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In-situ dilatometry and impedance spectroscopy characterization of single walled carbon nanotubes blended LiNi0.6Mn0.2Co0.2O2 electrode with enhanced performance

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ABSTRACT

Enhancing lithium-ion batteries (LiBs) cycle life is essential from both economic and sustainability perspective. In addition, to make their application in electric vehicles (EVs) even more feasible, the energy and power density have to be enhanced as well. Improvement in the electrical conductivity of battery electrodes can lead to an augmentation in power density and this can be achieved by using highly conductive carbon nanomaterials in the electrode fabrication. On the other hand, cycle life of LiBs is affected by dilation of both positive and negative electrodes during lithium ion (de)-insertion, and this can be also tailored by electrode design. In this work, ozonated long single walled carbon nanotubes (SWCNTs) are utilized to improve electrical conductivity of a LiNi0.6Mn0.2Co0.2O2 (NMC622) positive electrode along with enhancement of the mechanical strength. The enhancement effect of the ozone-treated SWCNTs on the NMC622 positive electrodes is demonstrated by means of electrochemical impedance spectroscopy and in-situ dilatometry. Compared to a conventional conductive carbon containing electrode, the presence of SWCNTs in an NMC622 electrode decreases irreversible height change occurring during a formation cycle from 276 nm to 86 nm and decreases overall electrode height change ~5.5 times. Furthermore, coulombic and energy efficiencies of the Ozonated SWCNT NMC622 electrodes are improved by 1.2% and 6.4%, respectively, compared to the reference NMC622 electrode after 250 cycles in a three-electrode assembly, showing great potential for SWCNTs to be used in LiBs. Hence, addition of optimized amount of modified SWCNTs is capable of enhancing both power density and cycling stability of LiBs simultaneously.

1. Introduction

Lithium-ion batteries (LiBs) are the most used energy storage technologies for mobile applications. With increasing demand for electrification of transportation, it is crucial to increase their energy density and efficiency along with incrementing the power density. The forecasted increasing demand for LiBs leads to significantly increasing global need for lithium and cobalt, and for example, the demand for Li is expected to reach 1.7 Mtons by 2030 [1]. LiBs raw materials are limited and expensive, and thus increasing their cycle life is important from both economic and sustainability point of view. amongst many positive electrode materials, LiNi0.2Mn0.8O2 (x + y + z = 1, NMC) are superior to other electrode materials, such as LiMO2 (M = Ni, Co, Mn) and lithium iron phosphate (LFP), in combining reasonable specific energy and cycling stability. In NMCs, Ni provides a high specific capacity whereas Co and Mn provide structural integrity and decrease the internal resistance [2,3]. The largest disadvantage of NMCs is the high price of the transition metals, mostly Co, and lower stability compared to e.g. LFP or LiCoO2. The NMC stability should be enhanced to prolong safe operation period of LiBs and to improve LiBs and NMCs sustainability as material acquisition and processing are currently energy and waste intensive. Therefore, further investigation on NMC positive electrodes has to be done to address the increasing demand of the energy storage systems.

1.1. Dilatometry of NMC electrodes

In LiBs, the energy storage is based on the spontaneous and non-spontaneous electrochemical reactions at the electrodes occurring during battery discharge and charge, respectively. Insertion and de-insertion of Li ions into the crystalline structure of the electrodes
causes expansion and contraction of the positive and negative electrodes, which can be considered as a macro scale visualization of crystalline distortions and phase transformations in molecular scale. This dilation is more significant in the most commonly used graphite negative electrodes compared to the positive electrodes. Yet, as shown here, and reported also earlier [4], positive electrodes also contribute to the Li-ion battery cell volume changes. However, based on previous works on some NMC stoichiometries, such as NMC111 [5], the swelling of a positive electrode can be negligible compared to the dilation of the negative electrode as the latter is considered to be around one order of magnitude higher [6,7]. For a graphite negative electrode this expansion is ~10% and with addition of Si to an electrode this value increases up to ~300% for pure Si anodes [8]. For different types of positive electrodes, expansions between 0 and 2% have been reported [4] while active material nature, electrode structural details, temperature, cycling potential window and applied pressure affect the dilatometry results. Despite these relatively low overall positive electrode volume changes, the anisotropic dilation in repetitive charge-discharge cycles can cause the increase of stress in electrode active materials. Higher Ni content in the NMC positive electrodes tolerates higher Li extraction (81% extraction of Li+ up to 4.3 V vs. Li+/Li) and therefore increases embedment of the electrode to the cycling stress [9]. The effect of the applied stress is typically observed in emergence of microcracks in primary particles [10] which cause structural degradation originating from unwanted side reactions with electrolyte penetrating deeper into the particles. This results in formation of a thicker surface film and irreversible volume changes which will cause capacity loss [11,12]. During charge, NMC materials typically expand up to approximately 4.0 V, which is followed by a sudden contraction with continued charging. The behavior is reversed during discharge. Hindering such behavior enables enhanced cycle life and more sustainable designs of batteries [13].

1.2. Improvement of NMC with aminated single walled carbon nanotubes (SWCNTs)

Although lithium transition metal oxides, such as NMC, have a relatively high capacity, they suffer from low conductivity and transition metal dissolution [14,15]. The electrical conductivity of these transition metal oxides varies in the semiconductor range from 10−4 to 103 mS/cm [16] while for composite electrodes the overall conductivity decreases even further because of mixing with non-conductive polymer-based binders (PVDF in this work) [14]. Therefore, it is crucial to add conductive materials to the electrode composition, and usually carbon black is used for this purpose. The carbon nanoparticles disperse around electrode active material particles and provide conductivity through point-to-point pathways. Compared to 0D carbon black, 1D carbon nanotubes (CNTs) can provide conductivity by forming a 3D network. Such a network can increase the conductivity by one order of magnitude compared to normal carbon black electrodes [17]. In addition, higher conductivity is not the only benefit from such a 3D network as the formed structure also provides mechanical reinforcement. Many studies have been devoted to applying CNTs to such positive electrodes of lithium ion batteries as LiFePO4 [18], LiCoO2 [19] and LiNi0.5Mn0.3Co0.2O2 [20], but only few investigations related to NMCs [21] exists.

