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(71) Applicant: **LAWRENCE LIVERMORE NATIONAL SECURITY, LLC** [US/US]; 7000 East Avenue, Livermore, California 94550 (US).

(72) Inventors: **SCHWARTZ, Johanna Jesse**; c/o Lawrence Livermore National Laboratory, 7000 East Avenue, P.O. Box 808, L-703, Livermore, California 94550 (US). **WOOD, Marissa**; c/o Lawrence Livermore National Laboratory, 7000 East Avenue, P.O. Box 808, L-703, Livermore, California 94550 (US). **YE, Jianchao**; c/o Lawrence Livermore National Laboratory, 7000 East Avenue, P.O. Box 808, L-703, Livermore, California 94550 (US). **JAYCOX, Adam W.**; c/o Lawrence Livermore National Laboratory, 7000 East Avenue, P.O. Box 808, L-703, Livermore, California 94550 (US). **ZHONG, Xiaoting**; c/o Lawrence Livermore National Laboratory, 7000 East Avenue, P.O. Box 808, L-703, Livermore, California 94550 (US). **GONGORA, Aldair Ernesto**; c/o Lawrence Livermore National

(54) Title: HIGH THROUGHPUT MATERIALS SCREENING

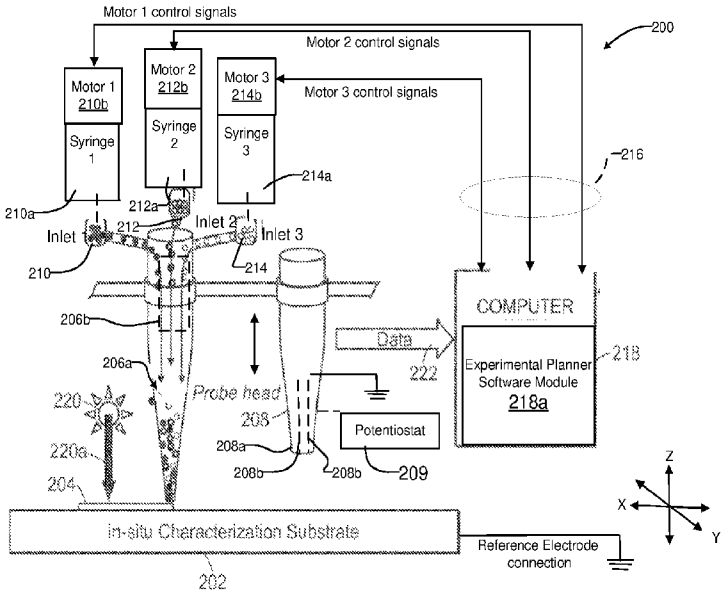


FIG. 2

(57) Abstract: The present disclosure relates to systems and methods for screening a formulation of a material being printed in an additive manufacturing process, in situ, to enable rapid analysis, modeling and modification of at least one characteristic associated with the material formulation. In one embodiment the system includes a computer and an experimental planning software module that includes a historical database of sample material test results, a machine learning software module, and a new batch formulation generation software module. The experimental planning software module enables new material formulations to be determined in situ and in real time, using one or more machine learning models, and new material samples to be printed in accordance with newly determined material formulations, for closer inspection and evaluation of at least one desired characteristic of the sample materials.

WO 2024/059302 A1

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Laboratory, 7000 East Avenue, P.O. Box 808, L-703, Livermore, California 94550 (US).

(74) **Agent: ELCHUK, Mark D.**; Harness, Dickey & Pierce, P.L.C., 5445 Corporate Drive, Suite 200, Troy, Michigan 48098 (US).

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HIGH THROUGHPUT MATERIALS SCREENING

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application is a PCT International Application and claims priority of United States Patent Application No. 17/932,723 filed on September 16, 2022. The entire disclosure of the above application is incorporated herein by reference.

STATEMENT AS TO RIGHTS TO APPLICATIONS MADE UNDER FEDERALLY SPONSORED RESEARCH AND DEVELOPMENT

[0002] This invention was made with Government support under Contract No. DE-AC52-07NA27344 awarded by the United States Department of Energy. The Government has certain rights in the invention.

BACKGROUND

Field of Endeavor

[0003] The present application relates to materials screening and more particularly to high throughput materials screening.

State of Technology

[0004] This section provides background information related to the present disclosure which is not necessarily prior art.

[0005] Polymer materials formulation and optimization has been generally limited to mixing by hand, as polymers have a wide range of viscosities. A high throughput approach is therefore needed to enable faster screening of polymers optimized for targeted applications. Systems that mix multi-materials with disparate viscosities are known [Example U.S. Patent No 10,071,350]. The inventors have developed active mixing direct-ink-write (DIW) additive manufacturing to facilitate the 3D printing of multi-material films. The inventors have developed an automated platform for materials by coupling mixing systems with *in-situ* characterization systems combined with machine learning systems.

SUMMARY

[0006] Features and advantages of the disclosed apparatus, systems, and methods will become apparent from the following description. Applicant is providing this description, which includes drawings and examples of specific embodiments, to

give a broad representation of the apparatus, systems, and methods. Various changes and modifications within the spirit and scope of the application will become apparent to those skilled in the art from this description and by practice of the apparatus, systems, and methods. The scope of the apparatus, systems, and methods is not intended to be limited to the particular forms disclosed and the application covers all modifications, equivalents, and alternatives falling within the spirit and scope of the apparatus, systems, and methods as defined by the claims.

[0007] Applicant's apparatus, systems, and methods provide screening for screening a material that includes providing active mixing direct-ink-writing of the material, providing in situ characterization substrates or probes that receive the material, and providing active learning planning for screening the material. The providing active mixing direct-ink-writing of the material prints multiple films. In one embodiment the providing active mixing direct-ink-writing of the material prints five to ten films. In another embodiment the providing active mixing direct-ink-writing of the material prints one to twenty films. The providing in situ characterization substrates or probes includes printing multiple films on the substrates or probes with a first set of constituents. The providing active learning planning for screening the material includes providing machine learning that takes the first set of constituents and uses the first set of constituents to dictate a next batch of films to achieve improved additional sets of constituents.

[0008] In one aspect the Applicant's system relates to a system for screening a formulation of a material being printed in an additive manufacturing process, in situ, to enable rapid analysis, modeling and modification of at least one characteristic associated with the material formulation. The system may comprise a computer. A substrate may be included on which the material formulation is printed. A deposition print head may be included for depositing the material formulation on the substrate as at least one material sample. The substrate may include at least one component for enabling the characteristic of the material formulation printed thereon to be at least one of measured or determined. A probe is included which is configured to be moved into contact with the material formulation after the material formulation is printed on the substrate as a sample material. The probe provides an output to the computer representing data from which the characteristic can be evaluated by the computer and a new material formulation determined. An experimental planning software module may be included which has a machine learning software module. The machine learning

software module is configured to use the data collected by the probe and to determine, using the machine learning software module, a new material formulation which better optimizes the characteristic being evaluated.

[0009] In another aspect the deposition print head of the system includes at least first and second input ports for receiving first and second components of the material formulation being supplied to the deposition print head.

[0010] In another aspect the system further comprises at least first and second syringes for containing the first and second components, respectively, of the material formulation, and which first and second motors associated with the first and second syringes, respectively. The first and second motors are responsive to control signals from the computer for controllably providing the first and second components to the deposition print head in accordance with the control signals from the computer.

[0011] In another aspect the computer generates the control signals in real time, and in situ, at least one of while or before the material sample is being printed.

[0012] In another aspect the experimental planning software module further includes a database for storing information and/or data associated with previously screened test materials. The database is configured to be updated in real time with new material screening results provided by the probe output and updated formulation suggestions by the machine learning software module. A new batch formulation software module is also included for receiving information from the database and generating new formulations for a new batch of material samples to be printed.

[0013] In another aspect the machine learning software module comprises at least one of a random forest model, a gaussian process model or a neutral network model.

[0014] In another aspect the machine learning module comprises a Bayesian optimization framework for carrying out Bayesian modeling and decision making.

[0015] In another aspect, the at least one component of the substrate comprises a grid of spatially separated electrodes which are used to complete electrical paths as the probe contacts different areas of the material sample after the material sample is printed on the substrate, to thus enable the probe to generate the output to the computer.

[0016] In another aspect the probe comprises a two point probe head including a first component which makes contact with the material sample, and a second

component which extends through the material sample and into contact with at least one of the electrodes.

[0017] In another aspect the at least one component of the substrate comprises an environmental sensor.

[0018] In another aspect the at least one component of the substrate comprises stress sensors.

[0019] In another aspect the at least one component of the substrate comprises an impedance sensor.

[0020] In another aspect the at least one component of the substrate comprises at least one of an O2 sensor, a thermal sensor or a pH sensor.

[0021] In another aspect cells are included in the material formulation when the material sample is printed on the substrate by the deposition print head. The cells provide information enabling the characteristic to be evaluated.

[0022] In another aspect a microscopy or fluorescence imaging subsystem is included for assisting in evaluating the material sample.

[0023] In another aspect the build plate comprises at least one of an embedded gas or a chemical sensor for generating information to assist the computer in evaluating the material sample printed on the build plate.

[0024] In another aspect substrate and deposition print head are located inside a controlled environment.

[0025] In another aspect the controlled environment includes a stimulus to assist in evaluation of the material sample.

[0026] In another aspect a secondary environmental chamber is included which communicates with the controlled environment to enable further study of a component present in the controlled environment.

[0027] In another aspect the present disclosure relates to a method for screening a formulation of a material being printed in an additive manufacturing process, in situ, to enable rapid analysis, modeling and modification of at least one characteristic associated with the material formulation. The method may comprise printing the material formulation as at least one material sample on a substrate, and then using at least one component associated with the substrate for enabling the characteristic of the material formulation printed thereon to be at least one of measured or determined. The method may further include using a probe to obtain information concerning the characteristic from the material sample. The method may include causing the probe to

provide an output to a computer, and then causing the computer to use software to evaluate the material sample. The software includes machine learning software to evaluate historical data concerning previously printed material samples, and to assist in determining updated formulations for new material samples to be printed on the substrate in subsequent printing operations and further analyzed.

[0028] The apparatus, systems, and methods are susceptible to modifications and alternative forms. Specific embodiments are shown by way of example. It is to be understood that the apparatus, systems, and methods are not limited to the particular forms disclosed. The apparatus, systems, and methods cover all modifications, equivalents, and alternatives falling within the spirit and scope of the application as defined by the claims.

BRIEF DESCRIPTION OF THE DRAWINGS

[0029] The accompanying drawings, which are incorporated into and constitute a part of the specification, illustrate specific embodiments of the apparatus, systems, and methods and, together with the general description given above, and the detailed description of the specific embodiments, serve to explain the principles of the apparatus, systems, and methods.

[0030] FIG. 1A is a flowchart that illustrates one embodiment of a screening method for screening a material.

[0031] FIG. 1B is a flowchart that illustrates another embodiment of a screening method for screening a material.

[0032] FIG. 2 is an illustration of Applicant's apparatus, systems, and methods that involve three main components: Formulations loading and mixing, Deposition and measurement, and Analysis and experimental planning.

[0033] FIG. 2A is a high level block diagram illustrating in more detail the various components of the experimental planning software module;

[0034] FIG. 2B is a high level flowchart of one example of operations that may be performed by the machine learning software module contained in the experimental planning software module;

[0035] FIG. 3 is an illustration of automated high throughput polymer electrolyte screening.

[0036] FIG. 4 is an illustration of tuning mechanical strength 3D printed materials screening.

[0037] FIG. 5 is an illustration of tuning mechanical strength and other thermomechanical properties for 3D printed materials screening.

[0038] FIG. 6 is an illustration of a screening system for screening a material.

[0039] FIG. 7A is an illustration of another embodiment of a screening system for screening a material.

[0040] FIG. 7B is an illustration of yet another embodiment of a screening system for screening a material.

DETAILED DESCRIPTION OF SPECIFIC EMBODIMENTS

[0041] Referring to the drawings, to the following detailed description, and to incorporated materials, detailed information about the apparatus, systems, and methods is provided including the description of specific embodiments. The detailed description serves to explain the principles of the apparatus, systems, and methods. The apparatus, systems, and methods are susceptible to modifications and alternative forms. The application is not limited to the particular forms disclosed. The application covers all modifications, equivalents, and alternatives falling within the spirit and scope of the apparatus, systems, and methods as defined by the claims.

[0042] Applicant's apparatus, systems, and methods provide active-mixing direct ink write additive manufacturing enable mixing of materials with highly disparate viscosities, from liquids to pastes. By coupling a mixing system with in-situ characterization methods, and also with machine learning experimental planning systems, the inventors have developed an automated platform for materials discovery and optimization. The systems and methods of the present disclosure can handle complex hybrid formulations including, but not limited to, solvents, monomers, oligomers, polymers, and additives. Additives can be liquid or solid, including particles (nano and micro) of organic compounds, metals, salts, glasses, ceramics, conducting materials, and more. In-situ characterization using a suitable component, for example either through a probe or substrate matrix, enables information to be obtained to facilitate homing-in on desirable properties for target applications when coupled with use of an active learning experimental planning software to vary the composition during the printing process.

[0043] Referring now to the drawings and in particular to FIG. 1A, an illustrative view shows an embodiment of Applicant's apparatus, systems, and methods. This

embodiment is identified generally by the reference numeral 100a. FIG. 1A is a flowchart that illustrates a screening method for screening a material. The component steps of Applicant's method 100a illustrated in FIG. 1A are listed below:

[0044] Reference Numeral No. 102a – provide multiple selected samples,

[0045] Reference Numeral No. 104a – mix the samples,

[0046] Reference Numeral No. 106a – deposit the mixed samples on a substrate,

[0047] Reference Numeral No. 108a – measure the deposited samples,

[0048] Reference Numeral No. 110a – establish desired sample characteristics, and

[0049] Reference Numeral No. 112a – rate the deposited samples according to the sample characteristics.

[0050] The description of the steps of the Applicant's material screening method 100a having been completed, the operation and additional description of the Applicant's apparatus, systems, and methods will now be considered in greater detail.

[0051] The screening method 100a includes the steps of providing active mixing direct-ink-writing of the material, providing in situ characterization components such, for example substrates or probes, containing the material, and providing active learning planning for screening the material. The step of providing active mixing direct-ink-writing of the material may involve printing a select number of films, for example printing five to ten films. The step of providing in situ characterization substrates or probes includes printing multiple films on the substrates or probes with the multiple films having a first set of constituents. For example, the step of providing in situ characterization substrates or probes can include printing five to ten films on the substrates or probes with the five to ten films having a first set of constituents. In another example, the step of providing in situ characterization substrates or probes includes printing one to twenty films on the substrates or probes with the one to twenty films having a first set of constituents.

[0052] The step of providing active learning planning for screening the material includes providing machine learning that takes the first set of constituents and uses the first set of constituents to dictate a next batch of films to achieve improved additional sets of constituents. As illustrated in FIG. 1A, step 102a involves providing multiple samples. Step 104a involves mixing the samples. Step 106a involves depositing the mixed samples on a substrate. Step 108a involves measuring the deposited samples.

