

Aerosol Jet Printing as a Versatile Sample Preparation Method for *Operando* Electrochemical TEM Microdevices

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***Operando* electrochemical transmission electron microscopy (ec-TEM) is a promising tool for advanced characterization of energy systems close to their operating conditions. However, reliable sample preparation for the technique is particularly challenging due to spatial constraints. Here, a novel approach of manufacturing such samples is introduced and demonstrated for industrially relevant battery powders: NMC811 and LTO ($\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ and $\text{Li}_4\text{Ti}_5\text{O}_{12}$). Aerosol-jet printing is used to deposit microscale patterns of battery active material particles on the electrodes of commercial ec-TEM chips. This method provides high spatial resolution (line width $< 30\ \mu\text{m}$) and accuracy, ease of ink preparation, flexibility of materials, and ability to manufacture complex structures (layered or mixed materials). Size selectivity of aerosol jet printing and its positive implications for ec-TEM sample preparation are also discussed. This procedure is a promising solution to the difficult problem of micro-battery fabrication for ec-TEM and for other applications where high spatial resolution deposition from powders is required.**

a lot of emphasis is placed on studying the principles of their operation, degradation and eventually—failure. Investigating new routes to improve the capacity and lifetime of batteries requires careful characterization of the constituent materials at various stages of their operation or, even better, the ability to observe them *operando*, where information is acquired as the device operates. Among these approaches, *operando* liquid-cell transmission electron microscopy (also referred to as in situ liquid-cell transmission electron microscopy (TEM)) has received substantial attention in the literature.^[1–7] For this technique, micro-fabrication is used to create two silicon chips, each coated with a thin layer of amorphous silicon nitride (SiN_x). Silicon is then etched locally to form suspended, electron transparent SiN_x windows. One

1. Introduction

As new materials and chemistries for next generation batteries and other electrochemical devices are being developed,

of the chips is typically partly coated with a patterned photoresist that acts as a spacer defining the thickness of the cell. A thin layer of liquid can be sealed between the two Si chips (this is referred to as the liquid cell). A material deposited on the SiN_x window or dispersed in the liquid layer can be imaged with electrons in a liquid environment in the column of a TEM, circumventing the usually strict requirements for high vacuum. When such a method is to be used as an *operando* technique to study electrochemical systems, the chips are patterned with 2 or 3 electrical contacts and at least one of them (called the working electrode) is positioned over the SiN_x window area. Such an approach, further referred to as electrochemical-TEM (ec-TEM) has been used to study fuel cell and battery systems.^[1,3,8,9] One of the biggest challenges for ec-TEM is a reliable preparation of the electrode, which must be thin enough to allow electron transmission through the liquid cell and must be carefully positioned on the contact (requiring positioning accuracies on the order of $10\ \mu\text{m}$). Additionally, thin SiN_x windows can break easily under mechanical strain, and liquid cells can suffer from imperfect seals which can degrade the microscope vacuum. Therefore, many of the ec-TEM studies so far focused on systems where the material of interest (such as Li metal) is electrodeposited on the working electrode during the experiment.^[1,3,10] This way, the material of interest is confined to just the electrode and does not require extensive sample preparation prior to the experiment. Consequently, ec-TEM literature on industrially relevant materials is sparse, as they usually are incompatible

