

DESCRIPTION

TITLE OF THE INVENTION: A Plasma Printing Process to manufacture and produce battery electrodes and enhance current collectors

FIELD OF THE DISCLOSURE

[0001] Various embodiments of the disclosure relate generally to binder-free electrodes for electrochemical devices. More specifically, various embodiments of the disclosure relate to plasma printing of binder-free electrodes and solid-state batteries using a continuous, electrolytic plasma process.

DESCRIPTION OF THE RELATED ART

[0002] There is an ever-increasing demand for efficient and reliable energy storage devices. Electrochemical devices such as batteries and supercapacitors play an indispensable role in our daily lives with wide-ranging applications from mobiles to electric vehicles. Electrodes are central to electrochemical devices as they serve as the interface where electrochemical reactions occur, enabling storage and/or conversion of energy.

[0003] An electrode of the electrochemical device is typically formed by applying an active material on a current collector. The active material may be applied through a dry process, *i.e.*, in the absence of any solvent by way of a dry jet and mortar or dry powder coating method. The application of the active material through the dry process is quite complex and requires sophisticated machinery and techniques. Alternatively, a wet slurry technique may be employed for making the electrodes. In the wet slurry technique, the active material is mixed with a binder and dispersed in an organic solvent, or in an aqueous medium to form a wet slurry. The wet slurry is then applied to the current collector to form the electrode. However, due to the presence of the binder, it is a challenge to achieve high electrode density of the electrode and hence improved energy density of the battery. Further, drying of the electrode may take 12 to 24 hours thus impacting cost of production.

[0004] There is a need for a fabrication process that is cost-effective, and economical and addresses some of the drawbacks of existing processes.

[0005] Limitations and disadvantages of conventional and traditional approaches will become apparent to one of skill in the art, through comparison of described systems with some aspects of the present disclosure, as set forth in the remainder of the present application and with reference to the drawings.

SUMMARY

[0006] Embodiments of the present invention provide an electrode of an electrochemical device fabricated using a process. The process comprises steps of providing a chamber that is filled with a liquid electrolyte and comprising at least one plasma anode. The liquid electrolyte comprises an electroactive material. The process further comprises providing a current collector in the chamber, wherein the current collector and the at least one plasma anode are in relative motion with each other at a translation rate, and wherein the current collector, or the at least one plasma anode, or both is operable to move in and out of the chamber in a continuous manner. The process further comprises applying a voltage across the at least one plasma anode and the current collector to generate plasma, wherein the plasma is generated in an initial plasma zone between a portion of the current collector and the at least one plasma anode, and wherein the plasma induces the electroactive material to mechanically bond to the portion of the current collector to form a layer. The process further comprises positioning a next portion of the current collector to a next plasma zone by moving the at least one plasma anode, the current collector, or both to extend the layer of the electroactive material on the next portion of the current collector and repeating this step along a dimension of the current collector to obtain the electrode, and wherein a temperature of bulk liquid electrolyte in the chamber is not more than 100 °C during the process.

[0007] According to embodiments of the present invention, a continuous process for fabricating an electrode of an electrochemical device is provided. The process comprises steps of providing a chamber that is filled with a liquid electrolyte and comprising at least one plasma anode, wherein the liquid electrolyte is continuously fed and discharged from the chamber at a flow rate. The liquid electrolyte comprises an electroactive material. The process further comprises providing a current collector in the chamber, wherein the current collector and the at least one plasma anode are in relative motion with each other at a translation rate, and wherein the current collector, or the at least one plasma anode, or both is operable to move in and out of the chamber in a continuous manner. The process further comprises applying a voltage across the at least one plasma anode and the current collector to generate plasma, wherein the plasma is generated in an initial plasma zone between a portion of the current collector and the at least one plasma anode, and wherein the plasma induces the electroactive material to mechanically bond to the portion of the current collector to form a layer. The process further comprises positioning a next portion of the current collector to a next plasma zone by moving the at least one plasma anode, the current collector, or both to extend the layer of the electroactive material on the next portion of the current collector and repeating this step along a dimension of the current collector to obtain the

electrode, and wherein a temperature of bulk liquid electrolyte in the chamber is not more than 100 °C during the process.

[0008] In another embodiment, a continuous process for treatment of a current collector of a battery is provided. The process comprises steps of providing a chamber that is filled with a liquid electrolyte and comprising at least one plasma anode, wherein the liquid electrolyte is continuously fed and discharged from the chamber at a flow rate. The process further comprises providing the current collector in the chamber, wherein the current collector and the at least one plasma anode are in relative motion with each other at a translation rate, and wherein the current collector, or the at least one plasma anode, or both is operable to move in and out of the chamber in a continuous manner. The process further comprises applying a voltage across the at least one plasma anode and the current collector to generate plasma, wherein the plasma is generated in an initial plasma zone between a portion of the current collector and the at least one plasma anode, and wherein the plasma modifies a surface of the portion of the current collector in the initial plasma zone. The process further comprises positioning a next portion of the current collector to a next plasma zone by moving the at least one plasma anode, the current collector, or both to modify a surface of the next portion of the current collector and repeating this step along a dimension of the current collector to obtain a treated current collector, and wherein a temperature of bulk liquid electrolyte in the chamber is not more than 100 °C during the process.

[0009] In yet another embodiment, a method of fabricating a battery is provided. The method comprises steps of (i) providing a chamber that is filled with a first electrolyte and comprising at least one plasma anode, wherein the first electrolyte is continuously fed and discharged from the chamber at a flow rate, and wherein the first electrolyte comprises a first electroactive material. The method comprises step (ii) of providing a current collector in the chamber, wherein the current collector and the at least one plasma anode are in relative motion with each other at a translation rate, and wherein the current collector, or the at least one plasma anode, or both is operable to move in and out of the chamber in a continuous manner. The method further comprises step (iii) of applying a voltage across the at least one plasma anode and the current collector to generate plasma, wherein the plasma is generated in an initial plasma zone between a portion of the current collector and the at least one plasma anode, and wherein the plasma induces mechanical bonding of the first electroactive material over the portion of the current collector to form a layer. The method further comprises step (iv) of positioning a next portion of the current collector to a next plasma zone by moving the at least one plasma anode, the current collector, or both, to extend the layer of the first electroactive material on the next portion of the current collector and repeating this step along a dimension of the current collector to form a continuous layer on the current

collector to obtain a first electrode. The method further comprises step (v) of repeating steps (i) to (iv) with the first electrode and a second electrolyte, wherein the second electrolyte comprises solid-state electrolyte material. The solid-state electrolyte material is deposited on a surface of the first electrode, wherein the solid-state electrolyte material is mechanically bonded to the surface of the first electrode to form a solid-state electrolyte bonded electrode. The method further comprises step (vi) of repeating steps (i) to (iv) with the solid-state electrolyte bonded electrode and a third electrolyte, wherein the third electrolyte comprises a second electroactive material. The second electroactive material is deposited on a surface of the solid-state electrolyte bonded electrode, wherein the second electroactive material is mechanically bonded to the surface of the solid-state electrolyte bonded electrode to form a battery. The battery comprises the first electrode, the solid-state electrolyte, and the second electrode. A temperature of bulk first electrolyte, or bulk second electrolyte in the chamber is not more than 100 °C.

[0010] In yet another embodiment, a plasma apparatus for continuous fabrication of an electrode of an electrochemical device is provided. The plasma apparatus comprises a chamber having an inlet and an outlet to circulate a liquid electrolyte at a flow rate. The chamber is filled with the liquid electrolyte, wherein the liquid electrolyte comprises an electroactive material. The plasma apparatus further comprises at least one plasma anode disposed in the chamber, and optionally operable to move in and out of the chamber. The plasma apparatus further comprises a current collector disposed in the chamber at a distance from the at least one plasma anode, wherein the current collector is in relative motion to the at least one plasma anode at a translation rate, and wherein the current collector is optionally operable to move in and out of the chamber. The plasma apparatus further comprises a DC supply to apply a voltage across the current collector and the at least one plasma anode to generate a plasma, wherein the plasma generated induces mechanical bonding of the electroactive material on a surface of the current collector to form the electrode, and wherein the plasma is controlled by adjusting a composition of the electrolyte, a composition of the current collector, the translation rate, the flow rate, voltage, or combinations thereof.

