

Article

Mn-Rich NMC Cathode for Lithium-Ion Batteries at High-Voltage Operation

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Abstract: Development in high-rate electrode materials capable of storing vast amounts of charge in a short duration to decrease charging time and increase power in lithium-ion batteries is an important challenge to address. Here, we introduce a synthesis strategy with a series of composition-controlled NMC cathodes, including $\text{LiNi}_{0.2}\text{Mn}_{0.6}\text{Co}_{0.2}\text{O}_2$ (NMC262), $\text{LiNi}_{0.3}\text{Mn}_{0.5}\text{Co}_{0.2}\text{O}_2$ (NMC352), and $\text{LiNi}_{0.4}\text{Mn}_{0.4}\text{Co}_{0.2}\text{O}_2$ (NMC442). A very high-rate performance was achieved for Mn-rich $\text{LiNi}_{0.2}\text{Mn}_{0.6}\text{Co}_{0.2}\text{O}_2$ (NMC262). It has a very high initial discharge capacity of 285 mAh g^{-1} when charged to 4.7 V at a current of 20 mA g^{-1} and retains the capacity of 201 mAh g^{-1} after 100 cycles. It also exhibits an excellent rate capability of 138, and 114 mAh g^{-1} even at rates of 10 and 15 C ($1 \text{ C} = 240 \text{ mA g}^{-1}$). The high discharge capacities and excellent rate capabilities of Mn-rich $\text{LiNi}_{0.2}\text{Mn}_{0.6}\text{Co}_{0.2}\text{O}_2$ cathodes could be ascribed to their structural stability, controlled particle size, high surface area, and suppressed phase transformation from layered to spinel phases, due to low cation mixing and the higher oxidation state of manganese. The cathodic and anodic diffusion coefficient of the NMC262 electrode was determined to be around $4.76 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$ and $2.1 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$, respectively.

Keywords: Mn-rich NMC cathode; high voltage; Li-ion battery; Li^+ diffusion coefficient; cyclic voltammetry; electrochemical impedance spectroscopy



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1. Introduction

Owing to the increasing demands of the modern world for inexpensive, safe, clean and long-lasting energy storage solutions, a significant evolution in material development for lithium-ion batteries (LIBs) has been witnessed in the past few years [1–3]. Current research is predominantly focused on the next-generation LIBs materials (such as lithium- and manganese-rich transition metal oxides) to address the electrochemical shortcomings that currently hinder the implementation of these materials as high-capacity battery cathodes, particularly for the applications related to the automotive industry. The term rate capability corresponds to the “maximum charge/discharge rate” of a cell or a battery. In general, a battery system with high charge/discharge capability is sought-after for enhanced performance of hybrid electric vehicles (HEVs) [2,4].

Spinel LiMn_2O_4 is a commonly used cathode material for electrical vehicles. However, its limitations, such as low energy density, capacity deterioration and poor thermal stability, make this material less of an option for long-term utilization in EVs and HEVs [5,6]. Meanwhile, NMC cathodes, classified under layered ternary oxide cathode materials, with the general formula $\text{LiNi}_x\text{Mn}_y\text{Co}_{1-x-y}\text{O}_2$, are quite popular for their desirable features, including cost-effectiveness, high operating voltage, reversible capacity and enhanced

safety at elevated operational temperatures. Owing to these merits, NMC-based cathodes are considered as potent candidates for lithium-ion batteries with high energy density for HEVs [6–9]. NMC-based cathodes offer a high discharge capacity of 230 mAh g^{-1} compared to the traditional LiCoO_2 , LiMn_2O_4 , and LiFePO_4 cathodes, when operated above 4.6 V [10–13]. Nevertheless, fast capacity drop during the cycles at high voltage, poor rate capability, and significant loss in first irreversible capacity are the main setbacks that limit the practical application of these otherwise remarkable materials in lithium-ion battery cathodes [14,15].

To deal with the aforementioned issues, it is highly important to develop strategies that can lead to the improvement of overall performance, particularly an improved rate capability, for these high-capacity and low-cost NMC-based cathode materials. One prospect to march toward such advancements lies in the exploration of chemistries based on transition metal ratios, since the selection of chemical compositions of lithiated transition metal oxide-based cathode materials can significantly affect their feasibility for long-term operation in HEVs [9,16].

The oxidation states of Ni, Co and Mn in the NMC compounds are generally +2, +3 and +4, respectively; however, a small quantity of Ni^{3+} and Mn^{3+} ions can also coexist [8]. As a general concept, Ni and Co ions play an active role in the charge/discharge process, while Mn^{4+} ions are considered to be extremely vital for stabilization of the electrode [17]. Previous reports suggest that during high-voltage operation, a high concentration of Ni can be detrimental; meanwhile, the oxidation of Co^{3+} to Co^{4+} can enhance the capacity at higher voltages. However, the scarcity of Co is forcing researchers around the world to either look for better alternatives for Co or reduce the concentration of cobalt in LIBs to as low as possible [18,19].

While the chemistries of Ni and Co are quite established regarding the properties of NMC-based cathodes, the role of Mn is still unclear and not properly understood [7]. Recently, a theoretical study has reported that the reversibility in lithiated NMC cathodes is mostly controlled by the oxidation and spin states of manganese [7]. Although the Ni-rich and Co-rich cathode materials have been studied extensively, the experimental investigations on Mn-rich LIB cathodes are relatively limited [20–22]. Therefore, to explore the impact of Mn concentration on NMC-based cathodes and to understand the effect that composition can have on rate capability of these high energy density electrodes, a series of electrodes were prepared for the following compositions: $\text{LiNi}_{0.2}\text{Mn}_{0.6}\text{Co}_{0.2}\text{O}_2$, $\text{LiNi}_{0.3}\text{Mn}_{0.5}\text{Co}_{0.2}\text{O}_2$, and $\text{LiNi}_{0.4}\text{Mn}_{0.4}\text{Co}_{0.2}\text{O}_2$, which are hereafter denoted as NMC262, NMC352 and NMC442, respectively.

Generally, cobalt-poor NMC cathodes demonstrate better rate capability and long term cyclic performance [23,24]; therefore, the composition tuning was carried out in a way to investigate the cobalt-poor NMC cathodes with a varied Ni to Mn ratio, and a fixed low Co concentration. In this research, we shall experimentally demonstrate the effect of Ni/Mn ratio alteration in NMC on the significant electrochemical properties and rate capability of the resultant LIB cathodes.

