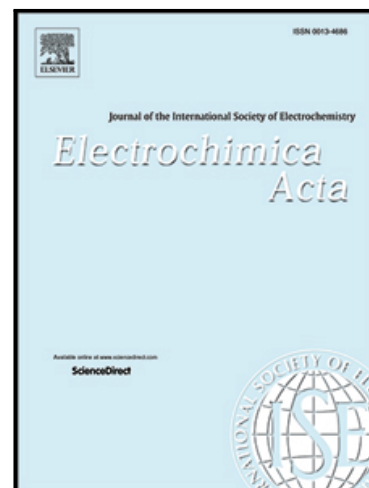


Journal Pre-proof

Reciprocal irreversibility compensation of $\text{LiNi}_{0.2}\text{Co}_{0.2}\text{Al}_{0.1}\text{Mn}_{0.45}\text{O}_2$ cathode and silicon oxide anode in new Li-ion battery

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Highlights

- A layered $\text{LiNi}_{0.2}\text{Co}_{0.2}\text{Al}_{0.1}\text{Mn}_{0.45}\text{O}_2$ cathode is synthesized and fully investigated
- The electrochemical process shows remarkable irreversible oxidation in the first cycle
- The material operates in Li half-cell at 3.8 V with specific capacity of 130 mAh g^{-1}
- The irreversible capacity is advantageously exploited to balance a Li-ion full cell
- The new Li-ion cell combines $\text{LiNi}_{0.2}\text{Co}_{0.2}\text{Al}_{0.1}\text{Mn}_{0.45}\text{O}_2$ with a silicon oxide composite

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Reciprocal irreversibility compensation of $\text{LiNi}_{0.2}\text{Co}_{0.2}\text{Al}_{0.1}\text{Mn}_{0.45}\text{O}_2$ cathode and silicon oxide anode in new Li-ion battery

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Keywords

$\text{LiNi}_{0.2}\text{Co}_{0.2}\text{Al}_{0.1}\text{Mn}_{0.45}\text{O}_2$ cathode; Silicon oxide anode; Synthesis; Li-ion battery; Cell balance.

Abstract

A layered $\text{LiNi}_{0.2}\text{Co}_{0.2}\text{Al}_{0.1}\text{Mn}_{0.45}\text{O}_2$ cathode is herein synthesized and investigated. Scanning electron microscopy (SEM) shows the layered morphology of the composite powder, while energy dispersion X-ray spectroscopy (EDS) confirms the achieved stoichiometry. X-ray diffraction (XRD) well identifies the layered structure unit cell, and Raman spectroscopy displays the corresponding M-O bonds motions. The cycling voltammetry (CV) of $\text{LiNi}_{0.2}\text{Co}_{0.2}\text{Al}_{0.1}\text{Mn}_{0.45}\text{O}_2$ in lithium half-cell reveals an electrochemical process characterized by a remarkable irreversible oxidation taking place at 4.6 V vs. Li^+/Li during the first scan, and subsequent reversible Li (de)intercalation

centered at 3.8 V vs. Li⁺/Li with interphase resistance limited to 16 Ω upon activation as indicated by electrochemical impedance spectroscopy (EIS). The relevant irreversibility during first charge is also detected by galvanostatic cycling in a lithium half-cell subsequently operating at an average voltage of 3.8 V with a stable trend, and a maximum specific capacity of 130 mAh g⁻¹. The initial irreversible capacity of the layered cathode is advantageously exploited for compensating the pristine inefficiency of the Li-alloying composite anode in a proof-of-concept cell Li-ion battery achieved by combining the LiNi_{0.2}Co_{0.2}Al_{0.1}Mn_{0.45}O₂ with a silicon oxide composite (SiO_x-C) without any preliminary pre-treatment of the electrodes. The full-cell displays a cycling behavior strongly influenced by the anode/cathode ratio, and the corresponding EIS response detected both on the single electrodes and on the Li-ion cell by using an additional lithium reference suggests a controlling role of the anode interphase and possible enhancements through a slight excess of cathode material.

1. Introduction

Lithium-ion batteries (LIBs) are presently the systems of choice for powering the portable electronics, the most promising candidate for driving the electric vehicles (EVs) to limit greenhouse gases emission [1,2], and a possible energy storage system from renewable sources to mitigate the high inflation related to pandemic and geo-political shocks [3]. The massive diffusion of this ground-breaking technology actually triggered a rapid development of EVs, and posed concerns on the present systems due to challenging market requirements such as the long driving autonomy, high safety level, and an adequate price [4,5]. Therefore, a remarkable deal of efforts are nowadays devoted towards LIBs optimization strategies including anode, cathode and electrolyte sides [4–7]. Accordingly, the typical LiCoO₂ layered cathode has been almost fully replaced by multi-metal oxides of the same structure such as Li(Ni_xCo_yMn_{1-x-y})O₂, in which the expensive and toxic cobalt is partially or totally substituted with other transition metals, thus achieving further bonuses such as adequate operating voltage, specific capacity, and thermal stability of the de-lithiated phase [8–11].

Despite the remarkable performance of widely employed electrodes such as $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (NMC333) and $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$ (NMC811) [12,13], the layered oxides still suffer from capacity decay upon prolonged cycling and possible safety issues due to phase changes involving material delamination and oxygen loss at the charged (de-lithiated) state [14,15]. This side reaction during the first cycle has also been reported as one of the main issue of voltage hysteresis during subsequent cycles, in particular in Li-rich layered oxides, which causes instability of the structure during redox processes [16]. Moreover, layered oxide cathodes with different alkali ions (e.g. Na) suffer from the same issue, reflected in a reorganization from P2 to O3-type structure that inhibits the cell performance [17,18]. Various strategies have been adopted to enhance the NMC stability, such as metal doping [19–21], acid treatment [22], and partial substitution of cobalt with aluminum which may represent a viable approach due to the stabilizing effect of Al already observed for the α - NaFeO_2 -type layered structure [23–25]. Regarding the anode side, the interest of the scientific community principally focused on Li-alloy composites including Si [26,27], Sn [28–30], Sb [31] SnO_2 [32,33], SiO_x [34–36], and Li-conversion oxides such as Fe_2O_3 [37], and NiO [38] due to the higher specific capacity delivered with respect to the conventional graphite [39]. On the other hand, the combination between substituted layered cathodes and Li-alloy conversion anodes is an attractive strategy to enhance the energy content and environmental compatibility of Li-ion batteries [40,41], despite the still open issues ascribed to these families of electrodes. Indeed, layered cathode materials may be affected by irreversible charge (de-lithiation) process during first cycle ascribed to a structural reorganization of the electrode by oxidation [42], while the alloy anodes suffer by a relevant irreversibility during first discharge (lithiation) due to matrix modification and solid electrolyte interphase (SEI) layer reductive formation concomitantly with the Li-alloying process [33]. This behavior posed intrinsic issues on the direct combination of the above electrodes in an efficient Li-ion cell, without *ad-hoc* designed *pre-activation* procedures including preliminary electrochemical or chemical lithiation of the electrodes, in particular of the anode, before their use [42,43]. In fact, possible irreversibility on the cathode or anode may lead to the loss of the cell

balance in terms of negative to positive (N/P) ratio and finally affect both the delivered capacity and the cycling stability of the Li-ion battery [44]. In this scenario, we propose and thoroughly characterize a multi-metal substituted $\text{LiNi}_{0.2}\text{Co}_{0.2}\text{Al}_{0.1}\text{Mn}_{0.45}\text{O}_2$ layered cathode for direct application in full Li-ion battery using a pristine carbon-coated SiO_x anode ($\text{SiO}_x\text{-C}$) without any further treatment of the electrodes before use in cell. Therefore, the remarkable irreversible capacity observed in the $\text{LiNi}_{0.2}\text{Co}_{0.2}\text{Al}_{0.1}\text{Mn}_{0.45}\text{O}_2$ cathode during the first charge due to its specific composition is advantageously exploited to balance the intrinsic $\text{SiO}_x\text{-C}$ anode irreversibility, thus allowing a preliminary control of the full-cell behavior by adequately selecting the N/P ratio. This novel combination, and the alternative approach adopted to achieve new Li-ion full-cells with promising performances may be of actual interest for allowing the exploitation of new materials with physical-chemical characteristics different than those of diffused electrodes in the commercially available LIBs.

2. Experimental Section

2.1. Synthesis of $\text{LiNi}_{0.2}\text{Co}_{0.2}\text{Al}_{0.1}\text{Mn}_{0.45}\text{O}_2$ cathode and $\text{SiO}_x\text{-C}$ anode

3 g of $\text{LiNi}_{0.2}\text{Co}_{0.2}\text{Al}_{0.1}\text{Mn}_{0.45}\text{O}_2$ material, subsequently indicated with the acronym LNCAM, was synthesized through a co-precipitation method, according to previous works principally focused on Na-layered electrode [45,46]. 1.3246 g of aluminum nitrate nonahydrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, Sigma-Aldrich, $\geq 98.0\%$), 2.0553 g of cobalt-(II)-nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Sigma-Aldrich, $\geq 99.0\%$), 2.0536 g of nickel-(II)-nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Sigma-Aldrich, $\geq 98.5\%$), and 3.9885 g of manganese-(II)-nitrate tetrahydrate ($\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, Sigma-Aldrich, $\geq 97.0\%$) were dissolved in 100 mL of deionized water to form a solution with a Al/Co/Ni/Mn molar ratio of 0.1:0.2:0.2:0.45. Then, 4.2370 g of NaOH pellets ($\geq 98\%$, Sigma-Aldrich) was dissolved in 212 mL of deionized water to obtain a 0.5 M NaOH aqueous solution which was added dropwise to the nitrate solution. A nitrate-NaOH solution using a 50 mol % excess of NaOH with respect to nitrate was stirred for 12 h to precipitate a hydroxide precursor that was filtered, washed with deionized

water and ethanol until a pH of 7, dried overnight at 70 °C in oven, and calcinated for 12 h at 120 °C (heating rate of 2 °C min⁻¹) in a dry air flow. Afterward, the hydroxide precursor was ground in an agate mortar with lithium hydroxide hydrate (LiOH·H₂O, ≥98%, Sigma-Aldrich) in the 1:1 molar ratio and the resulting mixture was pelletized and calcinated under a dry air flow at 500 °C (heating rate of 5 °C min⁻¹) for 5 h to obtain the material indicated with the acronym LNCAM500. The LNCAM500 precursor was ground in an agate mortar, pelletized and calcinated under a dry air flow at 1000 °C (heating rate of 5 °C min⁻¹) for 6 h to obtain the material indicated with the acronym LNCAM1000_6h, which was ground, pelletized and calcinated under a dry air flow at 1000 °C (heating rate of 5 °C min⁻¹) for 12 h to obtain the final cathode indicated with the acronym LNCAM1000_12h. All the thermal steps of the synthesis procedure were performed in a GHA 12/3000 (Carbolite) tubular furnace. The SiO_x-based anode material (indicated as SiO_x-C) was synthesized as reported in a previous paper [27]. 18 g of resorcinol was added to 58.5 g of formaldehyde at room temperature and 21 g of tetraethyl orthosilicate (TEOS) was dissolved in the homogeneous mixture. The achieved solution was heated at 70 °C and 2 mL of HCl (1 M) was added dropwise to catalyze the formation of a pink gel, which was aged for 24 h at room temperature, cut into pieces, washed with ethanol to remove residual HCl, and annealed at 1000 °C for 10 h under Ar-H₂ (5%) flow. The obtained SiO_x-C powder was finally ground in a mortar.

