Morphology-Controlled One-Step Synthesis of Nanostructured LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ Electrodes for Li-Ion Batteries

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ABSTRACT: Nanostructured electrodes effectively enhance the kinetics of the charge/discharge process in lithium-ion (Li-ion) batteries. However, the fabrication of these electrodes often involves complex processing steps. This study demonstrates a one-step improved flame spray pyrolysis synthesis approach to directly deposit the most common Li-ion battery cathode material LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ onto current collectors, which is identified as reactive spray deposition technology (RSDT). Because of the economical and continuous nature of RSDT, the industrial scale of manufacturing nanostructured electrodes for Li-ion batteries can be potentially developed. Morphologies of the electrodes are well controlled so that their electrochemical properties can be tailored to accommodate intended applications. In detail, by adjusting the precursor concentration in the solution feed during the operation of RSDT, the specific surface area of synthesized material can be fine-tuned accordingly. Although the electrodes prepared with low precursor concentration exhibit the highest surface area and deliver the highest initial discharge capacity of 192.1 mAh g$^{-1}$, the most stable cycling performance is demonstrated by the electrodes fabricated with high precursor concentration, retaining 93.6% of the initial capacity after 100 cycles in half-cell testing. This innovative direct deposition method considerably simplifies the manufacture process of high-performance nanostructured electrodes and enables effortless modification of their properties. Moreover, no hazardous waste is generated from this synthesis route.

INTRODUCTION

Until recent years, LiCoO$_2$ with layered structure has been the most widely applied cathode material in commercial lithium-ion (Li-ion) batteries due to its good cycling stability. However, high toxicity, high cost, and low practical capacity associated with this material considerably limit its scope of applications. To satisfy the need for novel cathode materials with enhanced properties to accommodate their use in portable electronics and electrical vehicles, one of the effective strategies is by engineering nanostructured LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ electrodes, as the diffusion lengths of electrons and ions are considerably reduced in this type of electrodes, so the kinetics of lithium storage can be effectively enhanced.

State-of-art synthesis methods for the preparation of nanostructured LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ electrodes are coprecipitation, spray pyrolysis, electrospinning, hydrothermal, and sol–gel. However, there are several shortfalls associated with these methods, such as complex time-intensive steps, irregular morphologies, and high equipment cost. Reactive spray deposition technology (RSDT), a flame combustion synthesis method in the open atmosphere, presents a superior alternative to fabricate the nanostructured electrodes. It is a single-step continuous process, offering the advantages of cost-
efficiency and scalability. In addition, the high combustion heat from the flame provides in-situ annealing to the electrodes and thus eliminates the need for postdeposition heat treatment.

The low-cost precursor materials (i.e. nitrates and acetylacetonates) and the highly combustible organic solvents (i.e. ethanol and xylene) are typically used to prepare the precursor solutions for RSDT. The atomization of the precursor solution creates a spray of aerosol droplets that are ignited to form a jet-flame. The precursors rapidly decompose in the high-temperature flame, followed by phase transition to vapor and homogeneous reactions to form the nanosized oxide particles. The particle formation and growth generally take place via the following mechanisms: homogeneous reactions, nucleation, coagulation, surface growth, cluster formation, coalescence, agglomeration, and aggregation. The nucleation and growth of the primary particles occur during time-of-flight. The synthesized materials are directly deposited onto the current collectors to form the electrodes. The intermediate steps required in the conventional pyrolysis and the conventional slurry-based electrode fabrication process are eliminated by RSDT. In addition, since the binder material is not required in this process, the energy density of the electrodes can be increased and the cost of the electrode fabrication can be reduced. More importantly, RSDT enables the effective control of the material properties via manipulation of the processing conditions. For example, by adjusting the precursor concentration, the synthesized material can be fine-tuned to the desired surface morphology and particle size distribution. In addition, no hazardous waste is generated from this synthesis route due to the complete combustion of the organic materials.