Step 110a involves establishing desired sample characteristics. Step 112a involves rating the deposited samples according to said sample characteristics.

[0053] Referring now to FIG. 1B, an illustrative view shows another embodiment of Applicant's apparatus, systems, and methods. This embodiment is identified generally by the reference numeral 100b. FIG. 1B is a flowchart that illustrates a screening method for screening a material. The component steps of Applicant's method 100b illustrated in FIG. 1b are listed below:

[0054] Reference Numeral No. 102b – provide multiple samples,

[0055] Reference Numeral No. 104b – mix said samples,

[0056] Reference Numeral No. 106b – deposit said mixed samples on a substrate,

[0057] Reference Numeral No. 108b – measure said deposited samples,

[0058] Reference Numeral No. 110a – establish desired sample characteristics,

[0059] Reference Numeral No. 112b – rate said deposited samples according to said sample characteristics,

[0060] Reference Numeral No. 114b – screening complete check, and

[0061] Reference Numeral No. 116b – provide new quantity of samples for further testing.

[0062] The description of the steps of the Applicant's material screening method 100b having been completed, the operation and additional description of the Applicant's apparatus, systems, and methods will now be considered in greater detail.

[0063] The screening method 100b includes the steps of providing active mixing direct-ink-writing of the material, providing in situ characterization substrates or probes containing the material, and providing active learning planning for screening the material. The step of providing active mixing direct-ink-writing of the material prints five to ten films. The step of providing in situ characterization substrates or probes includes printing multiple films on the substrates or probes with the multiple films having a first set of constituents. For example, the step of providing in situ characterization substrates or probes can include printing five to ten films on the substrates or probes with the five to ten films having a first set of constituents. In another example, the step of providing in situ characterization substrates or probes includes printing one to twenty films on the substrates or probes with the one to twenty films having a first set of constituents.

[0064] The step of providing active learning planning for screening the material includes providing machine learning that takes the first set of constituents and uses the first set of constituents to dictate a next batch of films to achieve improved additional sets of constituents. As illustrated in FIG. 1B step 102b provides multiple samples. Step 104b mixes the samples. Step 106b deposits the mixed samples on a substrate. Step 108b measures select characteristics or qualities of the deposited samples. Step 110b identifies one or more regions of the deposited samples for additional exploration, which may involve exploring unknown spaces between the deposited samples. Step 112b rates the deposited samples according to said sample characteristics. By "rates" it is meant evaluates the best sample(s) of interest according some at least one predetermined parameter (e.g., ionic conductivity). Step 114b involves making a check to determine if screening is complete. By "complete" it is meant that no additional space is available on the substrate or that a predetermined number of samples have been deposited. If this check produces a "NO" answer, then a new quantity of samples is provided at operation 116b, and steps 104b-114b are repeated. If the check at operation 114b produces a "YES" answer, then screening is completed.

[0065] Referring now to FIG. 2, an illustrative view shows another embodiment of Applicant's apparatus, systems, and methods. This embodiment is identified generally by the reference numeral 200. The components of Applicant's apparatus, systems, and methods 200 illustrated in FIG. 2 are listed below:

[0066] Reference Numeral No. 202 – In-situ Characterization Substrate,

[0067] Reference Numeral No. 204 – Deposited Formulation,

[0068] Reference Numeral No. 206 – Mixing and Deposition Head or Nozzle,

[0069] Reference Numeral No. 206a – Rotationally Driven Mixing Shaft Element,

[0070] Reference Numeral No. 208 – Probe Head,

[0071] Reference Numeral No. 208a – Probe Tip,

[0072] Reference Numeral No. 208b – Probe Push Pins,

[0073] Reference Numeral No. 210 – Inlet 1,

[0074] Reference Numeral No. 210a – Syringe 1,

[0075] Reference Numeral No. 210b – Motor 1,

[0076] Reference Numeral No. 212 – Inlet 2,

[0077] Reference Numeral No. 212a – Syringe 2,

[0078] Reference Numeral No. 212b – Motor 2,

[0079] Reference Numeral No. 214 – Inlet 3,

[0080] Reference Numeral No. 214a – Syringe 3,

[0081] Reference Numeral No. 214b – Motor 3,

[0082] Reference Numeral No. 216 – Signal bus,

[0083] Reference Numeral No. 218 – Computer,

[0084] Reference Numeral No. 218a – Experimental Planner Software Module for Analyzing Probe Data and Generating New Sample Formulation(s),

[0085] Reference Numeral No. 220 – Photocuring light source,

[0086] Reference Numeral No. 220a – Photocuring light, and

[0087] Reference Numeral No. 222 – Data from Probe Head.

[0088] The description of the structural components of the Applicant's apparatus, systems, and methods 200 having been completed, the operation and additional description of the Applicant's apparatus, systems, and methods will now be considered in greater detail. Applicant's apparatus, systems, and methods 200 involve three main components or operations: (1) Formulations loading and mixing, (2) Deposition and measurement, and (3) Analysis and experimental planning.

General Description of Operation of FIG. 2

[0089] Load test samples from syringes 210a, 212a and 214a into inlets 210, 212, and 214, respectively via control signals provided by the computer 218 to each of motors 210b, 212b and 214b, which force the test samples at desired flow rates out from their respective syringes and into the inlets 1, 2 and 3.

[0090] Use the deposition head 206 to mix and deposit 204 films in batches on the substrate 202.

[0091] Cure materials onto substrate 202 using photocuring light 220a.

[0092] Measure impedance through contact between the probe 208 and In-situ Characterization Substrate 202.

[0093] Record data of batch of just-deposited test samples on the computer 218.

[0094] Automated software 218a takes data from previous batches and analyzes the data relative to the data associated with the just-deposited samples, to determine samples to be used for the next batch printed 216.

[0095] Repeat until done (i.e., when substrate is filled or no more space is available for sample deposition onto the substrate 202– Applicant contemplates up to 100 samples in a single screening).

More Detailed Description of Operation of FIG. 2

[0096] Prior to deposition, sample materials of interest are first loaded into the inlets 210, 212, and 214 via suitable control signals applied to the motors 210b, 212b and 214b associated with the syringes 210a, 212a and 214a, respectively. It will be appreciated that this is but one suitable means for supplying the sample materials of interest to the Inlets 210, 212 and 214 of the print head 206. Any means of controlling the sample material flow into the inlets 210, 212 and 214 through electrical control signals from the computer 218 may be used to supply the sample material. The control signals applied to each motor 210b, 212b and 214b from the computer 206 via signal bus 216 control the flow rate of material out from the syringes 210a, 212a and 214a, respectively, so the quantity of each sample material can be closely controlled. Note that FIG. 2 shows the deposition nozzle 206 having three inlets; however, more inlets are contemplated and only three are shown for illustrative purposes. In some instances two inlets, or possibly even only one inlet, may be provided.

[0097] Each of the inlets 210, 212 and 214 of the deposition head 206 receives one of the sample materials of interest. Examples of the samples include polymer electrolyte resin formulations including components such as solvents, monomers, oligomers, polymers, initiators and curing agents, salts, stabilizers, plasticizers, and solid additives such as silica, ceramics, nanoparticles, and metals. Once the inlets 210, 212, 214 are loaded, this provides the sample formulation 204 which will be mixed within the deposition nozzle 206. The ratios of sample materials supplied to the inlets 210, 212 and 214 can be kept constant or varied throughout testing by suitable control signals from the computer 218, which serve to controllably vary the flow of the sample materials out from each of the syringes 210a, 210b and 210c, thus producing deposited materials with homogeneous, heterogenous, and/or graded compositions. Mixing of the sample materials within the deposition nozzle 206 can be achieved through static or active mixing techniques. Active mixing techniques are illustrated in FIG. 2 and utilize a rotating mixing shaft element 206b within the deposition head 206 to shear mix the inlet materials. Active mixing is generally chosen for polymer electrolytes, as homogenous mixing of formulations with viscosities ranging from liquids to gels and pastes is possible. The rotational rate of the mixing shaft 206b, coupled with the feed rate of the sample materials being supplied to the inlets 210, 212 and 214, impacts the mixing time and turbidity within the system 200, and thereby the homogeneity of each mixed sample formulation 204 which is deposited onto the substrate 202. The deposition

nozzle 206 may include shear, pressure, and thermal inputs to enable deposition and analysis of the mixed sample formulations 204. In one embodiment the mixing shaft may be controlled by the computer 218 or possibly by a separate controller associated with the deposition nozzle 206 (i.e., the printer system associated with the deposition nozzle).

[0098] Mixed sample formulations 204 are then deposited onto the substrate 202. Deposited samples formulations 204 can include liquids, gels pastes, and thermoplastics. With the inclusion of crosslinkers, the mixed sample formulations 204 can be cured using photo, thermal, chemical, or other curing mechanisms. In the case of polymer electrolyte formulations, traditional photocuring methods are used through the inclusion of light generated by photocuring light source 220 during printing. Curing enables the deposition of multiple stacked layers, and the system 200 can handle thin film and three-dimensional structures depending on the application. For screening, thin films are generally targeted. In the case of system 200, polymer electrolyte measurements are focused on impedance characterization. With contact between the two point probe 208 and the electrode connections on the substrate 202, electrical impedance spectroscopy measurements are made traditionally from frequencies of 7 MHz to 100 mHz. Ranges of 35 MHz to 10 μHz are possible. Over twelve measurements are possible for a single film, moving the probe head 208 spatially around on the thin film to position it at various points over the spatially varied electrode connections. Traditionally, 4-6 spatial measurements are done for each deposited thin film. Measurements are done in triplicate, and the average of all measurements for one film is used and recorded in the database for the sample for comparison. Additional probe heads and substrates contemplated for use in the system 200 include optical metrology and imaging, stress sensing, chemical compositional analysis, fluorescence, pH, and environmental measurements (temperature, humidity). In addition, probe head 208 and substrate 202 can be utilized to align and interact with deposited materials. This includes electromagnetic alignment of particles, electrochemical and surface chemistry interactions, and photo or thermal curing and interactions. Probe head 208 and substrate 202 inputs and measurement 220 information are controlled and recorded as data within the computer 218 and its respective experimental planner software module 218a. This data is kept for each print and formulation tested.

[0099] With specific regard to the probe head 208, in one embodiment the probe head 208 forms a “two-point” impedance probe head and includes a probe tip 208a

which when lowered that makes contact with the surface of the just-printed sample, and a pair of push pins 208b that can be lowered further to extend through the sample and make contact with a selection of two electrodes of the substrate 202, and thus complete an electrical path for an impedance measurement across the polymer electrolyte. In another embodiment the substrate 202 itself may include connections between the electrodes of the substrate and ground, which eliminates the need for the two-point feature of the probe head 208, allowing the probe to make contact only with the sample for impedance measurement. In another embodiment the substrate 202 itself may include connections between the electrodes of the substrate, the potentiostat, and ground, which eliminates the need for a probe head altogether. In still another embodiment three or more push pins 208b may be included in the probe to assist in making impedance spectroscopy measurements.

[0100] Referring briefly to Figure 2A, a high level block diagram can be seen of the experimental planner software module 218a that the system 200 includes. In this example the experimental planner software module 218a includes a database 218a1, a machine learning software submodule 218a2, and a new batch formulation generation software submodule 218a3. The database 218a1 receives and is updated with newly obtained screening results from the probe 208 in real time. The database 218a1 also receives updated/improved sample formulation(s) which are calculated by a machine learning software module 218a2. The new batch formulation generation software submodule 218a3 uses the most recently calculated batch formation(s) information generated by the machine learning software submodule 218a2 and generates the new material flow rates needed to apply to each constituent material in the syringes 210a, 212a and 214a, for the new sample material batch. The newly calculated feed rates are used by the computer 218 to generate the needed motor control signals to control the inlet 210, 212 and 214 sample material feed ratios during screening. Between tests, the machine learning models contained in the machine learning software submodule 218a2 are improved through repeated and strategic analysis of the full living database 218a1 of previous test materials screened. Machine learning models that may be included in the machine learning software submodule 218a2 may include, but are not limited to, for example, Bayesian optimization algorithms that use models such as Random Forest and Gaussian Processes, as well as large data models including Neural Networks. During sample deposition and testing, the latest model is used to analyze the data from previous batches of testing. From this data, a new batch of

formulations is generated by the experimental planning software module 218a for the next test or tests, which may include, but are not limited, for example, Bayesian optimization algorithms that use decision policies such as upper confidence bound (UCB), and printing continues. This new batch data is will again be analyzed by the experimental planning software module 218a against the next obtained sample data received from the probe 208, and again used to create still another new batch formulation. In other words, all data generated during a test, both historical and real time data, are used to make the new batch of testing, until testing is completed. Then this data is once again added to the database 218a1 and used to improve the calculated formulations generated by the experimental planning software module 218a. Critically, the experimental planning software module 218a enables full automation of the materials formulation screening, enabling rapid homing in on desirable properties (i.e., ionic conductivity) from the characterization and measurement data obtained by the probe 208 during testing.

Example of polymer electrolyte printing

[0101] 1) Material formulations are made using any combination, without limitation, of the following components: solvent, monomer, oligomer, polymer, crosslinkers, salts, photoinitiators, catalysts, stabilizers, dyes, liquid additives and solid additives. Viscosities from liquids to high viscosity gels and pastes are possible.

[0102] 2) Components making up formulations are loaded into the inlet syringes 210a, 212a, 214a and motor ratios are used to control the varying composition. Two to four different syringe inlets are possible, with traditional testing using two syringes to vary a single variable. Example variables include, without limitation, salt concentration, additive concentration, and polymer additive concentration.

[0103] 3) Components from each syringe 210a, 212a and 212b are mixed in the deposition nozzle 206 and deposited onto the characterization substrate 202. The rotational speed of each of the motors 210b, 212b and 214b, and pressures created therefrom in each syringe 210a, 212a and 214a, dictate turbidity, deposition rate, and homogeneity of the formulations fed into the deposition nozzle 206. Samples are generally printed at a fixed motor feed ratio (fixed composition), but compositions may be switched between samples in a given test. For sample quantity, depending on the dimensions of the characterization substrate 202, anywhere from 1-100 samples are possible in a single print run. Samples may also be graded or heterogeneous, with

ratios between components of the formulation being switched or modified mid-print. A dump region on the characterization substrate 202 is used to switch between different compositions between samples.

[0104] 4) UV or blue light is traditionally used to cure the samples during printing. Thermal, electrochemical, and catalytic curing methods are also possible.

[0105] 5) After curing, the probe head 208, which is connected to a potentiostat 209, is lowered to touch the electrical connections on the substrate 202. The deposition nozzle 206 is aligned such that it lowers into the dump region, or for example a hole in the board, to begin the transition to the next formulation and remove the unwanted formulation mix volume left within the deposition nozzle 206. With contact between the two point probe head 208 and the electrode connections on the substrate 202 (i.e., when the substrate 202 is an impedance characterization substrate), electrical impedance spectroscopy measurements are made traditionally from one or more selected frequencies, and in some embodiments frequencies of 7 MHz to 100 mHz and in some embodiments ranges of 35 MHz to 10 μHz are also possible. With the dimensions and probe locations on the present characterization substrate 202, over twelve measurements are possible for a single printed film by moving the probe head 208 around on the substrate 202 to varying electrode connections. Traditionally, 4-6 spatial measurements are done for each film. Measurements may be done in triplicate, and the average of all measurements for one film may be used and recorded in the database 218a1 for the sample for comparison.

