Lithium-ion batteries are important to many highly developed and evolving markets, including personal electronics, energy-storage solutions, electrical vehicles and more. As current manufacturing processes are large-scale and of high initial cost, production and integration of new battery types and geometries is a cost-intensive process. The need arises for highly customizable batteries at low cost, mainly to answer the requirements of small-scale markets that have no economically feasible route for production of custom battery geometries and are forced to rely on standard geometries that may not be optimal for specific applications.1

A promising low-cost route to the production of such cells is the employment of various types of 2D and 3D printing methods. While some work on this subject has been published in recent years, the processes of printing custom electrodes and batteries are still in early stages of development and commercialization.2–6 The possibility of electrode-printing by several types of printing technologies has been recently demonstrated.7 For the fabrication of printed lithium-ion cells, the choice of a specific printing technique has pivotal importance for the final result. In general, all printing technologies enable the application of predetermined designs onto a substrate and allow control over the final product and pattern. However, printing techniques themselves are vastly different in scale, resolution, cost and type of applicable substrates. With focus on research and development applications, we chose, in this study, to employ a digital printing method rather than traditional methods, such as screen printing that requires the use of a mask.

Several papers have been published in recent years on the printing of electrode materials by digital printing. Printing methods include traditional piezoelectric-crystal-actuated inkjet printing, which utilizes low-viscosity and low-surface-tension inks, or direct deposition of high-viscosity inks.3,4 Both show promising results, but pose significant limitations to the ink-formulation process. Low-viscosity inks, which are essential for inkjet printing, require low solids loading and other ink-formulation challenges, including limitations on the type of dispersed phase (relatively small particles are required). This also makes inkjet technique more suitable for very thin-layer printing, while making high-thickness printing (tens of micrometers) more prolonged. Direct deposition of high-viscosity inks by the extrusion of a continuous stream through an orifice or needle (rather than jetting or spraying ink onto the substrate) allows for facile high-thickness printing, but dictates relatively low active-material content and high content of the electrochemically inactive polymer binder. This is caused by the rheological-control requirements.

In the current work, we focus on drop-on-demand paste jet dispensing. In this commercially available process, droplets of liquid paste are forced through an orifice with the use of a piezoelectric crystal actuator plunger, enabling high-speed and high-accuracy jetting. In this method, one can dispense inks of much higher viscosity, and controlled drop size in customizable patterns. Because of the actuation mechanism, as the plunger is pressed against the orifice, a physical narrowing of the fluid path is achieved and drop formation is much less dependent on surface tension as compared to traditional inkjet technology. This flow profile also reduces the severe requirements concerning ink viscosity. Combination of this technique with inkjet and direct deposition enables the printing of a very wide range of inks for different applications.

Most of the commercial lithium-ion cells are based on cathodes of lithium cobalt oxide (LiCoO2). However, in recent years, several other cathode chemistries have been investigated for lower cost and increased energy and stability. These include: lithium manganese oxide (LiMn2O4), lithium nickel manganese cobalt oxide and lithium iron phosphate (LiFePO4, LFP).7

We chose to test LFP as a model cathode material because of its commercial availability, excellent electrochemical properties (long cycle life, high specific capacity, high power and high stability), and advantageous – its stability throughout the processing in a non-inert environment. LFP cathode powder is limited by low electrical conductivity and requires a carbon coating and, preferably, the addition of a conductive material to the final cathode formulation.8 In this study, we used carbon-coated LFP powder and added a carbon-black conductive additive to the cathode ink.

To summarize, we present here the structural and electrochemical properties of printed LFP cathodes by a drop-on-demand micro-dispensing technology, based on mechanical drop formation. As mentioned above, this technology has significant applicable advantages – it enables the formation of very thin electrode layers while retaining the ability to print viscous inks. This is an advantage in both the ink-formulation process and in the final product itself.

Experimental

We used LifePower P2 LFP powder (Clariant) as the active material. The entire study was carried out with the same batch of LFP...
powder in order to eliminate the possible influence of differences in carbon coating on ink rheology.\textsuperscript{9} C-Nergy Super C65 (Imerys) was used as a conductive additive. Sodium carboxymethylcellulose (NaCMC) was used as the binder. Triton X-100 was used as a dispersing agent for carbon.\textsuperscript{10}

In order to obtain the best and most stable cathode ink, we tested several different compositions, varying by the type and content of binder, the solid load and surface-active agents. The final electrode composition presented here includes a mixture of 80% (by weight) LFP, 10% carbon black and 10% binder. Deionized water was used as the solvent. The ink contained 20% solids and 0.5% Triton X–100.

