Electrospray Synthesis of Graphene Oxide–Mixed Metal Oxide Nanocomposites for Energy Storage

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Abstract

Synthesis of composite materials for an improved lithium-ion battery anode with the necessary attributes for a high performance anode prompted the examination of cobalt-manganese oxide because of its high capacity for lithium ions, and graphene oxide because of its high surface-to-volume ratio and high conductivity. Mixing these materials in a controlled manner is challenging at the nanoscale. To that end, the electrospray (ES) technique is used. The ES uses an electric field to emit droplets (in which said nanomaterials are encapsulated) that have a few key characteristics: 1) they are all homopolarly charged; 2) their size can be controlled with relative ease; and 3) both size and charge level are strongly dependent on the electric conductivity of the solution that can be varied by orders of magnitude. As a result, highly controlled sprays can be established in a broad range of droplet size and charge. A twin spray setup with opposite charges on the top and bottom sprays was used, in which a cobalt manganese oxide precursor was ejected from the top spray and the graphene oxide sheets were delivered from the bottom. The aerosolized graphene oxide appeared as either flat sheets or crumpled ones, which was tentatively attributed to different levels of dryness of the aerosol at the impaction on the substrate. Coupling of the graphene oxide with the mixed oxide nanoparticles showed sparse evidence of good mixing of the two. In addition, challenges with the precipitation of the graphene solution and with its electrospraying with negative polarity, as manifested by instabilities and corona discharge, prompted the on-going search for alternative ES synthesis methods either by layer-by-layer deposition or using a different source of carbon.

Introduction and Background

Most modern applications for Li-ion batteries, energy storage devices that rely on the transfer of lithium ions to produce electric current and power, are high power: computers, phones, and electric vehicles. The lithium-ion battery is a ubiquitous form of energy storage because of its simple structure and effectiveness as an energy storage medium. The battery consists of an electrolyte, a cathode and an anode. The anode acts as a temporary lithium ion holder. During discharge, the lithium ions travel through the electrolyte back to the lithium-containing cathode, producing a current and energy output. The cathode of the Li-ion battery has been very well researched and there are currently multiple lithium-containing compounds used commercially (Fergus, 2010; Taberna, Mitra, Poizot, Simon, & Tarascon, 2006). On the other hand, the only commercially used material used for the anode is carbon black, a carbon based material possessing an amorphous quasi-graphitic molecular structure. This work focuses on creating a new anode made of a more ideal material than carbon black.

When considering the effectiveness of an anode, there are two things that must be taken into account. The first is the capacity, or the amount of lithium ions that the material can store. The larger the capacity, the longer we can expect the battery life to last. The second is the conductivity. The conductivity is the ability to allow electrons to flow through the material (the generation of current). If a material has a high capacity, but does not allow the electrons to flow upon the movement of the lithium ions (i.e. low current), then the power that the battery can deliver—the energy over a length of time—is low.

Research has shown that carbon black has a theoretical capacity of approximately 400 milliamps hour/gram (Dominko et al., 2003). Cobalt manganese oxide, a promising mixed metal oxide that is used in this paper, has a theoretical capacity of approximately 1000 milliamps hour/gram (Zhi et al., 2008). Although the capacity is very high, the conductivity is too low for sole use as an anode. The goal is to mix this material with another that has a high conductivity and does not interfere with the capacity of the metal oxide. One such material is graphene oxide—cheap, single-molecule thick sheets of carbon that have a similar conductivity of carbon black, but a higher surface area to volume ratio, allowing more metal-to-carbon interaction(Mustafa et al., 2012).

In order to effectively mix the cobalt manganese oxide and graphene oxide, the electrospray (ES) technique will be used. The ES technique subjects liquid to an electric field at specific flow rates to form a cone from which droplets emerge. There are two distinct advantages to using the electrospray. The first is that the droplets are homopolarly charged, meaning that they repel each other and prevent coagulation, which preserves their size distribution (Cloupeau & Prunet-Foch, 1989; Fernández de La Mora, 2007). Since they are charged, their motion can be controlled if they are subjected to an external electric field. Secondly, the size of these droplets, which are monodisperse in nature, can be chosen (Cloupeau & Prunet-Foch, 1989; Fernández de La Mora, 2007). Since the droplets can be manipulated with such precision, the electrospray allows the engineering of materials at the nanoscale. The goal is to have every single nanoparticle of cobalt manganese oxide in electrical contact with a graphene oxide sheet to ensure a pathway for electron flow.

We aim to use the precise control provided by the electrospray to deposit our graphene oxide and mixed metal oxide to study the effect of this method in creating a better anode for the lithium ion battery.

Methodology

Chemicals

All chemicals were used as received from Sigma Aldrich. The chemicals used include 200 proof ethanol, ethylene glycol, acetic acid, hydrochloric acid, and 1-butanol.