[0106] In addition to impedance measurements, confocal machine vision techniques may also be used to measure the height of films as deposited on the substrate 202. These, in conjunction with images of the samples from above, and profilometry data (after deposition end), are used to train a machine learning model (e.g., one or more models of the machine learning software models 218a2) to accurately measure the height of the sample. These height measurements are used to generate corrected ionic conductivity measurements for each sample from the raw impedance measurements.

[0107] The average data from a batch of runs is then inputted into the experimental planning software module 218a, which uses this data to identify regions of uncertainty and interest. These regions are used to generate the deposition file for next batch of formulations tested. For example, if 12 samples were printed and the impedance of each measured, it may be that a region of uncertainty or interest worthy

of closer examination becomes apparent between the formulations used to print samples 3, 4 and 5. The experimental planning software module 218a may then be used to calculate a new batch of formulations to more closely explore the regions between defined between the previously printed samples 3-5.

[0108] This process continues (steps 3-7) until the substrate 202 is filled with samples and deposition concludes. After testing, identified films with high ionic conductivities are characterized further electrochemically and thermomechanically. This data is also included in the database 218a1.

[0109] In between testing, the models of the machine learning software module 218a2 are trained with all existing datasets and updated for the next round of testing.

[0110] The machine learning software module 218a2 includes, but is not limited to, small-data models like Gaussian Processes and Random Forest Ensembles, as well as large-data models including Neural Networks. Additionally, the machine learning software module 218a2 includes, but is not limited to, algorithms such as Bayesian optimization for modeling and decision-making. The exact machine learning model in use depends on the available data. These machine learning models are first trained with some initial test data, and then improved between tests when new materials are screened and the living materials database 218a1 grows. Specifically, during deposition and testing, some batches of data are produced at the beginning. The models of the machine learning software module 218a2 are trained using these initial batches of data and then used to help predict a new batch of formulations to print. A new batch of samples are printed for the predicted formulations and corresponding data is collected. This new batch of data is coupled to the previous batches to generate the following batch for further testing. In other words, all data generated during a test is used to make the new batch of testing, until testing is completed. Then this data is once again added to the database 218a1 and used to further improve the models within the machine learning software module 218a2 between tests. Critically, the machine learning software module 218a2 enables full automation of the materials formulation screening, and rapid homing in on desirable properties from the characterization and measurement data during testing.

[0111] Referring briefly to Figure 2B, one example of operations performed by the machine learning software module 218a2 is shown in flowchart 250. In this example, an initial operation 252 is performed where the machine learning software module 218a2 retrieves/queries relevant formulation data streams and/or historical

datasets collected from the probe 208. At operation 254 a predictive model is built/updated. The predictive model may be, without limitation, one or more Random Forest models, and/or one or more Gaussian Process models, and/or one or more Neural Network models. At operation 256 the predictive model is used to decide the next set of formulations to be tested. In one example this may be carrying out Bayesian optimization by using an acquisition function such as upper confidence bound (UCB). At operation 258 the next set of formulations are tested and relevant data are stored in the database. At operation 260 a check is made if sampling is complete, and if not, operations 252-256 may be repeated. If the check at operation 258 produces a "Yes" answer, then sampling is complete.

Automated High Throughput Polymer Electrolyte Screening

[0112] Referring now to FIG. 3, an illustrative view shows an embodiment of Applicant's apparatus, systems, and methods. This embodiment is identified generally by the reference numeral 300. The components of Applicant's system 300 illustrated in FIG. 3 are listed below:

[0113] Reference Numeral No. 302 – In-situ Characterization Substrate,

[0114] Reference Numeral No. 304 – Deposited Formulation,

[0115] Reference Numeral No. 306 – Mixing and Deposit Head,

[0116] Reference Numeral No. 308 – Probe Head,

[0117] Reference Numeral No. 310 – Inlet 1,

[0118] Reference Numeral No. 312 – Inlet 2,

[0119] Reference Numeral No. 314 – Inlet 3,

[0120] Reference Numeral No. 316 – Automated Compositional Control,

[0121] Reference Numeral No. 318 – Computer with database and experimental planner,

[0122] Reference Numeral No. 320 – Data from Substrate, and

[0123] Reference Numeral No. 322 – Data from Probe Head.

[0124] It will be appreciated that the system 300 in this example also includes the syringes and associated motors described in connection with the system 200, and those components may be controlled just as described for the system 200. Likewise, the experimental planner software module 318a may be identical or similar in construction to the module 218, and may include components identical to the database 218a1, the machine learning models 218a2 and the new batch formulation generation software module 218a3.

[0125] The description of the structural components of the Applicant's apparatus, systems, and methods 300 having been completed, the operation and additional description of the Applicant's apparatus, systems, and methods will now be considered in greater detail. Applicant's apparatus, systems, and methods 300 involve three main components: (1) Formulations loading and mixing, (2) Deposition and measurement, and (3) Analysis and experimental planning.

General Description of Operation of FIG. 3

[0126] Load test samples into inlets 310, 312, and 314.

[0127] Mix 306 and deposit 304 films in batches.

[0128] Data from Probe Head 322 and Data from Substrate 302 are sent to Computer 318 with database and the experimental planning software module 318a.

[0129] Measure characteristic of interest through contact between probe 308 and In-situ Characterization.

[0130] Record data of batch of test samples on computer 318.

[0131] Computer 318 takes data from previous batches to dictate next batch printed 316.

[0132] Repeat until done (when substrate is filled or no more space – Applicant contemplates up to 100 samples in a single screening).

More Detailed Description of Operation of FIG. 3

[0133] Prior to deposition, sample materials of interest are first loaded into the inlets 310, 312, and 314 of deposition nozzle 306. Note that FIG. 3 shows three inlets; however, more inlets are contemplated and only three are shown for illustrative purposes. Each of these inlets 310, 312 and 314 may receive samples. Examples of the samples include polymer electrolyte resin formulations including components such as solvents, monomers, oligomers, polymers, initiators and curing agents, salts, stabilizers, plasticizers, and solid additives such as silica, ceramics, nanoparticles, and metals. Once the inlets 310, 312, 314 are loaded and mixed within the deposition nozzle 306, deposited sample composition 304 is controlled through the apparatus 300, varying the ratio of material supplied into the inlets 310, 312 and 314 into the deposition nozzle 306. The ratios of the materials supplied to the inlets 310, 312 and 314 can be kept constant or varied throughout testing, producing deposited materials with homogeneous, heterogenous, and graded compositions. Mixing of the components within the deposition nozzle 306 can be achieved through static or active mixing

techniques as described herein for the deposition nozzle 206. Active mixing techniques are illustrated in FIG. 3 and utilize a rotating mixing shaft within the mixing head to shear mix the inlet materials. Active mixing is generally chosen for polymer electrolytes, as homogenous mixing of formulations with viscosities ranging from liquids to gels and pastes is possible. The rotational rate of the mixing shaft, coupled with the feed rate of inlets, impacts the mixing time and turbidity within the system, and thereby the homogeneity of 304. The deposition nozzle 306 may include shear, pressure, and thermal inputs to enable deposition and analysis of the mixed resin formulations 304.

[0134] Mixed formulations are then deposited as samples 304 (e.g., films) onto a substrate 302. Deposited samples 304 can include liquids, gels pastes, and thermoplastics. With the inclusion of crosslinkers, the formulations can be cured using photo, thermal, chemical, or other curing mechanisms. For screening, the samples 304, if they have been deposited in the form of thin films, are generally targeted. In the case of system 300, polymer electrolyte measurements are focused on impedance characterization. With contact between the two point probe head 308 and the electrode connections on the substrate 302, electrical impedance spectroscopy measurements are made traditionally from frequencies of selected frequencies, in some embodiments frequencies of 7 MHz to 100 mHz. The use of frequency ranges of 35 MHz to 10 μHz are possible and anticipated. In some embodiments over twelve measurements may be made for a single film, moving the probe head 308 around on the substrate 302 to varying electrode connections and locations on the deposited material 304 spatially. Traditionally, 4-6 spatial measurements are done for each deposited material film. Measurements may be done in triplicate, and the average of all measurements for one film is used and recorded in the internal database of the experimental planning software module 318 for the sample for comparison. Additional probe heads and substrates contemplated in the system 300 include, optical metrology and imaging, stress sensing, chemical compositional analysis, fluorescence, pH, and environmental measurements (temperature, humidity). In addition, probe head 308 and substrates 302 can be utilized to align and interact with deposited materials. This includes electromagnetic alignment of particles, electrochemical and surface chemistry interactions, and photo or thermal curing and interactions. Probe head 308 and substrate 302 inputs and measurement 320 information are controlled and recorded as data within the computer 318 and its respective software 318a. This data is kept for each print and formulation tested.

[0135] The experimental planning software module 318a for this system 300 is used to control the feed ratios of the materials applied to the inlets 310, 312 and 314 during screening. Between tests, machine learning models that are used in the experimental planning software module 318a are improved through analysis of the full living database of previous test materials screened. Machine learning models include, but are not limited to Bayesian optimization, random forest, and Gaussian processes, as well as large data models including neural networks. During deposition and testing, the latest model is used to analyze the data from the initial batches of testing. From this data, a new batch of formulations to test is generated, and printing continues. This new batch data is coupled to the previous batches to generate the following batch for further screening. In other words, all data generated during a test is used to make the new batch of testing, until testing is completed. Then this data is once again added to the database within the experimental software planning software module 318a and used to improve the module 318a. Critically, the experimental planning software module 318a enables full automation of the materials formulation screening, and rapid homing in on desirable properties from the characterization and measurement data obtained during testing.

Example of polymer electrolyte printing

[0136] Step 1 - Material formulations are made using any combination of the following components: solvent, monomer, oligomer, polymer, crosslinkers, salts, photoinitiators, catalysts, stabilizers, dyes, liquid additives and solid additives. Viscosities from liquids to high viscosity gels and pastes are possible.

[0137] Step 2 - Formulations are loading into inlet syringes, and motor ratios are used to control the varying composition. Two to four different syringe inlets for the deposition nozzle 306 are possible, with traditional testing using two syringes to vary a single variable. Example variables include salt concentration, additive concentration, and polymer additive concentration.

[0138] Step 3 - Inlet materials are mixed in the mixing body and deposited onto the impedance characterization substrate 302. The rotational speed and pressure of the mixing element within the deposition nozzle 306 dictate turbidity, deposition rate, and homogeneity of the formulations. Samples are generally printed at a fixed syringe motor feed ratio (fixed composition), and then compositions of the materials may be switched between samples in a given test. 1-100 samples are possible in a single run

with the substrate 302. Samples may also be graded or heterogeneous, switching ratios mid print. A dump region on the substrate 302 may be used to switch between different compositions between samples, as described herein before for the system 200.

[0139] Step 4 - UV or blue light is traditionally used to cure the samples during printing. Thermal, electrochemical, and catalytic curing methods are also possible.

[0140] Step 5 - After curing, the probe head 308 connected, may be connected to a potentiostat (such as potentiostat 209, but not shown in the Figure) is lowered to touch the electrical connections on the substrate 302. The deposition nozzle 306 is aligned such that it lowers into a dump zone, or a hole in the substrate 302, to begin the transition to the next formulation and remove the unwanted mix volume. With contact between the two point probe head 308 and the electrode connections on the substrate 302, electrical impedance spectroscopy measurements are made traditionally from selected frequencies, for example from 7 MHz to 100 mHz. Frequency ranges of 35 MHz to 10 μHz may also be used in some embodiments. Over twelve measurements are possible for a single film, moving the probe head 308 around on the substrate 302 to varying electrode connections. Traditionally, 4-6 spatial measurements are done for each film. Measurements may be done in triplicate, and the average of all measurements for one film may be used and recorded in the database of the experimental planning software module 318a for the sample for comparison.

[0141] Step 6 - In addition to impedance measurements, confocal machine vision techniques are used to measure the height of films as deposited. These, in conjunction with images of the samples from above, and profilometry data (after deposition end), are used to train a machine learning model (identical or similar to the machine learning models 218b2) of the experimental planning software module 318 to accurately measure the height of the sample. These height measurements are used to generate corrected ionic conductivity measurements for each sample from the raw impedance measurements.

[0142] Step 7 - The average data from a batch of runs is then inputted into the experimental planning software module 318a, which uses this data to identify regions of uncertainty and interest. These regions are used to generate the deposition file for next batch of formulations tested.

[0143] Step 8 - This process continues (steps 3-7) until the substrate 302 is filled with samples and deposition concludes. After testing, identified films with high ionic

conductivities are characterized further electrochemically and thermomechanically. This data is also included in the database.

[0144] Step 9 - In between testing, the machine learning models within the experimental planning software module 318a are trained with all existing datasets and updated for the next round of testing.

[0145] The experimental planning software module 318a of the system 300 that controls the inlet feed ratios during screening may be implemented with machine learning models as described above and as described for the system 200. The machine learning models include, but are not limited to small-data models like Gaussian Processes and Random Forest Ensembles, as well as large-data models like feed-forward Neural Networks. The exact machine learning model in use depends on the available data. These machine learning models are first trained with some initial test data, and then improved between tests when new materials are screened and the living materials database within the experimental software module 318a grows. Specifically, during deposition and testing, some batches of data is produced at the beginning. Machine learning models are trained using these initial batches of data and predicts a new batch of formulations to print. A new batch of samples are printed for the predicted formulations and corresponding data is collected. This new batch of data is coupled to the previous batches to create the following batch. In other words, all data generated during a test is used to make the new batch of testing, until testing is completed. Then this data is once again added to the database of the experimental planning software module 318a and used to improve the next round of material formulation. Critically, this experimental software module 318a enables full automation of the materials formulation screening, and rapid homing in on desirable properties from the characterization and measurement data during testing.

Tuning Mechanical Strength 3D Printed Materials Screening

[0146] Referring now to FIG. 4, an illustrative view shows yet another embodiment of Applicant's apparatus, systems, and methods. This system is identified generally by the reference numeral 400. The components of Applicant's system 400 as illustrated in FIG. 4 are listed below:

[0147] Reference Numeral No. 402 –Build Plate,

[0148] Reference Numeral No. 404 – Deposited Formulation,

[0149] Reference Numeral No. 406 – Mixing and Deposition Head,

[0150] Reference Numeral No. 408 – Environmental Sensors,

[0151] Reference Numeral No. 410 – Inlet 1,

[0152] Reference Numeral No. 412 – Inlet 2,

[0153] Reference Numeral No. 414 – Inlet 3,

[0154] Reference Numeral No. 416 – Automated Compositional Control,

[0155] Reference Numeral No. 418 – Computer ,

[0156] Reference Numeral No. 418a – Experimental Planning Software Module 418a,

[0157] Reference Numeral No. 420 – Load Cell, and

[0158] Reference Numeral No. 422 – Data from Probe Head and Load Cell and Environmental Sensors.

[0159] Reference Numeral No. 424 – Controlled environment

[0160] The description of the structural components of the Applicant's system 400 having been completed, the operation and additional description of the Applicant's system 400 will now be considered in greater detail.

