

Fabrication of high-capacity NMC cathodes using spray printing technique

Rafal Sliz, Esa Hannila, Ivy Saha Roy, Juho Valikangas, Palanivel Molaiyan, Ulla Lassi, and Tapio Fabritius

Abstract— While current Li-ion liquid electrolyte batteries provide satisfactory performance, there is a growing need for more adaptable and sustainable fabrication methods. Among the available printing methods, spray coating stands out as exceptionally adjustable, enabling easy up- and down-scaling, high-resolution features (down to tens of μm), 3D compatibility, and the use of a wide range of ink formulations, including those containing large particles ($>5 \mu\text{m}$). Moreover, spray coating generates little waste, making it a fully sustainable fabrication process that is also suitable for solid-electrolyte deposition. In this study, spray coating was used to fabricate $\text{LiNi}_{0.88}\text{Mn}_{0.03}\text{Co}_{0.09}\text{O}_2$ (NMC88) cathodes using dimethylformamide (DMF) ink instead of the toxic N-methyl-2-pyrrolidone (NMP). The printed cathodes had a relatively low roughness (R_q 3.4 μm and R_a 2.7 μm) prior to calendaring, as revealed by morphological analysis. Coin cells and pouch cells were then prepared using the fabricated cathodes for electrochemical characterization. The pouch cells demonstrated very repeatable behavior and 15 % capacity fade after 1000 cycles.

I. INTRODUCTION

Lithium-ion (Li-ion) batteries have revolutionized the concept of energy storage, with applications ranging from portable consumer electronics, through electric vehicles, and grid energy storage.[1] In Li-ion batteries, the cathode plays a crucial role as it determines the performance and safety of the battery. Nickel-manganese-cobalt oxide (NMC) is a popular cathode material in Li-ion batteries because of its high specific capacity, good cyclability, and thermal stability.[2] Especially promising are the high-nickel content materials, such as NMC 811 and NMC 88, with 80 % and 88 % of nickel content, respectively. Printing is a suitable method for producing batteries because it offers a range of advantages compared to conventional coating methods.[3] Printing methods, such as spray coating, inkjet printing, and screen printing, allow precise and controlled deposition of materials in a highly reproducible manner. These aspects enable the production of batteries with uniform thickness and composition, resulting in high performance and reliability. The attribute of controlled deposition is especially important in the fabrication of multilayer structures, for instance, in solid-state batteries.[4] Moreover, different printing methods can accommodate different ink and slurry compositions and formulations. Printing techniques allow the fabrication of batteries with complex geometries, making it possible to produce batteries of various shapes and sizes, including flexible and even wearable batteries.

Spray printing is a suitable method to print battery layers because it offers a few favorable properties over traditional printing methods, such as inkjet or screen printing. For example, spray printing allows the use of a wider range of materials, including viscous and high-solid content inks, which are not compatible with other printing techniques.[5] Additionally, spray printing can handle larger particle sizes, enabling the deposition of active materials with larger particle sizes, which can enhance the capacity and performance of the batteries. Spray printing is also a versatile technique that can be used to fabricate batteries with complex shapes and sizes, including curved, flexible, or even 3D geometries. Moreover, spray printing can be easily scaled up for mass production, which can potentially lower the cost of production and make batteries more affordable and accessible to consumers. During spray printing, the material intended for deposition is sprayed directly onto the substrate using a spray nozzle (Figure 1a).[6] The material can be in the form of a liquid or a powder, and is dispersed using a gas or a liquid. The behavior of the spray nozzle can be controlled to adjust the spray pattern, droplet size, and deposition rate.

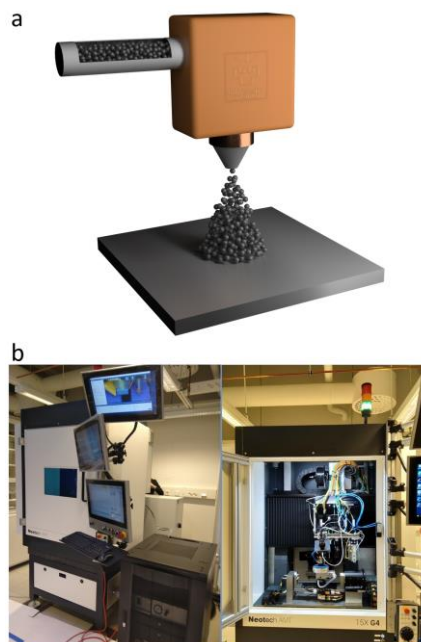


Figure 1. Spray printing technique. a) 3D representation of spray printer nozzle during the printing process. b) Neotech AMT 15X G4 printer used in this research for spray printing NMC 88 cathode layers.

