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(54) **ELECTROCHEMICAL SEPARATORS WITH
INSERTED CONDUCTIVE LAYERS**

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(52) **U.S. Cl.**

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(21) Appl. No.: **14/546,953**

(57)

ABSTRACT

(22) Filed: **Nov. 18, 2014**

Related U.S. Application Data

(60) Provisional application No. 61/905,678, filed on Nov. 18, 2013, provisional application No. 61/938,794, filed on Feb. 12, 2014, provisional application No. 61/985,204, filed on Apr. 28, 2014, provisional application No. 62/024,104, filed on Jul. 14, 2014.

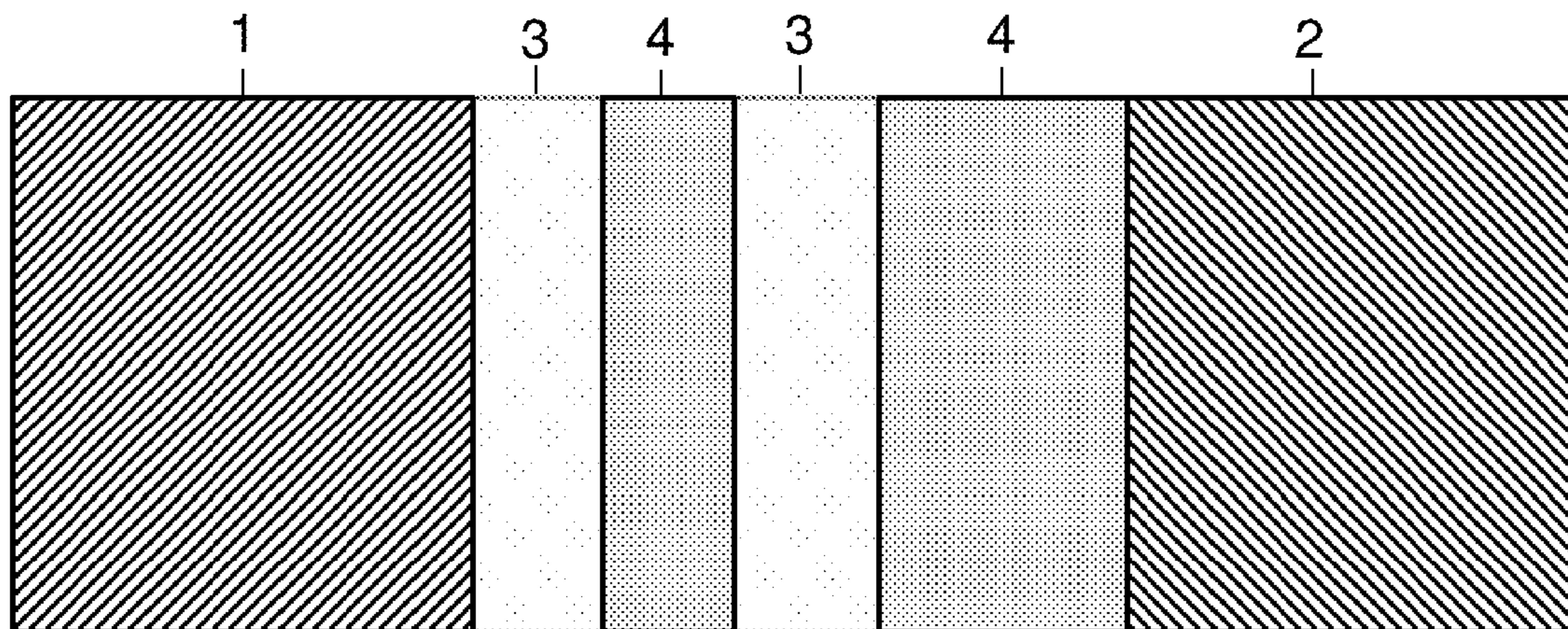
Disclosed are electrochemical cells including a composite separator capable of changing the performance of the cell by a) changing the internal electric field of the cell, b) activating lost active material, c) providing an auxiliary current collector for an electrode and/or d) limiting or preventing hot spots and/or thermal runaway upon formation of an electronic short in the system. An exemplary composite separator includes at least one electronically conducting layer and at least one electronically insulating layer. Another exemplary composite separator includes an electronically conducting layer and a solid ionic conductor. Also disclosed are methods for detecting and managing the onset of a short in an electrochemical cell and for charging an electrochemical cell.

Publication Classification

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H01M 2/16 (2006.01)

H01M 10/48 (2006.01)