2.2. Materials characterization

Scanning electron microscopy (SEM) images of the LNCAM_1000_12h sample were acquired by a Zeiss EVO 40 microscope with a LaB₆ thermionic source. Energy dispersive X-ray spectroscopy (EDS) was performed on the SEM images via a X-ACT Cambridge Instruments analyzer to record elemental maps and estimate the LNCAM1000_12h stoichiometry. The elemental composition of the sample was also determined via Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) technique. HNO₃ (70%, ≥99.999% trace metal basis, Sigma-Aldrich) and HCl (37%, for analysis-ISO, Carlo Erba reagents) were used without any further purifications. Ultrapure H₂O (18 MΩ cm)

was used for the dilution of the sample. 100 mg of LNCAM1000_12h was digested in 5 mL of aqua regia (HNO₃:HCl 1:3 molar ratio) at 120 °C for 1 h by using a Parr 4744 acid digestion vessel (Parr Instrument Company). After cooldown, the solution was diluted to the proper concentration prior the ICP-MS analysis. An ICP-MS Agilent 7500 (Agilent Technologies inc.) equipped with a 3 MHz quadrupole was used for the metal determination. X-ray diffraction (XRD) patterns of the LNCAM500, LNCAM1000_6h and LNCAM1000_12h materials were collected by performing scans in the 2θ range from 10° to 90° at a rate of 10 s step⁻¹ with step size of 0.02° through a Bruker D8 Advance instrument using a Cu-K α source and a graphite monochromator on the diffracted beam. Rietveld refinement of the LNCAM1000_12h pattern was carried out through the MAUD software [47] by using the reference parameters of the LiNi_{0.4}Co_{0.15}Al_{0.05}Mn_{0.4}O₂ layered oxide (*R*-3*m* space group, N. 166, ICSD #166715) [25]. The refinement was carried out by fixing atom occupancies to the values estimated by EDS and the isotropic atomic displacement parameters were set to the same value for Al, Mn, Co, and Ni upon the refinement. Raman spectroscopy was performed on the LNCAM1000_12h powder through a Czerny-Turner spectrometer (iHR320 Horiba Scientific) equipped with a diffraction grating of 1800 grooves mm⁻¹ and a laser source with $\lambda = 532$ nm. Thermogravimetric measurement on SiO_x-C powder was carried out under air flow employing a heating rate of 5 °C min⁻¹ in the 25 – 800 °C temperature range through a Mettler-Toledo TGA 2 instrument.

2.3. Electrode preparation

The electrode slurries were prepared by dispersing the active materials (either LNCAM1000_12h or SiO_x-C), polyvinylidene fluoride (PVDF 6020 Solef®) binding polymer and carbon black (Super P carbon, Timcal) mixed by the 8:1:1 weight ratio in *N*-methyl-2-pyrrolidone (NMP, Sigma-Aldrich) and were stirred at room temperature until homogenization (about 1 h). The slurries were cast by a doctor blade tool on either aluminum carbon-coated foils (thickness ~ 20 μ m, MTI Corporation) for LNCAM1000_12h or scratched copper foils (thickness ~ 30 μ m, MTI Corporation) for SiO_x-C.

The electrode tapes were dried for 3 h on a hot plate at 70 °C, cut into disks with diameter of either 10 mm or 14 mm, and dried for 3 h at 110 °C under vacuum to remove possible residual traces of water and NMP solvent. Prior to vacuum drying, LNCAM1000_12h electrodes were pressed with a hydraulic press (Silfradent) for 30 s at 115 bar. The final active material loading ranged from 4 to 4.5 mg cm⁻² for LNCAM1000_12h and from 1.2 to 1.8 mg cm⁻² for SiO_x-C, as normalized to the electrode geometric area (either 0.785 or 1.54 cm² for electrodes with a diameter of 10 mm or 14 mm, respectively). Carbon coated Al electrodes were prepared by the doctor blade casting procedure above described using Super P carbon and PVDF binder in the 80:20 weight ratio, cut into 10 mm disks, and dried overnight at 110 °C under vacuum.

2.4. Cell assembly

Two-electrode Swagelok T-type lithium half-cells were assembled by stacking a 10 mm-diameter LNCAM1000_12h cathode, a 10 mm-diameter lithium metal anode (MTI Corporation) and a 10 mm-diameter glass fiber Whatman® GF/B disk as the separator. The EC:DMC 1:1 v/v 1M LiPF₆ solution (Sigma-Aldrich) was used as electrolyte and consisted of ethylene carbonate (EC) and dimethyl carbonate (DMC) solvents mixed in the 1:1 volume ratio dissolving lithium hexafluorophosphate (LiPF₆) in concentration of 1 mol dm_{solution}⁻³ (1M). Three-electrode Swagelok T-type lithium half-cells were prepared with the same configuration by using an additional 10 mm lithium metal disk as the reference electrode at the top side of the T-cell. An additional three-electrode Swagelok T-type lithium cell was prepared using a 10-mm diameter Super P Carbon/PVDF electrode (SPC-Al) as cathode, a 10mm-diameter lithium metal anode, a 10-mm diameter Celgard 2400 as the separator, and an additional 10 mm lithium metal disk as the reference electrode. CR2032 coin-type lithium half-cells (MTI Corporation) were assembled by using the LNCAM1000_12h cathode and a lithium metal anode both with diameter of 14 mm separated by a 16 mm-diameter glass fiber Whatman® GF/B disk. Three-electrode Swagelok-type full-cells were assembled by stacking a 10 mm LNCAM1000_12h cathode, a 10 mm SiO_x-C anode, one 10 mm

glass fiber Whatman® GF/B separator and an additional 10 mm lithium metal disk as the reference electrode placed at the top side of the T-cell. An additional CR2032 coin-type full cell was assembled by using a 14 mm LNCAM1000_12h cathode, a 14 mm SiO_x-C anode, and one 16 mm glass fiber Whatman® GF/B separator. The SiO_x-C|LNCAM1000_12h full-cells were prepared by using negative to positive (N/P) capacity ratios of 0.98 or 0.84 (for Three-electrode cells), and 0.91 (for Coin-type cell), as determined by taking into account mass loadings and specific capacities of the two electrodes at the first charge of a full-cell including the irreversible part, that is, 300 mAh g⁻¹ for first cathode de-lithiation and 810 mAh g⁻¹ for first anode lithiation. Hence, electrode loadings of 1.53 mg_{anode} cm⁻² and 4.21 mg_{cathode} cm⁻² was used for N/P = 0.98, 1.26 mg_{anode} cm⁻² and 4.05 mg_{cathode} cm⁻² for N/P = 0.84, and 1.75 mg_{anode} cm⁻² and 5.19 mg_{cathode} cm⁻² for N/P = 0.91. All cells were assembled and sealed inside an Ar-filled glovebox (MBraun, O₂ and H₂O content lower than 1 ppm).

2.5. Electrochemical tests and ex-situ measurements

A preliminary Linear sweep voltammetry (LSV) was performed to evaluate the EC:DMC 1:1 v/v 1 M LiPF₆ electrolyte in lithium battery using a three three-electrode T-type cell with SPC-Al electrode at a scan rate of 0.1 mV s⁻¹ from the OCV condition of the cell to 6 V vs. Li⁺/Li. Cyclic voltammetry (CV) was performed using a three-electrode Li|LNCAM1000_12h half-cell at a scan rate of 0.1 mV s⁻¹ in the 2.5 – 4.9 V vs. Li⁺/Li potential range, while electrochemical impedance spectroscopy (EIS) was collected at the open circuit voltage (OCV) condition of the cell as well as after 1, 5, and 10 CV cycles by applying an alternate voltage signal of 10 mV in the 500 kHz – 100 mHz frequency range. Galvanostatic cycling measurements were performed using a CR2032-type Li|LNCAM1000_12h half-cells at the constant current rate of C/20 (1C = 298 mA g⁻¹) in the voltage ranges of 2.5 – 4.4 V, 2.5 – 4.8 V, and 2.5 – 4.9 V by adopting the constant-current constant-voltage (CCCV) mode, that is, by setting an additional constant voltage step during charge at either 4.4 V, 4.8 V, or 4.9 V, respectively, until a current value of ¼ of the initial C-rate was

reached. *Ex-situ* XRD measurements were performed on LNCAM1000_12h electrodes retrieved from two-electrode Swagelok-type lithium half-cells upon either 1 or 2 charge/discharge cycles at C/20 between 2.5 and 4.9 V by adopting the CCCV mode at 4.9 V during charge. XRD scans of the cycled electrodes and of a pristine one were collected by a Bruker D8 Advance instrument using a Cu-K α source and a graphite monochromator on the diffracted beam in the 10° – 60° 2 θ range at a rate of 10 s step⁻¹ and a step size of 0.02°. Prior to XRD investigation, the cycled electrodes were washed with DMC solvent and dried under vacuum for 30 min. A rate capability test was performed on a CR2032-type Li|LNCAM1000_12h half-cell by increasing the current rate from C/10 to C/8, C/5, C/3 and 1C every 5 cycles and lowering back to C/10 after 25 cycles. The test was performed between 2.5 and 4.8 V by adopting the CCCV mode at 4.8 V during charge. CR2032-type Li|LNCAM1000_12h half-cells were galvanostatically cycled at the constant current rate of either C/10 or C/5 between 2.5 and 4.8 V by using the CCCV mode at 4.8 V during charge. Full SiO_x-C|LNCAM1000_12h cells were galvanostatically cycled at the constant rate of C/10 (1C = 298 mA g_{cathode}⁻¹) in the 1.5 – 4.8 V voltage range by adopting the CCCV mode at 4.8 V during charge. EIS measurements were performed on the three-electrodes SiO_x-C|LNCAM1000_12h cells at the OCV condition and after 1 and 10 galvanostatic cycles by using an alternate voltage signal of 30 mV in the 500 kHz – 100 mHz frequency range. All the Nyquist plots recorded by EIS were analyzed through the non-linear least squares (NLLS) method by using Boukamp software and only fits with χ^2 values of the order of 10⁻⁴ or lower were accepted [48,49]. CV and EIS were carried out by a VersaSTAT MC Princeton Applied Research (PAR, AMETEK) instrument, while the charge/discharge cycling tests were performed by a MACCOR series 4000 battery test system. All the data were recorded at the room temperature (25°C).

3. Results and Discussion

The morphology of the LNCAM1000_12h cathode material is investigated by SEM-EDS analysis, as reported in Figure 1. The SEM images of the powder show flakes with size ranging from 3 to 25

μm characterized by a layered morphology (Figure 1a) stacked into submicrometric primary particles with nanometric thickness (Figure 1b). The corresponding EDS elemental maps acquired on SEM imaging (Figure 1c) of O (Figure 1d), Al (Figure 1e), Mn (Figure 1f), Co (Figure 1g), and Ni (Figure 1h) display a homogeneous distribution of the elements, without impurities as confirmed by the EDS spectrum in Figure S1 in the Supplementary Material. However, the elemental mapping in Figure 1g evidences the presence of more intense Co X-ray signals inferred from few regions suggesting a slight Co segregation and crystalline agglomeration in the sample already observed for similar materials [50]. The EDS also allows the determination of a $\text{LiNi}_{0.18}\text{Co}_{0.20}\text{Al}_{0.09}\text{Mn}_{0.43}\text{O}_2$ stoichiometry which well approaches the one designed during synthesis, i.e., $\text{LiNi}_{0.2}\text{Co}_{0.2}\text{Al}_{0.1}\text{Mn}_{0.45}\text{O}_2$ (see Table 1), thus suggesting the successful incorporation of the transition metals into the material [46]. A similar result, reported in Table 1, is obtained by ICP-MS measurement that likely confirms the material stoichiometry discussed above. XRD measurements are performed on LNCAM1000_12h as well as on the LNCAM500 and LNCAM1000_6h precursors to investigate the samples' structure, as reported in Figure 1i and Figure S2 in the Supplementary Material, respectively. The comparison between the XRD patterns of the LNCAM materials during the synthesis (Figure S2) displays the growth of the crystalline phase by the subsequent steps and the formation of the P3-type layered structure in the final LNCAM1000_12h sample. Moreover, the progressive definition of the (006)/(012) peaks couple at $37.82^\circ/38.32^\circ$ and the (018)/(110) one at $64.48^\circ/65.44^\circ$ indicates the consolidation of the hexagonal ordering of the LNCAM layered structure, which is confirmed by a R value of about 0.51 where R is defined as the $(I_{006}/I_{102})/I_{101}$ intensities ratio [51]. Additional structural insights are provided by the Rietveld refinement of the LNCAM1000_12h XRD pattern in Figure 1i carried out by constraining the atom occupancy according to the EDS results (Figure S1 in the Supplementary Material). The refined diffractogram (red dots in Figure 1i) confirms a trigonal cell unit (hexagonal $R\text{-}3m$ space group, table n. 166) without significant content of impurities, as also suggested by the difference profile [25]. The lattice parameters determined by refinement, that is, a , c , c/a and cell volume, are reported

