

SOLID-STATE BATTERY

RELATED APPLICATION

[0001] The following application claims priority to U.S. Nonprovisional No. 16/359,707 filed March 20, 2019, U.S. Nonprovisional No. 16/359,725 filed March 20, 2019, U.S. Nonprovisional 16/359,733 filed March 20, 2019, U.S. Provisional No. 62/646,521 filed March 22, 2018, and U.S. Provisional No. 62/691,819 filed June 29, 2018, the disclosures of which are incorporated by reference in their entireties.

FIELD OF THE INVENTION

[0002] The present invention relates to a solid-state battery which includes a printable lithium composition.

BACKGROUND OF THE INVENTION

[0003] Lithium and lithium-ion secondary or rechargeable batteries have found use in certain applications such as in cellular phones, camcorders, and laptop computers, and even more recently, in larger power application such as in electric vehicles and hybrid electric vehicles. It is preferred in these applications that the secondary batteries have the highest specific capacity possible but still provide safe operating conditions and good cyclability so that the high specific capacity is maintained in subsequent recharging and discharging cycles.

[0004] Although there are various constructions for secondary batteries, each construction includes a positive electrode (or cathode), a negative electrode (or anode), a separator that separates the cathode and anode, an electrolyte in electrochemical communication with the cathode and anode. For secondary lithium batteries, lithium ions are transferred from the anode to the cathode through the electrolyte when the secondary battery is being discharged, i.e., used for its specific application. During the discharge process, electrons are collected from the anode and pass to the cathode through an external circuit. When the secondary battery is being charged, or recharged, the lithium ions are transferred from the cathode to the anode through the electrolyte.

[0005] Historically, secondary lithium batteries were produced using non-lithiated compounds having high specific capacities such as TiS_2 , MoS_2 , MnO_2 , and V_2O_5 , as the cathode active materials. These cathode active materials were coupled with a lithium metal anode. When the

secondary battery was discharged, lithium ions were transferred from the lithium metal anode to the cathode through the electrolyte. Unfortunately, upon cycling, the lithium metal developed dendrites that ultimately caused unsafe conditions in the battery. As a result, the production of these types of secondary batteries was stopped in the early 1990s in favor of lithium-ion batteries.

[0006] Lithium-ion batteries typically use lithium metal oxides such as LiCoO_2 and LiNiO_2 as cathode active materials coupled with an active anode material such as a carbon-based material. It is recognized that there are other anode types based on silicon oxide, silicon particles and the like. In batteries utilizing carbon-based anode systems, the lithium dendrite formation on the anode is substantially avoided, thereby making the battery safer. However, the lithium, the amount of which determines the battery capacity, is totally supplied from the cathode. This limits the choice of cathode active materials because the active materials must contain removable lithium. Also, delithiated products corresponding to Li_xCoO_2 , Li_xNiO_2 formed during charging and overcharging are not stable. In particular, these delithiated products tend to react with the electrolyte and generate heat, which raises safety concerns.

[0007] New lithium-ion cells or batteries are initially in a discharged state. During the first charge of lithium-ion cell, lithium moves from the cathode material to the anode active material. The lithium moving from the cathode to the anode reacts with an electrolyte material at the surface of the graphite anode, causing the formation of a passivation film on the anode. The passivation film formed on the graphite anode is a solid electrolyte interface (SEI). Upon subsequent discharge, the lithium consumed by the formation of the SEI is not returned to the cathode. This results in a lithium-ion cell having a smaller capacity compared to the initial charge capacity because some of the lithium has been consumed by the formation of the SEI. The partial consumption of the available lithium on the first cycle reduces the capacity of the lithium-ion cell. This phenomenon is called irreversible capacity and is known to consume about 10% to more than 20% of the capacity of a lithium ion cell. Thus, after the initial charge of a lithium-ion cell, the lithium-ion cell loses about 10% to more than 20% of its capacity.

[0008] One solution has been to use stabilized lithium metal powder to pre-lithiate the anode. For example, lithium powder can be stabilized by passivating the metal powder surface with carbon dioxide such as described in U.S. Pat. Nos. 5,567,474, 5,776,369, and 5,976,403, the disclosures of which are incorporated herein in their entireties by reference. The CO_2 -passivated lithium metal powder can be used only in air with low moisture levels for a limited period of time before the lithium metal content decays because of the reaction of the lithium metal and air. Another solution is to apply a coating such as fluorine, wax, phosphorus or a

polymer to the lithium metal powder such as described in U.S. Patent Nos. 7,588,623, 8,021,496, 8,377,236 and U.S. Patent Publication No. 2017/0149052, for example.

[0009] There, however, remains a need for a solid-state battery having lithiated or prelithiated components for increased energy density and improved safety and manufacturability.