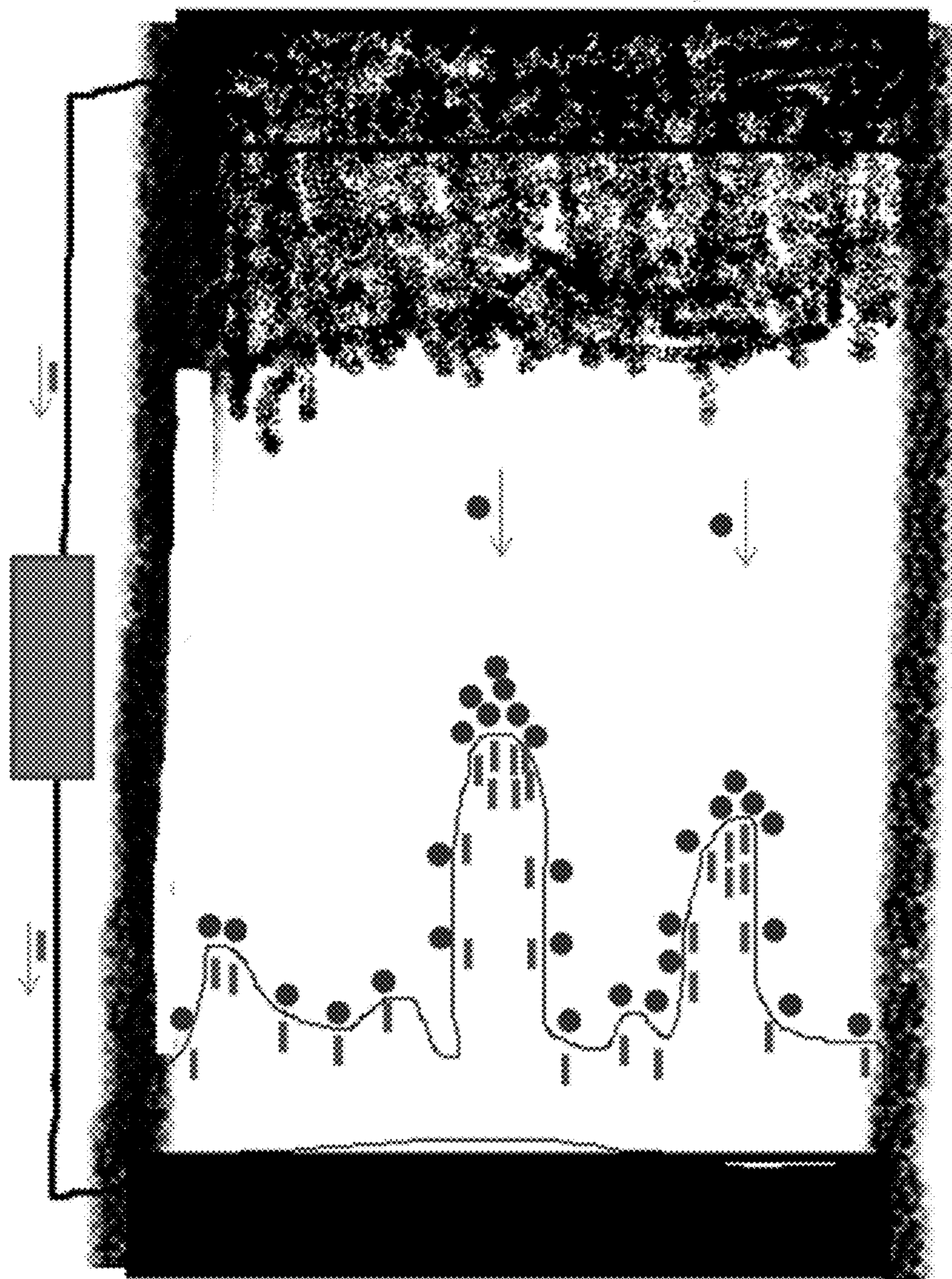


FIG. 1

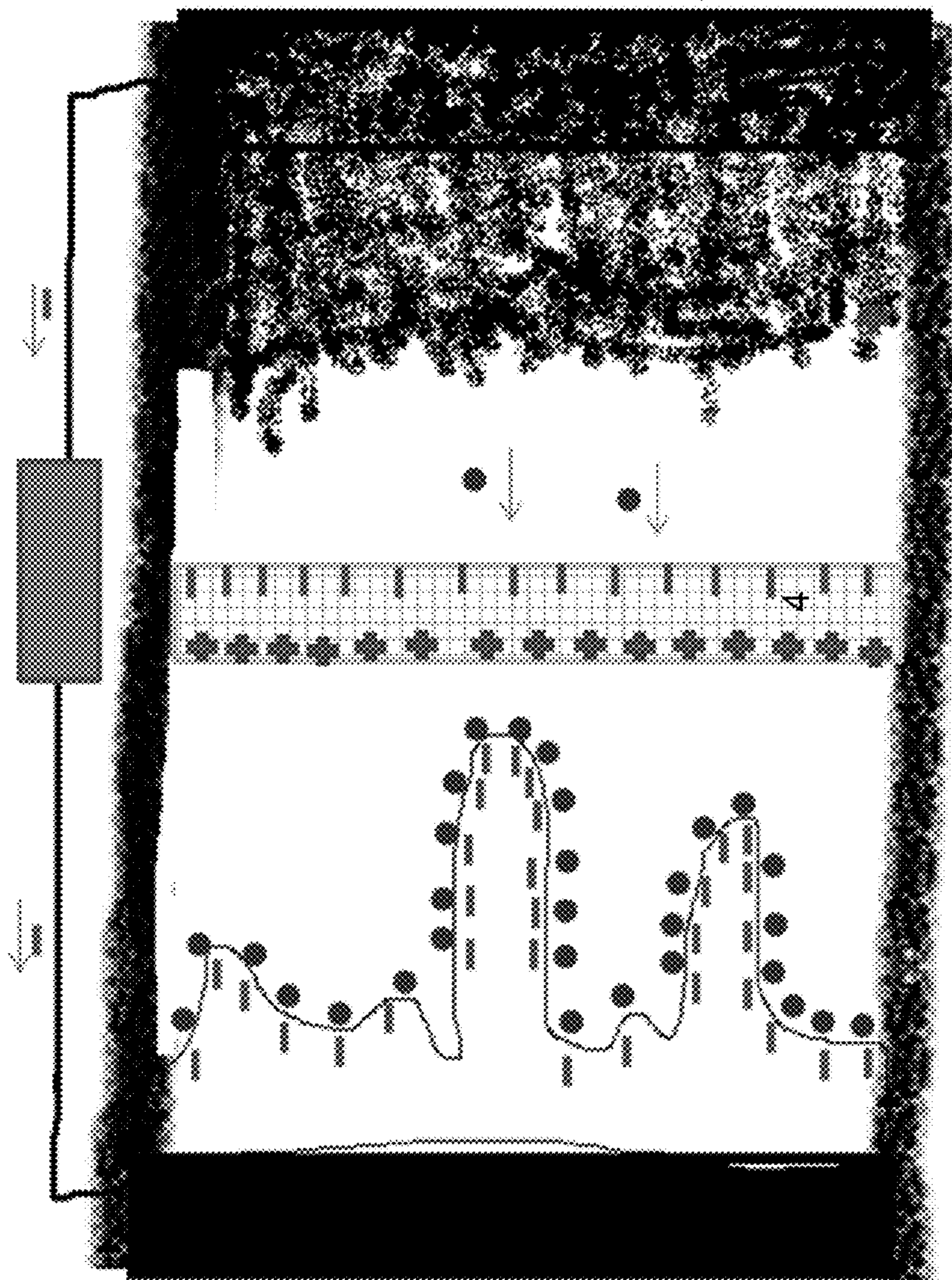


FIG. 2

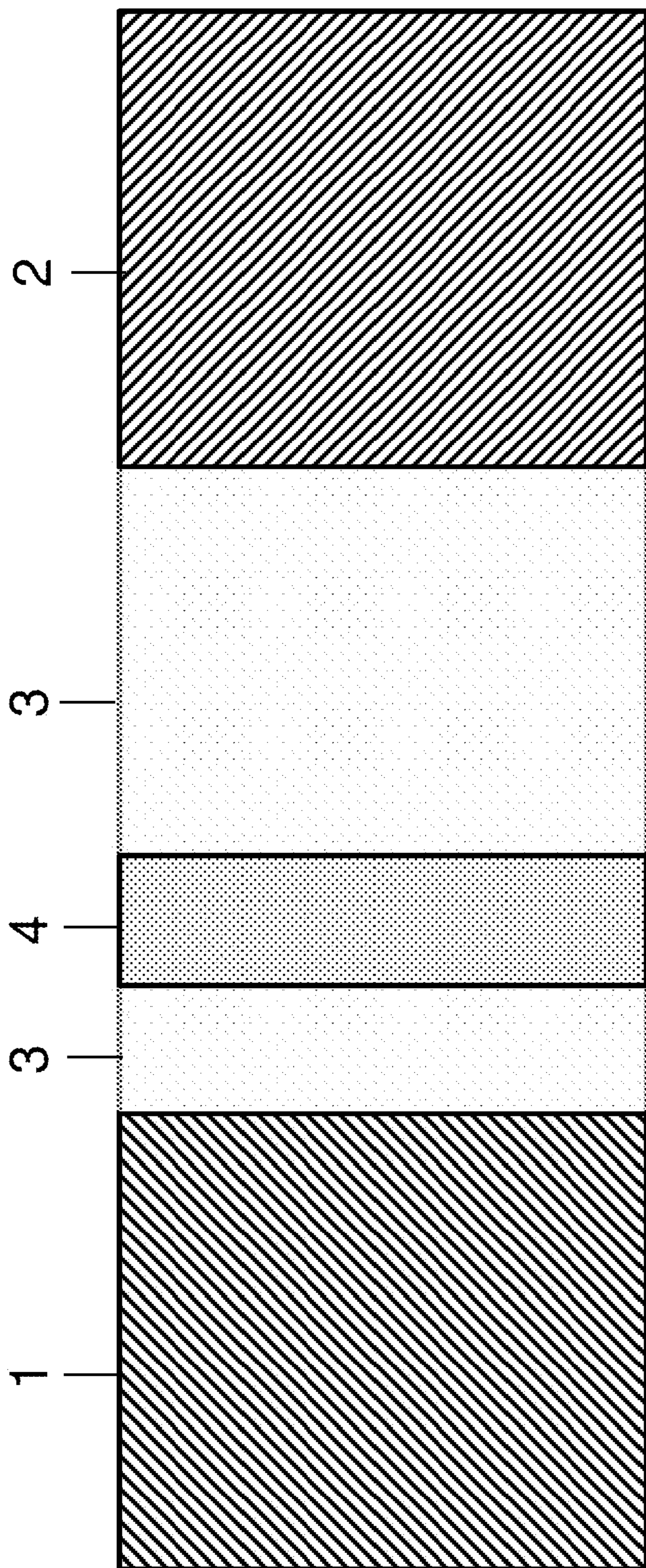


FIG. 3A

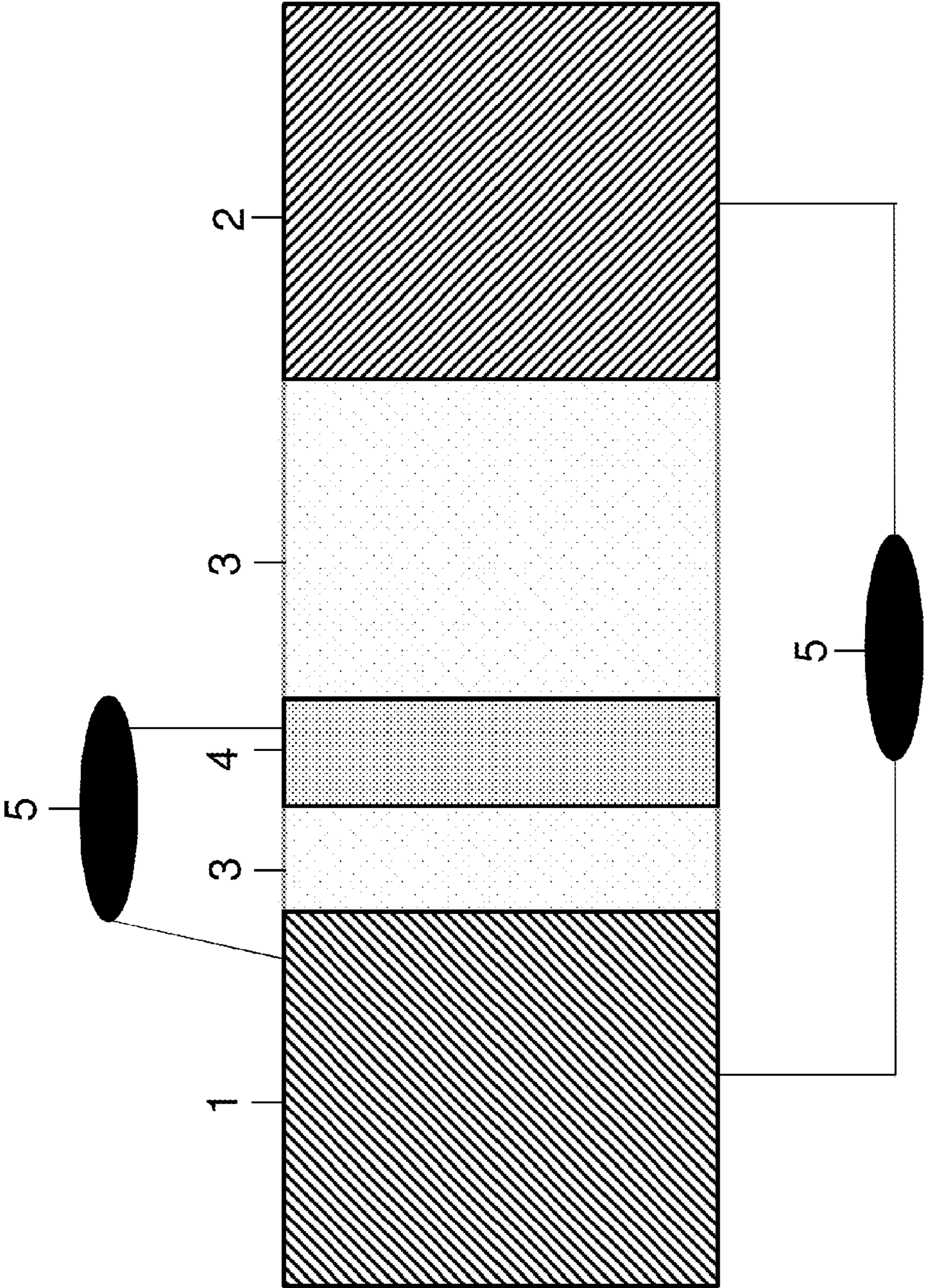


FIG. 3B

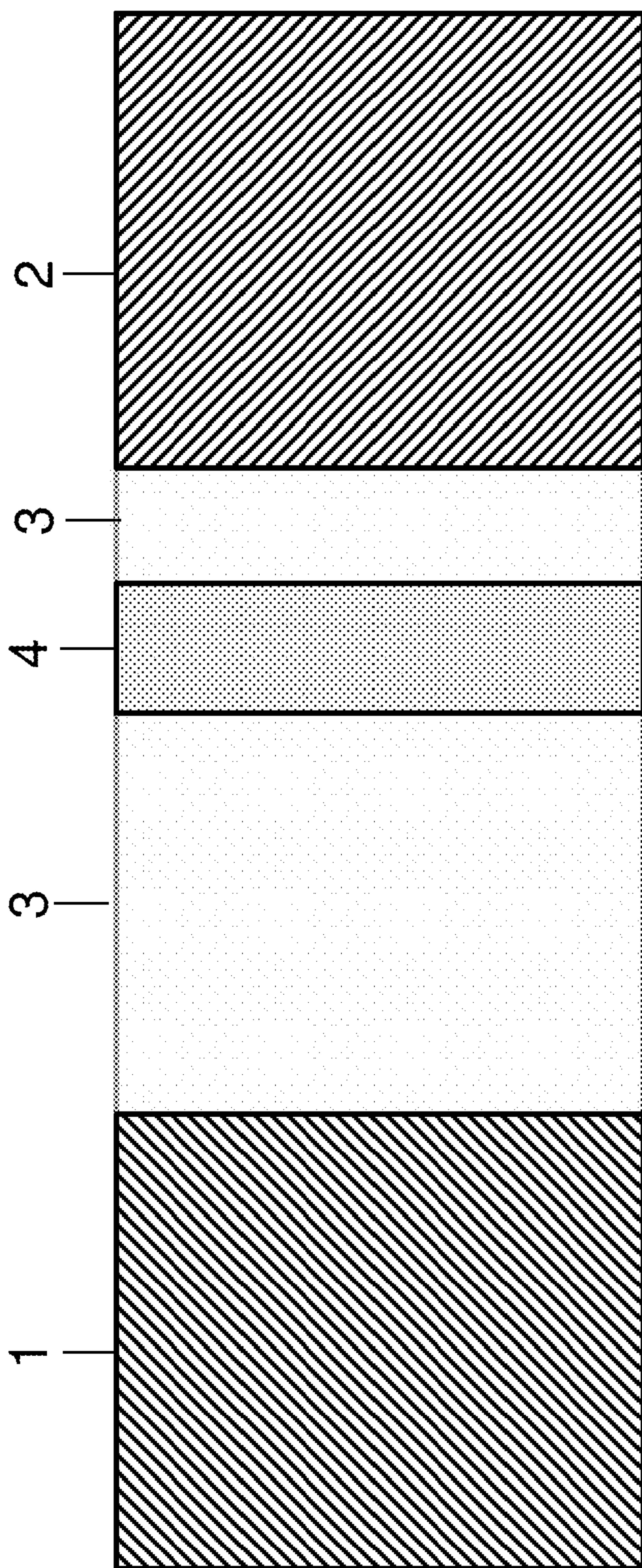


FIG. 4A

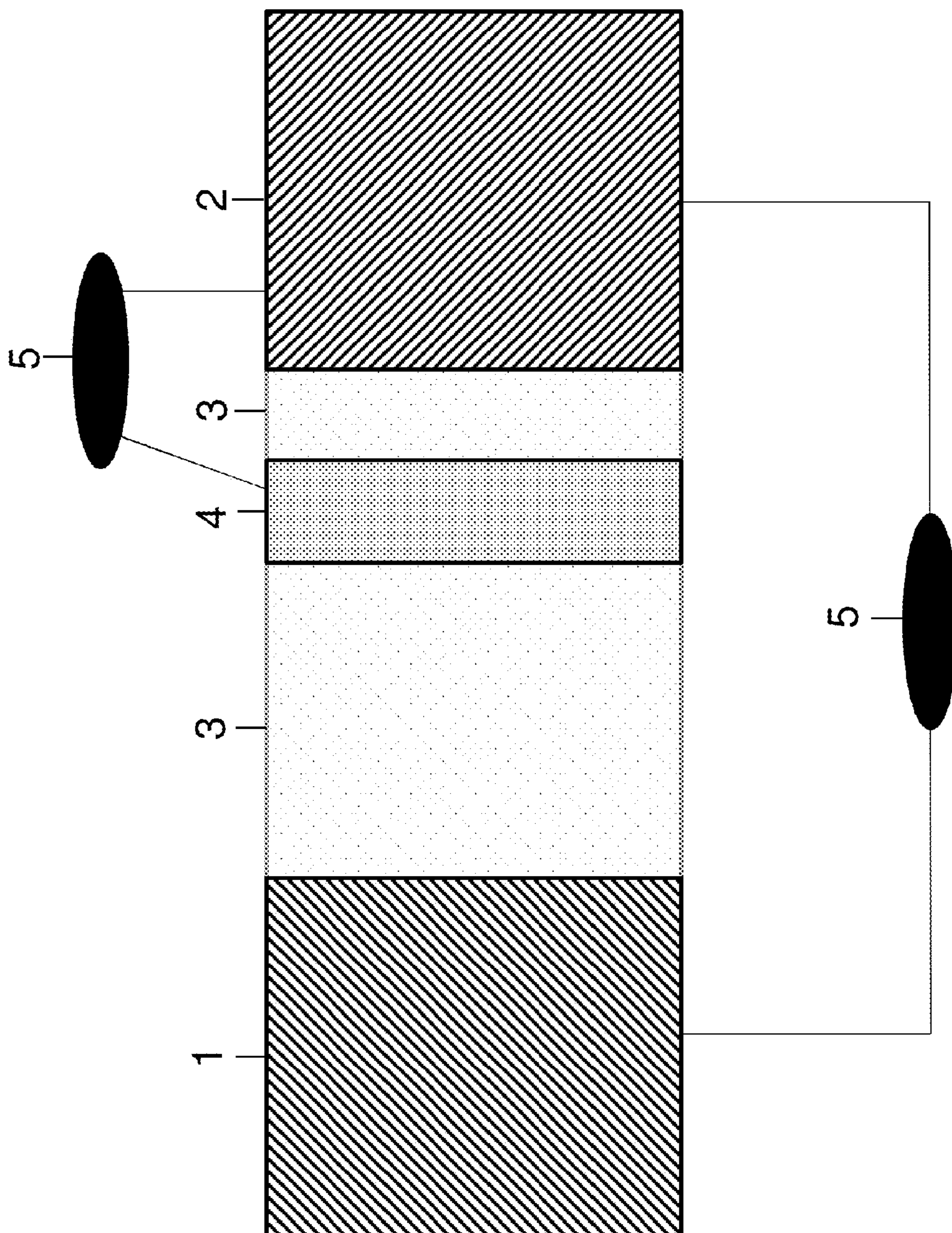


FIG. 4B

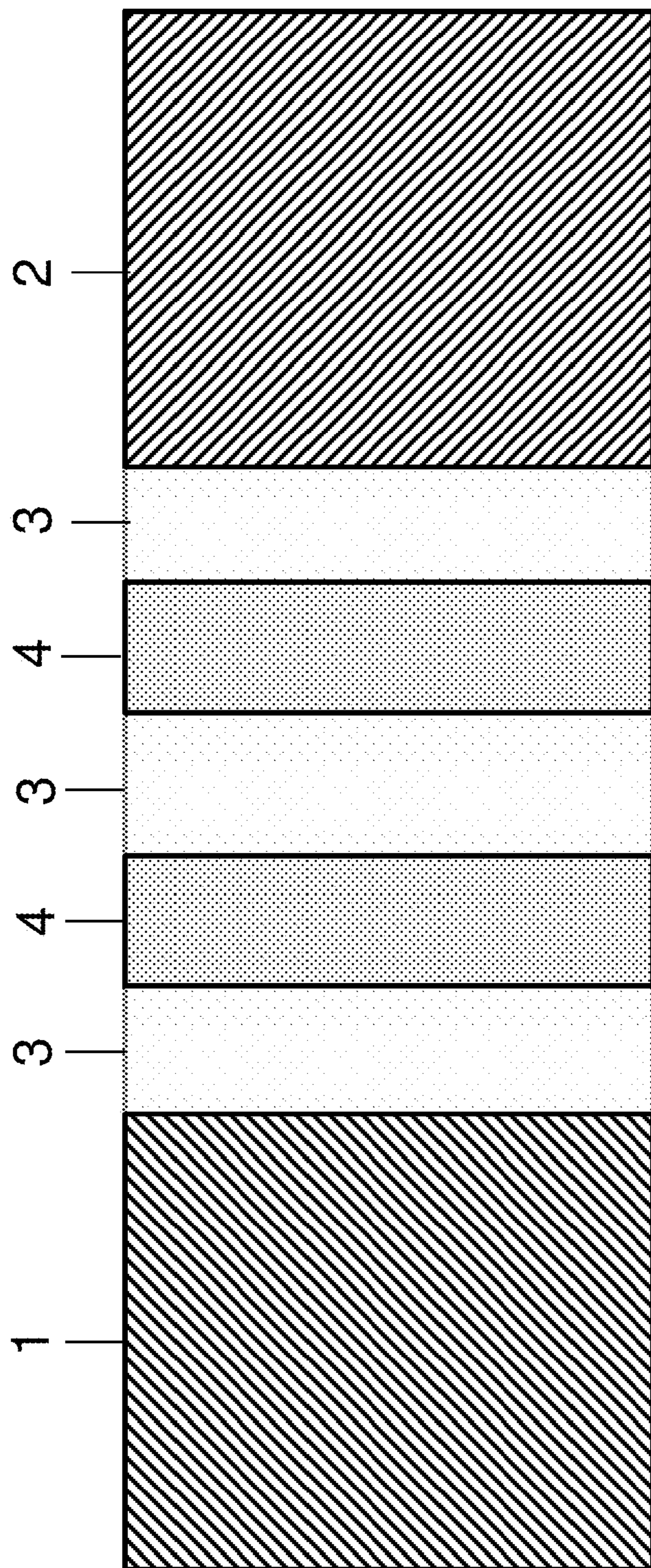


FIG. 5A

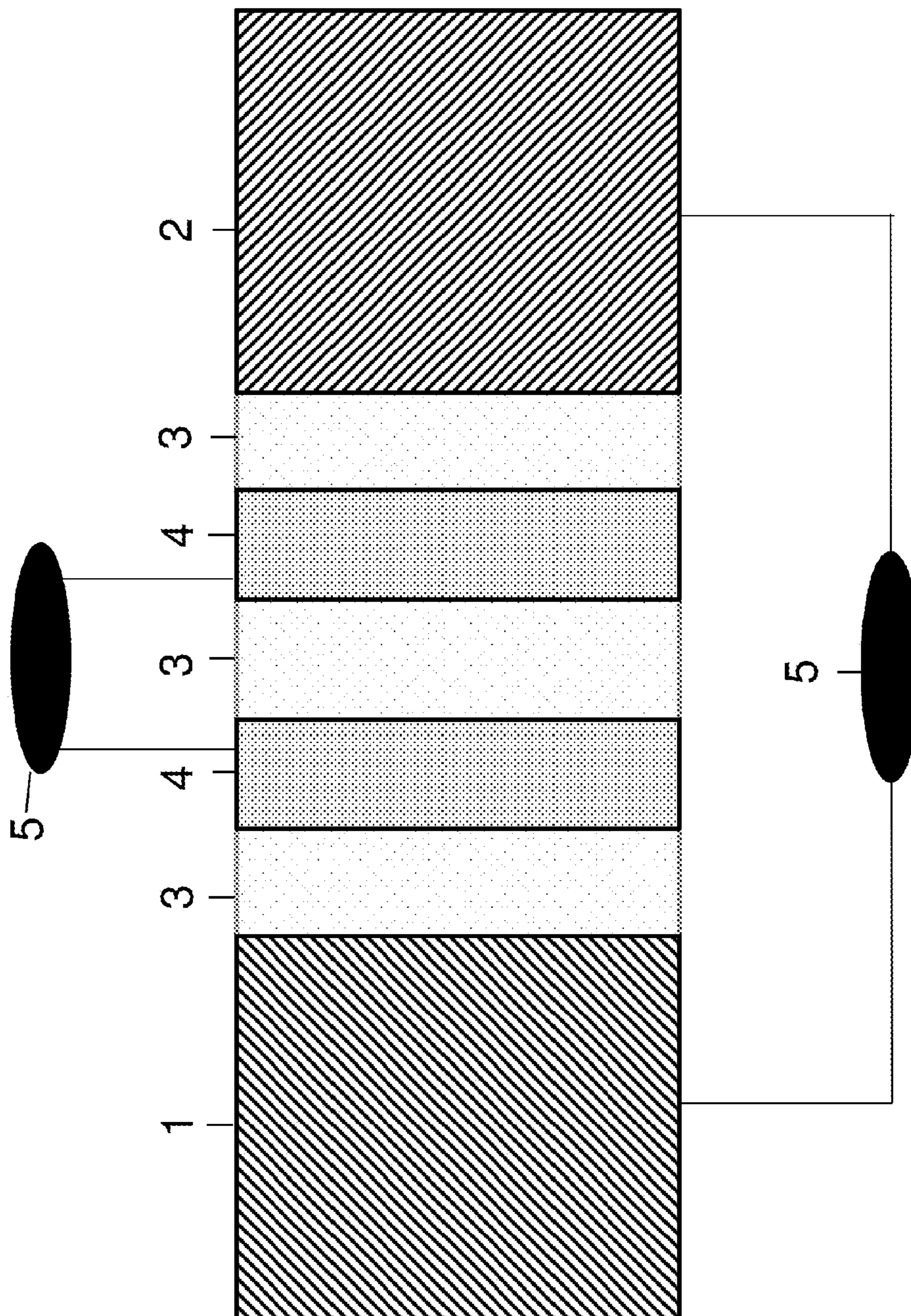


FIG. 5B

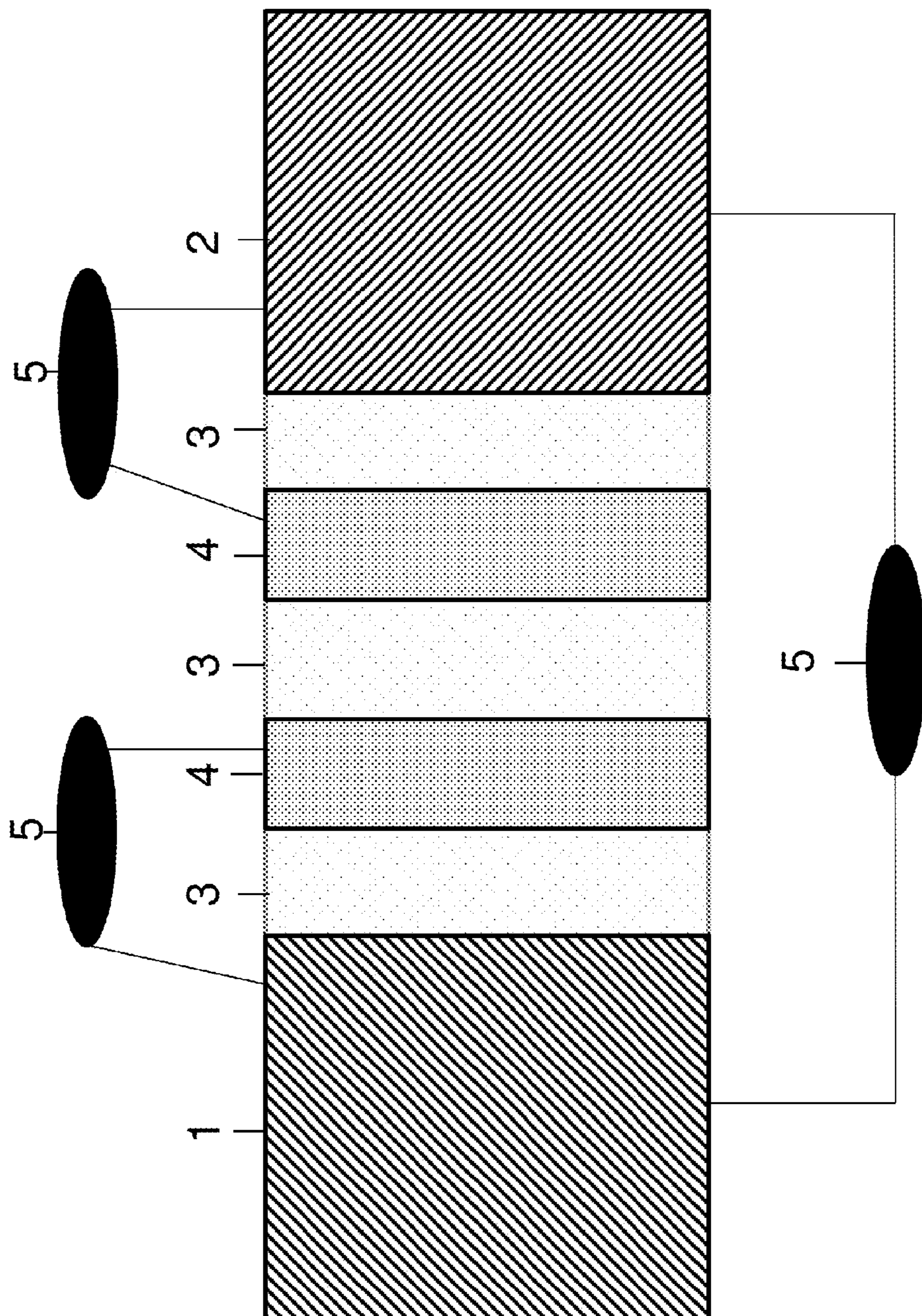


FIG. 5C

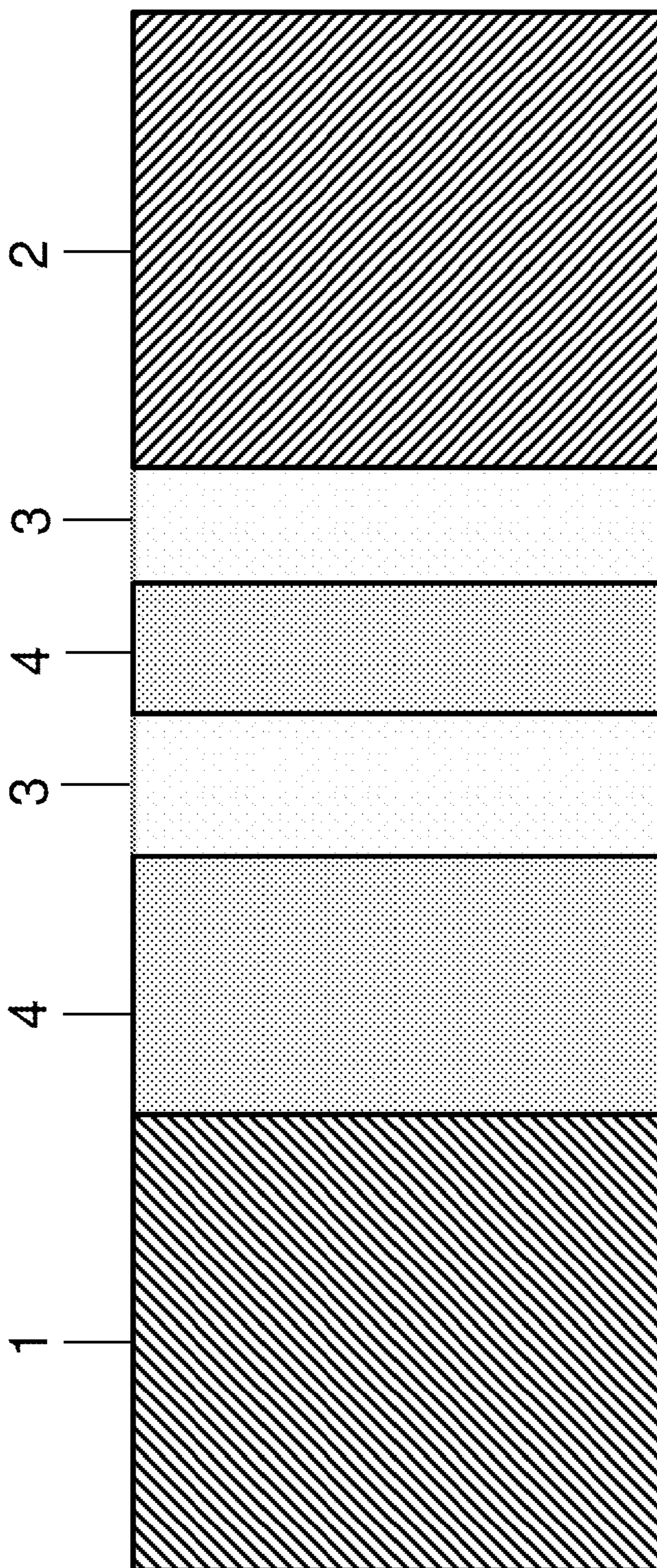


FIG. 6

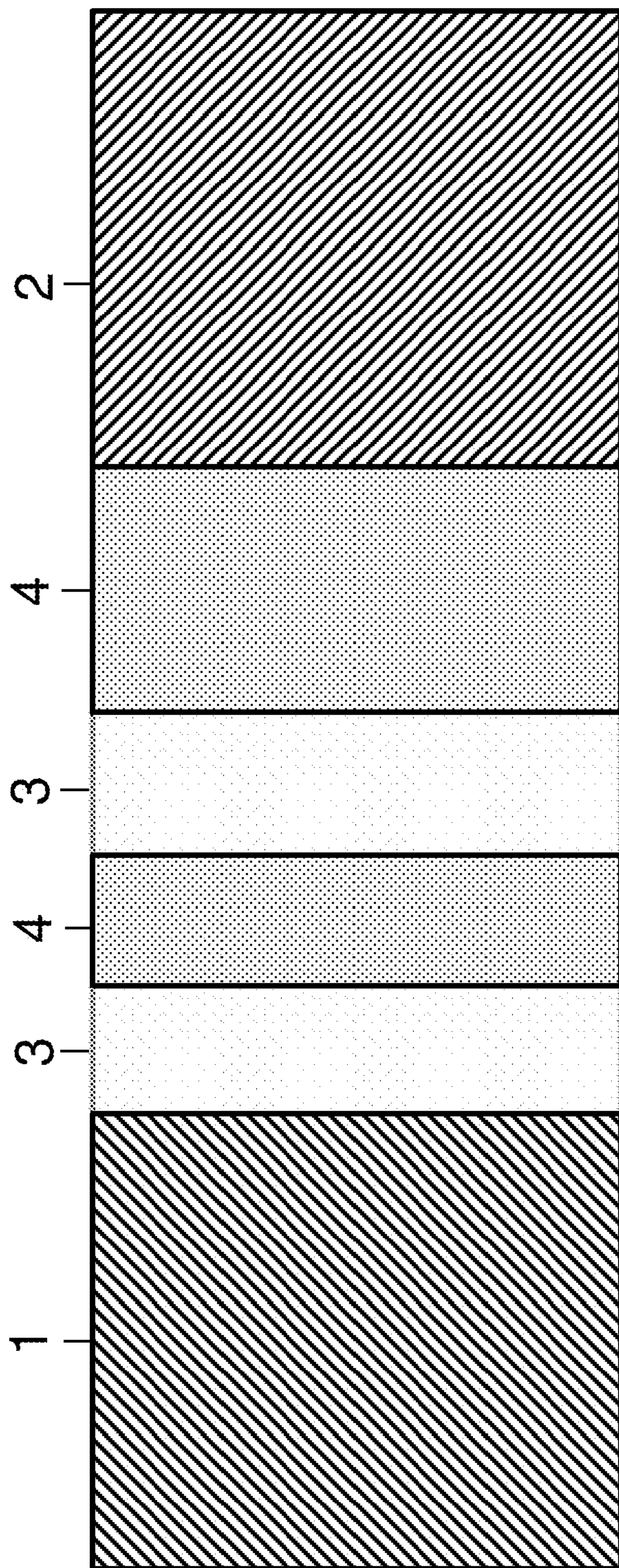


FIG. 7

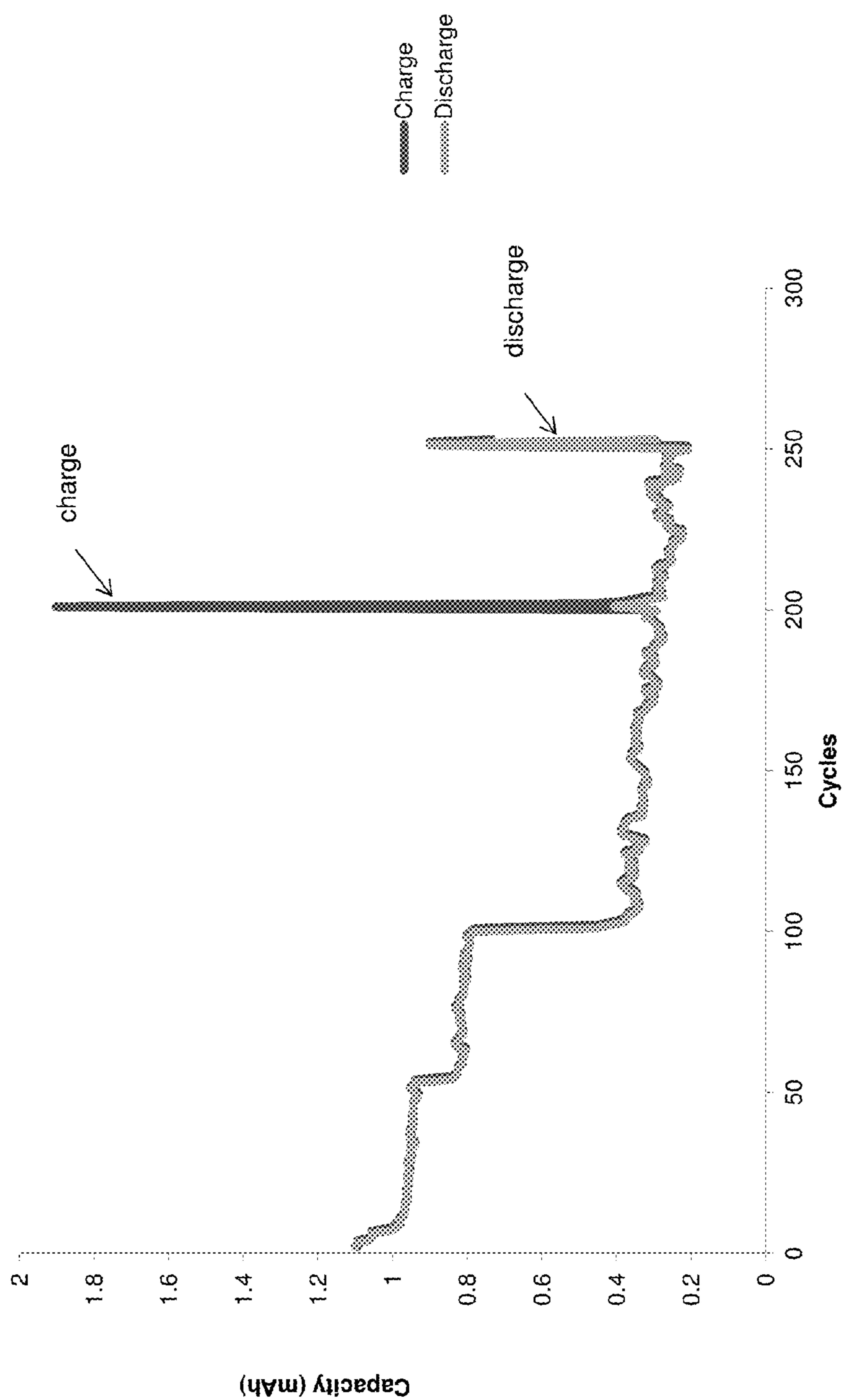


FIG. 8

Cycle	Current	mA
1	0.0001	0.1
4	0.0005	0.5
11	0.001	1
72	0.001	1

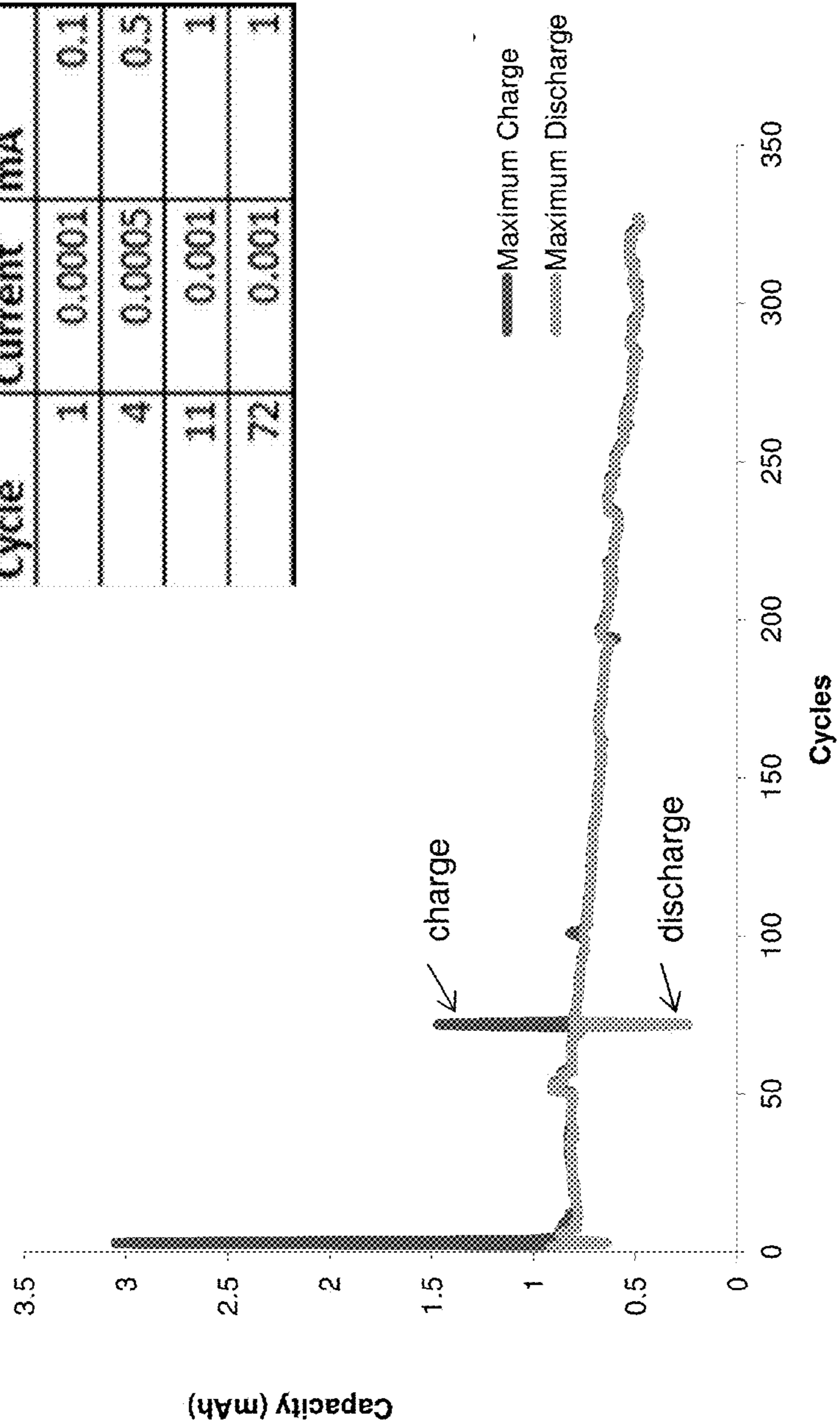


FIG. 9

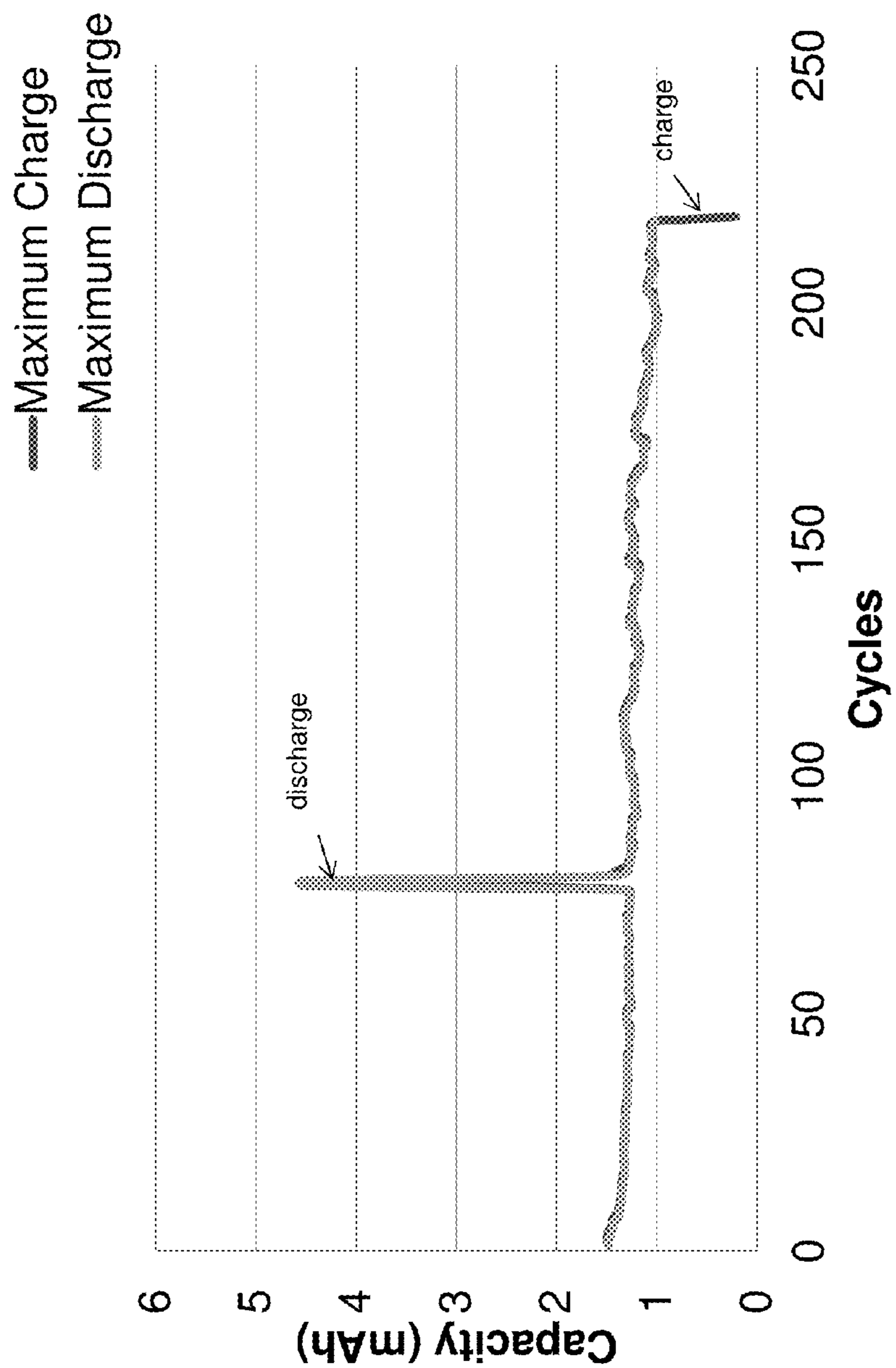


FIG. 10

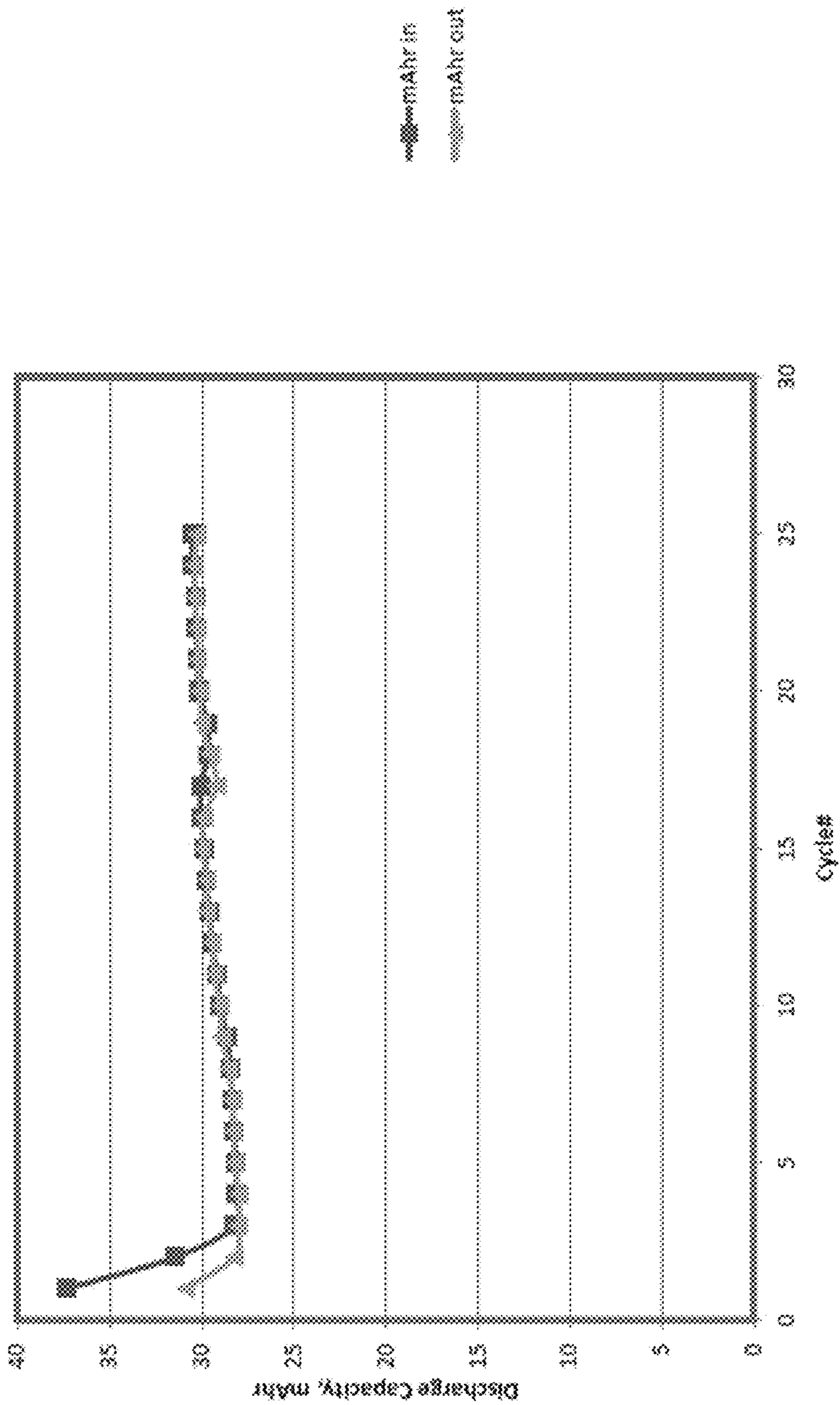


FIG. 11

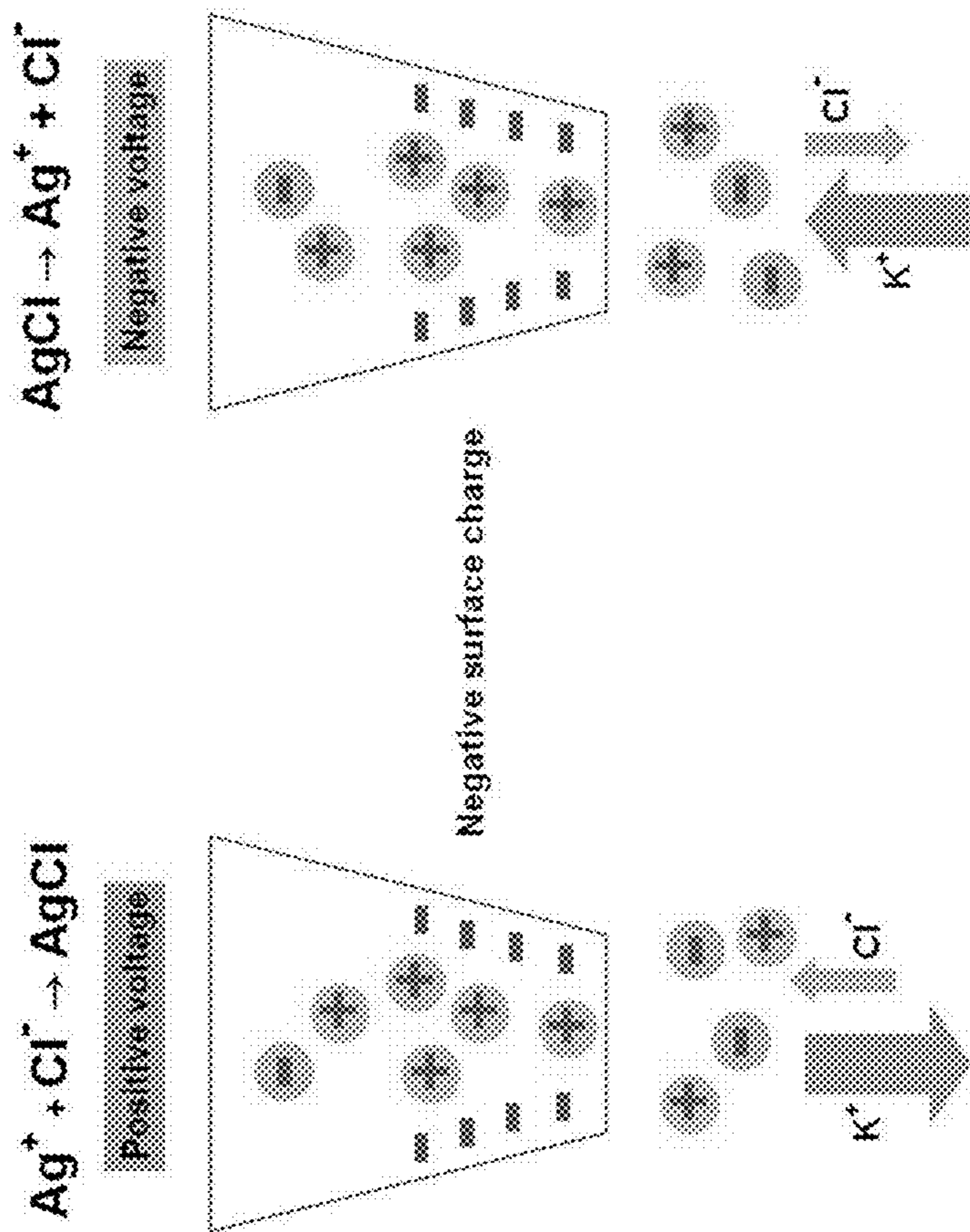


FIG. 12

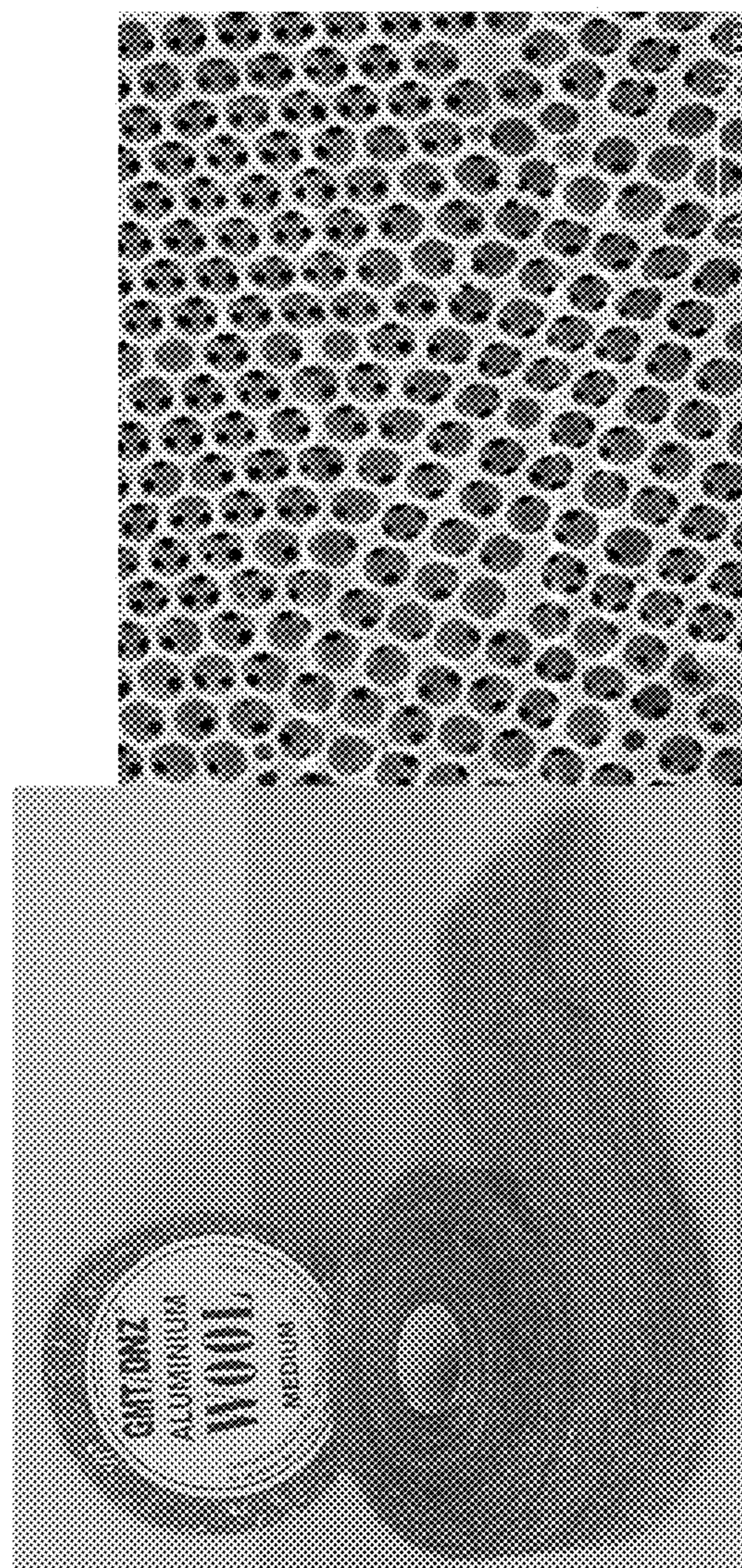


FIG. 13

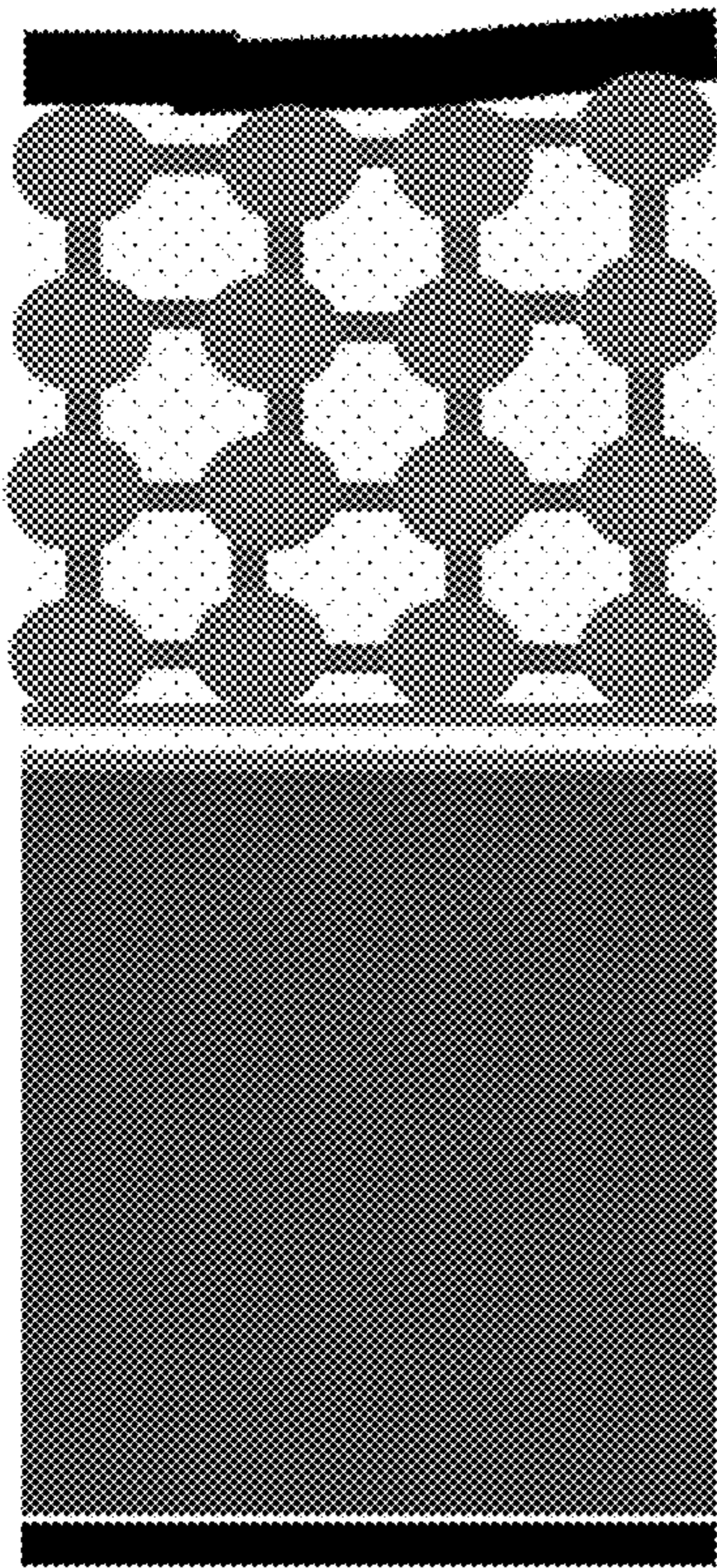


FIG. 14

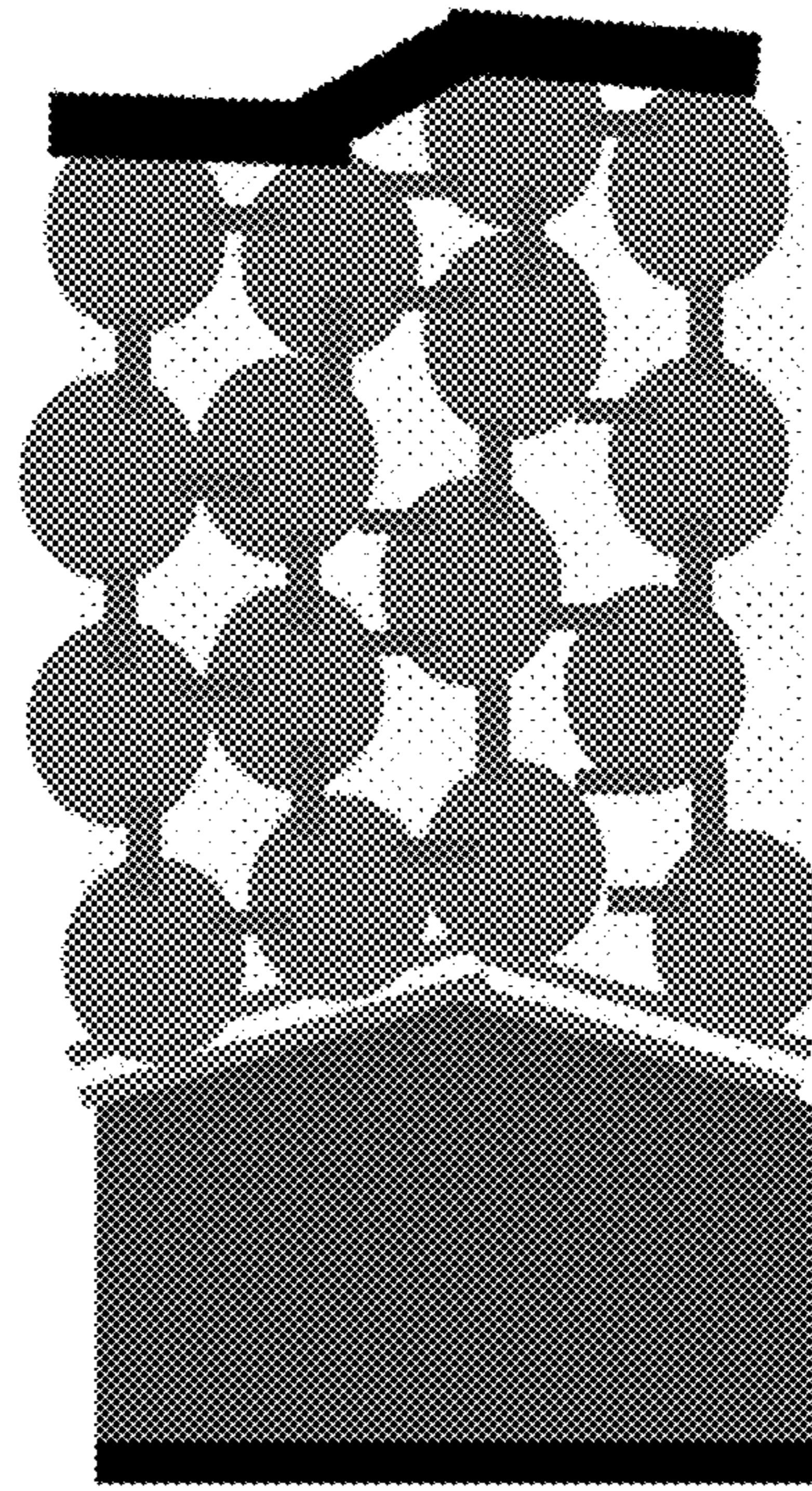


FIG. 15

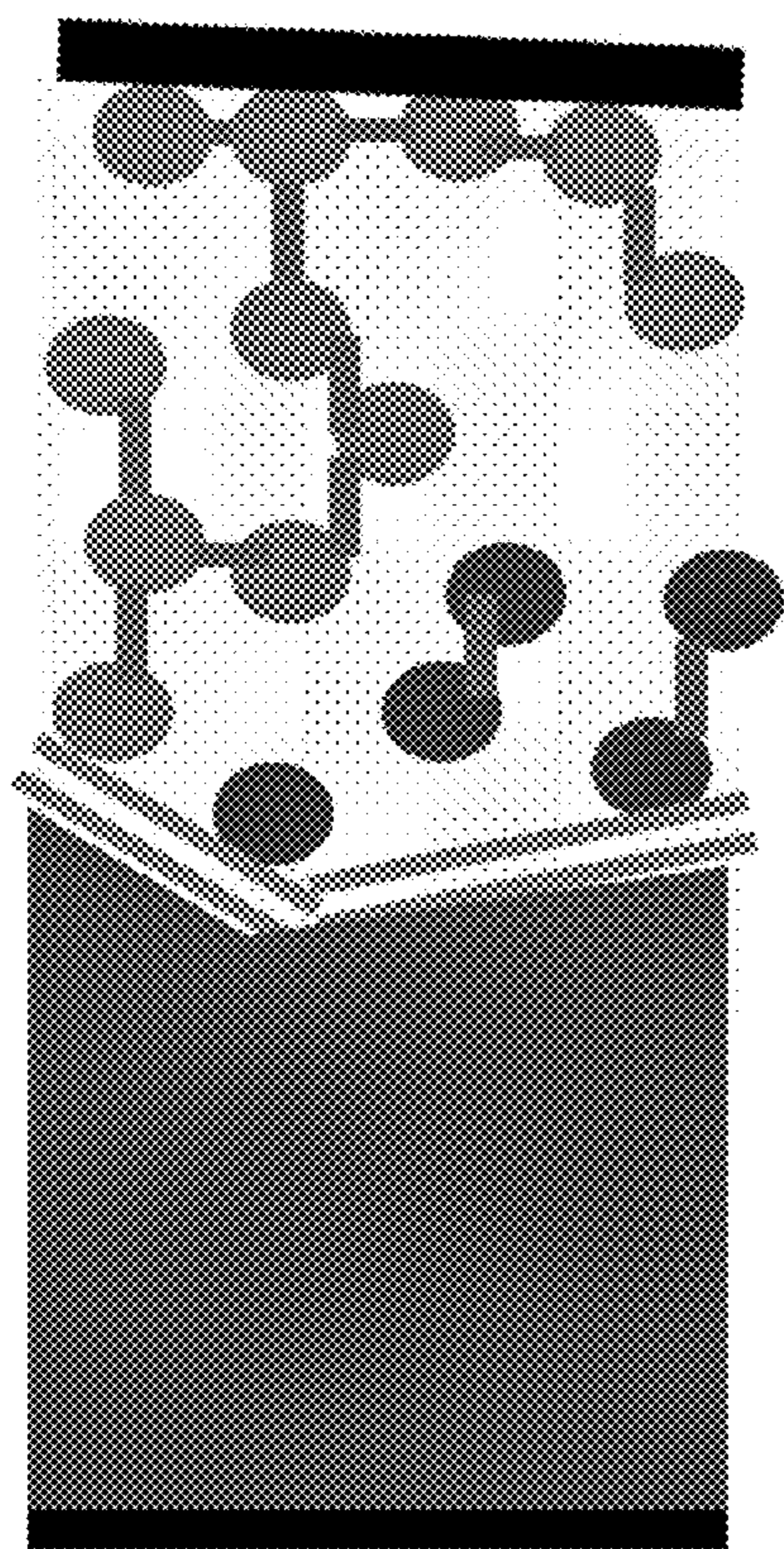


FIG. 16

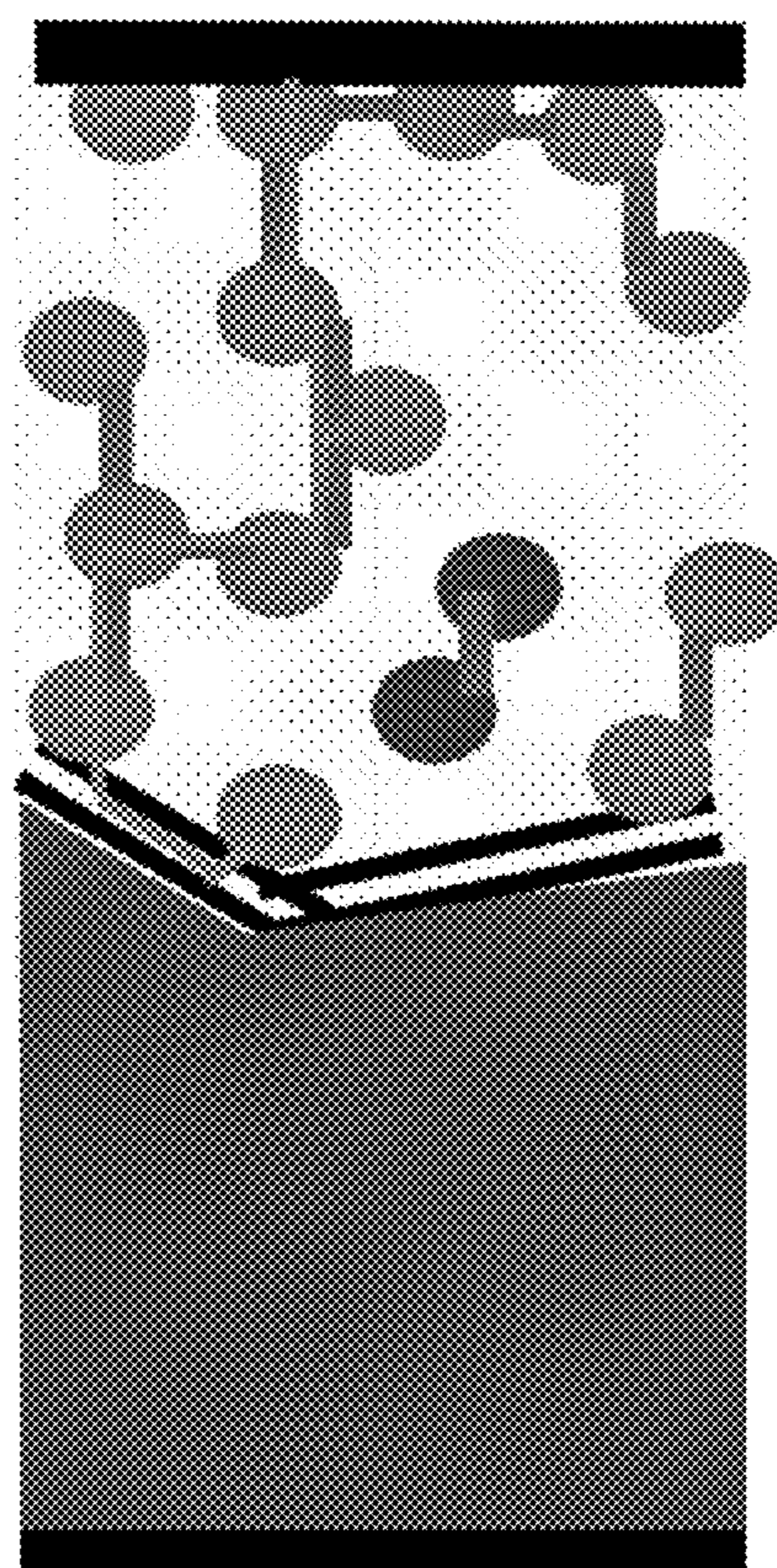


FIG. 17

- eNc-eC-eNc
- eNc-eC-eNc-eC
- eC-eNc-eC-eNc-eC
- eNc-eCS-eNc-eC
- eC-eNc-eCS-eNc-eC
- eC-eNc
- eC-eNc-eC
- eC-eNc-eCS
- eCS-eNc
- eCS-eNc-eCS
- eCS-eNc-eC

FIG. 18

ELECTROCHEMICAL SEPARATORS WITH INSERTED CONDUCTIVE LAYERS

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of and priority to U.S. Provisional Application No. 61/905,678, filed Nov. 18, 2013; U.S. Provisional Application No. 61/938,794, filed Feb. 12, 2014; and U.S. Provisional Application No. 61/985,204, filed Apr. 28, 2014 and U.S. Provisional Application No. 62/024,104, filed Jul. 14, 2014; all of which are hereby incorporated by reference in their entireties to the extent not inconsistent herewith.

BACKGROUND OF INVENTION

[0002] Over the last few decades revolutionary advances have been made in electrochemical storage and conversion devices expanding the capabilities of these systems in a variety of fields including portable electronic devices, air and space craft technologies, passenger vehicles and biomedical instrumentation. Current state of the art electrochemical storage and conversion devices have designs and performance attributes that are specifically engineered to provide compatibility with a diverse range of application requirements and operating environments. For