in Table 2 and compared with those of the $\text{LiNi}_{0.4}\text{Co}_{0.15}\text{Al}_{0.05}\text{Mn}_{0.4}\text{O}_2$ (ICSD #166715) [51,52]. The LNCAM1000_12h shows slightly different a and c values leading to a higher cell volume of 102.3 \AA^3 compared to the 101.99 \AA^3 of the reference, likely due to the higher content of Mn [53]. Furthermore, Table 2 reveals a c/a ratio of about 4.95, which indicates a well ordered structure of the sample [54], and a 003/104 peaks intensity ratio (I_{003}/I_{104} , see Figure S2 in the Supplementary Material for peaks indexing) exceeding 1.5, thus suggesting a low degree of cation mixing, in particular for the Ni^{2+} occupancy in the Li^+ sites, and likely an enhanced Li^+ ions mobility within the cathode [54]. The accuracy of the Rietveld refinement is suggested by a goodness-of-fit parameter (GOF) and weighted-profile R factor ($R_{\text{wp}}\%$) values lower than 2 and 20, respectively (Table 2) [55]. The Raman spectroscopy performed on LNCAM1000_12h in Figure 1j further confirms the layered structure by exhibiting two main peaks around 476 cm^{-1} related to the symmetric stretching vibration of the M–O bond (E_g symmetry) and at 590 cm^{-1} assigned to the O–M–O bending vibration (A_{1g} symmetry) [56,57]. In summary, LNCAM1000_12h displays defined layered morphology and structure with uniform distribution of the elements that are crucial parameters to enable the formation of a suitable electrode/electrolyte interphase in lithium cell and satisfactory cycling behavior [58], since irregular layer stacking or excessive aggregation may hinder the Li^+ ions diffusion in the material framework [59].

Table 1. Comparison of EDS and ICP-MS outcomes in terms of average atomic % (EDS), stoichiometric coefficient (EDS), concentration (ICP-MS), and stoichiometric coefficient (ICP-MS) for Li, Ni, Co, Al, Mn, and O. See corresponding EDS spectrum in Figure S1 Supplementary Materials and Experimental section for acronyms.

Element	EDS Average Atomic %	EDS Stoichiometric coefficient	ICP-MS Concentration (ppb)	ICP-MS Stoichiometric coefficient
Li	/	/	64.16	1.00
Ni	6.11	0.18	95.15	0.18
Co	6.76	0.2	99.33	0.18

Al	2.96	0.09	33.92	0.14
Mn	14.93	0.43	211.4	0.42
O	69.24	2.00	/	/

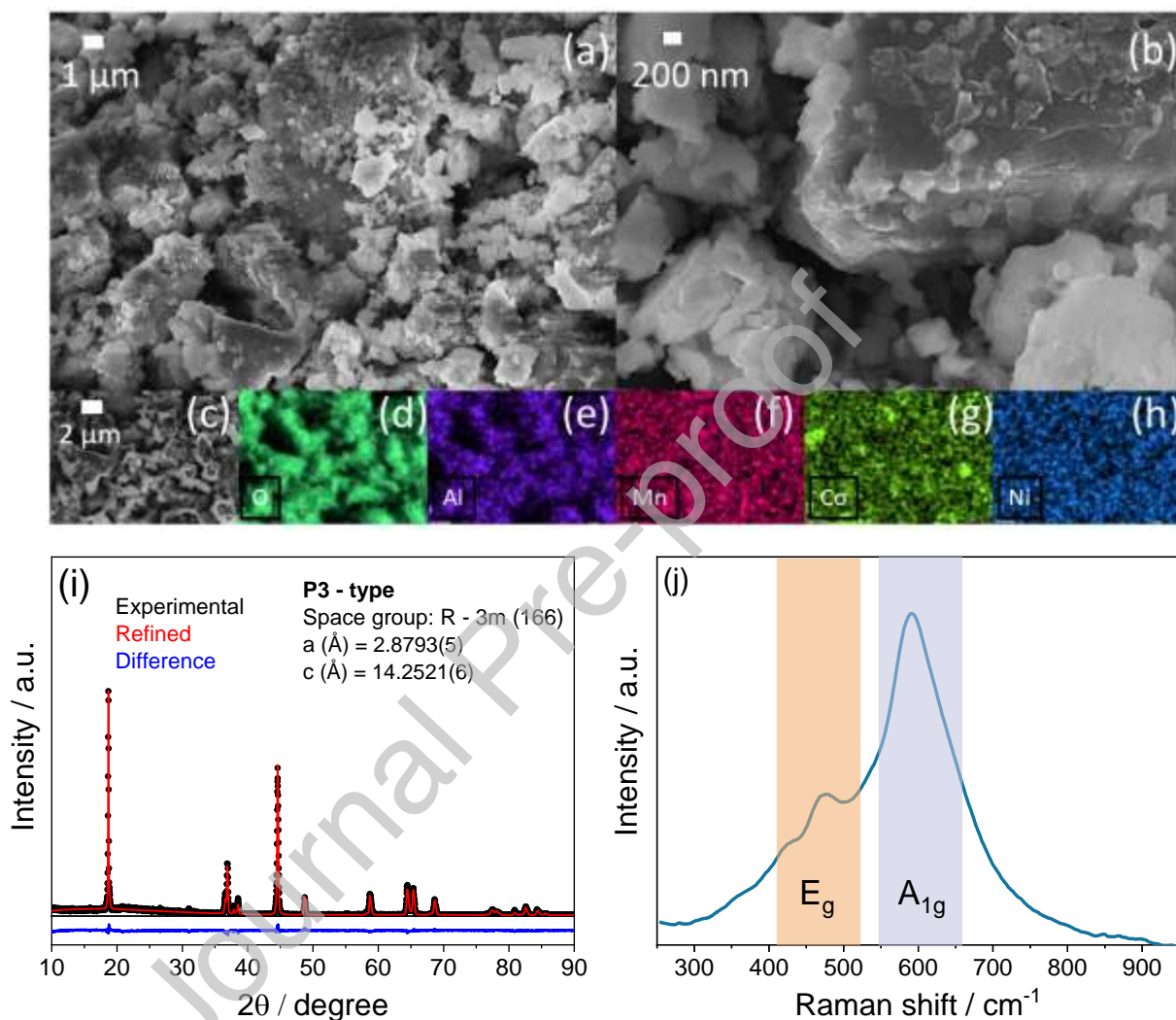


Figure 1. Characterization of the LNCAM1000_12h material. (a, b) SEM images at different magnifications; (c-h) SEM-EDS analyses with elemental maps of (d) O, (e) Al, (f) Mn, (g) Co and (h) Ni; (i) XRD and corresponding Rietveld refinement (R-3m space group, N. 166) showing experimental pattern (black dots), calculated pattern (red line) and difference profile (blue line); (j) Raman spectrum recorded in the 250 – 950 cm⁻¹ range. Highlighted regions report transitions identification. See the Experimental section for acronyms.

Table 2. Results of Rietveld refinement in terms of lattice parameters, unit cell volume, c/a parameters ratio, I_{003}/I_{104} intensities ratio, good-of-fit parameter (GOF), and weighted-profile R

factor ($R_{wp}\%$) of LNCAM1000_12h. Reference ICSD #166715 [25]. See corresponding diffractogram in Figure 1 and Experimental section for acronyms.

Material	a (Å)	c (Å)	c/a	V (Å ³)	I_{003}/I_{104}	GOF (σ)	Rwp %
LiNi _{0.4} Co _{0.15} Al _{0.05} Mn _{0.4} O ₂ (ICSD #166715)	2.872	14.273	4.969	101.99	1.848	/	/
LNCAM1000_12h	2.879(3)	14.252(1)	4.949(8)	102.32(5)	1.517(6)	1.50	17.18

Prior to testing the cell applicability of the LNCAM 1000_12h electrode, the anodic electrochemical stability window of the electrolyte (i.e., EC:DMC 1:1 v/v 1M LiPF₆) is checked in Figure S3 (Supplementary Materials). The LSV shows a small increase of the current around 5 V vs. Li⁺/Li and full oxidative decomposition at 5.2 V vs. Li⁺/Li, thus in full agreement with various literature reports [60–62]. The electrochemical process of the LNCAM1000_12h cathode is subsequently investigated in lithium half-cell by combining CV and EIS measurements, as reported in Figure 2. The CV response (Figure 2a) shows during the first cycle two oxidation peaks centered at 4.0 V and 4.6 V vs. Li⁺/Li and a single reduction wave merged at about 3.8 V vs. Li⁺/Li. The above irreversible oxidation peak at 4.6 V vs. Li⁺/Li is likely ascribed to partial oxygen loss due to structural rearrangement with possible phase modification of the cathode and concomitant partial electrolyte degradation [63], in particular the decrease of Co-O and Ni-O distances due to oxidation of the transition metals, despite negligible changes in Mn-O distance which holds Mn⁴⁺ oxidation state [64]. Nevertheless, the charge and discharge signals at 4.0 and 3.8 V vs. Li⁺/Li, respectively, are associated with the reversible (de)intercalation of the Li⁺ ions into the layered structure [65]. The irreversible lithium extraction related to the additional oxidation peak at the first cycle centered at about 3.4 V vs. Li⁺/Li may be ascribed to the presence of impurity traces in the electrolyte (e.g., water or other solvents) as well as to possible side Ni²⁺/Ni⁴⁺ oxidation process as suggested by literature reports [16]. However, the vanishing of the above peak during reduction and in the subsequent cycles suggests the formation of a suitable SEI layer at the electrodes surface [66]. During the subsequent voltammetry cycles, the electrochemical process reversibly evolves with a

single oxidation peak at 3.9 V vs. Li^+/Li reflected into the corresponding reduction signal at 3.7 V vs. Li^+/Li . The slight shift of the oxidation process to lower potential upon the first cycle further suggests a favorable reorganization of the material structure, while the modest polarization certainly indicates the formation of a suitable solid electrolyte interphase (SEI) at the electrodes surface [66,67]. This aspect is additionally investigated by EIS measurements performed at the OCV condition of the cell as well as after 1, 5, and 10 CV scans (Figure 2b).