Nanomaterials

The nanosheets used herein are mildly oxidized and fully oxidized graphene oxide sheets, abbreviated MOGO and GO respectively. These nanoparticles were received from the Wang Lab at the Yale Department of Chemistry, where they were synthesized using a modified hummers method (Wang et al., 2012)

Conductivity Measurement

For every solution used, the conductivity was measured by flowing the solution through a Teflon tube (inner diameter of 0.51mm). Two 22 gauge syringes were used on the sides of the Teflon tube, which ranged from 30-60 mm in length. One syringe contained 0.1-0.2 mL of the solution in question. Once both syringes were connected to either side of the tube, the liquid was pushed through so that the tube was completely filled with the desired liquid. The length of the Teflon tube from needle tip to needle tip was then measured for later calculations. One needle was connected to a power supply and the other was connected to ground. A known amount of current was then flowed through the liquid and the voltage was measured. This was done a total of five times.

The conductivity was then found by calculating the resistivity and taking the inverse of that value.

Physical set up of single spray

This homemade single spray electrospray setup consisted of a liquid dispenser connected to a needle (outer diameter of 0.4064 mm, inner diameter of 0.2032 mm).

To spray positively charged droplets, the needle was hooked up to a high voltage (HV) power supply. A brass extractor with a hole of approximate diameter 3.5 mm, also hooked up to a HV power supply, was placed 1-3 outer-diameters of the needle (0.4 mm to 1.2 mm) below the nozzle. A collector plate connected to ground was placed in varying distances from the needle and extractor, ranging from 4 cm to 20 cm. The voltage on the needle was increased in order to achieve the Taylor cone and spray. The difference between the two voltages was adjusted until the Taylor cone was formed. This value depended on the conductivity of the liquid, but was typically no greater than 2 kilovolts.

To spray in negative mode, the nozzle was connected to ground and the collector plate was hooked up to HV.

For liquids of high conductivity (ranging from high 10^{-2} to low 10^{-3} in magnitude), a voltage difference of about 2.5 kV was used. Fine adjustment of the nozzle voltage allowed was used to find the most stable cone jet possible. For solutions of lower conductivity (mid 10^{-3} or smaller in magnitude), a voltage difference of about 1.5 kV was used.

Calculating Droplet Size

To calculate the drop size, the conductivity measurement was used with the scaling law formed by de La Mora in his electrospray work. (Fernández de La Mora, 2007). The De La Mora scaling law for the drop diameter of liquids that are ejected out of Taylor cone of the electrospray is shown in equation 1. G(k) is an empirical function defined in the second line that is based on the dielectric constant (k) of the liquid used in units of F/m. Q is defined as the flow rate of the liquid through the nozzle in units of m^3/s. τ is defined as the dielectric constant (k, in F/m) multiplied by the permittivity of free space constant ϵ in (F/m) divided by the conductivity (K, in S/m) of the liquid.

$$(Eq. 1) \quad D_{diameter} = G(k)(Q\tau)^{\frac{1}{3}} \quad , where$$
$$G(k) = -10.87(k)^{-\frac{6}{5}} + 4.08(k)^{-\frac{1}{3}} \; and \; \tau = k\epsilon/K$$

Surface Tension Measurements

Individual droplets of the solution of question were suspended from a flat needle connected to a syringe. Images were captured at the point where the drop hung right before dripping off of the needle. Five images were taken for each solution. The resulting curvature of each drop was then taken and analyzed using a MatLab program written by the Dufresne Lab (Mechanical Engineering and Materials Science, Yale).

Spraying Graphene Oxide in Single Spray Setup

The ES setup detailed previously was used to spray solutions in the single spray setup. In order to spray the graphene oxide sheets, solutions that had a large enough jet diameter when put through the ES had to be used. Solutions were made with varying concentrations of ethanol, water, acetic and hydrochloric acids, ethylene glycol, 1-butanol, and graphene oxide.

Graphene Sheet Size Analysis/Imaging

In order to determine the size distribution of our graphene oxide sheets, scanning electron microscope (SEM) images of multiple, separate sheets were analyzed using Adobe® Photoshop® and ImageJ (Rasband, 2014). Entire sheets were outlined and filled in with a distinctly different color. The length of scale bars at the bottom of each imaged used were measured in ‘number of pixels’ for use in analysis. By removing background and insignificant parts of our image, an image of just the filled in areas was created. This image is then imported to ImageJ, where it is converted into an 8-bit image. Threshold values are set to include all relevant particles in the image. After setting the scale with our known scale value and length in number of pixels, the particles were analyzed for their area. The relevant information, in this case the square root of our area for each sheet (a characteristic length), was imported to Matlab (The MathWorks Inc.) to create a histogram of the data.

Twin Spray Setup

Two oppositely charged electrosprays worked in tandem in this setup. Graphene oxide solution was sprayed negatively in the bottom spray, while cobalt-manganese nitrate in solution was sprayed positively in the top spray. As the two sprays entered the mixing chamber, the opposite charges electrostatically attracted each other. The resulting collision between positively and negatively charged droplets yielded a composite material that then flowed with air (at a rate of 5 liters/minute) through a high-temperature tubular furnace at a temperature of 400ºC, allowing for a residence time of inside the furnace of 7.4 seconds.