example, advanced electrochemical storage systems have been developed spanning the range from high energy density batteries exhibiting very low self-discharge rates and high discharge reliability for implanted medical devices to inexpensive, light weight rechargeable batteries providing long runtimes for a wide range of portable electronic devices to high capacity batteries for military and aerospace applications capable of providing extremely high discharge rates over short time periods.

[0003] Despite the development and widespread adoption of this diverse suite of advanced electrochemical storage and conversion systems, significant pressure continues to stimulate research to expand the functionality of these systems, thereby enabling an even wider range of device applications. Large growth in the demand for high power portable electronic products, for example, has created enormous interest in developing safe, light weight primary and secondary batteries providing higher energy densities. In addition, the demand for miniaturization in the field of consumer electronics and instrumentation continues to stimulate research into novel design and material strategies for reducing the sizes, masses and form factors of high performance batteries. Further, continued development in the fields of electric vehicles and aerospace engineering has also created a need for mechanically robust, high reliability, high energy density and high power density batteries capable of good device performance in a useful range of operating environments.

[0004] Many recent advances in electrochemical storage and conversion technology are directly attributable to discovery and integration of new materials for battery components. Lithium battery technology, for example, continues to rapidly develop, at least in part, due to the discovery of novel electrode and electrolyte materials for these systems. The element lithium has a unique combination of properties that make it attractive for use in an electrochemical cell. First, it is the lightest metal in the periodic table having an atomic mass of 6.94 AMU. Second, lithium has a very low electrochemical oxidation/reduction potential (i.e., -3.045 V vs. NHE (normal hydrogen reference electrode)). This unique combination