General Description of Operation of the System 400 of FIG. 4

[0161] Applicant's system 400 provides tuning mechanical strength 3D printed materials screening.

[0162] Test sample formulations are loaded into inlets 410, 412, and 414. The deposited sample 404 can be test films or 3D samples.

[0163] The test sample 404 formulations are mixed in the deposition nozzle 406 and the test samples 404 are deposited on the build plate 402 providing test films or samples in batches. Deposited samples 404 may be standalone materials, or may be cured during or after deposition through stimulus such as, but not limited to, electromagnetic irradiation, acoustic wave, electric current, heat, and chemical crosslinking or interactions. Traditionally, light or heat are used to cure the deposited samples.

[0164] Information about the test films or samples 404 in batches on the build plate 402 is obtained from the load cell 420 and environmental sensors 408 and data 422 is provided to the computer 418 with its database and its experimental planning software module 418a. Environmental sensors can be used in tandem with controlled environments 424 such as oven heating, electromagnetic irradiation, humidifier, and non-ambient gas flow environments.

[0165] The automated software in the computer 418, which may be same or similar to the components described with the system 200, takes data obtained from previous batches to dictate next batch printed 416.

[0166] The above steps are repeated until done (when the substrate or build plate 402 is filled or no more space available – Applicant contemplates up to 100 samples in a single screening).

More Detailed Description of Operation of the System 400 of FIG. 4

[0167] Prior to deposition, sample materials of interest are first loaded into the inlets 410, 412, and 414. Note that FIG. 4 shows three inlets; however, more inlets are contemplated and only three are shown for illustrative purposes. Each of these inlets 410, 412, 414 will include samples. Once the inlets 410, 412, 414 are loaded, and mixed to the desired formulation, the test samples will be deposited on the build plate 404 providing test films or samples in batches. The deposited sample composition 404 is controlled through the system 400, varying the ratio of materials supplied to the inlets 410, 412, 414 of the deposition nozzle 406. The ratios of materials supplied can be kept constant or varied throughout testing, producing deposited materials with homogeneous, heterogenous, and graded compositions.

[0168] Mixing of the components within the deposition nozzle 406 can be achieved through static or active mixing techniques as described hereinbefore for the system 200. The deposition nozzle 406 may include shear, pressure, and thermal inputs to enable deposition and analysis of the mixed resin formulations 404.

[0169] Mixed formulations 404 are deposited onto the build plate 402. Deposited sample formulations 404 can include liquids, gels, pastes, and thermoplastics. Probe head 406 and build plate 402 inputs, controlled environment inputs 424, and measurements from the load cell 420 and the probe head 408 are controlled and recorded as data 422 within the computer 418 and its respective experimental planning software module 418a. This data is kept for each print and formulation tested. Applicant's system 400 and related and methods provide screening of the tuned mechanical strength of 3D printed materials to determine parameters for targeted applications.

[0170] The experimental planning software module for the system 400 is used to control the inlet feed ratios during screening. Between tests, machine learning models that are used in the apparatus's 400 experimental planning software module are

improved through analysis of the full living database of previous test materials screened, as explained herein for the module 218a. Machine learning models include, but are not limited to Bayesian optimization, random forest, and Gaussian processes, as well as large data models including neural networks. During deposition and testing, the latest model is used to analyze the data from the first batch of testing. From this data, a new batch of formulations to test is generated, and printing continues. This new batch data is analyzed relative to the previous batches to generate the following new batch of formulations for further testing. In other words, all data generated during a test is used to make the new batch of testing, until testing is completed. Then this data is once again added to the database of the experimental planning software module 418a and used to improve the experimental planner. Critically, this planner enables full automation of the materials formulation screening, homing in on desirable properties from the characterization and measurement data during testing.

Tuning Mechanical Strength 3D Printed Materials Screening

[0171] Referring now to FIG. 5, an illustrative view shows yet another embodiment of Applicant's apparatus, systems, and methods. The system of this embodiment is identified generally by the reference numeral 500. The components of the system 500 illustrated in FIG. 5 are listed below:

[0172] The components of Applicant's system 500 illustrated in FIG. 5 are listed below:

[0173] Reference Numeral No. 502 – Build Plate,

[0174] Reference Numeral No. 504 – Deposited Formulation,

[0175] Reference Numeral No. 506 – Mixing and Deposit Head,

[0176] Reference Numeral No. 508 – Environmental Sensors,

[0177] Reference Numeral No. 510 – Inlet 1,

[0178] Reference Numeral No. 512 – Inlet 2,

[0179] Reference Numeral No. 514 – Inlet 3,

[0180] Reference Numeral No. 516 – Automated Compositional Control,

[0181] Reference Numeral No. 518 – Computer,

[0182] Reference Numeral No. 518a - Experimental Planning Software Module 518a,

[0183] Reference Numeral No. 520 – Stress Sensors, and

[0184] Reference Numeral No. 522 – Data from Probe Head and Stress Sensors and Environmental Sensors.

[0185] Reference Numeral No. 524 – Controlled environment

[0186] The description of the structural components of the Applicant's apparatus, systems, and methods 500 having been completed, the operation and additional description of the Applicant's apparatus, systems, and methods will now be considered in greater detail.

General Description of Operation of the system 500 of FIG. 5

[0187] Applicant's system 500 and its related methods of operation provide tuning mechanical strength and other thermomechanical properties for 3D printed materials screening.

[0188] Test sample formulations are loaded into inlets 510, 512, and 514 of the deposition nozzle 506. The deposited sample 504 can be test films or 3D samples.

[0189] The test sample 504 formulations are mixed in the deposition nozzle 506 and then deposited on the build plate 504 providing test films or samples 504 in batches. Deposited samples 504 may be standalone materials, or may be cured during or after deposition through stimulus such as electromagnetic irradiation, acoustic wave, electric current, heat, and chemical crosslinking or interactions. Traditionally, light or heat are used to cure the deposited samples.

[0190] Information about the test films or samples 504 in batches on the build plate 504 is obtained from the Stress Sensors 520 and environmental sensors 508 and data 522 is provided to the computer 518 with its experimental planning software module 518 and internal database (similar or identical to the module 218a). The environmental sensors 508 can be used in tandem with one or more controlled environments 524 such as oven heating, electromagnetic irradiation, humidifier, and non-ambient gas flow environments.

[0191] The automated experimental planning software module 518a in the computer 518 with its database (e.g., the same or similar to the database 218a1) takes data obtained from previous sample 504 batches to analyzes the data to calculate formulations to be used for the next batch of materials 516 to be printed.

[0192] The above steps are repeated until done (when substrate is filled or no more space – Applicant contemplates up to 100 samples in a single screening).

More Detailed Description of Operation of the System 500 of FIG. 5

[0193] Prior to deposition, sample materials of interest are first loaded into the inlets 510, 512, and 514. Note that FIG. 5 shows three inlets being used with the deposition nozzle 506; however, more inlets are contemplated and only three are shown for illustrative purposes. Each of these inlets 510, 512 and 514 will be fed with samples from separate associated syringes (not shown but similar or identical to syringes 210, 212 and 214 of system 200). Once the inlets 510, 512, 514 are loaded, and mixed within the deposition nozzle 506 to the desired formulation, the test samples will be deposited on the build plate 504 providing test films or samples 504 in batches. The deposited sample composition 504 is controlled through the system 500, varying the ratio of materials supplied between the inlets 510, 512 and 514 into the deposition nozzle 506. The ratios of the materials supplied can be kept constant or varied throughout testing, producing deposited materials with homogeneous, heterogenous, and graded compositions.

[0194] Mixing of the components within the deposition nozzle 506 can be achieved through static or active mixing techniques as described hereinbefore. The deposition nozzle 506 may include shear, pressure, and thermal inputs to enable deposition and analysis of the mixed resin formulations 504.

[0195] Mixed formulations are deposited as samples 504 onto the build plate 502. Deposited samples 504 can include liquids, gels, pastes, and thermoplastics. Deposited samples 504 may be standalone materials, or may be cured during or after deposition through stimulus such as electromagnetic irradiation, acoustic wave, electric current, heat, and chemical crosslinking or interactions. Traditionally, light or heat are used to cure the deposited samples 504. Probe head 506 and build plate 502 inputs, controlled environment inputs 524, and measurements from stress sensors 520 and environmental sensors 508 are controlled and recorded as data 522 within the computer 518 and its respective experimental planning software module 518. This data is kept for each print and formulation tested. Applicant's system 500 and related methods provide screening of the tuned mechanical strength and other thermomechanical properties of 3D printed materials to determine parameters for targeted applications.

[0196] The experimental planning software module 500 for the system 500 is used to control the feed ratios of the materials supplied to the inlets 510, 512 and 514 during screening and is implemented through machine learning models of the

experimental planning software module 518a. Machine learning models may include, but are not limited to, Bayesian optimization, random forest, and Gaussian processes, as well as large data models like feed-forward neural networks. During deposition and testing, the latest model is used to analyze the data from the first batch of testing. From this data, a new batch of formulations to test is generated, and printing continues. This new batch data is coupled to the previous batches to generate the following batch for further screening. In other words. all data generated during a test is used to make the new batch of testing, until testing is completed. Then this data is once again added to the database and used to improve the experimental planning software module 518 and its machine learning models. Critically, experimental software planning module 518a enables full automation of the materials formulation screening, homing in on desirable properties from the characterization and measurement data during testing.

Long-term cell culture study

[0197] Referring now to FIG. 6, an illustrative view shows another embodiment of Applicant's apparatus, systems, and methods. This system of this embodiment is identified generally by the reference numeral 600. The components of Applicant's 600 as illustrated in FIG. 6 are listed below:

[0198] Reference Numeral No. 602 – Build Plate,

[0199] Reference Numeral No. 604 – Deposited Formulation,

[0200] Reference Numeral No. 606 – Mixing and Deposit Head,

[0201] Reference Numeral No. 608a – Thermal Sensors,

[0202] Reference Numeral No. 608b – Stress Sensors,

[0203] Reference Numeral No. 608c – pH Sensors,

[0204] Reference Numeral No. 608d – Impedance Sensors,

[0205] Reference Numeral No. 608e – O2, Glucose, Lactate Sensors,

[0206] Reference Numeral No. 610 – Inlet 1,

[0207] Reference Numeral No. 612 – Inlet 2,

[0208] Reference Numeral No. 614 – Inlet 3,

[0209] Reference Numeral No. 618 – Computer,

[0210] Reference Numeral No. 618a – Experimental Planning Software Module,

[0211] Reference Numeral No. 622 – Microscopy or Fluorescence Imaging Subsystem,

[0212] Reference Numeral No. 624 – Cells

[0213] Reference Numeral No. 626 – Environmental chamber

[0214] The description of the structural components of the Applicant's system 600 having been completed, the operation and additional description of the Applicant's system and its related methods of operation will now be considered in greater detail.

[0215] Applicant's system 600 provides materials screening.

[0216] Test sample formulations are loaded into inlets 610, 612, and 614 of the deposition nozzle 606. The deposited sample 604 can be test films or 3D samples.

[0217] The test sample formulations are mixed in the deposition nozzle 606 and the test samples 604 are deposited on the build plate 602 providing test films or samples in batches. Cells 624 can be seeded directly into the test sample 604 formulations or cultured onto the deposited films forming the samples 604 after printing. After printing, build plate 602 with samples is transferred to an environmental chamber 626 for continued study. Optionally, a microscopy or fluorescence imaging subsystem 622 may be disposed adjacent the build plate 602 and used to image a portion test samples to assist in the analysis of the test samples.

[0218] Information about the test films or samples 604 in batches on the build plate 602 and information from the cells 624 are obtained using the Thermal Sensors 608a, Stress Sensors 608b, pH Sensors 608c, Impedance Sensors 608d, and/or O_2, Glucose, Lactate Sensors 608e, and data is provided to the computer 618 with its experimental planning software module 618a and the internal database thereof (where the experimental planning software module 618 may by identical or similar in construction to the module 218a). In addition to measurements taken directly at printing, these sensors can be utilized to monitor samples and cell culture over time. The computer 618 with the experimental planning software module 618a and its internal database takes data obtained from previous batches to dictate next batch printed. Multiple build plates 602 can be loaded into the environmental chamber 626 at the same time, providing continued study of multiple screenings over prolonged periods of study.

[0219] The above steps are repeated until done (when substrate is filled or no more space – Applicant contemplates up to 100 samples in a single screening, multiple screenings per environmental chamber).

Environmental, permeability, and sample aging studies

[0220] Referring now to FIG. 7A, an illustrative view shows another embodiment of Applicant's apparatus, systems, and methods. This system of this embodiment is identified generally by the reference numeral 700a. The components of Applicant's system 700a as illustrated in FIG. 7A are listed below:

[0221] The components of Applicant's system 700a and its related methods of operation are listed below:

[0222] Reference Numeral No. 702a – Build Plate,

[0223] Reference Numeral No. 704a – Deposited Formulation,

[0224] Reference Numeral No. 706a – Mixing and Deposition Head,

[0225] Reference Numeral No. 708aa – Gas for Testing,

[0226] Reference Numeral No. 708ab –Sensors for Gas or Chemical,

[0227] Reference Numeral No. 708ac –Additional Sensors for Testing or Stimulus for Aging Study,

[0228] Reference Numeral No. 708ad –Environmental Sensors,

[0229] Reference Numeral No. 710a – Inlet 1,

[0230] Reference Numeral No. 712a – Inlet 2,

[0231] Reference Numeral No. 714a – Inlet 3,

[0232] Reference Numeral No. 716a – Deposition Nozzle,

[0233] Reference Numeral No. 718a – Computer,

[0234] Reference Numeral No. 718 a' – Experimental Planning Software Module;

[0235] Reference Numeral No. 724a – Controlled environment

[0236] The description of the structural components of the Applicant's system 700a having been completed, the operation and additional description of the Applicant's system and its methods of operation will now be considered in greater detail.

[0237] Applicant's system 700a provides materials screening.

[0238] Test sample formulations are loaded into inlets 710a, 712a, and 714a of the deposition nozzle 716. The deposited sample 704a can be test films or 3D samples.

[0239] The test sample formulations are mixed in the deposition nozzle 716a and the test samples are deposited on the build plate 702a providing test films or samples in batches. Deposited samples may be standalone materials, or may be cured during or after deposition through stimulus such as electromagnetic irradiation, acoustic wave,

electric current, heat, and chemical crosslinking or interactions. Traditionally, light or heat are used to cure the deposited samples.

[0240] Information about the test films or samples in batches on the build plate 702a is obtained in relation to responses to Gas, Chemicals, Stimulus, etc. 708aa. This includes gas and chemical permeability studies, aging studies, and stimuli-responsive material studies, for example. Sample responses are measured through embedded gas and chemical sensors 708ab in the build plate 702a. In addition, other embedded or drop-down sensors and stimuli may be incorporated for further testing , such as stress and thermal sensors, impedance sensors or electrode arrays, and imaging. With a controlled environment 724a, measurements can be made at initial printing, as well as over time through continued study. The controlled environment 724a can be envisioned as being present both around the deposition system 700a, as well as an external chamber for continued study after deposition. The use of an external chamber would also enable continued study of multiple screenings at the same time.

