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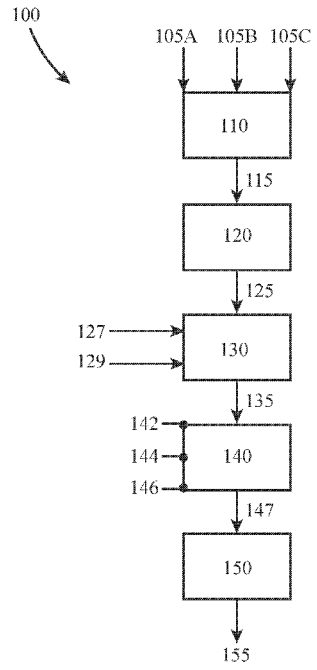

Figure 1A

(57) Abstract: The present disclosure relates to a method that includes reacting a mixture that includes a carrier gas and a precursor to form a first solid product and heating the first solid product to a temperature between 500 C and 1000 C to form a second solid product, where the precursor is a vapor, the reacting is performed using a plasma energized using a radio frequency (RF), the reacting is performed at an absolute pressure between 0.8 atms and 1.2 atms, the first solid product includes nickel and lithium, and the second solid product includes nickel, manganese, cobalt, lithium, and oxygen.

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RADIO FREQUENCY PLASMA FOR CATHODE MATERIAL SYNTHESIS AND RECYCLE

CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims priority from U.S. Provisional Patent Application Nos. 63/584,586, 63/588,339, and 63/656,266 filed on September 22, 2023, October 6, 2023, and June 5, 2024, respectively, the contents of which are incorporated herein by reference in their entirety.

CONTRACTUAL ORIGIN

This invention was made with government support under Contract No. DE-AC36-08GO28308 awarded by the Department of Energy. The government has certain rights in this invention.

BACKGROUND

Decades of research and investment have focused on developing technology crucial for the renewable energy transition, particularly in advancing energy storage solutions vital for electric vehicles, small electronics, and grid storage. Currently Li-ion batteries have a good combination of energy density, power density, and cycle stability. Traditional cathode synthesis for lithium-ion batteries is based on a large-scale solution synthesis with an initial mixing of the precursor salts, precipitation of product, and calcination of the product with a lithium source at temperatures up to 950 °C for as long as 12 hours. This final calcination step accounts for around 90% of the energy cost for cathode production. Nickel rich cathode materials (e.g., nickel, manganese, cobalt alloys) require the most energy with each kilogram of cathode powder produced requiring 6~8 kWh of electricity. In addition, the calcination kiln is not turned off as the heat up and cool down of the kiln is not feasible. Therefore, there is a need for improved methods and systems for producing materials for use in Li-ion batteries to, among other things, decrease the cost of electric vehicles to enable widespread adoption.

SUMMARY

An aspect of the present disclosure is a method that includes reacting a mixture that includes a carrier gas and a precursor to form a first solid product and heating the first solid product to a temperature between 500 °C and 1000 °C to form a second solid product, where the precursor is a vapor, the reacting is performed using a plasma energized using a radio frequency (RF), the reacting is performed at an absolute pressure between 0.8 atms and 1.2 atms, the first solid product includes nickel and lithium, and the second solid product includes nickel, manganese, cobalt, lithium, and oxygen. In some embodiments of the present disclosure, the RF may be between 1MHz and 200 MHz.

In some embodiments of the present disclosure, the RF may provide a power between 0.1 W/cm^3 and 50 W/cm^3. In some embodiments of the present disclosure, the reacting may be performed continuously. In some embodiments of the present disclosure, the carrier gas may flow through the reactor at a velocity between 0.01 m/s and 0.1 m/s based on a pure carrier gas feed basis. In some embodiments of the present disclosure, the precursor may flow through the reactor at a velocity between 0.01 to 0.5 m/s based on a pure precursor feed basis. In some embodiments of the present disclosure, the mixture may have a residence in the reactor between 0.01 seconds and 10 seconds.

In some embodiments of the present disclosure, the precursor may include a nickel salt, a manganese salt, a cobalt salt, and at least one of LiOH or lithium nitrate or a combination thereof. In some embodiments of the present disclosure, the nickel and cobalt may be present in the mixture at a molar ratio of nickel to cobalt (Ni:Co) between 10:1 and 0.5:1. In some embodiments of the present disclosure, the cobalt and manganese may be present in the mixture at a molar ratio of cobalt to manganese (Co:Mn) between 6:1 and 1:6. In some embodiments of the present disclosure, the LiOH may be present at a mass ratio of (Ni+Co+Mn):LiOH between 1:0.8 and 1:1.8. In some embodiments of the present disclosure, the mixture may further include a chelator and water. In some embodiments of the present disclosure, the precursor may be present in the mixture at a concentration between 0.01 M and 0.1 M.

In some embodiments of the present disclosure, the heating may result in the oxidizing of at least one of the cobalt, manganese, nickel, or a combination thereof. In some embodiments of the present disclosure, the heating may be performed for a period of time between 1 minute and 6 hours. In some embodiments of the present disclosure, the heating may be performed at an absolute pressure between 0.8 atms and 1.2 atms. In some embodiments of the present disclosure, the first product may include $LiNi_xMn_yCo_z$, where $0.95 \leq x \leq 8$, $0.5 \leq y \leq 3$, and $0.5 \leq z \leq 3$. In some embodiments of the present disclosure, the second product may include $LiNi_xMn_yCo_zO_2$, where $0.95 \leq x \leq 8$, $0.5 \leq y \leq 3$, and $0.5 \leq z \leq 3$.

An aspect of the present disclosure is a method that includes reacting a mixture that includes a carrier gas and a solid having a solid electrolyte interphase (SEI), where the solid includes at least one of nickel, manganese, cobalt, or a combination thereof, the solid further includes lithium and oxygen, the reacting is performed using a plasma energized using a radio frequency (RF), the reacting is performed at an absolute pressure between 0.8 atms and 1.2 atms, and the reacting removes at least a portion of the SEI.

An aspect of the present disclosure is a method that includes reacting a mixture that includes a carrier gas, a precursor, and a solid having a solid electrolyte interphase (SEI), where the precursor is a vapor, the solid includes at least one of nickel, manganese, cobalt, or a combination thereof, the solid further includes lithium and oxygen, the reacting is performed using a plasma energized using a radio frequency (RF), the reacting is performed at an absolute pressure between 0.8 atms and 1.2 atms, the reacting results in at least one of removing at least a portion of the SEI phase or the depositing of a layer on the solid, and the layer includes nickel and lithium.

An aspect of the present disclosure is a method that includes reacting a mixture that includes a carrier gas, a precursor, and a solid having a solid electrolyte interphase (SEI), where the precursor is a vapor, the solid includes at least one of nickel, manganese, cobalt, or a combination thereof, the solid further includes lithium and oxygen, the reacting is performed using a plasma energized using a radio frequency (RF), the reacting is performed at an absolute pressure between 0.8 atms and 1.2 atms, the reacting results in at least one of removing at least a portion of the SEI phase or the depositing of a layer on the solid, and the layer comprises nickel and lithium.

BRIEF DESCRIPTION OF THE DRAWINGS

Some embodiments of the present disclosure are illustrated in the referenced figures of the drawings. It is intended that the embodiments and figures disclosed herein are to be considered illustrative rather than limiting.

Figure 1A illustrates a system for synthesizing cathode materials and for recovering and recycling end-of-life cathodes using a plasma reactor, according to some aspects of the present disclosure.

Figure 1B illustrates an experimental plasma reactor for synthesizing cathode materials and for recovering and recycling end-of-life cathodes, according to some aspects of the present disclosure.

Figure 1C illustrates an experimental system for synthesizing cathode materials and for recovering and recycling end-of-life cathodes using a plasma reactor, according to some aspects of the present disclosure.

Figure 3 illustrates a scanning electron microscope (SEM) image of the synthesized cathode materials made using a plasma reactor as described herein, according to some aspects of the present disclosure.

Figure 4 illustrates cathode materials synthesized using a plasma reactor as described herein deposited on an X-ray diffraction (XRD) zero-background plate, according to some aspects of the present disclosure.

Figure 5 illustrates materials synthesized using a plasma reactor as described herein deposited inside the channel of the plasma reactor, according to some aspects of the present disclosure.

Figure 6 illustrates the reduced performance for aged nickel, manganese, cobalt (NMC) cathodes treated with plasma compared to aged NMC cathodes that are untreated by showing changes in voltage (Panel A) and cell resistance (Panel B), according to some aspects of the present disclosure.

Figure 7 illustrates scanning electron microscope (SEM) images that show differences in surface texture of aged lithium-nickel-manganese-cobalt-oxide (NMC) cathodes (Panel A) and then subsequently plasma treated NMC cathodes (Panel B), according to some aspects of the present disclosure.

Figure 8 illustrates XRD plots of the RF-plasma synthesized NMC before and after a heating step at 750 C°), according to some aspects of the present disclosure.

Figure 9 illustrates XRD plots of vaporized and condensed precursor run through an experimental setup without plasma and the effect of running the product through the same heating step that was used on the plasma produced product, according to some aspects of the present disclosure.

Figure 10 illustrates SEM images of RF-plasma synthesized NMC (Panels A-C) pre-heating step, (Panels D-F) post-heating step, according to some aspects of the present disclosure.

Figure 11 illustrates TGA plots of RF-plasma synthesized material mimicking a Muffle Furnace heating procedure, performed under atmospheric conditions, according to some aspects of the present disclosure.

Figure 12 illustrates (Panel A) discharge data for three cells with 45% loading of RF-plasma produced cathode material; (Panel B) C/10 charge and discharge, and (Panel C) C/3 charge and discharge), according to some aspects of the present disclosure.

Figure 13 illustrates electrochemical impedance spectroscopy of a representative cell with a 45% loading of RF-plasma produced cathode material, according to some aspects of the present disclosure.

REFERENCE NUMERALS

100.....system
105.....liquid precursor
110.....liquid precursor mixer
115.....liquid precursor mixture
120.....vaporizer
125.....vapor precursor mixture
127.....solid feed
129.....carrier gas
130.....vapor/gas/solid mixer (VGS mixer)
135.....feed stream
140.....plasma reactor
142.....radio frequency (RF) electrode
144.....ground electrode
146.....ignition electrode
147.....first solid product
150.....heater
155.....second solid product
200.....method
210.....mixing (precursors)
220.....vaporizing
230.....mixing (vapor/gas)
240.....reacting
250.....heating

DETAILED DESCRIPTION

The present disclosure relates to the use of plasma to induce chemical reactions and manipulate the growth of materials that may be used in Li-ion batteries. Further, in some embodiments of the present disclosure, plasma is used to treat recycled cathode materials to generate new cathode materials. Plasma synthesis may be used to synthesize a wide range of metal nanoparticles (including nickel, silicon, gold, iron, and platinum) and metal oxide nanoparticles (including nickel oxide, zinc oxide, and silicon dioxide). As used herein, "plasma" refers to a mixture of fully or partially ionized gas. A plasma may contain a significant portion of charged particles in any combination of ions or electrons, as well as neutral particles. As used herein "microplasma" refers to plasma confined to within a millimeter and/or sub-millimeter length scale in at least one dimension.

Among other things, the present disclosure relates to the use of a radio frequency (RF) atmospheric microplasma reactor for synthesizing nickel, manganese, cobalt (NMC-type) cathode materials and/or recycling NMC-type cathode materials. Liquid precursors containing hydrated metal ions may be vaporized using a vibrating transducer, e.g., ultrasound, and transported into the reactor using carrier gases such as one or more of argon, oxygen, and/or helium. For scale-up, a plurality of microplasma reactors may be configured in a parallel arrangement to produce large quantities of cathode materials and/or to treat large amounts of recovered and recycled cathode materials. Such an RF plasma array may use a common ground electrode for ease of manufacturability. Among other advantages, RF plasma may allow for longer residence times (e.g., longer than 10 mS) to form large particles (e.g., greater than 100 nm). In some embodiments of the present disclosure, the plasma may be generated using radio frequency ignition.

Another significant advantage of the methods and systems described herein, an RF microplasma reactor may use 85% less energy than traditional cathode synthesis processes (~36,750 J/g for a microplasma based method versus ~252,000 J/g for traditional methods). Traditionally, these materials are often synthesized using large kilns that require large amounts of energy to maintain the high temperature necessary to calcine the particles. Microplasma does not require large kilns and can create cathode particles by passing vaporized precursors through a plasma that requires significantly less heating time post-plasma treatment.

Figure 1A illustrates a system 100 for synthesizing cathode materials from precursor materials and/or for recovering and reusing spent cathodes to synthesize new cathode materials, according to some embodiments of the present disclosure. The central component of the system

100 is a plasma reactor 140 configured to facilitate reactions for synthesizing and/or recycling cathode materials such as NMC-type materials. The plasma reactor 140 illustrated is configured with an RF electrode 142, a ground electrode 144, and an ignition electrode 146. In some embodiments of the present disclosure, a plasma reactor 140 may be tubular in shape hollow through the center along the longitudinal axis, with an inlet and an outlet. In some embodiments f the present disclosure, a plasma reactor 140 may be a microplasma reactor and a microplasma reactor was utilized for collecting the experimental data described herein.

Solid, gaseous, and/or vapor materials, reactor feed 135, may be configured to flow into the inlet of a plasma reactor 140 and product, first solid product 147, may be configured to exit the outlet of a plasma reactor 140. A plasma rector 140 may be constructed of glass, alumina, zirconia, quartz and/or any other material that can withstand the plasma and operating conditions of the plasma reactor 140. A tubular plasma reactor 140 may have an inside diameter between 0.1 mm and 3 mm or between 0.5 mm and 1.5 mm or between 0.1 mm and 1.0 mm. A tubular plasma reactor 140 may have a length between 10 mm and 30 mm, or between 5 mm and 100 mm.

Referring again to **Figure 1A**, a feed stream 135 to a plasma reactor 140 may be a mixture of different phases. For the example of synthesizing new cathode materials from precursors, a feed stream 135 may be a mixture of a liquid vapor and a gas phase. For the example of recycling recovered solid cathode materials, a feed stream 135 may be a solid phase mixed with a gas phase and with or without an additional liquid vapor. In both cases, reacting a feed stream 135 in a plasma reactor 140 results in the formation of a first solid product 147, which, in some embodiments of the present disclosure, may be the final target product. However, in some embodiments of the present disclosure, a first solid product 147 may be directed to a downstream heater 150 for additional treating to form a second solid product 155. Such a heater 150 may, among other things, facilitate driving some reactions closer to completion, the forming of oxides, the removal of unreactive species, and/or the further crystallization of the first solid product 147 to form a second solid product 155.

For example, as shown herein, the reaction of liquid precursors (i.e., reactants) (105A-B) to form NMC-type cathode materials may proceed in a two-step process. A first step may result from the reaction of the liquid precursors (105A-B) occurring in the plasma reactor 140 to form a first solid product 147 containing crystalline nickel. Subsequently, the first solid product 147 may be directed to a heater 150 in which a second step occurs, e.g., one or more of oxidizing of at least a portion of the first solid product 147 due to the presence of O_2, resulting in the

additional reacting, and/or crystallizing, to form a second solid product 155 having each of nickel, manganese, and cobalt in a crystalline form, and metal oxides. Note that three precursors (105A-C) are specifically called out in **Figure 1A**. This is for illustrative purposes and a system or method may utilize one or more precursors 105, depending on the product targeted. The same applies for solid feed 127 and carrier gas 129: a system or method may utilize one or more solid feeds and/or one or more carrier gases.

