNT electrode (c) c-lattice and (d) a-lattice parameter evolution during the first cycle and (b) the 50th cycle. The NMC-1B-30CNT electrode (c) c-lattice and (d) a-lattice parameter evolution during the first and 50th cycles.

of the cycled cathodes shift towards a lower 2Θ angle compared to the fresh electrodes indicating lattice expansion along the c-axis. This phenomenon is observed in both electrodes after the cycling but is more prominent for the NMC-1B-0CNT electrode. Joonsup Kang et al. [38] reported a similar trend in the c-axis evolution after 50 cycles. Their ex-situ results showed 0.5 % and 0.2 % increase in the (003) peak position for the cycled reference electrode and modified electrode, respectively, while the NMC-1B-0CNT shows a 2.5 % increase, and NMC-1B-30 CNT shows a 1 % increase in their (003) peak position. Fig. 7b illustrates that all cycled electrodes display a decrease in the a-lattice parameter but an increase in the c-lattice parameter, ultimately resulting in a contraction of the unit cell volume. The c/a ratio is known to be sensitive to the SOC. In the case of the cycled NMC-1B-30CNT electrode, the lower c/a ratio observed in the discharge state after the cycling suggests the presence of a higher concentration of Li⁺ ions in the crystal structure compared to the cycled NMC-1B-0CNT electrode. The higher reaction reversibility of the NMC-1B-30CNT electrode is demonstrated by its performance. In electrochemical behavior, a larger change in the c/a ratio results in greater mechanical stress, which in turn leads to inferior cyclability. Therefore, reducing structural disordering and improving electron conductivity are effective ways to enhance the rate capability and cyclability of the NMC-1B-30CNT electrode, as demonstrated in its performance.

In addition to the ex-situ analysis, a set of operando XRD measurements were carried out during the 1st and 50th cycles for both the optimized CNT containing and the reference electrode (Fig. 8). The pouch cells were cycled in the potential range of 2.9-4.2 V at 1 C-rate while operando XRD data were collected to determine the structural evolution. From the operando XRD patterns, two features are of main importance. The 003 and 101 reflection peaks are attributed to the clattice and *a*-lattice parameters of the unit cell. In the beginning of the charge process, the shift of the (003) reflection shows the unit cell slowly expanding in the c-direction as Li ions de-intercalated from the structure, while the *a*-lattice parameter decreased gradually as the (101) reflection continuously shifts to the higher 2Θ angle. With more Li ions removed from the lattice, the c-axis contracts dramatically while the alattice parameter reaches its lowest value for both electrodes. In the NMC-1B-0CNT electrode, the fitted c-lattice parameter plotted in Fig. 8c experiences an expansion and an abrupt shrinking of the unit cell during cycling. Interestingly, the extent of cell collapse along the *c*-axis is more pronounced in the aged sample (50 cycles) as compared to the 1st cycle NMC-1B-0CNT. This indicates that the unmodified electrode underwent more extensive crystalline damage after cycling. Evidently, the greater cell contraction of the cycled electrode (50th cycle) reveals a clear asymmetricity in the c-axis evolution as compared to the 1st cycle electrode, distinctive feature of irreversible behaviors in cathode materials. The fitted a-lattice parameter (Fig. 8d) shows that the greater contraction experienced along the *c*-axis has also an impact on the *a*-axis reversibility. Contrary to NMC-1B-0CNT, the c-lattice parameter evolution of the NMC-1B-30CNT electrode (Fig. 8g) shows no further unit cell contraction of the c-lattice parameter for the cycled (50th cycle) electrode. Moreover, it is also clear from Fig. 8g how the extent of maximum expansion and sudden cell shrinking of the modified material NMC-1B-30CNT is smaller compared to NMC-1B-0CNT sample. These evidence extensively explain the improvement in cyclability for the modified electrode. Furthermore, the c-lattice parameter nearly reverts to its original value, resulting in a structurally stable configuration, as demonstrated by the reversible lattice change. The degree of the peak shift in the (101) reflection is consistent for both positive electrodes, irrespective of the composition. In fact, the fitted *a*-lattice parameters during cycling, plotted as a function of the SOC, indicated that Δa for both electrodes is limited to a maximum of -1 %, regardless of the composition which is contrary to the results obtained from the ex-situ XRD. It is important to highlight that the operando XRD results are based on 50 cycles, while the ex-situ XRD results are derived from 250 cycles and thus from more deteriorated electrodes. In comparison, the