SUMMARY OF THE INVENTION

[0010] To this end, the present invention provides a solid-state battery with one or more components prelithiated, or lithiated with a printable lithium composition. A solid-state battery comprising the printable lithium composition will have increased energy density and improved safety and manufacturability.

[0011] The printable lithium composition of the present invention comprises a lithium metal powder, a polymer binder, wherein the polymer binder is compatible with the lithium powder, and a rheology modifier compatible with the lithium powder and the polymer binder. A solvent may be included in the printable lithium composition, wherein the solvent is compatible with the lithium powder and compatible with (e.g., able to form suspension or to dissolve in) the polymer binder. The solvent may be included as a component during the initial preparation of the printable lithium composition or added later after the printable lithium composition is prepared.

BRIEF DESCRIPTION OF THE DRAWINGS

[0012] FIG. 1 is a schematic of a solid-state battery according to one embodiment of the present invention;

[0013] FIG. 2 is a temperature and pressure profile for the reactivity testing of SLMP/styrene butadiene/toluene printable lithium composition; and

[0014] FIG. 3 is a plot showing the cycle performance for a pouch cell with printable lithium derived thin lithium film as the anode vs. commercial thin lithium foil.

DETAILED DESCRIPTION OF THE INVENTION

[0015] The foregoing and other aspects of the present invention will now be described in more detail with respect to the description and methodologies provided herein. It should be appreciated that the invention can be embodied in different forms and should not be construed as limited to the embodiments set forth herein. Rather, these embodiments are provided so that

this disclosure will be thorough and complete, and will fully convey the scope of the invention to those skilled in the art.

[0016] The terminology used in the description of the invention herein is for the purpose of describing particular embodiments only and is not intended to be limiting of the invention. As used in the description of the embodiments of the invention and the appended claims, the singular forms "a", "an" and "the" are intended to include the plural forms as well, unless the context clearly indicates otherwise. Also, as used herein, "and/or" refers to and encompasses any and all possible combinations of one or more of the associated listed items.

[0017] The term "about," as used herein when referring to a measurable value such as an amount of a compound, dose, time, temperature, and the like, is meant to encompass variations of 20%, 10%, 5%, 1%, 0.5%, or even 0.1% of the specified amount. Unless otherwise defined, all terms, including technical and scientific terms used in the description, have the same meaning as commonly understood by one of ordinary skill in the art to which this invention belongs.

[0018] As used herein, the terms "comprise," "comprises," "comprising," "include," "includes" and "including" specify the presence of stated features, integers, steps, operations, elements, and/or components, but do not preclude the presence or addition of one or more other features, integers, steps, operations, elements, components, and/or groups thereof.

[0019] As used herein, the term "consists essentially of" (and grammatical variants thereof), as applied to the compositions and methods of the present invention, means that the compositions/methods may contain additional components so long as the additional components do not materially alter the composition/method. The term "materially alter," as applied to a composition/method, refers to an increase or decrease in the effectiveness of the composition/method of at least about 20% or more.

[0020] All patents, patent applications and publications referred to herein are incorporated by reference in their entirety. In case of a conflict in terminology, the present specification is controlling.

[0021] Referring now to Figure 1, a solid-state battery 10 comprising an anode 12, a cathode 14 and a solid electrolyte 16 is provided in accordance with one embodiment of the present invention. The solid-state battery may further include an anode current collector 20 and a cathode current collector 22. A printable lithium composition is applied or deposited to a current collector, electrode and/or solid electrolyte of the solid-state battery. For example, the printable lithium composition may be used to form a monolithic lithium metal anode of various thicknesses and widths for use in a solid-state battery, including solid-state batteries as

described in US Patent Nos. 8,252,438 and 9,893,379 and incorporated herein by reference in their entireties. In yet another embodiment, the printable lithium composition may be applied or deposited so as to form a solid electrolyte for a solid-state battery, and includes combining the ink composition with a polymer or ceramic material to form a solid electrolyte. The printable lithium composition comprises a lithium metal powder, one or more polymer binders, one or more rheology modifiers and may further include a solvent or co-solvent.

[0022] The printable lithium composition may be applied a current collector, electrode or solid electrolyte by various methods, including extruding, coating, printing, painting, dipping, and spraying as disclosed in US Application No. _____ (Attorney Matter ID 073396.1183, filed concurrently with this application and hereby incorporated by reference in its entirety). For example, the anode may be lithiated or prelithiated by printing the printable lithium composition onto the anode or a current collector, where the thin lithium film with controlled thickness and width could be formed, or coating the anode with the printable lithium composition.

