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[Ahmed Mohamed Ahmed Hashem](#)*, [Rasha Samir El-Tawil](#), [Somia Mohamed Abbas](#),
[Ashraf El-Sayed Abdel-Ghany](#), Luca Bargnesi, [Catia Arbizzani](#), [Alain Mauger](#), [Christian M. Julien](#)

Posted Date: 29 July 2024

doi: 10.20944/preprints202407.2320.v1

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Article

Properties of Co-free Ni-rich $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Fe}_{0.1}\text{O}_2$ as cathode material for lithium-ion batteries

Rasha S. El-Tawil ¹, Somia M. Abbas ¹, Ashraf E. Abdel Ghany ¹, Ahmed M. Hashem ^{1,*}, Luca Bargnesi ², Catia Arbizzani ², Alain Mauger ³ and Christian M. Julien ³

¹ Inorganic Chemistry Department, National Research Center, 33 El Bohouth St., (Former El Tahrir St.), Dokki, Giza, 12622, Egypt; r2samir@yahoo.com (R.S.E.-T.); somiamohamed119@yahoo.com (S.M.A.); achraf_28@yahoo.com (A.E.A.G.)

² Department of Chemistry "Giacomo Ciamician", Alma Mater Studiorum, University of Bologna, via F. Selmi 2, Bologna 40126, Italy; luca.bargnesi2@unibo.it (L.B.); catia.arbizzani@unibo.it (C.A.)

³ Institut de Minéralogie, de Physique des Matériaux et Cosmologie (IMPMC), Sorbonne Université, UMR-CNRS 7590, 4 place Jussieu, 75752, Paris, France; alain.mauger@sorbonne-universite.fr (A.M.); julienchristian@neuf.fr (C.M.J.)

* Correspondence: ahmedh242@yahoo.com

Abstract: This study throws more light on the new Co-free and Ni-rich $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Fe}_{0.1}\text{O}_2$ cathode material for lithium-ion batteries. This cobalt-free cathode material is prepared using a two-step process: the formation of an oxalate precursor by co-precipitation followed by a solid-state reaction with lithium hydroxide and iron citrate. The physico-chemical properties of $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Fe}_{0.1}\text{O}_2$ are characterized using X-ray diffraction, Raman spectroscopy, scanning electron microscopy, thermal gravimetric analysis, and energy dispersive X-ray spectroscopy, respectively. The $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Fe}_{0.1}\text{O}_2$ electrode tested at C/2 rate within voltage window of 3.0–4.4 V *vs.* Li^+/Li delivers a specific capacity of ~80 mAh g⁻¹ and retain about 45% of its initial capacity after 100 cycles.

Keywords: Co-free; Ni-rich cathode; Li-ion batteries; $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Fe}_{0.1}\text{O}_2$

1. Introduction

It is well known that lithium-ion batteries (LIBs) have become the main power sources for long-range electric vehicles (EVs). In these electrochemical devices, the cathode material is the most important, expensive and the heaviest compartment [1–3]. In the Ni-rich $\text{LiNi}_{1-x-y}\text{Mn}_x\text{Co}_y\text{O}_2$ (denoted as NMC) and $\text{LiNi}_{1-x-y}\text{Co}_x\text{Al}_y\text{O}_2$ (denoted as NCA) systems, cobalt is introduced to stabilize the structure, suppress the Li/Ni cation mixing (antisite defect) and improve their thermal stability [4]. However, in the short and medium term, cobalt is thought to pose the greatest material supply chain risk for electric vehicles due to its decreased abundance and geopolitical concerns [5,6]. Since, raw materials make up 50% to 70% of a battery's cost, the battery world is coming to the conclusion that it is necessary to reduce or remove cobalt in cathode materials without scarifying their performance due to societal, economic and security concerns [7,8]. Furthermore, despite the fact that cobalt is generally thought to improve rate performance, some studies have revealed that cobalt is much more harmful than nickel due to chemo-mechanical cracking and irreversible oxygen release at high voltage [9,10]. As a result, low-cobalt or cobalt-free have become a trend in cathode materials. In the search for the ideal booster cathode, an optimal candidate is the class of nickel-rich oxides that includes LiNiO_2 (LNO) exhibiting a high theoretical discharge capacity (~270 mAh g⁻¹) at a high average potential of 3.8 V *vs.* Li^+/Li . However, this cathode material poses serious technical challenges for commercial applications [11,12]. Even after more than twenty years of intensive research, LNO is still difficult to work because of its main drawbacks: (i) the mechanical problems brought on by large volume changes (up to ~7%), (ii) particle cracking, (iii) a variety of phase transitions that occur during cycling, and (iv) the surface instability during the delithiation process [13,14]. For better safety and

high-rate capability concerns, numerous promising strategies have been developed including bulk doping and surface passivation.

Cobalt-free $\text{LiNi}_{1-n}\text{Mn}_n\text{O}_2$ ($M = \text{Al}, \text{Mn}, \text{Mg}, \text{or Co}$) materials have been investigated by Dahn et al. [15], who showed that multiple phase transitions are suppressed throughout the charge and discharge processes when LiNiO_2 is doped with 5% Al, 5% Mn, or 5% Mg cations. The electrochemical characteristics and structural stability of $\text{Li}[\text{Ni}_{0.9}\text{Co}_{0.1}]\text{O}_2$ (NC90), $\text{Li}[\text{Ni}_{0.9}\text{Co}_{0.05}\text{Mn}_{0.05}]\text{O}_2$ (NCM90), and Co-free $\text{Li}[\text{Ni}_{0.9}\text{Mn}_{0.1}]\text{O}_2$ (NM90) of Ni-rich material were thoroughly compared by Sun et al. [16]. Positive opportunities for the development of Ni-rich $\text{LiNi}_{1-x}\text{Mn}_x\text{O}_2$ cathodes were observed since the NM90 cathode maintained a greater cycle stability than the Co-containing cathodes, especially under difficult cycling conditions (at higher cutoff voltage or at elevated temperature). Elmaataouy et al. [7] reported that $\text{LiNi}_{0.8}\text{Fe}_{0.1}\text{Al}_{0.1}\text{O}_2$ (NFA) synthesized by solid-state reaction demonstrates high-yield specific capacities of $\sim 180 \text{ mAh g}^{-1}$ at 0.1C rate, while Xi et al. [17] showed that $\text{LiNi}_{0.8}\text{Fe}_{0.1}\text{Mn}_{0.1}\text{O}_2$ (NFM) can deliver a specific capacity of 202.6 mAh g^{-1} (0.1C, 3.0–4.5 V). Muralidharan et al. [18] revealed that the cobalt-free material $\text{LiNi}_{0.85}\text{Fe}_{0.052}\text{Al}_{0.091}\text{O}_2$ delivers high capacity of 190 mAh g^{-1} at 0.1C. In a review article, Li et al. [19] presented the phase transition mechanism of Co-free Ni-rich cathode materials, the existing problems, and the state-of-the-art characterization tools employed to study the phase transition. The causes of crystal structure degradation, interfacial instability, and mechanical degradation are elaborated, from the material's crystal structure to its phase transition and atomic orbital splitting. Ni et al. [20] reported that single-crystalline, Co-free, Ni-rich $\text{LiNi}_{0.95}\text{Mn}_{0.05}\text{O}_2$ (NM95) cathode, successfully designed using a molten salt-assisted method, exhibits structural stability and cycling durability. Notably, the NM95 cathode achieves a high discharge capacity of 218.2 mAh g^{-1} , together with a high energy density of 837.3 Wh kg^{-1} at 0.1C, mainly due to abundant $\text{Ni}^{2+}/\text{Ni}^{3+}$ redox. Shen et al. [21] showed that $\text{LiNi}_{0.8}\text{Mn}_{0.18}\text{Fe}_{0.02}\text{O}_2$ outperforms widely the commercial polycrystalline $\text{LiNi}_{0.83}\text{Co}_{0.11}\text{Mn}_{0.06}\text{O}_2$ electrode and achieves a perfect equilibrium between material cost and electrochemical performance, which not only reduces the production cost by >15%, but also demonstrates excellent thermal stability and cycling performance. Recently, Kan et al. [22] evaluated the electrochemical performance of $\text{LiNi}_{0.94}\text{Mn}_{0.04}\text{Al}_{0.02}\text{O}_2$ (NMA) synthesized by a solid-phase sintering process. NMA has the smallest $\text{Li}^+/\text{Ni}^{2+}$ mixing and shows the capacity retention rate of 79.89% after 100 cycles.

