

Research Article

Effect of Solvents in Electrospray of Ni-Rich Layered Materials for High-Performance Cathodes in Lithium-Ion Batteries

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Electrospray, introduced to the coating process, enables the fabrication of porous electrodes, and electrosprayed cathodes exhibit improved cycle performance. Further, the solvent used in the cathode slurry of the electrospray coating plays a crucial role. This study investigated the effects of various solvents on the electrospray of Ni-rich layered materials for electrode fabrication as an alternative to conventional slurry coating using the doctor-blade method. The electrode performance of a typical doctor blade method using the N-methyl-2-pyrrolidone (NMP) solvent, which has various disadvantages (boiling and autoignition temperature), was compared with that of electrosprayed cathodes using NMP; N,N-dimethylformamide (DMF); and DMF/acetone solvents. The volatility difference between the three solvents resulted in the creation of individual cathodes with different porosities. For the DMF/acetone solvent, which had the highest volatility, the coated cathode showed 75.97% capacity retention after 100 cycles at 1C, which was significantly higher than those of the NMP (62.91%) and DMF (66.25%) solvents. Electrochemical impedance spectroscopy (EIS) showed a stable peak retention during cycling and a low increase in individual resistance for the DMF/acetone solvent cathode. To conclude, optimizing solvent selection in electrosprayed cathodes is highly critical for enhancing the cathode cycling performance, contributing to high-performance lithium-ion batteries.

Keywords: acetone; DMF; electrospray; electrospraying; lithium-ion batteries; NMP

1. Introduction

Lithium-ion batteries have attracted considerable attention and research as promising power sources for electric and hybrid electric vehicles (EVs and HEVs, respectively), and emergency stop signal (ESS) systems [1–5]. Among the prospective cathode materials for lithium-ion batteries, lithium nickel cobalt manganese oxide ($\text{LiNi}_{1-x-y}\text{Co}_x\text{Mn}_y\text{O}_2$), also referred to as NCMs, exhibits several advantageous properties, including relatively low cost, high capacity, and good rate capability [6–8]. However, NCMs are structurally and thermally unstable in high-charge states, owing to poor cycling characteristics [9]. This is because the structural modification of the oxide surface results in an increase in cathode impedance within the Li-ion battery, which in turn leads to a reduction in the battery's cycle life [10]. Various techniques, such as coating [11], doping [12], and nanostructure [13], have been applied to improve the

electrochemical performance of NCM cathodes. Furthermore, research has been conducted on the thickness of the electrode [14] and modifications to the morphology of the cathode based on the solvent used in casting [15, 16].

Conventional electrode processes typically involve coating a slurry on aluminum foil using a slot-die, comma, or blade coater [15]. However, these coatings have various challenges, as reported in previous studies, and electrospray has been introduced to the coating process to improve them. Unlike conventional blade coatings, electrospray enables the fabrication of porous electrodes [17]. During the charge/discharge reaction, a porous, electrosprayed cathode reacts with the entire electrode, unlike cathodes provided by conventional coatings, delaying the degradation of the electrode [18]. Consequently, electrosprayed cathodes exhibit improved cycle performance, compared with conventional cathodes [17].

TABLE 1: Comparison of properties of the conventional cathode-slurry solvent, NMP, and DMF.

Solvent	Boiling temperature (°C)	Autoignition temperature (°C)	Surface tension γ (mN/m)	Viscosity η (mPa·s)	δ_D (MPa ^{0.5})
NMP	202	252	40.3	1.7	18.0
DMF	155	445	35.2	0.9	17.4

Note: DMF is N-dimethylformamide; NMP is N-methyl-2-pyrrolidone; δ_D = Hansen solubility parameter for polyvinylidene fluoride (PVDF) of the energy form dispersion forces between molecules [22, 23].

The solvent used in the cathode slurry of the electrospray coating plays a crucial role. In Electrospray, the concentration of the solution is low, so the electric field causes the solution to break down and create microdroplets. The evaporation rate of the solvent plays an important role in this process: higher volatility solvents evaporate quickly as the droplets form, causing the solid portion to form earlier, which can result in a highly developed porous structure. In contrast, lower volatile solvents will take a longer time for the droplets to form and for the solution inside them to evaporate, resulting in a dense structure. In other words, in electrospray, the size of the droplets and the rate at which they evaporate will have a significant impact on the structure of the electrode [19].

In general, N-methyl-2-pyrrolidone (NMP) is the solvent used for slurry mixing in conventional electrode processes. As a highly polar solvent, NMP has high solubility compared to other organic solvents, making it highly useful for many chemical reactions that require an inert medium. Moreover, NMP is chemically and thermally stable, making it a popular solvent in the pharmaceutical, chemical, and battery industries [15, 20, 21]. However, NMP is a toxic solvent, and considerable research on alternatives has been conducted. N,N-dimethylformamide (DMF) is a suitable alternative solvent for NMP [22]. DMF has a lower boiling and higher autoignition temperature than NMP, requiring less energy to dry and consequently improved stability. As shown in Table 1, low surface tension improves wettability, and low viscosity allows for more cathode-active material-concentrated slurries [22, 24]. In addition, mixing polyvinylidene fluoride (PVDF) binder and solvent changes the color of the affected slurry solution. In the NMP slurry, PVDF can form hydrofluoric acid (HF) when exposed to strongly alkaline conditions and C=C bonds similar to thermal degradation; therefore, PVDF-NMP slurries suffer from dehydrofluorination degradation [23, 25]. Finally, DMF has a similar solubility to NMP; therefore, the slurry solvent conversion from NMP to DMF has many advantages for many battery applications.

DMF is mainly used as the solvent in PVDF-based electrospinning. In addition, acetone has been added as a binary solvent to control fiber morphology and diameter. The reason for using acetone in electrospinning is to improve the volatility of the solvent to reduce evaporation time and improve crystallinity [26–28]. Acetone is also present in the NCM cathode materials used in lithium-ion batteries. Tang et al. showed that when acetone reacts with NCM811, a 5-nm layer of NiO rock-salt phase is formed, which protects the structural framework of the particles. This NiO layer provides a significantly low internal resistance during the charge–discharge cycle, which improves the electrochemical performance [29].

The volatility of the solvent used in the cathode slurry substantially affected the electrochemical performance of the

cathode. Lee et al. formed mud cracks because of the difference in the volatility of the solvent used in the cathode slurry. They reported that the larger the crack density, the larger the active area of Li⁺ ions, and thus, the better the electrochemical performance [30]. Thus, the difference in the volatility of the solvent can be exploited to significantly affect the performance of the NCM cathodes.

In our previous study, the electrospray coating method was introduced to enhance the electrochemical performance of Ni-rich NCM811 cathodes compared to the conventional blade coating method. The results demonstrated that electrospray coating significantly improved the cycling stability, achieving a capacity retention of 75.98% after 100 cycles at 1C, compared to 47.13% for blade-coated cathodes. The enhanced performance was attributed to the increased porosity and uniform dispersion of the conductive additive, which facilitated better lithium-ion transport and mitigated surface degradation [17].

Building upon these findings, this study further investigates the influence of different solvent systems on the electrosprayed NCM811 cathode. While the previous research confirmed the advantages of ES coating, the impact of the slurry solvent composition on electrode porosity, active surface area, chemical reaction, and overall electrochemical properties required further exploration. By examining NMP, DMF, and a binary solvent system (DMF + acetone), this study identifies an optimal solvent for electrospraying NCM811 cathodes, considering electrochemical performance, environmental impact, and cost efficiency. The results provide a deeper understanding of solvent effects and contribute to the refinement of electrospray-based electrode fabrication for next-generation lithium-ion batteries.