In this study, nanostructured LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ electrodes are fabricated by RSDT. By varying the precursor concentration in the solution feed, the physical and electrochemical properties of the electrodes are modulated accordingly. Crystal structures of the synthesized materials are analyzed by X-ray diffraction (XRD). Surface morphologies and microstructures of the electrodes are investigated by means of scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Electrochemical properties of the as-prepared electrodes are evaluated by cyclic voltammetry (CV), galvanostatic charge/discharge cycling, and electrochemical impedance spectroscopy (EIS).

## RESULTS AND DISCUSSION

### XRD Analysis

XRD patterns of the nanostructured LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ electrodes prepared by RSDT are shown in Figure 1. They can be indexed to the hexagonal lattice structure of α-NaFeO$_2$ with R$ar{3}$m space group. The intensities of the diffraction peaks are dependent on the precursor concentration in the feed solution. The particle size distribution is affected by the precursor concentration. The estimated particle sizes are in the range of 3 to 16 nm for NMC-1, 5 to 21 nm for NMC-2, and 7 to 32 nm for NMC-3. As the primary particles are formed via the coagulation of nuclei and/or monomer followed by complete sintering, an increase in the precursor concentration leads to higher initial particle number concentration and collision frequency, which together drive a higher rate of coagulation. Consequently, larger primary particles are produced. Subsequent collisions between the primary particles with partial sintering (necking between particles) leads to the formation of secondary phases with different particle sizes and morphologies. The secondary phase composition is dependent on the precursor concentration and the thermal treatment conditions. The secondary phase composition can be analyzed by XRD and other characterization techniques such as electron microscopy and spectroscopy. The secondary phases can affect the electrode performance, such as capacity retention and cycling stability. Therefore, it is important to understand the relationship between the secondary phase composition and the electrode performance.

### Microscopic Analysis

Surface morphologies of the nanostructured LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ electrodes are shown in Figure 2a–f. The uniform distribution of the cauliflower-shaped aggregates of the nanoparticles with interconnected pores on the current collector can be observed. As the precursor concentration increases, the aggregate size tends to gradually increase, coupling with a decrease in the specific surface area of the electrode material. The nitrogen adsorption/desorption isotherms of the as-synthesized LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ are shown as the inset images in Figure 2a–c, which correspond to the less-defined type IV with the hysteresis loops that are characteristic to the mesoporosity in the materials. The measured Brunauer–Emmett–Teller (BET) specific surface areas are 48.4, 22.9, and 9.8 m$^2$ g$^{-1}$ for NMC-1, NMC-2, and NMC-3, respectively. The primary mechanisms that account for the particle growth in the flame are coagulation and coalescence. It is expected that higher precursor concentration increases the initial concentration of particles in the flame, leading to a higher coagulation rate and higher degree of sintering. As a result, larger and more compact aggregates with lower specific surface area are deposited on the current collector. In the meantime, the electrode appears less porous with higher precursor concentrations. Upon closer inspection, no cracks or significant morphology variation can be detected in the electrodes, which suggests that the organic solvents are fully combusted before the particles reach the substrates.

TEM images of LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ nanoparticles are shown in Figure 2d–f. The aggregates are primarily consisted of spherical nanoparticles. Sheet particles with lattice fringes can be observed, demonstrating high crystallinity. It also shows a trend of increasing primary particle size with higher precursor concentration. The estimated primary particles sizes are in the range from 3 to 16 nm for NMC-1, 5 to 21 nm for NMC-2, and 7 to 32 nm for NMC-3. As the primary particles are formed via the coagulation of nuclei and/or monomer followed by complete sintering, an increase in the precursor concentration leads to higher initial particle number concentration and collision frequency, which together drive a higher rate of coagulation. Consequently, larger primary particles are produced. Subsequent collisions between the primary particles with partial sintering (necking between particles) leads to the formation of secondary phases with different particle sizes and morphologies. The secondary phase composition is dependent on the precursor concentration and the thermal treatment conditions. The secondary phase composition can be analyzed by XRD and other characterization techniques such as electron microscopy and spectroscopy. The secondary phases can affect the electrode performance, such as capacity retention and cycling stability. Therefore, it is important to understand the relationship between the secondary phase composition and the electrode performance.