To synthesize cathode materials, many research groups have used a hydroxide co-precipitation method [25,26]. In such hydroxide co-precipitation methods, Mn ions are precipitated in an aqueous solution as $\text{Mn}(\text{OH})_2$ (Mn^{2+}) and oxidized gradually so that the valence state is changed to Mn^{3+} (MnOOH) or Mn^{4+} (MnO_2). Hence, using this method for precursor preparation is quite difficult. Meanwhile, with carbonate co-precipitation, the +2 valence of Mn and the cations are stable in an aqueous solution. Therefore, the carbonate co-precipitation method is considered to be more effective for industrial applications due to the ease of reproducibility. In this work, we have performed a systematic study of layered lithiated NMC cathodes by a carbonate co-precipitation method [27,28].

Composition-controlled NMC electrodes for this study were prepared using carbonate co-precipitate powders for 9 h and calcined at 900°C for 15 h. NMC262 demonstrates the highest discharge capacities and best rate performance when compared to NMC442 and NMC352, during the high-voltage operation. The Mn-rich electrodes show good structural

stability, which is attributed to the higher concentration of Mn ions in the structure. In addition, the reduction from Mn^{4+} to Mn^{3+} favors their cyclability. Meanwhile, the high surface area and controlled particle size favors the lithium intercalation/deintercalation process, making lithium-rich NMC262 a high-capacity and high-rate electrode among the other prepared NMC compositions.

2. Experimental Section

2.1. Synthesis of Materials

NMC powders were synthesized using a carbonate co-precipitate method. For the preparation of the carbonate powders $\text{Ni}_{0.2}\text{Mn}_{0.6}\text{Co}_{0.2}\text{CO}_3$, $\text{Ni}_{0.3}\text{Mn}_{0.5}\text{Co}_{0.2}\text{CO}_3$, and $\text{Ni}_{0.4}\text{Mn}_{0.4}\text{Co}_{0.2}\text{CO}_3$, we used $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$, $\text{MnSO}_4 \cdot \text{H}_2\text{O}$, $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$, and Na_2CO_3 as the starting materials. The detailed carbonate co-precipitation route is well described in our previous work [28].

To prepare $\text{Ni}_{0.2}\text{Mn}_{0.6}\text{Co}_{0.2}\text{CO}_3$, $\text{Ni}_{0.3}\text{Mn}_{0.5}\text{Co}_{0.2}\text{CO}_3$, and $\text{Ni}_{0.4}\text{Mn}_{0.4}\text{Co}_{0.2}\text{CO}_3$ powders, carbonate co-precipitation was carried out for 9 h of reaction time. The co-precipitated $\text{Ni}_{0.2}\text{Mn}_{0.6}\text{Co}_{0.2}\text{O}_3$ powders were preheated at 500 °C for 5 h in air. During the preheating process, the mixed carbonate powders were decomposed into metal oxide. A mixture containing a stoichiometric amount of metal oxide and an excess amount of $\text{LiOH} \cdot \text{H}_2\text{O}$ powder was preheated at 500 °C for 5 h, and then finally calcined at 900 °C for 15 h in air to achieve $\text{LiNi}_{0.2}\text{Mn}_{0.6}\text{Co}_{0.2}\text{O}_2$ (NMC262).

2.2. Characterizations

The NMC powders' morphology was characterized by field emission scanning electron microscopy (FE-SEM; FEI Nova600). High-resolution transmission electron microscopy (HR-TEM) was performed to observe structural changes after charge–discharge cycles. The crystal structure of the samples was analyzed with the help of X-ray diffraction (XRD; Bruker D8 Discover) with $\text{CuK}\alpha$ ($\lambda = 1.541 \text{ \AA}$) at a scan speed of $0.02^\circ \text{ s}^{-1}$ at the range of $10\text{--}80^\circ$ (2θ). The Rietveld method with GSAS-EXPGUI software was used for the collected data fitting or for structural refinement. Additionally, the preferential orientation was corrected using the March–Dollase algorithm. The Brunauer–Emmett–Teller (BET) method was used to determine the surface area where the nitrogen adsorption/desorption data were obtained using the Micromeritics TriStar 3000. Energy dispersive X-ray analysis (EDX) was carried out for all three samples using TESCAN SEM.

2.3. Electrode Preparation

To measure electrochemical performance, 3 mg of NMC powder was weighed and mixed with 2 mg of teflonized acetylene black (TAB-2) conducting binder in an agate mortar. The electrode was pressed onto the stainless steel with the area of 2 cm^2 . The electrodes were dried at 160 °C for 5 h in a vacuum oven. The cell was assembled in an argon environment in a glovebox. The working and counter electrodes were $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$ and Li foil. Two pieces of glass fiber filter (ADVANTEC, GB-100R, Japan) were used as a separator in 2032 coin-type cells. In addition, 1 M LiPF_6 -EC (ethylene carbonate): DMC (dimethyl carbonate) (1:2 by volume) was used as an electrolyte. The galvanostatic charge–discharge cycles were measured using an Arbin 16 channel instrument in the voltage range of 4.7 V–2.0 V, with a current density of 20 mA g^{-1} at room temperature. The C rate ($1 \text{ C} = 240 \text{ mA g}^{-1}$) was measured at different currents of 20, 40, 80, 120, 240, 480, 1200, 2400, and 3600 mA g^{-1} , respectively. The cyclic voltammetry was run between 4.7 and 2.0 V with a scan rate of 1 mV s^{-1} , using a SP200 Biologic potentiostat. Electrochemical impedance spectroscopy (EIS) of the NMC262 electrode was measured in the range of 100 mHz–5 MHz for the Li^+ diffusion coefficient.