In this article, we have optimized single walled carbon nanotube (SWCNT) content in NMC622 positive electrodes for high power lithium-ion batteries. Electrochemical half-cell measurements show improved rate capability attributed to improved kinetics, which is induced by the improved electron transfer. Measurements with EIS and dilatometry show that SWCNTs enhance the cycling stability by providing mechanical reinforcement. This is the first research in which the dilatometry of SWCNT modified electrodes has been investigated to our best knowledge. As a conclusion, SWCNTs beneficial effects cover improved positive electrode reaction efficiency and cycle life, and this potentially enables the manufacturing of more sustainable LiBs.

2. Experimental

2.1. Electrode preparation

The Reference NMC622 electrode was prepared first. PVDF (Solvay, Solfet 5130) was dissolved in N-methyl-2-pyrrolidone (NMP, Alfa Aesar) to obtain 5% solution. This solution was left standing overnight to remove air bubbles, and a slurry with the composition of NMC622 95% (LiNi0.6Mn0.2Co0.2O2, Targray), PVDF 3% and carbon black 2% (Timcal Super C65) was prepared. SWCNT (TUBALL, 93% purity, length ~15 μm and 5 nm diameter) was used as received for the “pristine SWCNT NMC” electrode. Then SWCNTs were functionalized using an ozone generator (OZX-300ST, Enerly) for 40 min at full power. The electrode composition optimization was performed by replacing a part of the carbon powder with SWCNTs, the mass percentages being 0.25, 0.5, 0.75 and 1% of the whole electrode. First, SWCNTs were dispersed in the PVDF/NMP solution and then conductive carbon and NMC622 were added, respectively. The ratios of NMC622 and PVDF were maintained constant and only carbon and SWCNT ratios were changed. NMP was used to fix solid mass percentage at 60%. The prepared slurries were uniformly coated on an Al foil (MTI, 20 μm thick) and subsequently dried at 80 °C for 4 h. The compositions of the electrodes prepared in this study are reported in Table 1.

2.2. Material characterisation

The morphological investigation of the electrodes was performed using a scanning electron microscope (SEM, Tescan Mira3, in-beam secondary electrons). The prepared electrodes could be investigated as they were, but the powder SWCNT sample was first mixed with 1 mg/ml isopropanol (Honeywell, >99.9%), then casted on Cu foil and finally dried before the measurement could be done. The surface composition of the samples was investigated using X-ray photoelectron spectroscopy (XPS, Kratos Axis Ultra DLD) with monochromatic Al Kα X-ray radiation. The SWCNTs were also analyzed via a Raman spectrometer (Renishaw, inVia confocal Raman microscope) using a 532nm argon ion laser as the source of excitation in the range of 50–3000 cm−1. The structural changes of the electrodes were measured using X-ray diffraction (XRD, PANalytical X’Pert Pro-MPD, CuKα-radiation). The room temperature conductivity of the NMC622 electrodes were determined by using the four-point-probe instrument (Jandel, model RM3000).

2.3. Electrochemical evaluation

- Two-electrode cell assembly

The prepared electrodes (active material loading ~1 mAh/cm2) were cut in 14 mm diameter discs and after being pressed with 3 tons/cm2 pressure, were dried in vacuum oven (~0.05 mbar, 80 °C) for 12 h and transferred to a glove box (Jacomet GP Campus) without exposure to air. Subsequently, half-cells (Hohsen 2016) were assembled with a Li foil as a counter electrode (Alfa Aesar, 0.75 mm thick). 200 μL of lithium

<table>
<thead>
<tr>
<th>Sample name</th>
<th>NMC 622</th>
<th>Binder</th>
<th>Conductive additive Carbon (Pristine or oxidized) SWCNT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference NMC</td>
<td>95 wt. %</td>
<td>3%</td>
<td>2 wt. %</td>
</tr>
<tr>
<td>0.25% SWCNT NMC</td>
<td>95 wt. %</td>
<td>3%</td>
<td>1.75 wt. %</td>
</tr>
<tr>
<td>0.5% SWCNT NMC</td>
<td>95 wt. %</td>
<td>3%</td>
<td>1.5 wt. %</td>
</tr>
<tr>
<td>0.75% SWCNT NMC</td>
<td>95 wt. %</td>
<td>3%</td>
<td>1.25 wt. %</td>
</tr>
<tr>
<td>1% SWCNT NMC</td>
<td>95 wt. %</td>
<td>3%</td>
<td>1 wt. %</td>
</tr>
</tbody>
</table>
hexafluorophosphate (LiPF$_6$) solution (BASF, LP300, 1:1 EC/DMC solution) was added as an electrolyte and glass fiber (Whatman GF/A, 19 mm diameter, 0.26 mm thick) was used as a separator. The prepared coin cells were analyzed by galvanostatic rate capability tests (Neware battery test system, TC53) in the potential range of 3.0 to 4.4 V. The discharge current density for rate capability tests varied from 0.1 to 10.0 C, and the charge current density was kept constant at 0.2 C followed by a constant voltage charge at 4.4 V with 0.03 C rate cut-off. The C-rates were calculated based on theoretical capacity of 175 mAh/g for NMC622. Three repeats of each sample were prepared to confirm the results.

