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Characterization of Ultrasonic Precursor Solution Spraying for Battery Material Synthesis

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Characterization of Ultrasonic Precursor Solution Spraying for Battery Material Synthesis

Patrick Champlin[a)]

The effects of various conditions on the operation of an ultrasonic atomizer for battery material precursor solution spraying were investigated. The diameter of the droplets formed from this device was expected to roughly match that of the orifices from which they originated; however, two distinct modes of operation were observed for ejection from arrays of 17 μm and 55 μm orifices: 1) orifice-size dependent jetting and 2) generation of a mist of small droplets (< 10 μm), the size of which was frequency independent. Experiments were conducted at the first and second half-wave resonances of a 1.2 mm high chamber (0.63 and 1.05 MHz respectively), though extensive characterization was limited to the second resonance. In most cases, the flow rate was proportional to applied voltage on the piezoelectric drive, after a threshold amplitude was exceeded. The ability to generate sub-10 μm droplets from larger orifices was not expected, but this capability should prove advantageous for the production of atypical battery materials by spray pyrolysis.

With increasingly imminent dangers posed by air quality and global warming, a transition of energy generation away from hydrocarbon and coal-based combustion plants is inevitable as new and sustainable sources are already beginning to replace them. But these sources are not without their own problems, as the rise of hybrid and electric vehicles, efficient power grid management techniques, and even portable electronics have brought attention to a growing need for reliable and compact rechargeable power sources. Due then to their significant energy density, flexibility, and lifespan,[1] lithium-ion batteries have presented themselves as good candidates to fulfill this need.

Despite the fact that these devices show great potential, they nonetheless face a number of serious questions. Besides the difficulty associated with procurement of their necessary components, lithium-ion battery development has been historically slowed by complications in designing suitably functional material interfaces.[1] Though much work on the optimization of battery chemistries has been devoted to this subject, in particular demonstrating $Li_{1.2}Mn_{0.54}Ni_{0.13}Co_{0.13}O_2$ to behave admirably as a high-performance cathode material,[2] recent reviews have now proven the geometry of the particles used in the formation of these materials also plays a major role in their final efficacy. Specifically, nanoporous particles on the order of microns in diameter are most desirable.[3,4] Unfortunately, these particles are limited in how large they can grow without becoming hollow, which corresponds to reduced performance. Conventional procedures such as spray pyrolysis have issues producing non-hollow particles above 2 μm in size, while more innovative methods such as slurry spray pyrolysis, which includes the added step of mixing the particulate matter from an initial spray pyrolysis with the precursor of a second, have been able to push this value up to 5 μm.[3] In either case though, the final particle size is dependent on the diameter of the droplet from which the particle is formed, where a precursor droplets of diameter 10 μm or less are required so as not to produce hollow particles.[3] This issue is illustrated in Figure 1.[5]

A device capable of accurately and rapidly producing liquid droplets of a given size is desirable to reliably manufacture the particles needed for these battery materials. Existing systems that could be used for this purpose produce droplets either with too wide of a size distribution or far too slowly.[6] Thus, in order to address this need, we introduced ultrasonic Microarray Spray Tuning, or uMIST. This device consists of a lead zirconate titanate or PZT-8 piezoelectric

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[a)] Under the supervision of Dr. J. Mark Meacham.

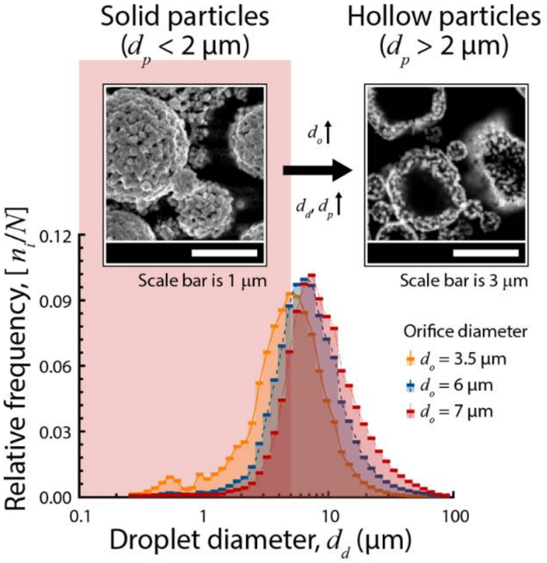

FIG. 1. The formation of hollow particles.[5]