Referring again to **Figure 1A**, liquid precursors (105A-C) may pass through one or more upstream unit-operations to create a feed stream 135, before directing the liquid precursors to a plasma reactor 140. For example, individual liquid precursors (105A-C) may be directed to a precursor mixer 110 configured to mix the liquid precursors to form a homogeneous liquid precursor mixture 115 having the targeted elements (e.g., nickel, cobalt, and manganese), each at a desired starting concentration. In some embodiments of the present disclosure, a precursor mixture 110 may be formed in a batch, semi-batch, and/or continuous fashion. A precursor mixer 110 may include at least one of a stirred-tank reactor, a continuous stirred-tank reactor, and/or a static mixer. Once created, a liquid precursor mixture 115 may be directed to a vaporizer 120 to form a vapor precursor mixture 125. In some embodiments of the present disclosure, a vaporizer 120 may include a device configured to use ultrasound to convert a liquid precursor mixture 115 to a vapor precursor mixture 125 of fine droplets having particle sizes between 10 nm and 10,000 nm.

Once the liquid precursors (105A-C) have been vaporized, a vapor precursor mixture 125 may be combined with a carrier gas 129 in a vapor/gas/solid mixer 130 (VGS mixer 130) to form a feed stream 135 having both a vapor phase and a gas phase, which may then be directed to a plasma reactor 140 to produce a first solid product 147. A carrier gas 129 may be an inert gas such as at least one of helium, argon, neon, krypton, and/or xenon. Among other things, a carrier gas 129 may be utilized to adjust the flowrate and/or residence time for the precursors (105A-C) flowing through a plasma reactor 140. Further, a carrier gas 129 may provide electrons and ions to facilitate precursor ionization and dilute the reactants to facilitate better control of the reactions and/or minimize side-reactions occurring in the plasma reactor 140.

In some embodiments of the present disclosure, a feed stream 135 having a combination of a vapor precursor mixture 125 and a carrier gas 129 may be directed to a plasma reactor 140 to synthesize new cathode materials. Further, in some embodiments of the present disclosure, recovered cathode materials may be combined with a carrier gas 129 and/or a vapor precursor mixture 125 to create recycled cathode materials. For example, passing a feed stream 135

having a solid feed 127 through a plasma reactor 140 may result in the at least partial removal of solid layers that accumulated and/or developed during the lifespan of the recovered solid cathode materials, e.g., a solid electrolyte interphase (SEI). Further, the treating of a solid feed 127 in a plasma reactor 140 may result in a change of the crystalline structure of the solid feed 127 to a form having better physical properties and/or performance metrics, including increased specific capacity of the plasma treated material. In addition, in some embodiments of the present disclosure, the treating of a feed stream 135 having both a solid feed 127 and a vapor precursor mixture 125 in a plasma reactor 140 may result in at least some of the same benefits described above, however, may also result in the forming of a new layer of new cathode material covering at least a portion of the recovered solids making up the solid feed 127. For example, when a solid feed 127 is provide in the form of a fine particulate, the vapor precursor mixture 125 component of a feed stream 135 may react to form a shell of new cathode material covering a core of the recovered cathode material, thereby forming a first solid product 147 having a core-shell architecture.

To convert a solid feed 127 to a form that can be utilized in a plasma reactor 140, some pre-processing of a starting, recovered cathode material may be necessary. For example, in some embodiments of the present disclosure, a used cathode may be directed to a ball-mill, hammermill and/or knife-mill to break the various components of a cathode into smaller pieces. These pieces may then be directed to a separator configured to separate the cathode material from other components, e.g., a substrate. Such a separation may be achieved gravimetrically, by size differences, and/or magnetically. Once a cathode's active material has been recovered, it may be subjected to one or more additional unit-operations configured to reduce the cathode material to a particle size suitable for injection into a plasma reactor 140. In some embodiments of the present disclosure, size reduction of recovered cathode materials may be achieved using at least one of a hammermill and/or a ball-mill. For example, recovered cathode material may be reduced in size to form a solid feed 127 of particles having an average particle size between 1 μm and 20 μm. Among other things, a solid feed 127 in particulate form may provide more surface area per unit volume, with the increased surface area providing more area for reactions to occur. In addition, smaller particles may enable easier entrainment of the solid feed 127 into a carrier gas 129 at lower carrier gas flow rates.

Once made, a solid feed 127 in a powder form needs a mechanism for entering the system 100. In some embodiments of the present disclosure, such a feed system (not shown in **Figure 1A**) may include a hoper and an auger. A solid feed 127 in powder form may be directed to and

stored in the hoper. The auger rotational speed may be varied to accurately meter the solid feed 127 powder into a VGS mixer 130 where it may be combined with a carrier gas 129 and/or a vapor precursor mixture 125, which mix with and entrain the solid feed 127 to form a two-phase or three-phase feed stream 135, which may then be directed to the plasma reactor 140. In some embodiments of the present disclosure, the hoper and/or the auger may be configured with a carrier gas supply line (in addition to or replacing carrier gas 129). In some embodiments of the present disclosure, a VGS solid mixer 130 may be as simple as a union having two or three tubes that converge together, a first tube for a vapor precursor mixture 125, a second for a solid feed 127, and a third for a carrier gas 129, with a fourth tube directing the resultant mixed feed stream 135 to a plasma reactor 140.

As described previously, a first solid product 147 exiting a plasma reactor 140, either new virgin cathode materials and/or cathode materials that include materials originating from recovered, end-of-life cathode materials, may be directed to a heater 150 for additional treating to form a downstream target product, i.e., a second solid product 155. Further, as is described in more detail below, other compounds may be added to a liquid precursor mixture 115. For example, a liquid precursor mixture 115 may include a lithium-containing compound to produce a lithiated first solid product 147 and/or a lithiated second solid product 155. In addition, a liquid precursor mixture 115 may include water and/or a chelator.

Figure 1B illustrates a hollow tubular plasma reactor 140 for the synthesis of cathode materials using RF plasma, according to some aspects of the present disclosure. The precursor and carrier gases were configured to enter the plasma reactor 140 from the top. The hollow tube plasma reactor was a quartz tube. An RF electrode 142, a ground (GND) electrode 144, and an ignition electrode 146 were connected to the hollow tube reactor. The first solid product flowed freely from the bottom of the tube, i.e., the plasma reactor 140.

Figure 1C illustrates a system for synthesizing cathode materials using RF plasma, according to some aspects of the present disclosure. This exemplary system included a plasma chamber containing the hollow tubular plasma reactor 140 illustrated in **Figure 1B**. An ignition coil provided the spark to the reaction vessel, igniting a glow discharge of the carrier gas. A liquid trap was used to remove/capture any condensed precursor vapor before it entered the plasma reactor 140. A vapor chamber (i.e., a liquid precursor mixer 110) mixed the liquid precursors and carrier gases used during the synthesis. A power supply was used to supply power to the plasma reactor. A matching network matched the reactor impedance to that of the power supply impedance to minimize reflected power to the supply. At least one mass flow controller (MFC)

controlled the flow rate of the carrier gases and a MFC controlled the flow rate of the fully mixed and vaporized liquid precursors. The power source generated an electric field in the plasma reactor, generating a glow discharge. The plasma chamber and reactor does not need to be vacuum sealed and operated at or near atmospheric pressure (an absolute pressure between 0.8 atm and 1.2 atm).

Figure 2 illustrates a method 200 that utilizes a system 100 having a plasma reactor 140 as illustrated in **Figures 1A-1C** and describe above, according to some embodiments of the present disclosure. The plasma reactor 140 is central to the method 200 as the reactions for synthesizing virgin cathode materials and/or for recycling recovered end-of-life cathode materials occur therein. Thus, the method 200 includes a step of reacting 240 a feed stream 135, where the feed stream 135 is a mixture of one or more liquid precursors 105 (three are shown, labeled 105A-C) and a carrier gas 129, or a mixture of a solid feed 127 and a carrier gas 129, or a mixture of liquid precursors (105A-C), a solid feed 127, and a carrier gas 129. However, as described previously for a system 100, before a feed stream 135 can be directed to a reacting 240 step, a feed stream 135 may need to be prepared using one or more upstream processing steps.

For example, as illustrated in **Figure 2**, one or more precursors 105 may be directed to a mixing 210 step to produce a liquid precursor mixture 115 having the desired elemental stoichiometries and concentrations. For synthesizing NMC-type cathode materials, precursors 105 may include three metal salts; e.g., a nickel salt, a manganese salt, and a cobalt salt. In some embodiments of the present disclosure, a metal salt may include at least one of an acetate, a sulfate, and/or a nitrate. Further, in some embodiments of the present disclosure, a salt precursor 105 may be hydrated. Examples of nickel salt precursors 105 include $Ni(CH_3COO)_2 \cdot 4H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $NiSO_4 \cdot 6H_2O$, $NiSO_4 \cdot 7H_2O$, $NiSO_4 \cdot H_2O$, and $NiSO_4$. Examples of manganese salt precursors 105 include $Mn(CH_3COO)_2 \cdot 4H_2O$, $Mn(NO_3)_2 \cdot 4H_2O$, $Mn(NO_3)_2 \cdot 6H_2O$, $MnSO_4 \cdot H_2O$, $MnSO_4 \cdot 4H_2O$, $MnSO_4 \cdot 5H_2O$, and $MnSO_4$. Examples of cobalt salt precursors 105 include $Co(CH_3COO)_2 \cdot 4H_2O$, $Co(CH_3COO)_2$, $Co(NO_3)_2 \cdot 6H_2O$, $CoSO_4 \cdot 7H_2O$, $CoSO_4 \cdot H_2O$.

Among other things a mixing 210 of liquid precursors 105 may be used to achieve the elemental stoichiometries desired in the first solid product 147 and/or the second solid product 155. In some embodiments of the present disclosure, a nickel precursor 105A and cobalt precursor 105B may be provided to a mixing 210 step such that the resultant liquid precursor mixture 115 and downstream mixtures and/or streams have a molar ratio of nickel to cobalt (Ni:Co)

between 10:1 and 0.5:1 or between 3:1 and 1:1. In some embodiments of the present disclosure, a nickel precursor 105A and cobalt precursor 105C may be provided to a mixing 210 step such that the resultant liquid precursor mixture 115 and downstream mixtures and/or streams have a molar ratio of (Co:Mn) between 6:1 and 1:6 or between 2:1 and 1:2.

To form a lithiated first solid product 147 and/or a lithiated second solid product 155, a mixing 210 of liquid precursors 105 may include a lithium-containing compound such as at least one of LiOH or lithium nitrate or a combination thereof. In some embodiments of the present disclosure, a lithium-containing compound may be provided to a mixing 210 step such that the resultant liquid precursor mixture 115 and downstream mixtures and/or streams have a molar ratio of (Ni+Co+Mn):Li between 1:0.8 and 1:1.8 or between 1:1.1 and 1:1.2. In some embodiments of the present disclosure, a mixing 210 step of precursors 105 and/or a lithium-containing compound may also include mixing at least one of a chelator and/or water to solvate the metal ions and reduce the likelihood of forming metal hydroxides. Examples of a chelator include citric acid, oxalic acid, and ethylenediaminetetraacetic acid (EDTA). In some embodiments of the present disclosure, a chelator may be added to a mixing 210 step to form a liquid precursor mixture 125 having a concentration between 0.5 wt% and 10 wt% or between 1 wt% and 3 wt%. In some embodiments of the present disclosure, water may be added to a mixing 210 step to form a liquid precursor mixture 125 having a total precursor 105 concentration between 0.01 M and 0.1 M or between 0.05 M and 0.5 M. As described previously, mixing 210 of liquid precursors 105, etc., may be achieved using at least one of a stirred-tank reactor, a continuous stirred-tank reactor, and/or a static mixer.

Referring again to **Figure 2**, with a liquid precursor mixture 115 successfully mixed, it may then be directed to a vaporizing 220 step. For the experiments described herein, a vibrating transducer (i.e., ultrasound) was used to create a vapor cloud at a volumetric rate between 100 mL/hr and 500 mL/hr or between 10 mL/hr and 3000 mL/hr, which was carried to the plasma reactor. In some embodiments, a nebulizer may be used when an array of reactors is used to scale the process to large production rates. In some embodiments of the present disclosure, a carrier gas 129 flow having a velocity between 5 m/s and 200 m/s or between 5 m/s and 50 m/s may be used to transport a liquid precursor mixture 115 through a vaporizing 220 step using a vibrating transducer (this carrier gas stream is not shown in **Figure 2**).

Referring again to **Figure 2**, a vapor precursor mixture 125 may then be directed to a second mixing 230 step, in which the vapor precursor mixture 125 is combined with and mixed with a carrier gas 129 and/or a solid feed 127. For the case of mixing a vapor precursor mixture 125

with a carrier gas 129, mixing 230 may be achieved in a union of a first tube supplying the vapor precursor mixture 125 with a second tube supplying the carrier gas 129. In some embodiments of the present disclosure, a vapor precursor mixture 125 may be combined and mixed with a carrier gas 129 using a static mixer. Supplying a solid feed 127 may be somewhat more involved, as described above.

Whether single phase (e.g., vapor phase), two phase (e.g., vapor/gas or solid/gas), or three phase (e.g., vapor/gas/solid), once mixing 230 is complete, the resultant feed stream 135 may be directed to the reacting 240 step. An advantage to the system 100 and method 200 described herein is that the reacting 240 may be completed at or near atmospheric pressure. In some embodiments of the present disclosure, reacting 240 may be completed at an absolute pressure between 0.8 atms and 1.2 atms. In some embodiments of the present disclosure, reacting 240 may be completed in a plasma reactor 140 by heating the feed stream to a temperature between 500 °C and 1000 °C. These temperatures are achieved using plasma generated in the plasma reactor 140, with the plasma energized using a radio frequency (RF) between 1MHz and 200 MHz or between 10 MHz and 20 MHz. In some embodiments of the present disclosure, a RF may provide a power between 0.1 W/cm^3 and 50 W/cm^3 or between 1 W/cm^3 and 10 W/cm^3.

In some embodiments of the present disclosure, a plasma reactor's 140 inner diameter and a carrier gas 129 flow rate may be set such that the carrier gas 129 flows through the plasma reactor 140 at a velocity between 0.01 m/s and 0.1 m/s, on a pure carrier gas feed basis. In some embodiments of the present disclosure, a plasma reactor's 140 inner diameter and a combined precursor 105 flow rate may be set such that the liquid precursor mixture 125 flows through the plasma reactor 140 at a velocity between 0.01 m/s and 0.1 m/s, on a pure precursor feed basis (including water, NiMnCo components, Li-containing precursor, and chelator). In some embodiments of the present disclosure, a feed stream 135 flow rate and a plasma reactor's 140 dimensions (length and inner diameter) may be set such that the feed stream 135 (all components, vapor precursor mixture 124, carrier gas 129, and solid feed 127) has a residence time in the plasma reactor 140 between 0.01 seconds and 10 seconds or between 0.02 seconds and 1.0 seconds.

In some embodiments of the present disclosure, a method 200 may include directing an oxygen containing stream (not shown) to a reacting 240 step. The addition of oxygen to the reactions occurring in a plasma reactor 140 may result in process simplification by achieving the oxidation and/or crystallization of all three nickel, manganese, and cobalt elements that was observed to occur in the downstream heating 250 step, as described below.