of properties enables lithium based electrochemical cells to have very high specific capacities. State of the art lithium ion secondary batteries provide excellent charge-discharge characteristics, and thus, have also been widely adopted as power sources in portable electronic devices, such as cellular telephones and portable computers. U.S. Pat. Nos. 6,852,446, 6,306,540, 6,489,055, and "Lithium Batteries Science and Technology" edited by Gholam-Abbas Nazri and Gianfranco Pistoia, Kluwer Academic Publishers, 2004, which are hereby incorporated by reference in their entireties, are directed to lithium and lithium ion battery systems.

[0005] Advances in electrode materials, electrolyte compositions and device geometries continue to support the further development of Li based electrochemical systems. For example, U.S. Patent Application Publication US2012/0077095, published on Mar. 29, 2012, and International Patent Application publication WO 2012/034042, published on Mar. 15, 2012, disclose three-dimensional electrode array structures for electrochemical systems including lithium batteries.

[0006] Despite substantial advances, practical challenges remain in connection with the continued development of Li and Zn based electrochemical systems. A significant issue, for example, relates to dendrite formation in secondary zinc and lithium based systems and to electronic conductivity loss in Si anode and sulfur or air cathode lithium ion batteries. It is generally known that Li or Zn deposition in many electrolytes is highly dendritic which make these systems susceptible to problems involving shorting, mechanical failure and thermal runaway. Safety concerns relating to dendrite formation are currently a barrier to implementation of metal Li and Zn anodes in rechargeable systems. A number of strategies have been pursued to address safety in connection with dendrite formation, particularly in the context of secondary batteries, including development of non-lithium anodes and internal safety systems able to monitor in real time problems associated with dendrite formation.

[0007] As will be generally recognized from the foregoing, a need currently exists for electrochemical systems, such as lithium based or alkaline based batteries, flow batteries, supercapacitors and fuel cells, exhibiting electrochemical properties useful for a range of applications. Specifically, lithium electrochemical systems capable of good electrochemical performance and high versatility for both primary and secondary lithium based batteries are needed.