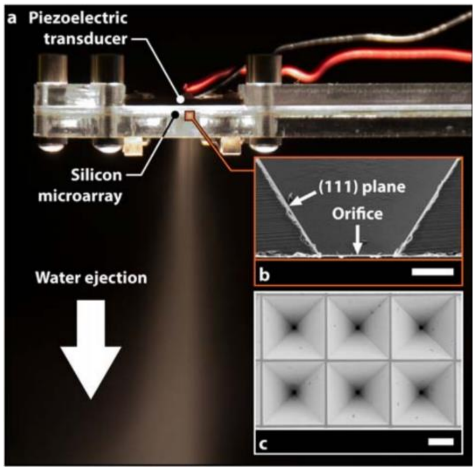

FIG. 2. (a) The uMIST device during operation. (b/c) SEM images of the nozzle geometry.[7]

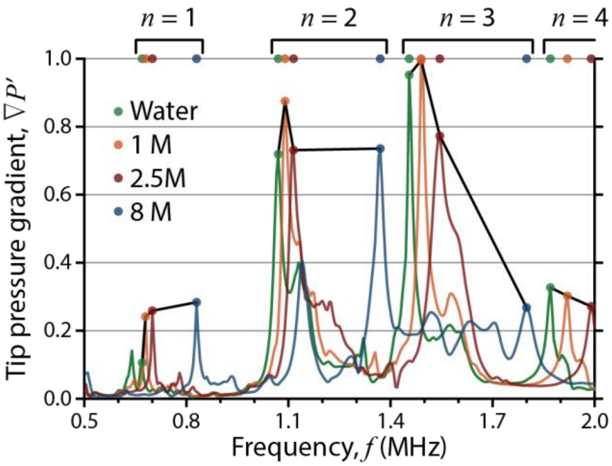

FIG. 3. Simulated resonant frequencies of the 1.2 mm high chamber for various fluid compositions.[5]

transducer, a reservoir and spray chamber for the precursor solution, an aluminum layer to couple the piezoelectric and the chamber, and a silicon microarray of nozzles. When driven by a standard function generator and amplifier at certain resonant frequencies of the chamber, the piezoelectric will develop an acoustic pressure field that pushes fluid through the orifices – while automatically pulling additional fluid from the reservoir. The device can be seen during operation in Figure 2,[7] while results of a simulation predicting resonant frequencies of a representative 2D chamber loaded with various precursor solutions are provided in Figure 3.[5] Piezoelectric actuation at ultrasound frequencies creates a robust and continuous spray, while simultaneously allowing for accurate droplet size selection by simple modification of the spray parameters.

We investigated the effects of altering spray parameters on the operation of the device and characteristics of resulting battery particles. For this purpose, two reservoir heights (1.0 and 1.2 mm) and two orifice sizes (17 to 55 μm) were used, and the piezoelectric was driven at the first two resonances of each reservoir height. Note that these resonances are functions of the height of the chamber and the speed of sound characteristic of the fluid, with approximate values of 0.63 and 1.05 MHz corresponding to water in a 1.2 mm high chamber.[5] Three operating fluids were used, water, NaCl salt solutions representing the precursor, and finally the precursor itself. The frequency of operation for each case was found simply by altering the frequency of the input until a spray was obtained, while the size of the produced droplets was estimated via high-speed imaging.