- **Three-electrode cell assembly**
  
  Three-electrode assemblies (EL-CELL®, ECC-Ref model) were prepared to perform cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) tests. CV measurements were done using a Bio-Logic potentiostat (MPG-205) by applying potential of 3.0–4.4 V vs. Li/Li$^+$ at 0.02, 0.05 and 0.10 mV/s scan rates. Parallel samples were also prepared in three-electrode assembly and were used to analyze EIS of the cells. EIS measurements were performed using an Autolab potentiostat (PGSTAT302 N, Nova 2.1 software). Alternating potential amplitude of 5 mV was applied to the cells in the frequency range of 100 kHz-15 mHz. The cells were cycled in constant current mode up to 250 cycles in Neware cycler, and EIS at SOC 50% was measured every 50 cycles.

- **Dilatometry**
  
  An ECD-3-nano electrochemical dilatometer with a displacement range of 250 µm, and displacement resolution of 1 nm was used in this work (Fig. 1). The heart of the ECD-3-nano consists of an electrochemical cell, which is completely tight against ambient atmosphere. Two electrodes inside are separated by a stiff glass frit that is fixed in position. The upper (working) electrode is sealed by means of a thin metal membrane through which any charge-induced height change is transmitted towards the sensor/load unit above. The dilatometer was placed inside a climate chamber and the temperature was fixed at 25 °C during the whole time of the measurement.

3. **Results and discussion**

3.1. **Materials characterization**

To enhance the performance of NMC622 electrodes, replacement of conventional conducting carbon black by SWCNT with excellent conductivity and (electro)chemical stability is investigated [17]. Conventional carbon black and SWCNTs conductive additives have different morphologies, which is expected to affect the electrode structure. Hence, the morphology of the electrodes fabricated utilizing these carbons were investigated with a SEM. The reference NMC electrode fabricated with only conventional carbon black as a conductive agent is depicted in Fig. 2(c,d) with different magnifications. In these electrodes, spherical micro-sized NMC622 secondary particles are uniformly spread and arranged with the PVDF binder. The carbon nanospheres with ~50 nm diameter are dispersed amongst the NMC622 secondary particles and interconnect them with the PVDF fibers. To identify SWCNTs in the NMC622 electrode, the pure SWCNTs casted on a Cu foil are shown in Fig. 2(a,b) in which SWCNT bundles (nanotubes connected to each other by van der Waals bonds) are observed. In Fig. 2(e,f) different magnifications of the ozonated SWCNT NMC electrodes illustrate SWCNTs connecting the NMC622 secondary particles together. SWCNT bundles are clearly distinguishable from the PVDF transparent fibers [21]. While the SWCNTs casted on a Cu foil are observed to agglomerate and form clusters, in the electrode environment this occurs less. Instead, the SWCNT bundles are observed to form two dimensional layers, and these layers cover the surface of the NMC622 secondary particles. Since insufficient dispersion can result in agglomeration of nanotubes cause non-homogeneous coating and thus decrease the electrical conductivity, it is essential to disperse SWCNTs well in the NMP/PVDF coating solution. As the SWCNTs seem to be quite evenly distributed in the sample, these SEM results are therefore promising in terms of good conductivity.

In this study, utilization of pristine and ozone treated SWCNTs is compared to gain insight into effect of conductivity and surface groups
on the NMC622 electrodes performance. Recently these materials have been used as an electrocatalyst support [22] where hydrophilicity induced by the ozonation is observed to improve the wettability and enhance electrochemical reactions. The increased wettability is ascribed to various oxygen containing groups formed on the SWCNT surface and the earlier reported elemental compositions obtained with an XPS [22] are collected in Table S1. Those results show that before the ozone treatment SWCNTs contain 0.7% oxygen but after the treatment the content increases to 2.9%, verifying that the SWCNTs are indeed functionalized.

In the work by Noh et al [23], it is proved that functional groups on the electrode surface improve lithium-ion insertion into porous structure. Therefore, to obtain structural information on SWCNTs, Raman measurements were carried out. Fig. 3. shows the Raman spectra of pristine and ozonated SWCNTs. Both samples show characteristic peaks related to SWCNTs; the D-band, G-band and the radial breathing mode (RBM) at 1343, 1590 and 120 to 300 cm$^{-1}$ Raman shifts, respectively. The RBM feature is a specific characteristic of SWCNTs, which indicates that the materials are indeed SWCNTs. Using Eq. (1) yields information about the diameter distribution of SWCNTs [24].

$$\omega = \omega_0 + \beta \frac{d}{n}$$  \hspace{1cm} (1)

where $\omega_0$ is the frequency of the 2D graphite (cm$^{-1}$), which is zero for the RBM mode. Diameter ($d$) dependence of the peaks are characterized by $\beta$ coefficient (cm$^{-1}$•nm) and $n$ exponent. In the RBM mode diameter coefficient is 248 cm$^{-1}$•nm and $n$ value is considered to be 1 [25]. Based on Eq. (1), the average value for SWCNTs diameter is ~2 nm.

The G/D ratio value is a good indicator of the disorder in SWCNTs structure, the lower G/D value indicating higher disorder. The G band is related to an in-plane vibrational mode of bond stretching between two atoms in a graphene unit cell. The D band corresponds to a hybridized vibrational mode associated with grain edges, which indicates the presence of disorder in the structure [26]. The obtained G/D ratios for

Fig. 2. SEM images of (a,b) the SWCNTs, (c,d) the Reference NMC and, (e,f) the Ozonated SWCNT NMC electrode.