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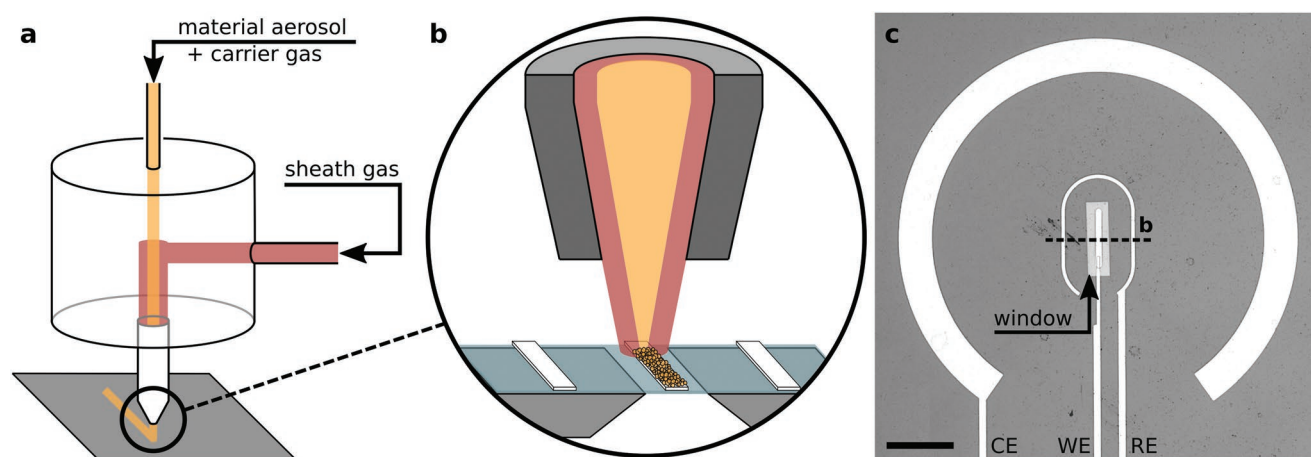


Figure 1. Schematic of the aerosol jet printing approach for ec-TEM sample preparation. a) Schematic of the print head, where material aerosol (yellow) and sheath gas (red) are fed into the nozzle. b) Close-up schematic of the aerodynamic focusing of the ink aerosol, which is used to print fine lines on ec-TEM chips. The chip is made of silicon (gray), has a suspended silicon nitride membrane (blue) and electrical contacts patterned on top of it (white). c) Optical microscope image of a commercial ec-TEM chip (Protochips ECT-24). Scale bar—200 μm . Platinum electrical contacts (white) are arranged so that they can be used as a working electrode (WE), counter electrode (CE) and pseudo-reference electrode (RE). The WE is extending over a rectangular silicon nitride window. Dashed line indicates a region that is schematically represented in (b).

with electrodeposition techniques. One of the first works to study such materials ($\text{NMC622—LiNi}_{0.6}\text{Mn}_{0.2}\text{Co}_{0.2}\text{O}_2$) on ec-TEM chips used drop casting of ball-milled particles to prepare the samples.^[11] Such sample preparation methods are lacking in resolution and are not reproducible enough to be used routinely.

To overcome this challenge, we propose a new approach for deposition of materials on *operando* ec-TEM chips based on aerosol jet printing (AJP). The principle is schematically shown in Figure 1a,b. In short, the material(s) of interest are made into a suspension in a suitable solvent, forming an ink. The ink is then put into a dedicated vessel and into an atomizer (ultrasonic or pneumatic), which generates an aerosol of the ink. The aerosol is then carried into the printing nozzle by a carrier gas. This aerosol stream is surrounded by an annular sheath gas stream that focuses it down into a small spot ($<20\text{ }\mu\text{m}$) on the substrate. By changing gas flow rates, nozzle size, distance to the substrate and surface properties of the substrate, it is possible to tune the rate of deposition, uniformity and size of printed features. The substrate is then moved by a motorized XY stage under a stationary nozzle to enable printing of pre-programmed patterns. Compared to other additive manufacturing methods, aerosol jet printing can take a wide range of inks, including suspensions of metal and ceramic nanoparticles, polymers and biological materials.^[12,13] Moreover, the ink preparation is relatively simple and does not have as strict viscosity requirements as ink-jet printing.^[12,13] Additionally,

aerosol jet printing can achieve feature sizes of less than $10\text{ }\mu\text{m}$ and positioning accuracy on the order of $5\text{ }\mu\text{m}$, which is needed for reliable sample preparation for ec-TEM.^[12,13] In this paper, we use AJP to manufacture ec-TEM microbatteries using commercially available, industrially relevant anode and cathode materials. We will also demonstrate high resolution, versatility and reliability of the approach.

2. Experimental Section

In this section the experimental approach for creating an ec-TEM sample starting from commercially available powders of conventional battery materials is outlined. $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ (NMC811) powder was acquired from Targray. $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) and SuperP conductive carbon (CC) powders, were sourced from MTI Corporation. Scanning electron microscope (SEM) micrographs of as-received CC and LTO powders can be found in Figures S1 and S2 (Supporting Information) respectively, and of NMC811 in Figure S3. Inks were formed by dispersing powders in *N*-Methyl-2-pyrrolidone (NMP, anhydrous, Sigma Aldrich) in 5 wt% concentration (solids in NMP). All prepared ink formulations are listed in Table 1.