Referring again to **Figure 2**, following reacting 240, a first solid product 147 may be directed to a heating 250 step. Among other things, heating 250, when performed in the presence of O_2 or air may result in the oxidizing of the first solid product 147, resulting in the forming of a second solid product 155 containing oxides. Like the reacting 240, heating 250 may be performed at atmospheric or near-atmospheric conditions. In some embodiments of the present disclosure, heating 250 may be performed at a pressure between 0.8 atms and 1.2 atms. In some embodiments of the present disclosure, heating 250 may be performed by heating the first solid product 147 to a temperature between 500 °C and 800 °C. In some embodiments of the present disclosure, heating 250 may be performed by holding the first solid product 147 at the elevated temperature for a period of time between 1 minute and 6 hours or between 20 minutes and 90 minutes.

As described above, a heating 250 step may change at least one of the composition, structure, physical properties, and/or performance metrics of a first solid product 147 to form a second product 155. In some embodiments of the present disclosure, a first product 147 may have the composition $LiNi_xMn_yCo_z$, where $0.95 \leq x \leq 8$, $0.5 \leq y \leq 3$, and $0.5 \leq z \leq 3$. In some embodiments of the present disclosure, a second product 155 may have the composition $LiNi_xMn_yCo_zO_2$, where $0.95 \leq x \leq 8$, $0.5 \leq y \leq 3$, and $0.5 \leq z \leq 3$ with the hexagonal α-$NaFeO_2$-type structure of the $R\bar{3}m$ space group.

Figure 3 illustrates a scanning electron microscope (SEM) image of cathode material synthesized in a RF plasma reactor having a $Ni_5Mn_3Co_2$ stoichiometry, a first solid product, using systems and methods as describe above, according to some embodiments of the disclosure. The product shown in **Figure 3** was synthesized using a 5 W/cm^3 plasma power density with a 29 mm electrode gap, and a 0.2 m/s argon carrier gas flow. **Figure 4** illustrates photographs of the cathode materials shown in **Figure 3** on a zero-background plate, synthesized using systems and methods as described above, according to some embodiments of the disclosure.

Figure 5 illustrates the deposition of cathode materials onto the inside diameter of a quartz tube plasma reactor using systems and methods as described above. Note the inner volume of the quartz tube plasma reactor in **Figure 5** appears to be filled with solid product, which is not the case for the plasma reactor illustrated in **Figure 1B**. This build-up is not ideal. However, it occurs in most plasma-based systems. For the systems and methods described herein, such solids build-up is less of an operating expense as the plasma reactor, essentially a hollow tube,

is more consumable and easily replaced, whereas the plasma reactors for most incumbent technologies are large and expensive.

Figure 6 illustrates the reduced performance for aged NMC cathodes treated with plasma compared to aged NMC cathodes that are untreated by showing changes in voltage (Panel A) and cell resistance (Panel B), according to some embodiments of the present disclosure. Initial tests in full cells vs graphite anodes in Gen-2 electrolyte are shown in **Figure 6**. **Table 1** shows experimental data taken from traditionally recycled lithium-nickel-manganese-cobalt-oxide (NMC) cathode materials and aged NMC cathode materials treated with plasma, according to some embodiments of the present disclosure. The data shows a greater than ~20 % increase in the performance of the plasma processed aged NMC cathode materials.

Table 1. Performance data for non-treated and plasma-treated recycled NMC cathode materials

Sample (Full Cells)	**Last C/10 Capacity (mAh/g) (Charge/Discharge)**
Recycled no Plasma 1	70/68
Recycled no Plasma 2	63/60
Recycled no Plasma 3	64/62
Treated with Plasma 1	82/80
Treated with Plasma 2	85/73
Treated with Plasma 3	80/77

Figure 7 illustrates the difference in surface texture of the aged lithium-nickel-manganese-cobalt-oxide (NMC) cathodes (Panel A) and the aged then plasma treated NMC cathodes (Panel B) using a scanning electron microscope (SEM), according to some embodiments of the present disclosure. The difference in the surface texture of the aged and plasma treated NMC cathodes can be seen in the images shown in **Figure 7**. The secondary structure (many small crystallites loosely held together) of the plasma treated material suggests that the crystallites may now be fused together. This may be significant as the cracking of these small crystallites remains a primary contributing factor in cathode aging. In some embodiments of the present disclosure, the plasma power used for treating recovered cathode materials may be significantly higher than when generating new cathode materials. Additionally, during recycling as described herein, the plasma environment (i.e., the precursors within the plasma chamber) may not contain metal salts and the electrode spacing may be different from what is used during new cathode synthesis. Further, the concentration of carrier gas (i.e., Ar) may be lower during recovered solids treating compared to what may be used during the synthesis of new cathode materials.

A system like that illustrated in **Figures 1A-1C** was utilized for the treating of used cathode materials using RF atmospheric plasma, according to some aspects of the present disclosure. Aged NMC 532 ($LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$) was introduced into argon (Ar) plasma. The bright pink color is emission due to lithium ionization. This suggests that lithium-containing cathode/electrolyte degradation products (such as lithium fluoride) are being removed from the cathode surface. These degradation products are difficult to remove by other means, and suggests atmospheric plasma has an advantage over those methods.

Materials synthesis: **Figure 1B** illustrates a schematic of the plasma reactor 140 utilized, with argon carrier gas 129 supplied to the to the reactor inlet using an Alicat mass flow controller (MFC) at 35 sccm. The feed stream 135 was directed to the plasma reactor 140 through another line with another MFC. The feed line for the carrier gas 129 and the feed line for the feed stream 135 were joined at a union, which acted as a VGS mixer 130 and the mixed feed stream 135 was fed to the plasma reactor, which was a 4 mm OD, 2 mm ID, quartz tube with copper RF and ground electrodes connected to the exterior 29 mm apart along the longitudinal axis. The RF power was supplied by a Kengineering Technical Services (KTS) RF-600 RF generator connected to a KTS Fastmatch RC-4 matching network.

In some embodiments of the present disclosure, the liquid precursor mixture 115 had a molar ratio of 90:5:5 for the nickel, cobalt, and manganese acetate hydrates and a 1:1.1 ratio of LiOH, in a 0.075 M solution with DI water and citric acid as a chelator. The liquid precursor mixture 115 was then vaporized using a ultrasonic transducer at 300mL/hr vaporizer 120, the resultant vapor precursor mixture 125 was then mixed with the argon carrier gas 129 in the union, and the resultant two-phase (vapor/gas) feed stream 135 was directed to the plasma reactor 140 at a flow rate of 250 sccm. The power of the plasma was held at 95 W during the runs, for a time period between 20 minutes and 90 minutes, with a production rate of around 50 mg of first solid product 147 an hour. This first solid product was then sintered to form a second solid product 155, i.e., heated, in a muffle furnace, first with a ramp from room temperature to 750 °C over the span of an hour, followed by a constant hold at 750 °C for an hour, all under atmosphere.

Physical characterization: The first solid product 147 produced from the plasma reactor 140, as well as the second solid product 155 after the 1 hour heating 250 step at 750 °C were examined physiochemically using XRD, SEM, and TGA. The XRD diffractogram from the plasma treated particles pre- and post-heating is shown in **Figure 8**. The first solid product XRD diffractogram has peaks corresponding to Ni nanoparticles with peaks around 44°, 51°,

and 76°, and Li_2CO_3 with the various peaks also indicated. The RF-microplasma reactor produced a first solid product of Ni-nanoparticles at atmosphere. The change in crystallinity occurring after the 1 hour heating 250 step is apparent in the second solid product with the appearance of peaks corresponding to the $R\bar{3}m$ space group after the baking process, in particular the (003) peak at ~18.7° and the (104) peak at ~44.4°, along with the doublets of the (006)/(012) peak at ~38° and the (108)/(110) peak at ~65°.

This work demonstrates the unique conversion of a first solid product of Ni-nanoparticles produced in a plasma reactor 140 to a second solid product of NMC-type cathode materials via a downstream heating 240 step. The lack of observable peak splitting at the (006)/(012) and at the (108)/(110) peak suggests a reduction in layering quality. The $I_{(003)}/I_{(104)}$ peak ratio of 0.776 indicates the degree of disorder within the crystal structure, in particular Li/Ni cation mixing. This higher ratio is also consistent with NMC chemistries with higher nickel content, but generally in those chemistries the $I_{(003)}/I_{(104)}$ peak ratio is between 1 and 1.2. The increased cation mixing could be a factor of calcination temperature or time, something which was not optimized in this research. If the structure is not fully oxidizing, due to the reduced calcination time it could allow for the transition metal migration that results in the $I_{(003)}/I_{(104)}$ peak ratio of 0.776. The extra peaks observed and not assigned to the NMC structure are Li_4SiO_4, resultant from the sputtering of the quartz tube by the plasma during the synthesis process.

The vital role the plasma plays in this synthesis procedure can be seen in **Figure 9**, which shows the XRD diffractogram resultant from a vaporized precursor run through the system *without* plasma and from the subsequent heating of this condensate. There are no defined peaks in either diffractogram before or after heating the condensed precursor. The diffractogram in **Figure 9**, in contrast to the diffractogram in **Figure 8**, is clear evidence for the plasma assisted chemical vapor synthesis occurring in the plasma reactor, which takes the metal acetate precursor salts and nucleates into nanoparticles, as only after the heating step of the plasma produced product (i.e., first solid product) is NMC (second solid product) formed. This NMC synthesis route mirrors co-precipitation, in which the metallic precursors are precipitated out of solution into partially crystalline metal oxides, similar to what was produced in the RF-microplasma setup, but the co-precipitated products are then sintered for longer durations, with a lithium source, such as Li_2CO_3, to produce NMC material. Pulling from the similarities of coprecipitation, the RF-microplasma setup is assumed to work in a similar way, where the plasma forms crystalline Ni-nanoparticles (first solid product), as seen in **Figure 8**, through

plasma assisted chemical vapor synthesis which are then oxidized and lithiated, with Li_2CO_3 (second solid product) during an abridged heating step, when compared to co-precipitation.

The SEM from the pre- and post-bake samples (e.g., first solid product and second solid product) show the distinct morphology change resulting from the heating (see **Figure 10**). The first solid sample particles show similar morphology to other chemical vapor synthetic techniques with small, independently nucleated particles. The second solid product NMC particles (see panels d- f of **Figure 10**) have the distinct secondary structure seen in most NMC particles comprised of the smaller primary particles. The particle size increases during the heating step as the single Ni-nanoparticles, e.g., the firs solid product, with sizes around 1 μm agglomerate into secondary particles with sizes in excess of 6 μm. These particle sizes are unique for plasma-based methods and system producing NMC-type materials. These are far larger than the other plasma assisted cathode synthesis methods with listed particle sizes of < 200 nm. The larger particles produced using the methods described herein result in less surface area and less parasitic reactions on the cathode particles' surface. The SEM micrographs of the second solid product also shows a large amount of material located in smaller clusters not the usual larger secondary particles. The heating step has a clear effect on the morphology of the product as it forms the characteristic NMC secondary structure from the independently nucleated Ni-particles.

TGA measurements were taken to examine the process of lithiation and oxidation of the metal nanoparticles, the first solid product, produced during the RF-microplasma synthesis process. The TGA was done on the plasma produced particles to mirror the heating step described previously. As seen in **Figure 11**, the weight loss before 700 °C can likely be attributed to the decomposition, combustion, and vaporization of the residual organics on the RF-microplasma product. The decomposition of Li_2CO_3 takes place around 720 °C and leads to more reactive lithium species. Finally, the increase of mass around 70 minutes, may be the oxidation of the metal nanoparticles into metal oxide particles, starting around 750 °C. The results demonstrate that the 1 hour hold at 750 °C does not allow for the oxidation step to fully plateau, indicating that the bake time might be increased or an increase of the air contact of the powder to maximize oxidation.

As evidenced by the XRD and SEM, the RF-microplasma setup can synthesize NMC. This product appears to have some irregularities when compared to traditional synthesis routes with the $I_{(003)}/I_{(104)}$ peak ratio and lack of peak splitting at the (006)/(012) and at the (108)/(110) peaks, demonstrating a lack of layering structure and Ni/Li cation mixing. The SEM shows

characteristic NMC secondary particles formation, along with evidence of un-agglomerated primary particles still present in the material. The lack of a plateau in the TGA during the NMC oxidation process points out that a longer hold at 750 °C could be a potential route to address some of the problems seen in the XRD and SEM, as a lack of oxidation could lead to more cation mixing and reduced layering quality.

Electrochemical characterization: The synthesized material, second solid product, was also examined electrochemically in half-cells. Differential capacity (DQ/DV) is the derivative of voltage with respect to the charge or discharge capacity, as shown in Equation 1.

$$DQ/DV = \frac{dQ}{dV} = \frac{\Delta Q}{\Delta V} = \frac{Q_{t+1} - Q_t}{V_{t+1} - V_t} \quad (1)$$

The first cycle shown was at a higher current density ~4μAcm^{-2}, which distorted the cathodic and anodic peaks to a higher and lower potential respectively as the higher current density leads to a higher overpotential within the cell. The cycles post formation at the more reasonable current density ~1μAcm^{-1} (cycles 7,8,9 and 15), display the more realistic differential capacity plot for the chosen cell. The cathodic and anodic peaks at 3.7 V, are associated with the main phase shift in NMC from H1 to M and correspond to the lithiation and delithiation of the NMC. There is a small peak at around 4.0 V, seen in cycles post formation, as the high rate does not allow for the phase shift, which is the M to H2 phase conversion, but there is no apparent peak for the H2 to H3 conversion which is usually seen in NMC with higher nickel content around 4.2 V. There is a slight rise starting around 4.1 V which might be related to the H2 to H3 phase shift, and is seen in all cycles post formation. The cathodic peak shift to a lower potential and the anodic peak shift to a higher potential relate to degradation of the cathode material as the oxidation of nickel, Ni^{3+} / Ni^{4+}, begins to happen at lower potentials around cycle 9, which is early in the cycle life of the material.

The cycling performance of the cathode half cells using second solid product is shown in **Figure 12**. The overall performance of the three cells on test is around 60 mAh/g below what is expected for the high nickel content NMC that was believed to be synthesized with the highest C/10 discharge capacity peaking at 140 mAh/g with an average around 100 mAh/g at a C/3 rate (see Panel A of **Figure 12**). Various cycles at a C/10 rate are shown in Panel C of **Figure 12**, with a capacity increase seen during cycling. This same trend is seen in Panel C of **Figure 12** except at a C/3 rate. The increase in capacity over time could be attributed to an initial lack of lithium inventory due to incomplete lithiation during synthesis, and the capacity would increase during cycling due to the unlimited lithium reservoir of a half-cell.

Additionally, the lower than expected cycling performance can be explained due to a potential lack of oxygen in the structure, as an analogous situation is seen in high-nickel chemistry NMCs as structural degradation leads to a loss of oxygen and lower capacities during cycling. The lack of lithium in the initially synthesized structure, as shown through the capacity increase during cycling, would also allow for an increase in cation mixing, again resulting in the lower capacities as compared to pristine high nickel NMCs.