Fig. 3. Raman Spectra of pristine and ozonated SWCNT.
pristine and ozonated SWCNTs are ca. 33.3 and 5.7, respectively. The presented values reveal expectedly that the amount of disordered carbon and lithiophilic groups such as carboxyl and hydroxyl groups increases with the ozone treatment, which in turn increases the lithiophilicity of the SWCNTs [23].

3.2. Electrochemical evaluation

To find the effect of pristine and ozonated SWCNTs on the NMC622 positive electrode electrochemical performance, rate capability tests were carried out with different electrode compositions. In these experiments the total amount of the conductive carbon is fixed to 2 wt-%. The Reference NMC electrode has only conventional carbon black while the share of carbon black and pristine or ozonated SWCNTs varies for the other samples (Table 1). The discharge rate capability of all the investigated compositions of the SWCNT NMC electrodes are shown in Fig. 4, and their performance is compared to that of the Reference NMC prepared using carbon black as the conductivity enhancing agent Figs. 4.(a, b) show that 0.5% of pristine and ozonated SWCNT in the electrode composition has the optimum discharge rate capability performance, and the electrodes with this composition are further compared in Fig. 4 (c). The 0.1C rate capacities are different for all samples, being 185 mAh/g, 191 mAh/g and 193 mAh/g for reference, pristine-SWCNT and ozonated-SWNT NMCs, respectively. The higher capacity of SWCNT modified NMC622 electrodes is attributed to better charge-transfer performance of these electrodes as discussed in the context of impedance results below. It is observed from Fig. 4(c) that up to 2C rate both the 0.5% SWCNT NMC samples (pristine and ozonated) have the same performance, the capacity being 163 mAh/g for both. However, at high rates of 5C and 10C, the 0.5% Ozonated SWCNT NMC electrode shows better performance, the 10C capacities being 118 mAh/g and 135 mAh/g for pristine SWCNT NMC and ozonated SWCNT NMC, respectively. Notably, the capacity of the Reference NMC at 10C is only 60 mAh/g, which indicates that the pristine SWCNTs improve the performance notably as well. The improvement induced by the ozonated-SWNT sample, however, is even higher.

It is worth mentioning that ozonation of the SWCNTs has contradictory effects on the electrode performance: it improves lithiophilicity in one hand, and on the other hand decreases electrical conductivity and adversely hinders charge-transfer between SWCNTs and lithium ions [23]. The intensity of the G band in the Raman spectra (Fig. 3) implies that both pristine and ozonated SWCNTs provide enough electrical conductivity during the rate capability measurements and this is clearly confirmed in the rate capability investigations at 10C rate (Fig. 4). On the other hand, defects and heteroatoms on the ozonated SWCNT (Table S1) increase lithiophilicity of the composite electrode and provide better electrochemical performance at higher C-rates compared to the pristine SWCNT sample. As a summary, these results show that increasing electrode lithiophilicity by ozonation of the SWCNTs is beneficial for the overall rate capability performance and outweighs the adverse effects of conductivity decrease. However, the best rate capability of the 0.5% pristine SWCNT NMC electrode is unexpected because the conductivity of SWCNTs is intrinsically higher compared to the carbon black [21]. Therefore, a higher content of SWCNT in the electrode structure can be expected to result in higher rate capability performance. This unexpected behavior can be explained by structural factors. First, physical characteristics of the SWCNT powder could explain the difference. SWCNTs used in this research are long and have very low density, and this feature was observed to affect the consistency of the slurry used in electrode preparation in a high extent. Insertion of the SWCNTs into the electrode slurry increases the viscosity significantly and when using higher contents, above 0.5% of the total mass, it is necessary to add more NMP to compensate the solvent adsorption by nanotubes. This in turn affects the viscosity, the slurry casting conditions and may lead to inhomogeneous material distribution in the electrode. Second and more likely explanation for the best performance of 0.5% SWCNT NMC could be the higher surface area of the SWCNTs (1000 m²/g) compared to the carbon black (62 m²/g). Hence, SWCNTs provide a higher surface area for side reactions, which lead to formation of resistive interfacial layers. Therefore, it is possible that while 0.5% is an optimal content for the SWCNTs, at 1% the formation of the interfacial layer is intensified and thus counteracts the advantage of the high conductivity of SWCNTs [27]. As the 0.5% Ozonated SWCNT NMC electrode show the highest rate capability, it is selected as the optimum sample for further investigations.

The electrochemical behavior of the optimal sample is further studied using cyclic voltammetry, and cyclic voltammograms of the 0.5% Ozonated SWCNT NMC and Reference NMC samples are presented in Fig. 5(a). The first cycle is performed at 0.02 mV/s scan rate. At this scan rate, voltammograms of both the samples show the same potentials for the anodic (3.78 V vs. Li/Li⁺) and cathodic (3.71 vs. Li/Li⁺) peaks and similar current densities Fig. 5(b) shows the anodic and cathodic peaks differences (ΔE_p) at different scan rates, and at 0.02 mV/s they are 66 mV and 61 mV for the Reference NMC and 0.5% Ozonated SWCNT sample, respectively. Due to the complex mechanism of redox reactions in Li ion batteries, it is not appropriate to use ΔE_p values as a direct criterion to evaluate the reversibility (using Nernst equation), but still the lower ΔE_p value correlates to faster kinetics. After increasing the scan rate to 0.05 and 0.1 mV/s, the potential difference of the peaks increases more for the Reference NMC sample than for the 0.5% Ozonated SWCNT NMC. ΔE_p value at 0.1 mV/s for the reference sample is 347 mV while it is 160 mV for the 0.5% Ozonated SWCNT sample, which indicates that the SWCNT enhances the reversibility of the electrode reaction considerably. Based on the literature, during the charge,
The electrical resistance of the NMC111 cathode materials is higher at 3.7–3.9 V vs. Li⁺/Li compared to higher potentials [28]. Thus, the superior performance of the 0.5% Ozonated SWCNT NMC electrode at Li de-insertion peak could be attributed to the compensation of the high electrical resistance by highly conductive SWCNTs.

