

LiCoO₂ Texturing by Laser Induced Forward Transfer for Printed Microbatteries

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ABSTRACT

Laser induced forward transfer (LIFT) is used to print Li-ion battery electrodes. We show a preferred orientation of LiCoO₂ particles in the (003) direction relative to non-laser transferred materials. While the laser energy does not alter the degree of orientation, the number of passes and transfer distance both have a significant influence on the observed texturing. We use a geometric argument based on the arrangement of plate-like particles on the substrate to explain the observations. When the plate-like particles encounter a perfectly flat substrate, they are able to align flat, causing (003) domains parallel to the substrate to be over 30 times more predominant than either (101) and (104) domains. From this maximum degree of orientation subsequent passes decrease the overall texturing of the samples as transferred particles encounter increasingly rough surfaces. At larger transfer distances, the areal density of particles reaching the substrate decreases, resulting in increased available substrate surface area and therefore more predominant particle orienting.

Keywords: Li-ion microbattery, Lithium cobalt oxide, crystal orientation, LIFT, laser direct write, laser printing, battery electrode

1. INTRODUCTION

As advances in electronic devices have enabled smaller and lower power consumption systems, the development of small scale energy storage to meet the power demands of these systems has continued to grow. Secondary lithium-ion batteries are desirable in these systems due to their relatively high energy density and long cycle life¹. These favorable properties also make such batteries promising as integratable micropower sources for autonomous microsensors, implantable medical devices, smart cards, and microelectromechanical systems².

In order to take full advantage of the benefits of miniaturization in electronic systems, specialized battery fabrication technologies have emerged as necessary counterparts to standard lithographic processing. One such technology is the laser induced forward transfer (LIFT) printing process, which uses a pulsed laser beam to transfer material from a donor to a receiving substrate with high spatial accuracy³. In the case of small scale energy storage, LIFT is especially advantageous as it allows direct integration of the power source into an electronic circuit, eliminating a significant amount of weight and resistive losses associated with conventional packaging^{4,5}.

In the past, LIFT has shown to be a promising method for fabricating Li-ion microbattery electrodes⁶⁻⁸. However, little research has examined the effects of laser processing parameters on battery performance. In particular, the orientation of the particles in the electrode can have a significant effect on the electrochemical performance⁹⁻¹². In this paper, we discuss the orientation and texture of LiCoO₂ electrodes produced in the LIFT process. We find that the orientation is independent of the laser energy, but dependant on other aspects of the laser transfer process including the distance between the donor and receiving substrates and the volume of material transferred. These results are analyzed and understood in the context of the geometrical constraints of the platelet-like particles composing the electrode. By determining the effects of laser processing parameters on transferred-particle orientation, an understanding of this important fabrication technique is established.

2. EXPERIMENT

The basic LIFT approach is shown schematically in Figure 1. The laser used for the transfer process is a frequency tripled Nd:YVO₄ laser, operating at 355 nm with 30 ns pulses. For all experiments described here, the beam size is set at approximately 50 μm and laser energy of 25 μJ per pulse is used. A donor substrate composed of a glass microscope

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slide with an ink of the desired material is positioned using variable thickness spacers above a glass receiving substrate. The donor/receiver substrate assembly is placed on an xyz manipulation stage and is moved at a rate of 50 mm/s in increments of 60 μm between pulses so as to raster the laser pulses across the 1 cm x 1 cm transfer area. Multiple passes are used to increase the amount of ink transferred to the sample. The weight of material transferred is determined using a microbalance before and after transfer.