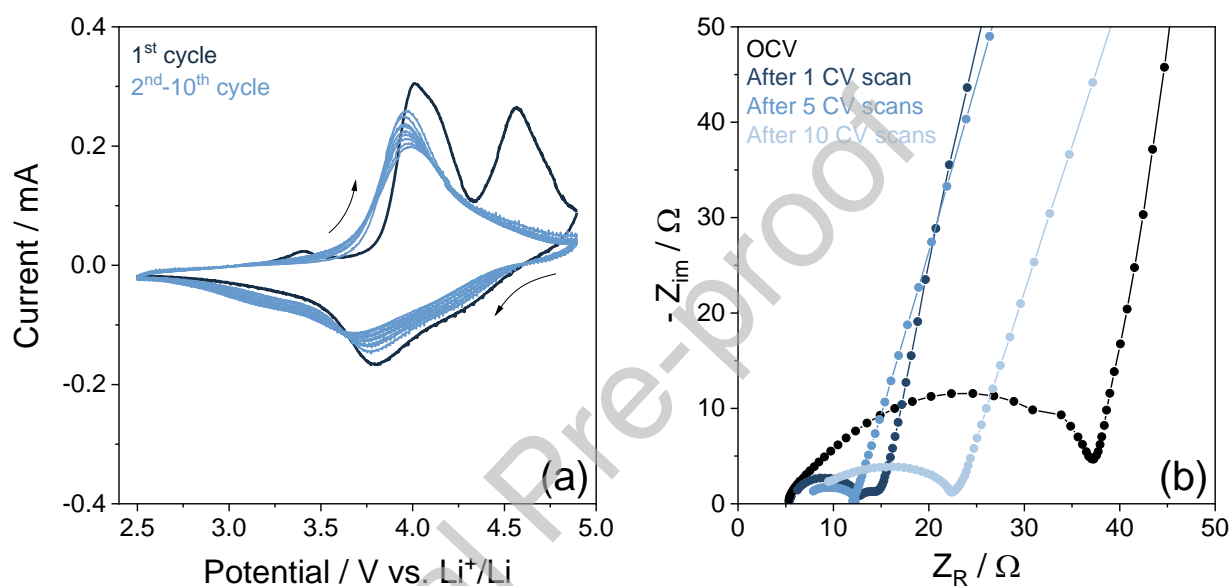


Figure 2. (a) CV and (b) EIS measurements performed on the $\text{Li}|\text{EC}:\text{DMC}$ 1:1 v/v 1M $\text{LiPF}_6|\text{LNCAM1000}_{12\text{h}}$ three-electrode cell using a Li reference electrode. CV potential range 2.5 – 4.9 V vs. Li^+/Li ; scan rate 0.1 mV s^{-1} . EIS carried out at the OCV of the cell and after 1, 5 and 10 cycles; frequency range: 500 kHz – 100 mHz; alternate voltage signal: 10 mV. See the Experimental section for the sample's acronym.

The reported Nyquist plots are analyzed by NLLS method and the results are reported in Table 3 [48,49]. The graphs in Figure 2b display a semicircle in the medium-high frequency region accounting for the Li^+ ion exchange through the electrode/electrolyte interphase, and a low-frequency almost vertical tilted line likely representing the cell geometrical capacity [68]. Therefore, the EIS can be represented by the $R_e(R_iQ_i)Q_g$ equivalent circuit, where R_e is the electrolyte resistance determined by the high-frequency intercept in the corresponding plot, the

(R_iQ_i) elements reflect the main semicircle with a total resistance corresponding to the charge transfer at the electrode/electrolyte interphase and the SEI layer at the electrodes surface, while Q_g is a constant phase element related the cell capacitance [48,49]. Only after one cycle, splitting of the SEI and charge transfer related features is clearly evidenced, thus allowing the fit of the two separate contributions, detailed in Table 3. Table 3 also reveals a trend by which an initial total interphase resistance at the OCV is 32Ω , then decreases to about 5Ω after 5 cycles and stabilizes at 16Ω at the end of the test. This behavior well supports the above mentioned formation of a suitable SEI and the favorable structural rearrangement of the cathode that may boost the reaction kinetics in lithium cell and enhance the corresponding performance [52].

Table 3. NLLS analysis of the Nyquist plots reported in Figure 2 recorded by performing EIS on a Li|LNCAM1000_12h three-electrode cell. NLLS analyses were performed through a Boukamp software and only fits with a χ^2 value of the order of 10^{-4} or lower were considered suitable [48,49]. See Experimental section for acronyms.

Cell condition	Equivalent circuit	R_1 (Ω)	R_2 (Ω)	$R_i = R_1 + R_2$ (Ω)	χ^2
OCV	$R_e(R_1Q_1)Q_g$	32.3 ± 0.5	/	32.3 ± 0.5	6×10^{-4}
After 1 CV scan	$R_e(R_1Q_1)(R_2Q_2)Q_g$	7.6 ± 0.1	1.8 ± 0.1	9.4 ± 0.1	2×10^{-5}
After 5 CV scans	$R_e(R_1Q_1)Q_g$	5.2 ± 0.2	/	5.2 ± 0.2	3×10^{-4}
After 10 CV scans	$R_e(R_1Q_1)Q_g$	16.2 ± 0.2	/	16.2 ± 0.2	1×10^{-4}

The LNCAM1000_12h is evaluated in Figure 3 by galvanostatic cycling in lithium half-cell performed by increasing the charge voltage cutoff from 4.4 V (panels a, b) to 4.8 V (panels c, d) and to 4.9 (panels e, f) at the constant rate of C/20 ($1C = 298 \text{ mA g}^{-1}$) in order to verify the effects of the irreversible oxidation on cell response and stability. As expected by the CV previously discussed in Figure 2, the cycling test with voltage range restricted between 2.5 V and 4.4 V (Figure

3a, b) shows at the first cycle (inset of Figure 3a) only the single-step charge and discharge processes centred around 4.0 V ascribed to the Li^+ (de)intercalation process. On the other hand, the first cycle reveals a remarkably higher charge specific capacity (207 mAh g^{-1}) compared to discharge (106 mAh g^{-1}) due to the above mentioned cathode structural rearrangement and partial electrolyte decomposition which appear affecting the cell even with a charge cutoff limited to 4.4V. The subsequent cycles in Figure 3a reveal a highly reversible charge/discharge process, which is confirmed by the cycling trend in Figure 3b with a stable discharge capacity of 106 mAh g^{-1} retained for over 96 % at the end of the test, and a coulombic efficiency raising from 50 % at the first cycle over 98 % at the steady state. Despite the stability, the specific capacity delivered by LNCAM1000_12h in the 2.5 – 4.4 V voltage range barely exceeds 1/3 of the theoretical value (298 mAh g^{-1}), which may possibly limit its practical application in fields in which high energy density is requested [69,70]. The cycling tests performed by using the wider voltage ranges of 2.5 – 4.8 V (Figure 3c, d) and 2.5 – 4.9 V (Figure 3e, f) show during the first cycle (insets in Figure 3c and e, respectively) irreversible oxidation process leading to charge capacity values of 397 mAh g^{-1} at 4.8 V (Figure 3c) and 370 mAh g^{-1} at 4.9 V (Figure 3e), reflected into respective discharge capacities of 146 mAh g^{-1} and 148 mAh g^{-1} ; this behavior confirms the irreversibility evidenced in CV profiles (see Figure 2a). The slightly higher capacity observed at the first cycle charging process in the 2.5 – 4.8 V voltage range (397 mAh g^{-1}) in comparison with the 2.5 – 4.9 V voltage range (370 mAh g^{-1}) is related to the irreversible oxidation process ascribed to electrolyte with partial oxygen loss from cathode [63]. This process may be also affected by the amount of the active material in the electrode, particularly affecting the electrolyte oxidation, which may slightly differ in the various samples taken into account. In spite of the excessive side oxidation capacity observed during the first cycle, the cells of Figure 3c and e surprisingly exhibit the typical sloping profiles centered at 3.9 V, a discharge capacity approaching 150 mAh g^{-1} , and a well improved reversibility during the subsequent cycles. On the other hand, the increase of the charge cutoff from 4.8 V to 4.9 V clearly affects the capacity decay of the cell as evidenced by the cycling trends reported in Figure 3d and f,

respectively. This behavior may be related to charge compensation of the irreversible oxygen loss and possible Ni reduction process at the first cycle accompanied by hysteresis [16]. Indeed, the cell cycled between 2.5 V and 4.8 V shows a capacity retention of 83 % and a coulombic efficiency that increases from 37 % to about 98 %, while the cell tested between 2.5 and 4.9 V reveals a retention of 77 % and initial coulombic efficiency of 40 % raising to 98 % at the end of the test. Considering the comparable delivered capacity and the better retention achieved by adopting the 2.5 – 4.8 V voltage range compared to 2.5 – 4.9 V, the former is considered a suitable compromise to achieve satisfactory energy and stability which are key factors for the successful application of the layered oxide cathode in lithium-ion batteries [39]. In addition, the relevant side oxidation of the first cycle (efficiency ~ 40%) which typically represents a severe issue for battery application may be exploited to compensate the typical irreversibility affecting the Li-alloy materials as will be demonstrated hereafter. It is worth mentioning that the LNCAM1000_12h delivers a capacity ranging from 110 to 150 mAh g⁻¹, depending on the voltage cutoff, which is actually lower than the one delivered by commercial NMC (typically of about 190 mAh g⁻¹). The lower capacity value is ascribed to the inert Al used for stabilizing the P3-type structure [25], and the Jahn-Teller distortion ascribed to the high amount of manganese instead of Co in the electrode formulation [71]. Despite the lower capacity, the substitution of the toxic and expensive Co with Al and Mn leads to notable reduction of the economical and environmental impact of the electrode.

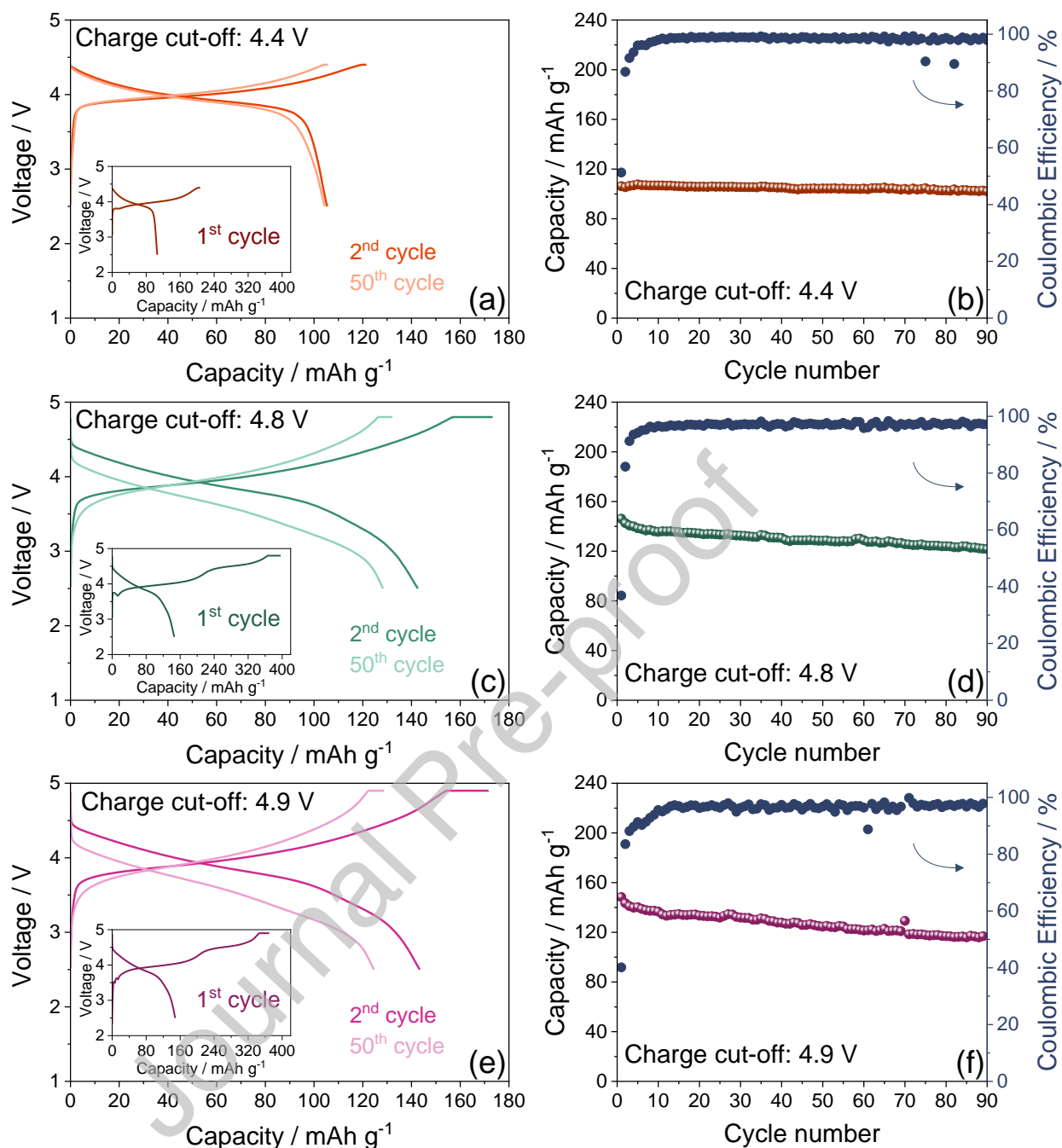


Figure 3. Galvanostatic cycling performances of the Li|EC:DMC 1:1 v/v 1M LiPF₆|LNCAM1000_12h cell at the constant current rate of C/20 (1C = 298 mA g⁻¹) in terms of (a, c, e) voltage profiles of (insets show first cycle) and (b, d, f) discharge capacity trend reporting coulombic efficiency on left y-axes. Voltage ranges: (a, b) 2.5 – 4.4 V, (c, d) 2.5 – 4.8 V, and (e, f) 2.5 – 4.9 V. Measurements performed employing an additional constant voltage step at either 4.4 V, 4.8 V, or 4.9 V, respectively, held until a current value of ¼ of the nominal C-rate is reached (CCCV mode). Room temperature (25 °C). See the Experimental section for sample's acronym.