At the end of this furnace, the deposit was collected electrostatically on a charged silicon wafer. Samples were taken for 30 min – 1 hour for varying concentrations of deposition.

Results and Discussion

The use of graphene oxide sheets as the scaffolding of the cobalt manganese nitrate generated some problems in this setup. Although the desired deposition was not achieved, it was important to establish that due to certain properties, graphene oxide sheets are not the ideal material to mix with cobalt manganese oxide in the ES.

Determination of which Graphene Oxide Sheets to Use

When considering which type of graphene oxide sheets to use, MOGO or GO, there were two important characteristics to take into account. The first was the size distribution of the sheets and the second was its ability to suspend in solution.

Size distributions were calculated by outlining the area of over 300 sheets of each type of graphene oxide (mildly oxidized and fully oxidized) and processing that area in ImageJ for an area in nm^2. The square root of each area (a characteristic length) was then calculated for each sheet and then plotted in a histogram. The distribution of the mildly oxidized sheets was much more standard than the distribution of the oxidized sheets (Figure 1). Whereas the fully oxidized sheets were skewed right and showed a higher chance for any given sheet to be larger than our cone jet, the mildly oxidized sheets had a much smaller skew in the right direction. Approaching this from a size perspective, this data concludes that in terms of size, the mildly oxidized graphene sheets are more ideal for the ES setup.

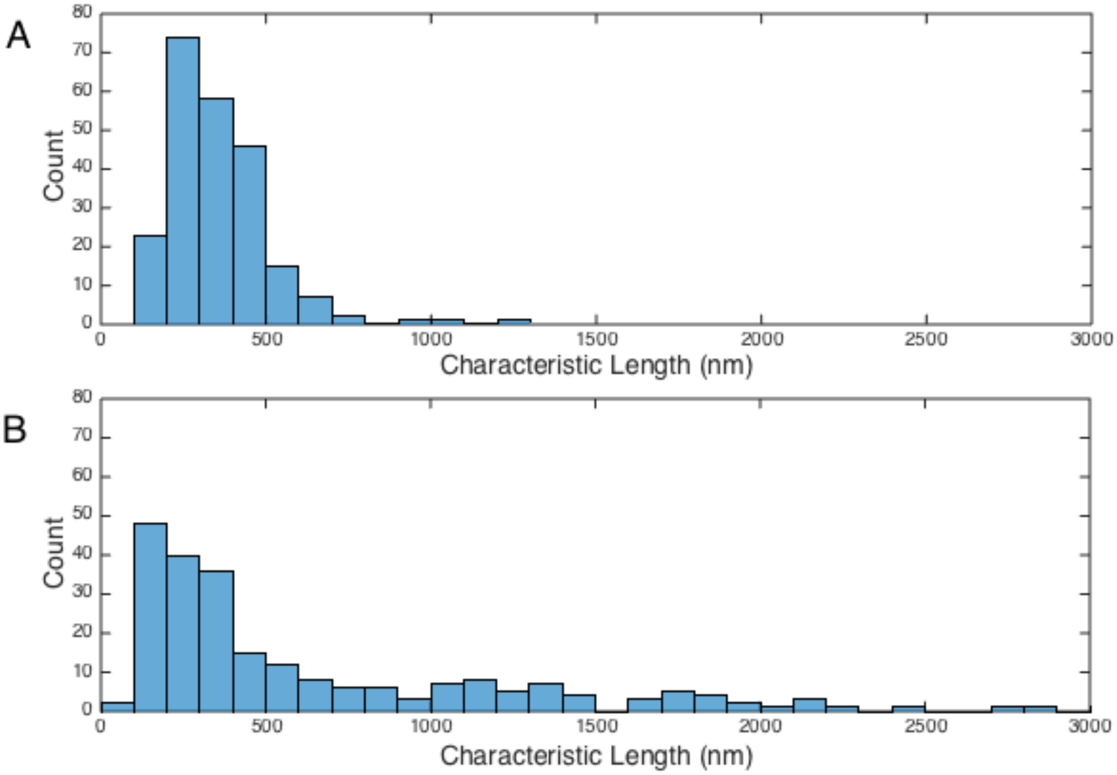

Figure 1: Size distribution of mildly oxidized graphene oxide (MOGO) sheets (A) and fully oxidized graphene oxide (GO) sheets (B). Average characteristic lengths are 355.2 nm and 440.1 nm for the

MOGO and GO, respectively. The MOGO distribution also shows a more normalized curve for the MOGO than the GO, indicating that the MOGO is more ideal for a dual spray setup as we can reduce the error produced by random breaks in the spray.