[0023] In one embodiment, the printable lithium composition may be used to prelithiate a solid electrolyte as described in US Patent No. 7,914,930 herein incorporated by reference in its entirety. One example of a solid-state secondary battery may include a positive electrode capable of electrochemically absorbing and desorbing lithium; a negative electrode capable of electrochemically absorbing and desorbing lithium, the negative electrode including an active material layer that comprises an active material, the active material layer being carried on a current collector; and a non-aqueous electrolyte. A method includes the steps of: reacting lithium with the active material of the negative electrode by bringing the printable lithium composition into contact with a surface of the active material layer of the negative electrode; and thereafter combining the negative electrode with the positive electrode to form an electrode assembly.

[0024] As disclosed in US Application No. _____ (Attorney Matter ID. 073396.1116, filed concurrently with this application) and hereby incorporated by reference in its entirety, the printable lithium composition comprises a lithium metal powder, a polymer binder, a rheology modifier and may further include a solvent. The polymer binder may be compatible with the lithium metal powder. The rheology modifier may be compatible with the lithium metal powder and the polymer binder. The solvent may be compatible with the lithium metal powder and with the polymer binder.

[0025] The lithium metal powder may be in the form of a finely divided powder. The lithium metal powder typically has a mean particle size of less than about 80 microns, often less than about 40 microns and sometimes less than about 20 microns. The lithium metal powder may be

a low pyrophoricity stabilized lithium metal power (SLMP®) available from FMC Lithium Corp. The lithium metal powder may also include a substantially continuous layer or coating of fluorine, wax, phosphorus or a polymer or the combination thereof (as disclosed in U.S. Pat. Nos. 5,567,474, 5,776,369, and 5,976,403). Lithium metal powder has a significantly reduced reaction with moisture and air.

[0026] The lithium metal powder may also be alloyed with a metal. For example, the lithium metal powder may be alloyed with a Group I-VIII element. Suitable elements from Group IB may include, for example, copper, silver, or gold. Suitable elements from Group IIB may include, for example, zinc, cadmium, or mercury. Suitable elements from Group IIA of the Periodic Table may include beryllium, magnesium, calcium, strontium, barium, and radium. Elements from Group IIIA that may be used in the present invention may include, for example, boron, aluminum, gallium, indium, or thallium. Elements from Group IVA that may be used in the present invention may include, for example, carbon, silicon, germanium, tin, or lead. Elements from Group VA that may be used in the present invention may include, for example, nitrogen, phosphorus, or bismuth. Suitable elements from Group VIIB may include, for example, nickel, palladium, or platinum.

[0027] The polymer binder is selected so as to be compatible with the lithium metal powder. “Compatible with” or “compatibility” is intended to convey that the polymer binder does not violently react with the lithium metal powder resulting in a safety hazard. The lithium metal powder and the polymer binder may react to form a lithium–polymer complex, however, such complex should be stable at various temperatures. It is recognized that the amount (concentration) of lithium and polymer binder contribute to the stability and reactivity. The polymer binder may have a molecular weight of about 1,000 to about 8,000,000, and often has a molecular weight of 2,000,000 to 5,000,000. Suitable polymer binders may include one or more of poly(ethylene oxide), polystyrene, polyisobutylene, natural rubbers, butadiene rubbers, styrene-butadiene rubber, polyisoprene rubbers, butyl rubbers, hydrogenated nitrile butadiene rubbers, epichlorohydrin rubbers, acrylate rubbers, silicon rubbers, nitrile rubbers, polyacrylic acid, polyvinylidene chloride, polyvinyl acetate, ethylene propylene diene termonomer, ethylene vinyl acetate copolymer, ethylene-propylene copolymers, ethylene-propylene terpolymers, polybutenes,. The binder may also be a wax.

[0028] The rheology modifier is selected to be compatible with the lithium metal powder and the polymer binder. The rheology modifier provides rheology properties such as viscosity. The rheology modifier may also provide conductivity, improved capacity and/or improved stability/safety depending on the selection of the rheology modifier. To this end, the rheology

modifier may be the combination of two or more compounds so as to provide different properties or to provide additive properties. Exemplary rheology modifiers may include one or more of carbon black, carbon nanotubes, graphene, silicon nanotubes, graphite, hard carbon and mixtures, fumed silica, titanium dioxide, zirconium dioxide and other Group IIA, IIIA, IVB, VB and VIA elements/compounds and mixtures or blends thereof.

[0029] Solvents compatible with lithium may include acyclic hydrocarbons, cyclic hydrocarbons, aromatic hydrocarbons, symmetrical ethers, unsymmetrical ethers, cyclic ethers, alkanes, sulfones, mineral oil, and mixtures, blends or cosolvents thereof. Examples of suitable acyclic and cyclic hydrocarbons include n-hexane, n-heptane, cyclohexane, and the like. Examples of suitable aromatic hydrocarbons include toluene, ethylbenzene, xylene, isopropylbenzene (cumene), and the like. Examples of suitable symmetrical, unsymmetrical and cyclic ethers include di-n-butyl ether, methyl t-butyl ether, tetrahydrofuran, glymes and the like. Commercially available isoparaffinic synthetic hydrocarbon solvents with tailored boiling point ranges such as Shell Sol® (Shell Chemicals) or Isopar® (Exxon) are also suitable.