EIS is helpful in understanding the internal impedance observed within the electrochemical cell containing the NMC cathode material, second solid product. As seen in **Figure 13**, the high-frequency x-axis intercept denotes that the overall bulk solution resistance is close to ideal, as it is near the origin. The radius of the semicircle corresponds to the charge transfer resistance found in the cell which is similar to other NMC type cathode materials with Z' values around 150 Ω and -Z'' values around 50 Ω. The Warburg resistance consists of the tail of the spectra at lower frequencies and relating to the resistance of the diffusion of elements across the electrochemical cell. The EIS spectra shows an electrochemical cell with no obvious differences in terms of its impedance, with bulk, charge transfer, and Warburg impedance all similar to other routes for NMC synthesis.

Materials characterization: X-Ray diffraction (XRD, Rigaku, Cu Kα radiation) was performed to examine the crystalline phase of the various precursors and products over a 2Θ range of 10°-80°. The samples were run in the Rigaku Smart lab system on a silicon zero-background plate. The XRD was set to a tube voltage of 40 kV and a tube current of 44 mA, with the incident slit at ½° and receiving slit at 20 mm. The morphological characteristics of the produced product were examined via scanning electron microscopy (SEM, Hitachi S-4800). Thermogravimetric analysis was performed in parallel to the bake out of the RF-microplasma produced product with a ramp from room temp to 750 °C over 1 hour, then held at 750 °C for 1 hour, all under atmosphere on a platinum pan (TGA, TA Q500).

Electrochemical characterization: The electrochemical tests of the produced materials were carried out in coin cells (CR2032) with a lithium metal counter electrode, 15 mm diameter, and a cathode with 14 mm diameter. The cathode slurries were made with ~45% produced active material, ~50% carbon-black (Super-P), and ~5% polyvinylidene fluoride, with N-methy-2-pyrrolidinone as a solvent. The slurry was then cast onto Al foil at atmosphere with a doctor blade and dried for 6 hours at 105 °C under vacuum. The cells were assembled using Gen2 electrolyte (Tomiyama Pure Chemical Industries, Ltd EC:EMC = 2.994:7 with 1.121 M $LiPF_6$). In addition, one piece of Celgard 2325 separator, 3/4" diameter, was used in the cell stack.

Following assembly in an argon glovebox, the cells were transferred into a Multi-Zone Temperature Chamber (MZTC; Arbin Instruments) connected to a multi-channel cycler (Arbin Instruments) and were allowed to wet for 5 hours and then cycled at various rates with the temperature set at 30 °C. Potentiostatic electrochemical impendence spectroscopy (EIS) was performed after the formation cycles, from a range of 100 kHz to 0.01 Hz, with a perturbation of 10 mV; the cells were held at 30 °C (GAMRY 5000E). The cells were originally formed at C/10 CC/CV, with the capacity calculated based upon a theoretical capacity for NMC 622, for four cycles in the potential range from 3.0 – 4.2 V. The capacities were then adjusted to the experimentally observed capacity and cycled at C/10 and C/3 rates with a 30 minutes CV step at the top of charge as well as a 5 minutes rests at the end of discharge over a potential range of 3.0 – 4.4 V.

Examples:

Example 1. A method comprising: reacting a mixture comprising a carrier gas and a precursor to form a first solid product; and heating the first solid product to a temperature between 500 °C and 1000 °C to form a second solid product, wherein: the precursor is a vapor, the reacting is performed using a plasma energized using a radio frequency (RF), the reacting is performed at an absolute pressure between 0.8 atms and 1.2 atms, the first solid product comprises nickel and lithium, and the second solid product comprises nickel, manganese, cobalt, lithium, and oxygen.

Example 2. The method of Example 1, wherein the RF is between 1MHz and 200 MHz.

Example 3. The method of Example 2, wherein the RF is between 10 MHz and 20 MHz.

Example 4. The method of Example 1, wherein the RF provides a power between 0.1 W/cm^3 and 50 W/cm^3 or between 1 W/cm^3 and 10 W/cm^3.

Example 5. The method of Example 1, wherein: the reacting is performed in a reactor comprising a reactor tube, and the reactor is configured with an RF electrode and a ground electrode.

Example 6. The method of Example 5, wherein the reacting is performed continuously.

Example 7. The method of Example 6, wherein the carrier gas flows through the reactor at a velocity between 0.01 m/s and 0.1 m/s based on a pure carrier gas feed basis.

Example 8. The method of Example 6, wherein the precursor flows through the reactor at a velocity between 0.01 to 0.5 m/s based on a pure precursor feed basis.

Example 9. The method of Example 6, wherein the mixture has a residence in the reactor between 0.01 seconds and 10 seconds or between 0.02 seconds and 1 second.

Example 10. The method of Example 1, wherein the precursor comprises a nickel salt, a manganese salt, a cobalt salt, and at least one of LiOH or lithium nitrate or a combination thereof.

Example 11. The method of Example 10, wherein at least one of the nickel salt, the manganese salt, the cobalt salt, or a combination thereof comprises at least one of an acetate, a nitrate, a sulfate, or a combination thereof.

Example 12. The method of Example 11, wherein at least one of the nickel salt, the manganese salt, the cobalt salt, or a combination thereof is hydrated.

Example 13. The method of Example 12, wherein the nickel salt comprises at least one of $Ni(CH_3COO)_2 \cdot 4H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $NiSO_4 \cdot 6H_2O$, $NiSO_4 \cdot 7H_2O$, $NiSO_4 \cdot H_2O$, $NiSO_4$, or a combination thereof.

Example 14. The method of Example 12, wherein the manganese salt comprises at least one of $Mn(CH_3COO)_2 \cdot 4H_2O$, $Mn(NO_3)_2 \cdot 4H_2O$, $Mn(NO_3)_2 \cdot 6H_2O$, $MnSO_4 \cdot H_2O$, $MnSO_4 \cdot 4H_2O$, $MnSO_4 \cdot 5H_2O$, $MnSO_4$, or a combination thereof.

Example 15. The method of Example 12, wherein the manganese salt comprises at least one of $Co(CH_3COO)_2 \cdot 4H_2O$, $Co(CH_3COO)_2$, $Co(NO_3)_2 \cdot 6H_2O$, $CoSO_4 \cdot 7H_2O$, $CoSO_4 \cdot H_2O$, or a combination thereof.

Example 16. The method of Example 10, wherein nickel and cobalt are present in the mixture at a molar ratio of nickel to cobalt (Ni:Co) between 10:1 and 0.5:1 or between 3:1 and 1:1.

Example 17. The method of Example 10, wherein cobalt and manganese are present in the mixture at a molar ratio of cobalt to manganese (Co:Mn) between 6:1 and 1:6 or between 2:1 and 1:2.

Example 18. The method of Example 10, wherein the LiOH is present at a mass ratio of (Ni+Co+Mn):LiOH between 1:0.8 and 1:1.8 or between 1:1.1 and 1:1.2.

Example 19. The method of Example 1, wherein the mixture further comprises a chelator and water.

Example 20. The method of Example 19, wherein the chelator comprises at least one of citric acid, oxalic acid, ethylenediaminetetraacetic acid (EDTA), or a combination thereof.

Example 21. The method of Example 19, wherein the chelator is present in the mixture at a concentration between 0.5 wt% and 10 wt% or between 1 wt% and 3 wt%.

Example 22. The method of Example 19, wherein the precursor is present in the mixture at a concentration between 0.01 M and 0.1 M or between 0.05 M and 0.5 M.

Example 23. The method of Example 1, wherein the heating results in the oxidizing of at least one of the cobalt, manganese, nickel, or a combination thereof.

Example 24. The method of Example 1, wherein the heating is performed for a period of time between 1 minute and 6 hours or between 20 minutes and 90 minutes.

Example 25. The method of Example 1, wherein the heating is performed at an absolute pressure between 0.8 atms and 1.2 atms.

Example 26. The method of Example 1, wherein: the first product comprises $LiNi_xMn_yCo_z$, $0.95 \leq x \leq 8$, $0.5 \leq y \leq 3$, and $0.5 \leq z \leq 3$.

Example 27. The method of Example 1, wherein: the second product comprises $LiNi_xMn_yCo_zO_2$, $0.95 \leq x \leq 8$, $0.5 \leq y \leq 3$, and $0.5 \leq z \leq 3$.

Example 28. The method of Example 1, further comprising, prior to the reacting, vaporizing the precursor from a liquid to the vapor.

Example 29. The method of Example 28, wherein the vaporizing is performed using ultrasound.

Example 30. The method of Example 29, wherein the vaporizing forms vapor droplets of the precursor having a droplet size between 10 nm and 10,000 nm.

Example 31. The method of Example 1, wherein the mixture further comprises O_2 to oxidize the cathode material during plasma processing and eliminate the need for futher heat treatment of the cathode material.

Example 32. The method of Example 1, wherein the first solid product comprises a plurality of particles having a particle size less than 1 μm.

Example 33. The method of Example 1, wherein the second solid product comprises a plurality of particles having a particle size greater than 6 μm.

Example 34. The method of Example 1, wherein the reacting is performed at a temperature between 500 °C and 1000 °C.

Example 35. A method comprising: reacting a mixture comprising a carrier gas and a solid having a solid electrolyte interphase (SEI), wherein: the solid comprises at least one of nickel, manganese, cobalt, or a combination thereof, the solid further comprises lithium and oxygen, the reacting is performed using a plasma energized using a radio frequency (RF), the reacting is performed at an absolute pressure between 0.8 atms and 1.2 atms, and the reacting removes at least a portion of the SEI.

Example 36. A method comprising: reacting a mixture comprising a carrier gas, a precursor, and a solid having a solid electrolyte interphase (SEI), wherein: the precursor is a vapor, the solid comprises at least one of nickel, manganese, cobalt, or a combination thereof, the solid further comprises lithium and oxygen, the reacting is performed using a plasma energized using a radio frequency (RF), the reacting is performed at an absolute pressure between 0.8 atms and 1.2 atms, the reacting results in at least one of removing at least a portion of the SEI phase or the depositing of a layer on the solid, and the layer comprises nickel and lithium.

Example 37. The method of either Example 35 or 36, wherein the RF is between 1MHz and 200 MHz.

Example 38. The method of any one of Examples 35-37, wherein the RF is between 10 MHz and 20 MHz.

Example 39. The method of any one of Examples 35-38, wherein the RF provides a power between 0.1 W/cm^3 and 50 W/cm^3 or between 1 W/cm^3 and 10 W/cm^3.

Example 40. The method of any one of Examples 35-39, wherein the reacting is performed continuously.

Example 41. The method of any one of Examples 35-40, wherein the carrier gas flows through the reactor at a velocity between 0.01 m/s and 0.1 m/s based on a pure carrier gas feed basis.

Example 42. The method of any one of Examples 35-41, wherein the mixture has a residence in the reactor between 0.01 seconds and 10 seconds or between 0.02 seconds and 1 second.

Example 43. The method of any one of Examples 35-42, wherein the reacting is performed at a temperature between 500 °C and 1000 °C.

Example 44. A method comprising: reacting a mixture comprising a carrier gas, a precursor, and a solid having a solid electrolyte interphase (SEI), wherein: the precursor is a vapor, the solid comprises at least one of nickel, manganese, cobalt, or a combination thereof, the solid

further comprises lithium and oxygen, the reacting is performed using a plasma energized using a radio frequency (RF), the reacting is performed at an absolute pressure between 0.8 atms and 1.2 atms, the reacting results in at least one of removing at least a portion of the SEI phase or the depositing of a layer on the solid, and the layer comprises nickel and lithium.

The embodiments described herein should not necessarily be construed as limited to addressing any of the particular problems or deficiencies discussed herein. References in the specification to "one embodiment", "an embodiment", "an example embodiment", "some embodiments", etc., indicate that the embodiment described may include a particular feature, structure, or characteristic, but every embodiment may not necessarily include the particular feature, structure, or characteristic. Moreover, such phrases are not necessarily referring to the same embodiment. Further, when a particular feature, structure, or characteristic is described in connection with an embodiment, it is submitted that it is within the knowledge of one skilled in the art to affect such feature, structure, or characteristic in connection with other embodiments whether or not explicitly described.

As used herein the term "substantially" is used to indicate that exact values are not necessarily attainable. By way of example, one of ordinary skill in the art will understand that in some chemical reactions 100% conversion of a reactant is possible, yet unlikely. Most of a reactant may be converted to a product and conversion of the reactant may asymptotically approach 100% conversion. So, although from a practical perspective 100% of the reactant is converted, from a technical perspective, a small and sometimes difficult to define amount remains. For this example of a chemical reactant, that amount may be relatively easily defined by the detection limits of the instrument used to test for it. However, in many cases, this amount may not be easily defined, hence the use of the term "substantially". In some embodiments of the present invention, the term "substantially" is defined as approaching a specific numeric value or target to within 20%, 15%, 10%, 5%, or within 1% of the value or target. In further embodiments of the present invention, the term "substantially" is defined as approaching a specific numeric value or target to within 1%, 0.9%, 0.8%, 0.7%, 0.6%, 0.5%, 0.4%, 0.3%, 0.2%, or 0.1% of the value or target.

As used herein, the term "about" is used to indicate that exact values are not necessarily attainable. Therefore, the term "about" is used to indicate this uncertainty limit. In some embodiments of the present invention, the term "about" is used to indicate an uncertainty limit of less than or equal to ±20%, ±15%, ±10%, ±5%, or ±1% of a specific numeric value or target. In some embodiments of the present invention, the term "about" is used to indicate an

uncertainty limit of less than or equal to ±1%, ±0.9%, ±0.8%, ±0.7%, ±0.6%, ±0.5%, ±0.4%, ±0.3%, ±0.2%, or ±0.1% of a specific numeric value or target.

The foregoing discussion and examples have been presented for purposes of illustration and description. The foregoing is not intended to limit the aspects, embodiments, or configurations to the form or forms disclosed herein. In the foregoing Detailed Description for example, various features of the aspects, embodiments, or configurations are grouped together in one or more embodiments, configurations, or aspects for the purpose of streamlining the disclosure. The features of the aspects, embodiments, or configurations, may be combined in alternate aspects, embodiments, or configurations other than those discussed above. This method of disclosure is not to be interpreted as reflecting an intention that the aspects, embodiments, or configurations require more features than are expressly recited in each claim. Rather, as the following claims reflect, inventive aspects lie in less than all features of a single foregoing disclosed embodiment, configuration, or aspect. While certain aspects of conventional technology have been discussed to facilitate disclosure of some embodiments of the present invention, the Applicants in no way disclaim these technical aspects, and it is contemplated that the claimed invention may encompass one or more of the conventional technical aspects discussed herein. Thus, the following claims are hereby incorporated into this Detailed Description, with each claim standing on its own as a separate aspect, embodiment, or configuration.

CLAIMS

What is claimed is:

1. A method comprising:

reacting a mixture comprising a carrier gas and a precursor to form a first solid product; and

heating the first solid product to a temperature between 500 °C and 1000 °C to form a second solid product, wherein:

the precursor is a vapor,

the reacting is performed using a plasma energized using a radio frequency (RF),

the reacting is performed at an absolute pressure between 0.8 atms and 1.2 atms,

the first solid product comprises nickel and lithium, and

the second solid product comprises nickel, manganese, cobalt, lithium, and oxygen.

2. The method of claim 1, wherein the RF is between 1MHz and 200 MHz.

4. The method of claim 1, wherein the RF provides a power between 0.1 W/cm^3 and 50 W/cm^3 .

3. The method of claim 1, wherein the reacting is performed continuously.

4. The method of claim 3, wherein the carrier gas flows through the reactor at a velocity between 0.01 m/s and 0.1 m/s based on a pure carrier gas feed basis.