3. Results and Discussion

3.1. Structural Analysis

Figure 1a illustrates the XRD patterns for NMC262, NMC352 and NMC442. Figure 1b shows the layered crystal structure of NMC262. It is possible to observe morphological changes with the increase in Mn concentration in our NMC materials. The X-ray diffraction patterns of $\text{LiNi}_{0.4}\text{Mn}_{0.4}\text{Co}_{0.2}\text{O}_2$, $\text{LiNi}_{0.3}\text{Mn}_{0.5}\text{Co}_{0.2}\text{O}_2$, and $\text{LiNi}_{0.2}\text{Mn}_{0.6}\text{Co}_{0.2}\text{O}_2$ are shown in Figure 1a. The precursors of these materials were prepared by a carbonate co-precipitation method. The XRD technique was utilized to analyze the crystal structure of the carbonate co-precipitation precursors. As shown in Figure 1, all the synthesized materials exhibit a typical hexagonal $\alpha\text{-NaFeO}_2$ layered structure with space group $R\bar{3}m$ symmetry. The weak diffraction peaks between 20° and 25° for the NMC262 powder are due to the cation ordering of monoclinic Li_2MnO_3 unit cells $C2m$ [29,30]. No other peaks for any other impurities were detected in the whole patterns of the synthesized NMC442, NMC352, and NMC262 powders, thus indicating the high purity of the prepared samples. All the three materials show clear splitting of the (006)/(102) and (108)/(110) peaks with a high c/a ratio, which indicates that the materials prepared were formed of a pure phase with good crystallinity. The intensity ratio $I_{(003)}/I_{(004)}$ value of NMC262 was 1.73, suggesting an enhanced layered structure and negligible disordered arrangement of Li^+ and Ni^{2+} ions in the synthesized material.

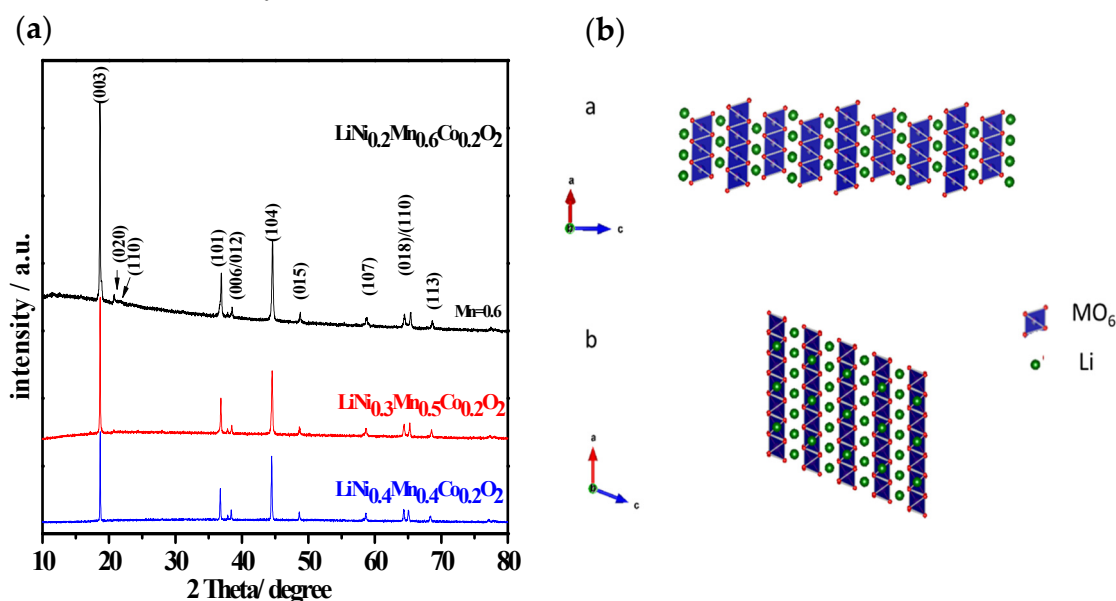


Figure 1. (a) X-ray diffraction patterns that correspond to NMC with different Mn ratios, (b) (a) integrated layered rhombohedral structure of the $\text{LiNi}_{0.2}\text{Mn}_{0.6}\text{Co}_{0.2}\text{O}_2$ cathode, and (b) (b) layered monoclinic phase that contains Li in the M-layer, which induces cation ordering in the structure (M-layer is the transition metal layer, comprising of Ni, Co and Mn).

SEM images are shown in Figure 2. The SEM images of NMC262 (Figure 2b) illustrate small round particles with diameters of 0.1–0.2 μm , aggregated to form large secondary particles of 1–3 μm in size with uniform shapes (Figure 2a). Meanwhile, in NMC352 and NMC442, the agglomeration of nanosized particles gave rise to larger secondary particles with uneven particle size distribution of 6 μm . EDX measurements were carried out using TESCAN SEM for all three samples of NMC, and all of the atomic ratio data are available in Table S2. According to this information, all three samples of NMC exhibit atomic ratios that are nearly comparable to the expected numbers.