The electrode material in this study is based on the active material LiCoO_2 (Aldrich, 99.8%). An ink containing 92.5 wt% LiCoO_2 , 4.2 wt% carbon black (Alfa Aesar, Acetylene, 50% compressed, 75 m^2/g , 99.9%), and 3.3 wt% polyvinylidene fluoride (PVDF) is mixed in a balance of 1-methyl-2-pyrrolidone (NMP; Sigma-Aldrich, 99.5%) that is 1.22 times the weight of the dry materials. The dry powders are first mixed at 2000 rpm for 2 minutes. Next, 70% of the NMP is added to the powders, mixed at 2000 rpm for 2 minutes, and ultrasonicated for approximately 20 seconds to break up any agglomerates. Finally, a premixed solution of NMP with 8 wt% PVDF is added to the mixture to achieve the appropriate concentrations and mixed at 2000 rpm for 5 minutes. The resulting ink is spread on a 1 mm thick glass slide using a wire coater (#6), resulting in a donor substrate of approximately 10-15 μm .

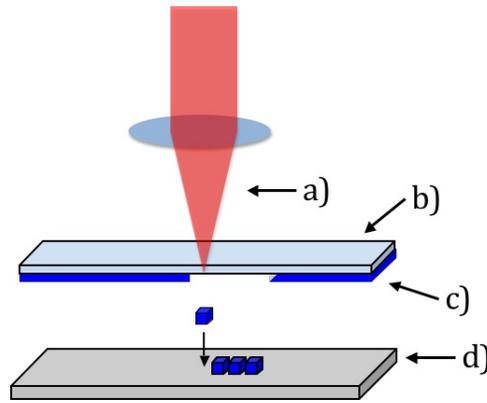


Figure 1: LIFT printing process: a) focused pulsed laser; b) transparent support (glass slide); c) donor substrate; d) receiving substrate.

Deposited materials are analyzed using scanning electron microscopy (SEM) and X-ray diffraction (XRD) to determine the morphology and crystal structure. SEM images are obtained on an FEI XL30, with a voltage of 5 kV in secondary electron imaging mode. XRD measurements are carried out using a Rigaku MiniFlex diffractometer equipped with a $\text{Cu K}\alpha$ source (1.5406 \AA) in the Bragg-Brentano configuration. The patterns are collected in the 2θ range of 10-80 $^\circ$, with a step size of 0.03 $^\circ$ and a speed of 1 $^\circ/\text{min}$. The resultant spectra are analyzed using MDI Jade software.

X-ray diffraction (XRD) is well suited to determine the orientation of crystalline particles because, in the conventional mode, the technique only detects the crystal planes parallel to the sample surface. Therefore, the integrated intensity, or area, of a specific peak in a spectrum is proportional to the total volume of the crystal domains having the associated crystal plane parallel to the sample surface. One method for quantifying the degree of orientation is to compute the volumetric ratio of crystal domains having particular crystal planes parallel to the sample surface, according to:

$$\left(\frac{V_1}{V_2}\right)_S = \frac{\left(\frac{P_1}{P_2}\right)_S}{\left(\frac{P_1}{P_2}\right)_R} \left(\frac{\mu_1}{\mu_2}\right)_S, \quad (1)$$

where P is the integrated intensity, the subscripts 1 and 2 correspond to the different domains, the subscript S indicates the sample, and the subscript R indicates the randomly oriented sample. The linear absorption coefficient, μ , is assumed to be constant^{13,14}.

An alternative method is to calculate the Lotgering factor, F , which is considered to be an estimate of the degree of orientation in a textured material¹⁵. The Lotgering factor, which varies from 0 for a random, non-oriented sample to 1 for a completely oriented sample, is calculated according to the following equation:

$$F = \frac{(P - P_o)}{(1 - P_o)}, \quad (2)$$

with,

$$P = \frac{\sum I_{(00l)}}{\sum I_{(hkl)}}, \quad (3)$$

where P is the sum of the integrated intensities for all $(00l)$ diffractions divided by the sum of the intensities of all (hkl) diffractions, and P_o is similarly defined for a randomly oriented sample.