![Figure 1. XRD patterns of LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ synthesized by RSDT with different precursor concentrations.](image-url)
formation of aggregates. Higher precursor concentration results in larger aggregates due to a faster sintering rate from more frequent collisions and more point contacts between the primary particles.

**Electrochemical Properties.** CV curves of the nanostructured LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ electrodes in the voltage window between 2.8 and 4.5 V are shown in Figure 3a. All of the samples demonstrate good electrochemical activity in the applied voltage window. Each type of the electrodes shows one pair of redox peaks that correspond to the redox reactions of Ni$^{2+}$/Ni$^{3+}$/Ni$^{4+}$ followed by Co$^{3+}$/Co$^{4+}$ during the intercalation/deintercalation process of Li$^+$ ions. No reduction peak of manganese with oxidation state of +4 is observed. These characteristics are consistent with those of the typical CV curves of LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ electrodes found in the literature.

Minor difference in the kinetics between the insertion and the extraction of Li$^+$ ions can be observed from the slightly higher anodic peaks than the cathodic peaks. Although the redox peaks of the electrodes appear to be symmetric, the peak separation enlarges with lower precursor concentration, which is 0.67, 0.49, and 0.36 V for NMC-1, NMC-2, and NMC-3, respectively. Smaller peak separation is an indication of better reversibility. Thus, NMC-3 has the highest reversibility among the three samples.

Figure 3b shows the specific discharge capacities and the corresponding Coulombic efficiencies of the nanostructured LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ electrodes fabricated by RSDT as a function of the cycle number, which are obtained galvanostatically in the voltage window between 3.0 and 4.5 V. NMC-1 delivers the highest initial specific discharge capacity of 192.1 mAh g$^{-1}$, but it also shows more pronounced capacity fading with a retention ratio of 68.9% at the end of 100 cycles. Although NMC-3 delivers the least initial specific discharge capacity among all three samples, which is 171.9 mAh g$^{-1}$, it
demonstrates the most stable cycling performance with a capacity retention ratio of 93.6%. In addition, the initial specific discharge capacity and the capacity retention ratio over 100 cycles of NMC-2 are 185.9 mAh g⁻¹ and 85.5%, respectively.

Table 1. Electrochemical Performance of the Bare LiNi₁/₃Co₁/₃Mn₁/₃O₂ Reported by Different Synthesis Methods