lattice parameter in the *c*-direction varies substantially depending on the composition, as shown for the (003) peaks in Fig. 8c and g. The calculated *c*-lattice parameters show a lower increase in the lattice expansion when the CNTs are introduced to the electrode composition. The maximum Δc for NMC-1B-30CNT is 1.25 %, while the maximum Δc for NMC-1B-0CNT is as high as 1.35 %.

4. Conclusion

The rate capability and cycling performance of the positive electrode with a high content of the active material (98 % NMC622) have been improved by creating a 3D electrically conductive network using an optimal mixture of carbon conductive additives and a binder. The electrochemical properties of the NMC622 positive electrodes were investigated by varying the CNT/C_{total} ratio (0–30 wt-%) and PVDF content (0.8–1.4 wt-%). At low C-rates, there is no significant difference in the specific charge and discharge capacities; however, at high C-rates, the CNT/C_{total} ratio and binder amount have an effect. Rate capability tests show that fixing the CNT/C_{total} ratio at 30 wt-% and using 1 wt-% binder produces the highest specific discharge capacity at high C-rates compared to other compositions. Thus, the electrode composite with 1 wt-% conductive additives (with a 30 wt-% CNT/C_{total} ratio), 1 wt-% binder (PVDF), and 98 wt-% active material (NMC622) is suitable for high-power applications.

The addition of CNTs create a more uniform conductive additive distribution, fully covering the primary particles, and forming a 3D conductive network which resulted in a higher specific discharge capacity at higher C-rates in rate capability measurement and higher capacity retention of 86 % after 250 cycles, compared to the reference electrode with 72 % of capacity retention. Additionally, the NMC-1B-30CNT electrode exhibits higher lithium diffusion compared to NMC-1B-0CNT, leading to improved reversibility due to the smooth transport of lithium during the charging and discharging processes.

Based on the post-mortem analysis, the enhanced capacity retention during the long-term cycling and improved structural integrity in the NMC-1B-30CNT electrode are ascribed to the outstanding mechanical stability of CNTs. This stability serves to suppress volume changes and prevents the propagation of microcracks. These conclusions are supported by structural characterization and electrochemical analysis. Moreover, results from dilatometry indicate that irreversible expansion is a significant factor contributing to the degradation and loss of capacity in the NMC622 electrode. Regarding the operando XRD results, the lattice parameters evolution demonstrate that CNTs also protects the NMC622 particles against the chemical-mechanical aging, resulting in higher Coulombic efficiency for the NMC-1B-30CNT electrode.

In conclusion, the use of CNTs reduces interfacial resistances and improves structural stability, enabling the electrode with CNTs to exhibit superior rate capability and cycling stability, even with a high content of the active material. These findings offer valuable insights into designing Ni-rich layered cathode active material-based electrodes with the desired high active material content for high-power Li-ion batteries that can achieve high performance and stability.

CRediT authorship contribution statement

Sara Hamed: Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Conceptualization. Filipp Obrezkov: Writing – review & editing, Investigation. Simo Huotari: Writing – review & editing, Investigation. Mattia Colalongo: Writing – review & editing, Formal analysis. Seyedabolfazl Mousavihashemi: Writing – review & editing, Formal analysis. Tanja Kallio: Writing – review & editing, Validation, Supervision, Resources, Project administration, Funding acquisition, Data curation.

Declaration of competing interest

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

Data availability

Data will be made available on request.