To satisfy the cost and performance benefits, in the present work, we synthesized a Co-free cathode material using iron to replace cobalt in the NMC structure. $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Fe}_{0.1}\text{O}_2$ (NMF811) is synthesized using a co-precipitation process assisted by oxalic acid as chelating agent. The structure, composition, morphology, and thermal stability of the as-prepared sample are characterized using X-ray diffraction (XRD), Raman scattering (RS) spectroscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM), energy dispersive X-ray spectroscopy (EDX), and thermogravimetry (TG). The NMF811 cathode can exhibit favorable electrochemical properties without sacrificing the structural stability owing to almost similar ionic radii of low-spin Ni^{3+} ($r_{\text{Ni}^{3+}} = 0.56 \text{ \AA}$) and Fe^{3+} ($r_{\text{Fe}^{3+}} = 0.55 \text{ \AA}$). Electrochemical properties of the NMF811 electrode are investigated by cyclic voltammetry (CV), galvanostatic charge discharge (GCD) experiments showing good cycle performance at 0.2C and good discharge capability under different C rates.

2. Materials and Methods

2.1. Materials Synthesis

The cobalt-free $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Fe}_{0.1}\text{O}_2$ cathode material was prepared using a two-step process using nickel(II) acetate tetrahydrate (AR), manganese(II) acetate tetrahydrate (AR), iron(III) citrate (AR), and lithium hydroxide (AR) as starting reagents. In the first step, an oxalate precursor was formed by co-precipitation. Nickel acetate tetrahydrate and manganese acetate tetrahydrate were dissolved in double-distilled water and then added drop wise to 1 mol L^{-1} of oxalic acid at 60°C . The precipitate of nickel and manganese oxalate was formed after vigorous stirring at 60°C then the mixture was filtered and washed with distilled water and then dried at 100°C overnight. In the second step, the dried precursor was grounded with stoichiometric amounts of $\text{LiOH}\cdot\text{H}_2\text{O}$ and iron citrate. The

mixture was precalcined at 450 °C for 5 h then grounded and calcined at 800 °C for 10 h in ambient atmosphere with intermittent grinding after the first 5 h. Figure 1 displays a scheme of the synthesis process assisted by oxalic acid chelating agent. For structural and electrochemical comparative studies, Ni-rich $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ (NMC811) was prepared by the same method using $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ as cobalt precursor.

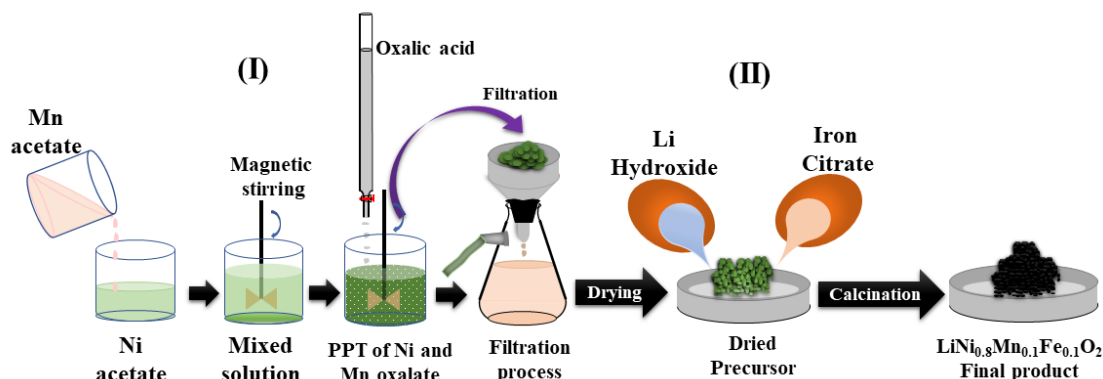


Figure 1. Schematic diagram of the two-step synthesis of the Co-free Ni-rich NMF811 cathode material: (I) co-precipitation process assisted by oxalic acid chelating agent followed by (II) solid-state reaction of oxalate with lithium hydroxide and iron citrate.

2.2. Materials Characterization

The phase composition and structure of the samples were analyzed by XRD using Philips X'Pert apparatus equipped with a $\text{CuK}\alpha$ X-ray source ($\lambda = 1.54056 \text{ \AA}$). Data were collected in the 2θ range $10\text{--}80^\circ$ at a step of 0.05° . The obtained XRD patterns were refined using the FULLPROF software (Toolbar Fullprof suit program (3.00), version June-2015). TGA measurements were carried out using a thermal gravimetric analyzer (Perkin Elmer, TGA 7 series) in the temperature range of $30\text{--}1000^\circ\text{C}$ in air at a heating rate of $10^\circ\text{C min}^{-1}$. The surface morphology of the as-fabricated samples was visualized using field emission scanning electron microscopy (Quanta, FEG 250). The microstructure and morphology of the materials were observed with a JEOL 2100F microscope operated at 200 kV and equipped with a Cs corrector to achieve atomic resolution better than 0.14 nm . BET surface area and pore size distribution of synthesized samples were determined from N_2 -adsorption experiments using (Belsorp max version 2.3.2). The Brunauer–Emmett–Teller (BET) specific surface area and pore size distribution were calculated from N_2 -adsorption experiments using a Belsorp max version 2.3.2 analyzer (Microstac Retsch GmbH, Haan, Germany). Raman scattering (RS) spectra were measured using a micro-Raman-laser spectrometer model Lab-Ram (Horiba-Jobin-Yvon, Longjumeau, France) equipped with $50\times$ microscope lens, D2 filter, aperture of $400 \mu\text{m}$, and a slit of $150 \mu\text{m}$. The spectra have been recorded with the 632 nm laser excitation.