| materials and compositions | synthesis method               | initial discharge capacity (mAh g⁻¹) | capacity retention after charge/discharge cycling test | rate capability (mAh g⁻¹) | references |
|----------------------------|---------------------------------|-------------------------------------|-------------------------------------------------------|---------------------------|------------|
| LiNi₁/₃Co₁/₃Mn₁/₃O₂        | flame spray pyrolysis           | 168 at 18 mA g⁻¹ (2.8 – 4.5 V)      | 71.4% after 30 cycles at 18 mA g⁻¹                    | not reported              | 30         |
| LiNi₁/₃Co₁/₃Mn₁/₃O₂        | spray pyrolysis                 | 133.7 at 0.5C (2.0 – 4.5 V)         | 97.1% after 20 cycles at 0.5C                         | 125.7 at 1C               | 31         |
| LiNi₁/₃Co₁/₃Mn₁/₃O₂        | ultrasonic spray pyrolysis      | 170 at 20 mA g⁻¹ (2.8 – 4.4 V)      | 96% after 50 cycles at 20 mA g⁻¹                      | 132.6 at 4C               | 32         |
| LiNi₁/₃Co₁/₃Mn₁/₃O₂        | combustion synthesis            | 150 at 1.25C (3.0 – 4.5 V)          | 68.7% after 100 cycles at 1.25C                       | 120 at 2.5C               | 33         |
| LiNi₁/₃Co₁/₃Mn₁/₃O₂        | nanoetching template            | 159.6 at 0.2C (2.8 – 4.3 V)         | 90% after 100 cycles at 1C                            | 135.5 at 5C               | 34         |
| LiNi₁/₃Co₁/₃Mn₁/₃O₂        | sol–gel                        | 175.7 at 0.5C (2.5 – 4.5 V)         | 72.4% after 100 cycles at 1C                          | 101.7 at 5C               | 35         |
| LiNi₁/₃Co₁/₃Mn₁/₃O₂        | sacrificial template            | 177.8 at 0.5C (2.5 – 4.5 V)         | 61.7% after 100 cycles at 1C                          | 126.0 at 5C               | 36         |
| LiNi₁/₃Co₁/₃Mn₁/₃O₂        | solid-state reaction            | 191.0 at 0.1C (2.5 – 4.5 V)         | 83.3% after 50 cycles at 0.1C                         | 90 at 5C                  | 37         |
| LiNi₁/₃Co₁/₃Mn₁/₃O₂        | coprecipitation                 | 178.4 at 0.1C (2.5 – 4.4 V)         | 93.7% after 100 cycles at 0.5C                        | 135 at 5C                 | 38         |
| LiNi₁/₃Co₁/₃Mn₁/₃O₂        | solid-state reaction            | 164.0 at 0.1C (2.7 – 4.3 V)         | 95.1% after 100 cycles at 1C                          | 114.5 at 5C               | 39         |
| LiNi₁/₃Co₁/₃Mn₁/₃O₂        | in situ sacrificial template    | 182 at 0.5C (2.5 – 4.4 V)           | 67.6% after 100 cycles at 0.5C                        | 78 at 3C                  | 40         |
| LiNi₁/₃Co₁/₃Mn₁/₃O₂        | solvo/hydrothermal              | 171 at 0.1C (2.5 – 4.5 V)           | 87.7% after 50 cycles at 0.1C                         | 120 at 10C                | 41         |
| LiNi₁/₃Co₁/₃Mn₁/₃O₂        | RSDT                            | 171.9 at 0.5C (3.0 – 4.5 V)         | 93.6% after 100 cycles at 0.5C                        | 122.8 at 5C               | this work  |

Figure 3. Electrochemical properties of the nanostructured LiNi₁/₃Co₁/₃Mn₁/₃O₂ electrodes fabricated by RSDT with different precursor concentrations: (a) CV curves in the potential range between 2.8 and 4.5 V at the scan rate of 1.0 mV s⁻¹; (b) cycling performance at 0.5 C in the potential range between 3.0 and 4.5 V; (c) galvanostatic charge/discharge curves for the 1st, 25th, 50th, 75th, and 100th cycles; (d) rate capabilities from 0.5 to 10 C.
The Coulombic efficiencies of the first charge/discharge cycle are 76.8, 83.9, and 90.7% for NMC-1, NMC-2, and NMC-3, respectively. It shows that NMC-1 suffers the most significant loss of the reversible capacity during the first cycle, which can be attributed to its high specific surface area resulting in the excessive side reactions with the electrolyte. However, the Coulombic efficiencies of all of the samples quickly increase after the initial cycle and maintain above ~98% after the fifth cycle. The charge/discharge curves of the nanostructured LiNi_{1/3}Mn_{1/3}Co_{1/3}O_{2} electrodes are shown in Figure 3c, which correspond to the typical behavior of the layered Li-Ni_{1/3}Mn_{1/3}Co_{1/3}O_{2} reported in the literature.\(^{3,7}\) The sloped plateaus stem from the redox couples of Ni\(^{2+}/Ni^{3+}\) and Ni\(^{3+}/Ni^{4+}\) during the charge/discharge process. The obtained electrochemical testing results suggest that high surface area of the nanostructured LiNi_{1/3}Mn_{1/3}Co_{1/3}O_{2} electrodes fabricated by RSDT is beneficial for enhancing the initial specific discharge capacity, which is due to increased contact area with the electrolyte, increased accessibility to the active sites, and increased utilization of the electrode capacity. However, there is more significant capacity loss associated with high surface area since a larger portion of the active materials are subjected to side reactions with the electrolyte solution.\(^{13}\) Consequently, there is a trade-off that needs to be made between the high initial discharge capacity and the cycling stability. In addition, the electrochemical performance of the nanostructured LiNi_{1/3}Mn_{1/3}Co_{1/3}O_{2} electrodes fabricated by RSDT is comparable to or superior to those reported for the state-of-the-art LiNi_{1/3}Mn_{1/3}Co_{1/3}O_{2} cathode materials prepared by both the pyrolysis/combustion route and the wet chemistry synthesis methods (Table 1). Hence, it demonstrates the feasibility of employing RSDT to prepare the high-performance nanostructured electrodes for the application in Li-ion batteries.