Ink was prepared in two stages. First, water was mixed with Triton X–100 and NaCMC for complete dissolution of the binder. In the second stage, LFP and carbon black powders were added to the solution and this was mixed with the use of a planetary mixer (Thinky ARE–250) at 2000rpm. Cathode ink was used within one hour of mixing (it was remixed for further use if needed).

We printed cathode ink with the use of a PICO Pµs3 (Nordson EFD) piezoelectric actuator valve installed on a Nordson EFD E3 dispensing robot. The orifice diameter for drop formation was 100µm. The current collector used as printing substrate was carbon-coated aluminum (MTI).

Physical characterization included visible-light bright-field imaging, confocal-laser imaging and profiling (Olympus LEXT 3100), scanning-electron-microscopy (SEM) imaging and energy-dispersive X-ray spectroscopy (EDS) analysis (FEI Quanta 200, Oxford INCA).

Electrochemical characterization was carried out with cells that consisted of the LFP cathode and metallic-lithium foil as counter electrode. Printed cathodes were vacuum-dried (pressure < 1 mbar) for at least 8 hours at 100°C. Cells were assembled in an argon-atmosphere glove box. We used the CR2032 coin-cell type setup. 12mm-diameter circular cathodes were used as printed (the current collector was die-cut to the desired geometry prior to printing). The separator was made of polypropylene (Celgard 2400). The electrolyte was 1M lithium hexafluorophosphate in ethylene carbonate/diethyl carbonate (1:1) with added vinylene carbonate (2%), used as received from Solvionic. Cycling was carried out in the voltage range of 2.6–3.8V at 30°C. Electrochemical-impedance-spectroscopy (EIS) tests were conducted by either varying the voltage around the OCV, or by varying the current, as outlined in the results. Equivalent circuit model was fitted to these measurements using the L-BFGS-B algorithm with parameters bound at a minimum of 0 and no maximum; tolerance was set to 10\textsuperscript{−11}, several orders of magnitude better than measurement accuracy. Four identical cells were assembled and tested, and similar results were obtained. Cycling currents were 10µA, 80µA, 150µA, 350µA and 500µA, corresponding to approximately 0.1C, 1C, 2C, 4C and 6C rates (rounded to one significant figure).

Results and Discussion

Printing and electrode geometry.—After optimization of the composition of the cathode ink on the requirements of high stability and appropriate viscosity (see Experimental), we were able to print a geometry of well-defined and separate cathode lines on the current collector. Two main factors were found to govern the final printing resolution. First, as the printing is done in a drop-by-drop formation and not in a continuous stream, the printed geometry is inherently not microscopically uniform. When printing several lines of cathode material, droplets are somewhat scattered around the exact printing-head position. The second factor is the wetting of the current collector. Droplets printed in close proximity, merge as a result of dynamic wetting effects and the dispersion of droplet placement. This limits separation of printed features and reduces the resolution of printing. Feature width is also limited by the small wetting angles and high dispersion of droplet placement. This is followed by widening of the produced features. Both negative phenomena can be somewhat mitigated by controlling droplet size, which is mainly limited by the opening size of the orifice.

![Figure 1](Image 312x552 to 515x717) SEM micrographs of single layer printed small- (top) and large-droplet (bottom) printed cathodes. Bar = 100µm.

Droplet size is readily adjusted in the printing process by controlling various parameters of the printing head, mainly piezoelectric cycle parameters (i.e. the voltage profile applied to the piezoelectric actuator, controlling the type of force and strain applied to the ink as it exits the printing head). Resolution can be also controlled by droplet size, but small droplets tend to scatter more and produce more satellite droplets (secondary droplets produced by inertial effects such as the impact of the droplet on the printing substrate), and so contaminate regions around the printed features, effectively worsening printing resolution.