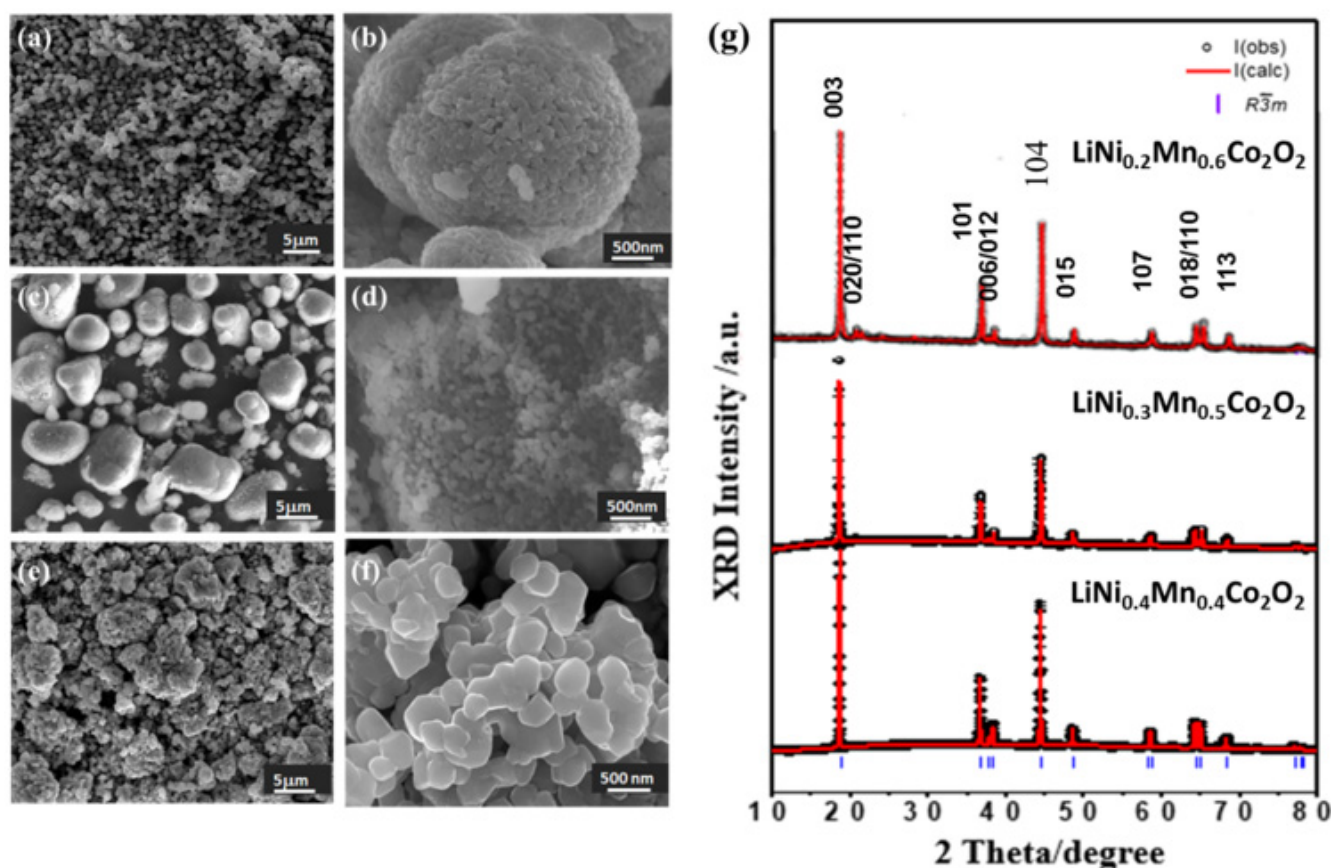


Figure 2. Scanning electron micrographs (a,c,e) and high-magnification scanning electron micrographs (b,d,f) for NMC262, NMC352 and NMC442, respectively. (g) XRD Rietveld analysis for NMC262, NMC352 and NMC442.

XRD Rietveld analysis for NMC262, NMC352 and NMC442 is shown in Figure 2g. The black circles represent the observed XRD intensity, while the red line marks the calculated intensity. The low reliability factor ($R_{wp}(\text{NMC262}) = 1.90\%$, $R_{wp}(\text{NMC352}) = 2.95\%$ and $R_{wp}(\text{NMC442}) = 3.53\%$) obtained for these NMC compositions, along with the reduced chi-square value close to unity, is indicative of the fact that the experimental data were fitted well by the Rietveld refinement, showing the rhombohedral and monoclinic structure. The refined profile is shown in Figure 2 and the lattice parameters c and a of NMC262, NMC352, and NMC442 are presented in Table 1.

Table 1. Structural composition, lattice parameters, intensity ratios and BET surface area of NMC cathodes with different compositions.

Composition	Space Group	a (Å)	c (Å)	c/a	Reduced χ^2	BET ($\text{m}^2 \text{g}^{-1}$)
$\text{LiNi}_{0.2}\text{Mn}_{0.6}\text{Co}_{0.2}\text{O}_2$	R-3m	2.8521 (6)	14.2423 (7)	4.9936	1.73	8.0
$\text{LiNi}_{0.3}\text{Mn}_{0.5}\text{Co}_{0.2}\text{O}_2$	R-3m	2.8596 (3)	14.263 (1)	4.9877	1.49	2.6
$\text{LiNi}_{0.4}\text{Mn}_{0.4}\text{Co}_{0.2}\text{O}_2$	Pm-3m	2.8670 (2)	14.253 (1)	4.9713	1.25	2.1

The surface area of different NMC samples was measured using the BET (Brunauer–Emmett–Teller) technique and the nitrogen adsorption–desorption plots obtained using BET analysis are presented in Figure 3. The BET surface areas obtained for NMC442, NMC352, and NMC262 were recorded as $2.1 \text{ m}^2 \text{g}^{-1}$, $2.6 \text{ m}^2 \text{g}^{-1}$ and $8.0 \text{ m}^2 \text{g}^{-1}$, respectively, for the as-synthesized samples. It was found that surface area increased with the increase in Mn concentration. Specific surface area is generally reported to decrease with an increase in Ni content, and increase with an increase in Mn percentage in the NMC materials [31,32].

Furthermore, particle shape and size could also affect the specific surface areas of cathode materials. From SEM analysis, it was found that the average particle size of NMC262 is much smaller than NMC352 and NMC442, which could lead to a higher surface area for Mn-rich materials.

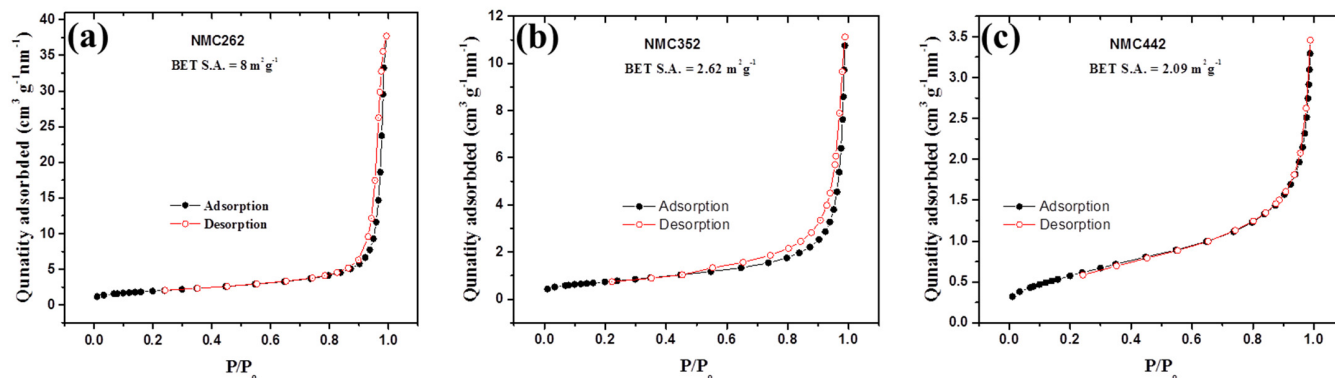


Figure 3. Nitrogen adsorption–desorption isotherm for (a) NMC262 (b) NMC352 and (c) NMC442.

3.2. Electrochemical Performance

The electrochemical charge–discharge cycles for all the samples were measured at room temperature with a constant current density of 20 mA g^{-1} with the voltage range of 2.0–4.7 V. The charge–discharge curves for the NMC262, NMC352 and NMC442 were obtained to study the lithium insertion and extraction behavior, as shown in Figure 4a–c.