SUMMARY OF THE INVENTION

[0008] Thermal runaway in batteries is triggered by portions of the battery reaching excessive temperatures and can occur as a result of an internal or external electrical or electronic short between the positive and the negative electrode. Causes of internal shorts include dendrites or foreign materials in the battery. In one aspect, the disclosure provides electrochemical cells including a composite separator capable of limiting or preventing hot spots and/or thermal runaway upon formation of an electronic short in the system. These electrochemical cells can enhance the safety of the cell and also prolong the cycle life. The disclosure also provides electrochemical cells including a composite separator which allows monitoring of cell performance and early detection of internal short formation. The disclosure also provides electrochemical cells including a composite separator which

allows control of the cell. Methods for reducing dendrite growth and for detection of electrical shorts are also provided.

[0009] In an embodiment, the disclosure provides an electrochemical cell comprising: a positive electrode; a negative electrode; one or more electrolytes positioned between said positive electrode and said negative electrode; said one or more electrolytes capable of conducting ionic charge carriers; and a composite separator comprising at least one electronically insulating layer and at least one electronically conductive layer; said separator positioned between said positive electrode and said negative electrode such that said ionic charge carriers are able to be transported between said positive electrode and said negative electrode but not electronic charge carriers; wherein the presence of the said electronically conductive layer(s) of the said separator affects the performance of the electrochemical cell performance upon formation of an electrical short between any of the said electrodes or the said electronically conductive layer.

[0010] In an embodiment, the disclosure provides electrochemical cells comprising a positive electrode, a negative electrode, one or more ionically conductive electrolytes positioned between said positive electrode and said negative electrode, and a composite separator comprising at least one electronically insulating layer and at least one electronically conductive layer. In a further embodiment, the disclosure provides electrochemical cells comprising a positive electrode, a negative electrode, one or more ionically conductive electrolytes positioned between said positive electrode and said negative electrode, and a composite solid electrolyte comprising a solid electrolyte and at least one electronically conductive layer. The composite separators are permeable to ionic charge carriers, but are not electronically conductive across their thickness.

[0011] In a further embodiment, the disclosure provides a composite solid electrolyte for an electrochemical cell comprising at least an electronically non-conductive layer, at least a porous layer of electronically conductive material and at least a group of fibers or particles filling the pores/holes of the porous layer.

[0012] In an aspect, the electronically conductive layer of the separator mitigates the effects of internal and/or external shorts between the positive and negative electrode. In embodiments, the cell either continues operating or fails without any thermal runaway' in the event of a short. In an embodiment, contact of a dendrite structure with the electronically conductive separator modifies the redox reactions taking place in the cell and the cell voltages. In an embodiment, the modification of the redox reactions and cell voltages is such that dendrite growth is not favored.

[0013] In an aspect, the electronically conductive layer of the separator provides an additional electronic path for active materials. In an embodiment, the electronically conductive layer is provided between said insulating layer and said positive electrode or said negative electrode to provide an additional electronic path for the active materials. In silicon or sulfur based electrodes the loss of electronic conductivity during cycling significantly decreases the cell capacity and cycle life. In an embodiment, contact of the separated active material with the electronically conductive separator creates an auxiliary current collector for the lost active material and improves the cycle efficiency of the cell.

[0014] In a further embodiment, the electronically conductive layer is a chemically reactive layer and a chemical reac-

tion happens between the electronically conductive layer and an electrical short (internal, such as a dendrite or a foreign metallic layer, or external) between the said electrically conductive layer of the said separator and said positive electrode or said negative electrode. In an embodiment the chemical reaction consumes and or dissipates energy. In an embodiment, a chemical reaction takes place between the material of the electronically conductive layer and the dendrite material after the dendrite contacts the layer of electronically conductive material.

[0015] In an embodiment, a multi-layer battery separator with at least one conductive layer is used to prolong the cycle life and safety enhancement of the cell. The conductive layer may have an external tab that can be used for monitoring the cell or be used to "control" the cell. The conductive layer prolongs the cycle life of the battery by one or more mechanisms. In the case with no auxiliary external tab: a) as a free standing physical barrier, stronger than conventional PP-PP separators, which limits the size of a short to the size of the pores of the conductive layer (an example is a 0.007 mm stainless steel or copper perforated film) and b) as a chemical reactive material to the short material, such that the reaction between the conductive layer and the short results in energy consumption and may stop or remove the short (an example is a 0.007 mm aluminum film or a 0.001 mm aluminum coating on one side of a porous polymer film, such as microporous PP-PP). When an external tab electronically connects the conductive layer to outside of the cell additional mechanisms include using the external to c) monitor the voltage between any of the electrodes and the conductive layer or d) apply a voltage or current between any of the electrodes and the conductive layer. Mechanism d) includes the mechanism of d1) burning the short, d2) activating solid electrolyte and d3) activating alloying with dendrite and d4) releasing other substances in the cell.

[0016] In an embodiment, an electrochemical cell comprises a positive electrode; a negative electrode; one or more electrolytes positioned between said positive electrode and said negative electrode; said one or more electrolytes capable of conducting ionic charge carriers; and a composite separator comprising at least one electronically insulating layer and at least one electronically conductive layer; said separator positioned between said positive electrode and said negative electrode such that said ionic charge carriers are able to be transported between said positive electrode and said negative electrode but not electronic charge carriers; wherein the said electronically conductive layer of the said separator has an external tab that can be used to monitor the performance of the cell by measuring the voltage or current. In an embodiment, sometimes the voltage doesn't change significantly but the current does slightly, for example the current change is equal C/100 rate or higher of the cell capacity, between the said tab and one of the electrodes.

[0017] In an embodiment, an electrochemical cell comprises: a positive electrode; a negative electrode; one or more electrolytes positioned between said positive electrode and said negative electrode; said one or more electrolytes capable of conducting ionic charge carriers; and a composite separator comprising at least one electronically insulating layer and at least one electronically conductive layer; said separator positioned between said positive electrode and said negative electrode such that said ionic charge carriers are able to be transported between said positive electrode and said negative electrode but not electronic charge carriers; wherein in the

said electronically conductive layer of the said separator has an external tab that can be used to modify the performance of the cell by applying a voltage or current between the said tab and one of the electrodes. In some embodiment the electronically conductive layer can have a source of active ions, for example can have a coating of lithium metal on it or can itself be made of lithium, in a lithium ion cells, which can be used to provide active ions to the cell, such as to compensate the ion loss or to make Li-ion cells with non-lithiated electrodes.

[0018] In an embodiment, an electrochemical cell comprises: a positive electrode; a negative electrode; one or more electrolytes positioned between said positive electrode and said negative electrode; said one or more electrolytes capable of conducting ionic charge carriers; and at least a composite solid electrolyte comprising at least an electronically non-conductive layer, at least a porous layer of electronically conductive material and at least a group of solid electrolyte fibers or particles filling the pores/holes of the porous layer; said solid electrolyte positioned between said positive electrode and said negative electrode such that said ionic charge carriers are able to be transported between said positive electrode and said negative electrode, but not electronic charge carriers. In an embodiment, the particles can consist of known solid electrolyte, such as known polymer or ceramic solid electrolytes. In another embodiment, the particles may have a source of active ions, for example can be lithium metal, in a lithium ion cells, which can be used to provide active ions to the cell, such as to compensate the ion loss or to make Li-ion cells with non-lithiated electrodes. In another embodiment, the said electronically conductive layer of the said solid electrolyte may have an external tab that can be used to modify the performance of the cell by applying a voltage or current between the said tab and one of the electrodes.

[0019] In an embodiment, the electronically conductive and chemically reactive layer reacts with a dendrite growing from the negative electrode. In an embodiment, the material of the electronically conductive and chemically reactive layer forms an alloy with the dendrite material. In an embodiment where lithium dendrite structures form at the negative electrode, the electronically conductive and chemically reactive layer comprises at least one of Al, Ti, Ni, Fe, conductive carbon, Super-P carbon, carbon black, Kenjen, stainless steel, Sn or Si. When Li_+ is one of the ionic charge carriers, the electrolyte may be nonaqueous. In an embodiment where zinc dendrite structures form at the negative electrode, the electronically conductive and chemically reactive layer comprises a metallic layer.

[0020] In a further embodiment, the electronically conductive and chemically reactive layer reacts with foreign material accumulated at the negative electrode. Foreign metallic materials which can occur in batteries and lead to internal defects include, but are not limited to Cu, Al, Fe, Stainless Steel, Mn, Ni or Co. The foreign materials can be introduced to the cell during the manufacturing or can be dissolved materials from a cathode active material or a current collector, due to over voltage.

[0021] In an embodiment, ionic charge carriers in the system deposit or electroplate on the electronically conductive layer once a dendrite or accumulation of foreign material makes contact with the electronically conductive layer.

[0022] In a further embodiment, the electronically conductive layer is thermally conductive. In an embodiment, the thermal conductivity of this layer allows the layer to dissipate heat and further reduce the likelihood that thermal runaway

will occur in the system. In the event that an electrical short between the positive and negative electrodes does occur, the electronically and thermally conductive layer can help dissipate the heat generated. In an embodiment, in the event of formation of an electrical short between the said electronically conductive layer of the said separator and said positive electrode or said negative electrode, said electronically conductive layer transports the heat away from the short location and reduces the likelihood of hot spots or thermal runaway. In an embodiment, the electronically and thermally conductive layer dissipates heat from the reaction between the dendrite and the layer. In an embodiment, the electronically conductive layer provides a substantially homogeneous thermal field within said electrochemical cell. In an embodiment, the electronically conductive layer is characterized by a thermal conductivity greater than $75 \text{ W}/(\text{m}\cdot\text{K})$ or selected over the range of $75 \text{ W}/(\text{m}\cdot\text{K})$ to $500 \text{ W}/(\text{m}\cdot\text{K})$. In an embodiment, the enhanced thermal conductivity of the cell interior decreases the probability of hot spots which increases the cell performance, safety and cycle life. It can further lessen the probability of nonuniform plating of active or foreign ions on the anode and can decrease the side reactions.

[0023] In an additional aspect, each of the electronically conductive layers of the composite separator comprises an external connection tab. The external connection tab may also be referred to as an external tab. In an embodiment, the electronically conductive layer comprising an external connection tab is used to monitor performance of the cell by measuring the voltage or current between the external connection tab and one of the electrodes. In another embodiment, the electronically conductive layer comprises an external connection tab that is used to modify the performance of the cell by applying a voltage or current between the external connection tab of the electronically conductive layer and either the external connection tab of one of the electrodes or of an additional electronically conductive layer in the composite separator.

[0024] In an aspect, the said separator has one or two electronically conductive layers, which can be used with external tabs to modify the electric field inside the cell, which can modify the performance of the cell. In one embodiments, the change of the electric field as a function of time can act as an ionic pump to redistribute the ions in the cell and prevent hot spots or dendrites.

[0025] In embodiments, the composite separator comprises a plurality of electronically conductive layers, such as 2, 3 or 4 independent conductive layers. In embodiments, the conductive layers have the same electric potential or have different electric potentials. Embodiments of this aspect include composite separators wherein the electronically conductive layers are provided in electrical contact (optionally in physical contact) with each other and, alternatively, wherein the electronically conductive layers are not provided in electrical contact. In an embodiment, the composite separator comprises a plurality of electronically conductive layers each independently having a selected electric potential. In an embodiment, the composite separator comprises a plurality of electronically conductive layers characterized by one or more selected potential differences between electronically conductive layers, for example, a composite separator comprising a first electronically conductive layer having a first electric potential and a second electronically conductive layer having a second electric potential characterized by a selected difference in voltage. Methods and systems of the invention

may further comprise independently electrically biasing one or more electronically conductive layers of the composite separator, for example, to establish an electric field within at least a portion of the electrochemical cell resulting in enhanced electrochemical or electronic performance, such as the avoidance or mitigation of dendrite formation and/or enhanced cycling performance and/or cycle life.

[0026] In an embodiment, the disclosure provides an electrochemical cell

[0027] comprising a positive electrode comprising a positive electrode active material and a first current collector in electronic communication with the positive electrode active material, the first current collection further comprising a first external connection tab;

[0028] a negative electrode comprising a negative electrode active material and a second current collector in electronic communication with the negative electrode active material, the second current collector further comprising a second external connection tab;

[0029] one or more electrolytes positioned between said positive electrode and said negative electrode; said one or more electrolytes being ionically conductive; and

[0030] a composite separator comprising at least one electronically insulating layer and at least one electronically conductive layer; said composite separator being positioned between said positive electrode and said negative electrode and being permeable to ionic charge carriers, but not electronically conductive across the composite separator;

[0031] wherein said electronically conductive layer further comprises a third external connection tab.

[0032] In an embodiment, the third external connection tab is not provided in electronic contact with said positive electrode or said negative electrode except through an optional connection through an external circuit. In an embodiment, the disclosure further provides an electrochemical system, the system comprising an electrochemical cell and a source of current or voltage connected between the third external connection tab connected to the electronically conducting layer and an external connection tab connected to one of the positive or negative electrode. In an embodiment, the source of current or voltage is also a controller of current or voltage.

[0033] In an aspect, the disclosure provides a method for detection of an electrical short in an electrochemical cell, the method comprising the steps of

[0034] a) providing said electrochemical cell comprising:

[0035] a positive electrode comprising a positive electrode active material and a first current collector in electronic communication with the positive electrode active material, the first current collection further comprising a first external connection tab;

[0036] a negative electrode comprising a negative electrode active material and a second current collector in electronic communication with the negative electrode active material, the second current collector further comprising a second external connection tab;

[0037] one or more electrolytes positioned between said positive electrode and said negative electrode; said one or more electrolytes being ionically conductive; and

[0038] a composite separator comprising an electronically insulating layer and an electronically conductive layer; said composite separator being positioned

between said positive electrode and said negative electrode and being permeable to ionic charge carriers, but not electronically conductive across the composite separator;

[0039] wherein said electronically conductive layer further comprises a third external connection tab and is not provided in electrical contact with said positive electrode or said negative electrode in the absence of said electrical short

[0040] b) monitoring the voltage or current of said electrochemical cell, wherein said electrochemical cell undergoes an observable change in voltage upon formation of an electrical short between the electronically conductive layer and said positive electrode or said negative electrode.

[0041] In an embodiment, the positive electrode comprises a positive electrode active material and a first current collector in electronic communication with the positive electrode active material, the first current collection further comprising a first external connection tab; the negative electrode comprises a negative electrode active material and a second current collector in electronic communication with the negative electrode active material, the second current collector further comprising a second external connection tab; one or more ionically conductive electrolytes positioned between said positive electrode and said negative electrode; and a composite separator comprising at least one electronically insulating layer and at least one electronically conductive layer; said composite separator being positioned between said positive electrode and said negative electrode and being permeable to ionic charge carriers, but not electronically conductive across the composite separator; wherein said electronically conductive layer further comprises a third external connection tab and is not provided in electronic contact with said positive electrode or said negative electrode except through an external circuit. In an embodiment, the third external connection tab is connected to an external connection tab of one of the positive or negative electrode through an external circuit and the voltage or current between the electronically conducting layer and the positive or negative electrode is monitored.

[0042] In a further aspect, the disclosure provides a method of reducing dendrite growth in an electrochemical cell; said method comprising the steps of:

[0043] a) providing said electrochemical cell comprising: a positive electrode; a negative electrode; one or more electrolytes positioned between said positive electrode and said negative electrode; said one or more ionically conductive electrolytes; and a composite separator comprising an electronically insulating layer and an electronically conductive layer; said composite separator being positioned between said positive electrode and said negative electrode and being permeable to ionic charge carriers, but not electronically conductive across the composite separator; and

[0044] b) charging said electrochemical cell, wherein said electronically conductive layer undergoes deposition, electrochemical plating or chemical reaction with a dendrite structure formed during discharge between the electronically conductive layer and said positive electrode, negative electrode or both.

[0045] In an aspect, the disclosure provides a method of operating an electrochemical cell, the method comprising the steps of:

- [0046]** a) providing said electrochemical cell comprising:
- [0047]** a positive electrode;
- [0048]** a negative electrode;
- [0049]** one or more electrolytes positioned between said positive electrode and said negative electrode; said one or more ionically conductive electrolytes; and
- [0050]** a composite separator comprising an electronically insulating layer and an electronically conductive layer; said separator positioned between said positive electrode and said negative electrode such that said charge carriers are able to be transported between said positive electrode and said negative electrode;
- [0051]** b) charging, discharging or charging and discharging said electrochemical cell.
- [0052]** In an aspect, the disclosure provides a method of operating an electrochemical cell, the method comprising the steps of:
- [0053]** a) providing said electrochemical cell comprising:
- [0054]** a positive electrode;
- [0055]** a negative electrode;
- [0056]** one or more electrolytes positioned between said positive electrode and said negative electrode; said one or more ionically conductive electrolytes; and
- [0057]** a composite separator comprising an electronically non-conductive layer, a porous or perforated layer of electronically conductive material and a plurality of fibers or particles located within the pores or holes of the layer of electronically conductive material; said separator positioned between said positive electrode and said negative electrode such that said charge carriers are able to be transported between said positive electrode and said negative electrode;
- [0058]** b) charging, discharging or charging and discharging said electrochemical cell

In an embodiment, said electronically conductive layer provides a substantially homogeneous electric field adjacent to and within said positive electrode, said negative electrode or both, thereby providing uniform ion deposition into said positive electrode, said negative electrode or both. FIGS. 2 and 4 schematically illustrate insertion of an electronically isolated electronically conductive layer (4) between the positive and negative electrodes. During charging, a surface charge develops on the conductive layer.

[0059] In a further embodiment, the electrodes and the electronically conducting layer comprise external connection tabs and the method further comprises the step of applying a voltage or current between the external connection tab and one of the electrodes. In embodiment, the applied voltage or current for each step of cycling is constant voltage or current or varying with time such as a sinusoidal, pulse or step wave. In an embodiment with the external tab for the conductive layer: the applied voltage or current can be fixed voltage or current or can vary with time, such as a sinusoidal, pulse or step voltage or current varying between different arbitrary values.

[0060] In embodiments, the application of a voltage or current between the electrodes and the electrically conducting layer achieves a variety of effects. In an embodiment, a solid electrolyte incorporated in the composite separator is activated by application of a voltage may varying between the

charge-discharge voltages of the electrolyte. In an embodiment, the application of voltage between the electronically conductive layer and the electrode is used to redistribute active material which has deposited at locations other than the desired electrode; in this embodiment, the application of voltage between the electronically conductive layer and the electrode can be used to “clean up” the cell. As an example it is known that active electrode material may be lost when charged particles deposit in the separator, such as zinc or zinc oxide particles in Zinc batteries or polysulfide particles in Li-ion batteries, which severely reduces the cell capacity and cycle life, applying a voltage between the conductive layer and the anode in this case, e.g., every 50 cycles, can deposit back the active materials from the separator to the anode and can result in higher cycle life. In further embodiment a layer of electrolyte additive or modifier is attached to the electronically conductive layer and the application of current or voltage to between the electronically conductive layer and the electrode is used to release electrolyte additive or modifier into the electrolyte. An additional example is shorting the conductive layer with the cathode that assists in oxygen evolution during charging in metal air batteries.

[0061] In an embodiment, the conductive layer can be used for charging or discharging, a specific example is shorting the conductive layer with the cathode that assists in oxygen evolution during charging in metal air batteries. Applying a voltage other than zero between the conductive electrode and the cathode or the anode can result in activating assisting materials, such as modifiers to decrease the cell temperature and assist in thermal runaway prevention.

[0062] Electrochemical Cell.

[0063] In an embodiment, the electrochemical cell is a secondary (rechargeable) electrochemical cell. In another embodiment, the electrochemical cell is a primary electrochemical cell. In embodiments, the electrochemical cell is a primary battery, a secondary battery, a fuel cell or a flow battery, a lithium battery, a lithium ion battery, a zinc anode-based battery, a nickel cathode-based battery, a semi-solid battery or a lead-acid-based battery. In additional embodiments, the electrochemical cell is a Li—S, Li—Air, Li—LiFePO₄, or Zn—Ni electrochemical cell. In further embodiments the cell is Mg based or Na based.

[0064] Negative Electrode

[0065] In an embodiment where the cell is a lithium ion cell, the active material of the negative electrode is lithium metal, a lithium alloy, silicon, a silicon alloy, silicon-graphite or graphite. In an embodiment where the cell is a zinc cell, the anode material is Zn metal, ZnO or Zn—ZnO. In an embodiment, the negative electrode comprises an active material in electronic communication with a current collector. In an embodiment, the current collector comprises an external connection tab; in an embodiment the external connection tab is integral with the current collector. In an embodiment, the current collector is an electronically conductive material such as a metal.

[0066] Positive Electrode

[0067] In embodiments where the cell is a lithium ion cell, the active material of the positive electrode is NMC (lithium nickel-manganese-cobalt oxide), sulfur, sulfur-carbon, carbon-air, LCO (lithium cobalt oxide, LiCoO₂) or LFP (lithium iron phosphate, LiFePO₄). In embodiments where the cell is a zinc battery, the cathode material is graphite, NiOOH, Ag, or AgO. In an embodiment, the positive electrode comprises an active material in electronic communication with a current

collector. In an embodiment, the current collector comprises an external connection tab; in an embodiment the external connection tab is integral with the current collector. In an embodiment, the current collector is an electronically conductive material such as a metal.

[0068] Electrolyte

[0069] In embodiments, the electrolyte is a liquid electrolyte, gel electrolyte, polymer electrolyte or ceramic electrolyte. In embodiments, the electrolyte is aqueous or nonaqueous. When the electrochemical cell is a lithium ion battery, the electrolyte is preferably nonaqueous. In an embodiment, the electrolyte comprises one or more lithium salts dissolved in a nonaqueous solvent.