At one point later in experimentation, it was found that in some solutions the MOGO precipitated out. In the same solution, only substituting GO for MOGO, the solution was perfectly stable. In accordance to Konios' paper on the suspension of graphene oxide and reduced graphene oxide, ethylene glycol was used as the primary solvent when spraying the graphene oxide because it suspended the materials best (Konios, Stylianakis, Stratakis, & Kymakis, 2014).

For the single spray setup and most of the twin spray setup, MOGO was used because of its smaller average size and more normal distribution. In the cases that MOGO precipitated out, GO was used.

Conductivity Measurements and the Ability to Spray Solutions with Graphene Oxide in the Single Spray Setup

Conductivity is the measure of electron (in metals) or ion (in liquids) flow, or induced current, through a medium. Both size and charge level are strongly dependent on the electric conductivity of the solution that can be varied by orders of magnitude. It is also useful in determining how small the jet will form from the cone in the ES setup and also allows for further calculations when trying to fit nanoparticles into the drops. A higher conductivity produces smaller droplets, while a lower one entails larger drops. In hopes of creating smaller droplets that would fit the nanoparticles, larger conductivities within the region from high 10^{-3} to mid 10^{-2} were sought after. For every solution that was tested, the conductivity was measured. This allowed for the creation of sprays in which nanosheets could spray without impeding the jet and flow of liquid, while also allowing the determination of the size of the drops that form. In Table 1, solutions and their respective conductivities are listed in the first two columns.

Of the main materials used (ethanol, hydrochloric and acetic acid, and water), ethanol was used because of its high volatility and low surface tension. Due to the high volatility, the droplets evaporated quickly, leaving behind the nanoparticle in the deposition. More importantly, ethanol has a low surface tension, which allows for the formation of the Taylor cone in the ES spray setup. Water and acid were used as a means to increase the conductivity, in turn decreasing the droplet size and allowing us to be within a reasonable range of droplet size and conductivity to spray the solution. Varying concentrations of graphene oxide were used to find which one created the best deposition.

Solution (by volume)	Conductivity (S/m)	Flow Rate (mL/hour)	Average Droplet Diameter (m)
100% EtOH	1.20×10^{-4}	0.60	7.85×10^{-6}
50% EtOH, 50% water	5.15×10^{-3}	0.50	1.07×10^{-6}
50% HCl, 50% EtOH	6.76×10^{-2}	0.05	4.55×10^{-7}
50% HCl, 50%	7.50×10^{-2}	0.01	2.57×10^{-7}

MOGO			
49.5% Water, 49.5% EtOH, 1% Acetic Acid	1.16×10^{-2}	0.05	8.19×10^{-7}
49.5% Water, 39.5% EtOH, 10% MOGO 1% Acetic Acid	1.09×10^{-2}	0.05	8.36×10^{-7}
75% 1-Butanol, 25% GO, 0.5mM HCl	1.635×10^{-3}	0.20	2.36×10^{-6}

Table 1: Measured Conductivities and Droplet Size for Specific Flow Rates for Each Solution Used. Solutions with acid had a much higher conductivity because of the presence of ions in solutions. The desired conductivity was one in the range of low 10^{-3} to mid 10^{-2}. The second and third columns detail the flow rates at which the solution were sprayed, and the droplet volume for that specific solution at the specified flow rate.

Blanks of 100% ethanol and 50:50 Ethanol/Water were sprayed to investigate how solutions acted alone. After doing so, graphene oxide sheets were added to solutions. Conductivities of the blanks of those solutions were also taken to investigate if the presence of graphene oxide increased or decreased the conductivity of the solutions. As shown with the 49.5% Water, 49.5% EtOH, 1% Acetic Acid and 49.5% Water, 39.5% EtOH, 10% MOGO 1% Acetic Acid solutions, the conductivity did not change significantly with the presence of graphene.

Acids were then added to the solutions to increase the conductivity and produce a solution that would create smaller droplets in the ES. Due to the presence of ions as the acids dissociated in solution, the conductivities increased in orders of magnitude upon their addition. Ethylene glycol was also added into solution to increase the time the graphene oxide spent within the solvent (before the solvent evaporated), which then provided a way to measure the size of our sheets due to the flattening of the wetted sheets onto a pristine silicon substrate. The addition of EG also did not drastically change the conductivity.

By changing the composition of the solutions, the conductivity was increased, therefore decreasing the drop size and producing more drops per unit volume. As long as the sheet size did not exceed the droplet size and a ratio of one sheet per droplet was maintained, a higher rate of graphene oxide sheet deposition could be created.

The solutions that worked best were those that had conductivities between 10^{-2} to 10^{-3} S/m. At this conductivity the volume of droplets being emitted from the electrospray lay in the range of about 10^{-6} m. As the average size of the sheets was 3.6×10^{-7} m and 4.4×10^{-7} m, this provided ample space for the sheets within the drop.