The printing was done using an Optomec Aerosol Jet 200 Printer equipped with an ultrasonic atomizer. To enable safe and reliable preparation of air- and moisture-sensitive specimens, the setup was positioned inside of an Ar-filled

Table 1. Ink formulations used in this work.

Label	Main material	Concentration [wt%]	Additive	Additive content [wt%]	Solvent
NMC	$\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$	5	n/a	–	NMP
CC	SuperP	5	n/a	–	NMP
LTO	$\text{Li}_4\text{Ti}_5\text{O}_{12}$	5	n/a	–	NMP
LTO+CC	$\text{Li}_4\text{Ti}_5\text{O}_{12}$	4.75	SuperP	0.25	NMP

glovebox. A 150 μm tip inner diameter nozzle was used throughout. Nitrogen was used as the carrier gas and the substrate temperature was kept at 80 $^{\circ}\text{C}$. The printing process was monitored using an optical microscope integrated into the printer, which allowed for monitoring of width, spread and coverage of printed traces and live optimization of the parameters. The printing parameters were optimized for the narrowest possible line width (based on the optical microscope images) at the beginning of every printing session to account for slight differences in ink parameters. The optimization procedure was performed on Al foil flattened out on a glass slide. When printing was done on ec-TEM chips, the substrate was subsequently changed to a Protochips ECT-24 ec-TEM chip with Pt electrodes (shown in Figure 1c). The ec-TEM chips were oxygen plasma treated for 2 min before printing to clean the surface, increase its hydrophilicity, and avoid excessive ink spreading. The ec-TEM chip was immobilized on a glass slide using custom-made Kapton-tape pockets to avoid any damage to the chip and to avoid the stream of gases moving the chip. The electrode was aligned with the nozzle under an optical microscope to ensure that the printed line overlapped with the electrode. After the system reached thermal equilibrium, a pre-programmed pattern was printed on the ec-TEM chip and repeated as necessary to control coverage. Printed lines were imaged under a FEI Nova 450 NanoSEM microscope equipped with a field emission gun operated at 10 kV unless otherwise specified. An Everhart–Thornley detector was used, with collection of both backscattered and secondary electrons. Image processing was performed in ImageJ.^[14] Printed (dry) ec-TEM working electrodes were imaged using FEI Tecnai F20 TEM operated at 200 kV. A Gatan OneView 4k camera was used to acquire bright-field TEM micrographs.

To evaluate the electrochemical response of a printed material, an LTO electrode (LTO ink, Table 1) was printed as described above, but in the pattern of a 12 mm diameter circle, on electrochemical grade Al foil. The printed area was cut out using a 12 mm diameter disk cutter, which was then dried in a vacuum oven at 120 $^{\circ}\text{C}$ for 24 h. 2032-type coin cells (Hohsen) were assembled with a printed LTO working electrode, a Li metal counter/reference electrode (15.6 mm diameter, LTS Research Laboratories) and a Celgard 2325 separator (19 mm diameter, PI-KEM) soaked in 40 μL of LP57 electrolyte (1 M LiPF_6 in ethylene carbonate (EC):ethyl methyl carbonate (EMC) 3:7 by weight, SoulBrain). After assembly, the half-cells were cycled galvanostatically (low current channel, Biologic VMP3) at 0.01 $\mu\text{A cm}^{-2}$ between 1.0–3.0 V versus Li/Li^+ . Similar cells with blank Al foil as the working electrode were also constructed for comparison. As a reference, an LTO electrode was also cast using traditional methods in which a 90:5:5 ratio (by weight) of LTO, polyvinylidene fluoride binder (PVDF, Sigma Aldrich) and SuperP CC, respectively, was mixed together with NMP in a planetary centrifugal mixer (Thinky) to form a slurry. The slurry was then cast onto Al foil and dried under vacuum at 120 $^{\circ}\text{C}$ for 24 h. Circular electrodes with 12 mm diameter and mass loading of 1.0 $\text{mg}_{\text{LTO}} \text{cm}^{-2}$ were punched and constructed into coin cells. Cells with cast LTO electrodes were cycled galvanostatically (CT2001A, Lahne) in a climate chamber set

at 25 $^{\circ}\text{C}$ for 2 cycles between 1.0 and 3.0 V versus Li/Li^+ at C/20, and then at a C/2 rate assuming a practical capacity of 175 $\text{mAh g}^{-1}_{\text{LTO}}$ (i.e., per gram of LTO).