[0011] These and other features and advantages of the present disclosure may be appreciated from a review of the following detailed description of the present disclosure, along with the accompanying figures in which like reference numerals refer to like parts throughout.

BRIEF DESCRIPTION OF DRAWINGS

[0012] FIG. 1 is a flow chart of a continuous process for treating a current collector of an electrochemical device, in accordance with an embodiment of the disclosure;

[0013] FIG. 2 is a schematic diagram of a plasma apparatus for continuous fabrication of an electrode of an electrochemical device; and

[0014] FIG. 3 is a Scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX) image of an electrode fabricated according to embodiments of the disclosure.

[0015] Further areas of applicability of the present disclosure will become apparent from the detailed description provided hereinafter. It should be understood that the detailed description of embodiments is intended for illustration purposes only and is, therefore, not intended to necessarily limit the scope of the present disclosure.

DETAILED DESCRIPTION OF EMBODIMENTS

[0016] The following description illustrates some embodiments of the disclosed disclosure in detail. Those of skill in the art will recognize that there are numerous variations and modifications of this disclosure that are encompassed by its scope. Accordingly, the description of a certain embodiment should not be deemed to limit the scope of the present disclosure.

[0017] The term “comprising” as used herein is synonymous with “including” or “containing” and is inclusive or open-ended and does not exclude additional, unrecited elements, or method steps.

[0018] All numbers expressing quantities of ingredients, property measurements, and so forth used in the specification are to be understood as being modified in all instances by the term “about.” Accordingly, unless indicated to the contrary, the numerical parameters set forth herein are approximations that may vary depending upon the desired properties sought to be obtained.

[0019] The term “plasma printing” as used herein has the connotations of a fast and continuous process, similar to traditional printing methods. Plasma printing technology utilizes plasma to modify a surface, or deposit a material onto the surface of a substrate. In the present disclosure, a reducing atmosphere plasma is generated by a plasma printer, or a plasma apparatus using an electrolytic plasma process where a liquid electrolyte contains desired material(s) for deposition. The material may be deposited irrespective of the nature, particle size, and form (for example, gas, liquid, or solid) of the material, and is described in detail in the following description. In the context of the present disclosure, the substrate refers to a current collector, and the material that is deposited is an electroactive material, an additive, or both. The term “process” as used herein refers to “plasma printing”, or a “continuous, electrolytic plasma deposition process”. The term “process” also refers to a continuous, electrolytic plasma process for treatment of current collectors.

[0020] As used herein, the term “electrode density”, is defined as the volumetric mass density of electrode material including active material, binder, and any remaining solvent in the electrode.

[0021] As used herein, the term “electrochemical device” refers to devices that generate electricity from a chemical reaction, and include batteries, solid-state batteries, electrolytic capacitors, and supercapacitors.

[0022] The term “battery”, as used herein, includes rechargeable, and non-rechargeable batteries. A typical battery consists of an anode, a cathode, an electrolyte, a separator, and two current collectors corresponding to the anode and the cathode. The anode and the cathode are collectively termed as electrodes. The electrolyte can be a liquid or a solid. The batteries including solid electrolytes are referred to as solid-state batteries.

[0023] An “electrolytic capacitor”, as used herein refers to a type of capacitor that uses an electrolyte as one of the electrodes. The electrolytic capacitor consists of two plates, an anode and a cathode. The anode is typically made of a metal that forms an insulating oxide layer that acts as the dielectric for the capacitor. A solid, liquid, or gel electrolyte covers a surface of the oxide layer which acts as the cathode. The three main electrolytic capacitor series are based on aluminum, tantalum, and niobium. “Supercapacitors” are high-capacity electrolytic capacitors that can store 10 to 100 times more energy than a typical electrolytic capacitor.

[0024] As used herein, the term “cathode”, when used in context to a battery refers to an electrode that supplies electrons during the charging of the battery and is present as part of a redox reaction. As used herein, the term “anode”, when used in context to a battery refers to an electrode that accepts electrons during charging and is present as part of the redox reaction. The terms “cathode” and “anode”, as used herein may refer to the cathode and the anode of the electrolytic capacitors or supercapacitors, respectively.

[0025] As used herein, the term “electrolyte” may refer to a material that allows ions to migrate therethrough but does not allow electrons to conduct therethrough, and is used in context to electrochemical devices. The term “liquid electrolyte” refers to an electrolyte used in a plasma chamber.

[0026] As used herein, the term “current collector” refers to a bridging component that collects electrical current generated at the electrodes through external circuits.

[0027] A rechargeable, metal-ion battery functions by reversible intercalation and deintercalation of metal ions between the anode and the cathode of the battery. During a discharge cycle, an oxidation half-reaction at the anode forms metal ions and electrons. The anode releases the metal ions to the cathode through the electrolyte, while electrons flow through an external circuit from the anode to the cathode through current collectors. During a charge cycle, an electric current is applied through the external circuit releasing metal ions from the cathode to the anode through the electrolyte.

[0028] Commercially, the electrodes of a metal-ion battery are formed by coating current collectors with a slurry comprising electroactive material. As used herein, the term “electroactive material” or “active material” may refer to a material that produces electrical energy from chemical reactions during the battery discharge. The cathode is formed by coating the cathode current collector with a slurry comprising a cathode active material. The anode current collector is coated with a slurry comprising an anode active material to obtain the anode. The slurry may additionally include binders. The binder refers to compounds that hold the active materials together and may also enhance binding between the active material and the current collector.

[0029] Most commonly used metal-ion batteries are based on alkali metal ions such as lithium, potassium, and sodium. The alkali metal ions being monovalent, the amount of electrical energy which may be stored and recovered from a given weight of electroactive material, typically metal salts, is limited as it yields only a single electron/ion transfer per unit weight of metal. Bivalent alkaline earth ions, such as calcium, magnesium, and strontium; multivalent transition metals such as yttrium, niobium, molybdenum, titanium, tungsten; and lanthanide compound sources, such as lanthanum, europium, and samarium, are known. For the purpose of this invention, the term “battery” includes batteries utilizing the above-mentioned metal ions.

[0030] Metal-air batteries are another type of battery consisting of a metal anode, a porous air cathode, and an electrolyte. A typical air cathode comprises a current collector, a catalytic layer, and a hydrophobic diffusion layer facing an air side of the air cathode. Non-limiting examples of metal-air batteries include zinc-air, iron-air, aluminum-air, magnesium-air, lithium-air, sodium-air, potassium-air, and silicon-air battery. For the purpose of this invention, the term “battery” includes the above-listed metal-air batteries.

[0031] Organic batteries are yet another type of battery where an organic compound, such as small organic molecules or polymers is responsible for charge storage. For the purpose of this invention, the term “battery” includes organic batteries.

[0032] Embodiments of the present invention provide an electrode of an electrochemical device fabricated using a process. The process comprises steps of providing a chamber that is filled with a liquid electrolyte and comprising at least one plasma anode, wherein the liquid electrolyte is continuously fed and discharged from the chamber at a flow rate. The liquid electrolyte comprises an electroactive material. The process further comprises providing the current collector in the chamber, wherein the current collector and the at least one plasma anode are in relative motion with each other at a translation rate, and wherein the current collector, or the at least one plasma anode, or both is operable to move in and out of the chamber in a continuous manner. The process further comprises applying a voltage across the at least one plasma anode and the current collector to generate plasma, wherein the plasma is generated in an initial plasma zone between a portion of the current collector and the at least one plasma anode, and wherein the plasma induces the electroactive material to mechanically bond to the portion of the current collector to form a layer. The process further comprises positioning a next portion of the current collector to a next plasma zone by moving the at least one plasma anode, the current collector, or both to extend the layer of the electroactive material on the next portion of the current collector and repeating this step along a dimension of the current collector to obtain the electrode, and wherein a temperature of bulk liquid electrolyte in the chamber is not more than 100 °C during the process.