Thus far all of the solutions were run in positive mode. When run in negative mode, more problems arose, and it was found that most solutions could not be sprayed in this setup. Specifically, the phenomena of coronal discharge, where the air ionizes before the liquid can form the Taylor cone, thus halting current flow through the liquid, occurred faster in the negative mode than in the positive mode. This created a setup in which a more limited amount of voltage could be used to create the Taylor cone than in the positive mode. One path to overcome the coronal discharge and inability to spray was to investigate (and ultimately reduce) the surface tension of the solutions.

There was significant difficulty in spraying solutions with graphene oxide in negative mode. To test if the inability to spray was the fault of the graphene sheets, a blank solution was tested. Specifically, a solution (percentages by volume) of 50% EG, 24.5% EtOH, 25% GO, and 5% 100 mM HCl (0.5mM) was tested and failed to produce a cone jet in negative mode. The blank version, 50% EG, 49.5% EtOH, and 5% HCl (0.5mM), was also tested. The resulting spray was not a perfect cone (it resembled more of a funnel than a cone), but resembled the structure of a stable one much more than in the previous solution. One hypothesis was that the surface tension of the liquid was being enhanced by the graphene oxide sheets. To test this, the surface tension was taken for these solutions and plotted on a graph of percent GO vs surface tension (Figure 2).

Three different liquids were used, all with the same basic composition and with varying amounts of graphene oxide. If the graphene oxide were increasing the surface tension and therefore inhibiting the creation of the cone in the ES, it would have been expected to see an increase in the surface tension measurements as the amount of graphene oxide increased. As shown in Figure 2, this was not the case, and the surface tension stayed the same with only a slight difference that can be explained as random error. Verified by the data graphene oxide does not significantly change the surface tension of the solution. As graphene oxide is the only differing component between solutions that do and do not function in the negative mode of the spray, there must be another characteristic of the graphene oxide that explains this phenomenon.

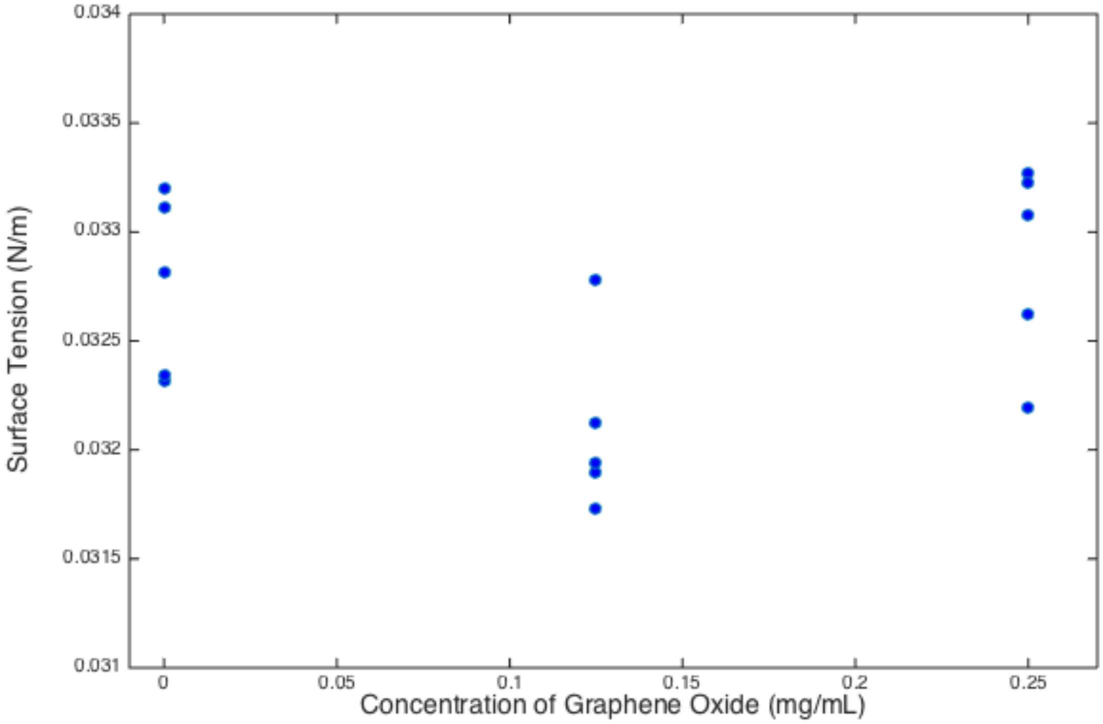

Figure 2: Surface Tension of Graphene Oxide in 50% Ethanol, 50% Ethylene Glycol, 0.5mM HCl. Three different solutions were measured for surface tension. The first was a blank with no graphene oxide present. This solution was almost able to spray in negative mode. The second consisted of .125 mg/mL GO in the same solution. The third consisted of .25 mg/ mL GO. Both the second and third solutions could not be sprayed in negative mode. 5 drops were analyzed for each solution. The average of these 5

drops for each sample were 0.0328, 0.0323, and 0.0329 in increasing order of concentration of GO. There was no positive trend as expected, and from these averages it can be asserted that the presence of GO does not affect the surface tension (at least not at these concentrations).