Rate capabilities of the as-prepared LiNi_{1/3}Mn_{1/3}Co_{1/3}O_{2} electrodes are investigated by galvanostatic cycling at the stepwise increased discharge current rates from 0.5 to 10 C. The corresponding results are shown in Figure 3d. It can be observed that the specific discharge capacities of the electrodes decrease gradually as the discharge rate is increased from 0.5 to 10 C. NMC-2 demonstrates the best rate performance compared with other samples, retaining a high capacity of 92.2 mAh g\(^{-1}\) at 10 C, which is 49.8% of the capacity at 0.5 C. It also recovers 97.1% of the capacity when the current rate returns to 0.5 C. Modestly high specific surface area and small particle size are likely contributing factors to the excellent rate capability. The contact area between the electrode and electrolyte is sufficiently increased, whereas the diffusion path lengths for both electrons and ions are reduced. In comparison, NMC-3 with lower surface area and larger secondary particle size delivers a lower discharge capacity of 77.6 mAh g\(^{-1}\) at 10 C, which is 45.4% of the capacity at 0.5 C. Surprisingly, NMC-1 that exhibits even higher surface area and smaller particle size compared to those of NMC-2 performs poorly in the rate capability test. It only delivers a specific discharge capacity of 67.6 mAh g\(^{-1}\) at 10 C, which is 35.4% of the capacity achieved at 0.5 C. It is likely that the excessive side reactions (i.e., acid/base reactions and transition-metal dissolution) from large surface area of the active material in direct contact with the electrolyte solution give rise to increasing electrode resistance and lead to the accelerated loss of capacity.\(^{13,29}\)

To reveal the resistance changes of the nanostructured LiNi_{1/3}Mn_{1/3}Co_{1/3}O_{2} electrodes before and after the galvanostatic cycling, EIS measurements and equivalent circuit analysis are performed. Nyquist plots before and after 100 charge/discharge cycles are displayed in Figure 4a,b. The sum of the intrinsic resistances of the electrode material and the cell components, the contact resistance between the active material and the current collector, and the ionic resistance of the electrolyte is represented by the intercept on the Z' axis in the high-frequency region, which is denoted by R\(_{0}\). The semicircle in the high-intermediate frequency region refers to the charge-transfer resistance (R\(_{ct}\)) at the electrode/electrolyte interface and the diffusion resistance (R\(_{D}\)) of Li\(^{+}\) ions through the surface films (i.e., solid electrolyte interface). The constant phase elements (CPE\(_{1}\) and CPE\(_{2}\)) that represent the non-ideal capacitance of the surface films are used for the modeling of the depressed semicircle. The Warburg diffusion (Z\(_{w}\)) is reflected by the sloping straight line in the low frequency region, which corresponds to the solid-state diffusion of Li\(^{+}\) ions in the bulk of the electrode material.\(^{32,43}\) The single semicircle present in the