3.3. Long-term cycling and EIS measurements

In order to understand the reasons for the improved performance in the ozonated SWCNT modified NMC622 electrodes, EIS analysis was performed in three-electrode half-cell assembly. A Li foil and Li wire were used as counter and reference electrodes, respectively. Previous works have proved that the Li metal reference electrode prevents the interference of the counter electrode in EIS results [29]. Thus, the Reference NMC and 0.5% Ozonated SWCNT NMC cells were cyclic at 250 cycles at 1C in constant current mode. The cells were interrupted every 50 cycles and charged to 3.8 V vs. Li/Li⁺ with a constant current mode. The energy efficiency, coulombic efficiency, and specific capacity of the samples during the cycling is presented in Fig. 6. Based on the cycling results, the 0.5% Ozonated SWCNT NMC electrode has higher specific capacity than the reference sample from the beginning of the cycling, and after 250 cycles it also has better capacity retention of 69% compared to 56% for the reference. The capacity retentions of the reference and ozonated SWCNT NMC electrodes are nearly similar in early cycles, but the difference increases during the cycling, most likely due to the differences in the energy efficiencies as depicted in Fig. 6.

Fig. 7 shows the Nyquist plots of the positive electrode samples at the different stages of ageing. The shape of the EIS response of both the samples remains consistent during the cycling, while the overall impedance of the electrodes increases. The Nyquist plots obtained for both the samples show two small semicircles in high and medium frequency range and a large semicircle followed by a sloping line in medium to low frequencies. The first semicircle is attributed to the current collector and electrode material interface and also the interface of the used research type cell (ECC-Ref) and the electrode current collector foil ($Q_i, R_i$). The second and the third semicircles are attributed to the cathode electrolyte interface (CEI) ($Q_{cei}, R_{cei}$), and charge-transfer resistance ($Q_p, R_p$), respectively [30–32]. The diffusion tail at the low frequency is ascribed to the Li-ion diffusion in the porous structure ($Q_d$).

The experimental data obtained from the EIS measurements was analyzed using Z-view software and the data for the selected fitted elements in the used equivalent circuit are reported in Tables S2 and S3, Figs. 8 (R values) and 9 (Q values). According to the fitting analysis performed, the error percentage of each element is below 5% and chisquared below 10⁻⁶.

The equivalent series resistance ($R_s$) of both the samples increases with the ageing of the material (Fig. 8(a)), which is attributed to the side reactions of the carbonate based solvents changing the Li ion concentration. This is a plausible explanation as any deviation from the optimum concentration of 1 M is known to result in an increase in the solution resistance [33]. Although the electrode modified with SWCNTs shows a lower equivalent series resistance due to higher electrical conductivity of SWCNTs, the values and the trend of increment in the resistance is similar for both the samples. The reduction in the resistance originating from the inherently better conductivity of SWCNTs is evidenced by four-probe in-plane electrical conductivity measurement of the composite electrodes. These show for the Reference NMC (0.8 S/m) and 0.5% Ozonated SWCNT NMC (16.7 S/m) electrodes that partial...
Fig. 7. Nyquist plots of (a) the Reference and (b) 0.5% Ozonated SWCNT NMC samples during cycling at 1C-rate (3.8 V vs. Li/Li$^+$ was applied as D.C. potential). End point of first and second semicircles denoted by 7943 and 63 Hz, respectively. End point of third semicircle at cycle 50 was 100 mHz which shifted to 19 mHz at higher cycles. The marked frequencies apply for both Reference NMC and 0.5% Ozonated SWCNT NMC samples.

Fig. 8. Values of different resistance elements— (a) Equivalent series resistance, (b) the current collector, (c) CEI and (d) charge-transfer during the cycling for both the Reference and 0.5% Ozonated SWCNT NMC samples.
substitution of carbon black with ozonated SWCNT increased electrical conductivity ~20 times.

Fig. 8(b) depicts the resistance values assigned to the interface between the current collector and electrode material ($R_i$). The interface resistance is observed to be clearly larger for the Ozonated SWCNT NMC, being ca. 4.6 $\Omega$ after 50 cycles while for the Reference NMC it is ca. 0.9 $\Omega$. The interface resistance of the Reference NMC increases to only 1.2 $\Omega$ when the cycling is continued to 250 cycles, but for the Ozonated SWCNT NMC the change is very large, to 7.2 $\Omega$. Birrozzi and co-workers have previously confirmed by measuring EIS of NMC electrodes calendared with different pressures [29], that a higher pressure enhances the electrical contact between the material and the current collector. In this work all samples were prepared using the same pressure of 3 ton/cm$^2$. Hence, these results indicate that the 0.5% Ozonated SWCNT NMC sample has higher interfacial resistance, and this resistance increases with higher intensity compared to the Reference NMC electrode. The reason for this difference could be the poorer adhesion of the electrode materials to the aluminium current collector in the presence of SWCNTs.