5. The method of claim 3, wherein the precursor flows through the reactor at a velocity between 0.01 to 0.5 m/s based on a pure precursor feed basis.

6. The method of claim 3, wherein the mixture has a residence in the reactor between 0.01 seconds and 10 seconds.

7. The method of claim 1, wherein the precursor comprises a nickel salt, a manganese salt, a cobalt salt, and at least one of LiOH or lithium nitrate or a combination thereof.

8. The method of claim 7, wherein nickel and cobalt are present in the mixture at a molar ratio of nickel to cobalt (Ni:Co) between 10:1 and 0.5:1.

9. The method of claim 7, wherein cobalt and manganese are present in the mixture at a molar ratio of cobalt to manganese (Co:Mn) between 6:1 and 1:6.

10. The method of claim 7, wherein the LiOH is present at a mass ratio of (Ni+Co+Mn):LiOH between 1:0.8 and 1:1.8.

11. The method of claim 1, wherein:

the first product comprises $LiNi_xMn_yCo_z$,

$0.95 \leq x \leq 8$,

$0.5 \leq y \leq 3$, and

$0.5 \leq z \leq 3$.

12. The method of claim 1, wherein:

the second product comprises $LiNi_xMn_yCo_zO_2$,

$0.95 \leq x \leq 8$,

$0.5 \leq y \leq 3$, and

$0.5 \leq z \leq 3$.

13. A method comprising:

reacting a mixture comprising a carrier gas and a solid having a solid electrolyte interphase (SEI), wherein:

the solid comprises at least one of nickel, manganese, cobalt, or a combination thereof,

the solid further comprises lithium and oxygen,

the reacting is performed using a plasma energized using a radio frequency (RF),

the reacting is performed at an absolute pressure between 0.8 atms and 1.2 atms, and

the reacting removes at least a portion of the SEI.

14. A method comprising:

reacting a mixture comprising a carrier gas, a precursor, and a solid having a solid electrolyte interphase (SEI), wherein:

the precursor is a vapor,

the solid comprises at least one of nickel, manganese, cobalt, or a combination thereof,

the solid further comprises lithium and oxygen,

the reacting is performed using a plasma energized using a radio frequency (RF),

the reacting is performed at an absolute pressure between 0.8 atms and 1.2 atms,

the reacting results in at least one of removing at least a portion of the SEI phase or the depositing of a layer on the solid, and

the layer comprises nickel and lithium.

15. A method comprising:

reacting a mixture comprising a carrier gas, a precursor, and a solid having a solid electrolyte interphase (SEI), wherein:

the precursor is a vapor,

the solid comprises at least one of nickel, manganese, cobalt, or a combination thereof,

the solid further comprises lithium and oxygen,

the reacting is performed using a plasma energized using a radio frequency (RF),

the reacting is performed at an absolute pressure between 0.8 atms and 1.2 atms,

the reacting results in at least one of removing at least a portion of the SEI phase or the depositing of a layer on the solid, and

the layer comprises nickel and lithium.

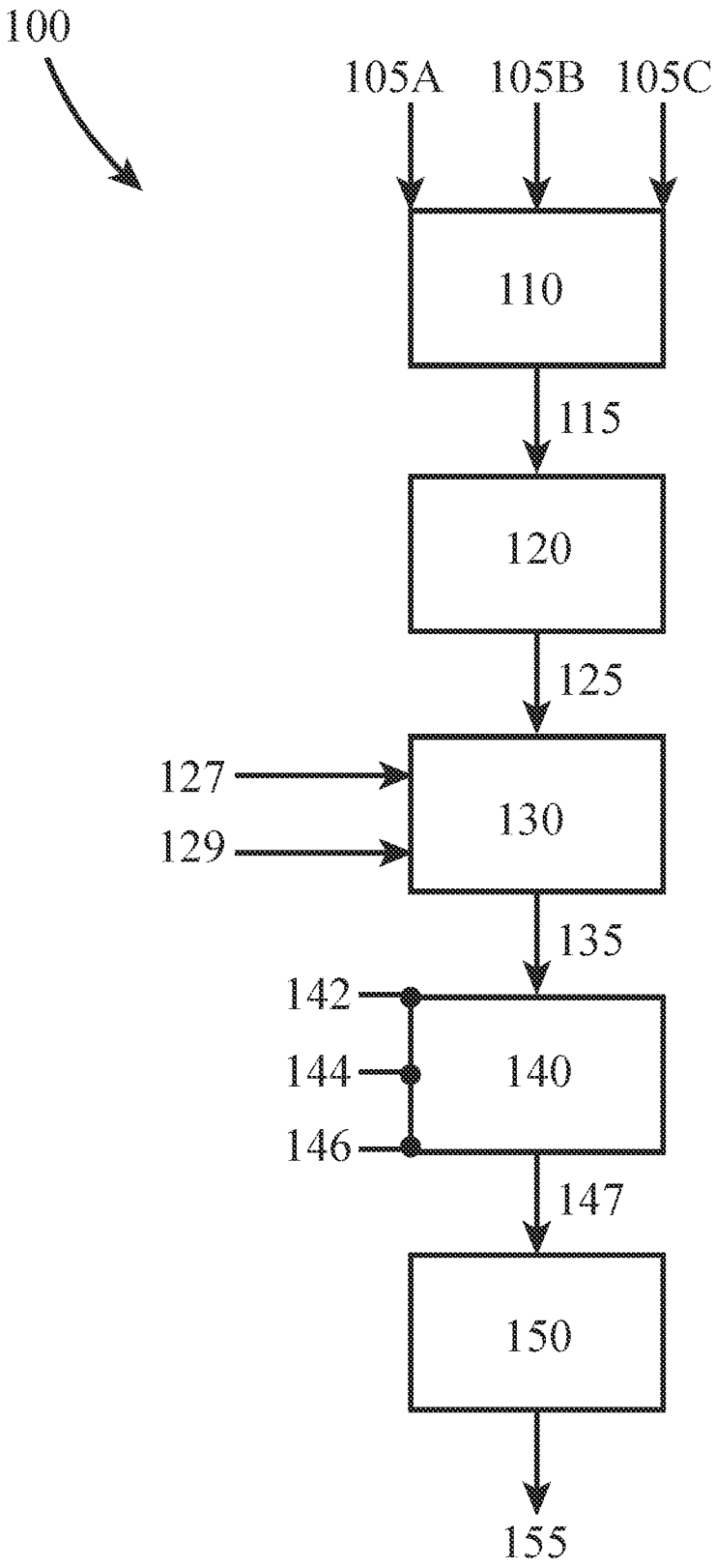
100
105A
105B
105C
110
115
120
125
127
129
130
135
142
144
146
140
147
150
155

Figure 1A

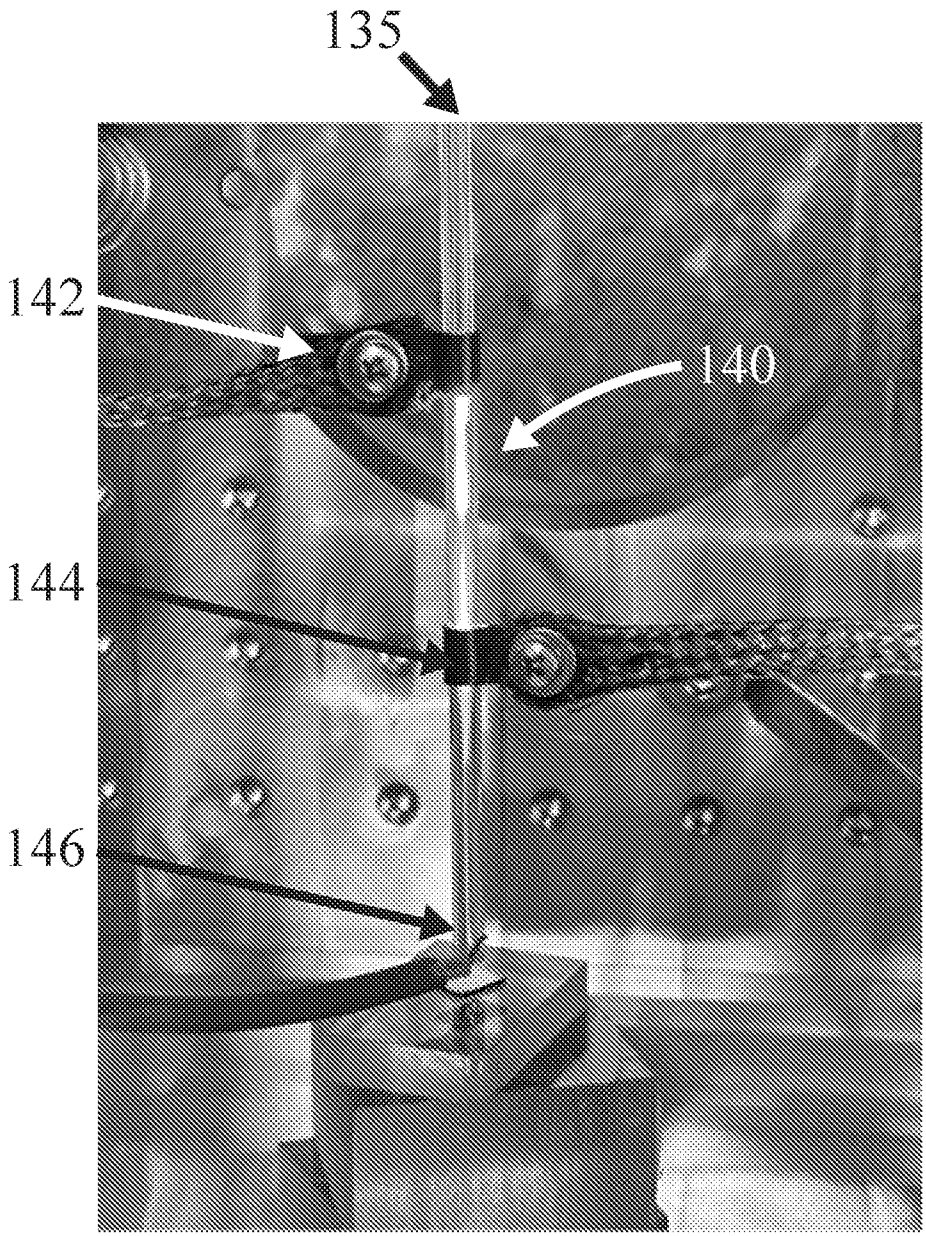

Figure 1B

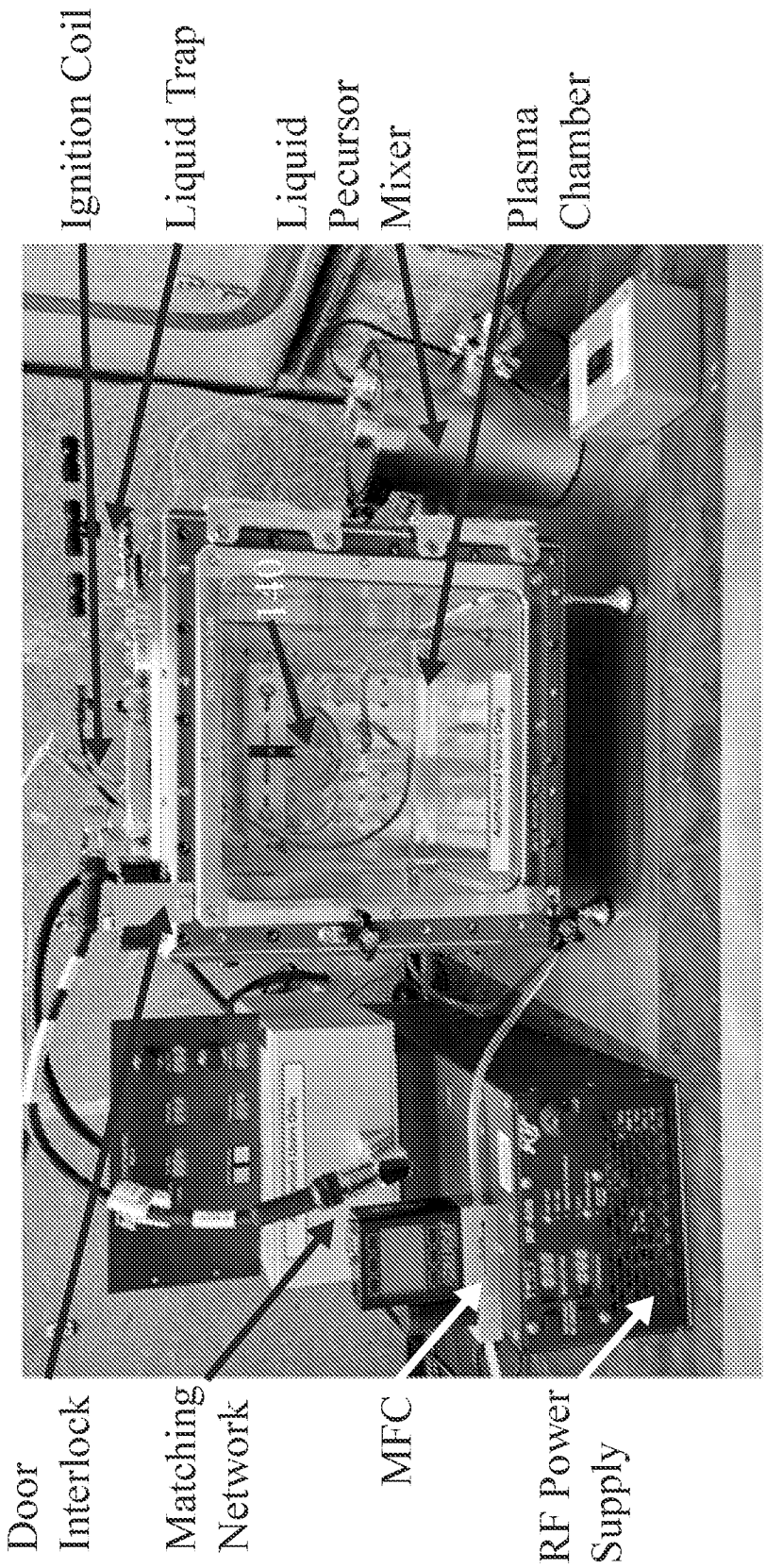
Ignition Coil
Liquid Trap
Liquid Pecursor Mixer
Plasma Chamber
Door Interlock
Matching Network
MFC
RF Power Supply