To create a solution that worked with the presence of graphene oxide, a new solvent needed to be used. The surface tension of the 50% ethanol, 50 % ethylene glycol was on average 0.0328 N/m. Pure ethanol, which can be sprayed with ease, has a surface tension of 0.022 N/m. Water, which cannot be sprayed at all, has a surface tension of 0.072 N/m. Ethylene glycol was used because of its low volatility (which decreased Coulombic fissions) and high surface tension (which promoted stable suspension of graphene oxide), but still did not produce a spray with graphene oxide in negative mode. 1-butanol was tested as a new solvent because of its low volatility and low surface tension (when compared to ethylene glycol). It has a surface tension of about 0.024 N/m and is very chemically similar to other alcohols, including ethanol, which is known to spray well.

The 1-butanol solvent did not change the conductivity drastically and was shown to work with the graphene oxide in negative mode. It was thus chosen as the solvent for the graphene oxide solution for future use.

Twin Spray Setup

The twin spray setup was the means with which the combination of graphene oxide and cobalt manganese oxide was to occur. Depositions were collected by spraying two solutions at one another (one containing the cobalt manganese nitrate, the precursor to the desired cobalt manganese oxide; and the other containing the graphene oxide), flowing them through a high temperature tubular furnace, and finally collecting the resulting composition electrostatically. The furnace 1) evaporated any excess solvent on our mixed cobalt manganese oxide and graphene oxide, 2) induced the thermal decomposition of the nitrate from the cobalt manganese nitrate, and 3) oxidized the cobalt manganese (due to the presence of air). In single spray, the particles move too quickly to have them spend enough time in the furnace to create the cobalt oxide due to their high charging level. A method was needed to discharge the drops to increase their residence time in the high temperature zone. In the twin spray setup, the droplets are discharged and are thus only subject to the air flow that moves slowly enough to provide enough time inside the furnace for the aforementioned chemical reactions to occur.

Shown in Figure 3 are the possible outcomes of the twin setup. There are two possible paths of deposition as the negative and positive charges cancel one another. The first is just cobalt oxide that forms as a result from the positive droplets discharging with the negative ions. The second is the desired mixed cobalt manganese oxide and graphene oxide deposition. Both of these possibilities were verified with SEM imaging, but the desired sheet-cobalt manganese oxide mixture was too scarce to consider the experiment a success. A third and unexplained deposit was also seen on the SEM—the presence of lone graphene oxide sheets. Given the current hypothesis and explanation, this shouldn’t be a possible outcome. Further experimentation and TEM imaging must be done to verify if this is in fact a lone graphene sheet or a graphene sheet covered in a conformal layer of cobalt manganese oxide.