3. RESULTS

LiCoO₂ has the α -NaFeO₂ layered structure with rhombohedral symmetry ($R\bar{3}m$ spacegroup). In this ABO₂-type rock salt superstructure oxide, the oxygen anions form a cubic close-packed (CCP) structure, and the cobalt ions occupy the 3a sites of the octahedron, while the lithium ions occupy the octahedral 3b interstices. This structure exhibits alternating Co³⁺ and Li⁺ planes in an ABCABC stacking arrangement, with lithium in octahedral sites between O-Co-O sheets¹⁶⁻¹⁸. Due to the layered nature of the α -NaFeO₂ structure, intercalation and deintercalation of the lithium ions in LiCoO₂ is facile. However, because of the anisotropy of the structure, the electrochemical insertion and extraction of lithium depends heavily on the orientation of the crystal. For the purposes of this investigation, we consider three main planes that are prominent in the XRD spectra, the (003), (101), and (006) planes, as shown in Figure 2. As we can see from the picture, one can envision easier transport of Li along the (003) plane as compared to the other planes.

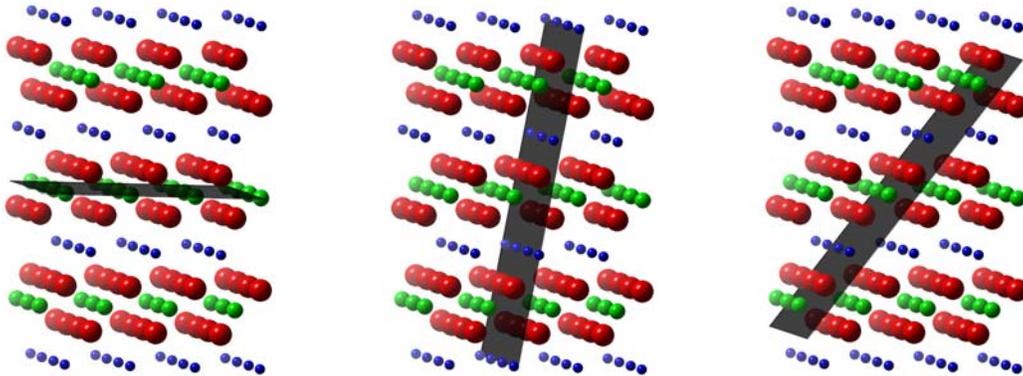


Figure 2: LiCoO₂ structure highlighting different planes: a) (003); b) (101); c) (104). Green = lithium, blue = cobalt, red = oxygen.

To establish a baseline, the XRD spectrum of non-transferred LiCoO₂ ink is collected, and is shown in Figure 3a. In this case, the mixed ink is spread on a glass substrate with a spatula and the spectrum is obtained. The peak assignments are those of LiCoO₂ (PDF #44-0145), and we see the prevalence of the (003), (101), and (104) planes as expected. As a comparison, the powder XRD spectrum as predicted for LiCoO₂ by standard structural model is shown in Figure 3b. It is immediately apparent that the spectrum for non-transferred ink shows a shift in peak heights, indicating a preference for the (003) orientation.

The increase in the (003) direction for non-transferred samples is related to the geometry of the starting LiCoO₂ material. Rather than a powder with randomly distributed shapes, orientations, and sizes, the starting material is plate-like in appearance as shown in the SEM image of Figure 4. Here we see the presence of large plates of LiCoO₂ that are intermixed with the conductive graphite additive. Such structures will therefore preferentially exhibit the orientation of the larger facet. The (003) plane is the most closely packed plane (Figure 2), and has the lowest surface energy and the slowest growth direction¹⁰. These arguments confirm the experimental observation of preferred (003) orientation in the plate-like films.

If we examine the XRD of laser-transferred material, we observe a drastic change in the particle orientation (Figure 5). As can be seen in the XRD spectrum of the sample made at 82 μJ , the (003) diffraction peak is more intense relative to the other peaks when compared to the same peak in the non-transferred ink spectrum (Figure 3). In order to understand this effect, we look at the parametric dependence of the orientation with respect to processing parameters.