As a starting point, to demonstrate printing capabilities, we printed a geometry of parallel straight lines on the current collector. To analyze printing performance, we prepared electrodes printed with multiple layers of relatively small droplets, printed repeatedly on top of one another. For electrochemical analysis, we prepared electrodes with cathode loading of 0.9-1 mg/cm\textsuperscript{2} based on a single layer of printing, but of much larger droplets.

![Figure 2](Image 427x526 to 435x540) Figure 2. 3D profile of 100 layers printed LFP cathode, characterized by scanning laser confocal microscopy.
clearly dispersed around the maxima, presumably the exact location of the droplets. The approximate width of the final printed line is 150–170 µm, the approximate maximum height is 90 µm.

**Electrochemical performance of printed electrodes.**—The theoretical capacity of LFP is 170mAh/g. Practical discharge (lithiation) capacity of uncoated LFP cathodes is generally less than 110mAh/g/LFP. Various types of carbon coating were shown to significantly improve this capacity, to about 160mAh/g LFP, at low current densities (up to C/10).11,12 We used carbon-coated LFP in this study (LifePower P2 LFP powder, Clariant). At low cycling rates (0.1C), the printed cathodes showed initial capacity of more than 140mAh/g/LFP (Figure 3). The reversible discharge capacity, which is about 130–140mAh/gLFP, is scarcely affected by a one-order-of-magnitude increase of the cycling rate (from 0.1C to 1C rate). After 100 cycles at 1C rate, the discharge rate was increased in several steps to 2C, 4C, and up to 6C, in order to evaluate the rate capability of the DoD printed cathode. A capacity as low as 80mAh/g was obtained at the 6C-rate, still close to 50% of the theoretical value. This reduced capacity is generally attributed to the diffusion-limited lithiation process, which is particularly pronounced at high current densities. Lowering the C rate back to 1C, after 165 cycles, resulted in a capacity increase back to its 1C value (about 130 to 140 mAh/g) indicating good capacity retention. This shows that the capacity decrease is not associated with deterioration of the active material itself (Figure 3). At all cycles and at all discharge rates, the faradaic efficiency is high, averaging 98.6% for 1C cycling and 98.2% overall, showing no increase in the attendant undesirable phenomena due to the printing procedure.

Another goal was to fully understand the effects of the charge and discharge rates on the voltage profiles and battery capacity. Figure 4 depicts several voltage/capacity curves at 1, 2, 4 and 6C (all in the same cell). At mid SOC and SOD, the gap between the curves rises from 90mV at 1C, up to 290mV at 6C. As an approximation we may say (neglecting the overvoltage on the lithium counter electrode) that the total cathode overvoltage on charge and discharge is half of the gap, i.e. 45mV at 1C and 145mV at 6C. However, as the OCV at mid-SOD is 3.42V, the total overpotential for charge (delithiation) is approximately 50mV (at 1C) and that for discharge (lithiation) is approximately 40mV. The OCV of about 3.42V is retained for the span of most states of charge, from 5% to 98%.13 Thus, the overvoltage values at 95% SOD and that at 95% SOC are very high, over 600mV and 200mV, respectively.

The cell impedance is the sum of several resistors in series, including: bulk (electrolyte and separator) resistance ($R_b$); lithium SEI resistance ($R_{EIS}$); cathode-activation resistance ($R_{ac}$) (lithiation-delithiation); lithium diffusion in the LFP particles ($R_d$); the resistance of the electrolyte in the porous structure of the cathode ($R_e$, calculated from the diameter of the second semicircle in Fig. 6) and diffusion ($R_d$), or Warburg impedance ($W$).14 In order to estimate the contribution of each of these resistances, we used the EIS technique. The Nyquist plots were fitted to the equivalent circuit (Figures 5, 6 and 7).

EIS tests were performed in several schemes on printed electrodes. Repeated EIS measurements were performed after lithiation at 1C, immediately after the process and after increasing rest periods (Figure 6). These measurements were done under OCV conditions, at 20mV AC amplitude for a fully lithiated cathode. Analysis of EIS spectra is a complex issue and we are presenting our best hypotheses for the processes contributing to each section of the EIS spectrum. The measured EIS spectra are typical for LFP cathode/metallic lithium cells.14,15