[0241] The automated experimental planning software module 718a' in the computer 718, with its internal database, takes data obtained from previous batches to determine the formulations for the next batch of samples to be printed.

[0242] The above steps are repeated until done (when substrate is filled or no more space – Applicant contemplates up to 100 samples in a single screening, multiple screenings studied over time simultaneously).

[0243] Referring now to FIG. 7B, an illustrative view shows another embodiment of Applicant's apparatus, systems, and methods. The system of this embodiment is identified generally by the reference numeral 700b. The components of Applicant's system 700b are listed below:

[0244] Reference Numeral No. 702b – Build Plate,

[0245] Reference Numeral No. 704b – Deposited Formulation,

[0246] Reference Numeral No. 706b – Mixing and Deposition Head,

[0247] Reference Numeral No. 708ba – Gas or Stimulus for Curing, and/or Gas or Stimulus for Aging Study (UV light, stress, etc.),

[0248] Reference Numeral No. 708bb –Sensors for Gas or Chemical,

[0249] Reference Numeral No. 708bc –Additional Sensors for Testing or Stimulus for Aging Study,

[0250] Reference Numeral No. 708bd –Environmental Sensors,

[0251] Reference Numeral No. 710b – Inlet 1,

[0252] Reference Numeral No. 712b – Inlet 2,

[0253] Reference Numeral No. 714b – Inlet 3,

[0254] Reference Numeral No. 716b – Deposition Nozzle,

[0255] Reference Numeral No. 718b – Computer,

[0256] Reference Numeral No. 718b' – Experimental Planning Software Module

[0257] Reference Numeral No. 724b – Controlled environment, and

[0258] Reference Numeral No. 724b – Secondary chamber for prolonged study.

[0259] Reference Numeral 726b – Secondary environmental chamber for continued study.

[0260] The description of the structural components of the Applicant's system 700b having been completed, the operation and additional description of the system will now be considered in greater detail.

[0261] Applicant's system 700b provides materials screening.

[0262] Test sample formulations are loaded into inlets 710b, 712b, and 714b of the deposition head 706b. The deposited sample 704b can be test films or 3D samples.

[0263] The test sample formulations are mixed in the nozzle and deposition head 706b and the test samples are deposited on the build plate 702b providing test films or samples 704b in batches. Deposited samples 704b may be standalone materials, or may be cured during or after deposition through stimulus such as electromagnetic irradiation, acoustic wave, electric current, heat, and chemical crosslinking or interactions 708ba. Traditionally, light or heat are used to cure the deposited samples.

[0264] Information about the test films or samples 704b in batches on the build plate 702b is obtained in relation to responses to Gas, Chemicals, Stimulus, or Gas for Age Study Testing or Stimulus for Aging Study (UV light, humidity, stress, heat, etc,) 708ba. This includes gas and chemical permeability studies, aging studies, and stimuli-responsive material studies, for example. Sample responses are measured through embedded gas and chemical sensors 708bb. In addition, other embedded or drop-down sensors and stimuli may be incorporated for further testing 708bc, such as stress and thermal sensors, impedance sensors or electrode arrays, and imaging. With a controlled environment 724b, measurements can be made at initial printing, as well as over time through continued study. Controlled environment 724b can be envisioned as being present both around the deposition system 700b, as well as an external chamber for continued study after deposition. The external chamber also enables continued

study of multiple screenings at the same time. The secondary environmental chamber 726b may be in communication with the controlled environment 724b and may be used for further prolonged study of a component present in the controlled environment 724b.

[0265] The automated experimental planning software module 718b' (similar or identical to the module 218a of system 200) within the computer 718b, with its internal database, takes data obtained from previous batches to determine the formulations for the next batch of samples to be printed.

[0266] The above steps are repeated until done (when the substrate 702b is filled or no more space – Applicant contemplates up to 100 samples in a single screening, multiple screenings studied over time simultaneously). A Secondary chamber 724b is provided for prolonged study.

[0267] Although the description above contains many details and specifics, these should not be construed as limiting the scope of the application but as merely providing illustrations of some of the presently preferred embodiments of the apparatus, systems, and methods. Other implementations, enhancements and variations can be made based on what is described and illustrated in this patent document. The features of the embodiments described herein may be combined in all possible combinations of methods, apparatus, modules, systems, and computer program products. Certain features that are described in this patent document in the context of separate embodiments can also be implemented in combination in a single embodiment. Conversely, various features that are described in the context of a single embodiment can also be implemented in multiple embodiments separately or in any suitable subcombination. Moreover, although features may be described above as acting in certain combinations and even initially claimed as such, one or more features from a claimed combination can in some cases be excised from the combination, and the claimed combination may be directed to a subcombination or variation of a subcombination. Similarly, while operations are depicted in the drawings in a particular order, this should not be understood as requiring that such operations be performed in the particular order shown or in sequential order, or that all illustrated operations be performed, to achieve desirable results. Moreover, the separation of various system components in the embodiments described above should not be understood as requiring such separation in all embodiments.

[0268] Therefore, it will be appreciated that the scope of the present application fully encompasses other embodiments which may become obvious to those skilled in

the art. In the claims, reference to an element in the singular is not intended to mean "one and only one" unless explicitly so stated, but rather "one or more." All structural and functional equivalents to the elements of the above-described preferred embodiment that are known to those of ordinary skill in the art are expressly incorporated herein by reference and are intended to be encompassed by the present claims. Moreover, it is not necessary for a device to address each and every problem sought to be solved by the present apparatus, systems, and methods, for it to be encompassed by the present claims. Furthermore, no element or component in the present disclosure is intended to be dedicated to the public regardless of whether the element or component is explicitly recited in the claims. No claim element herein is to be construed under the provisions of 35 U.S.C. 112, sixth paragraph, unless the element is expressly recited using the phrase "means for."

[0269] While the apparatus, systems, and methods may be susceptible to various modifications and alternative forms, specific embodiments have been shown by way of example in the drawings and have been described in detail herein. However, it should be understood that the application is not intended to be limited to the particular forms disclosed. Rather, the application is to cover all modifications, equivalents, and alternatives falling within the spirit and scope of the application as defined by the following appended claims.

THE CLAIMS ARE:

What is claimed is:

1. A system for screening a formulation of a material being printed in an additive manufacturing process, in situ, to enable rapid analysis, modeling and modification of at least one characteristic associated with the material formulation, the system comprising:

a computer;

a substrate on which the material formulation is printed;

a deposition print head for depositing the material formulation on the substrate as at least one material sample;

the substrate including at least one component for enabling the characteristic of the material formulation printed thereon to be at least one of measured or determined;

a probe configured to be moved into contact with the material formulation after the material formulation is printed on the substrate as a sample material, the probe providing an output to the computer representing data from which the characteristic can be evaluated by the computer and a new material formulation determined; and

an experimental planning software module including a machine learning software module, configured to use the data collected by the probe and to determine, using the machine learning software module, a new material formulation which better optimizes the characteristic being evaluated.

2. The system of claim 1, wherein the deposition print head includes at least first and second input ports for receiving first and second components of the material formulation being supplied to the deposition print head.

3. The system of claim 2, further comprising:

at least first and second syringes for containing the first and second components, respectively, of the material formulation;

first and second motors associated with the first and second syringes, respectively, and response to control signals from the computer, for controllably providing the first and second components to the deposition print head in accordance with the control signals from the computer.

4. The system of claim 3, wherein the computer generates the control signals in real time, and in situ, at least one of while or before the material sample is being printed.

5. The system of claim 1, wherein the experimental planning software module further includes:

a database for storing information and/or data associated with previously screened test materials, the database configured to be updated in real time with new material screening results provided by the probe output and updated formulation suggestions by the machine learning software module; and

a new batch formulation software module for receiving information from the database and generating new formulations for a new batch of material samples to be printed.

6. The system of claim 1, wherein the machine learning software module comprises at least one of:

a random forest model;

a gaussian process model; or

a neutral network model.

7. The system of claim 1, wherein the machine learning module comprises a Bayesian optimization framework for carrying out Bayesian modeling and decision making.

8. The system of claim 1, wherein the at least one component of the substrate comprises a grid of spatially separated electrodes which are used to complete electrical paths as the probe contacts different areas of the material sample after the material sample is printed on the substrate, to thus enable the probe to generate the output to the computer.

9. The system of claim 8, wherein the probe comprises a two point probe head including a first component which makes contact with the material sample, and a second component which extends through the material sample and into contact with at least one of the electrodes.

10. The system of claim 1, wherein the at least one component of the substrate comprises an environmental sensor.

11. The system of claim 1, wherein the at least one component of the substrate comprises stress sensors.

12. The system of claim 1, wherein the at least one component of the substrate comprises an impedance sensor.

13. The system of claim 1, wherein the at least one component of the substrate comprises at least one of:

an O2 sensor;

a thermal sensor;

a pH sensor.

14. The system of claim 1, further comprising cells that are included in the material formulation when the material sample is printed on the substrate by the deposition print head, the cells further providing information enabling the characteristic to be evaluated.

15. The system of claim 1, further comprising a microscopy or fluorescence imaging subsystem for assisting in evaluating the material sample.

16. The system of claim 1, wherein the build plate comprises at least one of an embedded gas or a chemical sensor for generating information to assist the computer in evaluating the material sample printed on the build plate.

17. The system of claim 1, wherein:

the substrate and deposition print head are located inside a controlled environment.

18. The system of claim 17, wherein the controlled environment includes a stimulus to assist in evaluation of the material sample.

19. The system of claim 18, further comprising a secondary environmental chamber in communication with the controlled environment to enable further study of a component present in the controlled environment.

20. A method for screening a formulation of a material being printed in an additive manufacturing process, in situ, to enable rapid analysis, modeling and modification of at least one characteristic associated with the material formulation, the method comprising:

printing the material formulation as at least one material sample on a substrate;

using at least one component associated with the substrate for enabling the characteristic of the material formulation printed thereon to be at least one of measured or determined;

using a probe to obtain information concerning the characteristic from the material sample;

causing the probe to provide an output to a computer;

causing the computer to use software to evaluate the material sample, and wherein the software includes machine learning software to evaluate historical data concerning previously printed material samples, and to assist in determining updated formulations for new material samples to be printed on the substrate in subsequent printing operations and further analyzed.

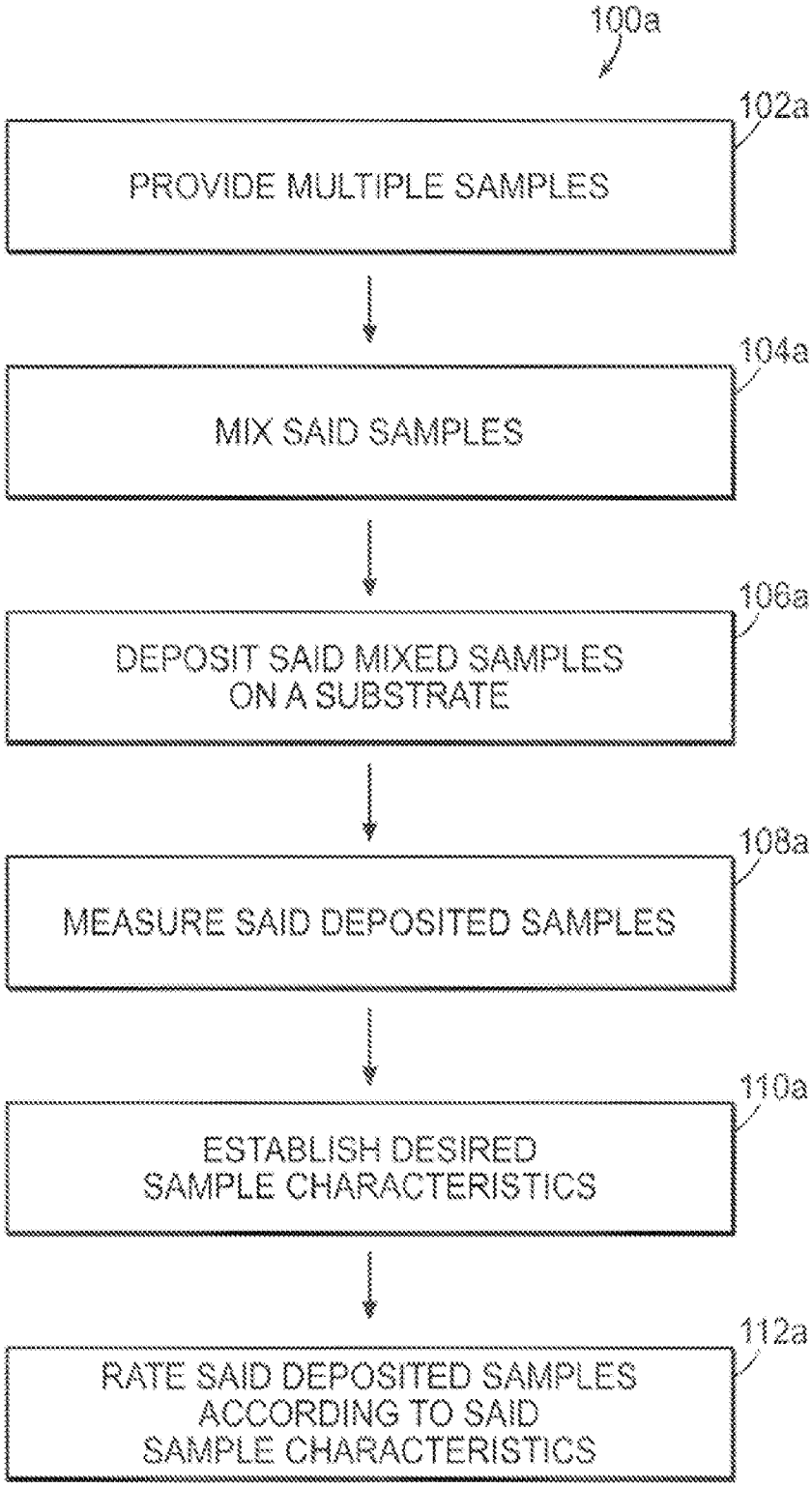

100a
102a
PROVIDE MULTIPLE SAMPLES
104a
MIX SAID SAMPLES
106a
DEPOSIT SAID MIXED SAMPLES ON A SUBSTRATE
108a
MEASURE SAID DEPOSITED SAMPLES
110a
ESTABLISH DESIRED SAMPLE CHARACTERISTICS
112a
RATE SAID DEPOSITED SAMPLES ACCORDING TO SAID SAMPLE CHARACTERISTICS