2. Experimental

2.1. Materials and Solution Preparation. The precursor of P_x-Ni_{0.8}Co_{0.1}Mn_{0.1}(OH)₂ was prepared through a coprecipitation reaction under an N₂ atmosphere, by mixing LiOH · H₂O (Li:TM = 1:1.02) and calcining under an O₂ atmosphere at 775°C for 12 h. Therefore, we constructed the NCM811 for use in our experiment. NCM811, carbon black, and Solef 6020 PVDF (Solvay, Brussels, Belgium), serving as active material, conductive additive, and binder, respectively, were mixed in a 94:3:3 mass ratio, and NMP anhydrous 99.5 (Sigma Aldrich, St. Louis, MO, USA), DMF (Guaranteed Reagent, Daejung Chemicals, Siheung, Korea), and DMF + acetone (Guaranteed Reagent, Daejung Chemicals) in a 5:5 volume ratio were added to obtain the appropriate viscosity. The solution was stirred at 2000 rpm for 5 h using a PH-91 homogenizer (SMT Co., Ltd., Tokyo, Japan).

2.2. Electrospray. Electrospray is a technique used for nano-micro scale film. In this study, extremely low solution concentrations were used to fabricate porous thin electrodes. The process employed a single-nozzle setup (nozzle adaptor, NanoNC, Seoul, South Korea), with a syringe pump (Fusion 100-X, dual-channel precision dosing pump, Chemyx, Stafford, TX, USA) maintaining a steady flow rate of 2.5 mL/h. A drum-type collector (NNC-DC90H, NanoNC) was used as the conveyor belt line in the electrode process. The distance between the nozzle tip and the rotating drum was fixed at 15 cm, and an electric field of 11–13 kV was applied to initiate the electrospray process. To prevent clogging due to the passage of NCM811 particles through the nozzle, a 20-gauge plastic tip (inner diameter: 0.6 mm; outer diameter: 0.9 mm; NanoNC) was attached to the syringe.

2.3. Electrochemical Characterization. All electrochemical tests were conducted using a 2032 coin cell. The cathode was mixed with the active material, carbon black, and PVDF binder in a weight ratio of 94:3:3. Subsequently, the cathode slurry was coated on Al foil, which was then dried at 120 °C for 30 min and finally roll-pressed. The battery was assembled within a glovebox [argon atmosphere, oxygen concentration (<0.01 ppm), and water concentration (<0.01 ppm)]. The opposite electrode was composed of lithium, and the electrolyte, a solution containing 1 mol/L LiPF_6 , was added. The solvent was a 3:7 (v/v) mixture of ethylene carbonate (EC) and ethyl methyl carbonate (EMC). Constant current charge–discharge measurements were performed using a battery tester (Wontec, City, Abb. State, Country). The NMP, DMF, and DMF + acetone experiments were subjected to electrochemical testing under identical conditions, with performance evaluated at 1C between 3.0 and 4.3 V versus Li/Li^+ at room temperature. The active material loadings of the NMP, DMF, and DMF + acetone samples are 4.087, 4.193, and 4.04 mg/cm^2 , respectively.

2.4. Analysis. Field-emission structural equation modeling (FE-SEM, SIGMA300, Carl Zeiss, Oberkochen, Germany) was used to analyze deposition conditions, porosity, and morphology of the electrodes. The crystal structure of the NCM811 cathode composite was characterized by X-ray diffraction (XRD) using $\text{Cu K}\alpha$ radiation (New D8-Advance, Bruker-AXS, Billerica, MA, USA). To analyze the surface chemical composition of the NCM811 cathode, X-ray photoelectron spectroscopy (XPS) (K-alpha, Thermo Fisher Scientific, Waltham, MA, USA) was used. A field emission transmission electron microscope (FE-TEM; JEM-F200, Jeol Ltd., Tokyo, Japan) was used to analyze the NiO protective layer of the NCM811 particles. FE-SEM, XRD, and XPS measurements were performed for electrodes before and after 100 cycles in a half-cell. The cathode was soaked in dimethyl carbonate (DMC, 99%, Acros Organics, Geel, Belgium) for a certain period before measurement.

3. Results and Discussion

All samples were prepared using NMP, DMF, and DMF + acetone solvents at a ratio of 94:3:3 of cathode active material, carbon black, and PVDF (binder), respectively, to prepare the

cathode slurry. These electrodes were named NMP, DMF, and DMF + acetone cathodes (NC, DC, and DAC), respectively. The NCM811 cathode was fabricated by electrospray instead of conventional blade coating using these slurries. As shown in Figure S1, the cathode from the conventional blade coating exhibited a dense surface structure, whereas a porous structure was observed during the electrospray process (Figure 1a–c). The morphology and porosity of the resulting products depend on the volatility of the solution. Under high volatility, most of the solvent is easily volatilized before the slurry reaches the Al foil and aggregates during electrospraying. This was confirmed by the multiple spherical cathode morphologies. The solvents used in this experiment exhibited high volatility in the order $\text{NMP} < \text{DMF} < \text{DMF} + \text{acetone}$. Higher volatility led to more spherical structures on the surface, which increased the porosity and enlarged the active area of the Li^+ ions (Figure S2). To demonstrate that the porosity increased with the difference in volatility of the solvent, the density of each sample was measured (Table S1). The densities of the blade coating, NC, DC, and DAC electrodes were found to be 4.6842, 3.7841, 3.4784, and 2.9011 g/mL , respectively. This indicates that for the same weight of sample, the more volatile solvent has a lower density. This density proves that DAC has the highest porosity and NC has the lowest porosity. The porosity of an electrode significantly affects its electrochemical performance.

Orikasa et al. [18] reported that the lower the porosity of the electrode (the smaller the active area of Li^+ ions), the faster the degradation, because the reaction mainly occurs on the electrode surface during charge and discharge cycles. Therefore, it can be expected that the sample with the highest volatility, the DMF + acetone solvent, would have the best cycling characteristics. All samples exhibited a typical layered $\alpha\text{-NaFeO}_2$ structure (space group $R\bar{3}m$) with sharp (006)/(102) and (108)/(110) doublet splitting peaks before cycling, indicating a well-ordered hexagonal layered structure (Figure 1d–g). The different solvents in the coating slurry did not cause any structural changes through chemical reactions to the NCM active material. Furthermore, both cathodes produced by conventional blade coating and electrospray coating exhibited similar peaks and intensities (Figure S3a). However, one difference was observed in the coating method, where the NCM cathode cast via electrospray showed a slight shift of the (003) peak to a lower angle (Figure S3b). This is attributed to the increased layer spacing due to the electrostatic repulsion of the lithium-deficient lattice [31, 32], and is a structural defect caused by the high voltage used to cast onto the collector during the electrospray process. A small amount of Li-ion delithiation occurred during the process, which changed the oxidation number of Ni and needs to be further studied about this [33].