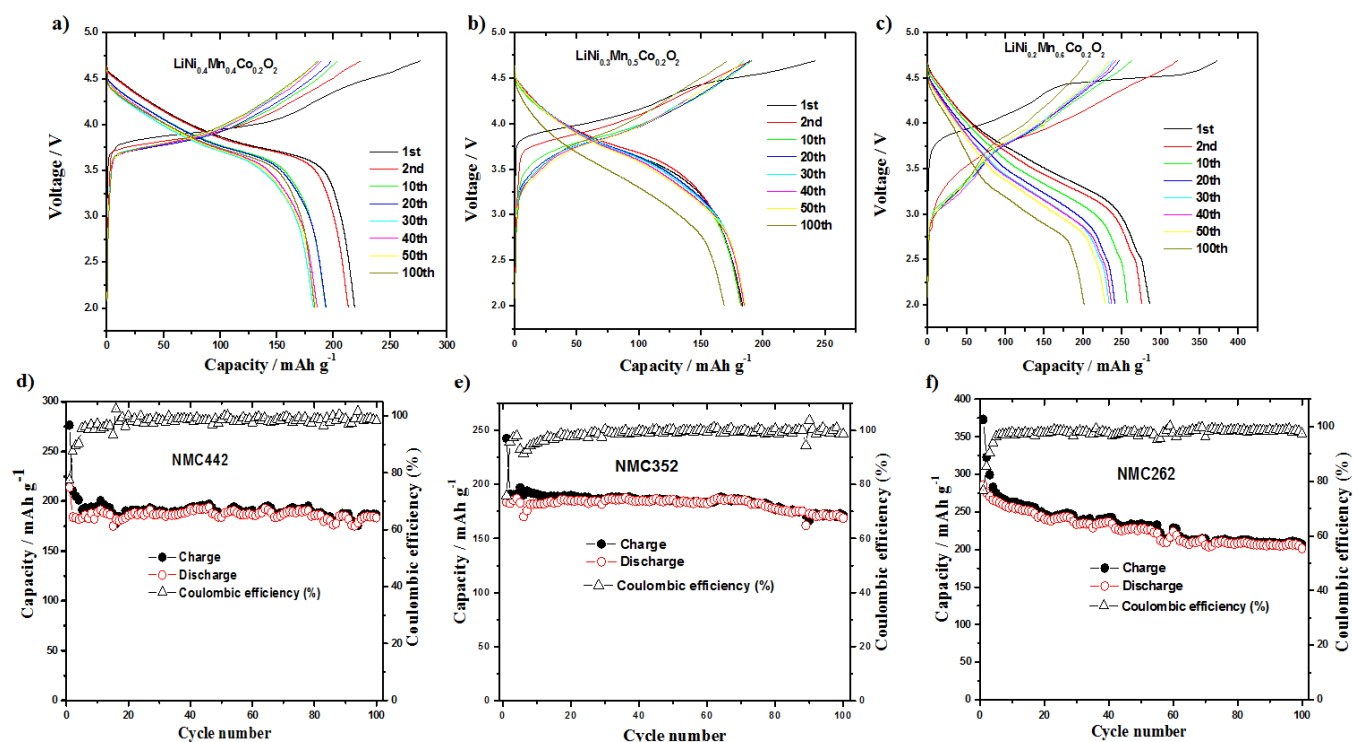


Figure 4. (a–c) Charge–discharge curves for NMC442, NMC352 and NMC262 at a current rate of 20 mA g^{-1} for the voltage range of 4.7–2.0 V. (d–f) Capacities versus cycle number of NMC442, NMC352 and NMC262 cathodes at the voltage range of 4.7–2.0 V with a current of 20 mA g^{-1} .

For NMC442, the initial discharge capacity was noted to be 214.2 mAh g^{-1} . The discharge capacity was reduced to the value of 184.3 mAh g^{-1} in the subsequent cycle, which could be attributed to the formation of electrolyte decomposition products [33,34]. The discharge capacity of 183.5 mAh g^{-1} was obtained after the 100th cycle, which indicates

the stable performance of the electrode. The initial discharge capacity of 183.7 mAh g^{-1} was obtained for NMC352, and the value was reduced to 168.8 mAh g^{-1} at the end of the 100th cycle. The highest initial discharge capacity among all the as-prepared cathodes was observed for the NMC262 electrode, which demonstrated 285.8 mAh g^{-1} discharge capacity. In the subsequent cycle, an irreversible capacity loss of 10 mAh g^{-1} was found, and the discharge capacity was 275.6 mAh g^{-1} . At the end of the 100th cycle, NMC262 still afforded a high discharge capacity of 201.3 mAh g^{-1} , which was much higher than the final discharge capacities attained by NMC352 and NMC442. The high capacity of the NMC262 electrode is considered to be due to the loss of oxygen from the lattice during the first charge cycle and the reduction in the transition metal ions at the end of the first discharge cycle [14,35].

However, the high-capacity layered cathode electrode usually suffers from a large irreversible capacity loss in the first charge–discharge cycle. The initial coulombic efficiencies of the NMC442, NMC352 and NMC262 electrodes are 77.4, 75.7 and 76.6%, respectively. The low initial coulombic efficiencies of NMC cathodes is due to the large capacity loss during the initial cycle, which resulted from the irreversible loss of Li_2O from the Li_2MnO_3 region. It is also referred to as the degradation of electrolytes, and a solid electrolyte interphase (SEI) film [34,36]. Among these, the removal of Li_2O from Li_2MnO_3 is the main cause for the low initial coulombic efficiency due to the irreversible process [29,37]. For stoichiometric NMC cathodes, Mn^{4+} is generally considered to be inactive during charge–discharge processes. Therefore, different charge behavior at high voltage regions could be related to different contents of $\text{Ni}^{2+/3+/4+}$ and $\text{Co}^{3+/4+}$ [38]. Nevertheless, the electrochemically inactive Li_2MnO_3 region is activated after the removal of Li_2O during the process of activation at about 4.5 V. The final coulombic efficiencies of the NMC442, NMC352 and NMC262 electrodes after 100 cycles were found to be 98.24, 98.56 and 97.36%, respectively. The large increment enhancement observed in the coulombic efficiency values between the 50th and the 1st cycles represents the highly reversible capacities of all the NMC cathodes.