3. Results and Discussion

To evaluate the quality, coverage and width of the printed features, LTO and NMC inks (Table 1) were printed in sets of 5 lines of 100 μm in length with increasing number of passes of the nozzle over an Al foil substrate, from 20 to 100 passes in steps of 20. The LTO and NMC were chosen to demonstrate the possibility of printing as-received industrially relevant anodes and cathodes, respectively, from powders. NMC is currently one of the most studied Li-ion battery cathode materials, while LTO was chosen as an anode material to complete a full cell on an ec-TEM chip for further studies because it is a well-studied, industrially relevant anode material with a flat potential profile and high redox potential, which avoids issues with the formation of a solid electrolyte interphase.^[15]

The printed specimens were dried and the resulting lines were imaged using an SEM. As shown in Figure 2a,b the width of all of the lines is within the 20–30 μm range, which is sufficient for ec-TEM sample preparation. The width increases with increasing number of passes by almost 50% from 20.2 μm for 20 passes up to 29.9 μm for 100 passes for the NMC ink and by 7% from 29 to 31 μm for the LTO ink. The width increase can result from (I) hysteresis when moving the stage back to the previous positions or (II) ink build-up, where the ink does not have sufficient time to dry before the next pass is done, leading to spreading of the ink on the substrate. Ink build-up could potentially be reduced by programming pauses in between passes, using a more volatile solvent or increasing the stage temperature. The thickness of the deposits also increases with the number of passes by about 230% between 20 and 100 passes which can be used to tune the density of the resulting film, at the cost of a small widening of the printed features. Details on how the width and thickness ratios (image intensity ratio, assuming intensity is proportional to thickness) of lines were calculated can be found in Note S1 (Supporting Information). A print pattern that would cover the Protochips' counter electrode shape (Figure 1c) was pre-programmed and printed on Al foil with the LTO ink as shown in Figure 2c to show the ability to print complex shapes and tune the printing process to the sample requirements. The results demonstrate the versatility of AJP as a method for ec-TEM sample preparation thanks to the ability to print a variety of industrially relevant active materials in arbitrary patterns.

We then moved to printing on commercially available ec-TEM chips. First, for the working electrode, NMC inks were used to print a linear pattern of 160 μm in length. Two different printing approaches were used: (1) a base layer of CC (50 passes) followed by a layer of NMC811 (80 passes) and (2) just NMC811 (240 passes) printed directly onto the chip. The CC base layer was added to demonstrate the possibility of creating composite samples through either a layered approach (as described above) or by mixing the materials during ink preparation as was the case for the counter electrode. There, LTO and CC powders were mixed with mortar and pestle before