The resistance related to the CEI ($R_{cei}$) implies that the Reference NMC electrode has a higher resistance than the electrode with SWCNTs (Fig. 8(c)), the values at 50 cycles being 5.2 $\Omega$ and 2.8 $\Omega$, respectively. However, the value decreases during the cycling for the reference sample but increases for the electrode with SWCNTs, and after 250 cycles the reference sample has a resistance of 4.8 $\Omega$ while the 0.5% Ozonated SWCNT NMC has 4.3 $\Omega$. Considering this interface as a layer on the cathode electrode, it can be concluded that the CEI layer of the composite cathode with SWCNTs gets thicker during cycling and hence provides higher resistance but simultaneously also protects the NMC622. For the Reference NMC sample, the resistance decreases during cycling suggesting that a protective CEI layer is degraded during the cycling. Finally, charge-transfer resistances ($R_p$) of the analyzed electrodes in Fig. 8(d) are observed to increase almost linearly with an increase in the cycle number. At 50 cycles the charge-transfer resistances of the Reference and Ozonated SWCNT NMCs are 14.0 $\Omega$ and 6.3 $\Omega$, respectively, and after 250 cycles 64 $\Omega$ and 24 $\Omega$. The linear regression of the obtained values for the $R_p$ reveals that the Ozonated SWCNT NMC electrode ageing occurs 2.5 times slower than that of the Reference NMC.

Obtained values for the constant phase elements of different interfaces are plotted in Fig. 9. The capacitance values of current collector Fig. 9. Values of different constant phase elements for the Reference and 0.5% Ozonated SWCNT NMC samples during cycling—(a) current collector, (b) CEI, (c) charge-transfer and (d) Li-ion diffusion.
interface \( (Q_d) \) for the Reference and Ozonated SWCNT NMC samples at 50 cycles are \( 6.5 \times 10^{-6} \text{ F s}^{(1-n)} \) and \( 3.5 \times 10^{-6} \text{ F s}^{(1-n)} \), respectively. Both the samples are in the order of \( 10^{-6} \text{ F s}^{(1-n)} \) which is in the range of the capacitance for the metal and electrolyte interface [29]. The current collector interface in the Reference NMC sample remains almost stable while the capacitance of the SWCNT modified electrode decreases with the cycling. This is most likely due to change in the electrolyte concentration caused by reactions between SWCNTs and the electrolyte, which results in the resistive interfacial layer formation.

The CEI layer capacitance \( (Q_{cei}) \) for the 0.5% SWCNT NMC electrode is higher than for the reference electrode during the first 100 cycles, e.g. at 50 cycles being 1.40 mF s\(^{(-1-n)}\) compared to the 0.85 mF s\(^{(-1-n)}\) of the reference, and after that becomes smaller. Eq. (2) shows the formula to calculate the capacitance of a double layer capacitor:

\[
C = \varepsilon \frac{A}{d} \tag{2}
\]

in which, \( C \) is the capacitance (F), \( \varepsilon \) is the dielectric permittivity (F/m), \( A \) is the area of capacitive layers (m\(^2\)) and \( d \) is the distance between two layers (m) which in here can be attributed to the thickness of the CEI layer. The decrease in the CEI capacitance for the SWCNT sample could be correlated to thickening of the interfacial resistive layer as SWCNTs tend to react readily with the electrolyte. On the other hand, this value increases for the Reference NMC sample during the cycling, which could be ascribed to crack formation exposing more NMC622 surface to the liquid electrolyte. Hence, the exposed NMC622 surface area increases, which is reflected as higher CEI capacitance (Eq. (2) and Fig. 9-d) [34].

The electrical double layer capacitance \( (Q_d) \), which is correlated to the (de-)insertion of Li ions in the electrode structure is the main feature in determining the cell performance. The \( Q_d \) is much higher for the 0.5% Ozonated SWCNT NMC electrode compared to the reference electrode, being 0.011 F s\(^{(-1-n)}\) and 0.006 F s\(^{(-1-n)}\), respectively. This indicates that the presence of the ozonated SWCNTs improves the lithiophilicity of the active materials significantly and facilitates Li-ion (de-)insertion, as this electrode has nearly 2 times higher capacitance compared to the Reference NMC cathode. The capacitance of both the electrodes decreases slightly with increasing cycle number, which is correlated to the active material ageing during the long cycling (Fig. 9(c)). The values obtained for the constant phase element \( Q_d \) are assigned to the concentration gradient caused by Li-ion diffusion in the active material particles. Although the 0.5% Ozonated SWCNT NMC electrode shows higher capacitance \( (0.56 \text{ F s}^{(-1-n)} \) in the starting cycles, this value decreases during cycling and becomes smaller compared to Reference NMC (Fig. 9-d). The \( Q_d \) value is also a function of Li-ion concentration in the electrolyte, and side reactions of Li ions with SWCNTs during the cycling are expected to decrease the Li ion concentration. Hence, the \( Q_d \) value decreases more intensely for the 0.5% Ozonated SWCNT NMC electrode compared to Reference NMC.

Fig. 10(a) displays the charge and discharge profiles of the Reference and 0.5% Ozonated SWCNT NMC electrodes at cycles 50 and 250 versus specific capacity. It is obvious that the electrode material degradation is accompanied with higher overpotential during charge. To obtain a higher capacity, charge potential cut-off should be increased, but this could lead to larger decay in the electrode material due to the dissolution of transition metals from the electrode structure [35]. The average charge and discharge working potentials upon cycling for both samples are presented in Fig. 10(b). Both the charge and discharge overpotentials are observed to be higher for the Reference compared to the Ozonated SWCNT NMC sample during cycling, which is in agreement with the EIS results. It is also obvious that the average discharge potential of Reference NMC is more significantly affected by ageing than the average charge potential. Comparing the results plotted in Fig. 10(b) with cyclic voltammetry results (Fig. 5) reveals that lithium insertion is more sluggish than lithium extraction [36]. Considering the voltammograms, this phenomenon can be inferred from the shape of the CV peaks in which lithium extraction peaks are sharper than the lithium insertion for both samples, while the lithium insertion peaks for the Reference NMC sample are much wider compared to those of the 0.5% Ozonated SWCNT NMC electrode. In the case of galvanostatic charge and discharge cycling, it can be seen that both the samples show higher overpotential at the discharge compared to the charge. Enhanced lithiophilicity of the Ozonated SWCNT NMC electrode can thus be concluded to improve lithium insertion, and as is seen in Fig. 10(b), the discharge overpotential of the 0.5% Ozonated SWCNT NMC electrode is clearly lower than that of the Reference NMC electrode.