From these cycling durability data, it is strongly believed that the degradation of capacity after the initial charge/discharge cycle is due to the process of Li^+ extraction and O^{2-} oxidation [35]. The lower capacity retention of NMC262 is mostly due to the metal ion dissolution by manganese ions during the charge–discharge process. During discharge to low potential, Mn^{4+} is reduced to Mn^{3+} , which will damage the oxide surface and form a thicker SEI layer [37,39]. Surface coating with fluoride or oxide on Mn-rich NMC electrodes can improve cyclic performance and coulombic efficiency, as suggested in the literature [40].

Figure 5 shows the cyclic voltammetry of the as-synthesized NMC electrodes with variable Mn concentrations. The cyclic voltammetry was run between the voltage range of 4.7 and 2.0 V with a scan rate of 1 mV s^{-1} , for all the electrodes. The oxidation peak (anodic) is a result of the lithium extraction process and the reduction peak (cathodic) is due to the lithium insertion process. Figure 5a demonstrates the cyclic voltammetry results for NMC442, carried out at a current rate of 1 mV s^{-1} . During the first anodic cycle, the peak observed at 4.2 V shifts to 4.1 V for five cycles, which refers to the oxidation of Ni^{2+} and Co^{3+} to Ni^{4+} and Co^{4+} , respectively. Meanwhile, Li^+ ions are extracted from the layered structure of the NMC cathode; thus the peak observe at 4.6 V could be attributed to the activation of Li_2MnO_3 , as Li_2O is being released from the structure [41,42]. Meanwhile, the peak observed at 3.5–3.7 V, during the cathodic polarization cycle, refers to the lithium intercalation process.

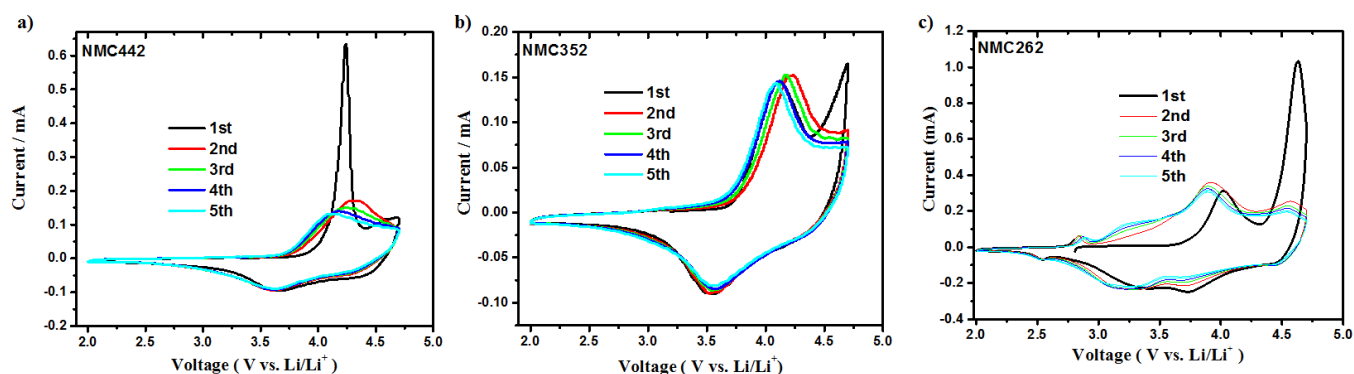


Figure 5. Cyclic voltammetry at the scan rate of 1 mV s^{-1} for (a) NMC442, (b) NMC352; (c) NMC262.

Cyclic voltammograms of NMC352 are presented in Figure 5b, while the graph of the peak current (I_p) versus square root of the scan rate (v) is presented in Figure S3. Together with Equation (2), the diffusion coefficient of NMC262 was calculated to be $2.2 \times 10^{-14} \text{ cm}^2 \text{ s}^{-1}$. During the charge process, the peaks in the range of 4.1–4.2 V correspond to Ni^{2+} and Co^{3+} oxidation to a tetravalent state. Once again, the peak observed at 4.69 V refers to the activation of Li_2MnO_3 due to the lithium extraction process. During the cathodic cycle, the peaks observed at 3.52–3.57 V indicate the lithium insertion process. Figure 5c demonstrates the current voltage curves for NMC262. The high redox potential around 4.4–4.5 V in NMC262 is due to the partial oxidation of Co^{3+} to Co^{4+} that corresponds to the transfer of the second electron. The high irreversible capacity reported in the first CV cycle of NMC262 after 4.62 V was indicated by a large anodic peak, as shown in Figure 5c. After the first CV cycle of all the NMC electrodes, all the successive CV peaks overlapped each other, showing no loss in capacity within the 2.0–4.7 V ranges. While charging to 4.7 V, the electrochemical activation of the Li_2MnO_3 component is followed by its decomposition to Li_2O and MnO_2 . Therefore, the peak observed at 3.18–3.25 V can be ascribed to the anodic oxidation peak of $\text{Mn}^{3+}/\text{Mn}^{4+}$ and reduction at 3.0 V of $\text{Mn}^{3+}/\text{Mn}^{4+}$ that takes place after the Li_2MnO_3 component is activated [29,43]. The partial transformation of $\text{Mn}^{4+}/\text{Mn}^{3+}$ confirms the redox activity of Mn, which was considered earlier to be electrochemically inert. Previous studies, however, have established that Mn^{3+} favors reversible cycling [7,44].

Figure 6 shows the comparison of the rate capability of NMC442, NMC352 and NMC242 at different current densities of 20, 40, 80, 120, 240, 480, 1200, 2400, and 3600 mA g^{-1} in the voltage range between 2.0 V and 4.7 V at room temperature. When the charging rate was increased in the aforementioned sequence, the discharge capacities of 187.5, 160.3, 129.4, 100.5, 93, 54.6, 21.1, 17.9, and 15.9 mAh g^{-1} were achieved for NMC442. Thereafter, upon reducing the current rate to 1200, 480, 240, 120, 80, and 40 mA g^{-1} , stable discharge capacities of 15.2, 15.4, 36, 65.8, 87.7 and 107.4 mAh g^{-1} were obtained, respectively.

For NMC352, the discharge capacities of 187.9, 143, 118.6, 107.7, 87.5, 66.9, 64.1, 64.2, and 63.9 mAh g^{-1} were obtained as the current was increased in the sequence described above. Afterwards, when the current rate was reduced to 1200, 480, 240, 120, 80, and 40 mA g^{-1} , discharge capacities of 62.1, 63.9, 85.0, 103.7, 116.2 and 140.2 mAh g^{-1} were achieved, respectively.