Electrode preparation was carried out by adding the powders of active material NMF811 and carbon black (CB) as conductive additive (C65 Carbon black, Imerys Graphite & Carbon) to a polyvinylidene fluoride (PVDF, Kynar HSW 900, >99%, Arkema) solution in N – Methyl – 2 – pyrrolidone (NMP, >99%, Honeywell Fluka). The electrode slurry was prepared with a ratio of 85: 7.5: 7.5 wt.% of NMF811, CB and PVDF respectively. The slurry was roll coated onto an aluminum sheet (0.02 mm) previously etched for 2 min in a 5 wt.% solution of potassium hydroxide (KOH, $\geq 85\%$, Merck KGaA). After drying at 60°C for 24 h, electrodes have been cut and heat treated at 120°C for 12 h under vacuum in an oven (B–585 Kugelrohr, BÜCHI Labortechnik AG). The obtained NMF811 electrode has an active mass loading in the range $1.5\text{--}1.9 \text{ mg cm}^{-2}$. Coin cells (CR2032, stainless steel 312, MTI corp.) and stainless steel T-shaped cells (Swagelok, Swagelok company) have been assembled in a glove box (Mbraun Labmaster SP, MBraun Inc.) in an inert argon atmosphere ($\text{O}_2 < 0.1 \text{ ppm}$ and $\text{H}_2\text{O} < 0.1 \text{ ppm}$) using NMF811 electrodes as working electrodes (0.636 cm^2), lithium metal (1.13 cm^2 , 0.75 mm thick, 99.9% Merck KGaA) with Celgard 2300 as separator, using 1 mol L^{-1} LiPF_6 in EC:DMC 1:1 wt.% (LP30, Solvionic SA) as the electrolyte solution. Electrodes were

electrochemically characterized by cyclic voltammetry (CV) in three electrodes mode, while galvanostatic charge/discharge (GCD) cycles using a potentiostat/galvanostat (VSP, Biologic).

3. Results

3.1. Structural Analysis

Figure 2a shows XRD patterns of the synthesized NMF811 and NMC811 samples. Well-resolved reflections with a very smooth background indicate a high crystallinity of Ni-rich layered oxides. All reflections are indexed to the characteristic Bragg lines of the α -NaFeO₂ type structure ($R\bar{3}m$ space group, JCPDS card No. 82-1495) without any residual impurities or secondary phases. This means that all Fe atoms were incorporated into the crystal α -NaFeO₂ type structure without the formation of impurities during the preparation process. A careful analysis of the X-ray diffractogram of the NMF811 sample indicates that the positions of the main peaks are shifted slightly toward the lower-angle region (Figure 2a) compared to XRD for pure NMC811. This shift confirms that low-spin Fe³⁺ ions with ionic radius (0.55 Å) were introduced into the crystal structure replacing Co³⁺ ions (ionic radius of 0.545 Å) that results in an increase of the c -axis parameter [17,23–25]. Some additional observations are recognized. (i) The $I_{(003)}/I_{(104)}$ intensity ratio which often used to identify the degree of cation mixing between Ni²⁺ ions and Li⁺ ions in Ni-rich NMC oxides, is slightly smaller for the synthesized NMF811 oxide (0.94) compared to Ni-rich NMC oxides. (ii) The (108)/(110) peak splitting, which reflects the well-ordered layered structure, is less evidenced for the NMF811 oxide, which can indicate the occupancy of some Fe³⁺ ions on Li⁺ sites [26–28]. Lattice parameters of as-prepared samples are listed in Table 1.

In order to characterize the phase purity as well as the phase composition, the full structural identification of the NMF811 sample was analyzed using Rietveld refinements. Figures 2b-c present the Rietveld refinements of NMF811 and NMC811 samples, respectively. In the NMC system, we already know that the presence of n Mn⁴⁺ ions with low-spin Ni³⁺ ions in the same TM slabs induces, due to charge compensation, equal amount of n Ni²⁺ which are distributed between the TM slabs and the Li interslab spaces. If iron is present as a substituent, Fe ions cannot be divalent in the presence of Ni³⁺ [29]. Therefore, the extra TM cations that must be in the Li site will be Ni²⁺ or Fe³⁺. Considering the respective ionic radii of Li⁺ ($r_{Li^+}^{CN=6} = 0.76$ Å), Ni²⁺ ($r_{Ni^{2+}}^{CN=6} = 0.69$ Å), and low-spin Fe³⁺ ($r_{Fe^{3+}}^{CN=6} = 0.55$ Å) [30] in an octahedral environment, it appears that the Li sites are simultaneously occupied by both 3d cation Ni²⁺ and Fe³⁺ ions [29,31,32]. This provides more evidence for the presence of some Fe³⁺ in the Li layer. Therefore, the chemical formula of the Li planes can be written as $[Li_{1-x} Ni_{x-y}^{+2} Fe_y^{+3}]_{3a}$. Moreover, Fe³⁺ preferentially occupies Li(3a) sites compared to Ni²⁺ [31], which sets the constraint $x-y < y$, or $x < 2y$. Therefore, the refinement process was based on fixing the Mn occupancy in transition metal (TM) (3b) sites and varying the ratios of the Ni and Fe occupancies on the TM (3b) and Li (3a) sites, *i.e.*, the 3a sites are occupied by Li⁺, Ni²⁺, and Fe³⁺, and the TM ions (Ni, Mn, and Fe) are located at the 3b sites, while the O²⁻ anions occupy the 6c sites. Since the total occupancy of each site 3a and 3b should be equal 1, we can propose the chemical formula for the NMF811 sample as follows:



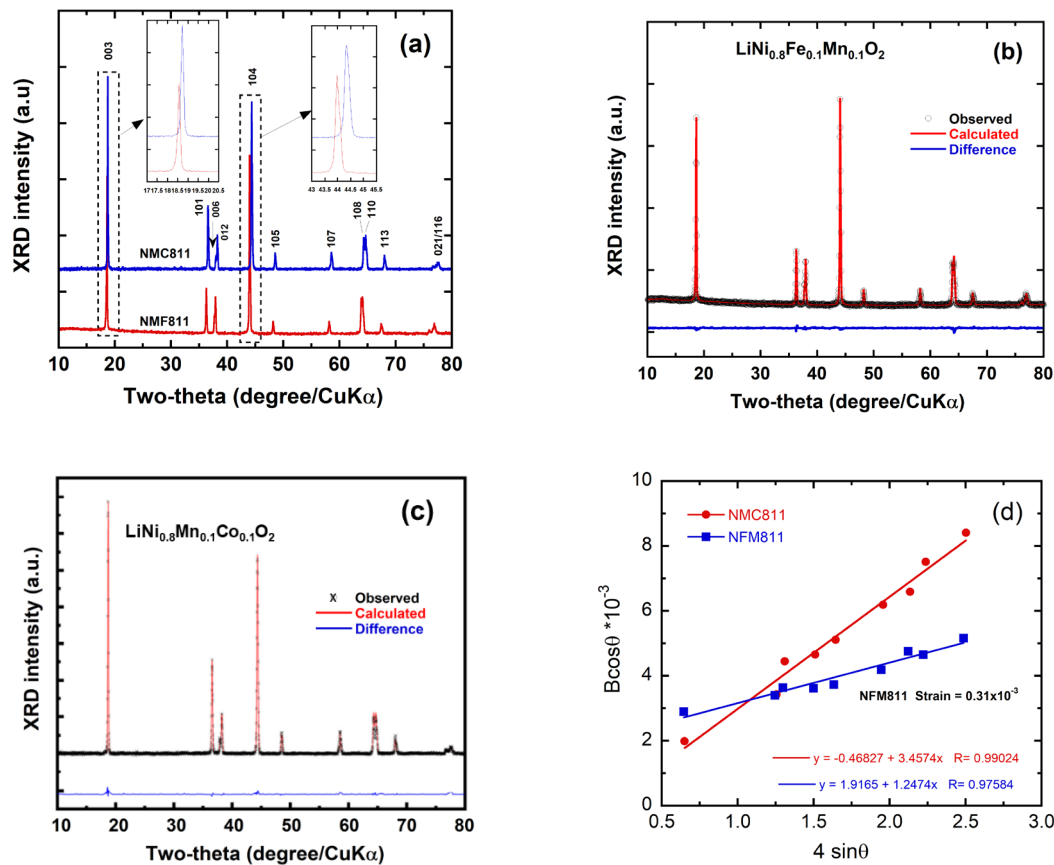


Figure 2. Structural properties of Ni-rich samples. (a) XRD patterns of NCM811 and NMF811 samples recorded with a CuK α X-ray source. (b) Rietveld refinements of XRD pattern of the NMF811 sample. (c) Rietveld refinements of XRD pattern of the NMC811 sample (d) Determination of the microstrain ϵ from the full-width at half-maximum, B_{hkl} of XRD reflections according to Equation (2).

Table 1. Structural parameters and site occupancy factors obtained from Rietveld refinements of X-ray diffractogram of NMC811 and NMF811 samples.

Crystal data	NMC811	NMF811
<i>Lattice parameters</i>		
$a=b$ (Å)	2.875(3)	2.881(1)
c (Å)	14.221(7)	14.29(9)
V (Å ³)	102.13	102.79
c/a	4.94(6)	4.96(3)
$I_{(003)}/I_{(104)}$	1.27±0.03	0.94±0.03
<i>2θ position (°)</i>		
$\langle 003 \rangle$	18.69	18.56
$\langle 104 \rangle$	44.29	44.08
<i>Reliability factors</i>		
R_p (%)	9.18	9.83
R_{wp} (%)	11.86	10.45
χ^2	1.24	1.56
<i>Occupancy (%)</i>		
Ni ²⁺ on Li-site	5.78	1.79
Fe ³⁺ on Li-site	-	2.32

The Rietveld refinements are shown in Figures 2b and 2c. In these figures, circles or crosses (in black) are experimental data and the solid lines (in red) are the calculated spectra. The difference

between calculated and experimental diffractograms (blue curves) shows the quality of the fit which validates the structural model. A good agreement between calculated diagrams and observed patterns was obtained assuming composition of NMF811 including a rhombohedral structure ($R\bar{3}m$ S.G.). In the XRD analysis, the phase fraction was refined with uncertainty of 0.1% and refined by minimization of the difference between experimental and calculated diffractogram. The best Rietveld fit for the NMF811 sample, which shows a good agreement between calculated and observed patterns is obtained with 1.79% $\text{Ni}^{2+}/\text{Li}^+$ anti-site defects and 2.32% $\text{Fe}^{3+}/\text{Li}^+$ anti-site defects.

Analyzing the data in Table 1, one may notice a slight increase in the a - and c -lattice parameters (i.e., 0.14% and 0.7%, respectively) of NMF811 compared to those of NMC811 due to the replacement of Fe for Co. Also, the structural refinements evaluate the Li-O and TM-O bond lengths and the thicknesses of the TM intraslab (i.e., metal–O₂ plane) $S_{(\text{MO}_2)}$ and that of the interslab ($I_{(\text{LiO}_2)}$) expressed by:

$$S_{(\text{MO}_2)} = 2(\frac{1}{3} - Z_{\text{oxy}})c, \tag{2}$$

$$I_{(\text{LiO}_2)} = c/3 - S_{(\text{MO}_2)}. \tag{3}$$

Results are given in Table 2. We notice that $S_{(\text{MO}_2)}$ and $I_{(\text{LiO}_2)}$ are slightly enlarged by 1.1% and 0.5% respectively, compared with those of NMC811sample [3]. This is another evidence of the presence of Fe^{3+} ions ($r_{\text{Fe}^{3+}}^{\text{CN=VI}} = 0.645 \text{ \AA}$) in both the Li(3a) and TM(3b) sites [25,33]. The presence of Fe^{3+} ions at the Li(3a) site can reduce the Li/Ni cation mixing. The percentage of Ni^{2+} ions in the Li(3a) site (1.79%) for NMF811 is lower than that observed for pristine NCM811 (5.57%), which attests the beneficial effect of the incorporation of Fe^{3+} ions into the Li(3a) site. Also, the refinement shows that the actual formula of the final sample is given by Equation (1), with a value $x-y \approx 0.0179$, for $y \approx 0.0232$. So, the value of $x = 0.0411$ and the final formula should be as followed $[\text{Li}_{0.9589}\text{Ni}_{0.0179}^{2+}\text{Fe}_{0.0232}^{3+}]_{3a}[\text{Ni}_{0.6988}^{3+}\text{Mn}_{0.0986}^{4+}\text{Fe}_{0.0808}^{3+}\text{Ni}_{0.0807}^{2+}]_{3b}[\text{O}_2]_{6c}$.

Table 2. Bond lengths and slab thickness for NMF811 sample, compared with data obtained from literature.

Material	Bond length (Å)		Slab thickness (Å)	
	Li-O	TM-O	Intraslab $S_{(\text{MO}_2)}$	Interslab $I_{(\text{LiO}_2)}$
NMC811	2.1135(1)	1.966(2)	2.114(2)	2.622(1)
NMF811	2.1150(2)	1.998(3)	2.137(2)	2.635(7)

Although the total cation mixing ratio ((Ni+Fe)/Li) increased in the presence of iron beside Ni^{2+} in Li(3b) sites (Table 1) which shows a negative effect on both the $I_{(003)}/I_{(104)}$ ratio and the (108)/(110) peak splitting [29], it is clear that the occupying Li sites with an amount of Fe^{3+} not only enhances the structural stability of the NMF811 system, but it also leads to improves the electrochemical properties that can be detected through different following points, firstly, the Ni/Li disorder decreased from 5.78 % in NMC811 to 1.79 % in NMF811, which allows less Ni^{2+} to enter the Li-sites, and as a result, more Ni^{2+} ions exist in the TM sites, i.e., more Ni^{2+} participates in the discharge reaction, secondly, occupation of Li^+ is more probable than that of Ni^{2+} in Li sites which will increase the number of Li ions that can be electrochemically active. Finally, Larger interlayer spacing of LiO_2 ($I_{(\text{LiO}_2)}$) with increased bond length of Li-O (i.e. lithium is weakly bonded to oxygen) as shown in Table 2, which reduces the activation barrier for Li hopping and facilitates lithium diffusion [34,35]. Therefore, the substitution of a small quantity of Fe will decrease the mixing of Ni^{2+} into the Li sites and improve the electrochemical properties of NMF811.

3.2. Thermal Characterization

As reported by Cui et al. [36], the thermal runaway of batteries is a direct result of the thermal decomposition of electrode materials and Ni rich is one of these materials. These authors reported also that the Ni-rich cathodes in contact with electrolyte can be thermally decomposed at temperature as low as 180–190 °C, with a heat release of over 1000 J g. In addition, these Ni-rich materials have considerable outgassing compared to other cathode materials such as LiFePO_4 (LFP) and LiMn_2O_4

(LMO) that react slowly with the electrolyte. So, increasing the thermal stability of Ni-rich cathode materials is important.