Prior to further testing in cell, the effects on the layered structure of the severe irreversibility affecting of the LNCAM1000_12h at high voltage are investigated by performing *ex-situ* XRD on electrodes retrieved from lithium cells after 1 and 2 cycles at C/20 between 2.5 and 4.9 V. Figure 4 displays the comparison between the XRD of pristine and cycled LNCAM1000_12h electrodes in the 10 – 60° range (Figure 4a), and provides additional focus of the (003) plane in 17 – 20° 2 θ region (Figure 4b) and the (104) reflection between 43° and 46° (Figure 4c). Figure 4a confirms the retention of the layered structures in the cycled electrodes (*R-3m* space group, table n. 166 [25]) which show the same diffraction peaks, along with a broad and weak signal extending from about 15° to 30° ascribed to the conducting carbon fraction in the electrode composition (see Experimental section). This experimental result justifies the evolution of the typical (de)intercalation profile of the layered cathode even upon the first cycle irreversibility as well as the relevant cell stability. Interestingly, the magnification of the 17 – 20° 2 θ region in Figure 4b reveals the shift of the (003) plane from 18.68° at the pristine condition to 18.54° after 1 charge/discharge cycle and then to 18.74° after 2 cycles in lithium cell (see peak indexing in Figure S2 in Supplementary Material). A similar trend can be observed for the (104) reflection in the magnified 43 – 46° 2 θ region in Figure 4c, which moves from 44.58° at the pristine state to 44.50° and to 44.70° upon 1 and 2 cycles, respectively. The shift of the (003) and (104) reflections well support the above mentioned structural variation for the LNCAM1000_12h material upon cycling in lithium with possible partial oxygen loss and aluminum insertion defective sites [25,70,72]. However, a contribution to the cell irreversible capacity of the side reaction with the electrolyte leading to the SEI layer formation at the electrode/electrolyte interphase cannot be neglected [73].

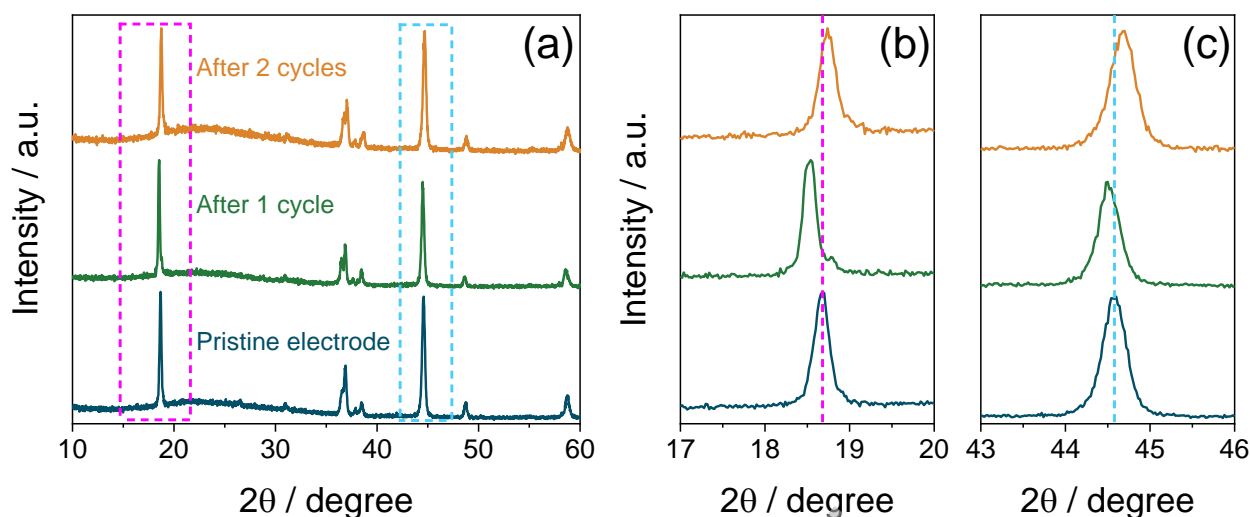


Figure 4. (a) XRD patterns of the LNCAM1000_12h electrode at the pristine state and after 1 and 2 charge/discharge cycles in lithium cell at the constant current rate of $C/20$ ($1C = 298 \text{ mA g}^{-1}$) between 2.5 and 4.9 V, with an additional constant voltage step at 4.9 V held until a current value of $1/4$ of the nominal C-rate is reached (CCCV mode). (b, c) Magnification of the (b) $17 - 20^\circ$ and (c) $43 - 46^\circ$ 2θ regions. See Experimental section for the samples' acronyms.

The cycling performance of the LNCAM1000_12h at higher current rates is also evaluated by additional galvanostatic charge/discharge measurements within the optimal 2.5 – 4.8 V voltage range. Figure S4 in the Supplementary Material shows a preliminary test performed on a Li|LNCAM1000_12h cell at C-rate increasing from $C/10$ to $C/8$, $C/5$, $C/3$ and $1C$. Selected voltage profiles from the above test (Figure S4a) display the single-step charge/discharge reversible process already observed in Figure 4, with increasing polarization from $C/10$ to $1C$ as expected by the ohmic drop promoted by the current increase. The corresponding cycling trend in Figure S4b reveals an initial discharge capacity of 134 mAh g^{-1} at $C/10$ which stabilizes at 117 mAh g^{-1} after 5 cycles, and values of 109, 96, 80 and 46 mAh g^{-1} at $C/8$, $C/5$, $C/3$ and $1C$, respectively. Lowering back the C-rate to $C/10$ after 25 cycles leads to a capacity of about 110 mAh g^{-1} , that is, the 82 % of the initial value, which suggests a moderate stability of the LNCAM1000_12h upon the stress triggered by the progressive raise of the current [53]. Prolonged galvanostatic cycling tests are reported in Figure 5 to determine the cycle life of the LNCAM1000_12h material at constant C-

rates of C/10 (Figure 5a, b) and C/5 (Figure 5c, d). Both cells show the expected irreversible double-plateau during charge at the first cycle (insets in Figure 5a and c), and exclusively the reversible Li^+ (de)intercalation in the subsequent cycles (Figure 5a, c) with more remarkable slope compared to the tests at C/20 (see Figure 3), due to the higher currents [74]. Maximum discharge capacities of 137 mAh g^{-1} and 129 mAh g^{-1} are respectively achieved at C/10 (Figure 5b) and C/5 (Figure 5d), retained over 73 % and 66 % after 100 cycles. As observed previously, low coulombic efficiency of about 50 % is achieved both at C/10 and C/5 during the first cycle, which subsequently increases and reach values of 98 % and 99%, respectively, at the end of the test. The promising performance exhibited by the LNCAM1000_12h cathode may be possibly improved upon optimization of the synthesis process in order to enhance the stability of the layered structure, mitigate the irreversible oxidation process, and limit the capacity decay.

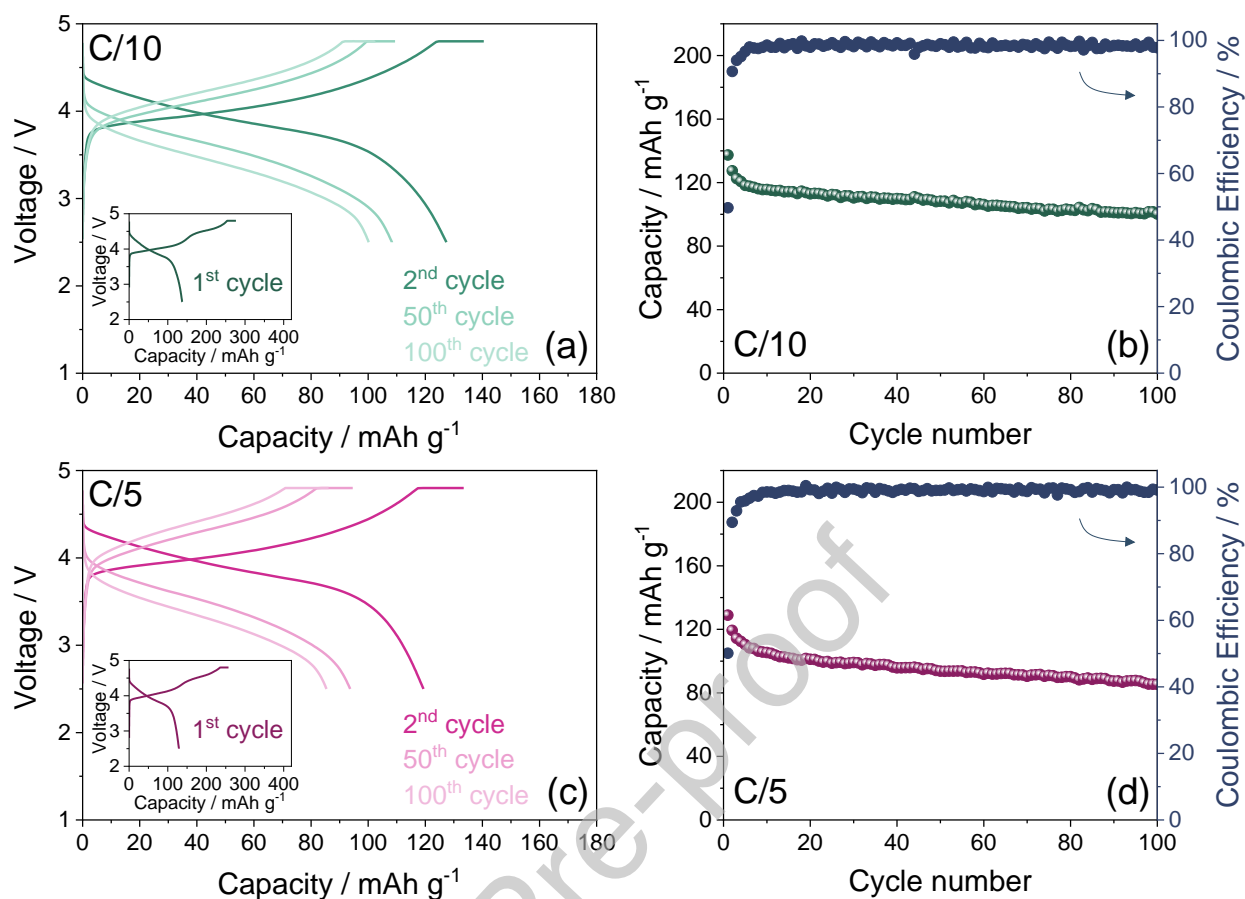


Figure 5. Galvanostatic cycling performances of the Li|EC:DMC 1:1 v/v 1M LiPF₆|LNCAM1000_12h cell at the constant current rate of (a, b) C/10 and (c, d) C/5, (1C = 298 mA g⁻¹) in terms of (a, c,) voltage profiles (insets show first cycle) and (b, d,) discharge capacity trend reporting coulombic efficiency on left y-axes. Voltage range: 2.5 – 4.8 V. Measurements performed with an additional constant voltage step at 4.8 V held until a current value of ¼ of the nominal C-rate was reached (CCCV mode). Room temperature (25 °C). See the Experimental section for the sample's acronym.