Figure 2a demonstrates the cycle performance of individual NC, DC, and DAC. For NC, DC, and DAC, the initial discharge capacities at 1C were 157.43, 163.44, and 167.4 mAh/g , while the discharge capacities after 100 cycles were 99.04 mAh/g with 62.91% cycle retention, 108.29 mAh/g with 66.25% cycle retention, and 127.17 mAh/g with the best retention of 75.97%, respectively. The decreased initial capacity of NC is probably attributed to the formation of PVDF-NMP slurry. When PVDF reacts with NMP, dehydrofluorination degradation

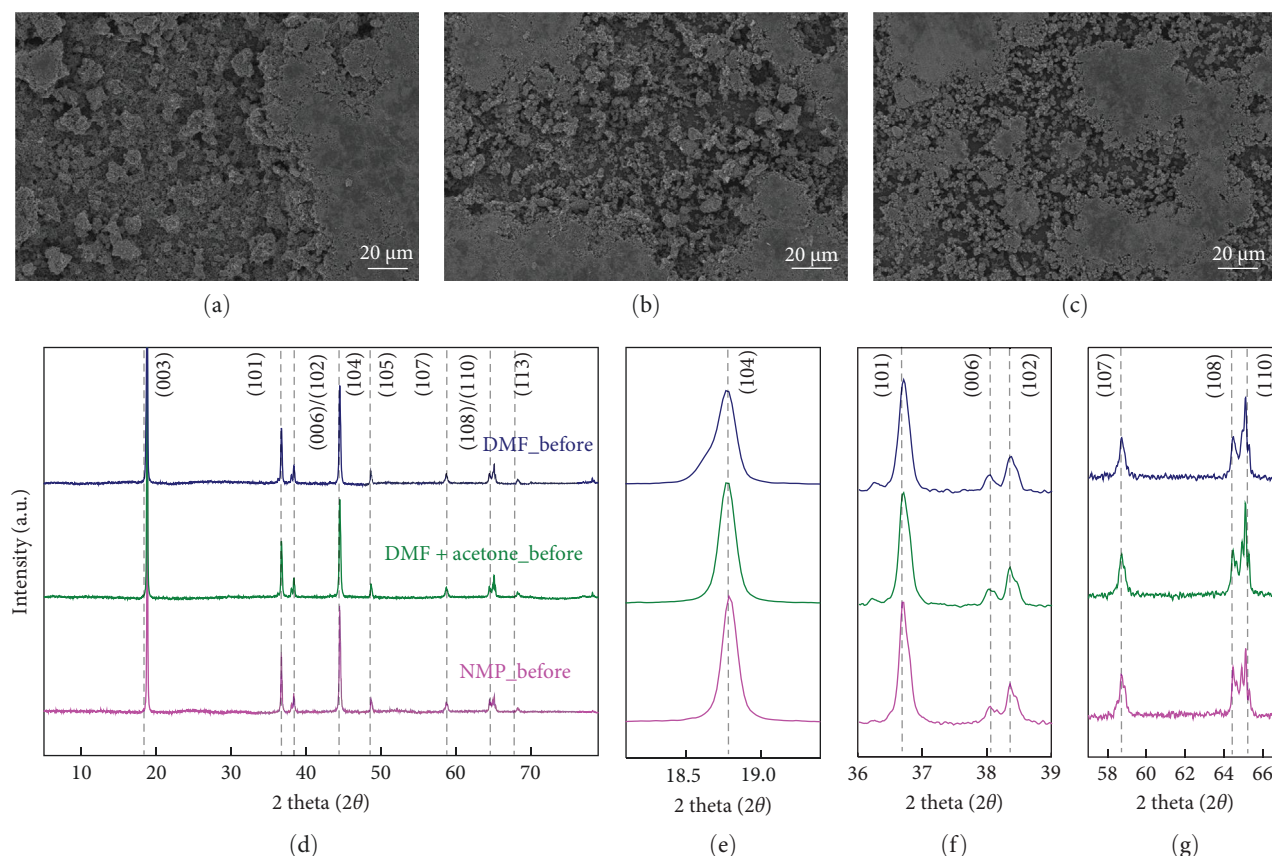


FIGURE 1: FE-SEM images of electrospayed NCM811 cathode according to the solvent in the cathode slurry before the cycle: (a) NMP, (b) DMF, and (c) DMF + acetone. XRD patterns before cycling of electrospay coated NCM811 cathode, using NMP, DMF, and DMF + acetone-slurry solvents. The 2θ ranges were (d) 5° – 80° , (e) 18.5° – 19.5° , (f) 36° – 39° , and (g) 57° – 67° .

occurs. This results in a color change from transparent to a brown or red color (Figure S4), the formation of C=C double bonding, and gelation of the PVDF, which leads to a decrease in the initial capacity of the NC [23, 25]. Furthermore, the initial capacity discrepancy between DC and DAC can be attributed to the reaction of high Ni cathode particles with acetone. When Ni-rich cathode particles and acetone were mixed, a ca. 5 nm NiO rock-salt layer was formed on the surface of DAC, which serves as a protective layer (Figure S5) [29]. A robust NiO layer formed on the surface of cathode particles can improve the structural stability with more stable cycling performance, as revealed in Figure 2a. Figure 2b displays a comparison of the rate performance of individual cathodes. NC exhibited discharge capacities of 229.46, 209.34, 181.76, 155.75, 122.08, and 53.48 mAh/g at 0.1, 0.2, 0.5, 1, 2, and 5C, respectively. When the C rate was subsequently changed to 0.2C after the rate test, the discharge capacity changed to 190.17 mAh/g, indicative of a 90.84% reduction in capacity relative to the initial 0.2C. In DC and DAC, significant decreases in discharge capacity were observed, compared with NC, from 0.1 to 2C. At 5C, these two electrodes displayed a similar capacity of 86.97 mAh/g and 89.35 mAh/g, respectively, indicating superior rate performance than that of NC. When the C rate was changed to 0.2C after 5C, DAC showed a capacity recovery of 98.1%, showing better cycle reversibility than NC (90.84%) and DC (93.98%).

Figure 3a,c,e shows the galvanostatic charge–discharge curves of NC, DC, and DAC between 3.0 and 4.3 V vs. Li/Li^{+} , respectively. After the 1st, 10th, 50th, and 100th cycles, the discharge capacities of NC were 157.43, 147.40, 120.41, and 99.04 mAh/g, respectively. For DC, the discharge capacities were 163.44, 158.91, 139.75, and 108.29 mAh/g, respectively, showing slightly better capacity retention than NC. However, DAC exhibited the best capacity retention, with discharge capacities of 167.4, 162.12, 149.13, and 127.17 mAh/g, respectively. The best cathode performance of the DAC can be attributed to the well-developed electrode morphology owing to the difference in the volatility of the selected solvents. During the electrospay process, the morphology and porosity are highly dependent on the volatility of the solvent. The solvents used in this experiment had high volatility in the order $\text{NMP} < \text{DMF} < \text{DMF} + \text{acetone}$, which resulted in a more developed porosity with spherical particle aggregation in DAC because of the highest volatility. This typical morphology is extremely helpful for better accessibility of lithium ions and provides sufficient space for mechanical relaxation during charge–discharge. This typical electrode structure can improve cycling properties by maintaining the interparticle ionic pathway.

To clarify the electrochemical behavior during cycling, the differential potential/voltage (dQ/dV) curves of the three cathodes were plotted, as shown in Figure 3b,d,f. For both DC and DAC, three phase transitions occurred during the

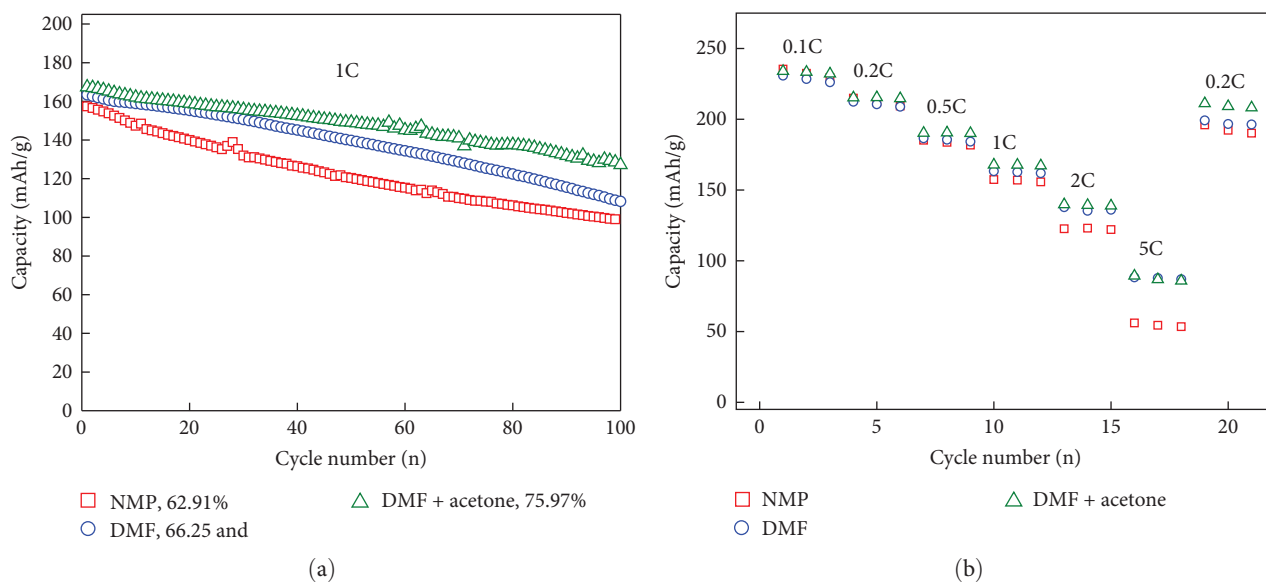


FIGURE 2: (a) Cycle stability at 1C and (b) rate performance of NMP, DMF, and DMF + acetone samples discharged at different current densities.