[0030] The polymer binder and solvents are selected to be compatible with each other and with the lithium metal powder. In general, the binder or solvent should be non-reactive with the lithium metal powder or in amounts so that any reaction is kept to a minimum and violent reactions are avoided. The binder and solvent should be compatible with each other at the temperatures at which the printable lithium composition is made and will be used. Preferably the solvent (or co-solvent) will have sufficient volatility to readily evaporate from the printable lithium composition (e.g., in slurry form) to provide drying of the printable lithium composition (slurry) after application.

[0031] The components of the printable lithium composition may be mixed together as a slurry or paste to have a high concentration of solid. Thus the slurry/paste may be in the form of a concentrate with not all of the solvent necessarily added prior to the time of depositing or applying. In one embodiment, the lithium metal powder should be uniformly suspended in the solvent so that when applied or deposited a substantially uniform distribution of lithium metal powder is deposited or applied. Dry lithium powder may be dispersed such as by agitating or stirring vigorously to apply high sheer forces.

[0032] In another embodiment, a mixture of the polymer binder, rheology modifier, coating reagents, and other potential additives for the lithium metal powder may be formed and introduced to contact the lithium droplets during the dispersion at a temperature above the lithium melting point, or at a lower temperature after the lithium dispersion has cooled such as described in U.S. Patent No. 7,588,623 the disclosure of which is incorporated by reference in

its entirety. The thusly modified lithium metal may be introduced in a crystalline form or in a solution form in a solvent of choice. It is understood that combinations of different process parameters could be used to achieve specific coating and lithium powder characteristics for particular applications.

[0033] Conventional pre-lithiation surface treatments require compositions having very low binder content and very high lithium; for example, see US Patent No. 9,649,688 the disclosure of which is incorporated by reference in its entirety. However, embodiments of the printable lithium composition in accordance with the present invention can accommodate higher binder ratios, including up to 20 percent on dry basis. Various properties of the printable lithium composition, such as viscosity and flow, may be modified by increasing the binder and modifier content up to 50% dry basis without loss of electrochemical activity of lithium. Increasing the binder content facilitates the loading of the printable lithium composition and the flow during printing. For example, in one embodiment the printable lithium composition comprises about 70% lithium metal powder and about 30% polymer binder and rheology modifiers. In another embodiment, the printable lithium composition may comprise about 85% lithium metal powder and about 15% polymer binder and rheology modifiers.

[0034] An important aspect of printable lithium compositions is the rheological stability of the suspension. Because lithium metal has a low density of 0.534 g/cc, it is difficult to prevent lithium powder from separating from solvent suspensions. By selection of lithium metal powder loading, polymer binder and conventional modifier types and amounts, viscosity and rheology may be tailored to create the stable suspension of the invention. A preferred embodiment shows no separation at greater than 90 days. This can be achieved by designing compositions with very high zero shear viscosity in the range of 1×10^4 cps to 1×10^7 cps. It is however very important to the application process that the compositions, when exposed to shear, exhibit viscosity characteristics in the ranges claimed.

[0035] The resulting printable lithium composition preferably may have a viscosity at $10s^{-1}$ about 20 to about 20,000 cps, and often a viscosity of about 100 to about 10,000 cps. At such viscosity, the printable lithium composition is a flowable suspension or gel. The printable lithium composition preferably has an extended shelf life at room temperature and is stable against metallic lithium loss at temperatures up to 60°C, often up to 120°C, and sometimes up to 180°C. The printable lithium composition may separate somewhat over time but can be placed back into suspension by mild agitation and/or application of heat.

[0036] In one embodiment, the printable lithium composition comprises on a solution basis about 5 to 50 percent lithium metal powder, about 0.1 to 20 percent polymer binder, about 0.1 to

30 percent rheology modifier and about 50 to 95 percent solvent. In one embodiment, the printable lithium composition comprises on a solution basis about 15 to 25 percent lithium metal powder, about 0.3 to 0.6 percent polymer binder having a molecular weight of 4,700,000, about 0.5 to 0.9 percent rheology modifier, and about 75 to 85 percent solvent. Typically, the printable lithium composition is applied or deposited to a thickness of about 50 microns to 200 microns prior to pressing. After pressing, the thickness can be reduced to between about 1 to 50 microns. Examples of pressing techniques are described, for example, in US Patent Nos. 3,721,113 and 6,232,014 which are incorporated herein by reference in their entireties.