Another set of measurements (Figure 7) was done after 20 cycles, for both lithiation (discharge) and delithiation (charge). The main notable features of the spectra include a semicircle at the high-frequency range, which is assigned to the SEI resistance ($R_{EIS}$) on metallic lithium. This arc may include some contribution of the charge-transfer process in the cathode. Another semicircle at a lower-frequency region (about 1Hz) is assigned to the diffusion of lithium in the LFP particles ($R_d$), in Figure 6. The last feature of the spectra is a diffusion region at very low frequencies. As LFP is a fast cathode, having low impedance, it is suggested that the first semicircle is dominated by SEI properties. This suggestion is supported by the value of the capacitance, about $10^{-5}$F/cm², which is typical for SEI on rough lithium metal, formed after 20 cycles. Figure 6 depicts the effect of rest time, from 10 minutes up to 11 hours, on the EIS spectra. It was found that $R_b$ (5Ω) does not change with time. The second semicircle varies slightly with time, but not in a consistent manner. The diffusion and Warburg regions, at low frequencies, are unaffected by the rest time, indicating no significant change in lithium-ion distribution within the cathode in the time scale of measurement.

![Figure 3](image-url) Cycle life of a printed LFP cathode in a geometry of lines.

![Figure 4](image-url) Charge/discharge curves at approximately 1C, 2C, 4C and 6C cycling rates, with respect to the state of charge in the specific cycle.

![Figure 5](image-url) Equivalent circuit model for LFP/Li cells.
While $R_{Sei}$ and $R_b$ do not change much over time (Figure 6) for a discharged cell (fully lithiated cathode), we found clear evidence that $R_d$, which is assigned to the diffusion resistance of lithium in the LFP particles, does change (Table I and Figure 6) over the course of the lithiation/delithiation cycle. To measure this change, we performed EIS measurements during charge and discharge processes (lithiation and delithiation of the cathode), without rest. This was done at a 1C rate, at SOC values of 10%, 50% and 90%. In order to acquire the EIS spectra we applied the relevant bias potential, at an AC current amplitude of 20μA. This was done for both lithiation and delithiation. As these measurements were performed operando (during cycling), they were kept as brief as possible and the frequency range was 1Hz–500kHz. The diffusion (Warburg) region is not observed at this frequency range (Figure 7).

Table I. Model fit parameters for the Li/LFP cathode cell – measurements at OCV. Model parameters are as in Figure 5.

| Time   | $R_1$ [Ω] | $R_2$ [Ω] | $C_2$ [F] | $R_3$ [Ω] | $C_3$ [F] | $R_4$ [Ω] | $C_4$ [F] | $A_1$ |
|--------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-------|
| After Discharge | 10 | 33 | $3.5 \times 10^{-5}$ | 35 | $2.7 \times 10^{-4}$ | 171 | $1.1 \times 10^{-2}$ | 58 |
| 10min  | 9.9 | 33 | $3.4 \times 10^{-5}$ | 42 | $2.0 \times 10^{-4}$ | 188 | $1.0 \times 10^{-2}$ | 55 |
| 20min  | 9.7 | 32 | $3.4 \times 10^{-5}$ | 37 | $2.2 \times 10^{-4}$ | 180 | $1.0 \times 10^{-2}$ | 49 |
| 30min  | 9.9 | 33 | $3.4 \times 10^{-5}$ | 34 | $2.7 \times 10^{-4}$ | 179 | $1.0 \times 10^{-2}$ | 49 |
| 40min  | 9.7 | 32 | $3.3 \times 10^{-5}$ | 40 | $2.1 \times 10^{-4}$ | 193 | $1.0 \times 10^{-2}$ | 50 |
| 50min  | 10  | 35 | $3.4 \times 10^{-5}$ | 40 | $2.3 \times 10^{-4}$ | 206 | $1.0 \times 10^{-2}$ | 51 |
| 1hr    | 10  | 36 | $3.5 \times 10^{-5}$ | 41 | $2.4 \times 10^{-4}$ | 214 | $1.0 \times 10^{-2}$ | 51 |
| 2hr    | 9.8 | 33 | $3.4 \times 10^{-5}$ | 40 | $2.1 \times 10^{-4}$ | 208 | $1.0 \times 10^{-2}$ | 54 |
| 11hr   | 8.7 | 25 | $3.3 \times 10^{-5}$ | 32 | $1.9 \times 10^{-4}$ | 186 | $1.0 \times 10^{-2}$ | 51 |
A model for the diffusion through the LFP particle was proposed by Srinivasan and Newman.\textsuperscript{13} The model suggests a biphasic structure of the LFP particle, a lithium-rich and a lithium-poor phase. The relative volume of each phase changes with the state of charge, and equilibrium between the phases is not reached within the time period of cycling. For lithiation, this causes a growing layer of fully lithiated LFP on the surface of the LFP particle, gradually increasing resistance to a further lithiation step. For delithiation, a lithium-depleted layer grows on the surface, increasing the extraction barrier of lithium ion from within the particle (and thus increasing the overpotential), Figure 8. Our tests show that $R_{sd}$ values measured at 10%, 50% and 90% SOC are in good qualitative agreement with the model of Srinivasan and Newman. However, direct comparison of measured resistances with the model would require some adjustments as this work used LFP particles significantly larger than those used for modelling; the LFP powder we used was sieved to $d_{50} \leq 700\text{nm}$, while the model used a mean particle diameter of 104nm.