To the best of our knowledge, this is the first time to investigate the thermal analysis of NMF811. The TGA curve for the synthesized NMF811 material (Figure 3) shows a good thermal stability as no obvious weight loss was recognized before 430 °C. Very slight weight loss upon heating was observed above 400 °C and reached to 1% at 875 °C. After this temperature additional slight weight loss started due to decomposition of the synthesized material and thermal volatilization or releasing of lithium. This synthesized NMF811 material shows comparable or better thermal behavior than NMC811 synthesized by Li et al. [37], as the weight loss in NMC811 noticed gradually upon heating until decomposition temperature of 750 °C. It seems that complete substitution of Co by Fe can postpone the decomposition reaction. Such a phenomenon was observed in $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ (NCA), due to the high bonding energy (low covalency) of Al [36]. It seems also Fe plays the same role in increasing the thermal stability of the $\alpha\text{-NaFeO}_2$ type structure.

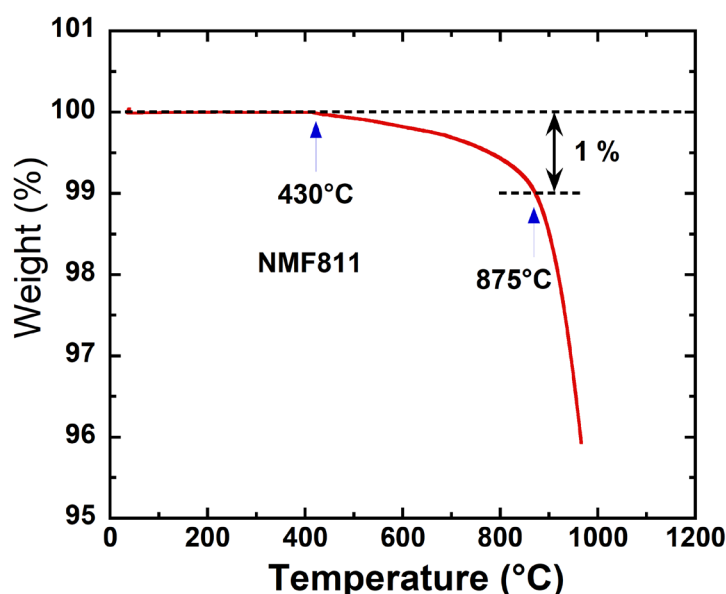


Figure 3. Thermogravimetric analysis of NMF811 carried out in ambient atmosphere.

3.3. Morphological Characterizations

The morphology of NMF811 powders was analyzed by SEM and TEM. From the SEM images shown in Figures 4a-b, it is evidenced that the combination between co-precipitation and solid-state methods plays a role in the morphology of the prepared material. It is obvious that the particles are faceted with smooth surface and clean edges. The microstructure the Co-free NMF811 particles with various magnifications was further investigated by TEM (Figures 4c and 4d) and SAED (inset of Figure 4d). From Figure 4c, the particle size distribution ranges from 50 to 95 nm. The HRTEM image (Figure 4d) clearly reveals the lattice fringes with an interplanar spacing of about 0.204 nm, which is consistent with the (104) planes of layered $\text{LiNi}_{0.8}\text{Co}_{0.1}\text{Mn}_{0.1}\text{O}_2$. The SAED pattern is conformed to the typical diffraction spots of the $R\text{-}3m$ space group [38].

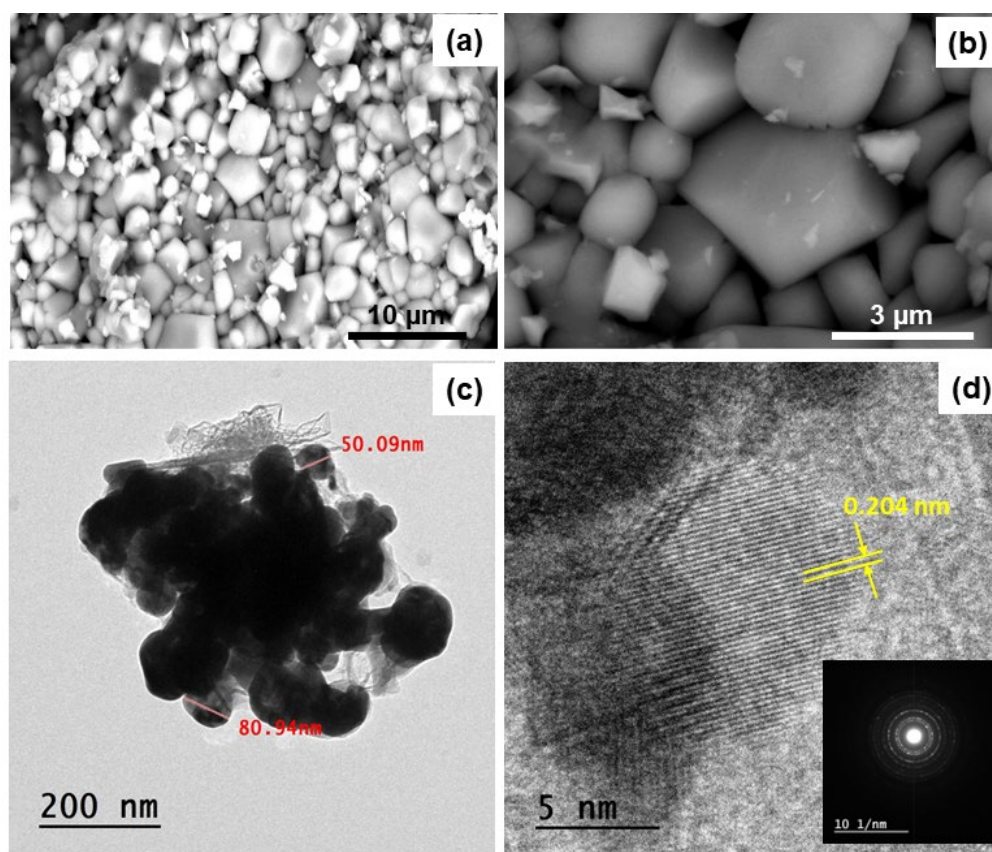


Figure 4. (a,b) SEM images and (c,d) HRTEM images of the NMF811 sample prepared by the two-step process including co-precipitation and solid-state reaction.

3.4. Compositional Analysis

In addition to Rietveld refinement, energy dispersive X-ray spectroscopy (EDX) experiments were used to determine the composition of the NMF811 sample. EDX $L\alpha$ peaks are observed in the 0.65-0.85 keV energy range, while $K\alpha$ peaks are pointed out at 5.6-7.7 keV. As shown in Figure 5, the EDX spectrum includes peaks attributed to the $K\alpha$ electron shell (~ 6.4 keV) and the $L\alpha$ shell (~ 0.7 keV) of iron. The experimental composition of the as-prepared NMF811 deduced from EDX analysis is $\text{LiNi}_{0.7801}\text{Mn}_{0.1096}\text{Fe}_{0.1101}\text{O}_2$. Here, the deviation from the content value of Ni, Fe, and Mn does not exceed 1.0 %, which means that a satisfactory agreement was obtained between EDX analysis and Rietveld refinement.