[0037] In one embodiment, the printable lithium composition is deposited or applied to an active anode material on a current collector namely to form a prelithiated anode. Suitable active anode materials include graphite and other carbon-based materials, alloys such as tin/cobalt, tin/cobalt/carbon, silicon-carbon, variety of silicone/tin based composite compounds, germanium-based composites, titanium based composites, elemental silicon, and germanium. The anode materials may be a foil, mesh or foam. Application may be via spraying, extruding, coating, printing, painting, dipping, and spraying, and are described in co-pending US Patent Publication No. _____ (Attorney Matter 073396.1183), filed concurrently herewith and incorporated herein by reference in its entirety.

[0038] In one embodiment, the active anode material and the printable lithium composition are provided together and extruded onto the current collector (e.g., copper, nickel, etc.). For instance, the active anode material and printable lithium composition may be mixed and co-extruded together. Examples of active anode materials include graphite, graphite-SiO, graphite-SnO, SiO, hard carbon and other lithium ion battery and lithium ion capacitor anode materials. In another embodiment, the active anode material and the printable lithium composition are co-extruded to form a layer of the printable lithium composition on the current collector. The deposition of the printable lithium composition including the above extrusion technique may include depositing as wide variety patterns (e.g., dots, stripes), thicknesses, widths, etc. For example, the printable lithium composition and active anode material may be deposited as a series of stripes, such as described in US Publication No. 2014/0186519 incorporated herein by reference in its entirety. The stripes would form a 3D structure that would account for expansion of the active anode material during lithiation. For example, silicon may expand by 300 to 400 percent during lithiation. Such swelling potentially adversely affects the anode and its performance. By depositing the printable lithium as a thin stripe in the Y-plane as an alternating pattern between the silicon anode stripes, the silicon anode material can expand in the X-plane alleviating electrochemical grinding and loss of particle electrical contact. Thus, the printing

method can provide a buffer for expansion. In another example, where the printable lithium formulation is used to form the anode, it could be co-extruded in a layered fashion along with the cathode and separator, resulting in a solid-state battery.

[0039] In one embodiment, the printable lithium composition may be used to pre-lithiate an anode as described in US Patent No. 9,837,659 herein incorporated by reference in its entirety. For example, the method includes disposing a layer of printable lithium composition adjacent to a surface of a pre-fabricated/pre-formed anode. The pre-fabricated electrode comprises an electroactive material. In certain variations, the printable lithium composition may be applied to the carrier/substrate via a deposition process. A carrier substrate on which the layer of printable lithium composition may be disposed may be selected from the group consisting of: polymer films (e.g., polystyrene, polyethylene, polyethyleneoxide, polyester, polypropylene, polypolytetrafluoroethylene), ceramic films, copper foil, nickel foil, or metal foams by way of non-limiting example. Heat may then be applied to the printable lithium composition layer on the substrate or the pre-fabricated anode. The printable lithium composition layer on the substrate or the pre-fabricated anode may be further compressed together, under applied pressure. The heating, and optional applied pressure, facilitates transfer of lithium onto the surface of the substrate or anode. In case of transfer to the pre-fabricated anode, pressure and heat can result in mechanical lithiation, especially where the pre-fabricated anode comprises graphite. In this manner, lithium transfers to the electrode and due to favorable thermodynamics is incorporated into the active material.

[0040] In additional embodiments, at least a portion of the printable lithium composition can be supplied to the anode active material prior to assembly of the battery. In other words, the anode can comprise partially lithium-loaded silicon-based active material, in which the partially loaded active material has a selected degree of loading of lithium through intercalation/alloying or the like.

[0041] In one embodiment, the printable lithium composition may be incorporated into a three-dimensional electrode structure as described in US Publication No. 2018/0013126 herein incorporated by reference in its entirety. For example, the printable lithium composition may be incorporated into a three-dimensional porous anode, porous current collector or porous polymer or ceramic film, wherein the printable lithium composition may be deposited therein.

[0042] In some embodiments, an electrode prelithiated with the printable lithium composition can be assembled into a cell with the electrode to be preloaded with lithium. A separator can be placed between the respective electrodes. Current can be allowed to flow between the electrodes. For example, an anode prelithiated with the printable lithium composition of the

present invention may be formed into a second battery such as described in U.S. Patent No. 6,706,447 herein incorporated by reference in its entirety.