As previously mentioned, the initial relevant irreversibility of the cathode can be potentially exploited to compensate similar side processes occurring during the first discharge of lithium-alloying anodes such as silicon or tin, which are typically promoted by excessive volume changes, electrolyte reduction, and partial lithiation of the electrode matrix [75]. Indeed, pre-activation processes including direct contact with lithium metal (chemical strategy [30]) and/or preliminary cycling in lithium half-cell (electrochemical strategy [44]) are usually necessary prior to the

application of the Li-alloying anodes in full Li-ion cell, in order to prevent parasitic reactions that would compromise the anode/cathode balancing. However, these efficient pre-activation procedures are still within a R&D stage which is mainly adopted for laboratory prototype cells [43,76,77]. Herein we avoid additional processes and directly combine a silicon oxide anode coated by 70 % (w:w) of carbon, as indicated by TGA in Figure S5 in the Supplementary Material [27], with the developed layered cathode in a full Li-ion cell by advantageously tuning the negative to positive (N/P) ratio estimated from the respective irreversible capacity. The N/P ratios were calculated taking into account mass loadings and specific capacities of the two electrodes at the first charge of a full-cell including the irreversible part, that is, 300 mAh g⁻¹ for first cathode de-lithiation and 810 mAh g⁻¹ for first anode lithiation (see Experimental Section for further details). As reported in Figure 6, a higher cathode content doesn't lead to lithium deposition, which is instead expected at much lower potential. Rather, the excess of cathode causes the irreversible electrolyte reduction at the anode side during the first cycle of the full cell with formation of a stable SEI, and holds the alloying material at sufficiently low potential to allow battery operation during the subsequent cycles. Figure 6 depicts the electrochemical behavior of two SiO_x-C|LNCAM1000_12h full-cells cycled at the constant current of C/10 as referred to the cathode (1C = 298 mA g_{cathode}⁻¹) using N/P ratio of either 0.98 or 0.84. The cell response is reported in terms of the voltage trend *vs.* time of the full-cells (Figure 6a and b for N/P of 0.98 and 0.84, respectively) as well as of the signals of the cathode (Figure 6c and d) and the anode (Figure 6e and f), which are concomitantly recorded using a lithium reference electrode (see Experimental section). The measurement clearly exhibits for the SiO_x-C|LNCAM1000_12h full-cells (Figure 6a, b) voltage profiles reflecting the combination of the respective cathode (Figure 6c, e) and anode (Figure 6d, f) signatures, and suggests a reciprocal compensation of irreversible capacities during the first charge, thus leading to a subsequent discharge fully in line with the one related to the Li|LNCAM1000_12h half-cell (compare voltage profiles of Figure 6c, d with insets of Figure 5a, c). Furthermore, the cathode side shows initial discharge capacity and cutoff remarkably depending on the N/P ratio with values of ~100 mAh g⁻¹

and ~ 3.7 in the cell using N/P of 0.98 (Figure 6c), and ~ 115 mAh g⁻¹ at ~ 3.5 V in the one using N/P of 0.84 (Figure 6d). The charge/discharge profiles of the full-cell with N/P ratio of 0.98 (Figure 6a) display more pronounced alteration. In fact, the working voltage of the electrodes is increased upon cycling more than the cell with N/P of 0.84 (Figure 6b). This difference suggests a better reciprocal compensation of the irreversible capacity ascribed to LNCAM1000_12h (Figure 6d) and SiO_x-C (Figure 6f) through N/P of 0.84 compared to 0.98 (Figure 6c, e, respectively). In detail, the LNCAM1000_12h cathode in the cell with N/P = 0.98 (Figure 6c) delivers irreversible charge capacity of 338 mAh g⁻¹ (1.12 mAh) at a final voltage cutoff of 4.971 V, while the cathode in the cell with N/P = 0.84 (Figure 6d) displays a first charge capacity of 299 mAh g⁻¹ (0.95 mAh) at 4.858 V cutoff. The respective SiO_x-C discharge capacities and voltage cutoff in the full-cell are of 933 mAh g⁻¹ (1.12 mAh) at 0.170 V (N/P = 0.98, Figure 6e) and 960 mAh g⁻¹ (0.95 mAh) at 0.056 V (N/P = 0.84, Figure 6f). Thus, as mentioned before, the results reveal that the use of a N/P ratio of 0.98 is insufficient to allow the anode a full Li-alloying process during first charge of the corresponding Li-ion cell with consequent low utilization of SiO_x-C indicated by the relatively high final reduction voltage (i.e., 0.170 V). Instead, the lower anode content achieved by setting up a N/P of 0.84 increases the utilized fraction of the alloying material as indeed evidenced by the final voltage cutoff of the SiO_x-C (i.e., 0.056 V) achieved by full-cell charge. As already mentioned, the first discharge of the full-cell further supports the improvement achieved by setting up a N/P of 0.84 which leads to capacity of 113 mAh g⁻¹ at 3.534 V cutoff for LNCAM1000_12h (Figure 6d) and 364 mAh g⁻¹ at 2.009 V for SiO_x-C (Figure 6f) with respect to 97 mAh g⁻¹ at 3.681 V and 275 mAh g⁻¹ at 2.163 V, respectively, related to N/P of 0.98 (Figure 6 c, e).

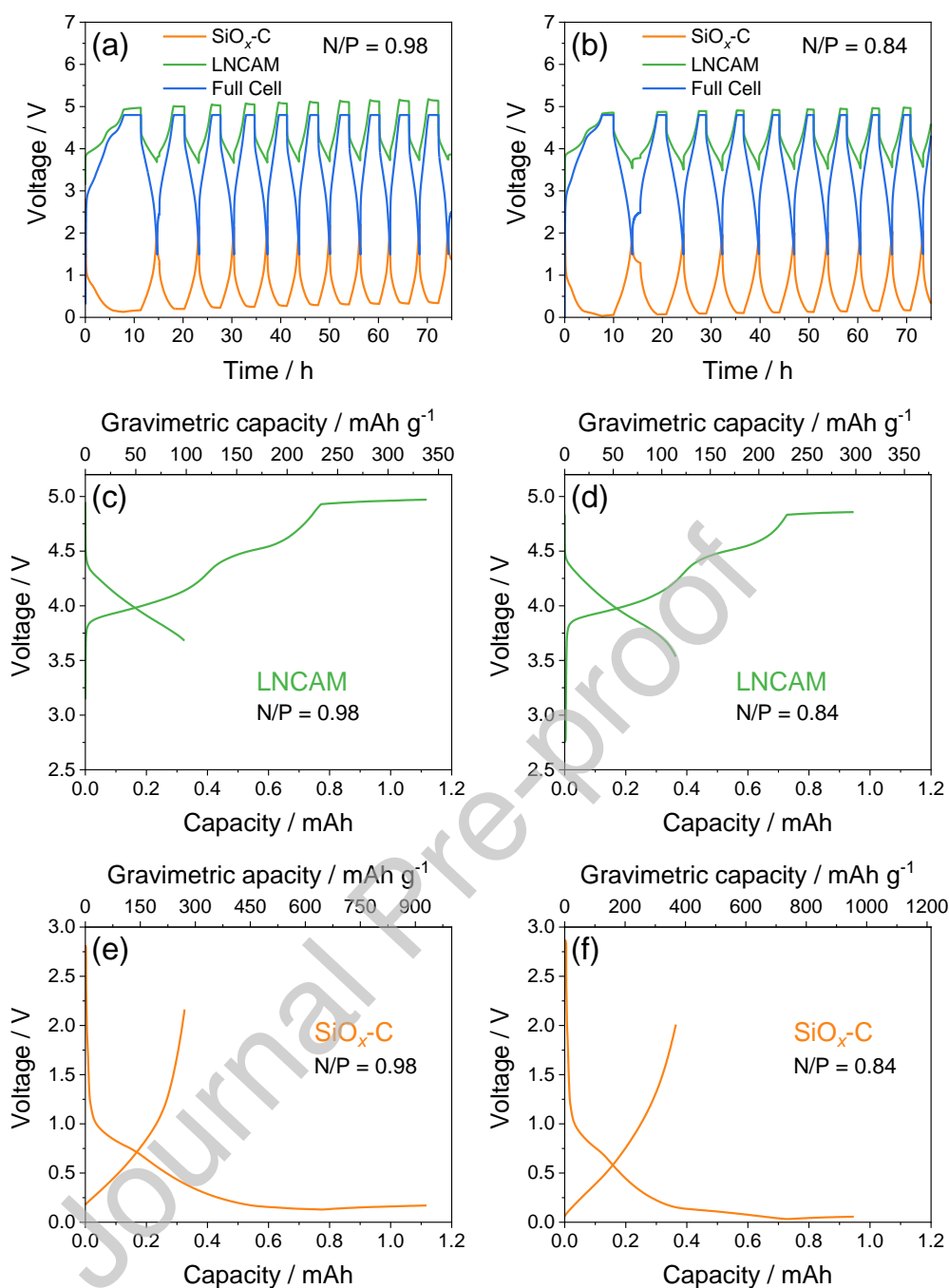


Figure 6. (a, b) Time evolution of the SiO_x-C anodes and the LNCAM1000_12h cathodes voltage concomitantly collected by using a Li reference and of the corresponding SiO_x-C|EC:DMC 1:1 v/v 1M LiPF₆|LNCAM1000_12h full-cells cycled at C/10 (1C = 298 mA g⁻¹) with N/P ratio of either (a) 0.98 or (b) 0.84; panels (c-f) show the first cycle in terms of voltage vs. capacity (mAh, bottom x-axes) and gravimetric capacity (mAh g⁻¹, top x-axes) related to (c, d) LNCAM1000_12h cathodes and (e, f) SiO_x-C anodes in the full-cells with N/P ratio of either (c, e) 0.98 or (d, f) 0.84. Voltage range: 1.5 – 4.8 V. Measurements performed with an additional constant voltage step at 4.8 V held until a current value of ¼ of the nominal C-rate was reached (CCCV mode). Room temperature (25 °C). See the Experimental section for the sample's acronym.

Figure 7 reports the cycling behavior of the above full $\text{SiO}_x\text{-C|LNCAM1000}_{12\text{h}}$ cells in terms of gravimetric capacity, calculated with respect to the active cathode mass (see Experimental section for details), delivered at C/10 with N/P ratio of either 0.98 (Figure 7a, c) or 0.84 (Figure 7b, d). The voltage profiles related to the cell with N/P = 0.98 (Figure 7a) show a higher irreversible charge capacity at the first cycle compared to the cell with N/P = 0.84 (Figure 7b), that is, 279 mAh g^{-1} and 258 mAh g^{-1} , respectively, reflected in subsequent discharge capacity of 99 mAh g^{-1} and 115 mAh g^{-1} and corresponding coulombic efficiency of 35% and 44%. Moreover, the cell with N/P ratio of 0.98 shows a more relevant capacity loss with a value of 60 mAh g^{-1} upon 10 cycles and lower final coulombic efficiency of 76 % compared to the cell with N/P ratio of 0.84 that has a capacity of 73 mAh g^{-1} and coulombic efficiency of 87 % at the end of the test. The voltage profiles displayed in Figure 7a show a polarization resulting from the combination of the slopping behavior of anode and cathode, as already mentioned in Figure 6, thus suggesting an effective reciprocal compensation of the irreversible capacity at the first cycle despite a further effort may be required to fully optimize the cell. These data confirm once more a better utilization of LNCAM1000_{12h} and $\text{SiO}_x\text{-C}$ by setting up a N/P of 0.84 in agreement with the performance of the single electrodes discussed in Figure 6. To further investigate the cycling behavior of the $\text{SiO}_x\text{-C|LNCAM1000}_{12\text{h}}$ system, a coin-type full cell with N/P of 0.91 was tested and the results are shown in Figure S6 in the Supplementary Material. The cell shows high irreversible charge capacity at the first cycle, that is 294 mAh g^{-1} , and discharge capacity of 104 mAh g^{-1} , with corresponding coulombic efficiency of 35%. Subsequently, the cell delivers a capacity of about 80 mAh g^{-1} during the initial cycling stages, which stabilizes at about 70 mAh g^{-1} after 20 cycles retained until the end of the test, with a coulombic efficiency approaching 85%. Therefore, the excess of the cathode in the $\text{SiO}_x\text{-C|LNCAM1000}_{12\text{h}}$ cell may represent a viable strategy to improve the cycling behavior, as demonstrate by the results discussed in Figure 6. In fact the cell with a N/P ratio of 0.91 delivers capacity and efficiency values close to the ones obtained for the cell with N/P with 0.84 (Figure 7b, d). These data suggest the need of further optimization of the electrode balancing to achieve a

higher capacity [57]. Moreover, a capacity retention of about 70% after 50 charge/discharge cycles could represent a promising result in terms of stability of the cell, despite enhanced synthesis pathway for the LNCAM material and further optimization of the cell can lead to performance of practical interest [33,57,78].