[0033] The current collector, of the present disclosure, corresponds to a current collector of a battery on which electroactive material is deposited to form the electrode. In another embodiment, the current collector corresponds to a material that forms part of an anode of an electrolytic capacitor.

[0034] In one embodiment, the current collector is a metal, a non-metal, a metal oxide, a polymer, or combinations thereof. A suitability of a material as a current collector for a particular electrode, capacitor and/or battery depends on electrical conductivity and potential stability of the material. For example, lithium-ion battery cathode has a higher potential between 3 to 4.5 V against lithium/lithium ion, while anode has a lower potential between 0.01 to 1.5 V against lithium/lithium ion. Aluminium (Al) metal is a good electrical conductor with 61% conductivity compared to copper. However, Al participates in electrochemical reactions at lower potential making it unsuitable for use as an anode current collector in lithium-ion battery. Aluminum can be used as a current collector at the cathode as it is stable at higher potential. In theory, any metals, non-metals, metal oxides, conducting polymers, and combinations of these may be used as a current collector if the battery electrode potentials match that of the material and the material has suitable electrical conductivity. The current collector is in the form of a sheet, a foil, a mesh, a porous body, or a non-woven body. In one embodiment, the current collector has a 3-dimensional structure, such as foam.

[0035] Non-limiting examples of metals include aluminum, manganese, cobalt, copper, nickel, titanium, stainless steel, platinum, zinc, tin, lithium, tungsten, molybdenum, tantalum, sodium, potassium, chromium, or alloys thereof. Non-limiting examples of metal oxides include indium tin oxide, fluorine-doped indium tin oxide, nickel oxide, cobalt oxide, manganese oxide, iron oxide, lithium oxide, titanium oxide, or combinations thereof. Non-limiting examples of non-metals include carbon, carbon fibers, carbon black, graphene, graphite, carbon nanotubes, fullerene, hard carbon, soft carbon, porous carbon, graphene oxide, silicon, silicon oxide; and semiconducting materials such as germanium, or combinations of these. Non-limiting examples of polymers include thermoplastic polymers, such as polyethylene terephthalate (PET), polyethylene naphthalate (PEN), or combinations thereof. The polymers may be made conducting by doping the polymers with a conducting agent such as graphite.

[0036] The electroactive material includes anode active material and cathode active material. The electroactive material comprises metal, metal salts, non-metals, non-metal salts, polymers, donor-acceptor organic molecules, or combinations thereof. Example electroactive materials include, but are not limited to, oxides, nitrides, oxynitrides, sulphates, phosphates, and sulphide salts of single metals, or mixed metals, or non-metals. The metal comprises lithium, sodium, titanium, aluminum, tin, zirconium, yttrium, magnesium, sodium, copper, niobium, nickel, manganese, cobalt, and iron. Non-metals include carbonaceous material, sulphur, boron, and silicon. As used herein, the term “carbonaceous material” includes carbon-based materials such as graphite, carbon black, graphene oxide, reduced-graphene oxide, carbon fibers, porous carbon, carbon nanotubes, fullerene, graphene, activated carbon, carbon black, amorphous carbon, soft carbon, hard carbon, or combinations thereof. Non-limiting examples of active material include lithium metal oxides, lithium mixed metal oxides, lithium phosphates, lithium oxynitride, lithium titanate, lithium mixed metal phosphates, lithium nitride, lithium sulphide, sodium metal oxides, sodium mixed metal oxides, sodium phosphates, sodium mixed metal phosphates, silica, silicon, metal alloys, chalcogenides, transition metal oxides, metal sulphides, metal nitrides, carbon nanotubes, graphite, graphene, or combinations thereof. Example electroactive material for a lithium-ion battery includes lithium metal oxides such as lithium manganese oxide (LMO), lithium nickel cobalt aluminium oxide (Li-NCA), lithium nickel manganese cobalt oxide (Li-NMC), lithium cobalt oxide (LCO), lithium nickel oxide (LNO), lithium nickel manganese oxide (LNMO), lithium nickel cobalt manganese oxide (LNCM), lithium iron phosphate (LFP), lithium manganese phosphate (LMP), and lithium cobalt phosphate (LCP). Non-limiting examples of polymers include polyvinylidene fluoride (PVDF), polyacrylic acid (PAA), perfluoroalkoxy alkanes (PFA), polythiophene, polypyrrole, polyacetylene, poly(tetramethylpiperidinyloxy methacrylate) (PTMA), or combinations thereof.

[0037] The electroactive material is in the form of a gas, a solid, or a liquid. The electroactive material may be dissolved in the liquid electrolyte, as in a typical electrolytic process. In another embodiment, the electroactive material is dispersed in the liquid electrolyte. In yet another embodiment, the electroactive material is nano-structured, or micro-structured. A particle size of the electroactive material may vary from as large as few micrometers to as small as nanometers. Further, the electroactive material may be porous, or non-porous.

[0038] On application of the voltage between two electrodes, *i.e.*, the current collector and the at least one plasma anode in the liquid electrolyte, plasma is generated. The voltage applied is about 1000 Volts (V), or less than about 1000 V. According to embodiments of the present disclosure, the plasma is generated for very short timescales of the order of picoseconds to nanoseconds to support mechanical bond formation between particles and/or molecules of the electroactive material and between the electroactive material and a surface of the current collector to support electroactive material deposition. The process ensures a continuous layer formation on the current collector to obtain the electrode, where the continuous layer comprises the electroactive material. As only mechanical bonds are formed during electrolytic plasma formation, the inventive process is chemistry agnostic, and hence any material may be deposited using the disclosed process.

[0039] The continuous layer formed over the current collector using the process is a conformal layer. The conformal layer is a uniform, continuous coating or deposition on the surface of the current collector irrespective of surface morphology or surface roughness or type of material of the current collector. In one embodiment, the continuous layer of the electroactive material on the current collector has a thickness in a range of 0.05 microns to 20 microns on a single pass of the current collector through the chamber.

[0040] In one embodiment, the continuous layer is multi-layered, wherein the continuous layer comprises a single electroactive material, or more than one electroactive material. A multi-layered structure may be obtained by disposing more than one plasma anode in the chamber to form a layer over layer, in one embodiment. In another embodiment, the current collector may be allowed to pass through the chamber more than once to deposit a layer over layer. In one embodiment, a multi-layered structure having a single electroactive material may be obtained by providing a single electroactive material in the liquid electrolyte. In yet another embodiment, the liquid electrolyte may include more than one electroactive material to form multilayered structure comprising more than one electroactive material. In another embodiment, after forming a layer over the current collector using a liquid electrolyte having a first electroactive material, the liquid electrolyte is fed in with a second electroactive material to form a

multi-layered electrode comprising the first electroactive material and the second electroactive material through multiple passes of the current collector through the chamber.

[0041] In some embodiments, the multi-layered continuous layer comprises a first layer over the current collector and a second layer over the first layer. The current collector comprises copper, steel, nickel, or aluminum. The first layer comprises graphene and the second layer comprises silicon, tin, lithium, or combinations thereof. In one embodiment, the first layer is an interfacial layer, and the electroactive material is deposited over the interfacial layer to form an electrode. The interfacial layers are sometimes used in electrode fabrication to enhance adhesion between electroactive material and current collectors.

[0042] In another embodiment, the continuous layer is a graded layer, wherein a concentration of the electroactive material varies across a cross-section, *i.e.*, in a transverse direction to the direction of deposition, of the continuous layer. In one embodiment, the graded layer may be formed by changing a concentration of the electroactive material in the liquid electrolyte during the process. In another embodiment, the graded layer may be formed by including two different electroactive materials in the liquid electrolyte, where concentrations of the two electroactive materials change across the layer. In yet another embodiment, pore-forming agents may be included in the electrolyte along with the electroactive material to change a concentration of the electroactive material across a cross-section of the continuous layer. The plasma parameters as discussed earlier may be utilized to form the multi-layered and the graded layer, for example by changing voltage, plasma composition changes which may change the composition of the layer comprising the electroactive material.