[0043] The cathode is formed of an active material, which is typically combined with a carbonaceous material and a binder polymer. The active material used in the cathode is preferably a material that can be lithiated. Preferably, non-lithiated materials such as MnO_2 , V_2O_5 , MoS_2 , metal fluorides or mixtures thereof, Sulphur and sulfur composites can be used as the active material. However, lithiated materials such as LiMn_2O_4 and LiMO_2 wherein M is Ni, Co or Mn that can be further lithiated can also be used. The non-lithiated active materials are preferred because they generally have higher specific capacities, lower cost and broader choice of cathode materials in this construction that can provide increased energy and power over conventional secondary batteries that include lithiated active materials.

EXAMPLES

Example 1

[0044] 10g of solution styrene butadiene rubber (S-SBR Europrene Sol R 72613) is dissolved in 90g toluene (99% anhydrous, Sigma Aldrich) by stirring at 21°C for 12 hours. 6g of the 10wt% SBR (polymer binder) in toluene (solvent) is combined with 0.1g carbon black (Timcal Super P) (rheology modifier) and 16g of toluene and dispersed in a Thinky ARE 250 planetary mixer for 6 minutes at 2000 rpm. 9.3g of stabilized lithium metal powder (SLMP®, Livent Corp.) having polymer coating of 20 to 200µm and d50 of 20µm is added to this suspension and dispersed for 3 minutes at 1000 rpm in a Thinky mixer. The printable lithium is then filtered through 180µm opening stainless steel mesh. The printable lithium suspension is then doctor blade coated on to a copper current collector at a wet thickness of 2mil (~50µm). Figure 3 is a plot showing the cycle performance for a pouch cell with printable lithium derived thin lithium film as the anode vs. commercial thin lithium foil.

Example 2

[0045] 10g of 135,000 molecular weight ethylene propylene diene terpolymer (EPDM) (Dow Nordel IP 4725P) is dissolved in 90g p-xylene (99% anhydrous, Sigma Aldrich) by stirring at 21°C for 12 hours. 6g of the 10wt% EPDM (polymer binder) in p-xylene (solvent) is combined with 0.1g TiO_2 (Evonik Industries) (rheology modifier) and 16g of toluene and dispersed in a Thinky ARE 250 planetary mixer for 6 minutes at 2000 rpm. 9.3g of stabilized lithium metal powder (SLMP®, Livent Corp.) having polymer coating of 20 to 200µm and d50 of 20µm is

added to this suspension and dispersed for 3 minutes at 1000 rpm in a Thinky mixer. The printable lithium is then filtered through 180 μ m opening stainless steel mesh. The printable lithium composition is then doctor blade coated on to a copper current collector at a wet thickness of 2mil (~50 μ m).

Shelf Life Stability

[0046] Printable lithium components must be selected to ensure chemical stability for long shelf life at room temperature and stability at elevated temperature for shorter durations such as during transport or during the drying process. The printable lithium composition stability was tested using calorimetry. 1.5g SLMP was added to a 10ml volume Hastelloy ARC bomb sample container. 2.4g of 4% SBR binder solution was added to the container. The container was fitted with a 24-ohm resistance heater and a thermocouple to monitor and control sample temperature. The bomb sample set-up was loaded into a 350ml containment vessel along with insulation. An Advance Reactive Screening Systems Tool calorimeter by Fauske Industries was used to assess the compatibility of the printable lithium solutions during a constant rate temperature ramp to 190°C. The temperature ramp rate was 2°C/min and the sample temperature was held at 190°C for 60 minutes. The test was conducted under 200psi Argon pressure to prevent boiling of the solvent. Figure 2 shows the temperature and pressure profiles for the reactivity testing of a SLMP/styrene butadiene/toluene printable lithium composition.

Printing Performance

[0047] The quality of the printable lithium composition with regard to printability is measured by several factors, for example, consistency of flow which directly impact one's ability to control lithium loading on a substrate or an electrode surface. An effective means of measuring flow is Flow Conductance which is an expression of the loading per square centimeter in relation to the factors which control the loading - the pressure during extrusion and the speed of the printer head. It can most simply be thought of as the inverse of flow resistance.

[0048] The expression is used to allow comparisons between prints of varying pressures and speeds, and changes in Flow Conductance can alert one to non-linear relationships of flow with pressure. These are important for scaling the loading for a printable lithium up or down depending on the need of the anode or cathode. An ideal printable lithium composition would behave in a linear fashion to changes in extrusion pressure.