FIG. 1A

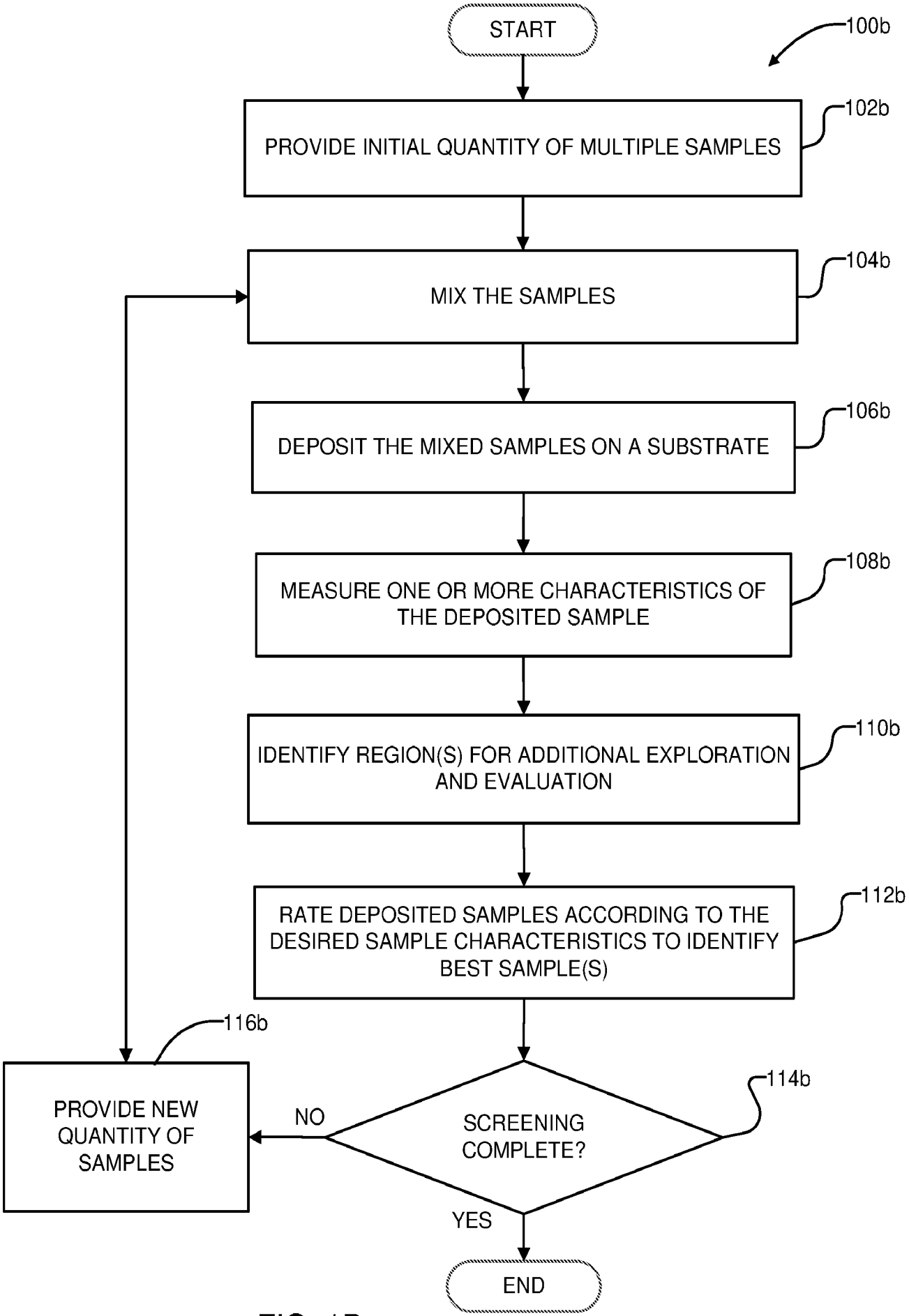

START
100b
PROVIDE INITIAL QUANTITY OF MULTIPLE SAMPLES
102b
MIX THE SAMPLES
104b
DEPOSIT THE MIXED SAMPLES ON A SUBSTRATE
106b
MEASURE ONE OR MORE CHARACTERISTICS OF THE DEPOSITED SAMPLE
108b
IDENTIFY REGION(S) FOR ADDITIONAL EXPLORATION AND EVALUATION
110b
RATE DEPOSITED SAMPLES ACCORDING TO THE DESIRED SAMPLE CHARACTERISTICS TO IDENTIFY BEST SAMPLE(S)
112b
SCREENING COMPLETE?
114b
NO
PROVIDE NEW QUANTITY OF SAMPLES
116b
YES
END

FIG. 1B

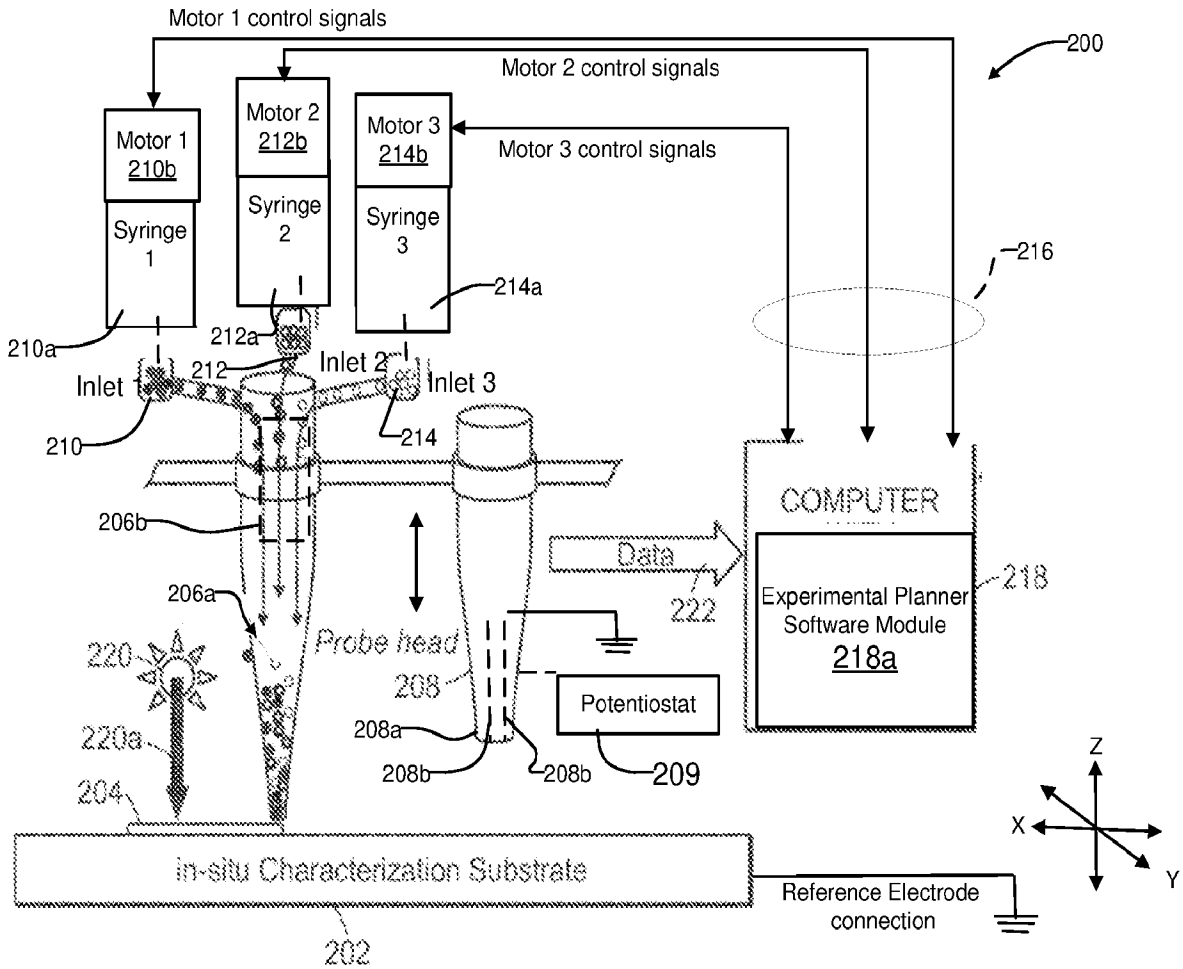

Motor 1 control signals
Motor 2 control signals
Motor 3 control signals
200
Motor 1
210b
Motor 2
212b
Motor 3
214b
Syringe
1
Syringe
2
Syringe
3
214a
216
210a
212a
212
Inlet 1
Inlet 2
Inlet 3
210
214
206b
206a
COMPUTER
Data
222
Experimental Planner
Software Module
218a
218
Probe head
208
220
Potentiostat
220a
208a
208b
208b
209
204
Z
X
Y
In-situ Characterization Substrate
Reference Electrode
connection
202

FIG. 2

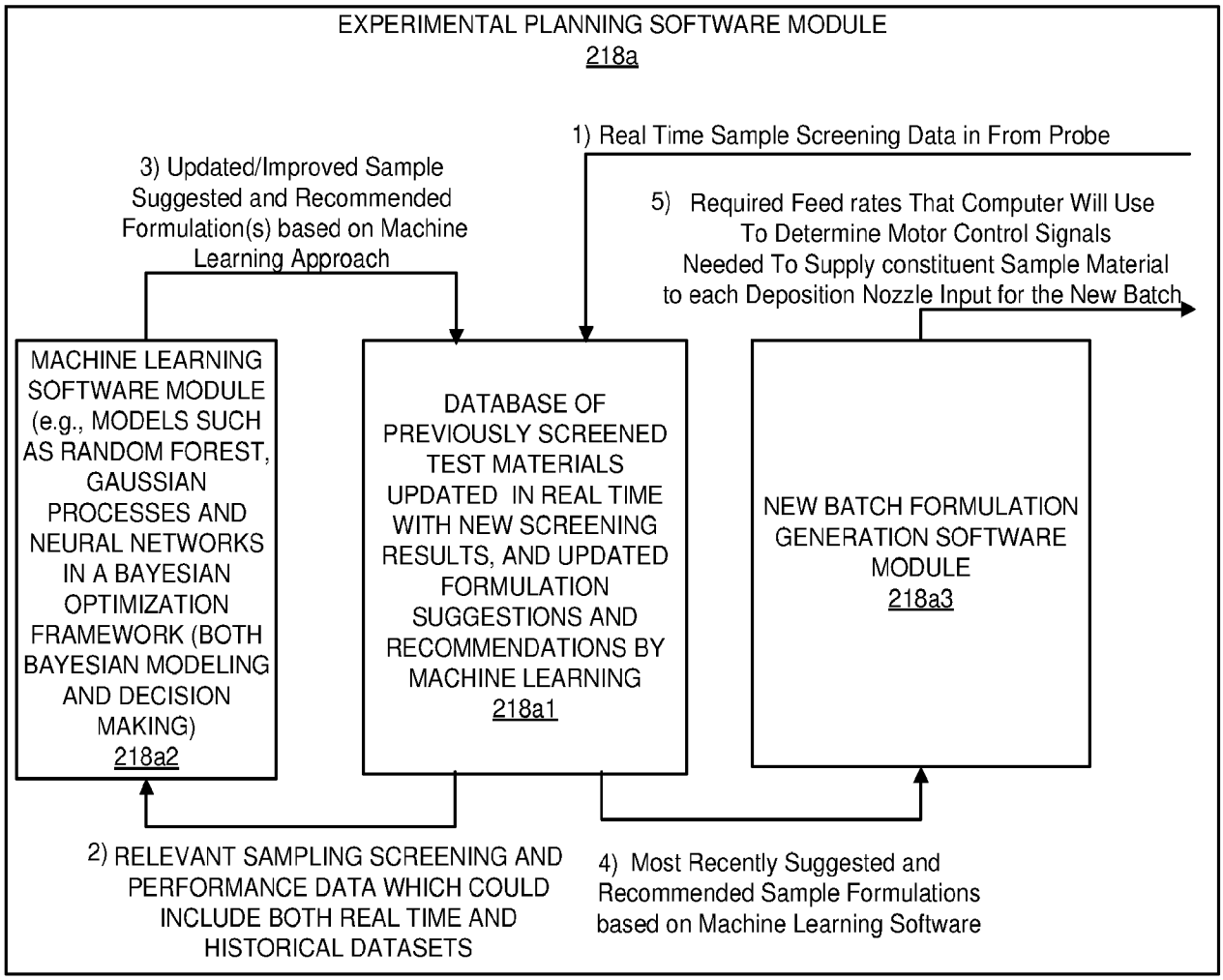

EXPERIMENTAL PLANNING SOFTWARE MODULE
218a
1) Real Time Sample Screening Data in From Probe
3) Updated/Improved Sample Suggested and Recommended Formulation(s) based on Machine Learning Approach
5) Required Feed rates That Computer Will Use To Determine Motor Control Signals Needed To Supply constituent Sample Material to each Deposition Nozzle Input for the New Batch
MACHINE LEARNING SOFTWARE MODULE (e.g., MODELS SUCH AS RANDOM FOREST, GAUSSIAN PROCESSES AND NEURAL NETWORKS IN A BAYESIAN OPTIMIZATION FRAMEWORK (BOTH BAYESIAN MODELING AND DECISION MAKING)
218a2
DATABASE OF PREVIOUSLY SCREENED TEST MATERIALS UPDATED IN REAL TIME WITH NEW SCREENING RESULTS, AND UPDATED FORMULATION SUGGESTIONS AND RECOMMENDATIONS BY MACHINE LEARNING
218a1
NEW BATCH FORMULATION GENERATION SOFTWARE MODULE
218a3
2) RELEVANT SAMPLING SCREENING AND PERFORMANCE DATA WHICH COULD INCLUDE BOTH REAL TIME AND HISTORICAL DATASETS
4) Most Recently Suggested and Recommended Sample Formulations based on Machine Learning Software