[0043] In one embodiment, the current collector of the electrode is aluminum, the electroactive material is graphene in combination with silicon or tin, and the additive is polyvinylidene fluoride.

[0044] In some embodiments, the current collector of the electrode comprises copper, aluminum, or nickel, and the electroactive material comprises graphite, porous carbon, carbon nanotubes, fullerene, graphene, activated carbon, carbon black, amorphous carbon, soft carbon, hard carbon, or combinations thereof.

[0045] In some embodiments, the current collector of the electrode comprises carbon, and the electroactive material comprises boron-doped carbon, boron nitride, boron carbide, graphite, porous carbon, carbon nanotubes, fullerene, graphene, activated carbon, carbon black, amorphous carbon, soft carbon, hard carbon, or combinations thereof.

[0046] FIG. 1 is a flow chart 100 that illustrates a continuous process for treating a current collector of an electrochemical device through exemplary steps 102 through 108, according to embodiments of the present disclosure. At step 102, a chamber is provided. The chamber is filled with a liquid electrolyte and the liquid electrolyte is continuously fed and discharged from the chamber at a flow rate.

[0047] The chamber, as used herein, refers to any closed-walled system to avoid contamination as well as to hold the liquid electrolyte. In a preferred embodiment, the chamber is maintained at room temperature and atmospheric pressure. In some embodiments, the chamber may be operated at elevated temperatures depending on process requirements. Optionally, a heater may be provided inside or outside of the chamber to heat the chamber, and/or contents of the chamber. In some embodiments, depending on the process requirement the chamber may be pressurized. The chamber, without any limitation, may be of any size and shape and is customizable as per process requirements. In one instance the chamber is rectangular in shape.

[0048] The liquid electrolyte is water-based, solvent-based, or ionic-liquid-based. It is preferred to have a water-based electrolyte. The liquid electrolyte dissociates to respective ions when an electric current or voltage is applied. The dissociation of ions of the liquid electrolyte should be a continuous process for stable plasma formation and sustenance. Non-limiting examples of solvents that may be used in solvent-based liquid electrolytes include alcohols, ethanol, methanol, acetonitrile, dimethyl sulphoxide (DMSO), N, N-dimethylformamide (DMF), ethylene carbonate, propylene carbonate or combinations thereof. Examples of ionic liquids include, but are not limited to, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, 1-butyl-3-methylimidazolium hexafluorophosphate, 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, pyridinium-based ionic liquids or combinations thereof. A composition and concentration of the liquid electrolyte may be controlled to control various parameters of the plasma such as temperature, and composition of the plasma. As used herein, the term “composition of the plasma” refers to ions, radicals, or gases constituting the plasma and their concentrations in the plasma.

[0049] The liquid electrolyte further includes additives, electroactive material, or both. The additive is in the form of a gas, a solid, or a liquid. The additives, in one embodiment, comprise metals, metal oxides, non-metals, non-metal salts, salts, binders, pore-forming agents, polymers, pro-electroactive material, or combinations thereof. In one embodiment, the metals comprise platinum, palladium, gold, silver, cobalt, copper, nickel, iron, manganese, or any alloys thereof, which are used as catalyst material in metal-air batteries. In yet another embodiment, the additive comprises transition

metal oxides and non-metals such as carbonaceous material. As used herein, the term “pro-electroactive materials” refers to materials when deposited using the inventive electrolytic plasma on the current collector functions as the electroactive material. Non-limiting examples of salts include halides, sulphates, and carbonates of alkali metals such as sodium chloride, potassium chloride, lithium chloride, potassium carbonate, sodium sulphate, or combinations thereof. The salt enhances conductivity of the liquid electrolyte by releasing respective ions in the liquid electrolyte necessary for plasma formation. The choice of salt is based on the conductivity of salt ions in the liquid electrolyte required for plasma generation and process requirements. For example, for a sodium-free process, non-sodium salts are preferred, as sodium salts may contaminate a resulting electrode.

[0050] The binders are added to the liquid electrolyte when the current collector is pre-treated with a slurry comprising electroactive material to bind the wet slurry to the current collector. However, the binders are eliminated during the electrolytic plasma treatment process. Non-limiting examples of binders include polyacrylic acid, carboxymethyl cellulose, styrene butadiene rubber, sodium alginate, polyvinylidene fluoride, or combinations thereof.

[0051] Pore-forming agents may be included in the liquid electrolyte. Example pore-forming agents include polymers or surfactants that can modify a surface tension and viscosity of the liquid electrolyte, leading to changes in the morphology and porosity of a deposited layer, or of a surface of the current collector. The porosity of the deposited layer may be influenced by the presence of nanoparticles in the liquid electrolyte. The presence of gases in the liquid electrolyte can affect the porosity of the deposited layer. In some embodiments, modulating processing parameters such as voltage, current, or frequency of power supply can control the porosity of the deposited layer.

[0052] The liquid electrolyte is continuously fed and discharged from the chamber at a flow rate. The circulation of the liquid electrolyte helps in maintaining a temperature of bulk liquid electrolyte, in one instance, to no more than 100 °C.

[0053] The chamber further comprises at least one plasma anode. The plasma anode forms one-half of a pair of electrodes required for plasma generation in the chamber. The at least one plasma anode may be positioned along a vertical axis or a horizontal axis of the chamber. The at least one plasma anode may be stationary. In some embodiments, the at least one plasma anode is movable.

[0054] At step 104, a current collector is provided in the chamber. The current collector corresponds to a current collector of a battery on which the electroactive material is deposited to form the electrode. In another embodiment, the current collector corresponds to a metal that forms part of an

anode of an electrolytic capacitor, or a supercapacitor. In one embodiment, the current collector is a metal, a non-metal, a metal oxide, a polymer, or combination thereof.

[0055] The current collector and the at least one plasma anode are in relative motion with each other at a translation rate. In one embodiment, the current collector is operable to move in and out of the chamber in a continuous manner. In some embodiments, the at least one plasma anode is operable to move in and out of the chamber and is in relative motion with the current collector. In yet another embodiment, the relative motion between the at least one plasma anode and the current collector is achieved by moving both in and out of the chamber in a continuous manner. In one instance, the at least one plasma anode, the current collector or both may be mounted over rollers for continuous motion.

[0056] The current collector functions as a cathode, the other half of the pair of electrodes, required for plasma generation. In one embodiment, the translation rate may be controlled to control the plasma.

[0057] In some embodiments, providing the current collector in the chamber comprises providing a current collector that is pre-coated with a slurry comprising electroactive material.

[0058] At step 106, a voltage is applied across the at least one plasma anode and the current collector to generate plasma, wherein the plasma is generated in an initial plasma zone between a portion of the current collector, and the at least one plasma anode, and wherein the plasma modifies a surface of the portion of the current collector in the initial plasma zone. The voltage is applied using a DC (Direct Current) power supply. A constant, steady voltage is required for stable, continuous plasma generation. Inherent variations in frequency of the DC supply are minimized by modulating the frequency to achieve the steady voltage.

[0059] The relative motion of the at least one plasma anode and the current collector combined with the frequency of the DC power supply results in a high frequency on and off plasma of short timescale of the order of picoseconds to nanoseconds. As the plasma is generated for a short timescale it results in surface activation of the current collector, electroactive material, and/or additives. The plasma may penetrate a surface of the current collector, additives and/or the electroactive material to a depth in a range of 5 to 10 nanometers to modify the surface. The activation of the surface, in one instance, enhances surface roughness or morphology of the surface that may promote adhesion or mechanical bond formation. The plasma promotes generation of ion and/or radicals of the liquid electrolyte comprising additives and/or the electroactive material that may assist in mechanical bonding or adhesion of the ions and/or radicals on the surface of the current collector.