- **Dilatometry**

Dilatometry is a method of measuring dimensional changes in a

![Fig. 10](image-url)
material under negligible load, while the material is exposed to a programmed change of the affecting parameters such as temperature or potential. All the affecting parameters should be strictly controlled and fixed during dilatometry. In-situ electrochemical dilatometry allows the measurement of the working electrode thickness changes while performing different techniques such as cyclic voltammetry, chronoamperometry and chronopotentiometry. The assembly of the dilatometer for the ECD-3 nano set-up (Fig. 1) is the same as for the three-electrode ECC-Ref cell, except for the top part of the dilatometer which is not mechanically fixed allowing a sensor to detect the breathing of the electrode. Special sealing parts prevent air or moisture contamination of the lithium-ion cell. Another difference between ECD-3 nano and ECC-Ref is the separator. In the latter, a flexible glass fibre separator is used, while in dilatometry a stiff glass frit separates the working and counter electrodes and thus allows monitoring of height changes related to the working electrode only. A metallic membrane on top of the working electrode acts as a seal along with connecting the sensor and working electrode. A small piece of Li metal is introduced close to the glass frit separator to be used as a reference electrode.

Here, dilatometry is used to investigate if the inclusion of ozonated SWCNTs affects the NMC622 electrode thickness changes during cycling, and the height change of the samples during a formation cycle is presented in Fig. 11(a). The Reference NMC and 0.5% Ozonated SWCNT NMC samples with similar thicknesses of 28±3 μm (Figure S1) show height changes of 892 nm and 116 nm during the whole cycle, respectively. Therefore, it appears that the SWCNTs prevent extreme volume change of the electrode at the wide potential window used here. Considering that the 0.5% Ozonated SWCNT NMC sample contains only 0.5 wt-% of SWCNTs, it suppresses the height changes in the electrode notably. Most likely the difference is caused by the superior mechanical strength of the SWCNTs which supports and protects the NMC622 particles upon cycling [21]. Reference NMC shows overall contraction behavior or height decrease after formation cycle and potential explanations include contraction of the working electrode as a result of the wetting by the liquid electrolyte or structural changes occurring in NMC622.

Fig. 11(a) shows that the 0.5% Ozonated SWCNT NMC sample has higher overpotentials during discharge which is opposite of the rate capability results (Fig. 4). The Reference NMC sample rely only on PVDF binding properties, which limit less volume changes during the lithium insertion. In contrast, the 0.5% Ozonated SWCNT NMC sample has nanotubes along with PVDF binder and this can impede Li insertion because of the restricted volume changes and consequently, increase the discharge overpotential. These observations about the NMC622 structural changes prevented by binding nature of the SWCNTs are supported by XRD measurements carried out for pristine, formatted and cycled electrodes depicted in Figure S2(a) (Supporting Information). Due to the Al current collector reflections, refinement of the NMC622 could not be...
carried out and therefore, conclusions about the NMC622 structural changes are based on the positions of the reflections. In Figure S2(b), the (003) reflection at 18.69° for the fresh samples shows an apparent shift to smaller values, to 18.52° and 18.65° for the cycled Reference NMC and 0.5% Ozonated SWCNT NMC electrode, respectively. The smaller shift for the latter suggest that the SWCNTs delay the increase in the lattice parameters caused by ageing [37,38]. It should also be noted that the flexible assembly of the dilatometer, in comparison to the highly pressurized coin cell assembly, can affect some of the electrochemical parameters and hence, the observed behavior.

Based on the cycling tests reported in Fig. 6, the decreased height change in 0.5% Ozonated SWCNT NMC does not seem to decrease the electrode specific capacity. On the contrary, the capacity is clearly higher in accordance with the rate capability measurements reported in Fig. 4. Fig. 11(b) shows the cycling results of the analyzed samples in the dilatometry. The height vs. time plot (left and bottom axis) shows the complete dilation behavior of the analyzed samples, while Max-Min vs. cycle plot (right and top axis) is obtained by calculating the difference between the maximum and minimum height of every cycle. All cycling measurements were performed at the potential range of 3.0–4.4 V vs. Li/Li° at 1 C-rate. Based on the long-term cycling of both the electrodes, the Reference NMC sample shows higher height change during each charge-discharge cycle starting from 552 nm in the beginning of cycling and decreasing to 284 nm at 80 cycles. The 0.5% Ozonated SWCNT NMC electrode shows very low height change during charge-discharge as its maximum height change is 110 nm. There is also a general tendency for both the electrodes to expand during the ageing. This behavior is intensified by irreversible expansions in every cycle. For this reason, the final height of the reference sample at 80th cycle is expanded to ~1.4 μm higher than the initial electrode, while the height change for the SWCNT sample is ~0.5 μm.