[0070] Solid Electrolyte

[0071] In an embodiment, the solid electrolyte can be a free standing layer or a coating layer. In another embodiment, the solid electrolyte is in the form of particles or fibers filling the holes-pores of an electronically insulating layer or the electronically conductive layer. In an embodiment, a layer is provided comprising at least a porous layer of electronically conductive material and at least a group of fibers or particles filling the pores or holes of the porous layer. A variety of solid electrolytes are known to the art and include, but are not limited to LISICON (Lithium super ionic conductor, $\text{Li}_{2+2x}\text{Zn}_{1-x}\text{GeO}_4$), PEO (polyethylene oxide), NASICON, and LIPON.

[0072] Insulator

[0073] In embodiments, the electronically insulating layer comprises a polymer, an oxide, a glass or a combination of these. In embodiments, the electronically insulating is nonwoven or a woven. In an embodiment, the insulating layer is polymeric such as microporous or nonwoven PE, PP, PVDF, polyester or polyimide. In a further embodiment the insulating layer is an oxide such as aluminum oxide. In an embodiment, said electronically insulating comprises a coating provided on at least one side of said electronically conductive layer. As an example, an aluminum oxide layer is provided on an aluminum layer. In an embodiment, the electronically insulating comprises one or more perforated or porous layers each independently having a porosity greater than or equal to 30%, from 30% to 80% or from 50% to 75%. In an embodiment, one or more perforated or porous layers each independently have a thickness selected over the range of 20 nm to 1 mm, 0.005 mm to 1 mm, from 1 μm to 500 μm or from 5 μm to 100 μm . In an embodiment, the separator comprises a first insulating layer having a plurality of apertures arranged in a first pattern and a second insulating layer having a plurality of apertures arranged in a second pattern; wherein said second pattern has an off-set alignment relative to said first pattern such that an overlap of said apertures of said first insulating layer and said apertures of said second insulating layer along axes extending perpendicularly from said first insulating layer to said second insulating layer is less than or equal to 20%. In an embodiment, there is no overlap of the apertures.

[0074] Electronically Conductive Layer

[0075] In embodiments, said electronically conductive layer comprises a chemically resistant material, a heat resistant material, a mechanically resistant material or any combination of these. In an embodiment, the conductive layer comprises a metal, alloy, carbon or a conductive polymer. In an embodiment, the electronically conductive layer comprises a metal foil, a metallic thin film, an electronically conductive polymer, a carbonaceous material or a composite material of any of these. In an embodiment, the metal or alloy

is selected from Al, Cu, Ti, Ni, Fe, stainless steel, Sn, Si, Au, Pt, Ag, Mn, Pb and their alloys and Zircalloy, Hastalloy, and superalloys. In an embodiment, the electronically conductive layer comprises a metal selected from the group consisting of Al, Ti, Cu, stainless steel, Ni, Fe, or any alloys or composites thereof. In an embodiment, the carbonaceous material is selected from conductive carbon, super-P, carbon black and activated carbon. In an embodiment, the electronically conducting polymer is selected from the linear-backbone "polymer blacks" (polyacetylene, polypyrrole, and polyaniline) and their copolymers, poly(p-phenylene vinylene) (PPV) and its soluble derivatives and poly(3-alkylthiophenes). In an embodiment, the electronically conducting layer does not react chemically or electrochemically with the electrolyte. In an embodiment, electronically conductive layer comprises a metal reactive with an active material of the negative or positive electrode. In an embodiment, the electronically conductive layer comprises a metal selected from the group consisting of Al and Sn. In embodiments, the thickness of the electronically conductive layer is greater than zero and less than 1 mm, greater than zero and less than 0.1 mm, from 0.001 mm to 1 mm, from 0.005 mm to 1 mm, from 0.005 mm to 0.5 mm, from 0.01 mm to 0.1 mm, from 0.075 mm to 0.2 mm or from of 25 nm to 0.5 mm. In an embodiment, the composite separator further comprises one or more additional electronically conductive layers.

[0076] In another embodiment, the electronically conductive layer or a coating on the electronically conductive layer provides a source of active ions. For example, in a lithium ion cells the electronically conductive layer may have a coating of lithium metal on it or may be made of lithium. In a further embodiment, the electronically conducting layer is porous or perforated and holes or pores in the electronically conducting layer are at least partially filled with particles or fibers comprising a source of active ions. The source of active ions is used to provide active ions to the cell, such as to compensate the ion loss or to make Li-ion cells with non-lithiated electrodes.

[0077] In a further embodiment, the electronically conducting layer is porous or perforated and holes or pores in the electronically conductive layer are at least partially filled by particles or fibers of an active material. Suitable active materials include, but are not limited to, traditional electrode active materials such as LiTiO_2 , silicon or graphite. In an embodiment, application of a voltage or current between the electronically conducting layer and one of the electrodes results in gain and release of ions by the fibers or particles, such that ionic charge carriers are able to be transported between said positive electrode and said negative electrode through the pores or holes of the electronically conducting layer. For example, a pulse or sinusoidal voltage between 1 and 2.5 V may be applied between a graphite anode and a layer comprising LiTiO_2 fibers inside a copper matrix in a Li-ion cell with a cathode such as air or sulfur.

[0078] In a further embodiment, the electronically conducting layer is porous or perforated and holes or pores in the electronically conductive layer are at least partially filled by particles or fibers of a redox shuffle material. In an embodiment, the redox shuffle material can be activated by application of a voltage or current between an external tab connected to the electronically conducting layer and an external tab connected to an electrode or another electronically conducting layer.

[0079] Exemplary Composite Separator Configurations:

[0080] FIG. 3A shows an exemplary configuration of an electrochemical cell including a multilayer separator with an electronically conductive layer (4) sandwiched between two electronically insulating layers (3). Cathode (1), Anode (2), Separator (3), Perforated or Porous Conductive Layer (4). Thickness of separator (3) is less between cathode (1) and conductive layer (4) than between anode (2) and conductive layer (4). FIG. 3B shows an exemplary configuration of a system including an electrochemical cell similar to that shown in FIG. 3A and devices (5) for monitoring or applying voltage or current. Cathode (1), Anode (2), Separator (3), Perforated or Porous Conductive Layer (4). A device (5) for monitoring or applying voltage or current is connected between the cathode and anode and also between the electronically conductive layer (4) and the cathode (1)

[0081] FIG. 4A. shows an exemplary configuration of an electrochemical cell including a multilayer separator with an electronically conductive layer (4) sandwiched between two electronically insulating layers (3). Cathode (1), Anode (2), Separator (3), Perforated or Porous Conductive Layer (4). Thickness of separator (3) is less between anode (2) and conductive layer (4) than between cathode (1) and conductive layer (4). FIG. 4B shows an exemplary configuration of a system including an electrochemical cell with a central electronically conductive layer and devices (5) for monitoring or applying voltage or current. Cathode (1), Anode (2), Separator (3), Perforated or Porous Conductive Layer (4). A device (5) for monitoring or applying voltage or current is connected between the cathode and anode and also between the electronically conductive layer (4) and the anode (2)

[0082] FIG. 5A shows an exemplary configuration of an electrochemical cell including a multilayer separator with two electronically conductive layers. Cathode (1), Anode (2), Separator (3), Perforated or Porous Conductive Layers (4). FIG. 5B shows an exemplary configuration of a system including an electrochemical cell with two electronically conductive layers and devices (5) for monitoring or applying voltage or current. Cathode (1), Anode (2), Separator (3), Perforated or Porous Conductive Layer (4). A device (5) for monitoring or applying voltage or current is connected between the cathode and anode and also between the two electronically conductive layers (4). FIG. 5C shows an exemplary configuration of a system including an electrochemical cell with two electronically conductive layers and devices (5) for monitoring or applying voltage or current. Cathode (1), Anode (2), Separator (3), Perforated or Porous Conductive Layer (4). A device (5) for monitoring or applying voltage or current is connected between the cathode and anode and also between one electronically conductive layer (4) and the cathode (1) and between the other electronically conductive layer (4) and the anode (2).

[0083] FIG. 6 shows an exemplary configuration of an electrochemical cell including a multilayer separator with two electronically conductive layers. One electronically conductive layer is in contact with the cathode (1) while the other is located between two separator layers (3). Cathode (1), Anode (2), Separator (3), Perforated or Porous Conductive Layers (4).

[0084] FIG. 7 shows an exemplary configuration of a multilayer separator with two electronically conductive layers. One electronically conductive layer is in contact with the anode (e) while the other is located between two separator

layers (3). Cathode (1), Anode (2), Separator (3), Perforated or Porous Conductive Layers (4).

[0085] In an aspect, the invention provides an electrochemical cell comprising: (i) a positive electrode; (ii) a negative electrode; (iii) one or more electrolytes positioned between said positive electrode and said negative electrode; said one or more electrolytes capable of conducting ionic charge carriers; and (iv) a composite separator comprising at least one electronically insulator layer and at least one electronically conductive layer; said separator positioned between said positive electrode and said negative electrode such that said ionic charge carriers are able to be transported between said positive electrode and said negative electrode but not electronic charge carriers; wherein the presence of the said electronically conductive layer(s) of the said separator affects the performance of the electrochemical cell performance upon formation of an electrical short between any of the said electrodes or the said electronically conductive layer.

[0086] In a further aspect, the invention provides an electrochemical cell comprising: (i) a positive electrode; (ii) a negative electrode; (iii) one or more electrolytes positioned between said positive electrode and said negative electrode; said one or more electrolytes capable of conducting ionic charge carriers; and (iv) a composite separator comprising at least one electronically insulator layer and at least one electronically conductive layer; said separator positioned between said positive electrode and said negative electrode such that said ionic charge carriers are able to be transported between said positive electrode and said negative electrode but not electronic charge carriers; wherein each said electronically conductive layer of the said separator further comprises an external connection tab and the cell further comprises a voltage or current applying circuit connected between each of said electrochemically conductive layers and one of the positive or the negative electrode, thereby allowing modification of the electric field and the performance of the electrochemical cell. In an embodiment, each said electronically conductive layer is a coating provided on at least a portion of said electronically insulating layer. In an embodiment, there are two electronically conductive layers and three electronically insulating layers, each electronically conductive layer being separated from the other and the positive and negative electrodes by an electronically insulating layer.

[0087] In an aspect, the invention provides an electrochemical cell comprising: (i) a positive electrode; (ii) a negative electrode; (iii) one or more electrolytes positioned between said positive electrode and said negative electrode; said one or more electrolytes capable of conducting ionic charge carriers; and (iv) a composite separator comprising at least one electronically insulator layer and at least one electronically conductive layer; said separator positioned between said positive electrode and said negative electrode such that said ionic charge carriers are able to be transported between said positive electrode and said negative electrode but not electronic charge carriers; wherein in the event of formation of an electrical short between the said electronically conductive layer of the said separator and said positive electrode or said negative electrode, chemical reaction happens between the electronically conductive layer and electronic short (internal, such as a dendrite or a foreign metallic layer, or external); which consumes and or dissipates energy.

[0088] In an aspect, the invention provides an electrochemical cell comprising: (i) a positive electrode; (ii) a negative electrode; (iii) one or more electrolytes positioned

between said positive electrode and said negative electrode; said one or more electrolytes capable of conducting ionic charge carriers; and (iv) a composite separator comprising at least one electronically insulator layer and at least one electronically conductive layer; said separator positioned between said positive electrode and said negative electrode such that said ionic charge carriers are able to be transported between said positive electrode and said negative electrode but not electronic charge carriers; wherein in the event of formation of an electronically short between the said electronically conductive layer of the said separator and said positive electrode or said negative electrode, the said electronically conductive layer transports the heat away from the short location and reduces the likelihood of hot spots or thermal runaway

[0089] In an aspect, the invention provides an electrochemical cell comprising: (i) a positive electrode; (ii) a negative electrode; (iii) one or more electrolytes positioned between said positive electrode and said negative electrode; said one or more electrolytes capable of conducting ionic charge carriers; and (iv) a composite separator comprising at least one electronically insulator layer and at least one electronically conductive layer; said separator positioned between said positive electrode and said negative electrode such that said ionic charge carriers are able to be transported between said positive electrode and said negative electrode but not electronic charge carriers; wherein in the said electronically conductive layer of the said separator has an external tab that can be used to monitor the performance of the cell by measuring the voltage or current. Optionally, sometimes the voltage doesn't change but the current does slightly, say the current=C/100 rate or higher of the cell capacity) between the said tab and one of the electrodes.

[0090] In an aspect, the invention provides an electrochemical cell comprising (i) a positive electrode; (ii) a negative electrode; (iii) one or more electrolytes positioned between said positive electrode and said negative electrode; said one or more electrolytes capable of conducting ionic charge carriers; and (iv) a composite separator comprising at least one electronically insulator layer and at least one electronically conductive layer; said separator positioned between said positive electrode and said negative electrode such that said ionic charge carriers are able to be transported between said positive electrode and said negative electrode but not electronic charge carriers; wherein in the said electronically conductive layer of the said separator has an external tab that can be used to modify the performance of the cell by applying a voltage or current between the said tab and one of the electrodes. Optionally, the electronically conductive layer can have a source of active ions, for example can have a coating of lithium metal on it or can itself be made of lithium, in a lithium ion cells, which can be used to provide active ions to the cell, such as to compensate the ion loss or to make li-ion cells with non-lithiated electrodes)

[0091] In an aspect, the invention provides an electrochemical cell comprising (i) a positive electrode; (ii) a negative electrode; (iii) one or more electrolytes positioned between said positive electrode and said negative electrode; said one or more electrolytes capable of conducting ionic charge carriers; and (iv) at least a composite solid electrolyte comprising at least an electronically non-conductive layer, at least a porous layer of electronically conductive material and at least a group of solid electrolyte fibers or particles filling the pores/holes of the porous layer; said solid electrolyte

positioned between said positive electrode and said negative electrode such that said ionic charge carriers are able to be transported between said positive electrode and said negative electrode, but not electronic charge carriers; Optionally, the particles can consist of known solid electrolyte, such as known polymer or ceramic solid electrolytes. Optionally, the particles may have a source of active ions, for example can be lithium metal, in a lithium ion cells, which can be used to provide active ions to the cell, such as to compensate the ion loss or to make li-ion cells with non-lithiated electrodes). Optionally, the said electronically conductive layer of the said solid electrolyte may have an external tab that can be used to modify the performance of the cell by applying a voltage or current between the said tab and one of the electrodes.

[0092] In an aspect, the invention provides a composite solid electrolyte for an electrochemical cell comprising at least an electronically non-conductive layer, at least a porous layer of electronically conductive material and at least a group of fibers or particles filling the pores/holes of the porous layer; wherein in the said electronically conductive layer of the said solid electrolyte has an external tab for changing the voltage between the particles and the electrodes by applying a voltage or current between the said tab and one of the electrodes; where in the applied voltage or current between the between the said embedded particles and the electrodes results in the gaining and releasing the ions by the fibers/particles, such that said ionic charge carriers are able to be transported between said positive electrode and said negative electrode, but not electronic charge carriers, through the solid electrolyte. Optionally, the solid particles can be a component of the electronically conductive layer, but: The solid particles can be a free standing layer or a coating layer; or the solid particles can be a component of the electronically non-conductive layer, e.g., particles or fibers filling the holes/pores of the electronically non-conductive layer. Optionally, the solid particles can be traditional electrode active material (transporting ions with appropriate voltage or current, such as LiTiO₂, Silicon or Graphite). Optionally, the applied voltage or current for each step of cycling can be constant voltage or current or a time variable such as a sinusoidal, pulse or step wave varying between the charge-discharge voltages of the nontraditional solid electrolyte.) Optionally, a pulse or sinusoidal between 1 and 2.5V applied between a graphite anode and the composite solid electrolyte (LiTiO₂ fibers inside a copper matrix) in a li-ion cell, for example with an air or sulfur electrode.

[0093] In an aspect, the invention provides an electrochemical cell comprising: (I) a positive electrode; (ii) a negative electrode; (iii) one or more electrolytes positioned between said positive electrode and said negative electrode; said one or more electrolytes capable of conducting ionic charge carriers; and (iv) at least a composite solid electrolyte comprising at least an electronically non-conductive layer, at least a porous layer of electronically conductive material and at least a group of fibers or particles filling the pores/holes of the porous layer; said composite solid electrolyte positioned between said positive electrode and said negative electrode such that said ionic charge carriers are able to be transported between said positive electrode and said negative electrode, but not electronic charge carriers; wherein in the said electronically conductive layer of the said separator has an external tab that can be used to modify the performance of the cell by applying a voltage or current between the said tab and one of the electrodes.

[0094] In an aspect, the invention provides an electrochemical cell comprising: (i) a positive electrode; (ii) a negative electrode; (iii) one or more electrolytes positioned between said positive electrode and said negative electrode; said one or more electrolytes capable of conducting ionic charge carriers; and (iv) a composite separator comprising at least one electronically insulator layer and at least one electronically conductive layer; said separator positioned between said positive electrode and said negative electrode such that said ionic charge carriers are able to be transported between said positive electrode and said negative electrode but not electronic charge carriers; wherein said electronically conductive layer(s) of the said separator changes the electrochemical cell performance upon formation of an electrical short between the electrically conductive layer and said positive electrode or said negative electrode

[0095] The conductive layer can be used for charging or discharging, a specific example is shorting the conductive layer with the cathode that assists in oxygen evolution during charging in metal air batteries. Applying a voltage other than zero between the conductive electrode and the cathode or the anode can result in activating assisting materials, such as modifiers to decrease the cell temperature and thermal runaway prevention.

[0096] As an another example it is known that active electrode material may be lost when charged particles deposit in the separator, such as zinc or zinc oxide particles in Zinc batteries or polysulfide particles in li-ion batteries, which severely reduces the cell capacity and cycle life, applying a voltage between the conductive layer and the anode in this case, e.g., every 50 cycles, can deposit back the active materials from the separator to the anode and can result in higher cycle life.

BRIEF DESCRIPTION OF THE DRAWINGS

[0097] FIG. 1. Electroplating (charging) without the conductive layer. The circles are the positive ions leaving the opposite electrode and depositing on the electrode of interest.

[0098] FIG. 2. Electroplating (charging) with the conductive layer (4) in the middle.

[0099] FIG. 3A. Exemplary configuration of an electrochemical cell including a multilayer separator with a central electronically conductive layer. Cathode (1), Anode (2), Separator (3), Perforated or Porous Conductive Layer (4). Thickness of separator (3) is less between cathode (1) and conductive layer (4) than between anode (2) and conductive layer (4).

[0100] FIG. 3B. Exemplary configuration of a system including an electrochemical cell with a central electronically conductive layer and devices (5) for monitoring or applying voltage or current. Cathode (1), Anode (2), Separator (3), Perforated or Porous Conductive Layer (4). A device (5) for monitoring or applying voltage or current is connected between the cathode and anode and also between the electronically conductive layer (4) and the cathode (1).

[0101] FIG. 4A. Exemplary configuration of an electrochemical cell including a multilayer separator with a central electronically conductive layer. Cathode (1), Anode (2), Separator (3), Perforated or Porous Conductive Layer (4). Thickness of separator (3) is less between anode (2) and conductive layer (4) than between cathode (1) and conductive layer (4).

[0102] FIG. 4B. Exemplary configuration of a system including an electrochemical cell with a central electronically

conductive layer and devices (5) for monitoring or applying voltage or current. Cathode (1), Anode (2), Separator (3), Perforated or Porous Conductive Layer (4). A device (5) for monitoring or applying voltage or current is connected between the cathode and anode and also between the electronically conductive layer (4) and the anode (2).

[0103] FIG. 5A. Exemplary configuration of an electrochemical cell including a multilayer separator with two central electronically conductive layers. Cathode (1), Anode (2), Separator (3), Perforated or Porous Conductive Layers (4).

[0104] FIG. 5B. Exemplary configuration of a system including an electrochemical cell with two electronically conductive layers and devices (5) for monitoring or applying voltage or current. Cathode (1), Anode (2), Separator (3), Perforated or Porous Conductive Layer (4). A device (5) for monitoring or applying voltage or current is connected between the cathode and anode and also between the two electronically conductive layers (4).

[0105] FIG. 5C. Exemplary configuration of a system including an electrochemical cell with two electronically conductive layers and devices (5) for monitoring or applying voltage or current. Cathode (1), Anode (2), Separator (3), Perforated or Porous Conductive Layer (4). A device (5) for monitoring or applying voltage or current is connected between the cathode and anode and also between one electronically conductive layer (4) and the cathode (1) and between the other electronically conductive layer (4) and the anode (2).

[0106] FIG. 6. Exemplary configuration of an electrochemical cell including a multilayer separator with two electronically conductive layers. One electronically conductive layer is in contact with the cathode (1) while the other is located between two separator layers (3). Cathode (1), Anode (2), Separator (3), Perforated or Porous Conductive Layers (4).

[0107] FIG. 7. Exemplary configuration of a multilayer separator with two electronically conductive layers. One electronically conductive layer is in contact with the anode (2) while the other is located between two separator layers (3). Cathode (1), Anode (2), Separator (3), Perforated or Porous Conductive Layers (4).

[0108] FIG. 8. Capacity (mAh) versus cycles for a LiTiO₂, Toray, Al, lithium cell.

[0109] FIG. 9. Capacity (mAh) versus cycles for a LiTiO₂, Celgard, Cu, lithium cell.

[0110] FIG. 10 Capacity (mAh) versus cycles for a LiTiO₂, Celgard, Ni, lithium cell.

[0111] FIG. 11. Capacity (mAh) versus cycles for a pouch cell containing EC: EMC (3:7 wt %)-1.2M LiPF₆, Toda NMC (111) vs. Li. Cathode active wt: 0.2021 g. Specific capacity at 12 mA discharge=148 mAh/g.

[0112] FIG. 12. Ionic diodes, in the form of a pair of one directional ion channels with opposite directions, as components of the separator and/or electrolyte.