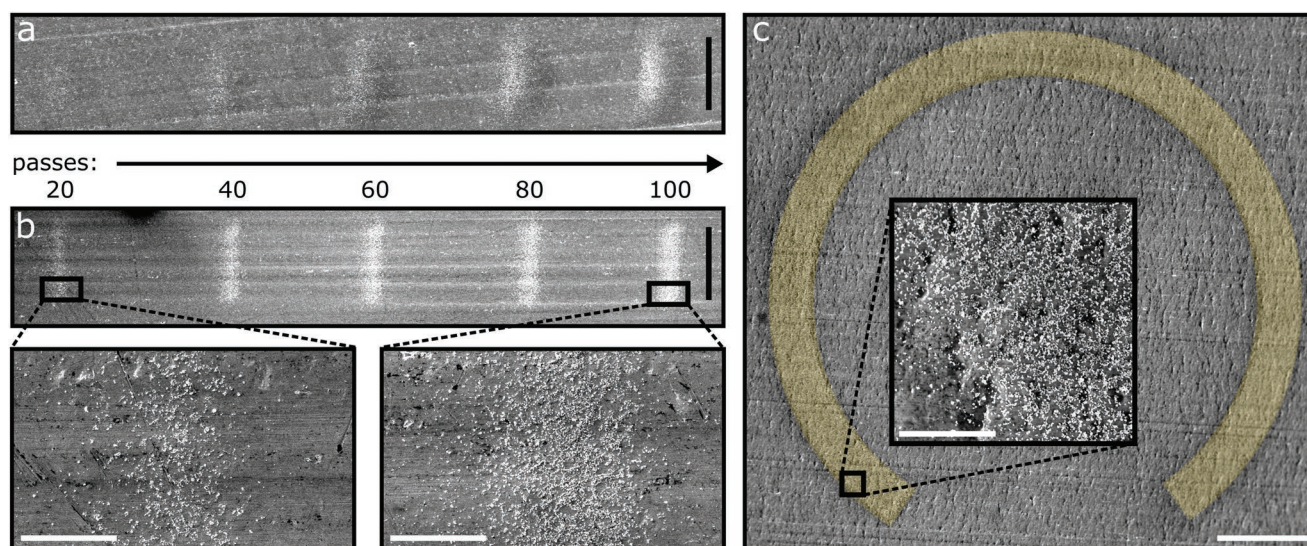


Figure 2. SEM micrographs of aerosol jet printed lines. a,c) LTO ink on Al foil, b) NMC811 ink on Al foil. In (c) part of the printed area has been false colored (orange) to highlight it and improve the clarity. Scale bar in (a) and top panel of (b) is 100 μm long, the same length as the programmed printing length. Scale bar in the bottom panel of (b) is 20 μm for both images; 200 μm in (c) and 20 μm in (c) inset.

suspending in NMP. LTO+CC ink was then used (Table 1) to print on the outer, counter electrode of the ec-TEM chip (see Figure 1c). In either case, CC is used to improve the electronic conductivity of the resulting electrodes, similar to commercial batteries. Similarly, a binder (such as polyvinylidene difluoride) could be added to the ink to improve the binding and robustness of the printed films if needed. However, here we decided not to include it as the films deposited are very thin and will not be experiencing mechanical stimuli in the liquid cell (no liquid flow, no stack pressure or calendaring like in macro-scale batteries).

The printed samples were imaged using an SEM and the micrographs of the working and counter electrodes are shown in Figure 3. The working electrode printed with just NMC811 shows a sparse film (Figure 3a,b), while the working electrode containing the base CC layer (Figure 3c,d) shows a more uniform film, due to higher printing efficiency of small CC particles compared to NMC811. LTO ink was printed on the counter electrode Pt contact (Figure 3e), forming a uniform film of the material. The printed NMC working electrodes were also imaged using a TEM (Figure 3g) to show that the NMC particles in proximity of the patterned Pt contact are visible and transparent to electrons, confirming the suitability of AJP for ec-TEM sample preparation. Using selected area electron diffraction, crystallinity of the printed NMC811 particles was confirmed, indicating that the printing process does not destroy the initial layered crystal structure of the material. A representative diffraction pattern and TEM image of the same area are shown in Figure S5 (Supporting Information).

High printing resolution was achieved on both Al foil substrates as shown in Figure 2 and discussed above as well as ec-TEM chips, on their Pt contact and partly on the SiN_x window. Figure S4 (Supporting Information) shows a comparison between printed line widths between the two substrates highlighting that printing on ec-TEM chips can be at least as high-resolution as on Al foil. It is also important to note

that the coverage of the deposited materials can be adjusted according to the needs of specific experiments (e.g., to avoid particle agglomerates or to increase the uniformity of the film) by changing the number of passes, concentration of the ink and gas flow rates.