Figure 1C

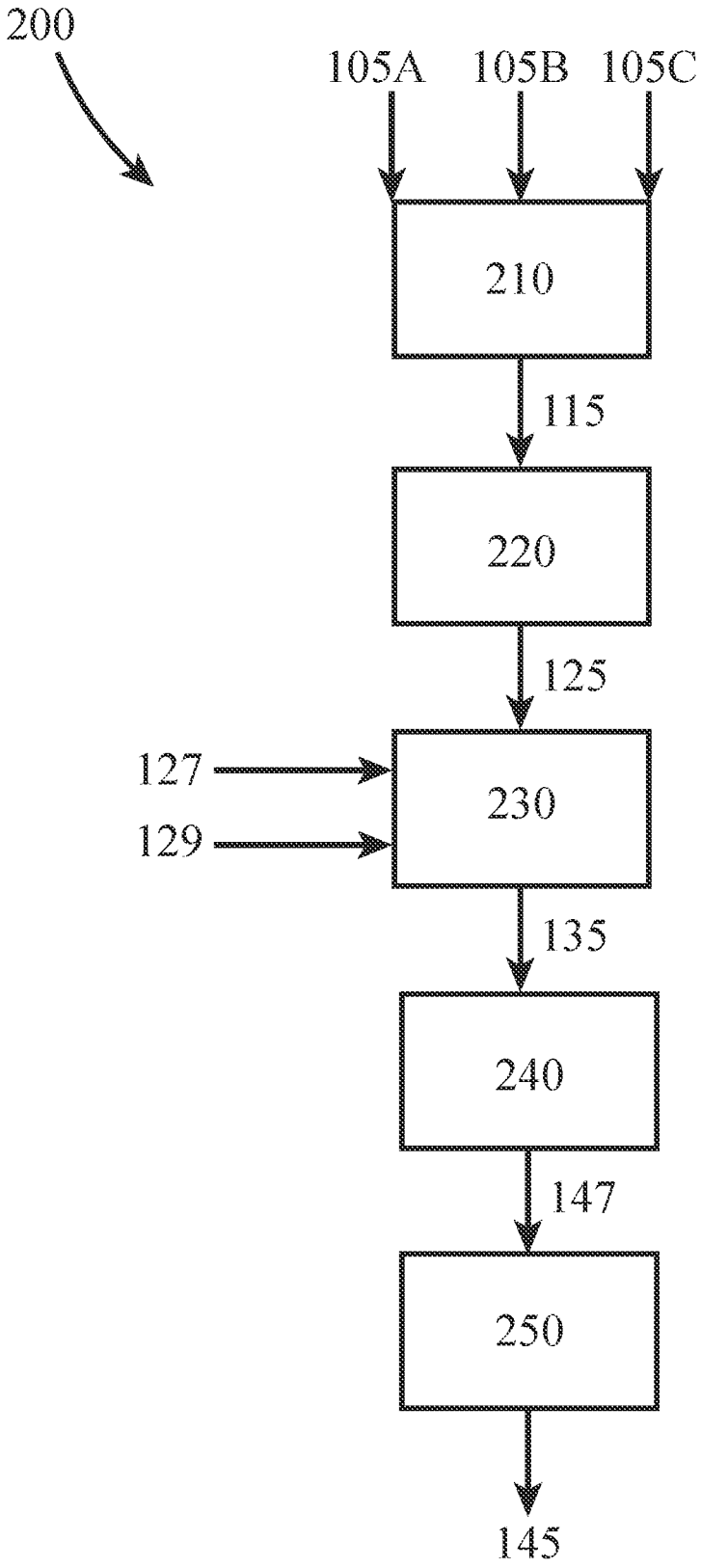
200
105A
105B
105C
210
115
220
125
127
129
230
135
240
147
250
145

Figure 2

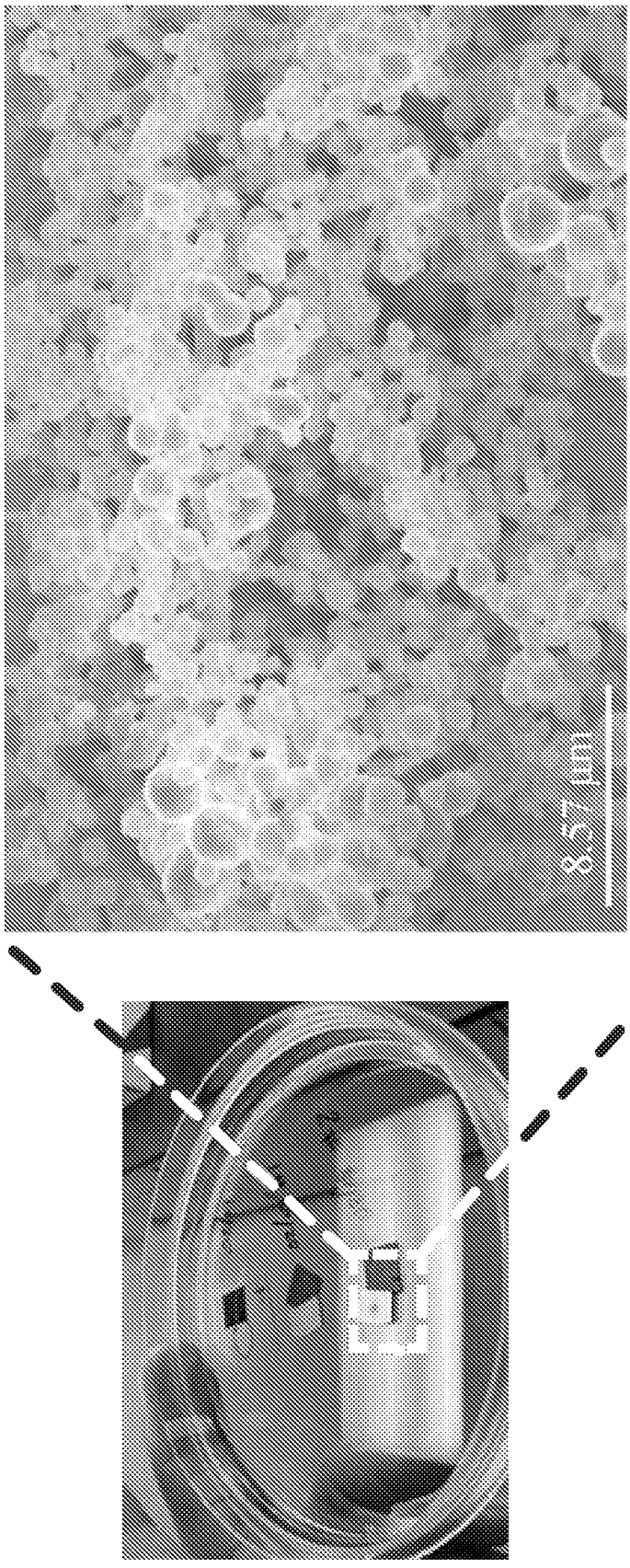

Figure 3

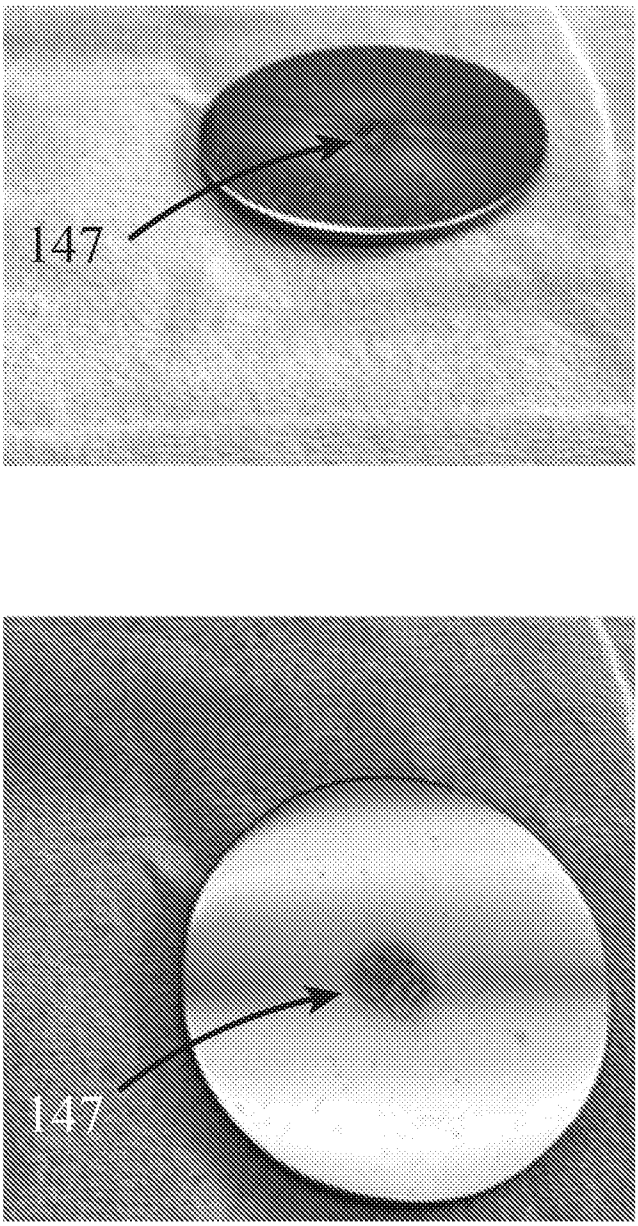

Figure 4

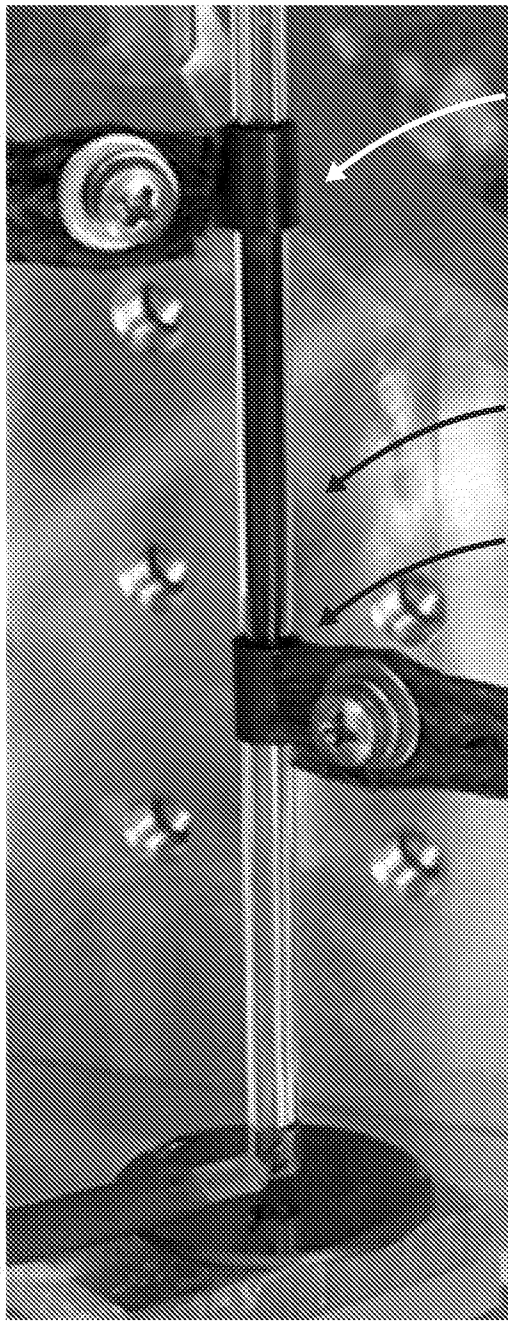

Figure 5

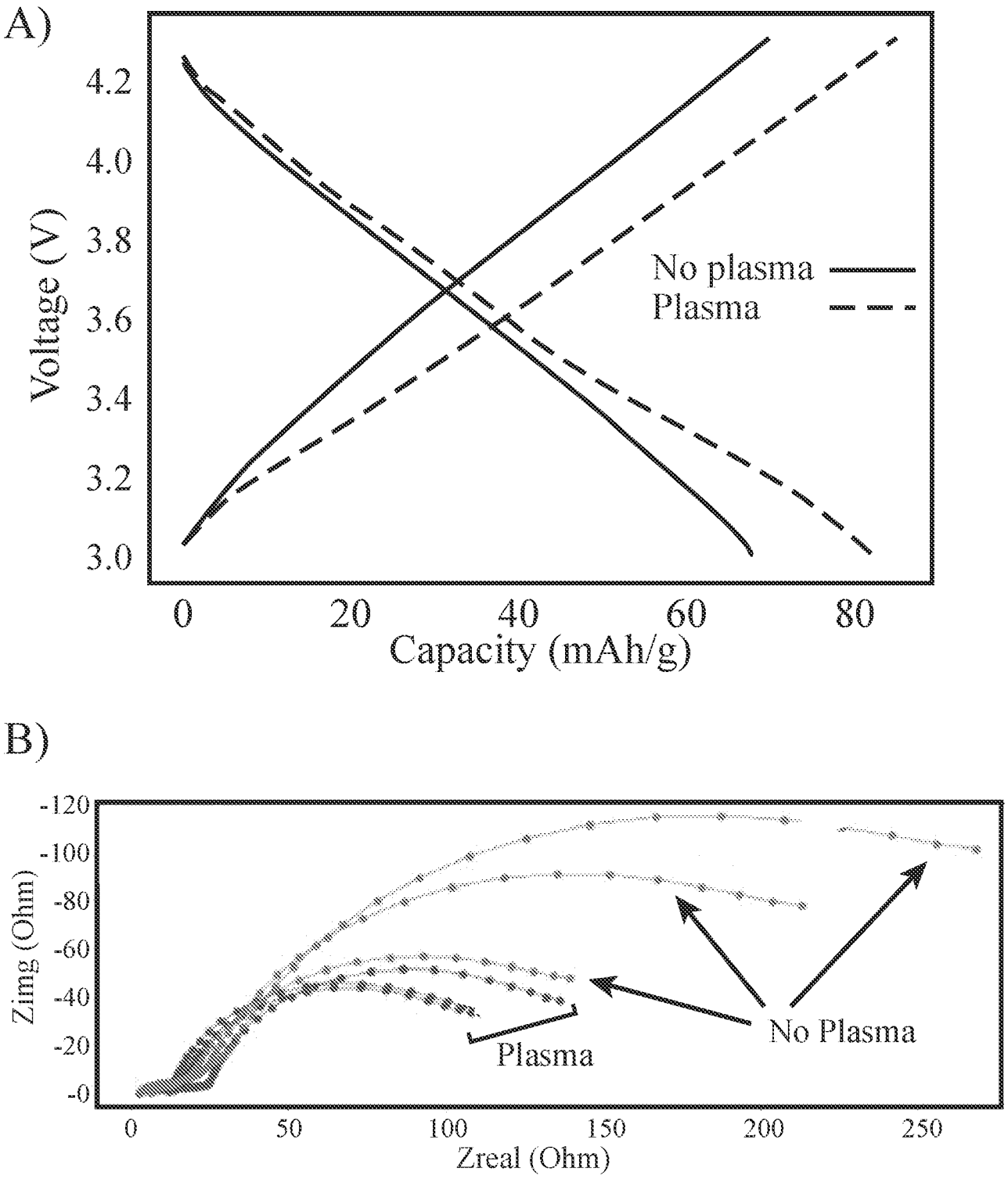
A)
4.2
4.0
3.8
3.6
3.4
3.2
3.0
Voltage (V)
No plasma
Plasma
0
20
40
60
80
Capacity (mAh/g)
B)
-120
-100
-80
-60
-40
-20
-0
Zimg (Ohm)
Plasma
No Plasma
0
50
100
150
200
250
Zreal (Ohm)