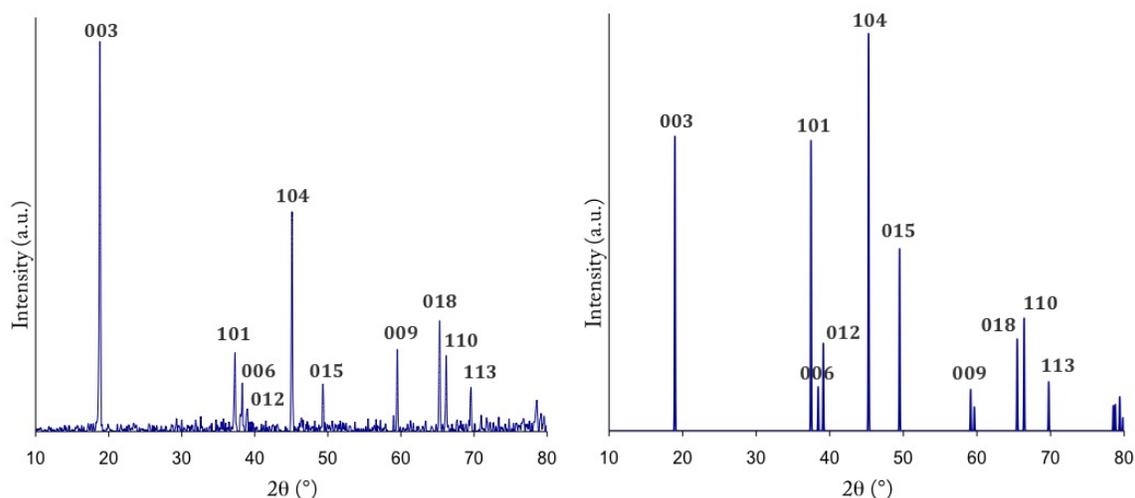


Figure 3: LiCoO₂ XRD spectra: a) non-transferred ink; b) model prediction

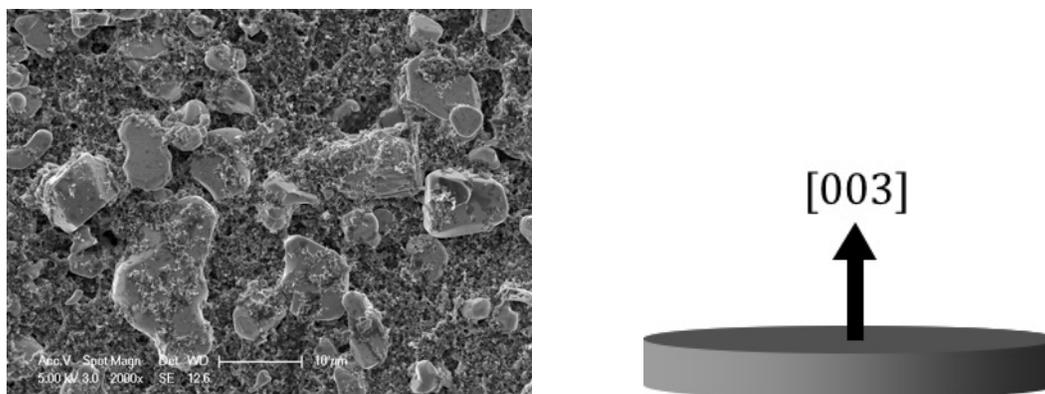


Figure 4: SEM of LiCoO₂ ink showing plate-like particles of LiCoO₂ intermixed with graphite (b) LiCoO₂ particle orientation.

The first processing parameter investigated is laser energy. Samples are made with laser energies between 28 and 136 μJ , keeping constant the transfer distance (200 μm) and number of passes (three). Figure 6 shows the degree of orientation relative to the (003) plane as determined by the Lotgering method. Most notably, we see the orientation is independent of the applied laser energy during LIFT. In addition, we see that the Lotgering factor for the transferred material is consistently greater than 0.7. This suggests that the laser transfer process does, in fact, alter the orientation of the LiCoO₂ particles relative to the random, non-laser transferred sample (Figure 3a).