To determine the influence of the printing process on the particle size distribution (PSD), the neat NMC811 ink was sonicated for 45 min in the ultrasonic atomizer of the printer. The suspension was then drop cast onto a carbon tape coated SEM stub for SEM analysis. PSD of the primary particles from the sonicated NMC811 and printed NMC811 on the ec-TEM chip are shown in a histogram in Figure 3f. Details on how they were acquired can be found in Note S2 (Supporting Information). Only particles below 1 μm in size were analysed as larger ones are not present in the printed features. PSD of the electrode printed using NMC811+CC ink is shown in Figure S4 (Supporting Information). Comparing the PSD histograms of sonicated and printed neat NMC811 (without CC) shows that there is an upper cut-off of about 0.6 μm for the printed NMC811. The apparent shift of the mode of PSD toward diameters for the printed particles is due to difficulty in recognising the printed particles from texture of the Pt contact itself. Therefore, only particles that were clearly distinguishable from the Pt substrate were measured. It has been shown previously, that the process of entraining particles into aerosol droplets strongly selects smaller particles which are more effectively incorporated in the 2–5 μm aerosol droplets,^[13] so this effect is not unexpected, but has an interesting implication for printing inks containing secondary agglomerates of primary particles (as is the case with the NMC ink): the process of sonication and printing leads to a breakdown of secondary particles and selective printing of individual primary particles. SEM images of as-received, sonicated and printed NMC811 are shown in Figure 4a–c. As demonstrated by SEM micrographs shown in Figure 4a, the as-received NMC811 was in a form of small (0.1–1 μm) primary particles packed into larger, near-spherical secondary particles of

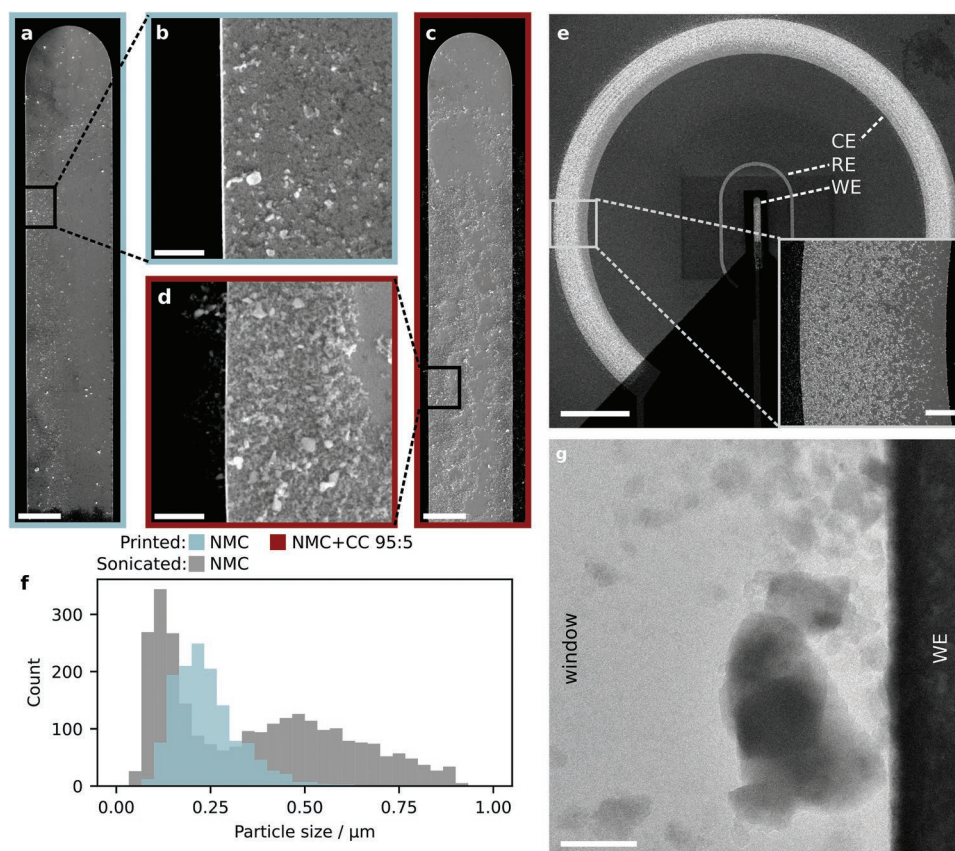


Figure 3. SEM micrographs of aerosol jet printed lines on the working electrode of a Protochips ec-TEM chip. a,b) Neat NMC811 ink (240 passes), c,d) Conductive carbon ink followed by NMC811 ink (50 and 80 passes respectively). Scale bars in (a) and (c) are 10 μm , (b) and (d) are 2 μm . e) Low magnification SEM micrograph of ec-TEM chip showing printed neat NMC working electrode and LTO+CC counter electrode. Scale bar 200 μm and 20 μm for the image inset. The electrodes are labeled as CE (counter electrode, Pt with printed LTO), RE (reference electrode, clean Pt contact) and WE (working electrode, Pt with printed NMC). f) Histograms comparing the particle size of the sonicated and printed NMC. g) Bright field TEM micrograph of the edge of a printed electrode showing NMC particles over the SiN_x window (scale bar 200 nm). The Pt contact is labeled as WE.

