Replacement of NMP solvent for more sustainable, high-capacity, printed Li-ion battery cathodes

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***Abstract* — The production methods of Li-ion batteries need to be adapted for the goals of a more sustainable future. This research focuses on replacing toxic NMP with less harmful solvents, without compromising the batteries' performance. From the perspective of printed electronics, the replacement is especially desirable because the aggressiveness of NMP has a negative impact on various components of printers. In this research, the novel NCM88 material has been used to fabricate the cathode layers of Li-ion batteries. Two fabrication methods (blade coating and screen printing) and two different slurry/ink formulations (NMP- and DMF-based) have been analysed. For the purpose of physicochemical and electrical characterization, the fabricated cathodes were used to assemble pouch cells and half-cells with metallic lithium as counter electrode. Results indicate that screen-printed cathodes fabricated with DMF-based slurries perform similarly to those fabricated through blade-coating NMP slurries.**

Keywords: sustainable, DMF, NMP, solvents, battery cathode, NMC, printed, screen printing.

I. Introduction

The rapid development of electronic devices and their demand for portability are creating pressure on developing more effective and longer lasting batteries. Also, recent advances related to electric vehicles and smart grid create additional needs for high-capacity battery systems. Regardless of the application, current battery fabrication methods are not energy efficient or environmentally friendly [1]. According to Ellingsen et al., the fabrication of a 26.6 kWh pack requires energy that is equivalent to approximately 4.6 tonnes of CO_2 emitted to the atmosphere [2]. Although technological advancements enable the introduction of more efficient fabrication methods, the ever-increasing demand for batteries poses challenges to meeting sustainability needs [3]. Another aspect is related to toxic and harmful solvents used during battery electrode fabrication. A recent study by Romare and Dahllof concluded that to fabricate a 26.6 kWh battery pack, approximately 23 kg of N-Methyl-2-Pyrrolidone (NMP) is used [4]. NMP belongs to the group of polar aprotic solvents widely used in the chemical industry. It offers high solvency for several organic and inorganic materials, high boiling point, and thermal stability [5, 6]. Although up to 99 % of the NMP can be recovered, the recovery process is energy demanding and requires additional investments [7]. Moreover, due to the toxicity of NMP, many countries are introducing legislation that limits its applications [8]. To overcome the problem of NMP usage, several alternatives have been proposed, such as employing water, DMSO, or Cyrene, to name a few [9–11]. Although these efforts provide promising results, they introduce additional challenges related to material solvability, poor adhesion, insertion of sulphur atoms, or delithiation [12], [13].

This work focuses on the replacement of NMP with Dimethylformamide (DMF) and introduces screen printing as a viable fabrication method for battery cathodes (Figure 1). Screen printing is especially promising because it offers controlled material deposition, the flexibility of implementation with a wide range of inks and slurries, the ability to create hybrid devices, and roll-to-roll compatibility [14–16]. Our efforts utilise NMC battery chemistry - Lithium-Nickel-Manganese-Cobalt-Oxide ($LiNiMnCoO_2$). NMC batteries offer high specific energy, sufficient lifetime, and high storage capacity. In particular, we utilise a high-capacity novel NMC88 with Ni-Mn-Co ratio of 88-08-03.

Compared to NMP, DMF offers a lower boiling point (153 ºC, NMP = 203 ºC), lower surface tension (37 mN/m, NMP = 41 mN/m), and lower viscosity (0.92 mPa s, NMP = 1.89 mPa s). All these aspects allow reduction of the energy consumption during electrode drying, improved slurry wetting, and better thermal control of the deposition process [17, 18].

Although DMF also belongs to a group of toxic solvents, thanks to the solvent recovery process and its advantageous physicochemical properties, it is a suitable candidate to replace more widely prohibited NMC. The archived results indicate that the DMF-based screen-printed cathodes offer similar performance as their blade-coated NMP-based counterparts.

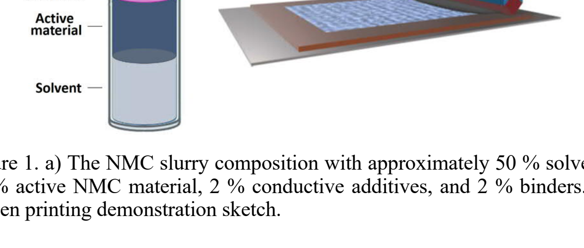

Figure 1. a) The NMC slurry composition with approximately 50 % solvent, 46 % active NMC material, 2 % conductive additives, and 2 % binders. b) Screen printing demonstration sketch.