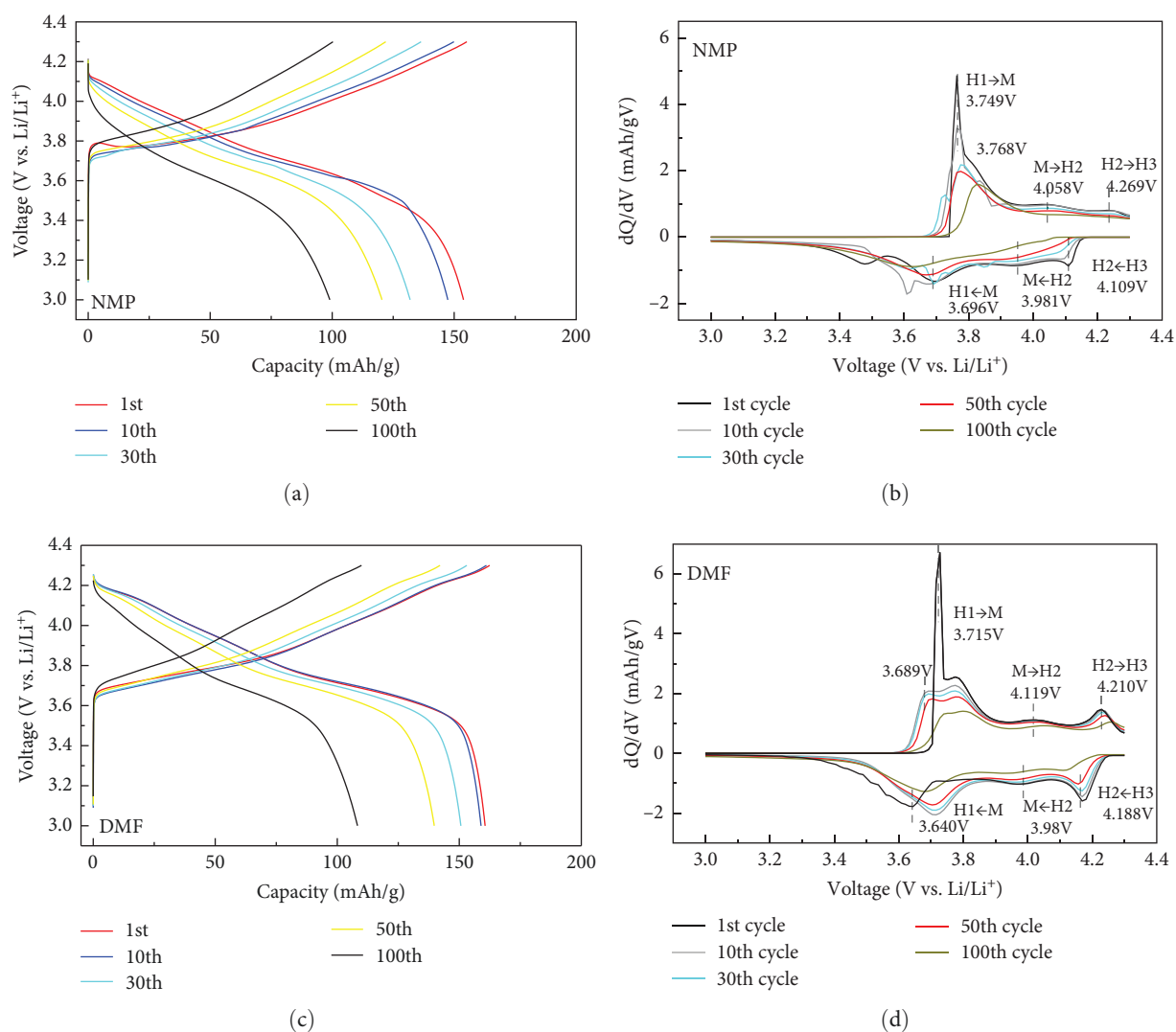


FIGURE 3: Continued.

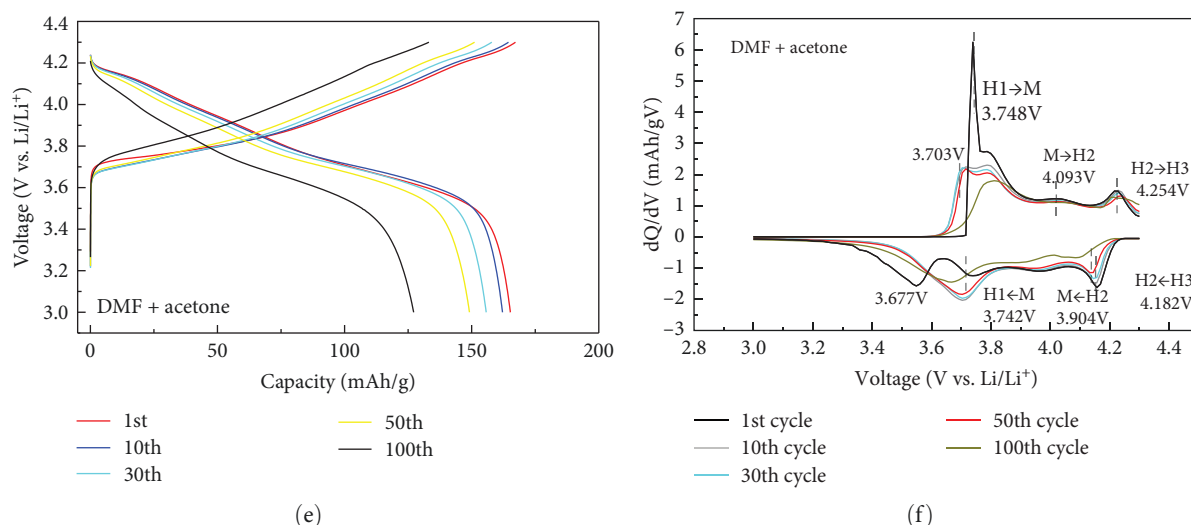


FIGURE 3: Charge/discharge profiles of the various cathode-slurry solvents at 1C: (a) NMP, (c) DMF, and (e) DMF + acetone. dQ/dV curves of various cathode-slurry solvents: (b) NMP, (d) DMF, and (f) DMF + acetone.

lithiation–delithiation process. For DAC, the 1st charge–discharge peak pair associated with the hexagonal 1 (H1)–monoclinic (M) phase transition was formed with a significantly small potential difference of 0.006 V (3.748–3.742 V). In contrast, those of the NC and DC were 0.053 V (3.749–3.696 V) and 0.075 V (3.715–3.640 V), respectively. This indicates that DAC exhibited the best reversibility during the first cycle. Furthermore, the shape and peak intensity of the dQ/dV curve in the DAC were well maintained with an increasing number of cycles, indicating the stable reversibility of individual electrochemical reactions during charge–discharge cycles. An additional reduction peak at ~3.677 V was observed in the first-cycle dQ/dV curve of the DAC electrode (Figure 3f). This peak can be attributed to the porous, low-density microstructure formed by the rapid evaporation of the DAC solvent system, which increases the lithium-ion accessible surface area and promotes surface or near-surface lithiation. This phenomenon shows that nanostructured, porous NCM electrodes exhibit additional dQ/dV features due to region-specific responses [34].