[0060] The surface of the portion of the current collector in the initial plasma zone is exposed to plasma for very short timescales. The surface modification in one instance, removes impurities from the surface of the current collector. In another embodiment, surface modification comprises removing undesirable oxides, sulfides, or nitrides from the surface of a metal current collector. In yet another embodiment, modifying the surface comprises modifying a morphology of the surface of the current collector.

[0061] In embodiments, where the liquid electrolyte comprises the electroactive material, the electrolytic plasma induces mechanical bonding between particles and/or molecules of the electroactive material, and between particles and/or molecules of the electroactive material and portion of the current collector to form the layer.

[0062] In embodiments, where the current collector is pre-coated with a slurry comprising the electroactive material, surface modification results in layer formation on the current collector, and the layer is devoid of any binders included in the slurry. The pre-coated current collector may be dried before plasma treatment. In one embodiment, the current collector is dried by providing an infrared source.

[0063] The plasma may be controlled by adjusting plasma parameters. The plasma parameters, include but are not limited to, composition of the liquid electrolyte, the flow rate, the voltage applied, composition of the current collector, and the translation rate. The plasma parameters are controlled during the process as these parameters are interdependent and dynamic. For example, as a layer is deposited over the current collector, the composition of the current collector changes, and as a result conductivity of the resulting current collector changes, and hence a voltage that has to be applied needs to be adjusted. As will be appreciated, the present disclosure by controlling plasma parameters ensures that plasma results only in mechanical bonding, without destroying a structure or chemical nature of particles and/or molecules of the electroactive material. As only mechanical bonds are formed on electrolytic plasma deposition, the inventive process is chemistry agnostic, and hence any material may be deposited using the disclosed process.

[0064] At step 108, a next portion of the current collector is positioned to a next plasma zone by moving the at least one plasma anode, the current collector, or both to modify a surface of the next portion of the current collector. The step 108 is repeated along a dimension of the current collector to obtain a treated current collector, and wherein a temperature of bulk liquid electrolyte in the chamber is not more than 100 °C during the process.

[0065] To obtain the continuous process, the current collector, the at least one anode, or both are moved which moves the initial plasma zone to the next plasma zone and thereby to the next portion of the current collector to modify the surface of the next portion. The step 108, is repeated along a dimension of the current collector. In one embodiment, the dimension corresponds to a length of the current collector. By placing the at least one plasma anode on both sides of a current collector, surface of both sides of the current collector may be modified during a single pass through the chamber.

[0066] During the process, a temperature of bulk liquid electrolyte in the chamber is not more than 100 °C.

[0067] The treated current collector, in one embodiment, comprises a cleaned current collector which may be used for depositing electroactive material over it to form the electrode. In another embodiment, the treated current collector is a current collector comprising a modified surface morphology.

[0068] In embodiments, where the liquid electrolyte comprises the electroactive material, performing step 108, forms a continuous layer over the current collector by mechanically bonding the electroactive material to a surface of the current collector. The treated current collector is an electrode where the electroactive material has been deposited as the continuous layer using the process.

[0069] The continuous layer has a thickness in a range of 0.05 microns to 20 microns on a single pass of the current collector through the chamber.

[0070] The continuous layer has a porosity in a range of 0.1 % to 80%.

[0071] A particular advantage of the process is the treatment of the current collector, or fabrication of electrodes does not require energy-intensive or expensive equipment such as clean rooms, or vacuum conditions, unlike commercial processes. The process is conducted in a closed liquid electrolyte system at atmospheric pressure and room temperature.

[0072] Commercial slurry-based deposition requires binders, that are dead-weight to battery and critically affect specific capacity. As used herein, the term “specific capacity” corresponds to an amount of electric charge (milliampere hours (mAh)) a material can deliver per gram of the material and is expressed as mAh per gram (mAh/g). Due to elimination of binders in electrodes, higher electroactive material loading may be achieved which may translate to higher specific capacity when compared to electrodes having binders. The mechanical bonding of the electroactive material to the current collector of the present disclosure provides for an electrode that is mechanically more stable than electrodes having

binders. Improved mechanical stability minimizes disintegration and delamination of the electroactive material during operation thus extending a life of the device.

[0073] The process substantially reduces or eliminates solvents, typically associated with solvent-based wet slurry methods. Moreover, the process does not require any drying time.

[0074] It is a particular advantage of the process that the electroactive material, or the additives may be dispersed in the liquid electrolyte thus widening the choice of materials that may be utilized in the process. Nanostructured or microstructured material may be used without losing its morphology.

[0075] In yet another embodiment, a method for fabricating a battery is provided. The method comprises providing a chamber filled with a first electrolyte and comprising at least one plasma anode. The first electrolyte is continuously fed and discharged from the chamber at a flow rate, and wherein the first electrolyte comprises a first electroactive material, at step (i). At step (ii), a current collector is provided in the chamber, wherein the current collector and the at least one plasma anode are in relative motion with each other at a translation rate, and wherein the current collector, or the at least one plasma anode, or both is operable to move in and out of the chamber in a continuous manner. A voltage is applied across the at least one plasma anode and the current collector to generate plasma, wherein the plasma is generated in an initial plasma zone between a portion of the current collector and the at least one plasma anode, and wherein the plasma induces mechanical bonding of the first electroactive material over the portion of the current collector to form a layer, at step (iii). At step (iv) a next portion of the current collector is positioned to a next plasma zone by moving the at least one plasma anode, the current collector, or both, to extend the layer of the first electroactive material on the next portion of the current collector and repeating this step along a dimension of the current collector to form a continuous layer on the current collector to obtain a first electrode. At step (v), the steps (i) to (iv) are repeated with the first electrode and a second electrolyte, wherein the second electrolyte comprises solid-state electrolyte material to deposit solid-state electrolyte material on a surface of the first electrode. The solid-state electrolyte material mechanically bonds to the surface of the first electrode to form a solid-state electrolyte bonded electrode. At step (vi), the steps (i) to (iv) are repeated with the solid-state electrolyte bonded electrode and a third electrolyte. The third electrolyte comprises a second electroactive material which is mechanically bonded to the surface of the solid-state electrolyte bonded electrode to form a battery. The battery comprises the first electrode, solid-state electrolyte, and the second electrode. The “first electrode” and the “second electrode” corresponds to an anode or a cathode of the battery.

[0076] A temperature of bulk first electrolyte, or bulk second electrolyte in the chamber is not more than 100 °C.

[0077] The current collector is a metal, a non-metal, a metal oxide, a polymer, or a combination thereof.

[0078] The first electrolyte and the second electrolyte, independent of each other, are water-based, solvent-based, or ionic-liquid-based. Non-limiting examples of solvents that may be used in solvent-based electrolytes include alcohols, ethanol, methanol, acetonitrile, dimethyl sulphoxide (DMSO), N,N-dimethylformamide (DMF), ethylene carbonate, propylene carbonate or combinations thereof. Examples of ionic liquids include, but are not limited to, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, 1-butyl-3-methylimidazolium hexafluorophosphate, 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, pyridinium-based ionic liquids or combinations thereof.