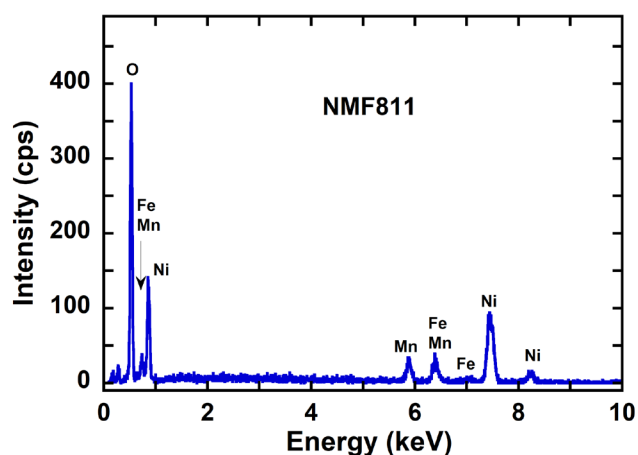


Figure 5. EDX analysis of the NMF811 sample.

3.5. Raman spectroscopy

Due to its sensitivity to the short-range oxygen coordination around cations in oxide frameworks, Raman spectroscopy was used to explore the structural characteristics of the synthesized NMF811. The atomic motion of cations towards their oxygen neighbors, make them highly responsive to the cationic local environment in the rhombohedral crystal lattice [27]. Layered NMC compounds exhibit D_{3d^5} spectroscopic symmetry, and the Raman active vibrational modes associated with three transition-metal ions are represented as $\Gamma = 3A_{1g} + 3E_g$, where A_{1g} and E_g species originate from M–O stretching and O–M–O bending vibrations, respectively [36]. The best fit of the Raman spectrum, starting from a prescribed set of six individual bands of Lorentzian shape that overlap to give rise to the two broad A_{1g} and E_g features as shown in Figure 6. The sets of Lorentzian bands for Ni, Fe and Mn ions, are centered at 468, 524 and 598 cm^{-1} for the E_g species and at 562, 656 and 695 cm^{-1} for the A_{1g} species, respectively. Note that the A_{1g} mode has greater oscillation strength and therefore exhibits higher peak intensity. For LiNiO_2 and for LiMnO_2 the Raman peaks attributed to the A_{1g} and E_g modes are located at 544, 465 cm^{-1} and at 605, 479 cm^{-1} , respectively [17]. It is obvious that these vibrational features are consistent with the formation of the LiNiO_2 - LiMnO_2 - LiFeO_2 solid solution [7,39,40]. For $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Fe}_{0.1}\text{O}_2$, we observe a significant increase of the Ni mode frequency by several cm^{-1} , which can be attributed to the fact that Ni occurs in two different oxidation states in NMF811 (Equation 1). The shift in the Mn mode frequency is due to the oxidation state +4 of Mn ions. Also, two additional bands are observed in Figure 6: (i) the low-frequency band at 185 cm^{-1} attributed to the Li-cage mode and (ii) the high-frequency broad peak assigned to the second-order Raman band.

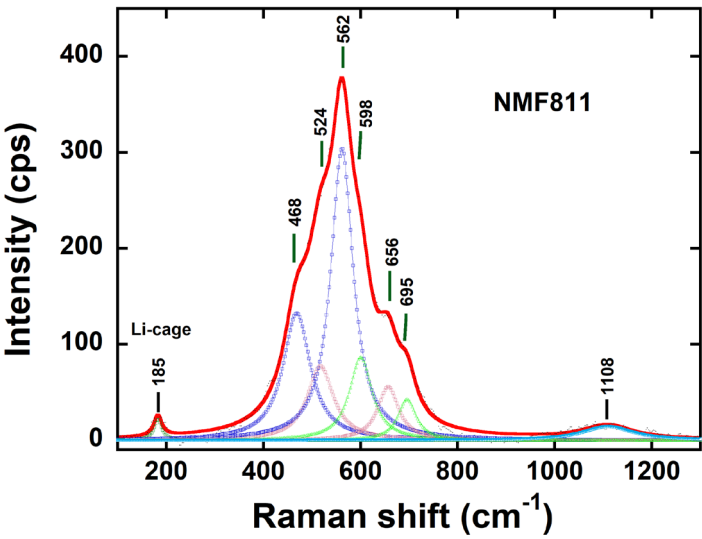


Figure 6. Typical spectral deconvolution of the Raman pattern of NMF811.

Table 3. Analysis of all Raman active modes for NMF811 sample using Lorentzian profiles. Band positions are given with an accuracy of $\pm 1 \text{ cm}^{-1}$.

Modes		Band position (cm^{-1})	Band width (cm^{-1})	Band area
v1	Li-cage	185	19	663
v2	E_g (Ni)	468	68	15669
v3	A_{1g} Ni)	562	56	30218
v4	E_g (Fe)	524	57	5300
v5	A_{1g} (Fe)	656	48	3242
v6	E_g (Mn)	598	55	5682
v7	A_{1g} (Mn)	695	42	3084
v8	2 nd order	1018	124	2556

3.6. Specific Surface Area Characterization

The specific surface area (SSA) of an electrochemically active material is an important parameter for the determination of the exchange-current at the electrolyte–electrode interface and kinetics of Li⁺ ions in electrode. The SSA of the NFM811 powders was measured by nitrogen adsorption method and the result is shown in Figure 7. The isotherm curve of NFM811 sample displays a hysteresis loop indicating the hierarchical nanoporous structure of powders. The isotherm increases with increasing p/p_0 and forms a H3-type hysteresis loop up to $p/p_0 \approx 1.0$ according to the IUPAC classification [41]. The BET specific surface area (S_{BET}) of NFM811 is $8.63 \text{ m}^2 \text{ g}^{-1}$ compared to $1.13 \text{ m}^2 \text{ g}^{-1}$ for NMC811 oxide, which reflects a significant increase in surface state and thus enhances transfer of Li⁺ ions into the secondary particles. The average nanopore size of 2.4 nm calculated using the Barrett–Joyner–Halenda (BJH) model correspond to the interconnecting voids existing between randomly packed nanoparticles within secondary particles. The equivalent particle size L_{BET} of 76 nm is calculated from BET measurements using the relationship $A = 3/(\rho L_{\text{BET}})$, where A is the specific surface area, ρ is the density (4.6 g cm^{-3} for NFM811) [41]. We observe a relatively good agreement between particle size values L_{BET} and L_{TEM} . It is also shown that the NFM811 powder has an open porosity and this ensures a better wettability relating to penetration through the electrolyte, and thus the diffusion paths in the cathode material are shorter, which promotes the Li⁺ transport.