To investigate the changes in the individual electrochemical reactions during cycling, electrochemical impedance spectroscopy (EIS) experiments were conducted on the three cathodes. For this purpose, the EIS spectra of the three cathodes were measured at 4.3 V after formation and after 10, 50, and 100 cycles. Changes in the overall Nyquist patterns are shown in Figure 4. From the nonlinear least squares fitting using the equivalent circuit within the inset, Table 2 lists the variations in film (R_f) and charge transfer (R_{ct}) resistance. The purpose of this analysis is to focus on the change in resistance from formation to 100 cycles, not the numerical value of resistance. Also, as shown in Figure S7 and Table S2, the resistivity values of the samples are not high enough to significantly affect the electrical conductivity. Therefore, the change in resistivity with increasing cycles is an important value for proper electrospray coating solvent studies. As listed, the R_f of NC increased by 13.129 Ω (from 8.731 to 21.86 Ω for formation and 50 cycles),

and a resistance increase of 5.28 Ω was observed from 50 to 100 cycles (from 21.86 to 27.14 Ω). In comparison, the R_f of DC increased by 7.05 and 4.98 Ω under similar measurement conditions, which is a smaller increase compared with that of NC. When NCM811 slurry is prepared using a mixed solvent of DMF and acetone, it is observed that acetone reacts with the NCM811 particle surface to form a 1–5 nm thick NiO protective layer, which can partially retard the crack formation during further cycling. In particular, the structural stability can be induced by a well-established NiO protective surface layer in the DMF + acetone sample. When using NMP or DMF solvent, on the contrary, the electrolyte can be further reacted with the newly created interface in the inner cracks within cathode particles. Hence, a more stable cathode–electrolyte interface (CEI) film could be formed in acetone case, showing the improved long-term cycle performance and durability. Also, the stable surface CEI film in the cathode under DMF and acetone solvent was confirmed by EIS spectra after 100 cycles, as shown in Figure 4 [29]. In addition, DAC exhibited the smallest increase in R_f among the three cathodes, as R_f change was 1.01 and 3.43 Ω , respectively. Furthermore, the R_{ct} of the DAC exhibited a pattern comparable to that observed for R_f . Similarly, DAC showed that R_{ct} increase was 13.76 Ω (from 27.14 Ω at 50 cycles to 40.9 Ω at 100 cycles), which was the smallest among those of the three cathodes. These resistance changes coincided with other electrochemical performance parameters, such as cycling, rate, and dQ/dV.

All the samples were disassembled after 100 cycles, and the individual cathodes were immersed in DMC to remove the SEI film on the surface. The three cathodes displayed no significant change from the initial to after cycles, indicating a limited structural change in the cathode particles (Figure 5a–c). The XRD peak positions of all three electrodes showed similar changes in the peak patterns from the initial to after 100 cycles (Figure 5d–f). Compared with those of the initial cathodes, the

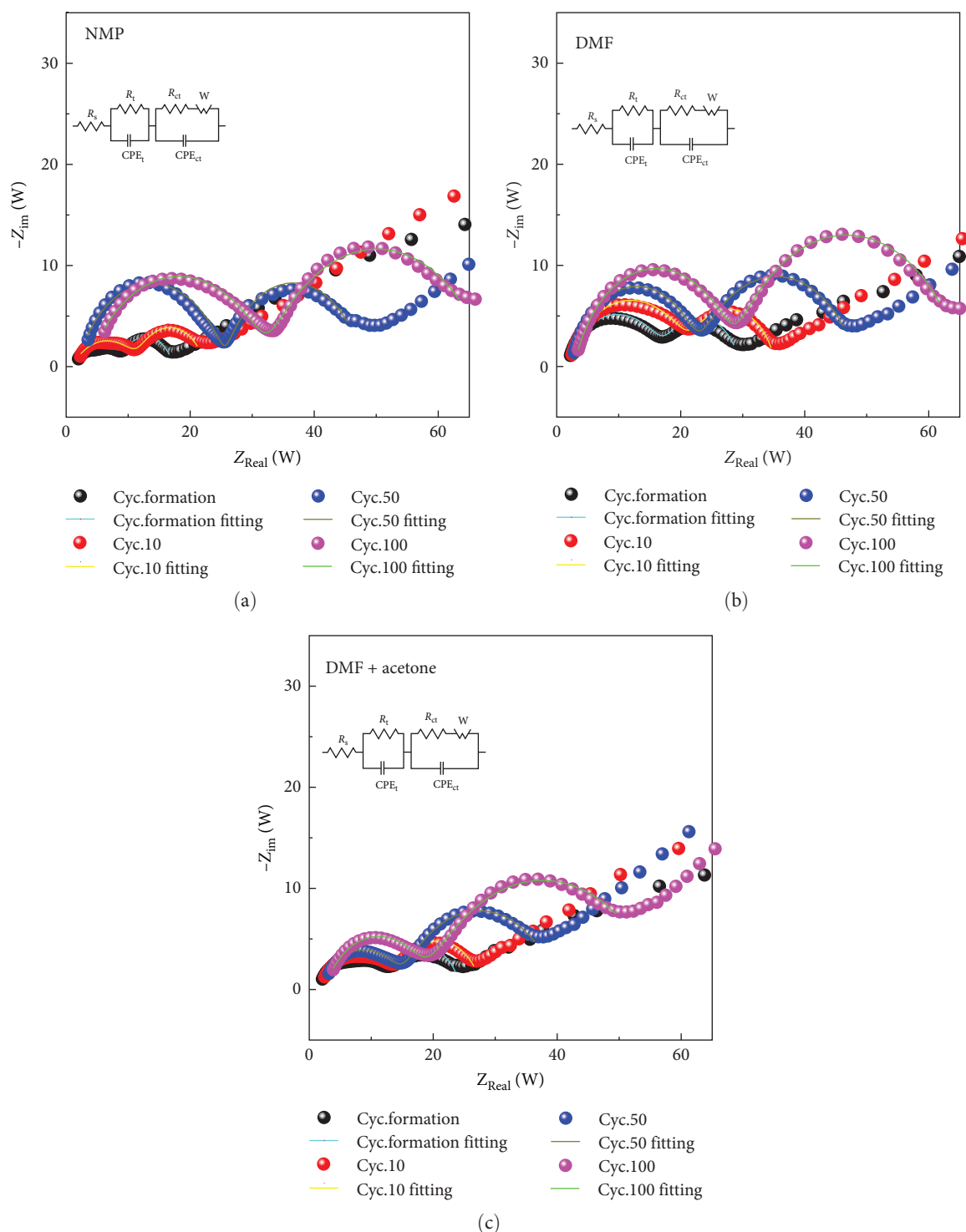


FIGURE 4: Nyquist plots of (a) NMP, (b) DMF, and (c) DMF + acetone at formation; 10th, 50th, and 100th cycles.

peak intensities of the three electrodes decreased, with unclear doublet peak splitting in the (006)/(102) and (108)/(110) lattices. Tables 3 and 4 outline the results of the calculations of the lattice parameters of the three cathodes, initially and after 100 cycles, respectively. Obviously, the intensity ratio of the (003) and (104) peaks, which usually represent cation mixing,

indicates that the degree of degradation was greater than 1.2, with limited contamination by rock-salt domains. This indicates the occurrence of retarded cation mixing [35]. Comparison of the findings presented in the two tables showed that the reduction ratio of $I(003)/I(104)$ was different for different solvents. The percentage decrease in the intensity ratio from the

TABLE 2: Nyquist analysis of the cells of various cathode-slurry solvents.