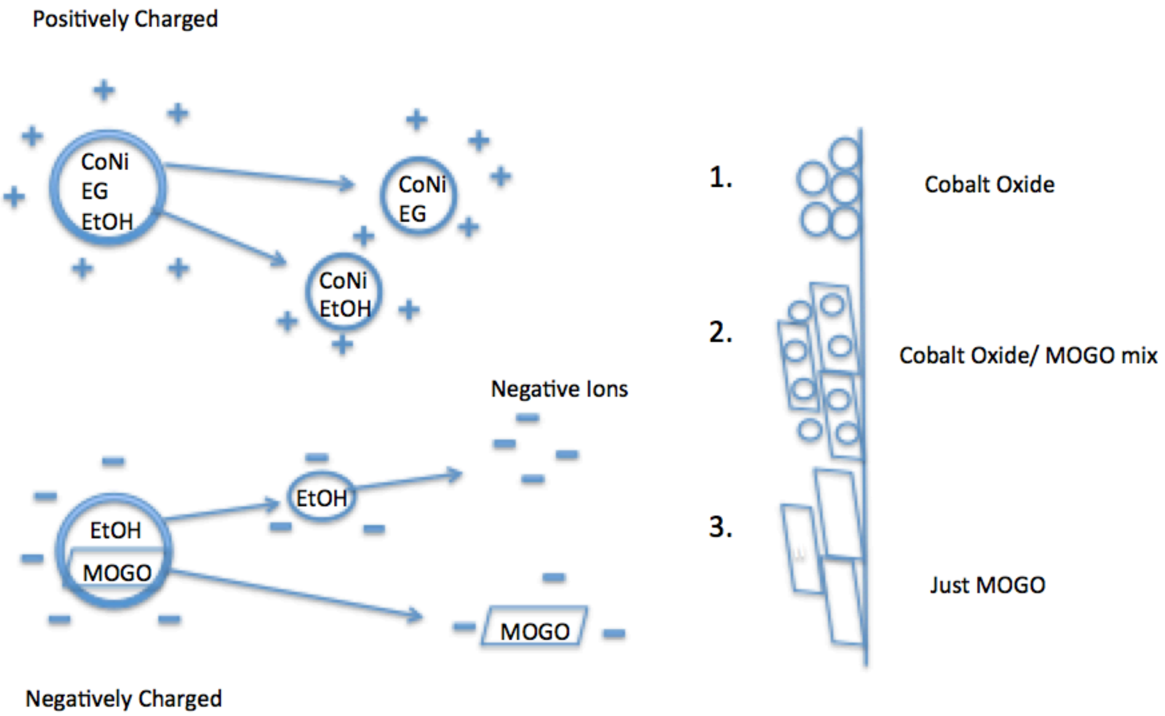

Figure 3: Possible Deposition Outcomes of the Twin Spray Setup. The bottom spray contains graphene oxide sheets in ethanol. As the drops fission, there are only two possibilities: the smaller drops contain only ethanol, which then dissolves leaving only negative ions; the drop contains ethanol and MOGO, resulting in a graphene oxide sheet that is negatively charged once the ethanol dissolves. The top spray contains dissolved cobalt nitrate. Even though this is only one metal of the overall cobalt manganese oxide final product, the cobalt nitrate is used for simplicity's sake—its results can be extrapolated and applied to the desired cobalt manganese oxide. As a result of Coulombic repulsion, the parent droplets that form from the ES disperse into smaller daughter droplets to reduce the charge to surface area ratio (Taflin, 1989). Cobalt nitrate (CoNi) can dissolve in both ethylene glycol (EG) and ethanol (EtOH), meaning that any interaction in the discharge of the drops in the top and bottom sprays must contain CoNi. As a result, the deposit should resemble 1 and 2, as they both contain cobalt nitrate. What was also found in SEM images was that there were sole graphene oxide sheets, represented in 3, which isn't explained by this model. Note that while the figure shows the droplets hitting at about a 30º angle, in reality the droplets are colliding at a 180º angle with respect to one another.

Even in the desired outcome of the deposition, the sheets were clumped, indicating that there was some instability in either the solution or the spray. To try and deposit a more even sample in which the sheets were not as clumped, the solution was sprayed immediately upon being made. This improved the distribution of the sheets in the deposition as shown in Figure 5, but they were still too sparse.

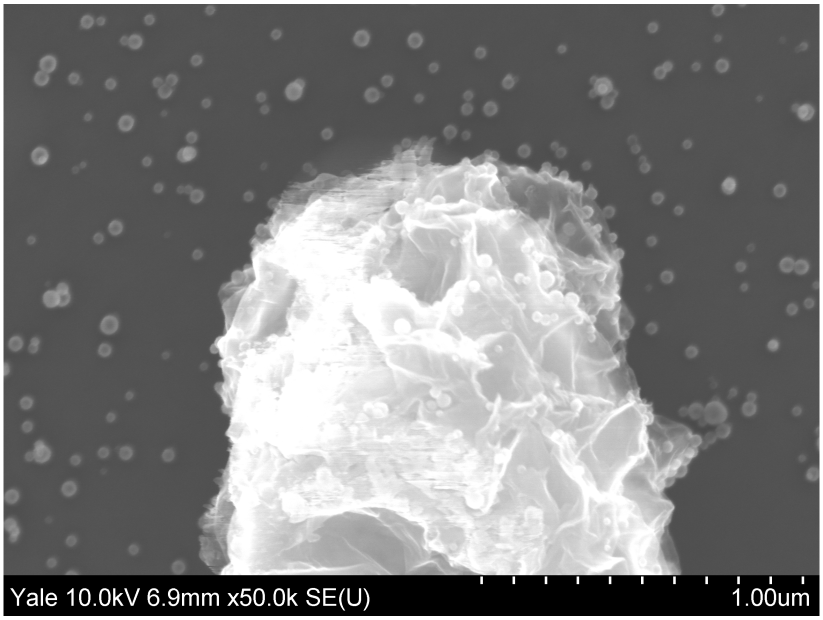

Figure 4: Preliminary Mixing of Cobalt Manganese Oxide and Graphene Oxide sheets. This SEM image validates the mixing of the two nanomaterials, but there is no even mixing. Instead, somehow the sheets coagulated into larger clumps. It was possible that this clumping occurred in solution or after the material sprayed.