[0113] FIG. 13. Porous metal structure Anode.

[0114] FIG. 14. Schematic illustration of a battery before use. All of the electrode particles are electronically connected.

[0115] FIG. 15. Schematic illustration of the battery after charging, the electrode particles have a large shape change

[0116] FIG. 16. Schematic illustration of the battery, with the conventional separator, after several cycling, some of the electrode particles have lost their electronic connection with the current collector and thus are in-active.

[0117] FIG. 17. Schematic illustration of the battery, with the new separator, after several cycling, some of the electrode particles have lost their conventional electronic connection with the current collector but the new separator provides a new path for some of the electrode particles. Green shows the new path of the electrons, due to the new separator.

[0118] FIG. 18. Example showing combinations of the multi-layer separators between anode and cathode electrodes

DETAILED DESCRIPTION OF THE INVENTION

[0119] In general the terms and phrases used herein have their art-recognized meaning, which can be found by reference to standard texts, journal references and contexts known to those skilled in the art. The following definitions are provided to clarify their specific use in the context of the invention.

[0120] Referring to the drawings, like numerals indicate like elements and the same number appearing in more than one drawing refers to the same element. In addition, hereinafter, the following definitions apply:

[0121] The term “electrochemical cell” refers to devices and/or device components that convert chemical energy into electrical energy or electrical energy into chemical energy. Electrochemical cells have two or more electrodes (e.g., positive and negative electrodes) and an electrolyte, wherein electrode reactions occurring at the electrode surfaces result in charge transfer processes. Electrochemical cells include, but are not limited to, primary batteries, secondary batteries and electrolysis systems. In certain embodiments, the term electrochemical cell includes fuel cells, supercapacitors, capacitors, flow batteries, metal-air batteries and semi-solid batteries. General cell and/or battery construction is known in the art, see e.g., U.S. Pat. Nos. 6,489,055, 4,052,539, 6,306,540, Seel and Dahn J. Electrochem. Soc. 147(3) 892-898 (2000).

[0122] The term “capacity” is a characteristic of an electrochemical cell that refers to the total amount of electrical charge an electrochemical cell, such as a battery, is able to hold. Capacity is typically expressed in units of ampere-hours. The term “specific capacity” refers to the capacity output of an electrochemical cell, such as a battery, per unit weight. Specific capacity is typically expressed in units of ampere-hours kg^{-1} .

[0123] The term “discharge rate” refers to the current at which an electrochemical cell is discharged. Discharge rate can be expressed in units of ampere. Alternatively, discharge rate can be normalized to the rated capacity of the electrochemical cell, and expressed as $C/(X t)$, wherein C is the capacity of the electrochemical cell, X is a variable and t is a specified unit of time, as used herein, equal to 1 hour.

[0124] “Current density” refers to the current flowing per unit electrode area.

[0125] Electrode refers to an electrical conductor where ions and electrons are exchanged with electrolyte and an outer circuit. “Positive electrode” and “cathode” are used synonymously in the present description and refer to the electrode having the higher electrode potential in an electrochemical cell (i.e. higher than the negative electrode). “Negative electrode” and “anode” are used synonymously in the present description and refer to the electrode having the lower electrode potential in an electrochemical cell (i.e. lower than the positive electrode). Cathodic reduction refers to a gain of electron(s) of a chemical species, and anodic oxidation refers to the loss of electron(s) of a chemical species. Positive electrodes and negative electrodes of the present electrochemical

cell may further comprise a conductive diluent, such as acetylene black, carbon black, powdered graphite, coke, carbon fiber, graphene, and metallic powder, and/or may further comprise a binder, such as a polymer binder. Useful binders for positive electrodes in some embodiments comprise a fluoropolymer such as polyvinylidene fluoride (PVDF). Positive and negative electrodes of the present invention may be provided in a range of useful configurations and form factors as known in the art of electrochemistry and battery science, including thin electrode designs, such as thin film electrode configurations. Electrodes are manufactured as disclosed herein and as known in the art, including as disclosed in, for example, U.S. Pat. Nos. 4,052,539, 6,306,540, and 6,852,446. For some embodiments, the electrode is typically fabricated by depositing a slurry of the electrode material, an electronically conductive inert material, the binder, and a liquid carrier on the electrode current collector, and then evaporating the carrier to leave a coherent mass in electrical contact with the current collector.

[0126] “Electrode potential” refers to a voltage, usually measured against a reference electrode, due to the presence within or in contact with the electrode of chemical species at different oxidation (valence) states.

[0127] “Electrolyte” refers to an ionic conductor which can be in the solid state, the liquid state (most common) or more rarely a gas (e.g., plasma).

[0128] “Standard electrode potential” (E°) refers to the electrode potential when concentrations of solutes are 1M, the gas pressures are 1 atm and the temperature is 25 degrees Celsius. As used herein standard electrode potentials are measured relative to a standard hydrogen electrode.

[0129] “Active material” refers to the material in an electrode that takes part in electrochemical reactions which store and/or deliver energy in an electrochemical cell.

[0130] “Cation” refers to a positively charged ion, and “anion” refers to a negatively charged ion.

[0131] “Electrical contact,” “electrical communication,” “electronic contact” and “electronic communication” refer to the arrangement of one or more objects such that an electric current efficiently flows from one object to another. For example, in some embodiments, two objects having an electrical resistance between them less than 100Ω are considered in electrical communication with one another. An electrical contact can also refer to a component of a device or object used for establishing electrical communication with external devices or circuits, for example an electrical interconnection. “Electrical communication” also refers to the ability of two or more materials and/or structures that are capable of transferring charge between them, such as in the form of the transfer of electrons. In some embodiments, components in electrical communication are in direct electrical communication wherein an electronic signal or charge carrier is directly transferred from one component to another. In some embodiments, components in electrical communication are in indirect electrical communication wherein an electronic signal or charge carrier is indirectly transferred from one component to another via one or more intermediate structures, such as circuit elements, separating the components.

[0132] A short in a battery refers to electronic connection between two electronically conductive layers with different charges (such as two electrodes), which can be internal (dendrite or foreign materials) or external (e.g., a wire between two opposite tabs). The term “electronical short” or “electric short” may also be used in place of “short”.

[0133] “Electrical conductivity” or “electrically conductive” refers to transfer of charges which can be ionic (ions) or electronic (electrons). “Electronic conductivity” or “electronically conductive” refers to transfer of charges which are electronic (electrons). As used herein, a separator element can permit passage of ions through pores or perforations present in element even though the material of the separator element is not ionically conductive. Such an element may be referred to as having low electronic resistance. As an example a perforated copper sheet can be ionically conductive as well as electronically conductive. “Ionic conductivity” or “ionically conductive” refers to transport of ionic charge carriers.

[0134] “Thermal contact” and “thermal communication” are used synonymously and refer to an orientation or position of elements or materials, such as a current collector or heat transfer rod and a heat sink or a heat source, such that there is more efficient transfer of heat between the two elements than if they were thermally isolated or thermally insulated. Elements or materials may be considered in thermal communication or contact if heat is transported between them more quickly than if they were thermally isolated or thermally insulated. Two elements in thermal communication or contact may reach thermal equilibrium or thermal steady state and in some embodiments may be considered to be constantly at thermal equilibrium or thermal steady state with one another. In some embodiments, elements in thermal communication with one another are separated from each other by a thermally conductive material or intermediate thermally conductive material or device component. In some embodiments, elements in thermal communication with one another are separated by a distance of 1 μm or less. In some embodiments, elements in thermal communication with one another are provided in physical contact.

[0135] “High mechanical strength” refers to a property of components of separator systems of the invention, such as first, second, third and fourth high mechanical strength layers, having a mechanical strength sufficient to prevent physical contact of opposite electrodes, sufficient to prevent short circuiting due to external objects within the cell, such as metallic particles from fabrication, and sufficient to prevent short circuiting due to growth of dendrites between positive and negative electrodes of an electrochemical cell, for example, during charge and discharge cycles of a secondary electrochemical cell. In an embodiment, for example, a high mechanical strength layer has a mechanical strength sufficient to prevent piercing due to external objects in the cell, such as metallic particles from the fabrication, and shorts due to the growth of dendrites between electrodes. In an embodiment, for example, a high mechanical strength layer has a mechanical strength sufficient to prevent shorting between the positive electrode and the negative electrode of an electrochemical cell due to external objects in the cell such as metallic particles from the fabrication and shorts due to the growth of dendrites between electrodes. In an embodiment, for example, a high mechanical strength layer is characterized by a Young’s modulus greater than or equal to 500 MPa, and optionally for some applications a Young’s modulus greater than or equal to 1 GPa, and optionally for some applications a Young’s modulus greater than or equal to 10 GPa, and optionally for some applications a Young’s modulus greater than or equal to 100 GPa. In an embodiment, for example, a high mechanical strength layer is characterized by a yield strength greater than or equal to 5 MPa, and optionally for some applications a yield strength greater than or equal to 50

MPa, and optionally for some applications a yield strength greater than or equal to 100 MPa, and optionally for some applications a yield strength greater than or equal to 500 MPa. In an embodiment, for example, a high mechanical strength layer is characterized by a propagating tear strength greater than or equal to 0.005 N, and optionally for some applications a propagating tear strength greater than or equal to 0.05 N, a propagating tear strength greater than or equal to 0.5 N, a propagating tear strength greater than or equal to 1 N. In an embodiment, for example, a high mechanical strength layer is characterized by an initiating tear strength greater than or equal to 10 N, and optionally for some applications an initiating tear strength greater than or equal to 100 N. In an embodiment, for example, a high mechanical strength layer is characterized by a tensile strength greater than or equal to 50 MPa, and optionally for some applications a tensile strength greater than or equal to 100 MPa, and optionally for some applications a tensile strength greater than or equal to 500 MPa, and optionally for some applications a tensile strength greater than or equal to 1 GPa. In an embodiment, for example, a high mechanical strength layer is characterized by an impact strength greater than or equal to 10 N cm, and optionally for some applications to an impact strength greater than or equal to 50 N cm, and optionally for some applications to an impact strength greater than or equal to 100 N cm, and optionally for some applications to an impact strength greater than or equal to 500 N cm.

[0136] “Chemically resistant” refers a property of components, such as layers, of separators and electrochemical systems of the invention wherein there is no significant chemical or electrochemical reactions with the cell active materials, such as electrodes and electrolytes. In certain embodiments, chemically resistant also refers to a property wherein the tensile retention and elongation retention is at least 90% in the working environment of an electrochemical system, such as an electrochemical cell.

[0137] “Thermally stable” refers a property of components, such as layers, of separators and electrochemical systems of the invention wherein there is no significant chemical or electrochemical reactions due to normal and operational thermal behavior of the cell. In certain embodiments, thermally stable also refers to materials wherein the melting point is more than 100 Celsius, and preferably for some embodiments more than 300 Celsius, and optionally the coefficient of thermal expansion is less than 50 ppm/Celsius. In an embodiment, thermally stable refers to a property of a component of the separator system such that it may perform in a rechargeable electrochemical cell without undergoing a change size or shape with the temperature that significantly degrades the performance of the electrochemical cell.

[0138] “Porosity” refers to the amount of a material or component, such as a high mechanical strength layer, that corresponds to pores, such as apertures, channels, voids, etc. Porosity may be expressed as the percentage of the volume of a material, structure or device component, such as a high mechanical strength layer, that corresponds to pores, such as apertures, channels, voids, etc., relative to the total volume occupied by the material, structure or device component.

[0139] In an aspect, the disclosure provides a multi-layer battery separator with at least one conductive layer to prolong the cycle life and safety enhancement of the cell. The conductive layer may have an external tab that can be used for monitoring the cell or be used to “control” the cell. The conductive layer prolongs the cycle life of the battery by

different mechanisms. In the case where the conductive layer does not include an auxiliary external tab the conductive layer may prolong by cycle life by one or all of the following mechanisms: a) as a free standing physical barrier, stronger than conventional PP-PP separators, which limits the size of a short to the size of the pores of the conductive layer (an example is a 0.007 mm thick stainless steel or copper perforated film) and b) as a chemically reactive material to the short material, such that the reaction between the conductive layer and the short results in energy consumption and may stop or remove the short (an example is a 0.007 mm aluminum film or a 0.001 mm aluminum coating on one side of a porous polymer film, such as microporous PP-PP). When an external tab electronically connects the conductive layer to outside of the cell additional mechanisms include c) use of the external tab to monitor the voltage between any of the electrodes and the conductive layer and d) use of the external tab to apply a voltage or current between any of the electrodes and the conductive layer. Mechanism d) includes the mechanisms of d1) burning the short, d2) activating a solid electrolyte, d3) activating alloying with dendrite and d4) releasing other substances in the cell.

[0140] In an embodiment, for example, the composite separator is provided in physical contact with the positive electrode and the negative electrode. In an embodiment, for example, the separator system with an electrolyte an ionic conductivity between the positive electrode and the negative electrode equal to or greater than 1×10^{-3} S/cm, optionally for some applications preferably greater than 1×10^{-2} S/cm. In an embodiment, for example, the separator system in the presence of an appropriate electrolyte provides a net ionic resistance from the positive electrode to the negative electrode selected over the range of 0.5 ohm cm^2 to 25 ohm cm^2 , and preferably for some applications less than 5 ohm cm^2 .

[0141] In an embodiment, for example, a layer permeable to ionic charge carriers has an ionic resistance less than or equal to 20 ohm- cm^2 , and preferably for some embodiments less than or equal to 2 ohm- cm^2 , and preferably for some embodiments less than or equal to 1 ohm- cm^2 .

[0142] Optionally, an ionically conductive and electronically insulating material has an ionic conductivity greater than or equal to 10^{-5} S/cm, greater than or equal to 10^{-4} S/cm, greater than or equal to 10^{-4} S/cm, greater than or equal to 10^{-3} S/cm, greater than or equal to 10^{-2} S/cm, greater than or equal to 10^{-1} S/cm, greater than or equal to 10 S/cm, selected from the range of 10^{-7} S/cm to 100 S/cm, selected from the range of 10^{-5} S/cm to 10 S/cm, selected from the range of 10^{-3} S/cm to 1 S/cm. Optionally, the first ionically conductive and electronically insulating material has an ionic conductivity selected from the range of 10^{-7} S/cm to 100 S/cm at an operating temperature of the cell.

[0143] In an embodiment, the electronically conductive separator has a thermal conductivity greater than or equal to $5 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$, greater than or equal to $10 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$, greater than or equal to $20 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$, greater than or equal to $50 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$, greater than or equal to $100 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ or greater than or equal to $200 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$. In an embodiment, the thermal conductivity is from $50 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ to $500 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$, or $100 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ to $500 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$, as measured at 25°C .

[0144] In embodiments, the layer permeable to ionic charge carriers is selected from the group consisting of a perforated polymer separator, a porous polymer separator, a perforated ceramic separator, a porous ceramic separator, a perforated

glass separator, a porous glass separator, a perforated metal or perforated alloy separator, a porous metal or porous alloy separator, a metal mesh and an alloy mesh. In an embodiment, for example, a layer permeable to ionic charge carriers is selected from the group consisting of a ceramic electrolyte, a glass electrolyte, a polymer electrolyte or another solid electrolyte. In an embodiment, for example, the layer permeable to ionic charge carriers comprises a glass electrolyte, such as Nafion or ZrO_2 or NASICON or LISICON or LIPON, or a polymer electrolyte such as PEO.

[0145] Optionally, the first ionically conductive and electronically insulating material comprises a solid electrolyte, a gel electrolyte, a polymer electrolyte, LISICON, NASICON, PEO, $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$, LIPON, PVDF, Li_3N , Li_3P , LiI, LiBr, LiCl, LiF, oxide perovskite, $\text{La}_{0.5}\text{Li}_{0.5}\text{TiO}_3$, thio-LISICON, $\text{Li}_{3.25}\text{Ge}_{0.25}\text{P}_{0.75}\text{S}_4$, glass ceramics, $\text{Li}_7\text{P}_3\text{S}_{11}$, glassy materials, $\text{Li}_2\text{S}-\text{SiS}_2-\text{Li}_3\text{PO}_4$, lithium nitride, polyethylene oxide, Doped Li_3N , $\text{Li}_2\text{S}-\text{SiS}_2-\text{Li}_3\text{PO}_4$, LIPON, $\text{Li}_{14}\text{Zn}(\text{GeO}_4)_4$, Li-beta-alumina, $\text{Li}_{3.6}\text{Si}_{0.6}\text{P}_{0.4}\text{O}_4$, $\text{Li}_2\text{S}-\text{P}_2\text{S}_5$, PEO- LiClO_4 , $\text{LiN}(\text{CF}_3\text{SO}_2)_2/(\text{CH}_2\text{CH}_2\text{O})_8$, NaPON, ZrO_2 , Nation, PEDOT:PSS, SiO_2 , PVC, glass fiber mat, alumina, silica glass, ceramics, glass-ceramics, water-stable polymers, glassy metal ion conductors, amorphous metal ion conductors, ceramic active metal ion conductors, glass-ceramic active metal ion conductors, an ion conducting ceramic, an ion conducting solid solution, an ion conducting glass, a solid lithium ion conductor or any combination of these

[0146] Optionally, the above-mentioned first ionically conductive and electronically insulating material has an average porosity less than 1%. Preferably, the first ionically conductive and electronically insulating material is non-porous. Optionally, the first ionically conductive and electronically insulating material has an average porosity selected from the range of 0% to 5%. Optionally, the first ionically conductive and electronically insulating material is substantially free of pinholes, cracks, holes or any combination of these. Optionally, the first ionically conductive and electronically insulating material is substantially free of defects. Optionally, the first ionically conductive and electronically insulating material is doped.

[0147] In an embodiment, the electronically insulating layers and the electronically conducting layers each independently have an average thickness selected over the range 25 nm to 1 mm, optionally for some applications selected over the range 25 nm to 15 μm , and optionally for some applications selected over the range of 1 μm to 100 μm , and optionally for some applications selected over the range of 5 μm to 1 mm. In an embodiment, for example, any of, and optionally all of, electronically insulating layers and the electronically conducting layers each independently have an average thickness selected over the range 10 nm to 2 μm or selected over the range 2 μm to 50 μm .

[0148] This invention is further explained with the following embodiments, which are not intended to limit the scope of this invention.

Example 1

Multilayer Separators Made of Materials that Upon Electronic Contact with an Electrode Result in an Observable Change in Voltage

[0149] The electrochemical cells in this disclosure include, but are not limited to, batteries, fuel cells, flow batteries and semi-solid batteries. Any of the electrode active materials can

be solid, liquid, gas, flowable semi-solid or condensed liquid composition. A flowable anodic semi-solid (also referred to herein as “anolyte”) and/or a flowable cathodic semi-solid (also referred to herein as “catholyte”) are/is comprised of a suspension of electrochemically-active agents (anode particulates and/or cathode particulates) and, optionally, electronically conductive particles (e.g., carbon). The cathodic particles and conductive particles are co-suspended in an electrolyte to produce a catholyte semi-solid. The anodic particles and conductive particles are co-suspended in an electrolyte to produce an anolyte semi-solid. All voltages are wrt Li_+/ Li .

[0150] Safer Batteries:

[0151] Overvoltage protection and Safe-short separators and electrochemical cells implementing them: multilayer separators made of materials that upon electronic contact with an electrode result in an observable change in the voltage. An electronic short between the opposite electrodes can be very dangerous, the suggested separators can not only give an early warning to the user before any catastrophic failure but can also reduce the severity of a battery failure. An example is an electrochemical cell with multilayer separators such that at least one of the separator layers is made of a metal (e.g. aluminum, titanium, copper, stainless steel, nickel, iron) or alloy or an electronically conductive material such as electronically conductive polymers for example such that the short can result in ion deposition on at least a part of the said separator. The said layer(s) can be porous or perforated to allow the passage of ions with the assistance of any electrolytes. The said separator can further have electronically insulating layers or coatings such that there is no electronic connection between the opposite electrodes inside the cell when separated with the said separator. Any internal electronic connection between the opposite electrodes e.g., due to external or internal objects (such as formed dendrites or initial defects from manufacturing) thus may reach the internal electronically conductive layer(s) which results in change of voltage and can further prevent the short between the opposite electrodes. As an example in a 3.7V lithium battery such as with lithium metal anode, LiCoO_2 cathode and non-aqueous electrolyte, implementing a separator which has aluminum as one of the components such as perforated aluminum foil, a short between the lithium metal and the aluminum due to dendrite formation, external metallic objects or high temperature inside the cell will change the voltage of the cell, further the dendrite can chemically prefer to stop growth as an electronic contact between the aluminum and lithium dendrite can change the electrochemical reactions. This is in addition to the benefit due to mechanically strong aluminum layer that may prevent the shorts or stop the dendrite. The excellent electronic and thermal conductivity of the metallic membrane can even affect the cell electrical and thermal fields such that the nucleation and growth of the dendrites is slowed down or stopped. All of these may help with better deposition of lithium upon recharging and prevention of catastrophic failure; it is noteworthy to mention that the aluminum layer may be electronically insulated from at least of one electrode by an electronically insulating layer or coating (made of materials such as conventional battery separators, conventional battery binders, PE, PP, polyester, polyurethanes, PVDF, PTFE, silicone, polyimide, Al_2O_3 , SiO_2 , TiO_2 , PEO, LIPON, etc.); this layer or coating can be selected such that the chance of any direct electronic contact between the opposite electrodes be minimized.