[0049] To test printability, a printable lithium composition is filtered through 180 μ m opening stainless steel mesh and loaded into a Nordson EFD 10ml syringe. The syringe is loaded into a Nordson EFD HP4x syringe dispenser and attached to a slot die print head. The slot die print head is equipped with a 100 μ m – 300 μ m thick shim with channel openings designed to deliver the desired printable lithium composition loading. The slot die head is mounted on a Loctite 300 Series robot. The print head speed is set to 200 mm/s and the printing pressure is between 20 and 200 psi argon, depending on shim and channel design. The print length is 14cm. In an example printing trial experiment, the printable lithium composition was printed 30 times from a single syringe at dispenser settings ranging from 80psi to 200psi. For this print trial experiment, the flow conductance average was $0.14 \frac{mg}{s \cdot cm^2} * \frac{lbf}{in^2}$ with standard deviation of 0.02. Although this printable composition does not behave in a perfectly linear fashion, the composition flow response to changes in dispenser pressure is predictable to allow one skilled in the art to fine tune lithium loading to the desired level. Thus, at fixed dispenser pressure conditions the loading of lithium can be controlled very consistently. For example, for a print of $0.275 \frac{mAh}{cm^2}$ lithium metal, the CV is about 5%.

Electrochemical Testing

[0050] The pre-lithiation effect of printable lithium composition can be evaluated by printing the required amount of printable lithium onto the surface of prefabricated electrodes. The pre-lithiation lithium amount is determined by testing the anode material in half-cell format and calculating the lithium required to compensate for the first cycle losses due to formation of SEI, or other side reactions. To calculate the necessary amount of printable lithium, the capacity as lithium metal of the composition must be known and is approximately 3600mAh/g dry lithium basis for the compositions used as examples.

[0051] The pre-lithiation effect is tested using Graphite-SiO/NCA pouch cells. The Graphite-SiO anode sheet has the following formulation: artificial graphite (90.06%) + SiO (4.74%) + carbon black (1.4%) + SBR/CMC (3.8%). The capacity loading of the electrode is 3.59 mAh/cm² with 87% first cycle CE (columbic efficiency). The printable lithium is applied onto a Graphite-SiO anode at 0.15 mg/cm² lithium metal. The electrode is dried at 80°C for 100 min followed by lamination at a roller gap approximately 75% of the thickness of the electrode. A 7 cm × 7 cm electrode is punched from the printable lithium treated anode sheet. The positive electrode has the following formulation: NCA (96%) + carbon black (2%) + PVdF (2%). The positive electrode is 6.8 cm x 6.8 cm with capacity loading of 3.37 mAh/cm². The NCA cathode

has 90% first cycle CE. The anode to cathode capacity ratio is 1.06 and the baseline for full cell first cycle CE is 77%. Single layer pouch cells are assembled and 1M LiPF₆ /EC+DEC (1:1) is used as the electrolyte. The cells are pre-conditioned for 12 hours at 21°C and then the formation cycle is conducted at 40°C. The formation protocol is 0.1C charge to 4.2V, constant voltage to 0.01C and 0.1C discharge to 2.8V. In the described test 89% first cycle CE was demonstrated.

[0052] Although the present approach has been illustrated and described herein with reference to preferred embodiments and specific examples thereof, it will be readily apparent to those of ordinary skill in the art that other embodiments and examples may perform similar functions and/or achieve like results. All such equivalent embodiments and examples are within the spirit and scope of the present approach.

That Which is Claimed is:

1. A solid-state battery comprising a cathode, an anode and a solid electrolyte, wherein at least the anode, cathode and/or solid electrolyte is formed from a printable lithium composition comprised of lithium metal powder, a polymer binder compatible with the lithium metal powder, a rheology modifier compatible with the lithium metal powder, and a solvent compatible with the lithium metal powder and with the polymer binder.
2. The solid-state battery of Claim 1, wherein the anode and/or cathode is formed by printing the printable lithium composition onto the anode and/or cathode.
3. The solid-state battery of Claim 1, wherein the anode is formed by printing the printable lithium composition onto a current collector.
4. The solid-state battery of Claim 1, wherein the anode and/or cathode is formed by coating the anode with the printable lithium composition.
5. The solid-state battery of Claim 1, wherein the anode and/or cathode is formed by depositing the printable lithium composition onto the anode using an electric current.
6. The solid-state battery of Claim 1, wherein the lithium powder is stabilized lithium metal powder.
7. The solid-state battery of Claim 1, wherein the rheology modifier is selected from the group consisting of carbonaceous materials, silicon-containing materials, tin-containing materials, Group IIA oxides, Group IIIA oxides, Group IVB oxides, Group VB oxides and Group VIA oxides.
8. The solid-state battery of Claim 7, wherein the carbonaceous material is selected from the group consisting of carbon black, carbon nanotubes, graphite, hard carbon, and graphene.
9. The solid-state battery of Claim 7, wherein the silicon-containing material is selected from the group consisting of silicon nanotubes and fumed silica.