On the basis of the analysis of the experimental data (Figures 5–8, Table I and Table II), we suggest that printing does not alter the charge/discharge mechanism of lithium iron phosphate.

Conclusions

We have presented a commercially viable and readily available drop-on-demand dispensing method of printing and patterning of LFP particles at high throughput, followed by a measurement of the electrochemical performance of printed cells. The results show that printing does not alter the charge/discharge mechanism of LFP. The Nyquist plots of the printed LFP cathode cell at different states of charge (10%, 50%, and 90%) are shown in Figure 7. The experimental data is compared with the model predictions in Figure 8. Table II summarizes the model fit parameters for the Li/LFP cathode cell at 1C. The model fit parameters are as in Figure 5.

| Lithiation | $R_1$ [Ω] | $R_2$ [Ω] | $C_2$ [F] | $R_3$ [Ω] | $C_3$ [F] | $R_4$ [Ω] | $C_4$ [F] |
|------------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| 10%        | 21        | 45        | $3.1 \times 10^{-5}$ | 251       | $6.0 \times 10^{-5}$ | 252       | $1.4 \times 10^{-3}$ |
| 50%        | 21        | 62        | $3.4 \times 10^{-5}$ | 330       | $6.2 \times 10^{-5}$ | 505       | $1.4 \times 10^{-3}$ |
| 90%        | 22        | 52        | $3.3 \times 10^{-5}$ | 209       | $7.0 \times 10^{-5}$ | 579       | $1.7 \times 10^{-3}$ |
| Delithiation | 21        | 45        | $3.2 \times 10^{-5}$ | 229       | $6.3 \times 10^{-5}$ | 262       | $1.7 \times 10^{-3}$ |
| 50%        | 20        | 60        | $3.4 \times 10^{-5}$ | 329       | $6.2 \times 10^{-5}$ | 475       | $1.5 \times 10^{-3}$ |
| 90%        | 21        | 59        | $3.5 \times 10^{-5}$ | 276       | $6.6 \times 10^{-5}$ | 774       | $1.7 \times 10^{-3}$ |

Figure 7. Nyquist plots of Li/printed LFP cathode cell at three states of cathode lithiation (10%, 50% and 90%), for both delithiation (top) and lithiation (bottom) processes. Dots – experimental values, solid lines – calculated using the equivalent circuit model (Figure 5), dashed lines – calculated only for the $R_tC_t$ circuit.

Measurements at 1C, $20\mu\text{A}$ amplitude, 1Hz–500kHz frequency range.

Table II. Model fit parameters for the Li/LFP cathode cell – measurements at 1C. Model parameters are as in Figure 5.
the LFP cathodes. Our results are completely reproducible, and the process is facile. This method can be generalized to other types of active materials.

We have shown that printing parameters and performance can be controlled. The main limiting factor in this method is the ink composition itself. A more complete characterization of the different parameters of ink composition, its preparation, the rheological behavior and optimization will be addressed in future work.

The electrochemical characteristics of the printed cathodes and the impedance components of the AC spectra of Li/LFP cells were shown to be unaffected by the printing procedure. The cycle-life, efficiency and cycling-rate capabilities were all shown to be very high and comparable to those of commercial cathodes.

Acknowledgments

Funding for this project is provided by the government of Israel.