II. Methods

The NMC slurries were prepared by mixing NMC88 material with conductive carbon black and PVDF binders in a weight ratio of (92:4:4) and concentration of 1 g/ml. To make a homogenous slurry, two different solvents were used (NMP and DMF) and mixed for 2h. Accordingly, the NMP-based slurry was used to blade-coat aluminum foil (thickness of 25 µm) serving as current collector, and exposed for drying at 80 ºC for 1 h. The DMF-based slurry was used for screen printing with an Ekra E2 screen printer and Koenen VA 165-0.05 mm W-Øx22.5º stencils. Consequently, the fabricated films were used for characterisation and battery assembly.

The Scanning Electron Microscopy (SEM) cross-sectional and in-plane images (Figure 2) and Energy-dispersive X-ray spectroscopy (EDS) characterisations of the fabricated NMC films were performed using Zeiss ULTRA plus FESEM Electron Microscope. The elemental analysis (EDS) depicted in Figure 4, was conducted to better understand the material distribution in relation to a fabrication method and solvent dependence. The surface morphology of the fabricated layers depicted in Figure 3 was acquired with Bruker ConturGT optical profilometer in VSI mode.

The fabricated cathodes were used to assemble half-cells (2016-type) with metallic lithium as the counter electrode and 1M $LiPF_6$ in EC:DEC:DMC (ratio 1:1:1), as the electrolyte [19]. The half-cells were used to extract information regarding voltage and specific capacity, depicted in Figure 5a.

Pouch cells were assembled using a graphite anode (Hitachi) material and an electrolyte of 1.15 M $LIPF_6$ at EC:DMC:EMC (2:4:4) ratio, with the addition of 1 % vinylene carbonate. The pouch batteries were cycled 100 times at a constant charge-discharge current 1C/1C (Figure 5b).

III. Results

The results depicted in Figure 1 indicate a very similar distribution of the NMC88 material, regardless of the used solvent and fabrication method. After the drying process, the average thickness of the NMC layers was 47.8 ± 2,1 µm and 46.3 ± 4,4 µm for NMP NMC88 Blade-coated and DMF NMC88 Screen-printed, respectively.

The SEM images reveal an interesting difference between samples, related to confinement of the NMC spheres in the layers. The cross-sectional images in Figures 2a and 2b indicate the difference in the surface morphology of the samples. The surface of the DMF NCM88 screen-printed sample is rougher than the surface of the NMP NCM88 blade-coated sample. Figures 2c and 2d demonstrate the distribution of the spheres on the surface of the samples. In the screen-printed sample, the spheres stand out from the surface more significantly than for the blade-coated sample.

The results of optical profilometry characterisation depicted in Figure 3 are in agreement with the previous SEM results, indicating that the DMF NMC88 Screen-printed layer is rougher than the NMP NMC88 Blade-coated layer.

The EDS characterisation of the cross-sectional images presented in Figure 4, shows that the conductive additives and binders are distributed uniformly in the structure of the layers, regardless of the used solvents and fabrication method.