The second processing parameter investigated is the number of passes used in fabricating the samples. Samples are made using between one and five passes of the laser, keeping constant the transfer distance (200 μm) and laser energy (66 μJ). Figure 7 shows the Lotgering factor and the volumetric domain ratios for each sample. As can be seen, the Lotgering factor for the single pass sample is almost unity (0.97), which indicates a nearly perfectly oriented sample. With each successive pass of the laser the Lotgering factor decreases, indicating that the overall orientation of the sample is reduced. While the degree of orientation clearly decreases with each pass, it is important to note that the (003) domain is still more prevalent than the other domains.

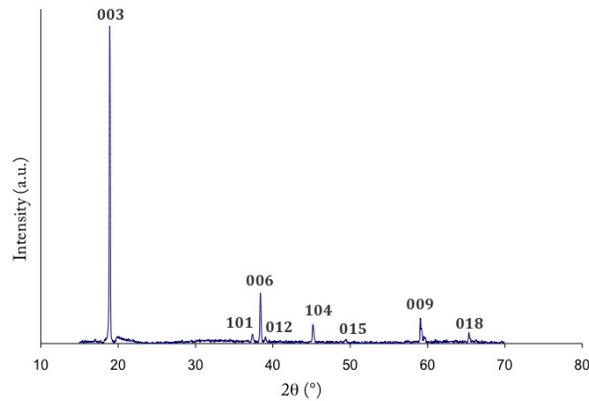


Figure 5: XRD spectrum of LiCoO₂ transferred onto glass at 82 μJ

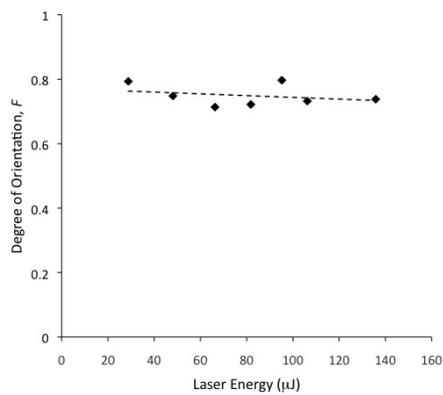


Figure 6: Lotgering factor for (003) orientation at different laser energies

The final processing parameter investigated is the distance between the support slide and the substrate, known as the transfer distance. Samples are made using transfer distances between 100 and 800 μm, keeping the laser energy (66 μJ) and number of passes (three) constant. Figure 8 shows the Lotgering factor for each sample. It is evident from the figures that the degree of orientation increases significantly as the transfer distance is increased. In fact, the Lotgering factor increases by 50%, from 0.60 to 0.90 over the range of this study.

In order to explain these experimental observations, we invoke the geometric constraints acting on the particles as they are transferred. Upon transfer, the particulate inks coalesce on the substrate. Excess solvent evaporates, leaving the solid particle film behind. This process is independent of laser energy and therefore we would not expect any changes in the film orientation properties. However, if we consider the initial processes occurring at the substrate we can understand the emergence of (003) texture under laser transfer. Consider a droplet of particles hitting the flat substrate. Regardless of the particle orientation when it hits the substrate, the particle will attempt to reach its most stable orientation. As the ink dries, surface tension will force the particle to lie flat against the surface, as this is the least energetic configuration. These flat-lying particles result in a very strong (003) peak in the diffraction pattern owing to the orientation of these plate-like particles.