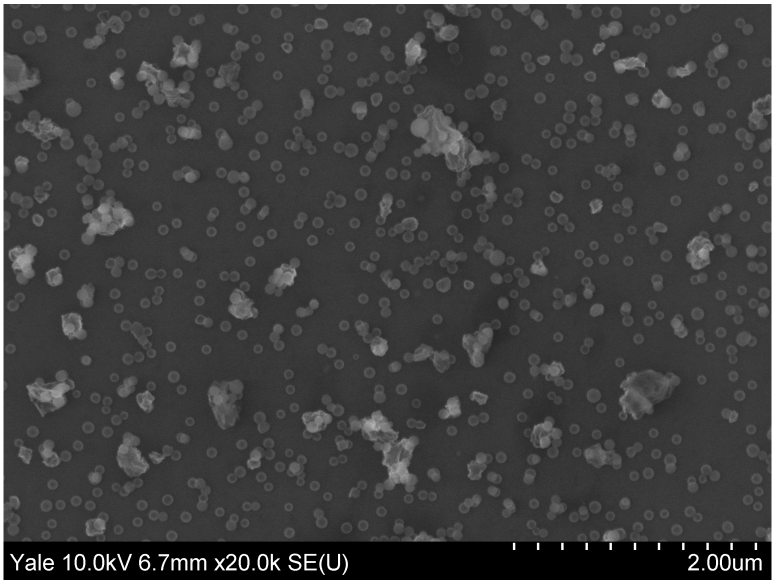

Figure 5: Graphene Oxide- Cobalt Manganese Oxide Mixing Immediately after Creation of Mixture. Although this image supports the mixing of the two nanomaterials, the deposition of graphene oxide is still too sparse compared to the ideal scenario of every single cobalt manganese oxide particle touching a graphene oxide sheet.

Although graphene sheets with nanoparticles were deposited, the twin spray setup did not allow for enough graphene oxide sheet coverage. The goal was to have every single sheet of cobalt manganese oxide touching a graphene oxide to ensure a pathway for electron flow.

Instead, there were many cobalt manganese particles left without contact with the sheets, and the unequal deposition of the sheets themselves did not allow for this to transpire. The comparison between the "fresh" solution and the solution that had been sitting for some time implies there is aggregation of the graphene oxide sheets while in the dispersion prior to spraying.

Although this method provided a means to spray and induce mixing of both materials, the deposition was not even enough to consider the scaling-up of the ES setup with graphene oxide sheets. This work did allow for the verification of the twin spray setup as a means to mix materials for the anode of the lithium ion battery, as well as the exploration of the properties and challenges of electrospraying graphene oxide. Future work will focus on using a new material, possibly sucrose, as the source of carbon and high conductivity for the anode to create an even better mixture between the two materials.

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References

Cloupeau, M., & Prunet-Foch, B. (1989). Electrostatic spraying of liquids in cone-jet mode. *Journal of Electrostatics, 22*(2), 135-159.

Dominko, R., Gaberscek, M., Drofenik, J., Bele, M., Pejovnik, S., & Jamnik, J. (2003). The role of carbon black distribution in cathodes for Li ion batteries. *Journal of Power Sources, 119–121*(0), 770-773. doi: http://dx.doi.org/10.1016/S0378-7753(03)00250-7

Fergus, J. W. (2010). Recent developments in cathode materials for lithium ion batteries. *Journal of Power Sources, 195*(4), 939-954. doi: http://dx.doi.org/10.1016/j.jpowsour.2009.08.089

Fernández de La Mora, J. (2007). The fluid dynamics of Taylor cones. *Annu. Rev. Fluid Mech., 39*, 217-243.

Konios, D., Stylianakis, M. M., Stratakis, E., & Kymakis, E. (2014). Dispersion behaviour of graphene oxide and reduced graphene oxide. *Journal of colloid and interface science, 430*, 108-112.

MATLAB version 8.4.0. Natick, Massachusetts: The MathWorks Inc., 2014.

Mustafa, M., Awais, M., Pooniah, G., Choi, K., Ko, J., & Doh, Y. (2012). Electrospray deposition of a graphene-oxide thin film, its characterization and investigation of its resistive switching performance. *Journal of the Korean Physical Society, 61*(3), 470-475. doi: 10.3938/jkps.61.470

Rasband, W.S., ImageJ, U. S. National Institutes of Health, Bethesda, Maryland, USA, http://imagej.nih.gov/ij/, 1997-2014.

Taberna, P. L., Mitra, S., Poizot, P., Simon, P., & Tarascon, J. M. (2006). High rate capabilities Fe3O4-based Cu nano-architectured electrodes for lithium-ion battery applications. *Nat Mater, 5*(7), 567-573.

Taflin, D. C. (1989). Electrified droplet fission and the Rayleigh limit. *Langmuir, 5*(2), 376-384. doi: 10.1021/la00086a016

Wang, H., Liang, Y., Gong, M., Li, Y., Chang, W., Mefford, T., . . . Dai, H. (2012). An ultrafast nickel-iron battery from strongly coupled inorganic nanoparticle/nanocarbon hybrid materials. *Nat Commun, 3*, 917. doi: 10.1038/ncomms1921

Zhi, L., Hu, Y.-S., Hamaoui, B. E., Wang, X., Lieberwirth, I., Kolb, U., . . . Mullen, K. (2008). Precursor-controlled formation of novel carbon/metal and carbon/metal oxide nanocomposites. *ADVANCED MATERIALS-DEERFIELD BEACH THEN WEINHEIM-, 20*(9), 1727.