[0079] The first electroactive material and the second electroactive material, independent of each other, comprises metal, metal salts, non-metals, non-metal salts, polymers, donor-acceptor organic molecules, or combinations thereof. Example electroactive materials include, but are not limited to, oxides, nitrides, oxynitrides, sulphates, phosphates, and sulphide salts of single metals, or mixed metals, or non-metals. The metal comprises lithium, sodium, titanium, aluminum, tin, zirconium, yttrium, magnesium, sodium, copper, niobium, nickel, manganese, cobalt, and iron. Non-metals include carbonaceous material, sulphur, boron, and silicon. As used herein, the term “carbonaceous material” includes carbon-based materials such as graphite, carbon black, graphene oxide, reduced-graphene oxide, carbon fibers, porous carbon, carbon nanotubes, fullerene, graphene, activated carbon, carbon black, amorphous carbon, soft carbon, hard carbon, or combinations thereof. Non-limiting examples of active material include lithium metal oxides, lithium mixed metal oxides, lithium phosphates, lithium oxynitride, lithium titanate, lithium mixed metal phosphates, lithium nitride, lithium sulphide, sodium metal oxides, sodium mixed metal oxides, sodium phosphates, sodium mixed metal phosphates, silica, silicon, metal alloys, chalcogenides, transition metal oxides, metal sulphides, metal nitrides, carbon nanotubes, graphite, graphene, or combinations thereof. Example electroactive material for a lithium-ion battery includes lithium metal oxides such as lithium manganese oxide (LMO), lithium nickel cobalt aluminium oxide (Li-NCA), lithium nickel manganese cobalt oxide (Li-NMC), lithium cobalt oxide (LCO), lithium nickel oxide (LNO), lithium nickel manganese oxide (LNMO), lithium nickel cobalt manganese oxide (LNCM), lithium iron phosphate (LFP), lithium manganese phosphate (LMP), and lithium cobalt phosphate (LCP). Non-limiting examples of polymers include polyvinylidene fluoride

(PVDF), polyacrylic acid (PAA), perfluoroalkoxy alkanes (PFA), polythiophene, polypyrrole, polyacetylene, poly(tetramethylpiperidinyloxy methacrylate) (PTMA), or combinations thereof.

[0080] The battery may further include a separator disposed between the first electrode and the second electrode. The separator separates the first electrode and the second electrode to avoid shorting of electrodes. In one embodiment, the separator is deposited over the first electrode, or the solid-state electrolyte bonded electrode by following the process as described in FIG.1. In another embodiment, a stand-alone separator may be provided in the chamber which is plasma treated to mechanically bond to a surface of the first electrode, the second electrode or on the surface of the solid-state electrolyte.

[0081] Example separator includes, but are not limited to, glass, ceramic, polymer, or combinations thereof.

[0082] Example solid-state electrolyte material includes lithium phosphorous oxynitride, lithium garnet ceramics, sulfide-based lithium compounds, polymer-based electrolytes, polyethylene oxide-based electrolytes, poly(diallyldimethylammonium) (PDADMA), or combinations thereof. In some embodiments, the solid-state electrolyte separates the anode and the cathode, and in such battery designs, a separator is absent.

[0083] FIG. 2 is a schematic diagram of a plasma apparatus 200 for continuous fabrication of an electrode of an electrochemical device, in accordance with an embodiment of the disclosure. The plasma apparatus 200 comprises a chamber 202 and a DC supply 204. The plasma apparatus 200 is also otherwise termed as a “plasma printer”.

[0084] The chamber 202 is filled with an electrolyte 206. The electrolyte is circulated in the chamber 202 and fed in through an inlet 208 and discharged through an outlet 210 at a flow rate. A set of at least one plasma anode 212 is disposed in the chamber 202. The at least one plasma anode 212 is optionally operable to move in and out of the chamber 202. In the illustrated embodiment, the set of at least one plasma anode 212 is placed parallel to each other. A current collector 214 is disposed in the chamber 202 at a distance from the at least one plasma anode 212, wherein the current collector is in relative motion to the at least one plasma anode at a translation rate. The distance between the current collector (214) and the at least one anode (212) is adjusted for stable plasma generation. The current collector 214 is optionally operable to move in and out of the chamber 202. In a roll-to-roll process as illustrated in FIG.2, the current collector 214 is introduced in chamber 202 via rollers 220, and after electrolytic plasma treatment a treated current collector 216, or an electrode (216) is taken out via rollers

220. The current collector 214, in this embodiment, is sandwiched between the set of at least one plasma anode 212 so that both surfaces of the current collector 214 are treated.

[0085] The DC supply 204 applies a voltage across the at least one plasma anode 212 and the current collector 214. On application of the voltage, a plasma is generated which induces mechanical bonding of the electroactive material on a surface of the current collector 214 to form a layer. The apparatus may be used for surface modification of the current collector 214, as described previously. The surface modification includes cleaning the surface, removing any impurities, or changing a morphology of the surface of the current collector (214).

[0086] By moving the current collector 214 on rollers 220, a next portion of the current collector falls into a next plasma zone and the process is repeated till both surfaces of the current collector 214 are completely coated to form a continuous layer on the current collector 214 to form the coated current collector 216. The coated current collector 216, or the electrode 216 is taken out from the chamber 202, in a single pass. In one embodiment, the coated current collector 216 may be taken to the chamber 202 to be coated over to complete a second pass and this process can be repeated a number of times to obtain a thicker coating. Alternately, a set of apparatus 200 may be set up in series, the coated current collector 216 is fed through a second apparatus to form a thicker layer. In another embodiment, the second apparatus may have a different electrolyte to form a coating of a second electroactive material over the coated current collector 216, where it is coated with the second electroactive material to form a graded multi-layer.

[0087] The plasma parameters, include but are not limited to, composition of the liquid electrolyte, the flow rate, the voltage applied, composition of the current collector, the translation rate, or combinations thereof.

[0088] The plasma apparatus 200 is customizable and can be tailored from a table-top system in laboratories to large-scale system for use in manufacturing. A series of plasma apparatus 200 may be combined to fabricate treated current collector, electrodes, or solid-state batteries.

[0089] Commercially, electrolytic plasma has been used for metal cleaning, or depositing oxide layers over metals. However, utilization of electrolytic plasma has been quite limited. This is because controlling plasma and achieving precise control over the electrolysis process is quite challenging, as variations in temperature, pressure, or plasma composition can critically affect an outcome leading to inconsistent results. Further, plasma treatment involves complex processes and intricate set-ups.

[0090] A continuous process for fabricating binder-free electrodes and solid-state batteries has been disclosed for the first time. As described, with respect to FIG. 1, the relative motion of the at least one plasma anode and the current collector combined with the frequency of the DC power supply results in a high frequency on and off plasma of short timescale of the order of picoseconds to nanoseconds. As the plasma is generated for a short timescale it results in surface activation of the current collector, electroactive material, and/or additives.

[0091] The coated current collector of the disclosure includes a layer comprising desired material, that is chemistry-agnostic. A morphology, thickness, or porosity of the layer can be varied as desired by adjusting plasma parameters.

EXAMPLES

The below example has been provided for preparation of electrodes

[0092] Electrode samples were fabricated by electrolytic plasma deposition of an electroactive material comprising graphene, tin, and silicon on various current collectors. A steel substrate was used as the current collector to form Sample 1. Sample 2 had copper foil as the current collector. Aluminum foil was used as the current collector in Sample 3.

[0093] A plasma apparatus, as shown in FIG.2, was used for electrolytic plasma deposition using a water-based liquid electrolyte. The liquid electrolyte included metal salts and conductive carbon to enhance conductivity of the liquid electrolyte. The solid electroactive materials were introduced as dispersions of graphene, silicon and tin in the liquid electrolyte at concentrations in weight percent of 45 %, 45% and 10%, respectively.

[0094] Plasma was generated on application of voltage across an anode of the plasma apparatus and the current collector to deposit electroactive material on the current collectors, namely steel, copper and aluminum. The electroactive material deposition resulted in the formation of continuous layers or coating over the current collectors to form Sample 1, Sample 2, and Sample 3, respectively. The electroactive layers were found to be mechanically-bonded to the surfaces of the current collector.

[0095] The conductivity of Samples 1 to 3 was found to be very similar to that of the current collectors showing well-formed layers providing low resistance to conduction of electric current.

[0096] The continuous layers of Sample 1, Sample 2, and Sample 3 were characterized using Atomic force microscopy (AFM) to assess surface smoothness of the layers. AFM revealed surface roughness of less than 50 nanometers on a 20 square micron area for Samples 1 to 3.