On the other hand we focus herein on a proof-of-concept Li-ion battery combining electrode materials without any pre-treatment or activation process to overcome one the main critical issues that avoids the large scale diffusion of these appealing energy storage systems.

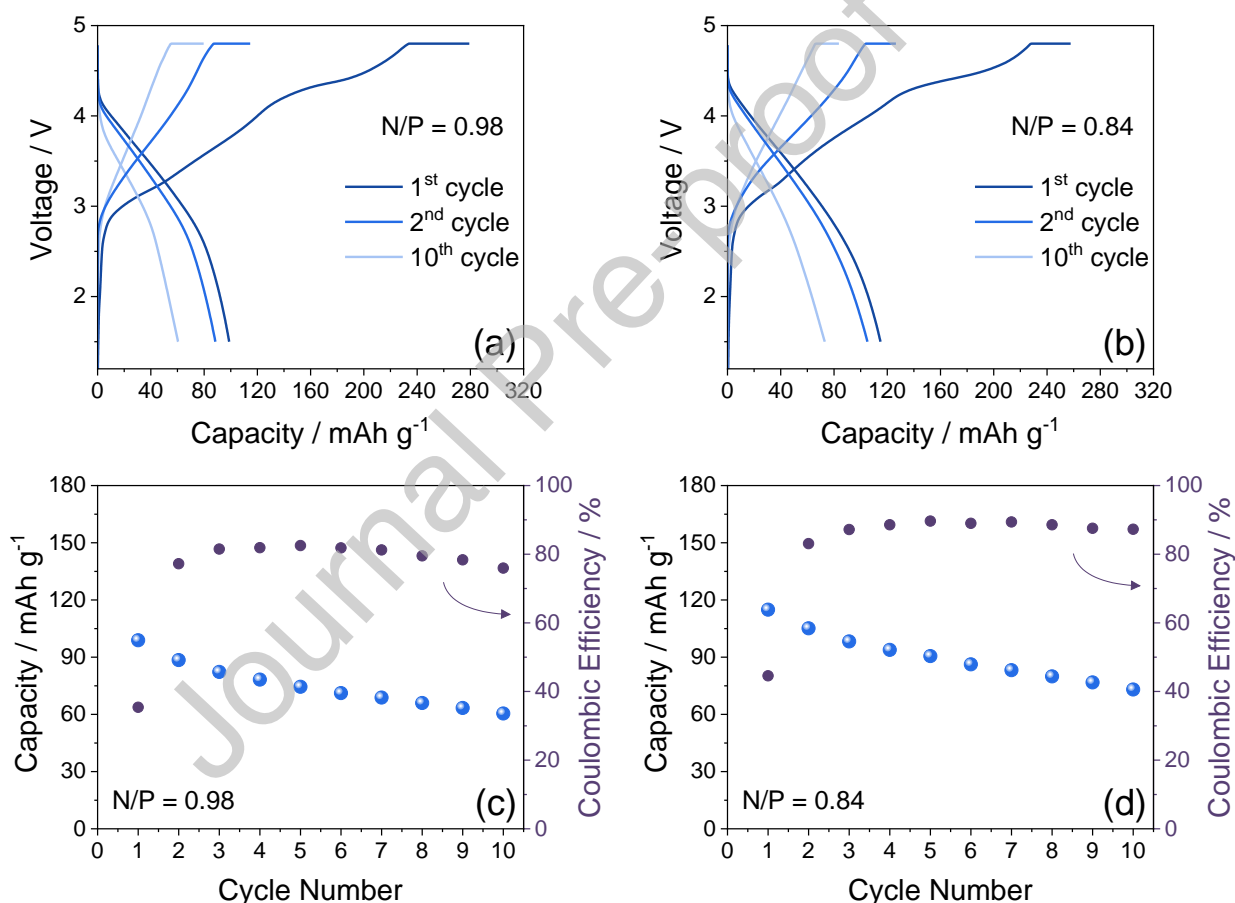


Figure 7. (a, b) Voltage profiles and (c, d) capacity trends (right y-axes show coulombic efficiency) of the SiO_x-C|EC:DMC 1:1 v/v 1M LiPF₆|LNCAM1000_12h full-cells with N/P ratio of either (a, c) 0.98 or (b, d) 0.84 cycled at the constant current rate of C/10 (1C = 298 mA g⁻¹). Cells assembled with a Li reference electrode. Voltage range: 1.5 – 4.8 V. Measurements performed with an additional constant voltage step at 4.8 V held until a current value of ¼ of the nominal C-rate was

reached (CCCV mode). Room temperature (25 °C). See the Experimental section for the sample's acronym.

With the aim of further investigating the effects of the selected N/P ratio, a detailed study of the electrode/electrolyte interphase is performed on the $\text{SiO}_x\text{-C|LNCAM1000}_\text{12h}$ cells by carrying out EIS at OCV and at full discharged states after 1 and 10 galvanostatic cycles, as reported in Figure 8. The use of an additional lithium reference electrode in the cells allows the study of three different sides of each cell, that is, $\text{SiO}_x\text{-C vs. Li}$ (Figure 8a, b), $\text{LNCAM1000}_\text{12h vs. Li}$ (Figure 8c, d) and $\text{SiO}_x\text{-C vs. LNCAM1000}_\text{12h}$ (Figure 8e, f) at OCV condition as well as after 1, 5 and 10 charge/discharge cycles. The NLLS analyses performed on the Nyquist plots of Figure 8 displayed in Table 4 reveal that all the considered systems can be generally represented by the $R_e(R_iQ_i)Q$ circuit, where R_e is the electrolyte resistance, R_i and Q_i account for the electrode/electrolyte interphase, and Q is a constant phase element that may refer to the cell geometric capacitance or to the Warburg-type Li^+ ions diffusion, depending on the system taken into account [48,49]. It is worth mentioning that Table 4 reports the overall resistance (R_e+R_i) instead of the single values to avoid differences ascribed to the cell geometry in the various configurations, in particular those referring to the third Li electrode. In fact, the latter T-setup involves a larger amount of electrolyte and typically higher resistances compared to a Li-ion cell closely stacking the $\text{SiO}_x\text{-C}$ anode and the $\text{LNCAM1000}_\text{12h}$ cathode (see experimental section for details). Indeed, the full-cell with N/P ratio of 0.98 exhibits a resistance value referred to the $\text{SiO}_x\text{-C/Li}$ system (Figure 8a) around 458 Ω at the OCV condition, that greatly increases to 8259 Ω upon 10 cycles (inset of Figure 8a). A similar trend is observed for the $\text{LNCAM1000}_\text{12h/Li}$ system of the same cell (Figure 8c) with initial resistance of 399 Ω , that reaches after 10 cycles a value of 7246 Ω (inset of Figure 8c). On the other hand, the full-cell assembled with $\text{N/P} = 0.84$ presents at the OCV condition a resistance of 268 Ω for $\text{SiO}_x\text{-C/Li}$ system (Figure 8b) and 345 Ω for $\text{LNCAM1000}_\text{12h/Li}$ (Figure 8d) that increase after 10 cycles to 5467 Ω (inset of Figure 8b) and 8282 Ω (inset of Figure 8d). Hence, the cell with N/P of 0.84 shows a much lower increase of the anodic side resistance compared to the

cell with N/P of 0.98, and a slightly higher increase of the cathodic side value by cycling, thus suggesting a less remarkable degradation of the $\text{SiO}_x\text{-C}$ anode interphase in the former cell compared to the latter, and a substantial similarity of the LNCAM1000_12h cathode interphase. On the other hand, the $\text{SiO}_x\text{-C/LNCAM1000_12h}$ cell with N/P = 0.98 (Figure 8e) and N/P = 0.84 (Figure 8f) display resistance values two order of magnitude lower compared to the corresponding ones referring to the third Li electrode due to the above mentioned geometry differences. Despite the similarity, the full-cell with N/P ratio of 0.98 reveals slightly higher resistances compared to the one with N/P of 0.84, with values increasing from 8.3 Ω at the OCV to 13.7 Ω in the former and from 7.5 Ω at the OCV to 12.2 Ω in the latter, which is in line with the combined trend of the corresponding electrodes detected referred to the lithium. Hence, the study of the $\text{SiO}_x\text{-C}$ or LNCAM1000_12h electrodes using the Li reference gives additional insights on the electrode/electrolyte interphases of cathode and anode which are not fully revealed by considering the combination of the two materials in a full Li-ion cell. In general the NLLS analyses suggest that the rapid capacity decay observed in Figure 7a for the full-cell using N/P ratio of 0.98 is mainly related with the excessive increase of the $\text{SiO}_x\text{-C}$ interphase resistance possibly due to the electrolyte degradation promoted by the voltage change during operation [79]. Instead, the full-cell with N/P ratio of 0.84 allows a limited increase of the $\text{SiO}_x\text{-C}$ interphase resistance, despite the limited increase of the value ascribed to the LNCAM1000_12h cathode which appears to have less effect on the cell decay. Interestingly, the two Li-ion cells have similar resistance values, whilst substantial differences between the anode and cathode detected by the Li reference which suggest a controlling role of the anode, and a better electrode/electrolyte interphase using N/P of 0.84 reflected into a better cycling performance [80].