As the film builds up, the subsequent transfers are not hitting a flat surface, but one on which there is existing material. In this case of multiple passes, the surface tension flattening mechanism is no longer valid. Rather, we look to the cartoon of Figure 9 to describe what happens. On the second pass, the transferred particles encounter parallel particles on top of the flat substrate with space between them. However, the overall surface is no longer flat, so neither surface tension nor the particle's inertia is able to force the particle into the parallel orientation. Instead, it is likely to encounter another particle and remain with a non-zero angle. On subsequent passes, this effect continues and intensifies, and each particle that is transferred encounters an increasingly rough surface. The result of this phenomenon is very strong preferred crystallographic orientation, or texturing, on the first pass, followed by decreased texturing with each successive pass of the laser.

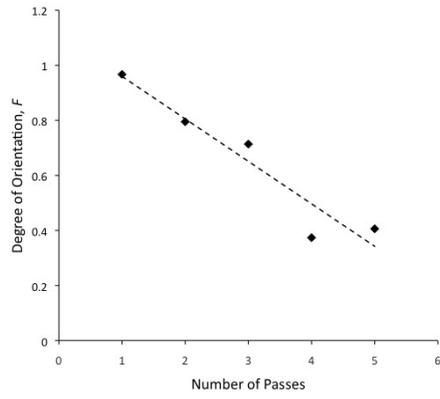


Figure 7: LiCoO₂ orientation for different passes

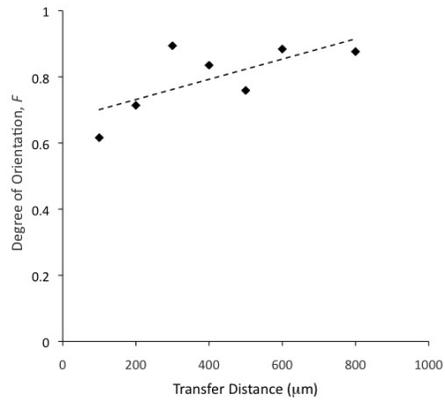


Figure 8: LiCoO₂ orientation for different transfer distances

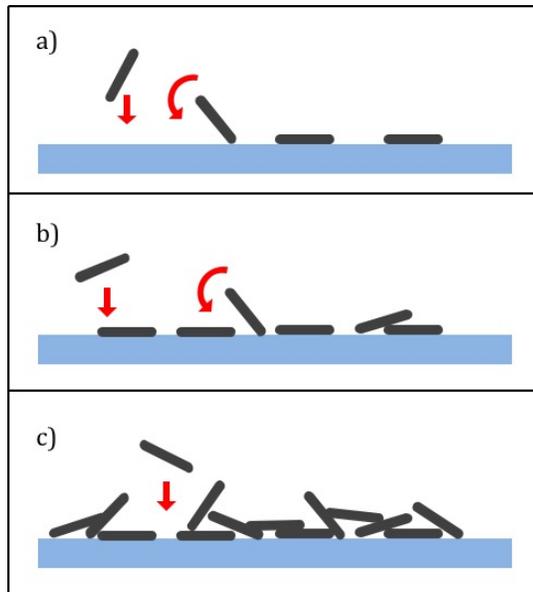


Figure 9: Proposed texturing mechanism: a) first pass; b) second pass; c) third pass

One indication of the validity of the proposed mechanism is the calculated layer thickness. Based on the density of LiCoO_2 (3.7 g/cm^3)¹⁹, an assumed particle fill factor of 75%, and a transfer area of 10 mm^2 , the average pass, which transfers about 1 mg of ink, results in a layer approximately $4 \text{ }\mu\text{m}$ thick. Thus, it is reasonable to assume that each layer of transferred ink is only a few particles deep.

The increase in texturing with increased transfer distance is consistent with the geometric texturing mechanism. When the transfer distance is short, the area on the substrate covered with ink due to a single pulse of the laser is relatively small and the areal density of material is large. Thus, there is not enough exposed substrate surface to allow all of the transferred particles to assume the parallel orientation (Figure 10). When the transfer distance is large, the transfer footprint is relatively large and the corresponding density is low. Therefore, transferred particles are more likely to find a flat surface. Furthermore, as the transfer distance increases, less material reaches the substrate (Figure 11), as indicated by the decrease in weight of transferred ink. Thus, both effects serve to reduce the areal density of particles, and a greater degree of texturing is to be expected.