[0097] Raman spectroscopic studies were carried out on Samples 1 to 3. Sample 1 had a thicker coating when compared to Samples 2 and 3, in a range of 80 to 150 microns with graphene features as small as 2 microns. Even though the process parameters were similar, changes in the composition of the current collector such as the material of the current collector might have resulted in the difference in coating thickness between Samples 1 to 3.

[0098] Scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX) analysis was performed on Sample 1 to analyze layer composition, at various positions within the layer. FIG. 3 is an image 300 of SEM-EDX at various positions, where 302 corresponds to bulk layer, 304 corresponds to steel substrate, 306 corresponds to interface between the bulk layer and the layer, and 308 corresponds to an interface between the steel substrate and the layer. Composition of carbon, oxygen, iron and manganese detected at these positions is as shown in Table 1. The presence of iron and manganese detected is most likely from the steel substrate. Within the layer, concentration of iron, and manganese varies from a maximum at steel substrate to a minimum at bulk layer, within less than 100 microns distance. This confirms that the inventive plasma printing process is a surface phenomenon without changing the material constituting the current collector or the electroactive material.

	Carbon relative percentage	Oxygen relative percentage	Iron relative percentage	Manganese relative percentage
Bulk layer (302)	80	19	<1	0
Steel (304)	6	0	93	0.6
Interface between bulk layer and interface (306)	28	0	64	0.3
Interface between steel and layer (308)	7	0	92	0

Table 1

[0099] The image 300 and the composition, as shown in Table 1, revealed intimate contact between the graphene and the steel current collector due to mechanical bonding on electrolytic plasma deposition. An anode of a lithium battery is often coated with a primer coating (such as an interfacial layer) to enhance bonding between electroactive material and current collector. As shown in this Example, electrolytic plasma deposition eliminates the need for such primer coating. Using the inventive method graphene may be coated over a metal, over which electroactive material may be deposited.

[00100] Samples 1 to 3 were incorporated as anodes in lithium half-cells to evaluate battery performance. The sample exhibited high coulombic efficiency in a range of 65% to 98 %. As used herein, the term “coulombic efficiency” is defined as the ratio of discharge capacity of the anode material to the theoretical discharge capacity derived from electrochemical calculations involving Faraday’s law. The lithium half-cells formed using Samples 1 to 3 displayed expected patterns of cell cycling for a new material. The terms “cycle life” or “cycling” refer to number of discharge-charge cycles the battery can undergo before it fails to meet the specific performance criteria. For example, electric vehicle (EV) batteries have a cycle life of more than 2000 times.

[00101] It is to be understood that the above description is intended to be illustrative, and not restrictive. Furthermore, many other embodiments will be apparent to those of skill in the art upon reading and understanding the above description. Although the present disclosure has been described with reference to specific embodiments, it will be recognized that the disclosure is not limited to the embodiments described, but can be practiced with modification and alteration within the scope of the appended claims.

CLAIMS

1. An electrode of an electrochemical device fabricated using a process, the process comprising steps of:
providing a chamber that is filled with a liquid electrolyte and comprising at least one plasma anode, wherein the liquid electrolyte comprises an electroactive material;

providing a current collector in the chamber, wherein the current collector and the at least one plasma anode are in relative motion with each other at a translation rate, and wherein the current collector, the at least one plasma anode, or both is operable to move in and out of the chamber in a continuous manner;

applying a voltage across the at least one plasma anode and the current collector to generate plasma, wherein the plasma is generated in an initial plasma zone between a portion of the current collector and the at least one plasma anode, and wherein the plasma induces mechanical bonding of the electroactive material to the portion of the current collector to form a layer;

positioning a next portion of the current collector to a next plasma zone by moving the at least one plasma anode, the current collector, or both to extend the layer of the electroactive material to the next portion of the current collector and repeating this step along a dimension of the current collector to form a continuous layer on the current collector to obtain the electrode, and wherein a temperature of bulk liquid electrolyte in the chamber is not more than 100 °C during the process.
2. The electrode as claimed in claim 1, wherein the electroactive material comprises metal, metal salts, non-metals, non-metal salts, polymers, donor-acceptor organic molecules, or combinations thereof.
3. The electrode as claimed in claim 2, wherein the electroactive material comprises lithium metal oxides, lithium mixed metal oxides, lithium phosphates, lithium mixed metal phosphates, sodium metal oxides, sodium mixed metal oxides, sodium phosphates, sodium mixed metal phosphates, silica, silicon, metals, metal oxides, metal sulphates, metal oxides, alloys, chalcogenides, transition metal oxides, metal sulphides, metal nitrides, carbon nanotubes, graphite, graphene, carbon black, fullerene, all kind of carbon and its composites or combinations thereof.

4. The electrode as claimed in claim 1, wherein the current collector is a metal, a non-metal, a metal oxide, a polymer, or a combination thereof.
5. The electrode as claimed in claim 1, wherein the continuous layer has a thickness in a range of 0.05 micrometer to 20 microns on a single pass of the current collector through the chamber.
6. The electrode as claimed in claim 1, wherein the continuous layer has a porosity in a range of 0.1 % to 80%.
7. The electrode as claimed in claim 1, wherein the continuous layer is multi-layered, and wherein the continuous layer comprises a single electroactive material or more than one electroactive material.
8. The electrode as claimed in claim 1, wherein the continuous layer is a graded layer, wherein a concentration of the electroactive material varies across a cross-section of the continuous layer.
9. The electrode as claimed in claim 1, wherein the current collector comprises copper, aluminum, or nickel, and wherein the electroactive material comprises graphite, porous carbon, carbon nanotubes, fullerene, graphene, activated carbon, carbon black, amorphous carbon, soft carbon, hard carbon, or combinations thereof.
10. The electrode as claimed in claim 1, wherein the current collector comprises aluminum, the electroactive material comprises graphene in combination with silicon or tin, and an additive comprising polyvinylidene fluoride.
11. The electrode as claimed in claim 1, wherein the current collector comprises carbon, and wherein the electroactive material comprises boron-doped carbon, boron nitride, boron carbide graphite, porous carbon, carbon nanotubes, fullerene, graphene, activated carbon, carbon black, amorphous carbon, soft carbon, hard carbon, or combinations thereof.
12. The electrode as claimed in claim 7, wherein the multi-layered continuous layer comprises a first layer over the current collector and a second layer over the first layer, wherein the current collector

comprises copper, steel, nickel or aluminum, wherein the first layer comprises graphene, and the second layer comprises silicon, tin, lithium or combinations thereof.

13. The electrode as claimed in claim 1, wherein the electrochemical device comprises a battery, a solid-state battery, an electrolytic capacitor, or a supercapacitor.

14. The electrode as claimed in claim 1, wherein the electrode is binder-free.

15. A continuous process for fabricating an electrode of an electrochemical device comprising steps of:

providing a chamber (102) that is filled with a liquid electrolyte and comprising at least one plasma anode, wherein the liquid electrolyte is continuously fed and discharged from the chamber at a flow rate, and wherein the liquid electrolyte comprises an electroactive material;

providing a current collector in the chamber (104), wherein the current collector and the at least one plasma anode are in relative motion with each other at a translation rate, and wherein the current collector, or the at least one plasma anode, or both is operable to move in and out of the chamber in a continuous manner;

applying a voltage across the at least one plasma anode and the current collector (106) to generate plasma, wherein the plasma is generated in an initial plasma zone between a portion of the current collector and the at least one plasma anode, and wherein the plasma induces mechanical bonding of the electroactive material over the portion of the current collector to form a layer;

positioning a next portion of the current collector (108) to a next plasma zone by moving the at least one plasma anode, the current collector, or both to extend the layer of the electroactive material on the next portion of the current collector and repeating this step along a dimension of the current collector to form a continuous layer on the current collector to obtain the electrode, and wherein a temperature of bulk liquid electrolyte in the chamber is not more than 100 °C during the process.