Acknowledgments

This work made use of the Aalto University Otanano and RAMI infrastructures, as well as the University of Helsinki X-ray Laboratory and Center for X-ray Spectroscopy infrastructures. This work was supported by the RM KIC HiQCarb (grant number 20049-HiQCarb).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jpowsour.2024.234549.

References

- Z. Yang, et al., High power density & energy density Li-ion battery with aluminum foam enhanced electrode: fabrication and simulation, J. Power Sources 524 (Mar. 2022) 230977, https://doi.org/10.1016/j.jpowsour.2022.230977.
- [2] H. Cho, J. Kim, M. Kim, H. An, K. Min, K. Park, A review of problems and solutions in Ni-rich cathode-based Li-ion batteries from two research aspects: experimental studies and computational insights, J. Power Sources 597 (Mar. 2024) 234132, https://doi.org/10.1016/j.jpowsour.2024.234132.
- [3] M. Feinauer, M. Wohlfahrt-Mehrens, M. Hölzle, T. Waldmann, Temperature-driven path dependence in Li-ion battery cyclic aging, J. Power Sources 594 (Feb. 2024) 233948, https://doi.org/10.1016/j.jpowsour.2023.233948.
- [4] C. Gervillié-Mouravieff, L. Albero Blanquer, C. Alphen, J. Huang, J.-M. Tarascon, Unraveling SEI formation and cycling behavior of commercial Ni-rich NMC Li-ion pouch cells through operando optical characterization, J. Power Sources 580 (Oct. 2023) 233268, https://doi.org/10.1016/j.jpowsour.2023.233268.
- [5] D. Chatzogiannakis, et al., Towards understanding the functional mechanism and synergistic effects of LiMn2O4 - LiNi0.5Mn0.3Co0.2O2 blended positive electrodes for Lithium-ion batteries, J. Power Sources 591 (Jan. 2024) 233804, https://doi. org/10.1016/j.jpowsour.2023.233804.
- [6] P.U. Nzereogu, A.D. Omah, F.I. Ezema, E.I. Iwuoha, A.C. Nwanya, Anode materials for lithium-ion batteries: a review, Appl. Surf. Sci. Adv. 9 (Jun. 2022) 100233, https://doi.org/10.1016/j.apsadv.2022.100233.
- [7] L. de Biasi, A.O. Kondrakov, H. Geßwein, T. Brezesinski, P. Hartmann, J. Janek, Between Scylla and charybdis: balancing among structural stability and energy density of layered NCM cathode materials for advanced lithium-ion batteries, J. Phys. Chem. C 121 (47) (Nov. 2017) 26163–26171, https://doi.org/10.1021/ acs.jpcc.7b06363.
- [8] J. Hoon Kim, et al., Highly efficient oxidation of single-walled carbon nanotubes in liquid crystalline phase and dispersion for applications in Li-ion batteries, Chem. Eng. J. 458 (Feb. 2023) 141350, https://doi.org/10.1016/j.cej.2023.141350.
- [9] X. Lu, et al., Effect of carbon blacks on electrical conduction and conductive binder domain of next-generation lithium-ion batteries, J. Power Sources 592 (Feb. 2024) 233916, https://doi.org/10.1016/j.jpowsour.2023.233916.
- [10] J. Shin, J.-H. Lee, J.K. Seo, W.T.A. Ran, S.M. Hwang, Y.-J. Kim, Carbon nanotubescoated Ni-rich cathodes for the green manufacturing process of lithium-ion batteries, Int. J. Energy Res. 46 (11) (2022) 16061–16074, https://doi.org/ 10.1002/er.8266.
- [11] C.W. Park, et al., Graphene collage on Ni-rich layered oxide cathodes for advanced lithium-ion batteries, Nat. Commun. 12 (1) (Apr. 2021), https://doi.org/10.1038/ s41467-021-22403-w.
- [12] J.H. Choi, et al., Improved electrochemical performance using well-dispersed carbon nanotubes as conductive additive in the Ni-rich positive electrode of lithium-ion batteries, Electrochem. Commun. 146 (Jan. 2023) 107419, https://doi. org/10.1016/j.elecom.2022.107419.
- [13] X. Tian, Y. Zhu, Z. Tang, P. Xie, A. Natarajan, Y. Zhou, Ni-rich LiNi0.6Co0.2Mn0.2O2 nanoparticles enwrapped by a 3D graphene aerogel network as a high-performance cathode material for Li-ion batteries, Ceram. Int. 45 (17) (Dec. 2019) 22233–22240, https://doi.org/10.1016/j.ceramint.2019.07.247.
- [14] S. Pedaballi, C.-C. Li, Using conductive carbon fabric to fabricate binder-free Nirich cathodes for Li-ion batteries, Int. J. Energy Res. 46 (4) (2022) 4671–4679, https://doi.org/10.1002/er.7462.