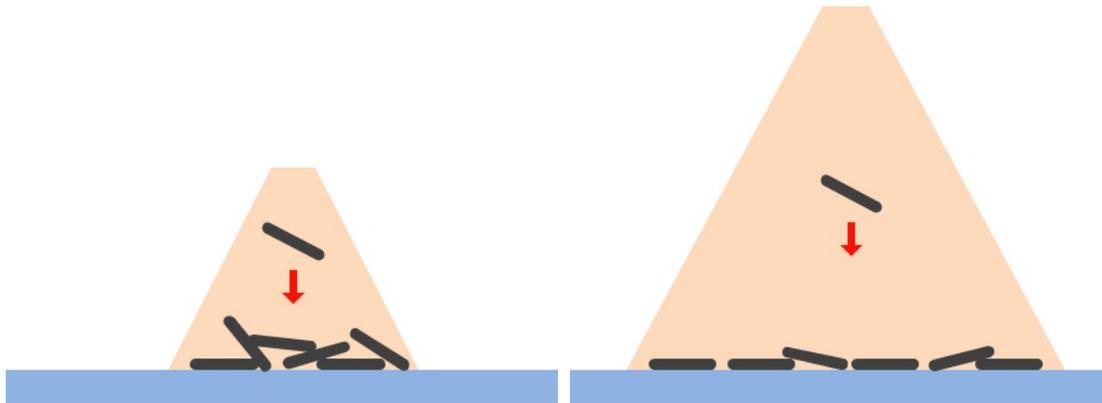


Figure 10: Proposed texturing mechanism: a) short transfer distance; b) long transfer distance

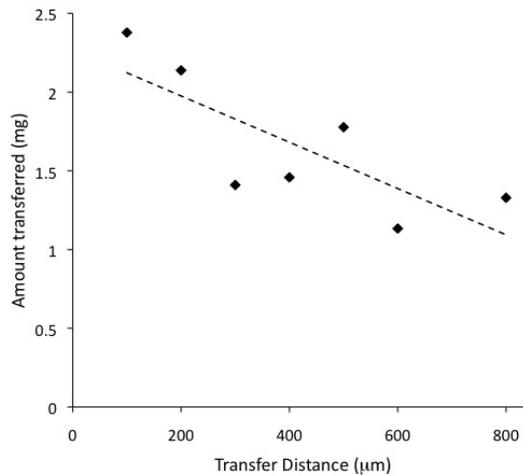


Figure 11: Effects of transfer distance on LiCoO_2 texturing on the mass of ink transferred

4. SUMMARY

A preferred orientation of LiCoO_2 particles is demonstrated to result from the laser induced forward transfer (LIFT) printing process. Composite inks of plate-like LiCoO_2 particles, carbon, binder, and solvent are laser-forward transferred onto glass substrates. The laser energy, number of passes, and transfer distance are systematically altered to determine the mechanism of texturing. We determine that particles orient with plate faces parallel to the substrate due to

energetic considerations when the particles encounter the receiving substrate. As the laser energy increases beyond the threshold level, the mechanism of forward transfer is not altered, and therefore the degree of orientation does not change. The number of passes, however, heavily influences the degree of particle orientation. On the first pass of the laser, the transferred particles encounter a perfectly flat substrate and therefore align flat, with (003) planes parallel to the substrate. After the first pass, the (003) domains parallel to the substrate are more than 30 times more predominant than the (101) and (104) domains, resulting in a Lotgering factor of 0.97. Subsequent passes decrease the overall texturing of the samples, as particles encounter increasingly rough receiving surfaces. As the transfer distance is increased, the areal density of particles decreases due to the dynamics of the explosive plume, resulting in increased substrate surface area and therefore more predominant particle ordering.

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