Figure 6

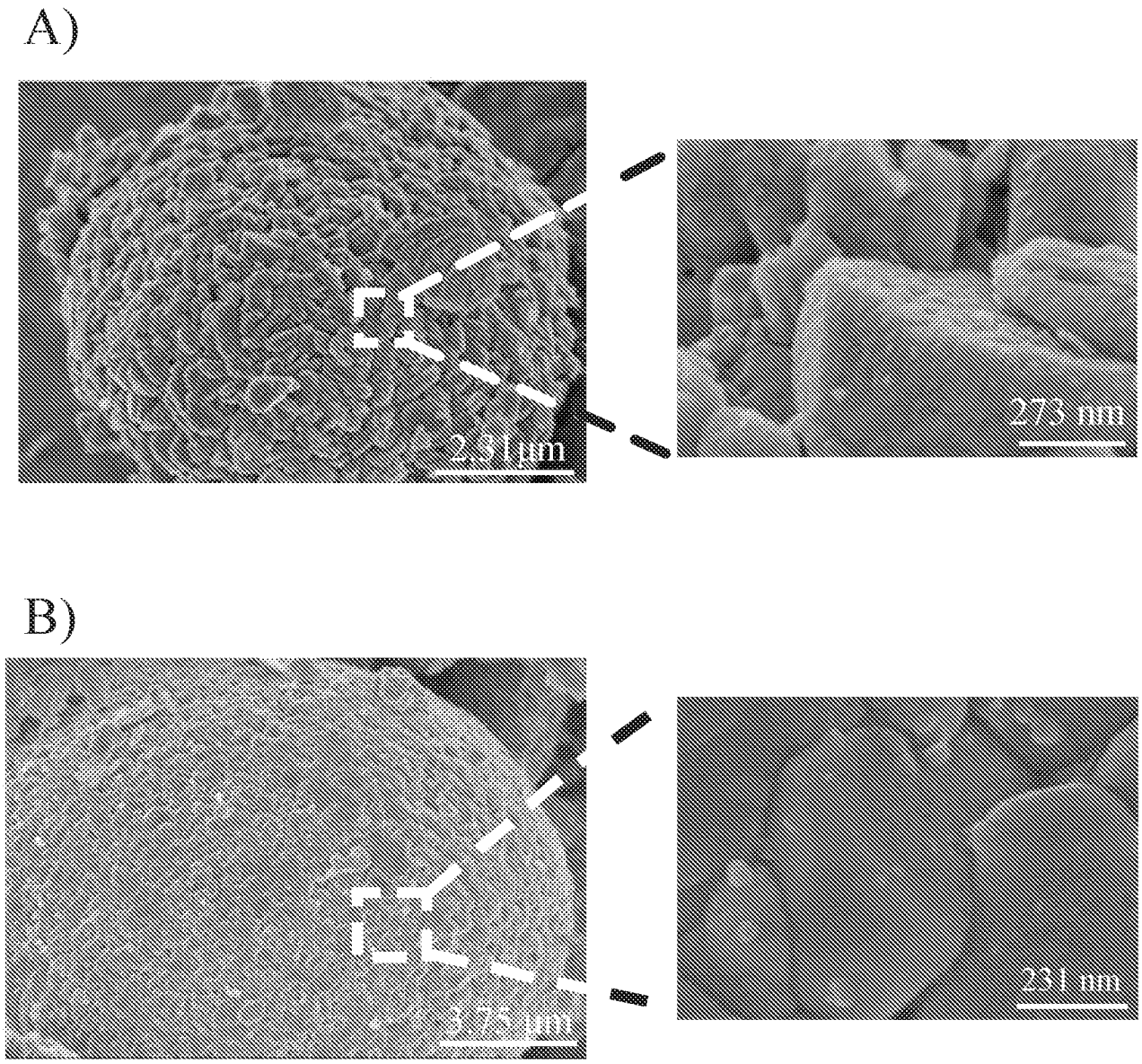

Figure 7

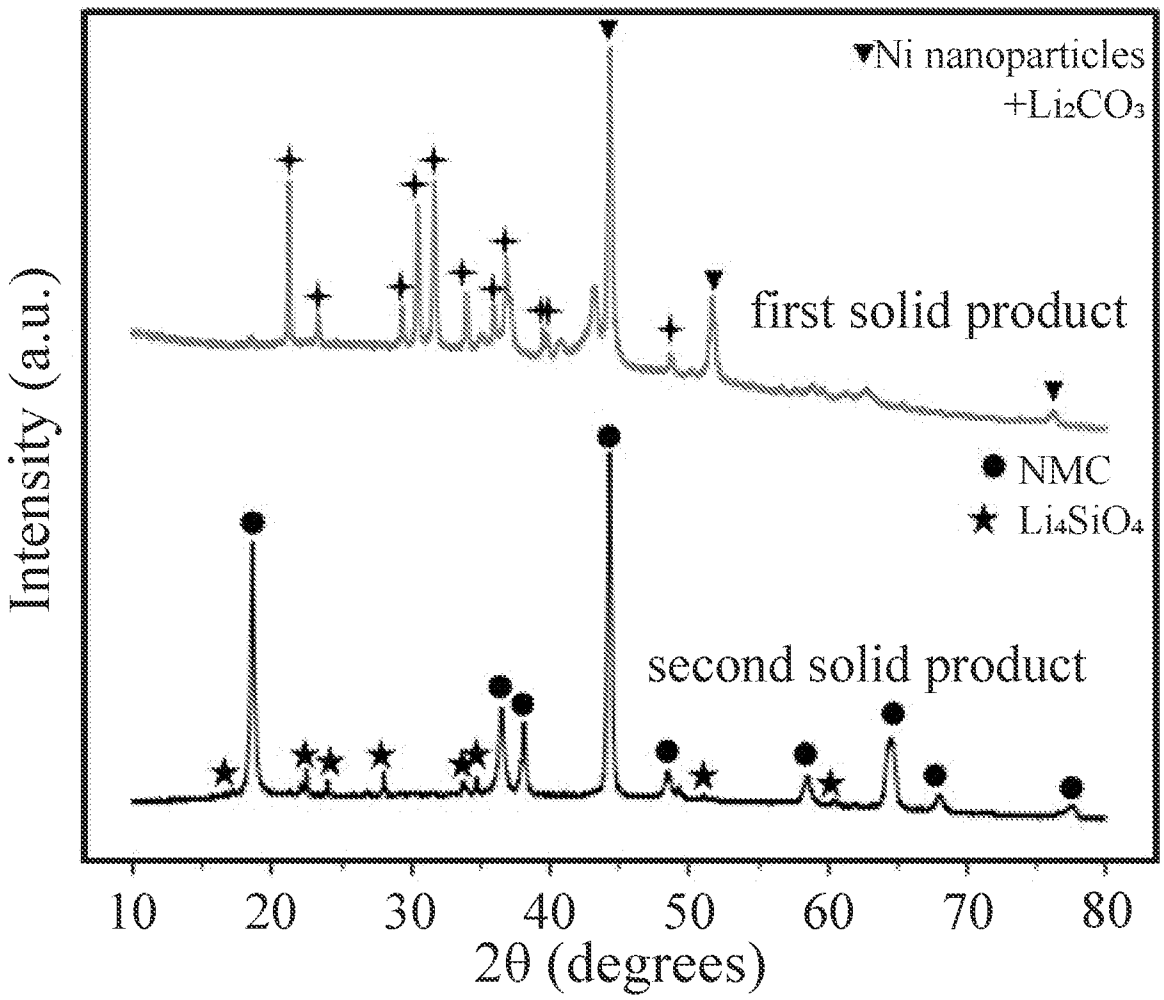
Ni nanoparticles
+Li2CO3
first solid product
NMC
Li4SiO4
second solid product
Intensity (a.u.)
10
20
30
40
50
60
70
80
2θ (degrees)

Figure 8

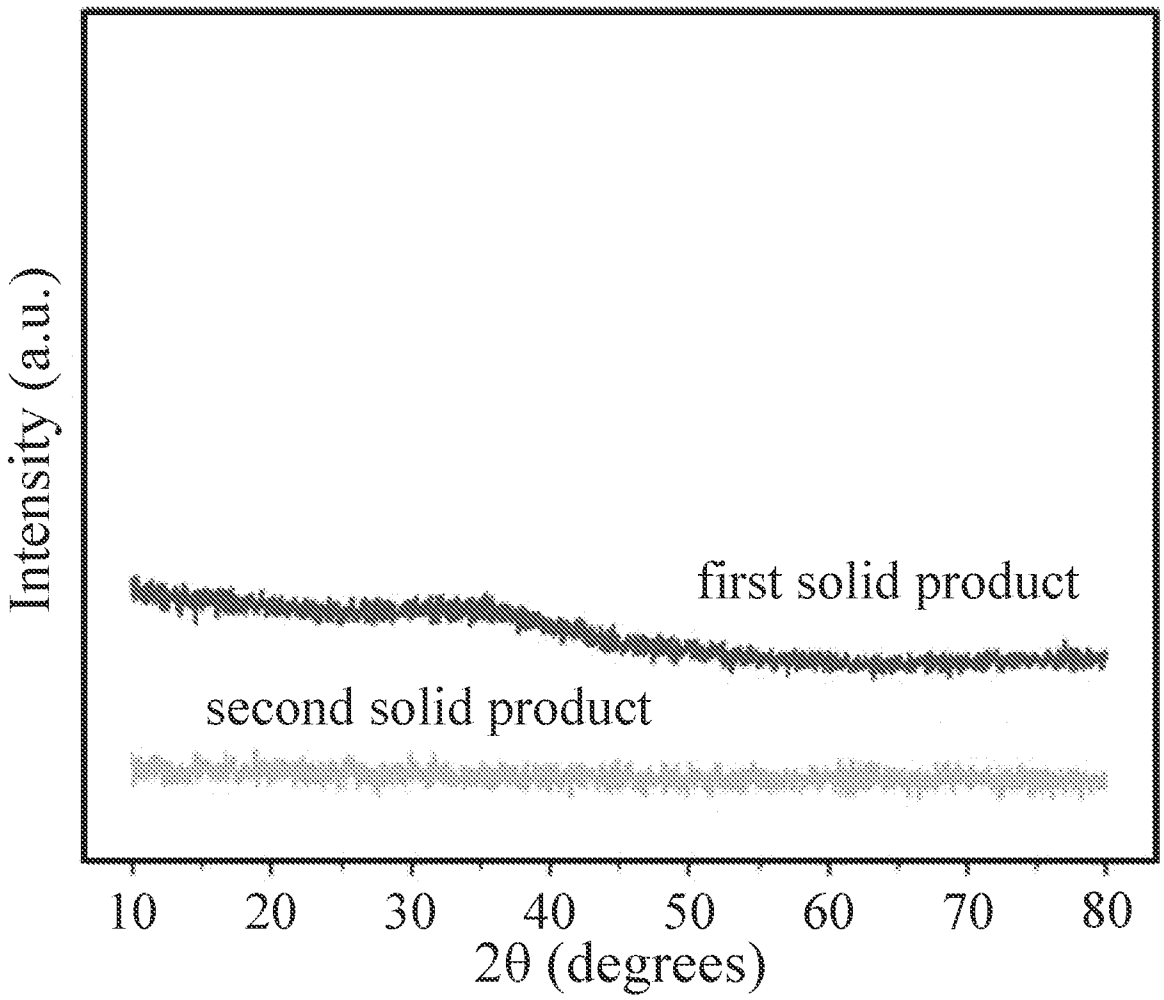
Intensity (a.u.)
first solid product
second solid product
10
20
30
40
50
60
70
80
2θ (degrees)

Figure 9

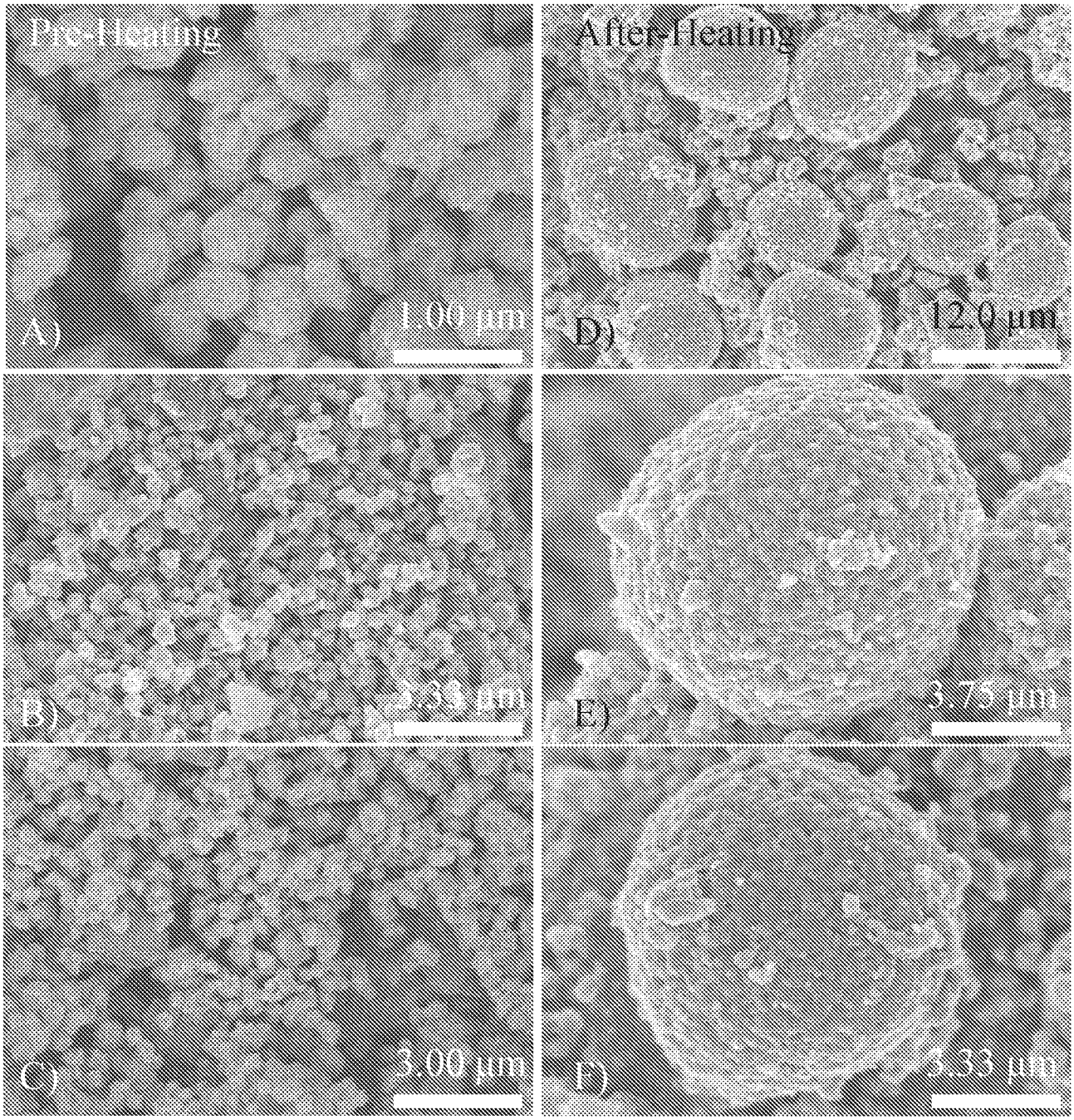
Pre-Heating
A)
100 µm
After-Heating
D)
12.0 µm
B)
3.33 µm
E)
3.75 µm
C)
3.00 µm
F)
3.33 µm