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**Figure 4.** EIS measurements and equivalent circuit modeling. Nyquist plots of the nanostructured LiNi_{1/3}Mn_{1/3}Co_{1/3}O_{2} electrodes: (a) before cycling and (b) after cycling.
high-intermediate frequency region suggests that $R_\alpha$ is the dominating resistance over $R_\Omega$. The increase in the diameter of the semicircle is observed for all three samples, which corresponds to a higher charge-transfer resistance. From Table 2, it shows that there is significant increase in both $R_\alpha$

| Electrode Sample | $R_\Omega$ ($\Omega$) | $R_\Omega$ ($\Omega$) | $R_\alpha$ ($\Omega$) |
|------------------|------------------------|------------------------|------------------------|
| NMC-1 before cycling | 6.54 | 6.05 | 6.15 |
| NMC-2 before cycling | 4.96 | 5.49 | 11.81 |
| NMC-3 before cycling | 4.54 | 6.39 | 13.02 |
| NMC-1 after cycling | 9.21 | 26.19 | 41.39 |
| NMC-2 after cycling | 8.16 | 11.79 | 28.93 |
| NMC-3 after cycling | 7.48 | 7.19 | 15.06 |

**Table 2. Equivalent Circuit Analysis**

and $R_\Omega$ of NMC-1. Meanwhile, NMC-2 has seen a less amount of increase in $R_\Omega$ and $R_\alpha$, whereas the resistance growth in NMC-3 is the least. These changes observed in the impedance measurements clearly indicate that the sample with higher external surface area suffers from considerably larger impedance increase upon galvanostatic cycling. Higher surface area is more susceptible to the detrimental side reactions with the electrolyte solution. The decomposition of the electrolyte salt (i.e., LiPF$_6$) generates hydrofluoric acid that attacks the bare Li-Ni$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ and leads to the dissolution of transition-metal ions into the solution. It is likely that the highly resistive LiF is formed on the surface of the active materials, which blocks the charge transfer between the particles and retards the kinetics of the electrochemical reactions. This leads to the accelerated capacity fading during the charge/discharge cycling and the inferior rate performance. The EIS measurements can serve as an explanation to the cycling performance and the rate capability of the nanostructured electrodes synthesized by RSDT. However, the degree of transition-metal ion dissolution and the quantification of the resistive species have not been determined, which requires further research work.

**EXPERIMENTAL SECTION**

Fabrication of Nanostructured LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ Electrodes by RSDT. Nanostructured LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ electrodes were fabricated by RSDT. The instrument setup and the operating procedures of RSDT have been previously described in detail.20,46—49 The stoichiometric amount of acetylene black of lithium, nickel, manganese, and cobalt (Sigma-Aldrich) were dissolved into 50:50 wt % methanol/xylene (ACS reagent grade, Sigma-Aldrich) solvent mixture, which was formulated according to a preliminary solubility study. The precursor concentrations used to prepare the electrodes for comparison study are 15, 30, and 45 mM, and the corresponding electrodes were denoted as NMC-1, NMC-2, and NMC-3. Water bath sonication was employed to obtain a clear solution. The precursor solution was filled into a pressure vessel. Sulfur-free liquid propane (Airgas East Inc.) was then added to the pressure vessel, which accounted for 18.5 wt % of the final solution. The solution was pumped through a capillary line to a custom-designed atomization nozzle at a flow rate of 6.0 mL min$^{-1}$. The atomization of the solution and the size reduction of the droplets exiting the nozzle were assisted by the supercritical expansion of the propane. The induction heating was provided to increase the temperature of the solution to 50—60 $^\circ$C before reaching the nozzle. The precursor solution exited the nozzle in the form of aerosol spray which was ignited by six pilot burners surrounding the nozzle to form a jet-diffusion flame. The main flame was supported by the high-purity oxygen (Airgas East Inc.) at a flow rate of 10 L min$^{-1}$ and sustained by the pilot burners that were consuming the premixed methane (Airgas East Inc., 0.85 L min$^{-1}$) and oxygen (Airgas East Inc., 0.85 L min$^{-1}$). The mass flow controllers (Alicat Scientific) were used to control the flow of the gases. The flame was enclosed by a quartz shroud to limit the dissipation of the combustion heat. Stainless steel current collectors were mounted on a custom-made substrate holder for the deposition of the synthesized material to form the nanostructured electrodes, which was secured on a computer-controlled motion platform that was programmed to follow a serpentine raster pattern to ensure the uniform deposition. During the operation of RSDT, a zero-diffraction silicon substrate was also mounted on the substrate holder to collect the synthesized materials for XRD analysis.