16. The continuous process as claimed in claim 15, wherein the liquid electrolyte comprises an additive, and wherein the additive comprises a metal, a metal oxide, a metal salt, a non-metal, a non-metal salt, a pro-electroactive material, a binder, a polymer, a pore-forming agent, or combinations thereof.

17. The continuous process as claimed in claim 15, wherein the electroactive material comprises metal, metal salts, non-metals, non-metal salts, polymers, donor-acceptor organic molecules, or combinations thereof.

18. The continuous process as claimed in claim 15, wherein the current collector is a metal, a metal oxide, a non-metal, a polymer, or combinations thereof.

19. The continuous process as claimed in claim 15, wherein providing the current collector in the chamber comprises providing a current collector that is pre-coated with an electroactive slurry.

20. The continuous process as claimed in claim 15, wherein the continuous layer has a thickness in a range of 0.05 to 20 microns on a single pass of the current collector through the chamber.

21. The continuous process as claimed in claim 15, wherein the continuous layer has a porosity in a range of 0.1 % to 80%.

22. The continuous process as claimed in claim 15, wherein plasma is controlled by adjusting a composition of the electrolyte, a composition of the current collector, the translation rate, the flow rate, voltage, or combinations thereof.

23. The continuous process as claimed in claim 15, wherein the process is a roll-to-roll process and the current collector is moved in and out of the chamber at a rate in a range of 1 to 400 meters per minute (m/min).

24. A method of fabricating a battery comprising steps of;

- i) providing a chamber that is filled with a first electrolyte and comprising at least one plasma anode, wherein the first electrolyte is continuously fed and discharged from the chamber at a flow rate, and wherein the first electrolyte comprises a first electroactive material;

- ii) providing a current collector in the chamber, wherein the current collector and the at least one plasma anode are in relative motion with each other at a translation rate, and wherein the current collector, or the at least one plasma anode, or both is operable to move in and out of the chamber in a continuous manner;
- iii) applying a voltage across the at least one plasma anode and the current collector to generate plasma, wherein the plasma is generated in an initial plasma zone between a portion of the current collector and the at least one plasma anode, and wherein the plasma induces mechanical bonding of the first electroactive material over the portion of the current collector to form a layer;
- iv) positioning a next portion of the current collector to a next plasma zone by moving the at least one plasma anode, the current collector, or both, to extend the layer of the first electroactive material on the next portion of the current collector and repeating this step along a dimension of the current collector to form a continuous layer on the current collector to obtain a first electrode;
- v) repeating steps (i) to (iv) with the first electrode and a second electrolyte, wherein the second electrolyte comprises solid-state electrolyte material to deposit solid-state electrolyte material on a surface of the first electrode, and wherein the solid-state electrolyte material is mechanically bonded to the surface of the first electrode to form a solid-state electrolyte bonded electrode; and
- vi) repeating steps (i) to (iv) with the solid-state electrolyte bonded electrode and a third electrolyte, wherein the third electrolyte comprises a second electroactive material to deposit the second electroactive material on a surface of the solid-state electrolyte bonded electrode, and wherein the second electroactive material is mechanically bonded to the surface of the solid-state electrolyte bonded electrode to form a battery, wherein the battery comprises the first electrode, solid-state electrolyte, and the second electrode; and wherein a temperature of bulk first electrolyte, or bulk second electrolyte in the chamber is not more than 100 °C.

25. The method as claimed in claim 24, wherein a separator is provided between the first electrode and the second electrode, wherein the separator comprises glass, ceramic, polymer, or combinations thereof.

26. The method as claimed in claim 24, wherein the current collector comprises a metal, a non-metal, a metal oxide, a polymer, or a combination thereof.

27. The method as claimed in claim 24, wherein the first electroactive material and the second electroactive material independently comprises metal, metal salts, non-metals, non-metal salts, polymers, donor-acceptor organic molecules, or combinations thereof.

28. The method as claimed in claim 24, wherein the solid-state electrolyte material comprises lithium phosphorous oxynitride, lithium garnet ceramics, sulfide-based lithium compounds, polymer-based electrolytes, polyethylene oxide-based electrolytes, or combinations thereof.

29. The method as claimed in claim 24, wherein the first electrode and the second electrode are binder-free.

30. A continuous process for treatment of a current collector of a battery comprising:
providing a chamber that is filled with a liquid electrolyte and comprising at least one plasma anode, wherein the liquid electrolyte is continuously fed and discharged from the chamber at a flow rate;
providing the current collector in the chamber, wherein the current collector and the at least one plasma anode are in relative motion with each other at a translation rate, and wherein the current collector, or the at least one plasma anode, or both is operable to move in and out of the chamber in a continuous manner;
applying a voltage across the at least one plasma anode and the current collector to generate plasma, wherein the plasma is generated in an initial plasma zone between a portion of the current collector and the at least one plasma anode, and wherein the plasma modifies a surface of the portion of the current collector in the initial plasma zone; and
positioning a next portion of the current collector to a next plasma zone by moving the at least one plasma anode, the current collector, or both to modify a surface of the next portion of the current collector and
repeating this step along a dimension of the current collector to obtain a treated current collector, and
wherein a temperature of bulk liquid electrolyte in the chamber is not more than 100 °C during the process.

31. The continuous process as claimed in claim 30, wherein the liquid electrolyte is water-based, solvent-based, or ionic liquid-based.

32. The continuous process as claimed in claim 30, wherein the liquid electrolyte comprises an additive, an electroactive material, or both.

33. The continuous process as claimed in claim 32, wherein the additive comprises a metal, metal oxide, metal salt, non-metals, non-metal salt, a pro-electroactive material, a binder, a polymer, or a pore-forming agent, or combinations thereof.

34. The continuous process as claimed in claim 32, wherein the additive, or the electroactive material is a gas, a solid, a liquid, or combinations thereof.

35. The continuous process as claimed in claim 32, wherein the liquid electrolyte comprises the electroactive material, and wherein modifying the surface of the current collector comprises forming a layer of the electroactive material that is mechanically bonded to the surface of the current collector.

36. The continuous process as claimed in claim 30, wherein the current collector is a metal, a metal oxide, a polymer, or combinations thereof.

37. The continuous process as claimed in claim 30, wherein providing the current collector in the chamber comprises providing a current collector that is pre-coated with an electroactive slurry.

38. The continuous process as claimed in claim 30, wherein modifying the surface comprises cleaning the surface of the current collector, or modifying a morphology of the surface of the current collector using plasma generated in the liquid electrolyte.

39. The continuous process as claimed in claim 30, wherein modifying the surface of the current collector is controlled by adjusting a composition of the electrolyte, a composition of the current collector, the translation rate, the voltage, the flow rate, or combinations thereof.

40. The continuous process as claimed in claim 30, wherein the process is a roll-to-roll process and the current collector is moved in and out of the chamber at a rate in a range of 1 to 400 meters per minute (m/min).

41. A treated current collector prepared according to the continuous process as claimed in claim 30.

42. A plasma apparatus for continuous fabrication of an electrode of an electrochemical device comprising:

a chamber (202) having an inlet (208) and an outlet (210) to circulate a liquid electrolyte (206) at a flow rate, wherein the chamber is filled with the liquid electrolyte (206), and wherein the liquid electrolyte (206) comprises an electroactive material;

at least one plasma anode (212) disposed in the chamber (202), and optionally operable to move in and out of the chamber (202);

a current collector (214) disposed in the chamber (202) at a distance from the at least one plasma anode (212), wherein the current collector (214) is in relative motion to the at least one plasma anode (212) at a translation rate, and wherein the current collector (214) is optionally operable to move in and out of the chamber (202); and

a DC supply (204) to apply a voltage across the current collector (214) and the at least one plasma anode (212) to generate a plasma, wherein the plasma generated induces mechanical bonding of the electroactive material on a surface of the current collector (214) to form the electrode (216), and wherein the plasma is controlled by adjusting a composition of the liquid electrolyte (206), a composition of the current collector (214), the translation rate, the flow rate, voltage, or combinations thereof.