5–20 μm in diameter. Figure 4b shows that the original particle size distribution becomes binomial after sonication with some large secondary particles as well as separate primary particles.

This can be explained by fracturing of the (brittle) secondary particles during ultrasonic atomization, and subsequent separation of primary particles. It is clear from Figure 4c that the

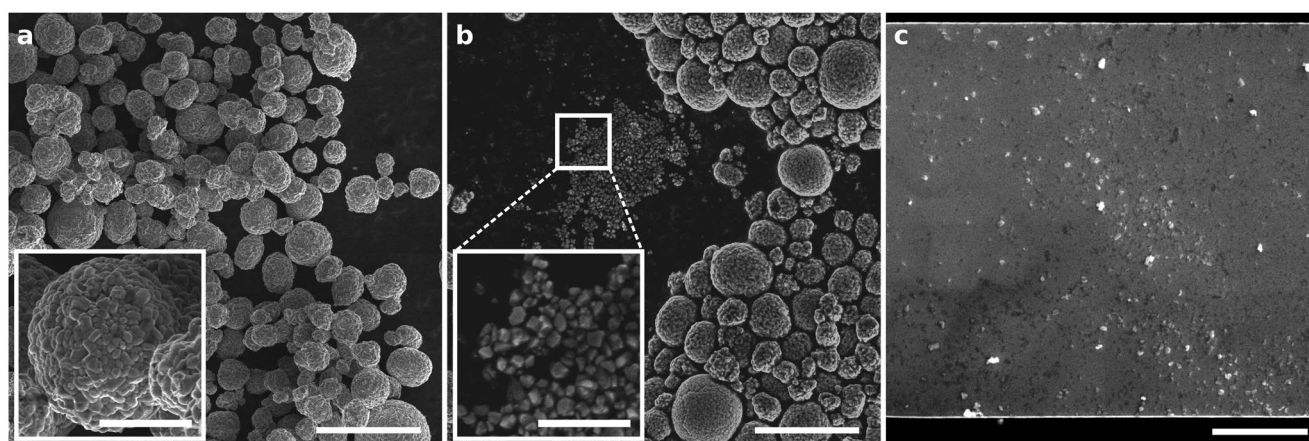


Figure 4. SEM micrographs of NMC811: a) as received particles (scale bar 20 μm), inset shows a secondary particle structure under higher magnification (scale bar 5 μm). b) Particles sonicated for 45 min in the printer (scale bar 20 μm), inset shows a higher magnification image of primary particles separated during sonication (scale bar 5 μm). Particles in (a, b) are deposited on carbon tape. c) Aerosol jet printed NMC811 particles on ec-TEM chip Pt WE (scale bar 5 μm).

size distribution of the printed particles is in a similar size range as the primary particles (0.1–1 μm). This size selectivity is not a detrimental property of the aerosol jet printing for preparing ec-TEM samples. In fact, it is advantageous, as the liquid cell has a spacer-determined thickness, which is typically 0.5 or 1 μm , and becomes larger with the bulging of windows due to pressure difference inside (atmospheric) and outside (UHV of the TEM) of the cell. Any particles larger than 1 μm might be in direct contact with both SiN_x windows, exerting local stress on the membrane, potentially leading to breakage of the window. Moreover, due to mean free paths of electrons in materials of the order of 100 nm, the smaller (thinner) the particles, the higher the resolution and visibility of features in the TEM images will be. However, in the ec-TEM with liquid, the smallest of particles would lack contrast to be distinguished from the liquid itself. However, the particles on the order of 100–200 nm that are present in the printed films would be suitable for ec-TEM imaging. Similarly sized particles have been previously studied in liquid cell TEM in the literature, such as LiFePO_4 in a study by Holtz et al.^[5] Of course, the average atomic number for STEM-HAADF imaging will be slightly different between LiFePO_4 and NMC811, but they can be expected to show similar contrast in the liquid cell.