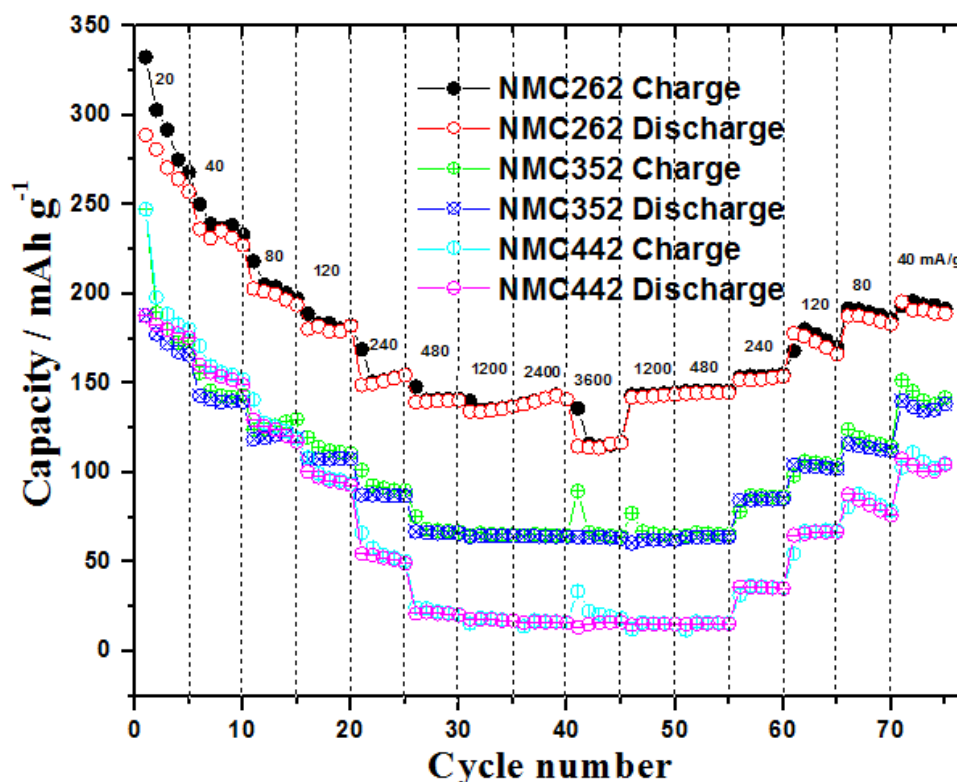


Figure 6. C-rate test of NMC262, NMC352 and NMC442 cathode materials in the voltage range of 2.0–4.7 V with current densities of 20, 40, 80, 120, 240, 480, 1200, 2400, and 3600 mA g^{−1}, respectively.

Meanwhile, the highest discharge capacities were observed for NMC262, i.e., 228.8, 236.2, 202.9, 180.5, 148.9, 139.3, 134, 138.2, and 113.9 mAh g^{−1}, which correspond to the charging rates of 20, 40, 80, 20, 240, 1200, 2400, and 3600 mA g^{−1}, respectively. When the current rate was decreased again to 1200, 480, 240, 120, 80, and 40 mA g^{−1}, discharge capacities of 142.2, 144.5, 151.7, 176.2, 187.7, and 195.5 mAh g^{−1} were obtained, respectively, implying the high structural stability of the NMC262 electrode even at high current rates.

These results indicate that Mn-rich NMC262 is an efficient material for high-rate lithium-ion battery cathodes, providing maximum power output and minimum charging time. The highly reversible capacity of NMC262, achieved after cycling at different current rates, can be ascribed to its high surface area, controlled particle size, and good structural stability, which helps in improving its electrochemical performance, as well as its high discharge capacity [45]. Thus, our research established that the carbonate co-precipitation method could be a good choice for synthesizing materials with a high discharge capacity and high tapping density; however, the synthesis condition should be carefully controlled to prepare material with proper particle sizes [46].

To further understand the reason behind the outstanding performance of NMC262, TEM analyses were carried out on the material after it was charged to 4.5 V, 4.7 V, and after 100 cycles of discharge at 2.0 V, as shown in Figure 7a–c, respectively. When charged to 4.5 V, the TEM image of NMC262 shown in Figure 7a illustrates regions of amorphous layers between the grains of the cathode material. Additionally, crystalline grains demonstrate the strain-induced modulation of the crystal structure, which is visible in the form of alternating bright and dark bands across some of the grains, as shown in Figure 7a. This could be attributed to the material's deterioration during the initial charge/discharge cycle and could be the reason behind the further capacity loss during cycling [47,48]. Figure 7b shows the TEM images of the electrode charged to 4.7 V. This sample shows larger grains that are free of strain, and demonstrate overall higher crystallinity. Additionally, some grains display clear high-contrast lattice fringes with the d-spacing of 4.7 Å that corresponds to the (003) plane of the composite structure, indicating excellent structural integration of the

$\text{Li}_2\text{MO}_3\text{-LiMO}_2$ components at the atomic level. The result of TEM analysis for the sample after 100 charge/discharge cycles is shown in Figure 7c. The amorphous surface is clearly apparent on the electrode after 100 cycles. The formation of a spinel-like phase due to the side reactions between the active material and electrolyte, is responsible for the gradual rise of 3 V in the composite electrode [49,50].

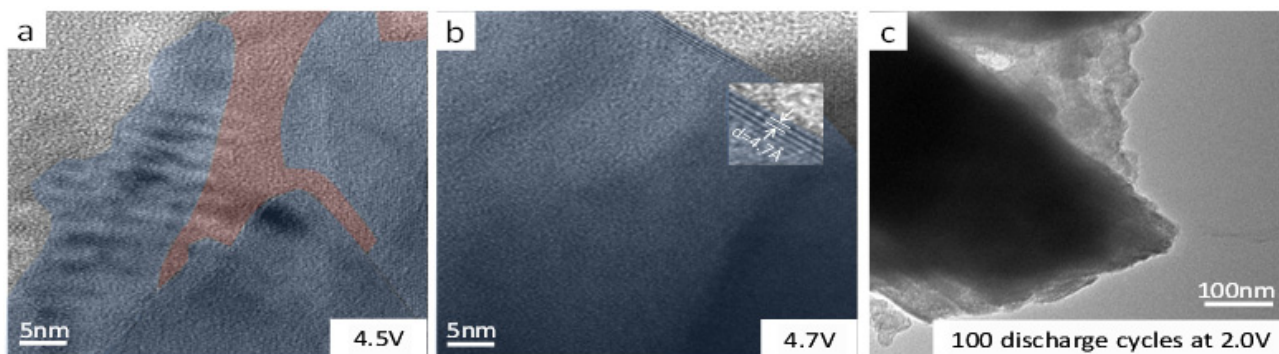


Figure 7. TEM micrographs of NMC262 after charging to (a) 4.5 V and (b) 4.7 V, and (c) after 100 cycles of discharge at 2.0 V.