10. The solid-state battery of Claim 7, wherein the Group IVB oxide is selected from the group consisting of titanium dioxide and zirconium dioxide.
11. The solid-state battery of Claim 7, wherein the Group IIIA oxide is aluminum oxide.
12. The solid-state battery of Claim 1, wherein the polymer binder has a molecular weight of 1,000 to 8,000,000 and is selected from the group consisting of unsaturated elastomers, saturated elastomers, thermoplastics, polyacrylic acid, polyvinylidene chloride, and polyvinyl acetate.
13. The solid-state battery of Claim 12, wherein the unsaturated elastomer is selected from the group consisting of butadiene rubber, isobutylene, and styrene butadiene rubber.
14. The solid-state battery of Claim 12, wherein the saturated elastomer is selected from the group consisting of ethylene propylene diene monomer rubber and ethylene-vinyl acetate.
15. The solid-state battery of Claim 12, wherein the thermoplastic is selected from the group consisting of polystyrene, polyethylene and polymers of ethylene oxide.
16. The solid-state battery of Claim 15, wherein the polymers of ethylene oxide is selected from the group consisting of poly(ethylene glycol) and poly(ethylene oxide).
17. The solid-state battery of Claim 1, wherein the solvent is selected from the group consisting of alkanes, toluene, ethylbenzene, cumene, xylene, sulfones, mineral oil, glymes, and isoparaffinic synthetic hydrocarbon solvents.
18. The solid-state battery of Claim 1, wherein the printable lithium composition comprises on a solution basis:
 - a) 5 to 50 percent lithium metal powder;
 - b) 0.1 to 20 percent polymer binder;
 - c) 0.1 to 30 percent rheology modifier;
 - d) 50 to 95 percent solvent.

19. The solid-state battery of Claim 1, wherein the lithium is deposited onto the solid electrolyte using the printable lithium composition.
20. A solid-state battery comprising a cathode, an anode and a solid electrolyte, wherein lithium is deposited onto the solid electrolyte with a lithium printable lithium composition comprised of lithium metal powder, a polymer binder compatible with the lithium metal powder, a rheology modifier compatible with the lithium metal powder and the polymer binder, and a solvent compatible with the lithium metal powder and with the polymer binder.
21. The solid-state battery of Claim 20, wherein lithium is deposited onto the solid electrolyte by printing the printable lithium composition onto the solid electrolyte.
22. The solid-state battery of Claim 20, wherein lithium is deposited onto the solid electrolyte by coating the solid electrolyte with the printable lithium composition.
23. The solid-state battery of Claim 20, wherein the lithium powder is stabilized lithium metal powder.
24. The solid-state battery of Claim 20, wherein the rheology modifier is selected from the group consisting of carbonaceous materials, silicon-containing materials, tin-containing materials, Group IIA oxides, Group IIIA oxides, Group IVB oxides, Group VB oxides and Group VIA oxides.
25. The solid-state battery of Claim 24, wherein the carbonaceous material is selected from the group consisting of carbon black, carbon nanotubes, graphite, hard carbon, and graphene.
26. The solid-state battery of Claim 24, wherein the silicon-containing material is selected from the group consisting of silicon nanotubes and fumed silica.
27. The solid-state battery of Claim 24, wherein the Group IVB oxide is selected from the group consisting of titanium dioxide and zirconium dioxide.
28. The solid-state battery of Claim 24, wherein the Group IIIA oxide is aluminum oxide.

29. The solid-state battery of Claim 20, wherein the polymer binder has a molecular weight of 1,000 to 8,000,000 and is selected from the group consisting of unsaturated elastomers, saturated elastomers, thermoplastics, polyacrylic acid, polyvinylidene chloride, and polyvinyl acetate.
30. The solid-state battery of Claim 29, wherein the unsaturated elastomer is selected from the group consisting of butadiene rubber, isobutylene, and styrene butadiene rubber.
31. The solid-state battery of Claim 29, wherein the saturated elastomer is selected from the group consisting of ethylene propylene diene monomer rubber and ethylene-vinyl acetate.
32. The solid-state battery of Claim 29, wherein the thermoplastic is selected from the group consisting of polystyrene, polyethylene and polymers of ethylene oxide.
33. The solid-state battery of Claim 32, wherein the polymers of ethylene oxide is selected from the group consisting of poly(ethylene glycol) and poly(ethylene oxide).
34. The solid-state battery of Claim 20, wherein the solvent is selected from the group consisting of alkanes, toluene, ethylbenzene, cumene, xylene, sulfones, mineral oil, glymes, and isoparaffinic synthetic hydrocarbon solvents.
35. The solid-state battery of Claim 20, wherein the printable lithium composition comprises on a solution basis:
- a) 5 to 50 percent lithium metal powder;
 - b) 0.1 to 20 percent polymer binder;
 - c) 0.1 to 30 percent rheology modifier;
 - d) 50 to 95 percent solvent.
36. The solid-state battery of Claim 20, wherein the anode is lithiated using the printable lithium composition.