Sample	Cycle	R_f (Ω)	R_{ct} (Ω)
NMP	Cyc.formation	8.731	8.007
	Cyc.10	9.256	14.18
	Cyc.50	21.86	25.85
	Cyc.100	27.14	44.02
DMF	Cyc.formation	13.27	16.86
	Cyc.10	16.78	18.5
	Cyc.50	20.32	26.23
	Cyc.100	25.3	41.38
DMF + acetone	Cyc.formation	11.26	13.52
	Cyc.10	11.69	16.02
	Cyc.50	12.42	27.54
	Cyc.100	16.01	40.79

Note: R_f , film resistance; R_{ct} , charge transfer resistance.

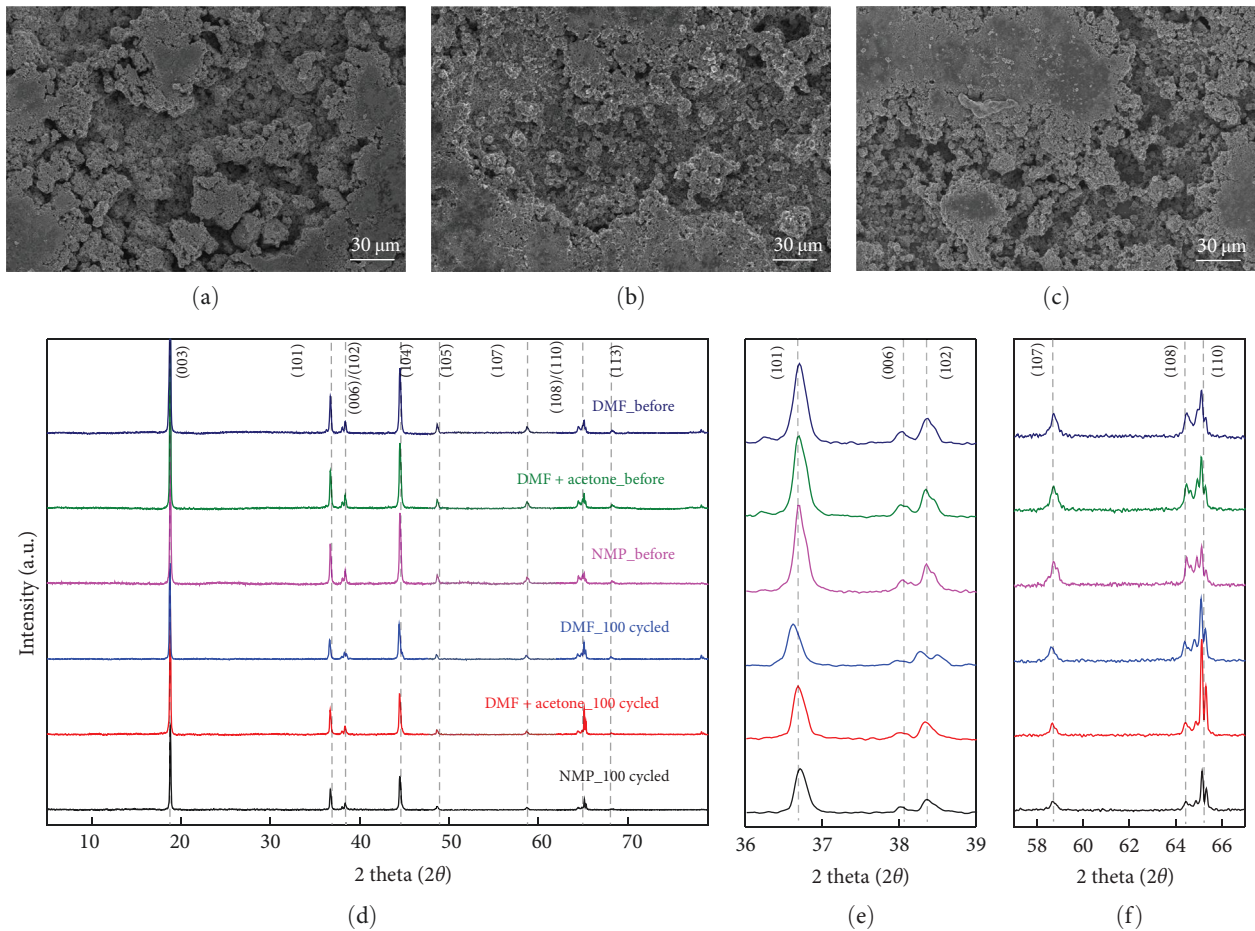


FIGURE 5: FE-SEM images of electrospayed NCM811 cathode according to the solvent in the cathode slurry after 100 cycles: (a) NMP, (b) DMF, and (c) DMF + acetone. XRD patterns before and after cycles of electrospay coated NCM811 cathode, using NMP, DMF, and DMF + acetone-slurry solvents. The 2θ ranges were (d) 5° – 80° , (e) 36° – 39° , and (f) 57° – 67° .

initial to after cycling for NC, DC, and DAC was -17% , -10% , and -3% , respectively. Although all three cathodes exhibited intensity ratios above 1.2, the results showed that the structural degradation was similar for all the cathodes.

In Ni-rich layered cathodes, the ionic state of Ni has a significant impact on battery performance [36]. Cation mixing occurs during the charge and discharge cycles, where the positions of Li^+ and Ni^{2+} , which have similar ionic radii, are

TABLE 3: Lattice parameters and peak intensity ratio before cycle of electrosprayed NCM811 cathode using various cathode-slurry solvents.

Before cycle	NMP	DMF	DMF + acetone
<i>a</i>	2.851	2.85	2.851
<i>c</i>	14.17	14.174	14.177
<i>c/a</i>	4.97	4.972	4.973
Volume	99.77	99.742	99.795
I(003)/I(104)	3.049	2.750	3.265

TABLE 4: Lattice parameters and peak intensity ratio after 100 cycles of electrosprayed NCM811 cathode using various cathode-slurry solvents.

After 100 cycle	NMP	DMF	DMF + acetone
<i>a</i>	2.850	2.854	2.851
<i>c</i>	14.174	14.193	14.174
<i>c/a</i>	4.973	4.972	4.971
Volume	99.712	100.143	99.794
I(003)/I(104)	2.558	2.485	3.162

reversed (Figure S6). When cation mixing occurs, the structure changes, and the NiO phase with poor ionic conductivity increases, which hinders the diffusion of Li^+ [37]. The XPS results demonstrate that the Ni 2p peaked, Ni-rich cathode materials split into two peaks, Ni 2p_{3/2} and Ni 2p_{1/2}, and that the peaks of Ni^{2+} and Ni^{3+} are important (Figure 6). Typically, as the contribution of the Ni^{2+} ions increases, more reduction from Ni^{3+} to Ni^{2+} occurs, which results in an increase in the rock salt NiO phase, leading to increased cation mixing [38]. By comparing the three cathodes before and after cycling, the ratio of $\text{Ni}^{2+}/(\text{Ni}^{2+} + \text{Ni}^{3+})$ of 2p_{3/2} via the peak intensity was quantitatively analyzed, indicating the extent of cation mixing and phase transformation. The $\text{Ni}^{2+}/(\text{Ni}^{2+} + \text{Ni}^{3+})$ ratios of NC, DC, and DAC in the initial state were 44.54%, 39.81%, and 39.19%, respectively, reaching 27.52%, 26.81%, and 17.75%, respectively, after 100 cycles. These results indicate that NC exhibits poor electrochemical performance, as shown in Figures 2 and 3, which is ascribed to greater cation mixing than that in the other two cathodes during cycling.