FIG. 2A

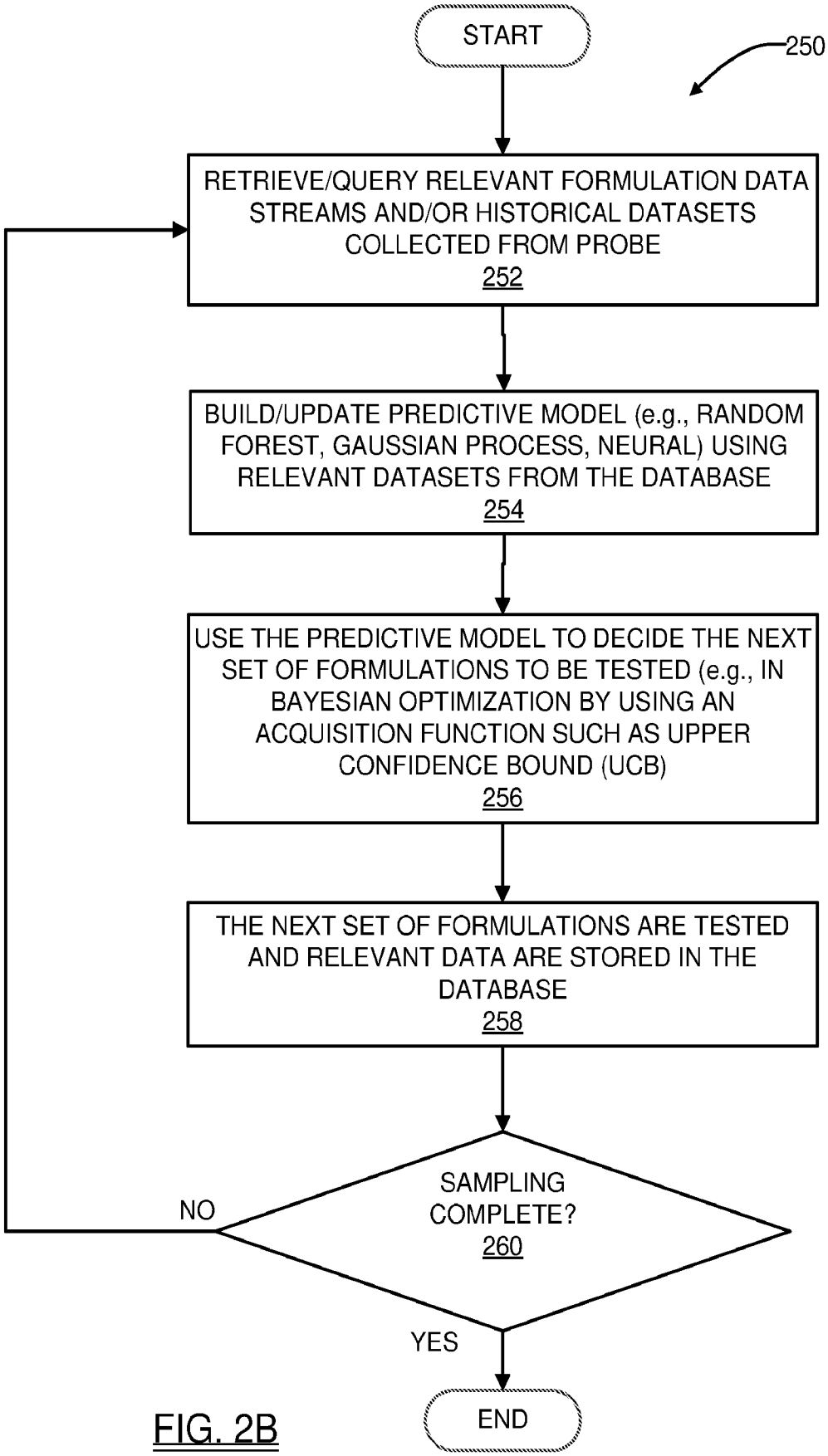

START
250
RETRIEVE/QUERY RELEVANT FORMULATION DATA STREAMS AND/OR HISTORICAL DATASETS COLLECTED FROM PROBE
252
BUILD/UPDATE PREDICTIVE MODEL (e.g., RANDOM FOREST, GAUSSIAN PROCESS, NEURAL) USING RELEVANT DATASETS FROM THE DATABASE
254
USE THE PREDICTIVE MODEL TO DECIDE THE NEXT SET OF FORMULATIONS TO BE TESTED (e.g., IN BAYESIAN OPTIMIZATION BY USING AN ACQUISITION FUNCTION SUCH AS UPPER CONFIDENCE BOUND (UCB)
256
THE NEXT SET OF FORMULATIONS ARE TESTED AND RELEVANT DATA ARE STORED IN THE DATABASE
258
SAMPLING COMPLETE?
260
NO
YES
END

FIG. 2B

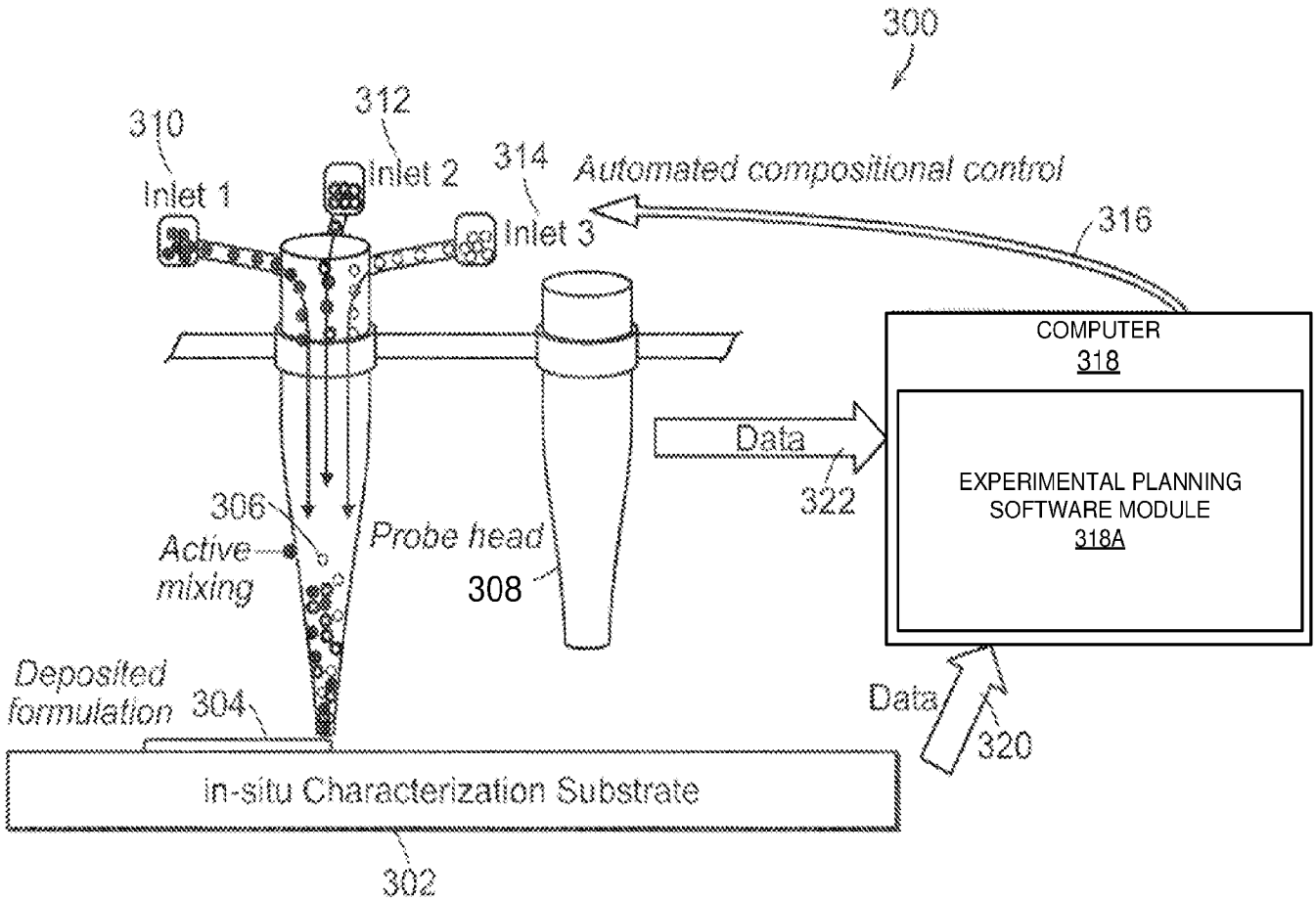

300
310
Inlet 1
312
Inlet 2
314
Inlet 3
Automated compositional control
316
COMPUTER
318
EXPERIMENTAL PLANNING
SOFTWARE MODULE
318A
Data
322
306
Active
mixing
Probe head
308
Deposited
formulation
304
Data
320
in-situ Characterization Substrate
302

FIG. 3

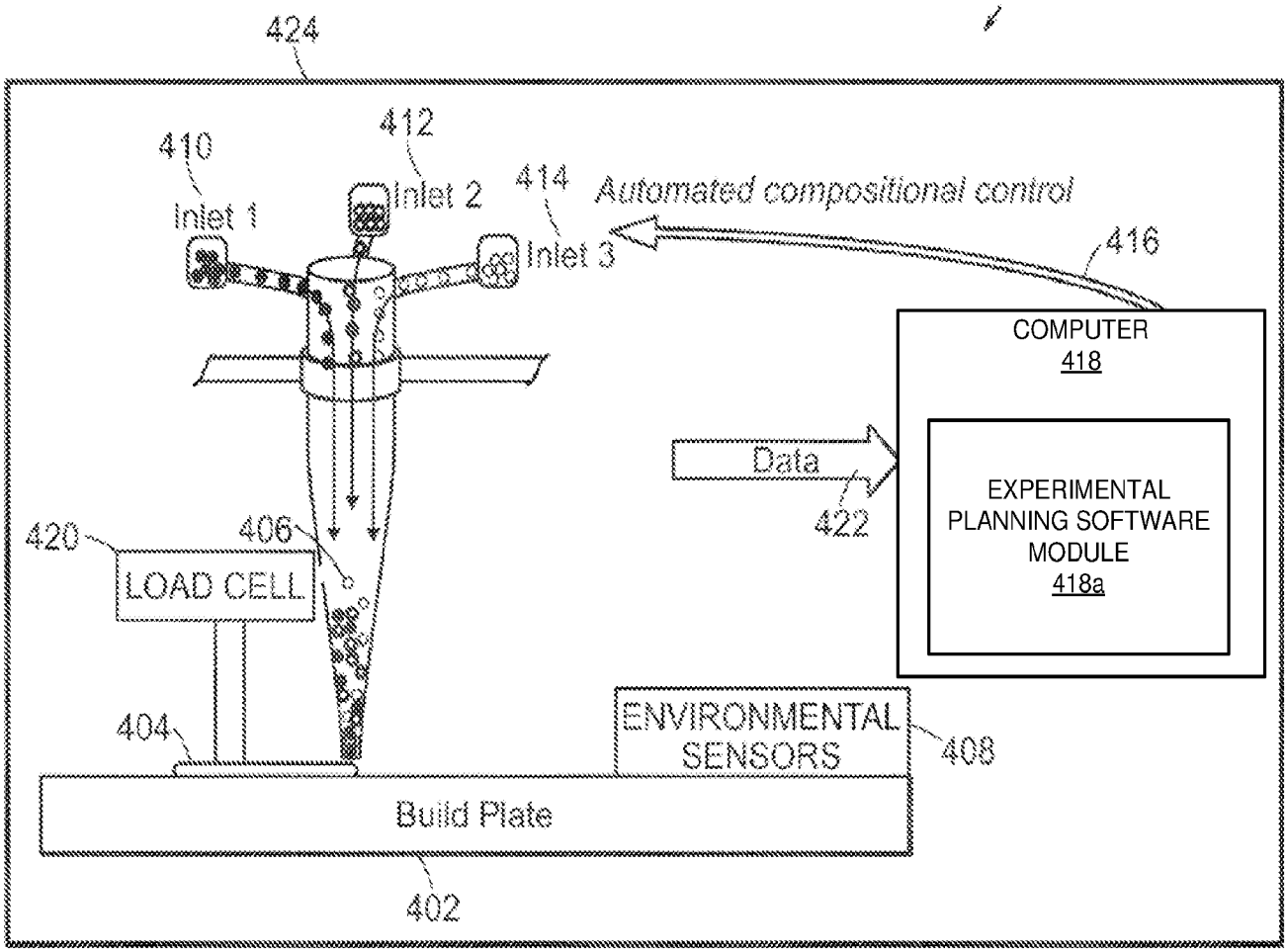

424
410
Inlet 1
412
Inlet 2
414
Automated compositional control
Inlet 3
416
COMPUTER
418
Data
422
EXPERIMENTAL
PLANNING SOFTWARE
MODULE
418a
420
406
LOAD CELL
404
ENVIRONMENTAL
SENSORS
408
Build Plate
402

FIG. 4

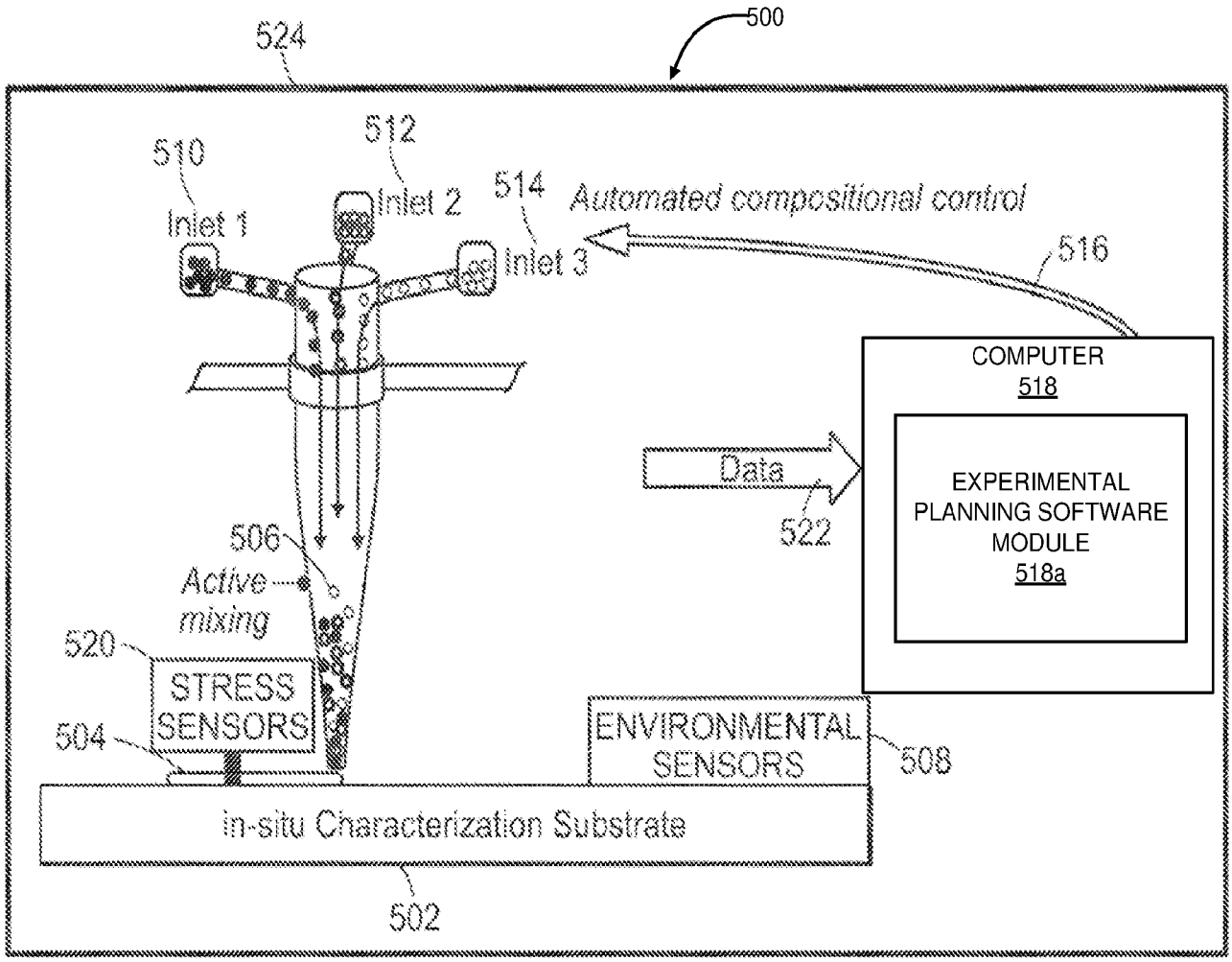

500
524
510
Inlet 1
512
Inlet 2
514
Inlet 3
Automated compositional control
516
COMPUTER
518
EXPERIMENTAL PLANNING SOFTWARE MODULE
518a
Data
522
506
Active mixing
520
STRESS SENSORS
504
ENVIRONMENTAL SENSORS
508
in-situ Characterization Substrate
502