As mentioned above, in the dilatometer assembly the working electrode has movement freedom in vertical direction. Since the Reference NMC sample does not have enough binding pressure provided by the PVDF polymer the height change behavior is not stable during galvanostatic charge and discharge cycling, but the 0.5% Ozonated SWCNT NMC electrode performance is more stable during the cycling. This also indicates that the SWCNTs participate in mechanical binding of the active materials in addition to enhancing the electrical conductivity of the whole electrode (as indicated by the EIS and electrical conductivity experiments discussed above). The porosity of the composite electrodes would also affect the volume change behavior, but addition of 0.5% of the ozonated SWCNTs does not change the porosity or volume of the electrodes comparable to the 500% volume change decrement observed in the dilatometry (Fig. 11b and porosity calculations in SI). The steadiness of the volume change in the 0.5% Ozonated SWCNT NMC electrode at the end of the long cycling also proves the stability of the ozonated SWCNTs in the composite electrode.

The differential capacities (dQ/dV) of the Reference and Ozonated SWCNT NMC samples are presented in Figs. 11(c) and 11(d) together with differential height (dH/dV). The differential capacity peaks indicate the potential at which the majority of Li enters or leaves the electrode, while the differential height peaks show the potential for the maximum expansion or contraction. Furthermore, the potentials at which dH/dV=0 correlate to the behavior change of the electrode from expansion to contraction or vice versa.

The apparition potentials of the differential peaks are collected in Table 2 for both the charge and discharge. The Reference NMC sample has a sharper differential charge peak with an intensity nearly 4 times higher compared to the 0.5% Ozonated SWCNT NMC sample. The potentials of the peaks are the same, being 3.74 V vs. Li/Li°. The different intensities reveal that Li extraction in the Reference NMC occurs faster. The intensity values of the dH/dV peaks during the charge for the Reference NMC and the 0.5% Ozonated SWCNT sample are 3.24 and 0.44, respectively. The difference between the dH/dV intensities shows that the Reference NMC sample expands ~7 times more compared to the 0.5% Ozonated SWCNT NMC (Figs. 11(c) and (d)). It should be noted that the height change reversal potential (from expansion to contraction) is shifted from 3.98 V vs. Li/Li° for the Reference NMC to 4.22 V vs. Li/Li° for the 0.5% Ozonated SWCNT sample. It can be concluded that ozonated SWCNTs induce a positive shift for the contraction of the electrode. As the positive electrode potential range is limited by the contraction of the active material which could cause a collapse in the crystalline structure at higher potentials [38], this suggests that the battery usable voltage range can be increased with by using the ozonated SWCNT in the electrode.

During the discharge, the reference sample shows an expansion peak at ~3.78 V vs. Li/Li° which is correlated to volume increasing caused by lithiation (Fig. 11(c)). For the 0.5% Ozonated SWCNT sample, the expansion peak appears at ~3.75 V vs. Li/Li° and has much lower intensity compared to the reference sample (Fig. 11(d)). Using full width at half maximum (FWHM) values obtained from expansion peaks, it is shown that the Reference NMC sample expands 4.6 times more than the 0.5% Ozonated SWCNT NMC sample, and this could explain faster degradation of the Reference NMC sample due to severe volume changes. As an overall conclusion, SWCNTs resist the severe volume change of the electrode during both the charge and the discharge processes and hence increase cycle life of the positive electrode during operation.

4. Conclusion

In this study, NMC622 positive electrodes were prepared with different compositions of pristine and ozonated SWCNTs. Electrochemical results show that SWCNTs improve cells performance significantly compared to the Reference NMC electrode with conventional carbon black conducting additive at a large range of current densities. Rate capability tests reveal that 0.5% of ozonated SWCNTs in the NMC electrode composition has a better discharge performance compared to pristine SWCNT NMC at rates higher than 2C. Hence, the 0.5% Ozonated SWCNT NMC composite electrode appears to be suitable for high power and higher potential window applications.

EIS analysis reveal that ozonated SWCNTs improve the cycling stability by enhancing the CEI layer strength during cycling. The charge-transfer resistance values obtained from the EIS results reveal that the aging of the electrodes in the presence of ozonated SWCNTs occurs ~2.5 times slower than for the reference electrode. A dilatometry test instrument was also used for in-situ investigation of the volumetric behavior for the Reference and Ozonated SWCNT modified electrodes during electrochemical measurements. Dilatometry results show that the SWCNTs prevent the severe contraction of the NMC622 at higher potentials while the dH/dV analysis reveals that the SWCNTs cause a 200 mV positive shift in electrode contraction threshold potential. Long-term cycling results show that the Reference NMC electrode dilation is ~5 times higher than that of the Ozonated SWCNT NMC sample in the early cycles and still ~3 times higher after 80 cycles due to higher capacity loss in the Reference NMC sample. Hence, the dilatometry results suggest that the irreversible expansion in the discharge profile at every charge - discharge cycle is one of the main reasons for the NMC622 electrode degradation and capacity loss. Overall, SWCNTs are concluded to diminish the composite electrode structural changes preventing loss
of electronic paths within the electrode porous structure and thus increasing the cycling stability and efficiency and reducing overpotentials.

CRediT authorship contribution statement

Seyadabolfazl Mousavihashemi: Investigation, Conceptualization, Methodology, Data curation, Formal analysis, Writing – original draft.
Katja Lahtinen: Writing – review & editing. Tanja Kallio: Conceptualization, Writing – review & editing, Supervision, Project administration, Funding acquisition.

Declaration of Competing Interest

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

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Supplementary materials

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References

[5] R. Amin, Y.-M. Chiang, Characterization of electronic and ionic transport in Li1-xNi0.50Mn0.20Co 0.30O 2 (NMC523) and Li1-xNi0.50Mn0.20Co 0.30O 2 (NMC523) as a function of Li content, J. Electrochem. Soc. 163 (B) (2016) A1512–A1517.