- [15] Z. Du, J. Li, M. Wood, C. Mao, C. Daniel, D.L. Wood, Three-dimensional conductive network formed by carbon nanotubes in aqueous processed NMC electrode, Electrochim. Acta 270 (Apr. 2018) 54–61, https://doi.org/10.1016/j. electacta.2018.03.063.
- [16] D. Pantea, H. Darmstadt, S. Kaliaguine, L. Sümmchen, C. Roy, Electrical conductivity of thermal carbon blacks: influence of surface chemistry, Carbon 39 (8) (Jul. 2001) 1147–1158, https://doi.org/10.1016/S0008-6223(00)00239-6.
- [17] J. Choi, et al., Analysis of electrochemical performance with dispersion degree of CNTs in electrode according to ultrasonication process and slurry viscosity for lithium-ion battery, Nanomaterials 12 (23) (Jan. 2022), https://doi.org/10.3390/ nano12234271.
- [18] Y. Wang, G.J. Weng, Electrical conductivity of carbon nanotube- and graphenebased nanocomposites, in: S.A. Meguid, G.J. Weng (Eds.), Micromechanics and Nanomechanics of Composite Solids, Springer International Publishing, Cham, 2018, pp. 123–156, https://doi.org/10.1007/978-3-319-52794-9_4.
- [19] S. Xue, et al., Mesoporous carbon as conductive additive to improve the high-rate charge/discharge capacity of lithium-ion batteries, Energy Technol. 10 (8) (2022) 2200472, https://doi.org/10.1002/ente.202200472.
- [20] M.-H. Woo, et al., Reinforcing effect of single-wall carbon nanotubes on the LiNi0.6Co0.2Mn0.2O2 composite cathode for high-energy-density all-solid-state Li-ion batteries, Appl. Surf. Sci. 568 (Dec. 2021) 150934, https://doi.org/10.1016/ j.apsusc.2021.150934.
- [21] Y. Liu, et al., Understanding the influence of nanocarbon conducting modes on the rate performance of LiFePO4 cathodes in lithium-ion batteries, J. Alloys Compd. 905 (Jun. 2022) 164205, https://doi.org/10.1016/j.jallcom.2022.164205.
- [22] D.W. Kim, S.M. Hwang, J.B. Yoo, Y.-J. Kim, Electrode engineering with CNTs to enhance the electrochemical performance of LiNi0.6Co0.2Mn0.2O2 cathodes with commercial level design parameters, Chemelectrochem 7 (12) (2020) 2621–2628, https://doi.org/10.1002/celc.202000283.
- [23] A. Coban, H. Gungor, The carbon-based 3D-hierarchical cathode architecture for Li-ion batteries, Arabian J. Sci. Eng. 47 (6) (Jun. 2022) 7147–7155, https://doi. org/10.1007/s13369-022-06725-5.
- [24] H. Song, Y. Oh, N. Çakmakçı, Y. Jeong, Effects of the aspect ratio of the conductive agent on the kinetic properties of lithium ion batteries, RSC Adv. 9 (70) (2019) 40883–40886, https://doi.org/10.1039/C9RA09609D.
- [25] CSS Certified Scientific Software." Accessed: February. 6, 2024. [Online]. Available: https://www.certif.com/.
- [26] E. Shahpouri, S. Hassani, H. Yousefi-Mashhour, S. Aghababaeian, M. M. Kalantarian, Insight into impact of carbon nanotubes on Li-ion cathode materials, Carbon Trends 13 (Dec. 2023) 100293, https://doi.org/10.1016/j. cartre.2023.100293.