FIG. 5

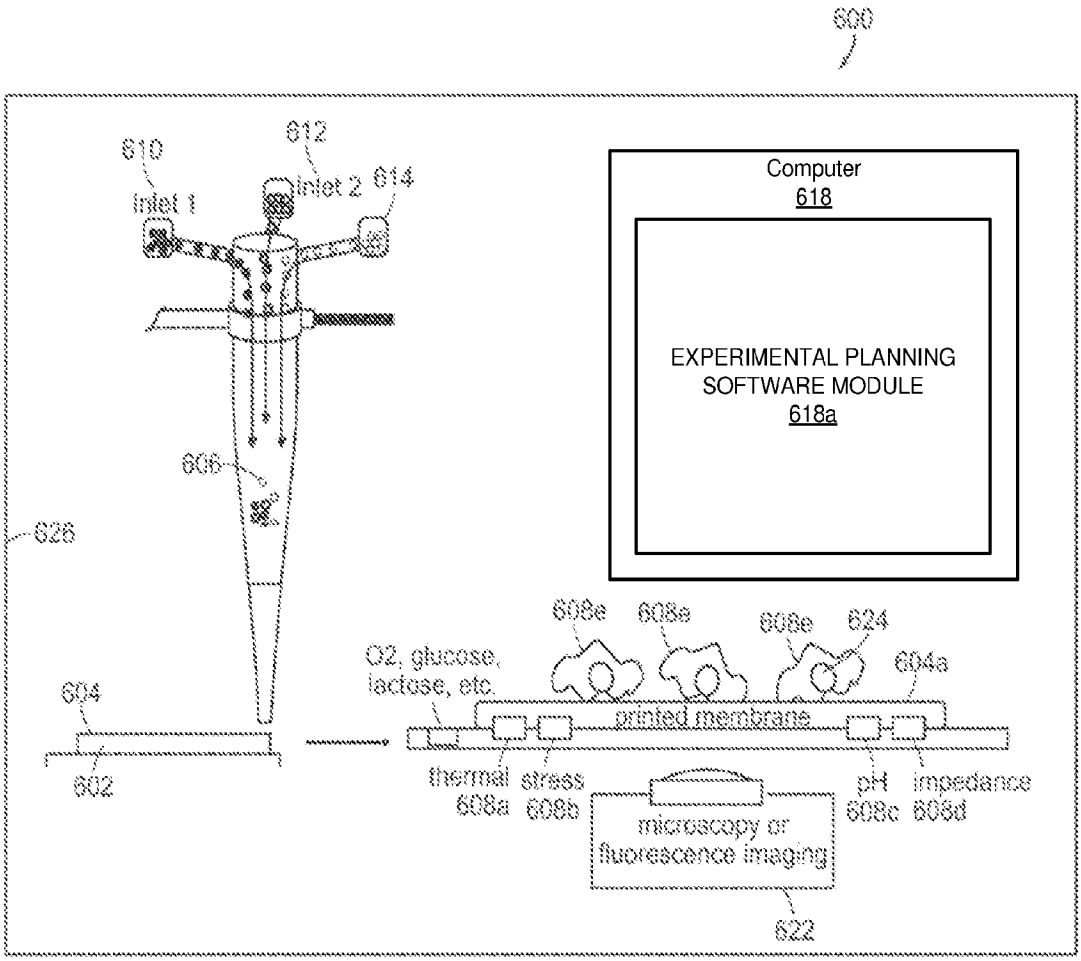

600
610
Inlet 1
612
Inlet 2
614
606
626
604
602
Computer
618
EXPERIMENTAL PLANNING SOFTWARE MODULE
618a
608e
608e
608e
624
604a
O2, glucose, lactose, etc.
printed membrane
thermal 608a
stress 608b
microscopy or fluorescence imaging
622
pH 608c
impedance 608d

FIG. 6

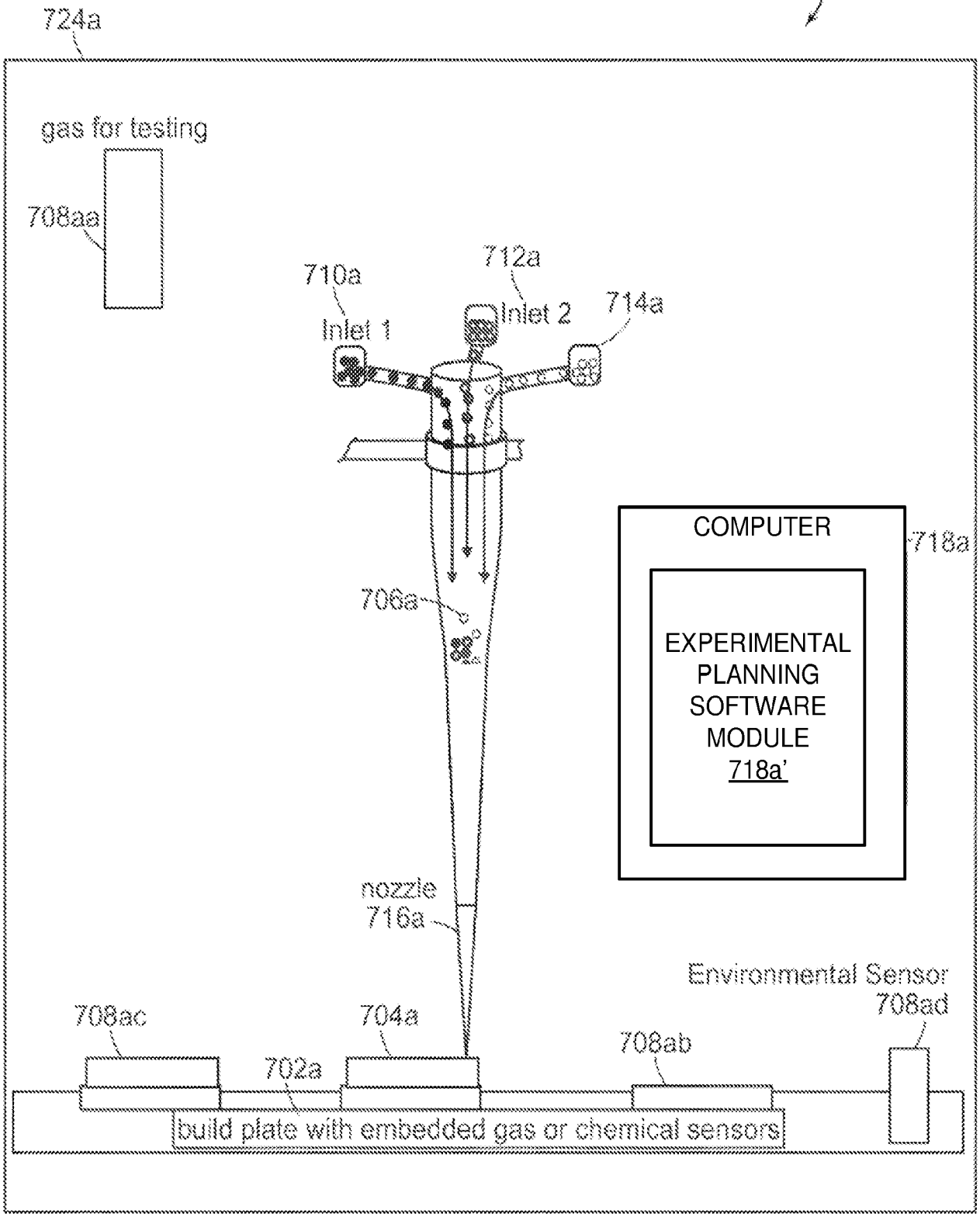

724a
gas for testing
708aa
710a
Inlet 1
712a
Inlet 2
714a
COMPUTER
718a
EXPERIMENTAL PLANNING SOFTWARE MODULE
718a'
706a
nozzle
716a
Environmental Sensor
708ad
708ac
704a
708ab
702a
build plate with embedded gas or chemical sensors

FIG. 7A

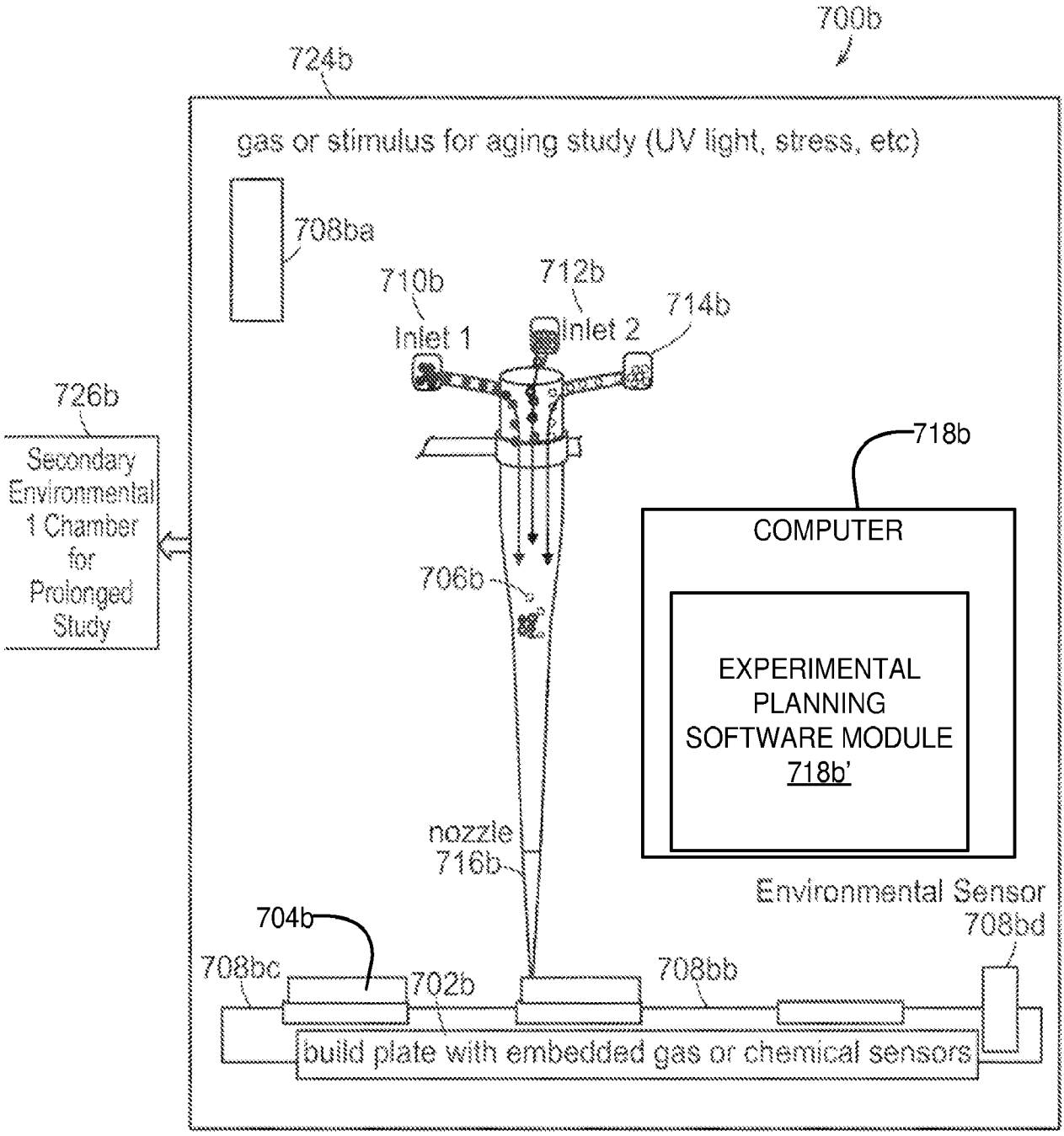

700b
724b
gas or stimulus for aging study (UV light, stress, etc)
708ba
710b
Inlet 1
712b
Inlet 2
714b
726b
Secondary Environmental 1 Chamber for Prolonged Study
718b
COMPUTER
706b
EXPERIMENTAL PLANNING SOFTWARE MODULE
718b'
nozzle
716b
Environmental Sensor
708bd
704b
708bc
702b
708bb
build plate with embedded gas or chemical sensors

FIG. 7B

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2023/032932

A. CLASSIFICATION OF SUBJECT MATTER

G01N 33/44(2006.01)i; **G01N 33/483**(2006.01)i; **G01N 35/00**(2006.01)i; **G06N 20/00**(2019.01)i; **B33Y 40/00**(2015.01)i; **B33Y 70/00**(2015.01)i

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)

G01N 33/44(2006.01); B01F 3/08(2006.01); B22F 10/25(2021.01); B22F 10/36(2021.01); B29C 64/153(2017.01); B29C 64/386(2017.01); B29C 64/393(2017.01); B41J 2/21(2006.01); G01N 21/17(2006.01)

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

Korean utility models and applications for utility models
Japanese utility models and applications for utility models

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

eKOMPASS(KIPO internal) & Keywords: screening, machine learning, probe, substrate, additive manufacturing

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2022-0266522 A1 (PALO ALTO RESEARCH CENTER INCORPORATED) 25 August 2022 (2022-08-25) claims 1, 9; paragraphs [0004], [0010]; figure 2	1-20
DA	US 10071350 B2 (PRESIDENT AND FELLOWS OF HARVARD COLLEGE) 11 September 2018 (2018-09-11) column 5, lines 31-46; column 6, lines 1-12; figure 2	1-20
A	US 2021-0197279 A1 (KOREA ADVANCED INSTITUTE OF SCIENCE AND TECHNOLOGY) 01 July 2021 (2021-07-01) the whole document	1-20
A	US 2020-0223146 A1 (CARL ZEISS INDUSTRIELLE MESSTECHNIK GMBH) 16 July 2020 (2020-07-16) the whole document	1-20

☑ 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
05 February 2024	**05 February 2024**

Name and mailing address of the ISA/KR	Authorized officer
Korean Intellectual Property Office **189 Cheongsa-ro, Seo-gu, Daejeon** **35208, Republic of Korea**	**HEO, Joo Hyung**
Facsimile No. **+82-42-481-8578**	Telephone No. **+82-42-481-5373**

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2023/032932

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2020-0384693 A1 (RAYTHEON TECHNOLOGIES CO.) 10 December 2020 (2020-12-10) the whole document	1-20

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/US2023/032932

Patent document cited in search report	Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
US 2022-0266522 A1	25 August 2022	None	
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		WO 2016-164562 A1	13 October 2016
US 2021-0197279 A1	01 July 2021	CN 113118461 A	16 July 2021
		KR 10-2226094 B1	11 March 2021
		US 11858040 B2	02 January 2024
US 2020-0223146 A1	16 July 2020	CN 110799286 A	14 February 2020
		CN 110799286 B	28 February 2023
		EP 3641965 A1	29 April 2020
		JP 2020-533481 A	19 November 2020
		JP 6845353 B2	17 March 2021
		US 11633918 B2	25 April 2023
		WO 2018-234331 A1	27 December 2018
US 2020-0384693 A1	10 December 2020	EP 3747571 A1	09 December 2020
		EP 3747571 B1	29 November 2023