The electrochemical behavior of printed LTO was evaluated. The charge voltage profiles for all half cells (first C/2 cycle of the cast LTO electrode and first cycle of the printed LTO electrode, as well as first cycle of the Al foil) are shown in Figure 5. The cast LTO shows a typical voltage profile with a plateau at 1.55 V versus Li/Li^+ .^[15] Due to very low mass loadings, the response of LTO printed on Al foil is mostly overshadowed by a response of the Al foil current collector, but still shows a clear plateau at 1.55 V, confirming its electrochemical activity. These electrochemical cycling data verify that the process of

aerosol-jet printing allows retention of the expected electrochemical behavior of the printed material.

Overall, based on the results shown above, the aerosol jet printing approach to ec-TEM sample preparation is promising. The features printed are small enough for the application, the ability to pre-program arbitrary shapes makes this method applicable to a range of ec-TEM chip geometries as well as potential other applications, where fine features are required for microdevices. Inks can be prepared out of a variety of materials, including mixed materials. The “side-effect” of size selectivity of aerosol jet printing is advantageous as TEM applications need small particle size to ensure electron transparency. Future work will focus on using the samples prepared as shown in this study to deepen the understanding of degradation of materials as they operate inside of the microscope.

4. Conclusions

We have proposed a new approach, based on aerosol jet printing, for creating full cell microbattery samples on a commercial chip for *operando* electrochemical TEM. In this work, we have shown that this approach can be used to deposit conventional, industrially relevant battery materials (NMC811, LTO, SuperP conductive carbon) starting from powders, with high spatial resolution (line width <30 μm) and in arbitrary, pre-programmed shapes. Moreover, materials can be either deposited as a mixture as shown with LTO+CC ink, or sequentially in layers of different materials (e.g., CC base layer, followed by NMC811 layer). We have demonstrated important implications of the size selectivity of aerosol jet printing to the deposition of materials with a broad range of particle sizes, resulting in a thin layer of particles <1 μm in size, which is advantageous for ec-TEM sample imaging. A confirmation of a typical electrochemical response from printed LTO was obtained for a coin cell geometry, paving the way to systematic ec-TEM testing. The combination of the versatility, flexibility, size selectivity, positioning accuracy and spatial resolution make aerosol jet printing a very promising candidate for *operando* TEM sample preparation. Moreover, a similar approach may enable other opportunities in a wide variety of studies where high-resolution material deposition is required.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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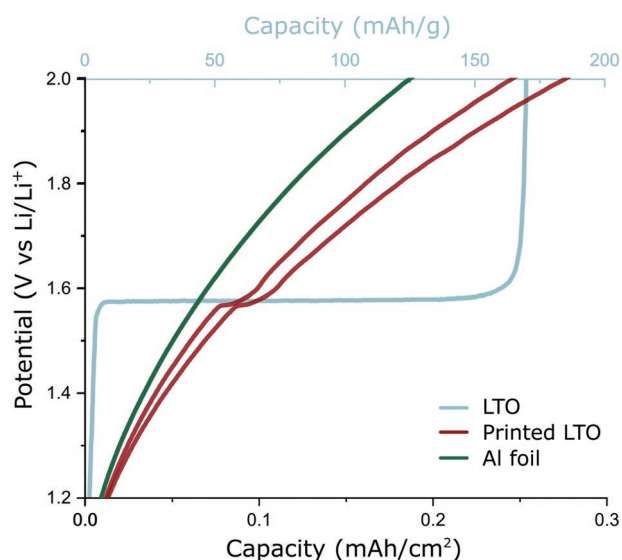


Figure 5. Charge voltage profiles of half cells with traditionally cast LTO, printed LTO and Al foil without an active material. Bottom axis is for the printed LTO and Al foil, top x-axis is for cast LTO. Note the different scale and units for the top and bottom x-axes. Two profiles for duplicate printed LTO samples are shown.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

aerosol jet printing, batteries, electrochemistry, microdevices, microdevice fabrication, operando TEM

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