Initially, it was believed that the size distribution of the droplets would be measured most accurately by a Phase Doppler Particle Analyzer (PDPA), but the device was eventually found to be giving erroneous results due to the nature of the produced spray. PDPA measurements suggested that 60 μm orifices were producing only a population of droplets as small as 7 μm in diameter. This in turn gave reason to believe that there was some instability in the droplets – which would normally be on the same spatial order as the orifice from which they were produced – causing them to burst, and that there would be a transition into this regime for larger orifice sizes. The measurement error was discovered while using high-speed video to image the droplet production process. We recognized that though the device was indeed producing a cloud of 7 μm droplets, it was doing so with very little volumetric flow. Instead, there were large streams of approximately 55 μm droplets at many orifices, which had simply been missed by the PDPA. It is thought that these larger droplets can be captured by PDPA if measurements are taken while scanning across the array; however for the current studies, the PDPA was essentially abandoned in favor of the high-speed video camera.

As for the effect of varying the height of the reservoir, the results were essentially what was anticipated. Resonant frequencies were found to decrease with increasing reservoir height, though it had very little impact on the size of the droplets that were produced. Interestingly, an anomalous mode between the first and second resonances was observed for the reservoir with 1.0 mm height. This special state was recognized as a unique mode actually established partially within the aluminum coupling plate and piezoelectric. The chamber resonant frequencies were found to change at near-constant rates between the different fluids as shown in Figure 3. With these results, we restricted further tests to the 1.2 mm reservoir.

Some parameters did alter the characteristics of the spray. As stated earlier, the most important of these parameters was the orifice diameter – with the size of the generated droplets of all three fluids following on average closely with this value. For example, the water droplets coming out of the 17 μm orifices were approximately 17 μm in size; with nearly all of the droplets fitting within a 14 to 22 μm range. Though one is limited to using the resonant frequencies corresponding to the chamber geometry and operating fluid, a possible frequency dependency discovered in earlier work might be used to more carefully fine-tune the size of the particles.[7]

Additionally, one could in general observe both a primary stream and a secondary mist, where the primary stream droplet diameter was roughly a function of the orifice size, and the secondary mist droplet diameter was more or less constant. Specifically, the larger orifices of 55 μm displayed a marked distinction, while conversely the two droplet sizes were nearly indistinguishable for the 17 μm orifices. Interestingly, the mist could almost be eliminated when the function generator was operated in “burst” mode, in which the device was pulsed at regular intervals, though it is unclear why this behavior was observed. This phenomenon is shown in Figures 4(a) and 4(b). Finally, the amplitude of the input signal was identified to have a direct influence on the volume of the produced spray, increasing alongside the voltage. This gain can be seen by comparing Figures 4(a) and 4(c).

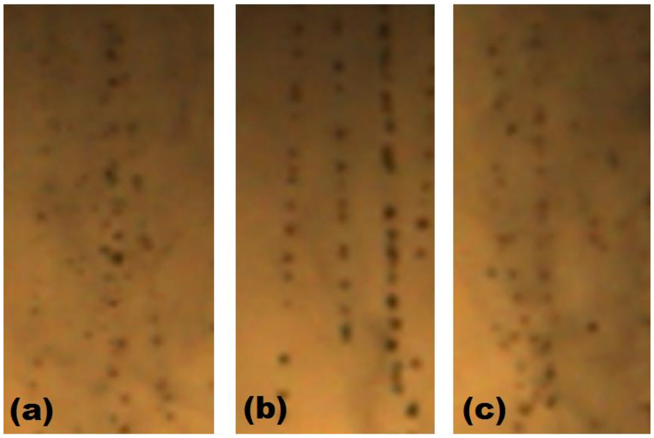

FIG. 4. Precursor spray from the device at (a) 300 mV, (b) 300 mV in burst mode, and (c) 500 mV.

In conclusion, the uMIST device was used under various conditions to test their effect on the behavior of its spray. The diameter of the droplets produced depended principally on the orifice diameter, though a secondary mist of much smaller droplets was also observed. Device resonant frequencies of operation decreased with an increase in reservoir height as expected, and the flow throughput was proportional to applied voltage. Lastly, the primary stream was found to be more easily distinguishable from the secondary mist for larger orifices and under burst mode operation. uMIST has demonstrated a number of desirable operating characteristics for the production of precursor droplets needed for the synthesis of novel cathode materials. In fact, work is underway to use the device to manufacture functional particles and batteries.

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