Figure 10

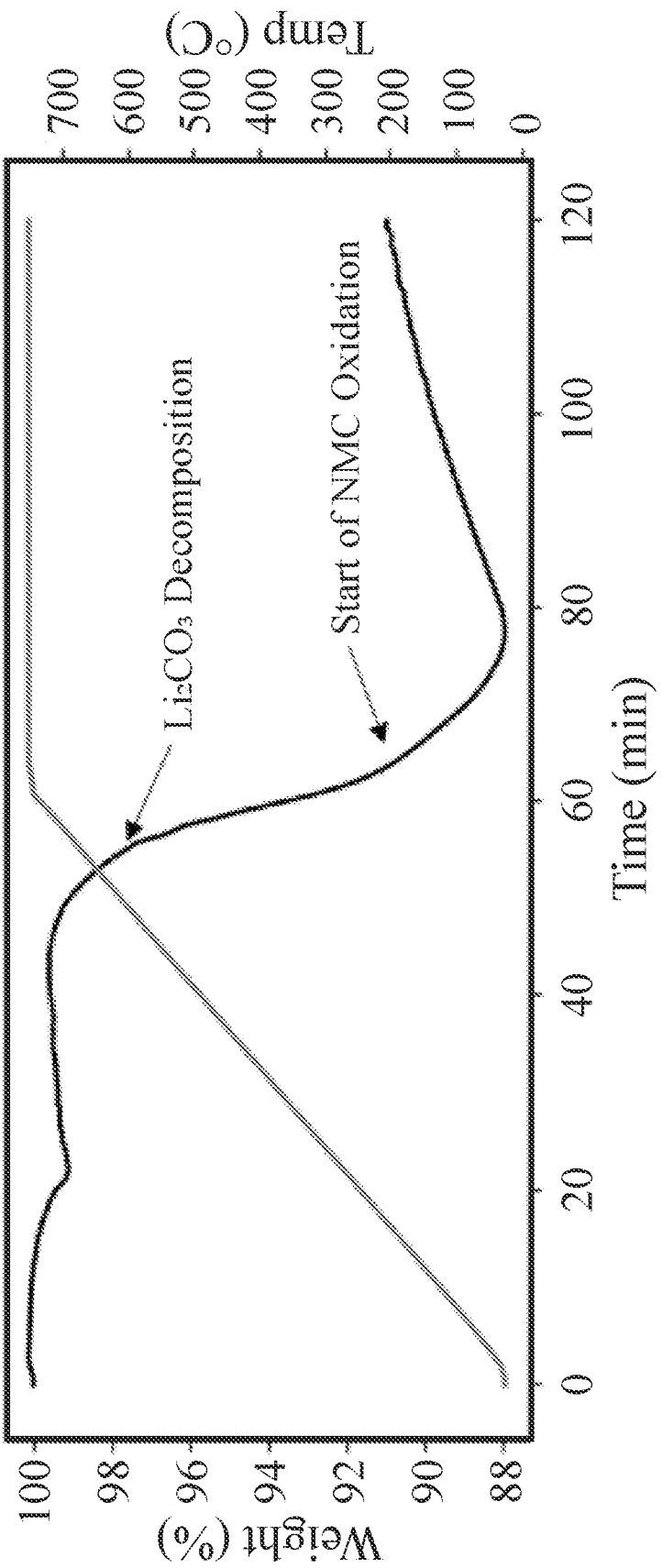
Weight (%)
100
98
96
94
92
90
88
Temp (°C)
700
600
500
400
300
200
100
0
Time (min)
0
20
40
60
80
100
120
Li2CO3 Decomposition
Start of NMC Oxidation

Figure 11

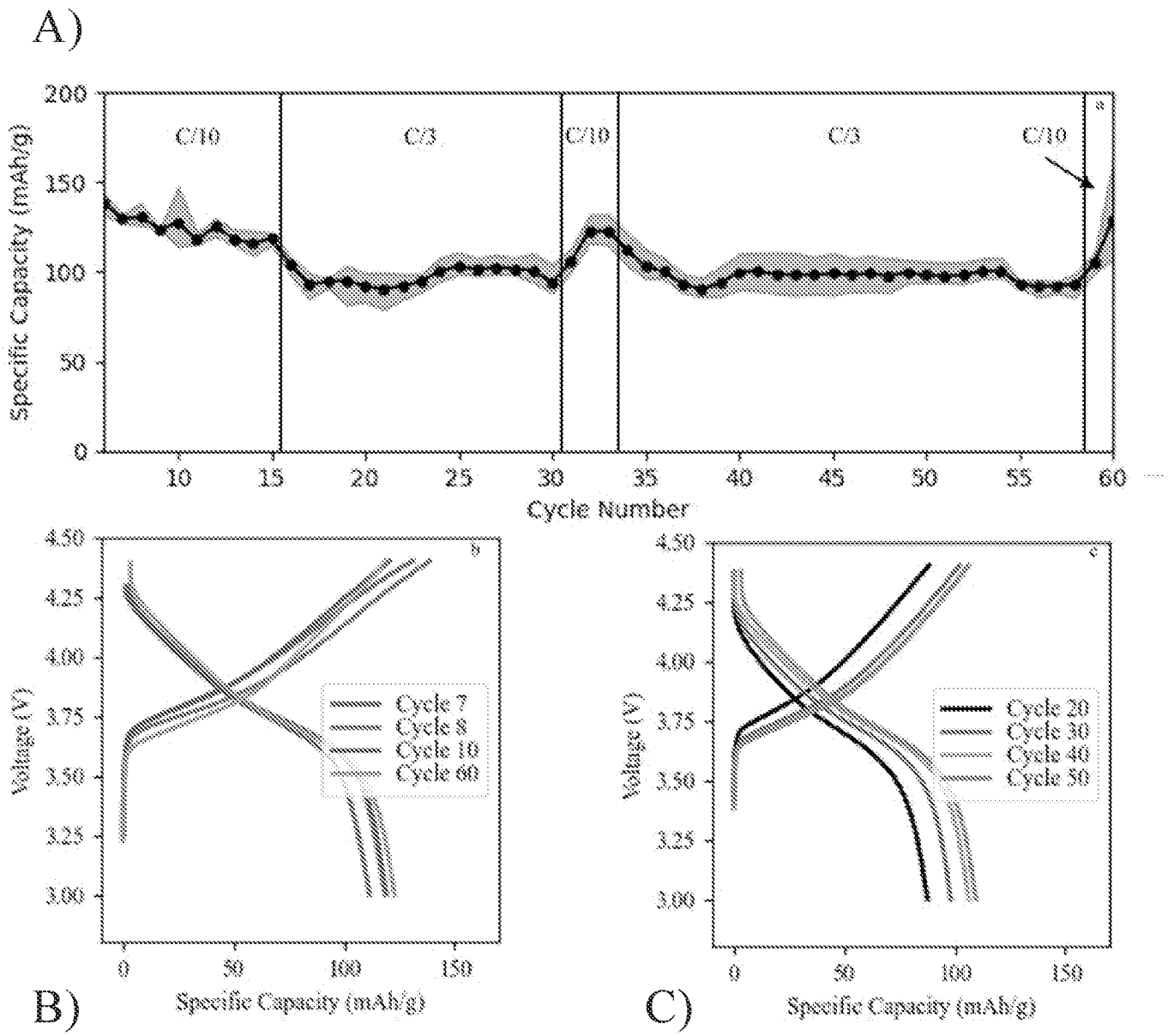
A)
Specific Capacity (mAh/g)
Cycle Number
C/10
C/3
C/10
C/3
C/10
a
B)
Voltage (V)
Specific Capacity (mAh/g)
Cycle 7
Cycle 8
Cycle 10
Cycle 60
b
C)
Voltage (V)
Specific Capacity (mAh/g)
Cycle 20
Cycle 30
Cycle 40
Cycle 50
c

Figure 12

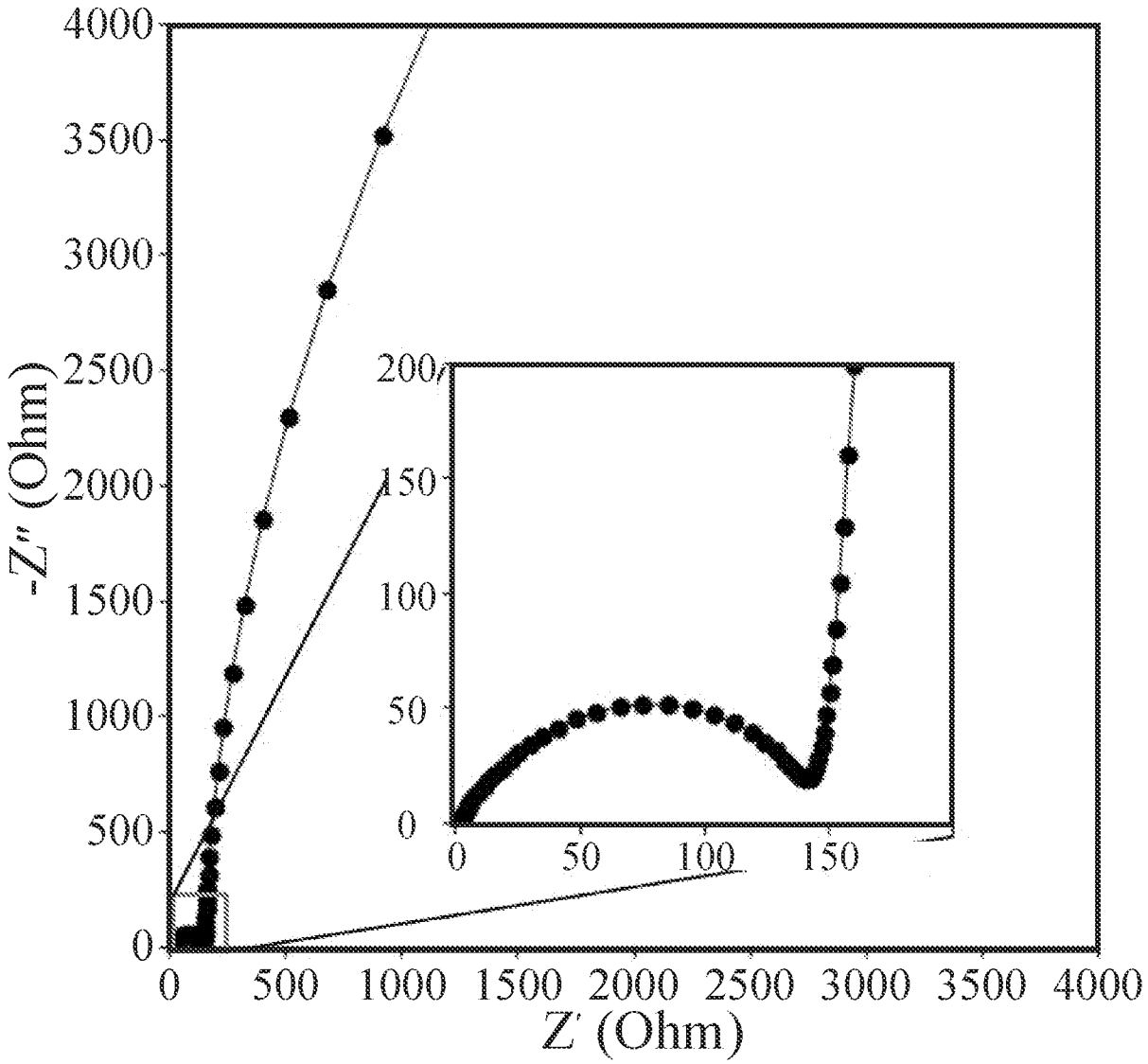
4000
3500
3000
2500
2000
1500
1000
500
0
-Z'' (Ohm)
200
150
100
50
0
0
50
100
150
0
500
1000
1500
2000
2500
3000
3500
4000
Z' (Ohm)

Figure 13

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2024/047996

A. CLASSIFICATION OF SUBJECT MATTER

IPC: ***C01D 15/00*** (2023.01); ***C01G 53/00*** (2023.01); *H01M 10/0525* (2023.01); *H01M 4/505* (2023.01); *H01M 4/525* (2023.01)

CPC: ***C01D 15/00; C01G 53/00;*** *H01M 10/0525; H01M 4/505; H01M 4/525*

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

See Search History Document

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

See Search History Document

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

See Search History Document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2021/0032117 A1 (UT-BATTELLE, LLC) 04 February 2021 (04.02.2021) entire document; especially Fig. 1A; para [0010]-[0012], para [0026], para [0046]	1-12
Y	WO 2021/048399 A1 (UMICORE et al.) 18 March 2021 (18.03.2021) entire document; especially pg. 15-16	1-12
A	WO 2022/129083 A1 (UMICORE) 23 June 2022 (23.06.2022) entire document	1-12

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"D" document cited by the applicant in the international application
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
26 December 2024 (26.12.2024)	**16 January 2025 (16.01.2025)**

Name and mailing address of the ISA/US	Authorized officer
COMMISSIONER FOR PATENTS **MAIL STOP PCT, ATTN: ISA/US** **P.O. Box 1450** **Alexandria, VA 22313-1450** **UNITED STATES OF AMERICA**	**KARI RODRIQUEZ**
Facsimile No. **571-273-8300**	Telephone No. **PCT Help Desk: 571-272-4300**

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2024/047996

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☑ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.: **1-12**

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2024/047996

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1.

Group I: Claims 1-12 are directed to a method comprising heating a first solid product to a temperature between 500 C and 1000 C to form a second solid product.

Group II: Claims 13-15 are directed to a method comprising a solid having a solid electrolyte interphase (SEI).

The groups of inventions listed above do not relate to a single general inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons:

Special Technical Features

Group I includes the special technical feature of heating the first solid product to a temperature between 500 C and 1000 C to form a second solid product, not included in the other group.

Group II includes the special technical feature of a solid having a solid electrolyte interphase (SEI), not included in the other group.

Common Technical Features:

The only technical feature shared by Groups I-II that would otherwise unify the groups is a method comprising reacting a mixture comprising a carrier gas and a precursor, wherein: the precursor is a vapor, the reacting is performed using a plasma energized using a radio frequency (RF),the reacting is performed at an absolute pressure between 0.8 atms and 1.2 atms, a solid comprises lithium, oxygen, at least one of nickel, manganese, cobalt, or a combination thereof. However, this shared technical feature does not represent a contribution over the prior art, because the shared technical feature is disclosed by US 2021/0032117 A1 to UT-Battelle, LLC (hereinafter "Battelle")

Battelle discloses a method comprising reacting a mixture comprising a carrier gas and a precursor, wherein: the precursor is a vapor, the reacting is performed using a plasma energized using a radio frequency (RF) (Fig. 1A; para [0010]-[0012]- the method includes subjecting a precursor material (e.g., a single material or mixture of materials) containing all elements desired to be in the resulting ionically conductive composition, as described above, to a thermal process in which the precursor material is at least partially vaporized...thermal process is a plasma process..inductive plasma processing...four different gases are used in the process, i.e., a quench gas, carrier gas, sheath gas, and the plasma gas..in the plasma process, precursor powders, liquids, and/or gases are passed through a radio-frequency plasma torch, where they are vaporized into atoms or molecular.), the reacting is performed at an absolute pressure between 0.8 atms and 1.2 atms (para [0046]- the method described herein can be practiced at standard pressure, typically about 1 atm.), a solid comprises lithium, oxygen, at least one of nickel, manganese, cobalt, or a combination thereof (para [0026]- The particles and films described above have an ionically conductive composition..at least two elements selected from the group consisting of oxygen (O)... lithium (Li).. manganese, iron, cobalt, nickel).

Accordingly, the inventions listed as Groups I-II above lack unity of invention under PCT Rule 13 because the do not share a same or corresponding special technical feature providing contribution over prior art.