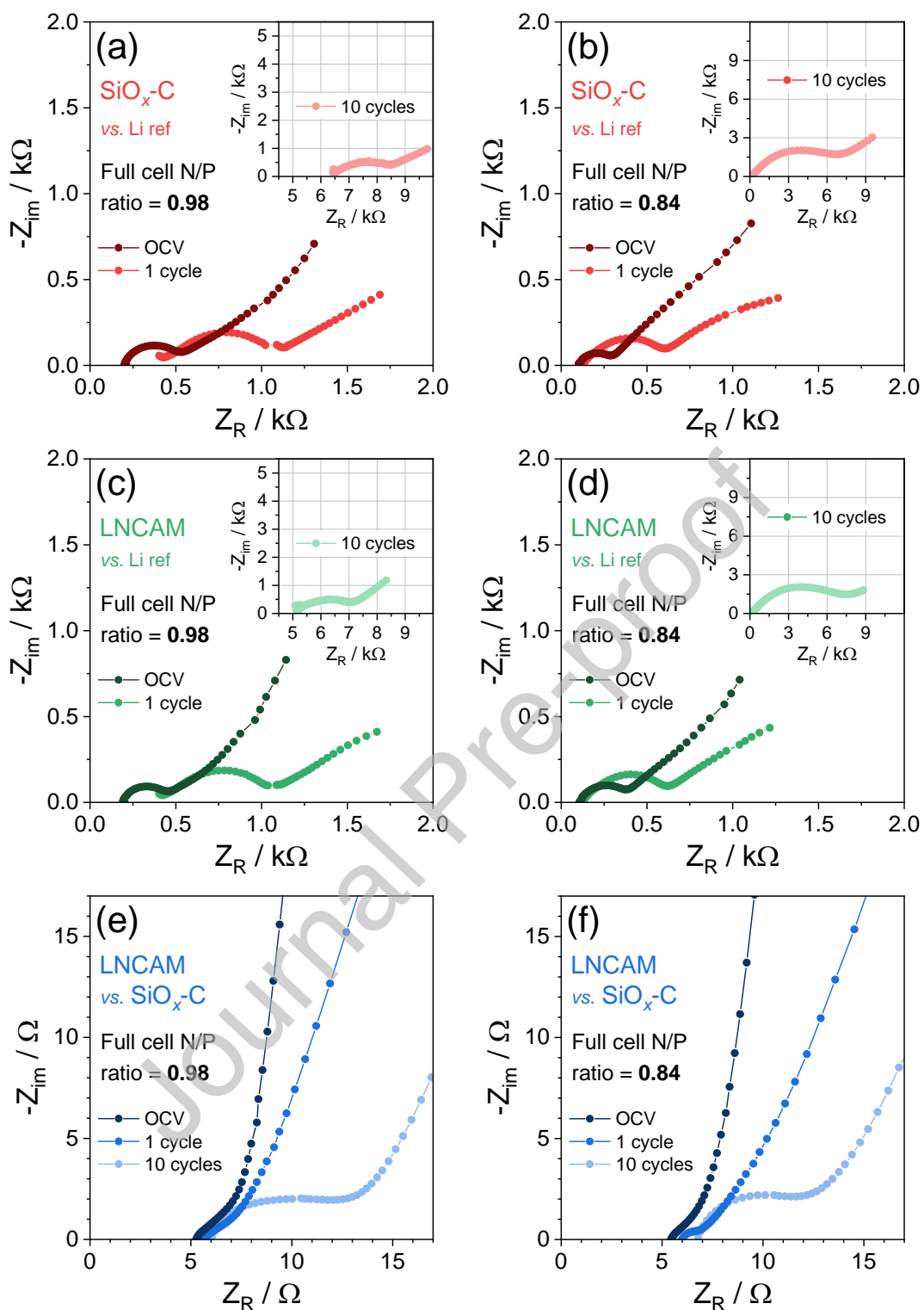


Figure 8. EIS measurements performed on $\text{SiO}_x\text{-C}|\text{EC:DMC 1:1 v/v 1M LiPF}_6|\text{LNCAM1000}_{12\text{h}}$ full-cells. In detail: Nyquist plots related to the (a, b) $\text{SiO}_x\text{-C}$ anode and (c, d) LNCAM1000_{12h} cathode collected concomitantly by using a Li reference electrode in (e, f) full-cells with N/P ratio of either (a, c, e) 0.98 or (b, d, f) 0.84; EIS carried out at the OCV of the cells and after 1 and 10

(insets) galvanostatic cycles depicted in Figure 6; frequency range 500 kHz – 100 mHz; alternate voltage signal: 30 mV. See the Experimental section for the sample's acronym.

Table 4: NLLS analysis of the Nyquist plots reported in Figure 8 recorded by performing EIS on $\text{SiO}_x\text{-C|LNCAM1000_12h}$ full-cells using a lithium reference and N/P ratio of either 0.98 or 0.84. The measurements were performed on three different sides of each cell, that is, $\text{SiO}_x\text{-C}$ vs. Li reference, LNCAM1000_12h vs. Li reference and $\text{SiO}_x\text{-C}$ vs. LNCAM1000_12h. NLLS analyses were performed through a Boukamp software and only fits with a χ^2 value of the order of 10^{-4} or lower were considered suitable [48,49]. See Experimental section for acronyms.

N/P ratio	Considered system	Cell condition	Circuit	$R_e + R_i$ [Ω]	χ^2
0.98	$\text{SiO}_x\text{-C}$ vs. Li reference	OCV	$R_e(R_iQ_i)Q$	458 ± 4	3×10^{-5}
		1 cycle	$R_e(R_iQ_i)Q$	1103 ± 22	3×10^{-4}
		10 cycles	$R_e(R_iQ_i)Q$	8259 ± 101	1×10^{-5}
	LNCAM1000_12h vs. Li reference	OCV	$R_e(R_iQ_i)Q$	399 ± 8	2×10^{-4}
		1 cycle	$R_e(R_iQ_i)Q$	1044 ± 14	1×10^{-4}
		10 cycles	$R_e(R_iQ_i)Q$	7246 ± 57	1×10^{-5}
	LNCAM1000_12h vs. $\text{SiO}_x\text{-C}$	OCV	$R_e(R_iQ_i)Q$	8.3 ± 0.2	4×10^{-5}
		1 cycle	$R_e(R_iQ_i)Q$	8.5 ± 0.3	3×10^{-5}
		10 cycles	$R_e(R_iQ_i)Q$	13.7 ± 0.3	2×10^{-4}
0.84	$\text{SiO}_x\text{-C}$ vs. Li reference	OCV	$R_e(R_iQ_i)Q$	268 ± 4	2×10^{-4}
		1 cycle	$R_e(R_iQ_i)Q$	594 ± 15	3×10^{-4}
		10 cycles	$R_e(R_iQ_i)Q$	5467 ± 150	1×10^{-4}
	LNCAM1000_12h vs. Li reference	OCV	$R_e(R_iQ_i)Q$	345 ± 5	1×10^{-4}
		1 cycle	$R_e(R_iQ_i)Q$	582 ± 14	4×10^{-4}
		10 cycles	$R_e(R_iQ_i)Q$	8282 ± 74	2×10^{-4}
	LNCAM1000_12h vs. $\text{SiO}_x\text{-C}$	OCV	$R_e(R_iQ_i)Q$	7.5 ± 0.2	4×10^{-5}
		1 cycle	$R_e(R_iQ_i)Q$	6.7 ± 0.1	4×10^{-5}
		10 cycles	$R_e(R_iQ_i)Q$	12.2 ± 0.3	2×10^{-4}

4. Conclusions

We reported herein the synthesis and characterization of a $\text{LiNi}_{0.2}\text{Co}_{0.2}\text{Al}_{0.1}\text{Mn}_{0.45}\text{O}_2$ layered oxide cathode material as well as its application in a Li-ion cell using a $\text{SiO}_x\text{-C}$ alloying anode without any pre-activation processes. SEM performed on the cathode revealed stacked submicrometric flakes forming layered micrometric particles, while EDS images suggested homogeneous distribution of the elements and a stoichiometry close to the expected one. XRD refinement confirmed the formation of the P3-type layered structure with trigonal cell unit (hexagonal $R\bar{3}m$ space group, table n. 166), supported by Raman spectroscopy that showed the corresponding M–O bonds vibration. The investigation of the electrochemical process in lithium half-cell by CV revealed an irreversible oxidation process during the first cycle centered at 4.6 V vs. Li^+/Li due to structural rearrangement with partial oxygen loss and SEI formation upon electrolyte oxidation. The subsequent voltammetry cycles indicated the exclusive presence of the single-step reversible Li^+ (de)intercalation process occurring between 3.7 and 3.9 V vs. Li^+/Li with low polarization. EIS measurements carried out upon CV suggested the formation of a suitable electrode/electrolyte interphase with resistance value decreasing from 32 Ω at the OCV condition to 16 Ω at the end of the test. Galvanostatic cycling performed in lithium half-cells using the layered cathode at the constant current rate of C/20 ($1\text{C} = 298 \text{ mA g}^{-1}$) indicated the 2.5 – 4.8 V voltage range as the most adequate operative condition to achieve fair compromise between delivered capacity (150 mAh g^{-1}), retention (83 % at the end of the test) and coulombic efficiency (98% upon initial cycles). The effect of the cycling tests on the layered structure was investigated by *ex-situ* XRD upon charge/discharge cycles at C/20 in lithium half-cell. The diffractograms revealed the shift of the (003) and (104) main reflections related to the LNCAM structure to lower 2θ upon 1 cycle and to higher angles after 2 cycles due to the occurring of the structural modifications already suggested by CV. Additional charge/discharge tests in half-cell at the constant rates of C/10 and C/5 between 2.5 and 4.8 V, performed to evaluate the cycling behavior of the cathode at higher current, revealed

a capacity of 137 mAh g^{-1} retained at the 73 % at C/10 and respective values of 129 mAh g^{-1} and 66 % at C/5. The $\text{LiNi}_{0.2}\text{Co}_{0.2}\text{Al}_{0.1}\text{Mn}_{0.45}\text{O}_2$ cathode has been subsequently coupled with the $\text{SiO}_x\text{-C}$ alloying anode in proof-of-concept Li-ion cells without any pre-activation process. The cells exploited a N/P ratio of either 0.98 or 0.84, tuned by taking into account the characteristic initial irreversibility affecting both the layered cathode and the silicon oxide anode. Galvanostatic cycling tests performed on the full-cell at the constant current of C/10 ($1C = 298 \text{ mA g}_{\text{cathode}}^{-1}$) have shown excessive degradation during the first charge for the cell with N/P = 0.98, leading to relevant increase of the voltage of both the electrodes and fast capacity decay. On the other hand, the cell using N/P ratio of 0.84 demonstrated a better cycling stability with a maximum delivered capacity of 115 mAh g^{-1} , retention of 63 % and final coulombic efficiency of 87 %. The use of a third Li reference electrode in the full-cells allowed the EIS investigation of cathode and anode interphases as well as the monitoring of the full-cell behavior. The study indicated a strong influence of the Li-ion cell balancing on the electrode/electrolyte interphase characteristics, and suggested substantial differences between the anode and cathode resistance trends. In particular, the EIS revealed the controlling role of the anode, and a better electrode/electrolyte interphase and cycling performance for the cell using a cathode excess adopting a N/P of 0.84 compared to the one with N/P of 0.98. In summary, the tests demonstrated that the direct combination of the $\text{LiNi}_{0.2}\text{Co}_{0.2}\text{Al}_{0.1}\text{Mn}_{0.45}\text{O}_2$ layered cathode and the $\text{SiO}_x\text{-C}$ alloying anode without additional pre-treatments may be a viable strategy to achieve efficient Li-ion systems, despite a further investigation may be required to determine the optimal N/P ratio.

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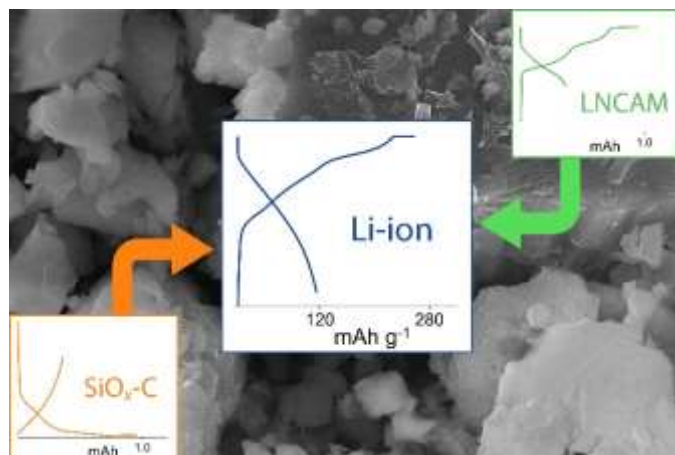
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Table of Content Entry



A layered $\text{LiNi}_{0.2}\text{Co}_{0.2}\text{Al}_{0.1}\text{Mn}_{0.45}\text{O}_2$ cathode is synthesized, fully investigated and combined with a $\text{SiO}_x\text{-C}$ alloying anode in a new Li-ion battery without any pre-activation processes

Credit Author Statement

Luca Minnetti: Investigation, Visualization, Formal analysis, Writing-Original Draft. **Vittorio Marangon:** Investigation, Visualization, Formal analysis, Writing-Original Draft. **Paolo Andreotti:** Investigation, Formal analysis. **Antunes Staffolani:** Investigation, Formal analysis. **Francesco Nobili:** Writing-Review & Editing, Supervision. **Jusef Hassoun:** Conceptualization, Writing-Original Draft, Writing-Review & Editing, Validation, Supervision, Project administration, Funding acquisition.

Declaration of interests

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.

The authors declare the following financial interests/personal relationships which may be considered as

potential competing interests:

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