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In this study, we validated the usability of spray printing as a feasible method of fabricating NMC 88 cathode layers. The printed cathodes were used to make coin and pouch cells that were electrochemically tested. In order to verify the capabilities of the system, various features were printed, and their morphology was analyzed. Figure 2 depicts the printed structures: (a) plane cathode for pouch cells, (b) shaped structures that can be utilized in 3D batteries.

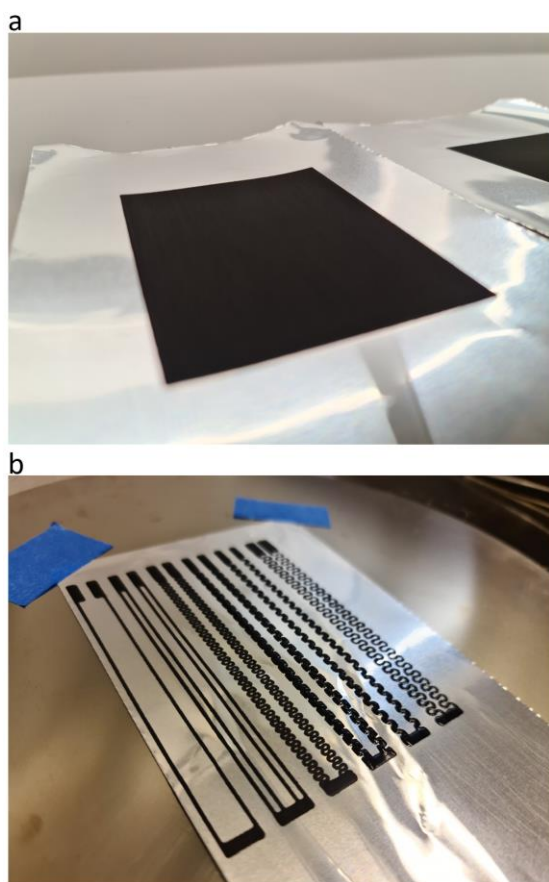


Figure 2. Spray-printed NMC 88 cathode material. a) Full cathode for pouch cells. b) Various-shaped cathodes to demonstrate the capabilities of the spray printer.

II. METHODS

A. Ink formulation and cathode printing

The ink was formulated using NMC 88 active material mixed with PVDF binder and carbon C45 conductive additives at a 92/4/4 ratio. Firstly, PVDF was dissolved in DMF and stirred at room temperature for 6 hours.[7] Consequently, NMC active material was dry-mixed with C45 carbon in a vortex mixer for 2 minutes and added to the PVDF solution for further mixing for 6 hours. The ready ink was transferred to the printer dispersing container. For printing, Neotech AMT 15X G4 printer with Nordson 100 μm printing nozzle was utilized. The aluminium foil was solvent-cleaned and plasma treated to improve the adhesion of the ink.[8] The printing process underwent several iterations of optimization to achieve desired thickness and surface morphology. The printed final cathodes were annealed at 50° C for 10 minutes and consequently at 120° C for 1 hour, to remove any solvent residues.

B. Cells assembly

For each sample foil, two coin cells of 2016-type were assembled with metallic lithium serving as the counter electrode and 1M LiPF₆ in 1:1:1 EC:DEC:DMC as the electrolyte. The cells underwent initial charging at a constant current until a cut-off voltage of 4.3 V was reached. Charging then continued with a constant voltage until the current decreased to 0.015 C for the first two cycles, and in subsequent charge cycles, the current threshold was raised to 0.02 C using the same method. For the first two discharge cycles, constant current discharge was done at 0.1 C until 2.6 V was reached, followed by constant voltage discharge until the current decreased to 0.015 C. A subsequent discharge was done to 3.0 V with a constant current. The cells were tested at 25 °C, and the theoretical capacity used to calculate the C-rate was 200 mAh/g.