- [27] F. Napolskiy, et al., On the use of carbon nanotubes in prototyping the high energy density Li-ion batteries, Energy Technol. 8 (6) (2020) 2000146, https://doi.org/ 10.1002/ente.202000146.
- [28] Y. Zhang, et al., Ultrahigh active material content and highly stable Ni-rich cathode leveraged by oxidative chemical vapor deposition, Energy Storage Mater. 48 (Jun. 2022) 1–11, https://doi.org/10.1016/j.ensm.2022.03.001.
- [29] Y.K. Lee, An optimization framework for enhancing cycle life of composite positive electrodes in lithium-ion batteries via composition ratio optimization, J. Electrochem, Soc. 170 (6) (2023), https://doi.org/10.1149/1945-7111/acdd28.
- [30] J. Yang, X. Liang, H.-H. Ryu, C.S. Yoon, Y.-K. Sun, Ni-rich layered cathodes for lithium-ion batteries: from challenges to the future, Energy Storage Mater. 63 (Nov. 2023) 102969, https://doi.org/10.1016/j.ensm.2023.102969.
- [31] J. Zhang, et al., Binary carbon-based additives in LiFePO4 cathode with favorable lithium storage, Nanotechnol. Rev. 9 (1) (Jan. 2020) 934–944, https://doi.org/ 10.1515/ntrev-2020-0071.
- [32] Z. Ahaliabadeh, X. Kong, E. Fedorovskaya, T. Kallio, Extensive comparison of doping and coating strategies for Ni-rich positive electrode materials, J. Power Sources 540 (Aug. 2022) 231633, https://doi.org/10.1016/j. ipowsour.2022.231633.
- [33] M. Zhang, et al., Electrochemical impedance spectroscopy: a new chapter in the fast and accurate estimation of the state of health for lithium-ion batteries, Energies 16 (4) (Jan. 2023), https://doi.org/10.3390/en16041599.
- [34] A.V. Babkin, et al., Single-, double-, and multi-walled carbon nanotubes as electrically conductive additives to lithium-ion battery cathodes, Dokl. Chem. 508 (1) (Jan. 2023) 1–9, https://doi.org/10.1134/S001250082360013X.
- [35] Z. Ahaliabadeh, et al., Understanding the stabilizing effects of nanoscale metal oxide and Li-metal oxide coatings on lithium-ion battery positive electrode materials, ACS Appl. Mater. Interfaces 13 (36) (Sep. 2021) 42773–42790, https:// doi.org/10.1021/acsami.1c11165.
- [36] H.-M. Kim, B.-I. Yoo, J.-W. Yi, M.-J. Choi, J.-K. Yoo, Solvent-free fabrication of thick electrodes in thermoplastic binders for high energy density lithium-ion batteries, Nanomaterials 12 (19) (Jan. 2022), https://doi.org/10.3390/ nano12193320.
- [37] L. Jing, et al., Faster and better: a polymeric chaperone binder for microenvironment management in thick battery electrodes, Energy Storage Mater. 45 (Mar. 2022) 828–839, https://doi.org/10.1016/j.ensm.2021.12.038.
- [38] J. Kang, H.Q. Pham, D.-H. Kang, H.-Y. Park, S.-W. Song, Improved rate capability of highly loaded carbon fiber-interwoven LiNi0.6Co0.2Mn0.2O2 cathode material for high-power Li-ion batteries, J. Alloys Compd. 657 (Feb. 2016) 464–471, https://doi.org/10.1016/j.jallcom.2015.10.127.