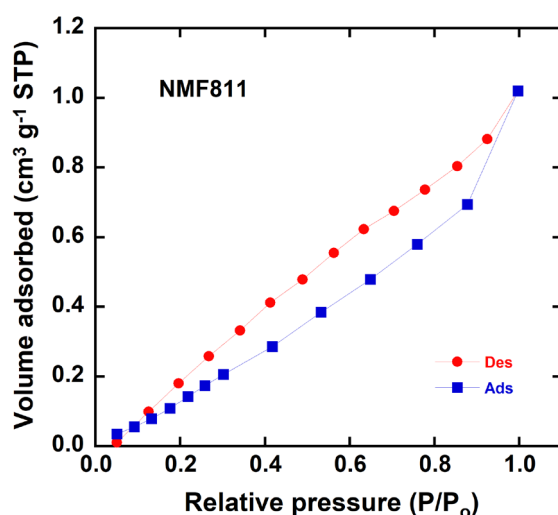
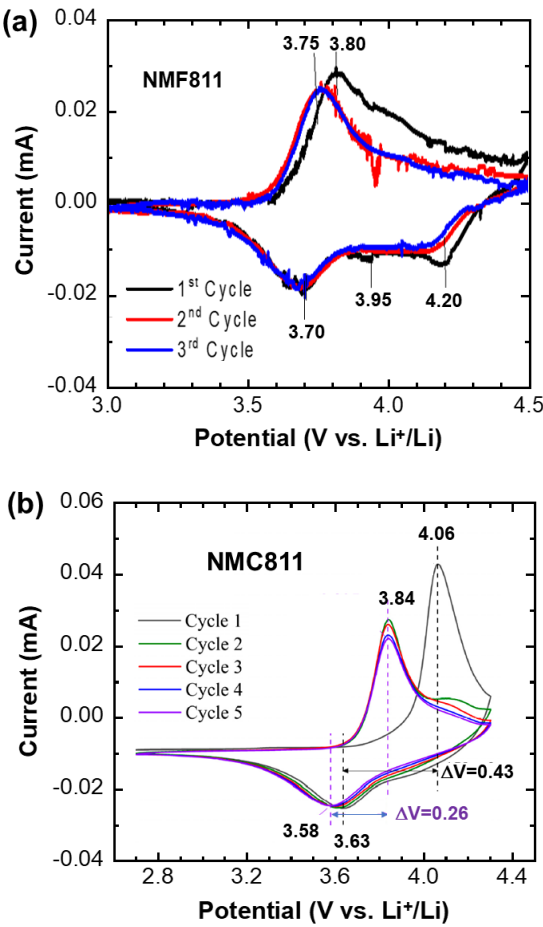


Figure 7. BET experiments showing N₂ adsorption–desorption isotherms of NFM811.

3.7. Electrochemical characterizations

Electrochemical assessments on the as-prepared sample NFM811 were performed in CR2032 coin-type cells using cyclic voltammetry and galvanostatic charge–discharge experiments. The voltammograms carried out at the scan rate of 0.01 mV s^{-1} in the potential range 3.0–4.5 V vs. Li⁺/Li are shown in Figure 8a, which reveal the electrochemical behavior during Li-ion intercalation/deintercalation associated with the corresponding crystallographic transitions. Three pairs of anodic and cathodic peaks located at around 3.70, 3.95, and 4.20 V correspond to Ni^{2+/3+,4+} redox processes and to the phase transition of hexagonal (H1) to monoclinic (M), monoclinic (M) to hexagonal (H2), and hexagonal (H2) to hexagonal (H3), respectively [17,26,42,43]. As shown in Figure 8a, the anodic peak located at 3.8 V exhibit a slight shift to 3.75 V after the 1st cycle. The voltage difference (ΔV) between anodic and cathodic peaks during the second and the third cycle is stabilized, which gives a good indication about improvement in cycle performance upon cycling. It is worth noting that the cyclic voltammograms of NFM811 are rather different from those NMC811 illustrated in Figure 8b for which the anodic peak at 4.06 V is shifted to 3.84 V after the 1st cycle.



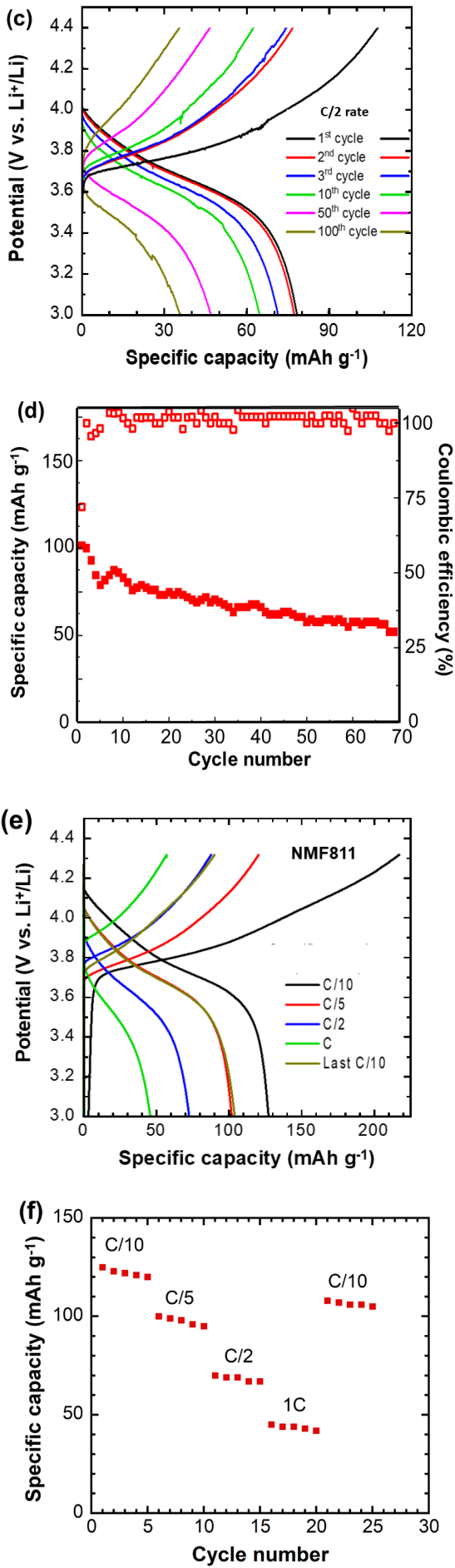


Figure 8. Electrochemical characterization of the layered oxide electrode. (a) CV profile of NMF811 and (b) CV profile of NMC811 recorded at low sweep rate of 0.01 mV s^{-1} in the potential range 3.0-4.5 V vs. Li^+/Li . (c) GCD profiles of the NMF811 electrode recorded at C/2 rate in the voltage range 3.0 - 4.4 V. (d) Cycleability of the NMF811 electrode tested at C/5 rate in the potential range 3.0 - 4.4 V. (e) GCD profiles of the NMF811 electrode recorded at different C-rate. (f) Rate capability of the NMF811 electrode.