For the pouch cells, a graphite anode (Hitachi), an electrolyte of 1.15 M LiPF₆ in EC:DMC:EMC (2:4:4), and 1 % vinylene carbonate were used to prepare one electrode pair pouch cell with a capacity of 50 mAh. After the formation cycles, the pouch cells were initially charged at a constant current of 1 C until 4.2 V was reached, followed by constant voltage charging until the current decreased to 0.03 C. The cells were discharged to 2.5 V at 1 C, and the theoretical capacity used to calculate the C-rate was 230 mAh/g. The cells were cycled at 1C/1C ratio, at 25 °C. Capacity check cycles (0.2C/0.2C) were performed every 100 cycles, but they were not plotted for clarity in the figures.

The batteries were assembled in a dry room conditions, at temperature 25 °C. Maccor Series 4000 battery cycler was used to conduct electrochemical testing of the cells.

C. Morphological and electrochemical characterization

To characterize the quality of printing and behavior of the cathode material, the scanning electron microscopy images were captured (Joel SEM Microscope) in two configurations: the edge of the printed cathode printed on the aluminium current collector, and the cross-section of the printed cathode. To analyze the surface morphology of the printed NMC layers, Bruker ConturGT optical profilometer was used (in VSI mode). Consequently, the Gwyddion software was used to process the images, and the final figures were rendered with the Paraview software.

III. RESULTS

The electrochemical results are presented in Figure 3. The plot in Figure 3a shows the behavior of two pouch cells cycled 1000 times. Throughout the cycling, the specific capacity of the cells decreases from 167 mAh/g to 142 mAh/g. Importantly, the capacity fade is almost identical for both cells. The same plot shows the Coulombic Efficiency that oscillates around 100 % throughout the entire cycling. The small variation between 100th and 250th cycle was caused by the temperature instability in the dryroom environment. Figure 3b represents the behavior of the coin cells during charging and discharging at various C-rates. Expectedly, the specific capacity drops at higher C-rates: 174 mAh/g and 197 mAh/g at 2C and 0.1C, respectively. This occurs due to lithium diffusion limitations and reduced electrochemical reaction rates.

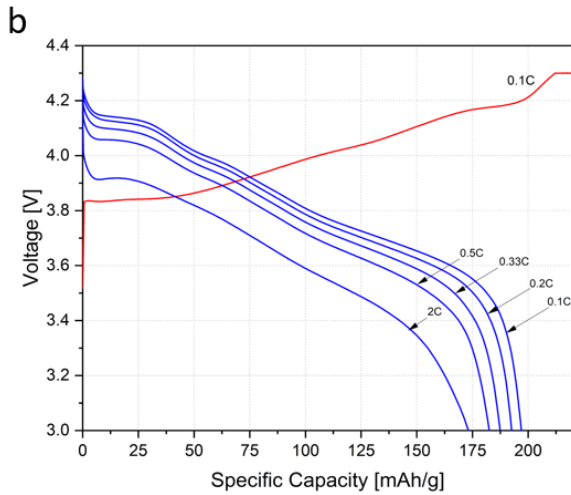
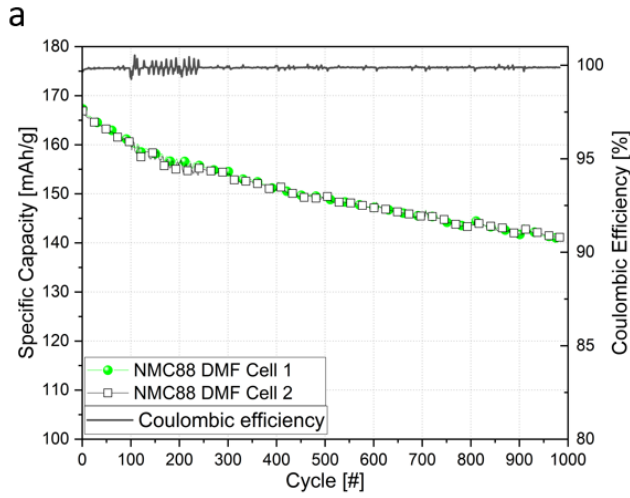


Figure 3. Electrochemical characterization of printed NMC batteries. a) Two pouch cells capacity fade and coulombic efficiency over 1000 charge and discharge cycles (1C/1C). b) 0.1C charge curve (red) and five different C-rate discharge curves (blue).