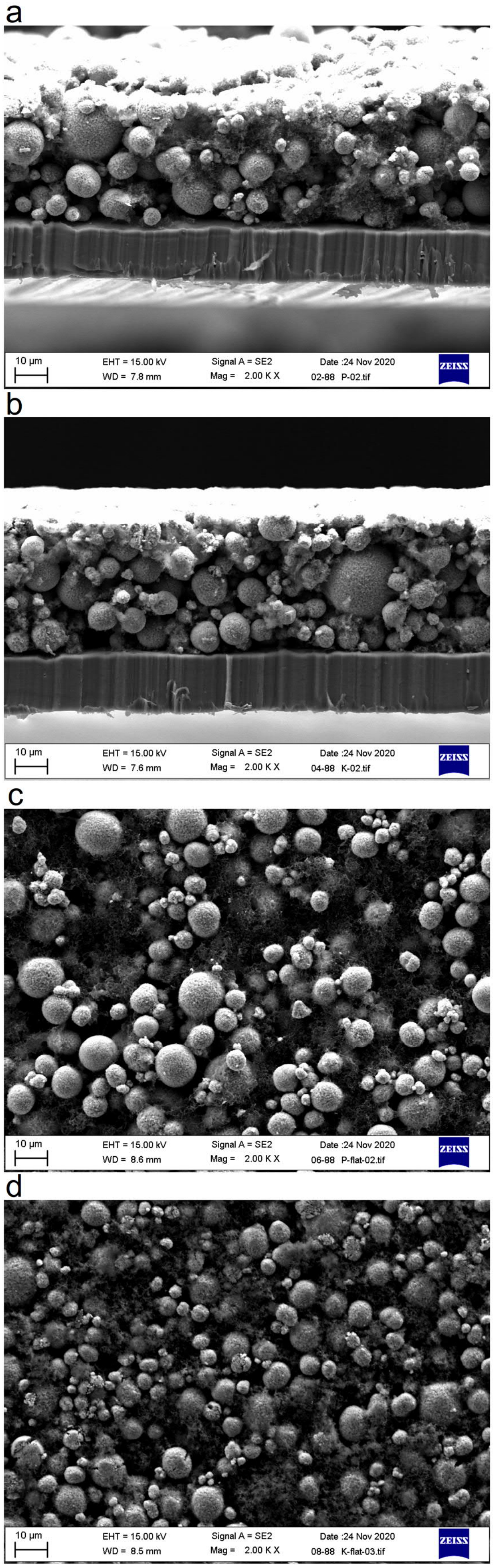

Figure 2. SEM images of the fabricated samples. a) Cross-sectional SEM image of DMF NMC88 Screen-printed. b) Cross-sectional SEM image of NMP NMC88 Blade-coated. c) In-plane SEM image of the DMF NMC88 Screen-printed sample. d) In-plane SEM image of NMP NMC88 Blade-coated sample.

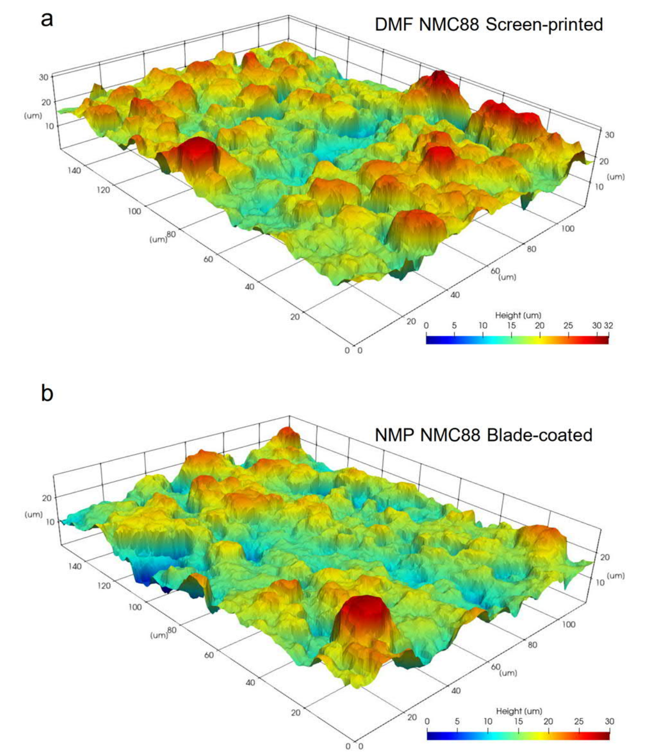

Figure 3. Surface morphology of the fabricated layers acquired with optical profilometry techniques. a) DMF NMC88 Screen-printed layer. b) NMP NMC88 Blade-coated layer.

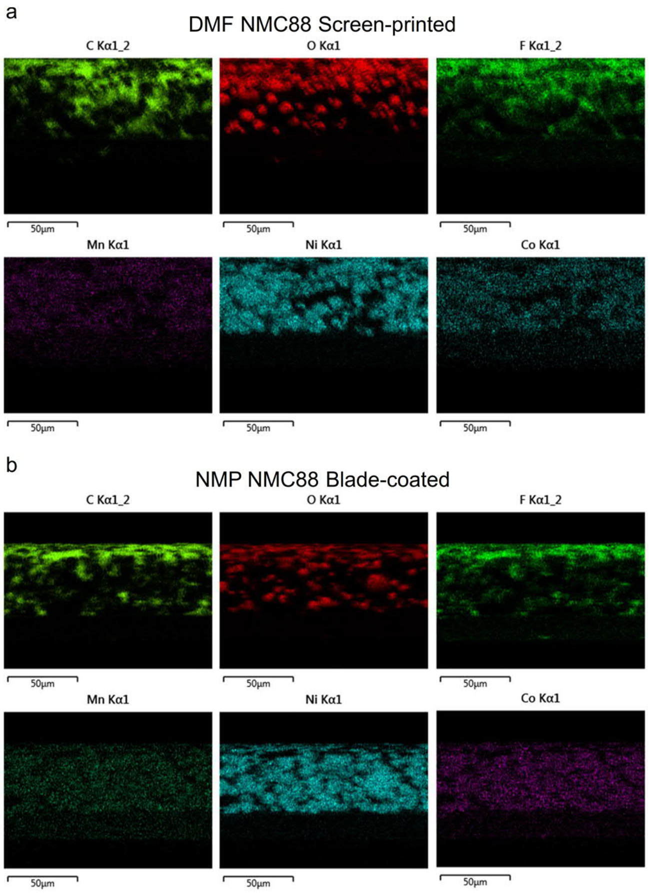

Figure 4. SEM-EDS cross-sectional images of differently fabricated NMC88 layers with an emphasis on elemental distribution of C, O, F, Mn, Ni, and Co. a) DMF NMC88 Screen-printed layer. b) NMP NMC88 Blade-coated layer.