Figure 7 shows the XPS results for the O and C bonding. Here, the Ni 2p XPS as well as the O 1s, Li 1s, and P 2p XPS results coincide with the electrochemical results in Figures 2 and 3. The O 1s data in this figure are split into C—O, C=O (Li_2CO_3), and metal oxide peaks. The higher the ratio of the metal oxide peaks, the fewer the defects formed on the surface. In addition, a higher ratio of the metal oxide peak correlated with a reduction in the structural defects occurring in the Ni-rich cathode crystal during the charge and discharge cycles. This is due to the reduced oxygen outflow during side reactions, which, in turn, minimizes the risk of thermal runaway [39]. A comparison of the metal oxide peaks of the three cathodes before and after cycling revealed the reduction ratios of the metal oxide peaks to be 65.67%, 56.42%, and 37.33%, respectively. This indicates fewer surface defects in the order of NC, DC, and DAC. Figure S8 shows the XPS peaks for Li 1s. The Li [40] 1s peaks of the cathodes correspond to three peaks of intercalated Li, LiOH, and Li_2CO_3 . The ratio of intercalated lithium in NC decreased by 32.64% after cycling compared

with that before cycling, whereas it decreased by 27.14% for DC and 20.31% for DAC. This indicates that DAC has the most intercalated lithium even after cycling, and that more available lithium ions can diffuse as the cycle continues with a high capacity. Finally, Figure S9 shows the XPS peak of P 2p, which enables the quantitative analysis of the impedance of the surface. The SEI film formed during the cycle was composed of LiPF_6 , $\text{Li}_x\text{PO}_y\text{F}_z$, and phosphor ions, and the higher peak ratio of $\text{Li}_x\text{PO}_y\text{F}_z$ indicated higher impedance [41]. As shown in Figure S9, compared with that of DC, the $\text{Li}_x\text{PO}_y\text{F}_z$ peak ratio of NC was higher both before and after cycling. These results support the Nyquist plots shown in Figure 4 and Table 2.

4. Conclusion

From the electrospray process for NCM811 cathodes, the solvent effects were investigated to replace the conventional doctor blade coating method. According to the volatility of the three solvents, the cathode surface area and porosity increased in the order of DMF + acetone, DMF, and NMP, and the highest capacity retention after 100 cycles at 1C was observed in DMF + acetone (75.97%), followed by DMF (66.25%) and NMP (62.91%). Due to the influence of acetone, a NiO protective layer was formed on the surface of DMF + acetone solvent, which showed the highest initial discharge capacity of 167.4 mAh/g at 1C. EIS analysis showed internal resistance increases with more charge and discharge cycles in the order of NMP, DMF, and DMF + acetone. With the change in solvent during the electrospray process, the surface structure and morphology changed owing to the difference in volatility, and the electrochemical performances were different. Table S1 shows that the electrodes prepared by the electrospray process have a less dense structure than the conventional blade coating method, indicative of a more developed porous structure in the former electrodes. One can expect that ionic transport is partially improved in more porous electrode, while electrical conductivity can be hindered due to less particle contact. However, it is more significant that stable cycle performance cannot be

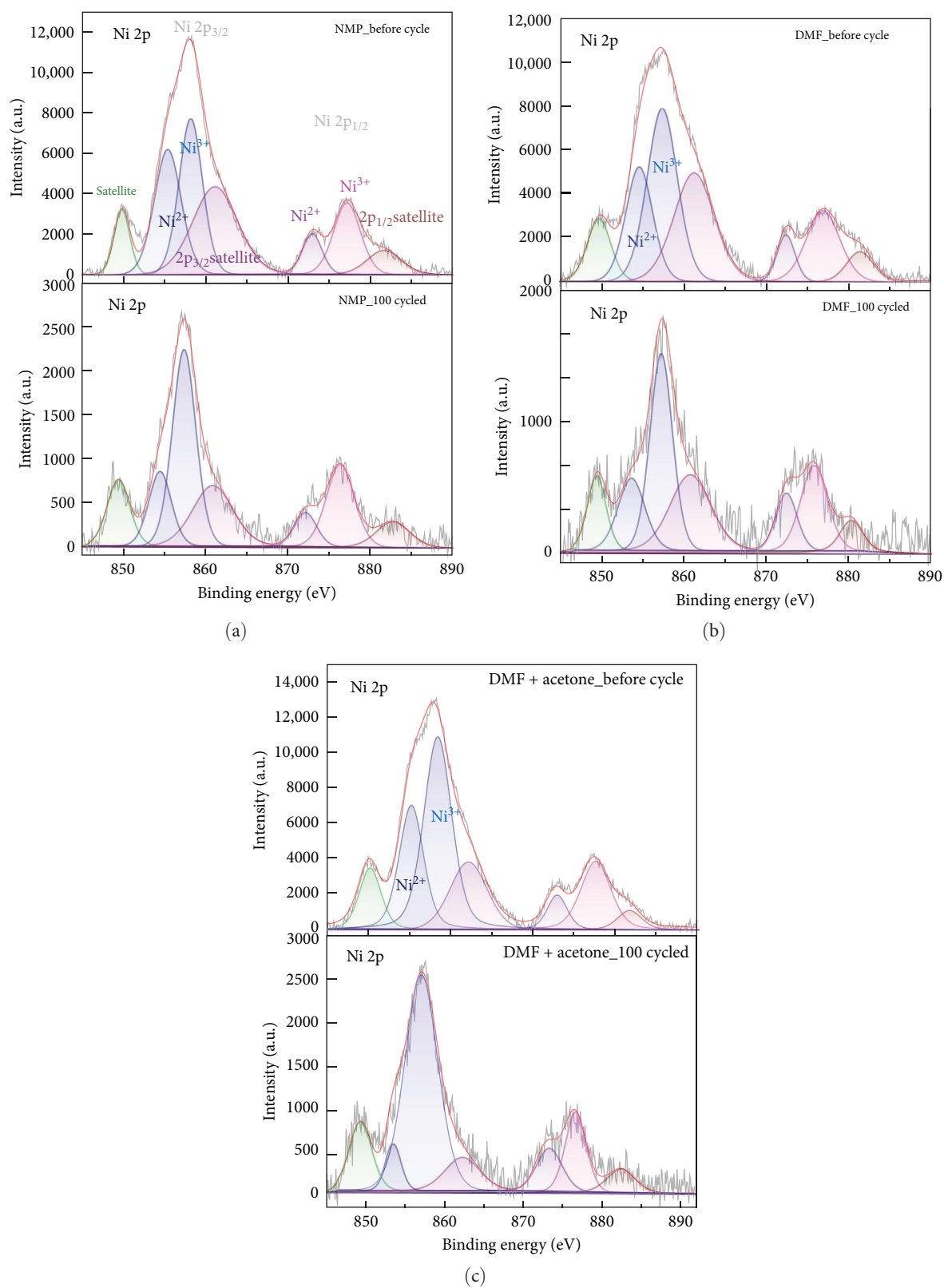


FIGURE 6: XPS spectra of Ni 2p before and after 100 cycles of NCM811 cathode using various cathode-slurry solvents: (a) NMP, (b) DMF, and (c) DMF + acetone.