The large initial irreversible capacity loss is due to Li_2O extraction and O-vacancy elimination in the lattice during the first charge cycle [14,51,52]. There is evidence of side reactions between the electrolyte and the extracted oxygen, which produce a thick electrolyte interface layer on the electrode surface that results in a rise in impedance and drastic capacity loss [53]. A large amount of the extracted Mn ions migrate to the vacant octahedral sites in the lithium layer through the adjacent tetrahedral sites [54]. The structural phase transformation results from the crystal surface cause the reconstruction of the surface layer with a gradual voltage drop during cycling. Overall, the TEM analysis after the charge and discharge cycles reveals that high-voltage operation does not cause structural degradation to NMC262, which could be ascribed to the high Mn concentration in the lattice of NMC262.

3.3. Lithium-Ion Diffusion Coefficient Studies

The diffusion coefficients of lithium ions in the high-capacity NMC262 cathode materials were determined using cyclic voltammetry (CV) with a scan speed of 0.1, 0.2 and 1 mV s^{-1} , as shown in Figure S2 and by electrochemical impedance spectroscopy (EIS) in Figure S4. For the EIS, the diffusion coefficient of lithium-ion was calculated using the following equation [55–57]:

$$D = \frac{R^2 T^2}{2 A^2 n^4 F^4 C^2 \sigma^2} \quad (1)$$

where R is the gas constant, T is the absolute temperature, A is the surface area of the cathode/electrolyte interface, which is 0.3848 cm^2 in this work, n is the number of electrons per molecule during oxidation ($n = 1$ for lithium ion intercalation/deintercalation), F is the Faraday constant ($96,486 \text{ C mol}^{-1}$), C is the concentration of lithium-ions, and σ is the Warburg factor, which obeys the following relationship [55–57]:

$$Z = R_e + R_{ct} + \sigma \omega^{-\frac{1}{2}} \quad (2)$$

where R_e is the resistance between the electrolyte and electrode, and R_{ct} is the charge transfer resistance, ω is the angular frequency and Z is the real part of Warburg impedance. The Warburg factor was determined from the slope of the linear fit of Z against the inverse square root of angular frequency, as shown in Figure S1, and the diffusion coefficient using EIS was calculated to be $4.99 \times 10^{-13} \text{ cm}^2 \text{ s}^{-1}$.

For the CV, the Randle–Sevcik equation was used to determine the Li-ion diffusion coefficient, by assuming a semi-infinite diffusion [55–57].

$$I_p = 0.4463F \left(\frac{F}{RT} \right)^{1/2} C v^{1/2} A D^{1/2} \quad (3)$$

In this equation, I_p is the peak current (A); F is the Faraday constant ($96,486 \text{ C mol}^{-1}$); A is the surface area of the electrode (cm^2); D is the diffusion coefficient of the Li ion ($\text{cm}^2 \text{ s}^{-1}$); C is the concentration of the Li ion (mol cm^{-3}); v is the CV scanning rate (V s^{-1}); and R is the gas constant. In Figure S3, the cathodic and anodic peak currents (I_p) were plotted against the square root of the scan rate v and the cathodic and anodic slopes were then used with Equation (3) to calculate the diffusion coefficient of the NMC262 electrode to be around $4.76 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$, and $2.1 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$, respectively. In this NMC262 electrode, the diffusion of Li^+ is around 2.3 times faster during the de-lithiation than lithiation, which is similar to Li^+ ion diffusion coefficient observed by cyclic voltammetry in the reported literature [58,59].

To further illustrate the irreversible capacity loss, an EIS study was carried out on a freshly prepared NMC262 cell, after which the same cell was cycled, and a second EIS study was performed. The EIS result plotted in Figure S4 showed an increase in both bulk and interface resistance after cycling, as detailed in Table S1. This increase in resistance can be attributed to the buildup of solid electrolyte interphase (SEI) during the formation cycle.

4. Conclusions

A cost-effective and scalable carbonate co-precipitation method was utilized to synthesize NMC material with various compositions for NMC cathodes that operate at high voltages. All three compositions demonstrated high discharge capacities, good rate capabilities and elongated cycle life. Nevertheless, the Mn-rich cathode outperformed the other NMC compositions in terms of discharge capacity obtained at the 100th cycle, which was 201.6 mAh g^{-1} for NMC262. Moreover, a phenomenal rate capability of 138, and 114 mAh g^{-1} at 10 and 15 C, respectively, was attributed to the structural stability and controlled particle size of NMC262. Owing to the remarkable performance of $\text{LiNi}_{0.2}\text{Mn}_{0.6}\text{Co}_{0.2}\text{O}_2$, this NMC composition can be considered as an efficient alternative cathode material for next-generation high-voltage lithium-ion batteries with enhanced rate capabilities.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/en15228357/s1>, Figure S1: Graph of Warburg Impedance (Z') vs inverse square root of angular frequency at varying temperatures. (Inset: Arrhenius plot of the apparent diffusion constants); Figure S2: Cyclic Voltammetry plot for NMC262 at different scan rate (0.1 mV/s , 0.2 mV/s , 1 mV/s) and 30°C ; Figure S3: Graphs of cathodic and anodic peak current (I_p) vs square root of scan rate (v); Figure S4: Impedance of half-cell with NMC262 before and after cycling. Inset is the Equivalent circuit model; Figure S5: SEM images of sample NMC 262 at magnifications of (a) 500, (b) 1000, (c) 2000 and EDS mappings of (d) Ni, (e) Mn, (f) Co and (g) O; Figure S6: SEM images of sample NMC 352 at magnifications of (a) 500, (b) 1000, (c) 2000 and EDS mappings of (d) Ni, (e) Mn, (f) Co and (g) O; Figure S7: SEM images of sample NMC 442 at magnifications of (a) 500, (b) 1000, (c) 2000 and EDS mappings of (d) Ni, (e) Mn, (f) Co and (g) O; Table S1: Impedance analysis of NMC262 half-cell before and after cycling; Table S2: Atomic ratios calculated based on EDS spectrums.

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