Figure 4 represents the morphology of the printed cathode conducted with the optical profilometer. The printed layer is smooth over a large area, with RMS roughness of (R_q) 3.4 μm and surface mean roughness (R_a) of 2.7 μm . Importantly, these values were acquired before the calendaring process, that reduces the roughness.

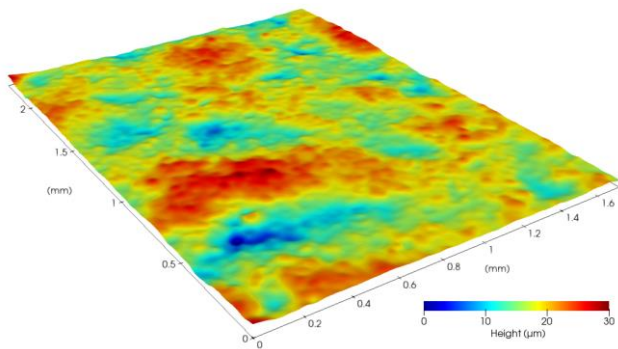


Figure 4. Morphology of the NMC cathode acquired with optical profilometry.

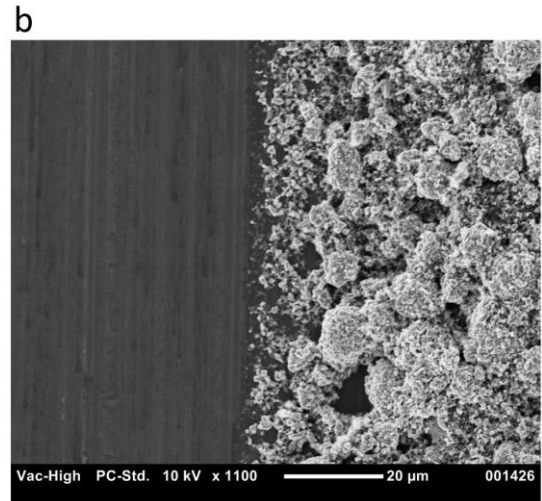
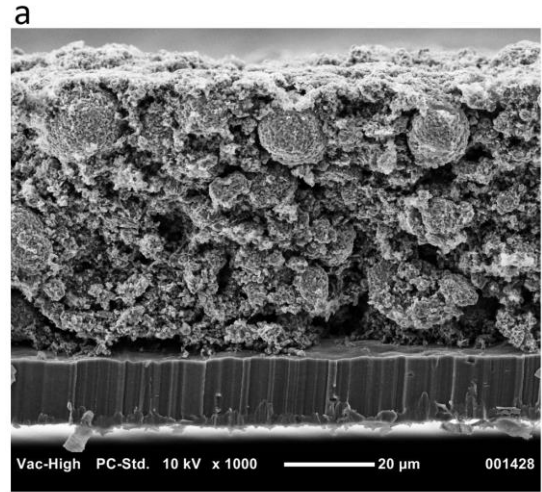


Figure 5. SEM images of the printed cathodes. a) Cross-sectional image of the NMC material printed on the surface of the aluminium current collector. b) SEM image of the cathode edge highlighting the quality of the print.

Figure 5 shows SEM images acquired from the cross-section of the cathode printed on the aluminium current collector (a) and the edge of the printed cathode (b). The printed cathodes have a thickness of approximately 50 μm and demonstrate an even distribution of the material across the entire structure. The SEM image suggests that spray printing allows relatively clean printing as the unprinted area remains clear of any material residues.

IV. DISCUSSION

The results achieved in this study suggest that spray printing is a suitable method for printing NMC-based cathodes. Although the technique is not as fast as slot-die coating, it allows printing of various shape cathodes that can be advantageous in customizing batteries. The electrochemical and profilometry results show that the printing process is repeatable, as the electrodes have almost identical performance and low-roughness surfaces. The cross-sectional imaging confirms that spray printing does not affect the material distribution within the cathode structure.

V. CONCLUSION

This work provides additional evidence about the suitability of spray printing to be used in battery fabrication, with an emphasis on batteries with unconventional shapes. Although this research demonstrates spray printing as a feasible method of printing cathodes, more research is needed to investigate its suitability for printing a full battery stack. The ability to spray print a full battery at an industrial scale would open new opportunities for the entire industry and allow the fabrication of novel electronic devices with extraordinary features.

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