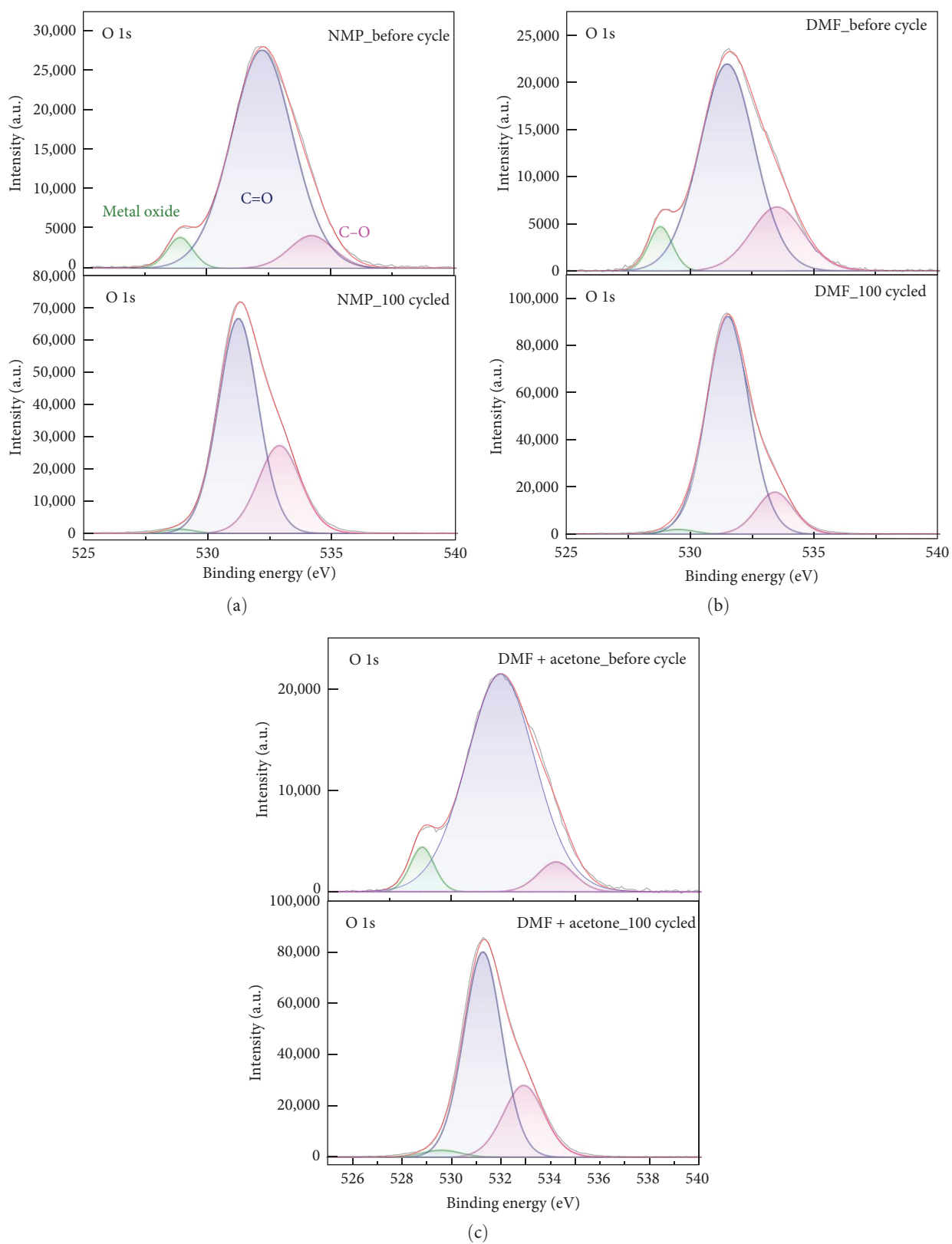


FIGURE 7: XPS spectra of O 1s for before and after the 100th cycle of the NCM811 cathode using various cathode-slurry solvents: (a) NMP, (b) DMF, and (c) DMF + acetone.

attained by a simple decrease of electrode density, which is discussed in the electrochemical analysis. Furthermore, there can be proposed several solutions to increase electrode density. (1) Optimization of the “roll press” process allows the electrode material to be more tightly bonded to the collector, which improves conductivity. A good contact with the collector optimizes the electron transport paths and increases the conductivity within the electrode. Furthermore, by increasing the particle density inside the electrode through roll press, the transport paths of ions and electrons are more efficiently connected, which also increases the conductivity. (2) Additional mixing of carbon black or CNTs to strengthen electron conduction pathways. This creates a 3D carbon network in the porous structure, which helps electrons pass through the electrode quickly without being diverted. (3) Optimize the electrospray process. Since there are many different parameters in the electrospray process, it is possible to control these parameters to optimize the porous structure for improved electrical conductivity. Forming a denser porous structure while maintaining porosity can provide the benefits of both electrical conductivity and Li-ion activity.

In terms of electrochemical, economic, and environmental aspects, DMF + acetone is considered the best solvent combination for electrosprayed cathodes. The reason for this is to reduce the amount of highly toxic DMF and NMP, and use acetone, which is less toxic and relatively inexpensive. Future studies should focus on further refining the electrospray parameters and exploring additional solvent systems to achieve even greater enhancements in battery performance. This study contributes to broader efforts to improve the efficiency and longevity of lithium-ion batteries, thereby supporting the advancement of EVs and other energy-storage applications.

Nomenclature

DMC:	Dimethyl carbonate
DMF:	Dimethylformamide
EIS:	Electrochemical impedance spectroscopy
ESS:	Emergency stop signal
EVs:	Electric vehicles
FE-SEM:	Field-emission structural equation modeling
FE-TEM:	Field emission transmission electron microscope
HEVs:	Hybrid electric vehicles
HF:	Hydrofluoric acid
$\text{LiNi}_{1-x-y}\text{Co}_x\text{Mn}_y\text{O}_2$:	Lithium nickel cobalt manganese oxide
NCM:	Nickel cobalt manganese oxide
NMP:	N-methyl-2-pyrrolidone
PVDF:	Polyvinylidene fluoride
XRD:	X-ray diffraction.

Data Availability Statement

The data that support the findings of this study are available upon request from the corresponding author. The data are not publicly available due to privacy or ethical restrictions.

Conflicts of Interest

The authors declare no conflicts of interest.

Author Contributions

JinUk Yoo and Dong Chul Kang: conceptualization, formal analysis, investigation, resources, writing – original draft. **Hyun Chul Kang:** data curation, validation, visualization. **Sung Gyu Pyo and Songhun Yoon:** writing – review and editing, supervision. JinUk Yoo and Dong Chul Kang contributed equally to this study.

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Supporting Information

Additional supporting information can be found online in the Supporting Information section. (*Supporting Information*) Figure S1: FE-SEM image of (a) blade-coated cathode and (b) electrosprayed cathode before cycle. Figure S2: FE-SEM image of NCM811 cathode using different cathode-slurry solvents before cycling at high magnification; (a) NMP, (b) DMF, and (c) DMF + acetone. Figure S3: XRD patterns before the cycle of the blade and electrospray-coated NCM811 cathode, using different slurry solvents; 2 range is (a) 5° – 80° and (b) 18.5° – 19.5° . Figure S4: Actual photo of PVDF-NMP and PVDF-DMF after reaction. Figure S5: Transmission electron microscope (TEM) of NCM811 active material particle using DMF + acetone slurry; (a) low and (b) high magnification. Figure S6: Schematic illustration of cation mixing in high nickel NCM cathodes. Figure S7: Nyquist plots of (a) blade-coated NCM811 and electrosprayed NCM811 using different solvents slurry; (b) NMP, (b) DMF, and (c) DMF + acetone at formation, 10th, 50th, and 100th cycles. Figure S8: XPS spectra of Li 1s for before and 100 cycles after of NCM811 cathode using various cathode-slurry solvents; (a) NMP, (b) DMF, and (c) DMF + acetone. Figure S9: XPS spectra of P 2p for before and 100 cycles after of NCM811 cathode using various cathode-slurry solvents; (a) NMP, (b) DMF, and (c) DMF + acetone. Table S1: The weight, thickness of active materials, and density of the Blade coating, electrosprayed cathode (using different solvents slurry) used to measure electrochemical performance. Table S2: Nyquist analysis of the cells of various cathode-slurry solvents.

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