The electrical analysis depicted in Figure 5 shows the electrical performance of the fabricated batteries. As seen in Figure 5a, both cathodes demonstrate similar charging capacity; however, they reach the plateau at different voltage levels. For the discharge process at various currents, both samples present almost the same behaviour. Figure 5b demonstrates the comparison of the cycling process of batteries with differently fabricated cathodes. Regardless of fabrication method, the batteries demonstrate similar capacity fading. The initial values of the specific capacity differ insignificantly in favour of NMP NMC88 Blade-coated samples. However, after x100 cycles, the capacity decreases by 3 % and 2 % for NMP NMC88 Blade-coated and DMF NMC88 Screen-printed, respectively, favouring the screen-printed sample.

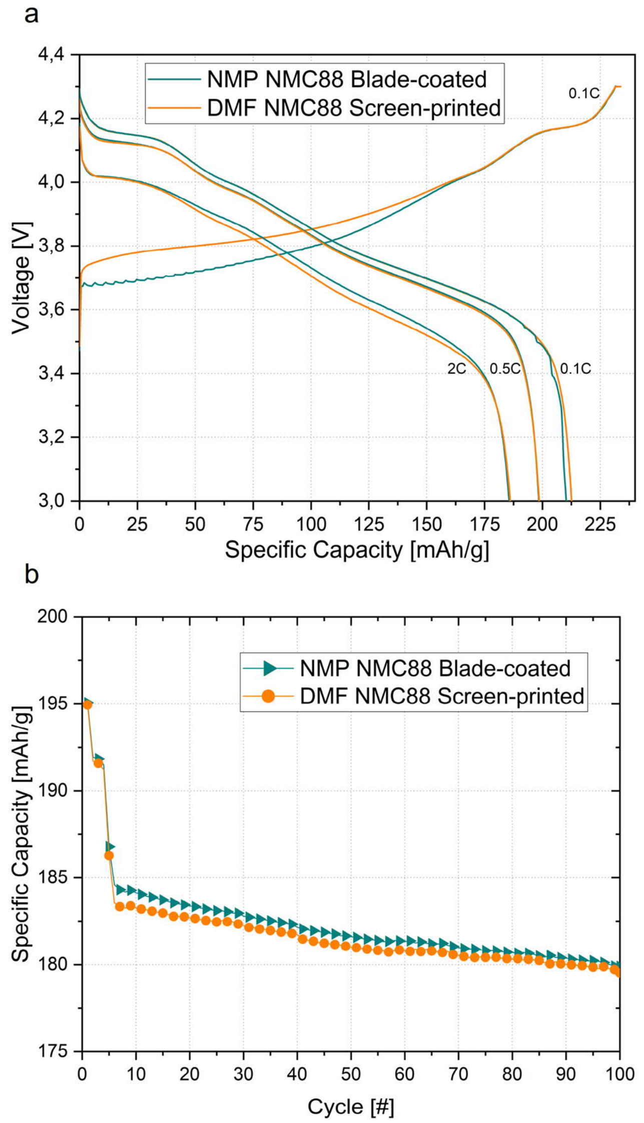

Figure 5. Electrical analysis of the fabricated batteries. a) Specific capacity vs voltage at various charge-discharge current (0.1C, 0.5C, 2C) for differently fabricated cathodes. b) Specific capacity during charging-discharging (1C/1C) process for differently fabricated cathodes.

IV. Discussion and Conclusions

Thanks to the physicochemical and electrical characterisations, this research provides evidence that DMF and screen printing could be viable replacements for toxic NMP and blade-coating. We assume that the morphology difference of the layers is associated with the fabrication method. In screen printing, the slurry is pressed through a mesh, while in blade-coating, the blade passes through the surface, allowing better confinement of the NMC spheres. Although the screen-printed layers are rougher, the roughness does not influence the performance of the fabricated batteries. This research could be further advanced by implementing more sophisticated characterisation techniques, such as AFM or electron probe micro analyser, to reduce the deficiencies of optical profilometry or EDS measurements. Furthermore, more cycling and reliability testing would provide additional insights and help in establishing the proposed approach as a viable cathode fabrication method.

The achieved results indicate high potential for the proposed method and ability to replace NMP without compromising the performance of the battery. Thanks to the flexibility and numerous materials compatibility (solvents and active materials), screen printing could be utilised to fabricate various cathode systems and ultimately enable fabrication of fully printed batteries [20].

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