**Physical Characterization.** Structural and phase analysis of the as-synthesized LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ were carried out by aBruker D8 Advance X-ray diffractometer, which had a monochromatic Cu K$\alpha$ ($\lambda = 1.5418$ Å) radiation and a LynxEye detector. Surface morphologies of the LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ electrodes were investigated using FEI Quanta 250 FEG that had a field emission source. Transmission electron microscopy (TEM) images were acquired on a FEI 200 kV probe-corrected Metrios DX S/TEM. The particle size distributions were obtained by the analysis of the TEM images using the image processing software ImageJ. TEM samples were prepared by scraping the active material off the electrode, dispersing in the electroactive sites and higher utilization of the electrodes, the excessive side reactions with the electrolyte are detrimental to the cycling stability of the electrodes. Future studies will explore the option of depositing a protective surface coating (i.e., metal oxides) on top of the active material to alleviate the detrimental effects from the electrolyte decomposition and to enhance the cycling performance of the electrodes with high surface area.

**CONCLUSIONS**

Nanostructured LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ electrodes with the interconnected pore network are fabricated in one step by RSDT. This innovative synthesis method presents a pathway to the simple and rapid manufacturing of high-performance nanostructured electrodes for Li-ion batteries. XRD analysis indicates a layered structure with minimal cation mixing of the nanostructured electrodes, which was secured on a computer-controlled motion platform that was programmed to follow a serpentine raster pattern to ensure the uniform deposition. During the operation of RSDT, a zero-diffraction silicon substrate was also mounted on the substrate holder to collect the synthesized materials for XRD analysis.
ethanol, and drop-casting onto 400 mesh copper grids that have ultrathin carbon film on lacy carbon support film (Ted Pella Inc.). The grids were dried in ambient environment overnight. Brunauer–Emmett–Teller (BET) surface area measurements of the samples were performed by Micromeritics ASAP2020 surface area analyzer using nitrogen as the adsorbent at 77 K. The samples were degassed at 200°C under vacuum before performing the measurements.

Electrochemical Measurements. The as-prepared Li-Ni$_{x}$/Mn$_{1/3}$Co$_{1/3}$O$_{2}$ electrodes were assembled into CR2032 type two-electrode coin cells (diameter 20 mm, height 3.2 mm) as the working electrodes. Microporous polyethylene membranes (Celgard 2400) were used as the separators, and pure lithium foils were used as both the counter electrodes and the reference electrodes. The mass loadings of the active materials were controlled between 0.8 and 1.0 mg. Lithium hexafluoro-phosphate (LiPF$_{6}$, 1 M) dissolved in a mixture of ethylene carbonate, diethyl carbonate, and dimethyl carbonate was used as the electrolyte. The coin cells were assembled in an argon-filled glovebox. The cells were galvanostatically charged and discharged in the voltage window of 3.0–4.5 V vs Li/Li$^+$ at multiple C-rates by means of a multi-channel Arbin battery tester. CV measurements were taken at scan rate of 1.0 mV s$^{-1}$ in the voltage window of 2.8–4.5 V vs Li/Li$^+$ by Solartron 1287 Potentiostat. EIS was conducted on a Gamry Reference 600 Potentiostat at the frequency range from 0.5 MHz to 0.1 Hz.

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Notes
The authors declare no competing financial interest.

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