Figure 8c presents the room-temperature galvanostatic charge/discharge tests of the NMF811 electrode performed at high rate of 0.5C within the potential range 3.0-4.4 V vs. Li^+/Li . The NMF811 electrode delivers an initial charge and discharge specific capacities of 108 and 79 mAh g^{-1} , respectively, giving an irreversible capacity of 29 mAh g^{-1} and an initial Coulombic efficiency (ICE) of 73 %. This looks better than pristine NCM811, which exhibits an irreversible capacity of 50 mAh g^{-1} and an ICE of 71 % at lower current density of 0.1C. This improved electrochemical performance may be explained by the interlayer linear $\text{Ni}^{2+}\text{-O}_2\text{-Fe}^{3+}$ generated when Co is completely replaced by Fe maintaining the layered structure of $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Fe}_{0.1}\text{O}_2$. This ternary layered oxide electrode material mitigates the 180° $\text{Ni}^{2+}\text{-O}_2\text{-Ni}^{2+}/\text{Mn}^{4+}$ linear super exchange effect alleviating or retarding Ni/Li mixing, which increases the diffusion rate of Li^+ [44,45]. Additionally, as observed by Ryu et al. [46] and Yang et al. [47], the full substitution of Co-by-Fe in the NCM811 cathode assists to avoid the detrimental effect of the $\text{H}_2 \rightarrow \text{H}_3$ phase transition at the end of the charge-process, which considerably affects its cycle stability. Hu et al. reported the mechanism of side reaction inducing capacity fading of Ni-rich cathode [48]. This phase transition causes expansion and contraction of crystal structure, which is closely related to cracks in grains that cause lattice distortion and induce internal strain accelerating the degradation of layered cathode material via an irreversible phase transition (IPT) from layered structure to spinel phase and NiO-like phase.

Figure 8d illustrates the cycleability of the NFM811 electrode tested in the same potential window 3.0 V - 4.4 V over 70 cycles at 0.2C rate. Using this lower C-rate, the electrode delivers an initial discharge capacity to 102 mAh g^{-1} (ICE 72%) and retained 52 mAh g^{-1} after 70 cycles with capacity retention of 51 % ($\text{CE} \cong 100\%$). This improvement in Coulombic efficiency may be ascribed to the incorporation of Fe that maintains the stability of the layered rhombohedral structure and inhibits the transition to a spinel-like structure, which ultimately results in the cubic rock-salt phase [49]. Furthermore, even in the extreme case of a high charging cut-off voltage, Fe doping prevents the local collapse of LiO_2 interslab space during cycling. In order to evaluate the rate capability of the NFM811 cathode, galvanostatic charge-discharge experiments were carried out at various C-rates in the range 0.1C-1C (Figures 8e and 8f). It is noted that the discharge capacities of NFM811 at 0.1C, 0.2C, 0.5C, 1.0C are 126, 101, 72, 46 and 103 mAh g^{-1} , respectively. This is another evidence for the possibility to rely on this new electrode material after further modification.

4. Discussion

The influence on the electrochemical performance of the Li/Ni cation mixing in Ni-rich cathodes has been widely documented as, in most cases, results in capacity degradation, structure evolution and poor thermal stability, especially at high cut-off potential [43,50,51]. Universal strategy to mitigate cation mixing has been achieved by surface doping, cation doping or compositional gradient. For instance, Wu et al. [50] reported the reduction of cation mixing from 6% to 5% via Li_2MnO_3 injection in NMC811 prepared by the mixture of $\text{LiOH}\cdot\text{H}_2\text{O}$ with the precursor powder $[\text{Ni}_{0.776}\text{Co}_{0.097}\text{Mn}_{0.117}](\text{OH})_2$ obtained by co-precipitation. Cui et al. [51] investigated the effect of cationic uniformity in the precursors on Li/Ni mixing of Ni-rich layered cathodes and reported cation mixing of 7.97% and 5.82% for NCM811 prepared by solid-state reaction and sol-gel method, respectively. Park et al. [43] quantified from a Rietveld refinement analysis that the ratio of Ni^{2+} existing in the 3a sites is 2.8% and 0.9% in pristine NMC and in 0.25% Fe doped NMC, respectively, indicative of the reduced cation mixing ratio upon iron introduction in the layered lattice. Herein, we observed the same tendency with 5.78% and 1.79% Ni^{2+} on Li(3a) sites for pristine NMC811 and NMF811, respectively.

Also, we can state that the complete substitution of Co^{3+} by Fe^{3+} has a positive effect on the electrochemical results. Generally, Fe^{3+} is an active cation that mitigates in occupying the position of Ni^{2+} so it reduces the degree of cation mixing between Ni/Li ions and increases the interlattice region between the layers. So, an increase in the diffusion coefficient of lithium (D_{Li^+}) in the oxide framework is expected with iron doping. In one side, Fe^{3+} lowers $\text{Li}^+/\text{Ni}^{2+}$ disordering due to the comparable ionic radius of Ni^{2+} ion (0.69 Å) to Li ion (0.76 Å) by the modification in TM slabs and Li slabs [52]. As Fe^{3+} ions located in transition metal layers (3b sites) can easily migrate and occupy into LiO_2 layers (3a sites) simultaneously along with Ni^{2+} , therefore, it could be predicted that parts of Fe^{3+} and Ni^{2+} ions reside in the 3a sites and hence it reduces the antisite of Ni^{2+} and the cation mixing is reduced (as evidenced from XRD section), this means that more Ni^{2+} participated in the discharge reaction, so as to obtain more specific discharge capacity. On the other side, Fe^{3+} ameliorate the lithium diffusion kinetics as reported by Mofid et al. [53], Fe^{3+} and Co^{3+} have the same role as they have the electronic configuration of ($t_{2g}^5 e_g^0$) and ($t_{2g}^6 e_g^0$), respectively, with almost similar ionic radius, i.e., 0.55 Å for low-spin Fe^{3+} and 0.545 Å for Co^{3+} . So, upon the replacement of Co by Fe ion the *a*-axis and *c*-axis became slightly larger and hence decreases the lithium diffusion barrier. Moreover, the high bond energy of Fe-O (390.4 kJ) lessens oxygen release and increases the lamellar layer structural stability from suffering phase transitions via occupying transition metal (TM) sites [54].

5. Conclusions

In this work, a Ni-rich Co-free oxide cathode has been designed by substituting Fe for Co. The compound $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Fe}_{0.1}\text{O}_2$ was synthesized via a two-step process: the formation of an oxalate precursor by co-precipitation followed by a solid-state reaction with lithium hydroxide and iron citrate. Two structural modifications can be observed upon iron substitution for cobalt: (i) a change in the TM layer spacing and (ii) a shift in the *c/a* ratio which ascribes to change in the anti-site defect concentration. However, as the ionic radius of low-spin Fe^{3+} (0.55 Å) is not substantially different than that of Co^{3+} (0.545 Å), the shift if the *c/a* ratio is expected to reflect primarily change in the anti-site defect concentration in the NFM811 material. More importantly, the mechanical inner strain is alleviated by the improved reversible H2-H3 phase transition, which can reduce the formation of cracks and improve the safety performance during long-term cycling. This Ni-rich Co-free cathode material can deliver a specific capacity of ~80 mAh g⁻¹ and retain about 45% of its initial capacity after 100 cycles at C/2 rate.

Author Contributions: Conceptualization, A.M.H. and C.A.; methodology, A.E.A.; formal analysis, R.S.E, S.M.A, A.E.A., and L.B.; investigation, R.S.E, S.M.A, A.E.A., and L.B.; data curation, A.E.A.; writing—original draft preparation, A.E.A and A.M.H.; writing—review and editing, A.M. and C.M.J.; supervision, A.M.H and C.A.; funding acquisition, A.M.H. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Egyptian Science, Technology, and Innovation Funding Authority (STIFA, STDF previously) through project number 42691 entitled (Microstructure-Based, Multi-Physics Simulation and Optimization to Improve Battery Performance).

Data Availability Statement: All data are provided in this article.

Conflicts of Interest: The authors declare no conflicts of interest.

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