[0152] An example is a Li-ion battery with conventional electrodes and electrolyte (e.g. Carbon anode, LCO cathode and LFP in EC-DMC-DME electrolyte) where the two electrodes are separated by a layer of perforated-porous aluminum sandwiched between two layers of PE or PP microporous layers (e.g., Setela or Celgard); the middle aluminum layer not only can help with the operational performance of the cell due to its excellent thermal conductivity and also electronic conductivity (easy charge separation on the surface) effect; in addition in the event of a dendritic short (e.g., cold temperature or fast charging) the multilayer separator is now mechanically much stronger than PE-PP separators of the same thickness and can force the dendrite to stop; Even if the dendrite penetrates the first PE-PP microporous layer, then no catastrophic failure may happen; this is because the lithium dendrite and aluminum contact can change the redox reactions and the voltage such that the dendrite won't be favorable, and may disappear at the following cycles; one possible mechanism is the that the lithium metal (from anode or dendrite) and the aluminum may perform an in-situ composite lithium-aluminum anode, similar to that known in the art.

[0153] Another example is a Li-ion battery with conventional electrodes and electrolyte (e.g. Carbon anode, LCO cathode and LFP in EC-DMC-DME electrolyte) where the two electrodes are separated by a layer of perforated-porous aluminum that is covered by metal oxides such as Al_2O_3 on the surface, where the metallic oxide may have been deposited on the metal (Al) surface or may have been formed as the oxidation of the metal (Al), for example Al_2O_3 forms on the surface by corrosion of the metal (Al); the middle aluminum layer not only can help with the operational performance of the cell due to its excellent thermal conductivity and also electronic conductivity (easy charge separation on the surface) effect; in addition in the event of a dendritic short (e.g., cold temperature or fast charging) the introduced separator is now mechanically much stronger than conventional separators of the same thickness and can force the dendrite to stop; Even if the dendrite penetrates the first metal oxide layer, then no catastrophic failure may happen; this is because the lithium dendrite and aluminum contact can change the redox reactions and the voltage such that the dendrite won't be favorable, and may disappear at the following cycles; one possible mechanism is the that the lithium metal (from anode or dendrite) and the aluminum may perform an in-situ composite lithium-aluminum anode, similar to that known in the art. The thickness of the aluminum can be 0.001-0.01 mm and the Al_2O_3 can be 0.0005-0.005 mm in this example. More than one metallic interlayer can be implemented, for example two aluminum perforated layers that are offset (US Patent Application Publication No. 2013/0224632) can be used, between the two layers can be another oxide layer or can be a conventional polymer separator or electrolyte such as PE-PP microporous or nonwoven films or a coating of PEO, PVDF, LIPON, LISICON or PTFE. Note that the dendrite between anode and the middle metal (say Al here) may melt during operation (e.g., with about 100 mV in less than 1 ms) which increases the safety of the cell.

[0154] Another example is a lithium battery with conventional electrodes or lithium metal anode and electrolyte (e.g. carbon anode, LCO cathode and LFP in EC-DMC-DME electrolyte) where least one layer of perforated-porous aluminum is in physical contact with an electrode, preferably the anode. Further the aluminum layer can be separated electroni-

cally and physically from the other electrode by means of conventional battery separators such as micro-porous PE-PP layers. At least one porous metal oxides layer such as Al_2O_3 may be deposited on at least one surfaces of the aluminum layer(s); the oxide layer can help with the wetting of the electrolyte surface and thus improve the performance of the electrochemical cell, where the metallic oxide may have been deposited on the metal (Al) surface or may have been formed as the oxidation of the metal (Al), for example Al_2O_3 forms on the surface by corrosion of the metal (Al); more than one layer of perforated-porous aluminum may be placed in the cell, for example two perforated layers with complementary patterns of apertures may be placed according to US Patent Application Publications No. 2013/0017432 and 2013/0224632; the multilayers of perforated-porous metal (e.g. aluminum foil) may be in physical contact or may not, if not in physical contact, then a thin microporous or nonwoven layers such as PE, PP separators or a layer such as PEO or pvdf or metal oxides can be placed at least in part of the space between the metal layers. The aluminum layer(s) not only can help with the operational performance of the cell due to its excellent thermal conductivity that results in more uniform heat distribution, but also improves the mechanical stability of the cell in the event of an external or internal shorts such as dendritic short (e.g., cold temperature or fast charging) where the introduced separator is now mechanically much stronger than conventional separators of the same thickness and can force the dendrite to stop; Even if an electronic connection between at least one electrode and the aluminum is made still no catastrophic failure may happen; this is because the lithium dendrite and aluminum contact can change the redox reactions and the voltage such that the dendrite won't be favorable, and may disappear at the following cycles; one possible mechanism is the that the lithium metal (from anode or dendrite) and the aluminum may perform an in-situ composite lithium-aluminum anode, similar to that known in the art. The thickness of the aluminum can be 0.005-0.01 mm and the Al_2O_3 can be 0.0005-0.005 mm in this example. More than a metallic interlayer can be implemented, for example two aluminum perforated layers that are offset (see, e.g., US Patent Application Publication no. 2013/0224632) can be used, between the two layers can be another oxide layer or can be a conventional polymer separator or electrolyte such as PE-PP micro-porous or nonwoven films or a coating of PEO, PVDF, LIPON, LISICON or PTFE. Note that a dendrite may melt during operation (e.g., with about 100 mV in less than 1 ms).

[0155] Another benefit of the highly thermal layer in the membrane is homogeneous distribution of heat inside the cell (reducing thermal gradient) that not only reduces the risk of catastrophic failure but also increased the cycle life of the battery.

Example 2

Electrochemical Systems with Inserted Conductive Layers

[0156] This example relates to methods in order to stop, slow down or control the dendrite formation in electrochemical plating such as in rechargeable electrochemical cells with lithium metal, zinc metal or aluminum metal anodes, for example in Li-air, Zn-air and Al-air batteries. This disclosure enables high energy, high rate and high cycle life (high performance) rechargeable batteries. Other applications such as

electroplating gold or other materials of interest such as other metals can also benefit from this disclosure.

[0157] Different methods are suggested for this purpose. One method is based on manipulating the electric field near the electrode of interest. In any electroplating, the electric field plays a role in the morphology and speed of the deposition. As an example, there may be some inhomogeneities or impurities (existing such as those from the substrate material or in situ forming such as those from the reactions between the electrolyte and the electrode materials) on the surface which can cause uneven deposition (for example by changing the nucleation energy or electric conductivity on the surface). This step may be governed by ionic diffusion, electric insulators or nucleation or other parameters not directly related to the electric field intensity, but after certain amount of electroplating growth or time, the electric field can start playing a key role. Electric field near any surface is affected by the geometry of the surface; areas with higher curvature have higher electric field near them, e.g., surface density of charges such as electrons and ions is much higher closer to the tips of a surface than on the flat area of the surface. This means that after certain amount of the growth of the deposition, the areas with higher curvature will attract more charges, which itself results in higher curvature and thus further growth; this is the phenomena that results in the uneven electroplating which gets worse with more deposition.

[0158] Different methods have been suggested in the past to overcome this mentioned uneven electroplating. One method is reducing the speed (rate) of electroplating; however in many applications such as in energy storage (e.g., batteries) there is a limit on the time that the user is willing to wait (for example in recharging a cellphone battery, the user does not want to wait hours to charge his cellphone), for this reason pulse electroplating (charging) is suggested, however, there a clear balance between the effectiveness of pulse electroplating (charging) and the total time of the electroplating (charging). Another suggested method that has been actively explored is changing the electrolyte (environment) of electroplating. This method tries to control the inhomogeneities or impurities (nucleation sites and their growth speed at least initially) rather than the electric field related growth (previous method). However this method may result in the electrolyte consumption in closed systems, such as in batteries, and the number of cycles can thus be limited due to the loss of active or supporting ions; many researchers observed great results in the lab scale with small amount of deposition quantity to electrolyte volume ratio (Ah/mL), but realized that the method causes another fading mechanism in practical applications, due to the limitation on deposition quantity to electrolyte volume ratio. Another suggested method to control electroplating (cycling) in electrochemical cells is applying out-of-plane pressure on the surface of the deposited area. This method has been shown to be very effective to mechanically suppress the uneven deposition (the mechanical force flattens the surface). This method has been proven difficult to be applied in practical situations (such as in a cylindrical battery); several novel methods have been developed to practically apply out-of-plane pressure on the surface and the results are very promising. In this Example the author introduces another novel method to control the surface of electroplating and ensuring high performance.

[0159] Changing the Electric Field:

[0160] The new method is based on changing the electric field in the vicinity of the electrode and can be used with or

without any other methods. In this method a layer capable of having surface charges without interrupting the ionic flow between the opposite electrodes is introduced into the space between the opposite electrodes. An example can be a thin (e.g., less than 0.025 mm thickness) perforated metallic (stainless steel, nickel, titanium, iron or aluminum) layer or a carbon layer covered by thin (e.g., less than 0.025 mm) insulating layer, coating or material to ensure that there is no electronic connection inside the cell between the opposite electrodes; thus the conductive layer is electronically separated from the electrode of interest, e.g., from lithium metal electrode in a rechargeable lithium battery. Examples of the thin insulating layer or coatings are separators such as celgard or any of those described in US Patent Publication no. 2013/0224632, or such as polymers; e.g., PVDF, PE, PP, parylene, PTFE, PET, PEEK, LIPON, polyester, epoxy or PEO or ceramics; e.g., alumina, titania, zirconia, silica, aluminum nitride, lithium nitride, titanium nitride or silicon nitride). The conductive layer allows surface charges on its surface such that the charge on surface of the conductive layer opposes the charge on the electrode it is facing, where the electroplating is happening. For example, the charge on the surface of the metallic layer facing lithium in a lithium metal battery is positive during charging. Conductive layers with high charge separation (such as those used in capacitors) are preferred so that they can affect the electric field better. Higher surface area of the conductive layer (m²/gram) can thus improve the results. The electric field changes due to the insertion of the conductive layer; that is the surface charges on the conductive layer facing the electrode of interest (e.g., lithium during charging) repels the same-sign charges, which results in more homogenous distribution of the ions in the electrolyte between the conductive layer and the electrode and thus a more uniform deposition in electroplating (or battery charging).

[0161] Changing the Thermal Field:

[0162] Another benefit of the conductive layer is that it can result in higher life cycle and less capacity fades in the electrochemical cells. Part of it can be because the conductive layer makes the electric field more uniform and thus fewer hot spots may form on the electrodes. Hot spots can form due to material impurities or due to areas with slightly higher voltage (overpotential) compared to their neighborhood and are known to result in loss of performance in the cells. Another benefit can be due to the fact that electronically conductive layers are also thermally conductive; thus the conductive layer may help with more uniform thermal field inside the cell and less temperature gradients, which results in better performance and higher cycle life of the cell. It can also significantly improve the safety of the cell, especially in larger cells, such as those used in electric driven vehicles, where a high temperature gradient may cause not only capacity loss, but may also result in fire and explosions.

[0163] Conductive Layer and the Opposite Electrode:

[0164] The conductive layer may or may not be electronically connected to the opposing electrode. Further, the conductive layer may or may not be physically connected to the opposing electrode. Decisions should be based on the chemistry and ionic and electronic conductivity of the opposite layer. It is expected that electronically connecting the conductive layer to the opposite electrode (not the one which we want to electroplate on) results in higher changes in the electric field near the surface of the electrode of interest, due to the help from external source of energy during charging (elec-

trode of interest—where we perform the electroplating such as the lithium metal electrode in a lithium metal battery) and thus can result in more uniform electroplating on the electrode of interest. On the other hand, electronically separating the conductive layer from the opposite layer can modify the electric field near the surface of the opposite electrode which has its own advantage, including pushing the ions deeper into the opposite electrode, which can help with making thicker electrodes and thus higher energy cells; it may also improve the rate capability of the cell by allowing better ionic and electronic conductivities. It is also expected that physical separation between the conductive layer and the opposite electrode results in better wetting of the opposite electrode by the electrolyte and thus better performance may be achieved; this is because the conductive layer may not be able to hold enough electrolyte on its surface, as opposed to battery separators which are designed to hold large amount of electrolyte; thus surface coating (at least partially) of the conductive electrode in vicinity of the opposite electrode may be needed to reduce the interface resistance on the surface of the opposing electrode layers. On the other hand, it is also expected that physical connection between the conductive layer and the opposite electrode results in higher electronic conductivity of the opposite electrode and thus better performance of the cell due to improving the electronic conductivity of the opposing electrode through the new path (secondary current collector) provided by the conductive layer; This can also help with making thicker electrodes and thus higher energy cells; it may also improve the rate capability of the cell by allowing better ionic and electronic conductivities.

[0165] In an embodiment, the conductive layer does not react chemically or electrochemically with any other component of the cell, including the electrolyte. Thus a chemically and electrochemically resistant coating may be applied to the conductive layer. Examples are polymers; e.g., PVDF, PE, PP, PTFE, PET, PEEK, polyester, epoxy, parylene, LIPON or PEO or ceramics; e.g., alumina, titania, zirconia, silica, aluminum nitride, titanium nitride, lithium nitride or silicon nitride. It is also preferred that the conductive layer and its potential coating layers have minimal effects to the ionic resistance of the cell, for this reason porous or perforated conductive layers are preferred. However, when increasing the porosity the overall performance of the conductive layer, e.g., uniform electric field and other aspects such as mechanical integrity, should be considered. Further, in some embodiments more than one conductive layer can be used. In some embodiments the conductive layer can be part of the separator of the electrochemical cell.

[0166] Please refer to FIGS. 1 and 2.

Example 3

Electrochemical Cells with Improved Safety and Performance

[0167] An electrochemical cell is introduced, consisting of an anode, a cathode, an electrolyte, one or more separator layer(s) and an electronically conductive layer.

[0168] The electronically conductive layer may have no electronic connections with one of the electrodes or may have no electronic connections with any of the electrodes.

[0169] The electronically conductive layer can be porous, perforated, nonwoven or thin coating. The size of the holes can be from 10 nm to 1 cm, depending on the chemistry of the cell. For example in a lithium ion battery it can be about 0.2

mm. In an alkaline battery (Zinc anode based or Nickel cathode based) it can be about 0.5 mm. The thickness of the layer can be less than 1 mm, preferably less than 0.1 mm depending on the chemistry. For example in li-ion battery it can be about 0.01 mm. In an alkaline battery (Zinc anode based or Nickel cathode based) it can be about 0.1 mm. The layer itself can be a coating on a non-conductive layer such as micro-porous or nonwoven PE-PP such as Celgard 2225. The thickness of the coating can be less than 0.005 mm, for example can be about 0.002 mm. The layer can also be made of metalized PET or metalized polyimides. The electronically conductive material can be made of any electronically conductive materials such as metals (e.g., stainless steel, copper, titanium, nickel, aluminum, Sn), from alloys (e.g., alloys of the said metals), from conductive polymers, from carbon, or any combinations thereof. The porosity of the layer can be at least 30%, for example 70%.

[0170] Electrolyte can be aqueous, non-aqueous, gel, polymer (such as PEO) or ceramics (such as LISICON or NASICON).

[0171] The electrochemical cells can be rechargeable or primary. They can be li-ion batteries, lithium metal batteries, Zinc anode based batteries, Nickel cathode based batteries, lead-acid based batteries or any other battery chemistry. They can further be any fuel cell or flow battery.

[0172] In some embodiments any or both of the separator layers can be in the form of coating layers on the said electronically conductive layer. In some embodiments, more than one conductive layer can be used.

[0173] This disclosure relates to new applications of the electronically conductive layer to an electrochemical cell, such as those known in the art of energy storage.

[0174] It is known in the art that the temperature generated during an internal short is the controlling parameter in any safety hazard. The electronically conductive layer prevents the expansion of any possible internal short in the cell, and can prevent the cell from thermal runaway, and thus can significantly reduce the risk of fire and explosion. In some occasions, the electronically conductive layer may even control the internal short, for example by burning out possible internal dendrites. This kind of dendrite shorts is the major culprit behind many fire incidents in the case of too fast charging or too much charging (voltage) which are known to result in dendrite forming on li-ion cells. Shorts may also happen in cells with metal anodes such as in lithium metal anode cells (e.g., Li—S, Li—Air or Li—LiFePO₄ cells) or zinc metal anode cells (e.g. rechargeable Zn—Ni cells).

[0175] In addition as most electronically conductive materials are also excellent thermally conductive materials, the layer can result in less heat gradients in the cell and more homogenous distribution of the heat in the cell not only in the event of a short (internal or external) but also during the normal performance. This is especially important in high power or fast charging rate situations. The outcome is not only safer energy storage systems but also longer life cycle of the system.

[0176] An example is an electrochemical energy storage system for a cellphone, electronics, vehicle or utility storage that implements li-ion chemistry in cells with this arrangement:

[0177] Copper, anode Current collector/Li-metal, 0.05 mm thick/celgard, 0.012 mm thick/perforated stainless steel, 0.01 mm/celgard, 0.012 mm/LiCoO₂, 0.1 mm/Al, cathode current collector.

[0178] In some embodiments the electronically conductive layer can have a surface charge. In some embodiments the surface charge can increase the cycle life of the energy storage system. As an example a positive surface charge may reduce the dendrite formation or growth; for example in a cell with metallic anode, such as lithium or zinc. As another example the surface charge may hinder the migration of polysulfide from a sulfur cathode to anode in a li-ion cell.

[0179] It is noted that the conductive layer should not react chemically or electrochemically with any other component of the cell, including the electrolyte, during the normal life of the electrochemical cell. In some embodiments, a chemically and electrochemically resistant coating may be applied to the conductive layer.

Example 4

Active Membranes: Conductivity Assisting Membranes and their Use as Active Separators in Electrochemical Cells Such as Batteries

Summary

[0180] In this disclosure, active membranes are introduced, especially as separators in electrochemical cells such as in batteries. In an embodiment, the disclosure provides a multi-layer membrane comprising two or more layers such that at least one of the layers at either of the ends of the membrane is electronically conductive; and at least one of the middle layers is electronically nonconductive such that there is no electronic connection between the two outer faces of the membrane. In embodiments, some of the layers are deposited or coated on each other. In an embodiment, some of the layers are deposited or coated on another layer or on either of the electrodes.

[0181] The multi-layer membranes of the present disclosure are capable of being used as a separator in an electrochemical cell. In an embodiment, the outer conductive layer results in a new electronic path for the outer particles of the adjacent electrode and thus increases the electronic conductivity of the adjacent electrode materials. In an embodiment, the outer conductive layer results in a change in electric field at least in the vicinity of the corresponding electrode

[0182] In an embodiment, each of the conductive layers is a porous or perforated layer or a mesh made of a metal such as stainless steel or aluminum or copper. In an embodiment, the porosity of the metallic layer is at least 30%. In an embodiment, a metallic conductive layer is between an electrode and an electronically non-conductive layer of the membrane. In an embodiment, a non-conductive layer is a coating on one side of the metallic layer; in an embodiment the coating is a polymer such as PTFE or PVDF or PEO or PMMA.

[0183] In embodiments, the total thickness of the membrane is less than 500 micrometers or less than 25 micrometers. In an embodiment the ionic resistance of the separator is less than 10 ohm·cm².

[0184] In an embodiment, an electrode material undergoes shape change due to charging-discharging, which can result in the loss of at least part of the electronic conductivity between the electrode materials and the corresponding current collector.

[0185] In an embodiment, the membranes of the present disclosure are used as a separator in an electrochemical cell such as a rechargeable lithium battery. In an embodiment, a lithium battery is made with separator of the present disclo-

sure. In an embodiment, the anode is silicon. In an embodiment, the cathode is lithium oxide or is sulfur or is carbon or air. In an embodiment, the electric field modifications due to the conductive layer of the separator result in a more uniform lithium deposition during charging and thus increases the performance, life cycle and efficiency of the electrochemical cell. In a further embodiment, an alkaline battery made with a separator of the present disclosure. In another embodiment, a metal air battery made with the separator of this disclosure.

[0186] In an aspect, the methods of the disclosure are used in electro-depositions such as in electro-depositing of a metal such as gold, silver or lithium or zinc or copper or an alloy.

[0187] An Example of the usage of the membrane as a separator in an electrochemical cell such as in a battery: FIGS. 14-17: black: current collectors (at extreme right and left), medium gray circles: active electrode particles (e.g. Silicon), medium gray line segments: carbon black, double gray lines: conventional separator, double black lines: our separator, darker gray circles are the in-active (lost) electrode material due to the lost electronic connectivity. Dark gray: opposite electrode. Electrolyte is white.

[0188] FIG. 14 shows the battery before use. All of the electrode particles are electronically connected.

[0189] FIG. 15 shows the battery after charging, the electrode particles have a large shape change.

[0190] FIG. 16 shows the battery, with the conventional separator, after several cycling, some of the electrode particles have lost their electronic connection with the current collector and thus are in-active.

[0191] FIG. 17 shows the battery, with the new separator, after several cycling, some of the electrode particles have lost their conventional electronic connection with the current collector but the new separator provides a new path for some of the electrode particles. The new path of the electrons, due to the new separator is shown in gray.

Example 5

Multi-Layer Separators

[0192] Abbreviations for layers:

[0193] eNc: electronically Nonconductive

[0194] eC(R): electronically Conductive, Reactive with dendrite

[0195] eC(nR): electronically Conductive, non-Reactive with dendrite

[0196] eC(R/nR): part nonreactive, part reactive with the electrolyte (for example a coating of reactive on a non-reactive).

[0197] eCS: a matrix of electronically conductive with solid material fibers or particles (the solid electrolyte particles fill the pores-holes of the matrix). The solid electrolyte fiber particles can be a known solid electrolyte such as known polymer or ceramic solid electrolytes. In an embodiment, this layer comprises a porous layer of electronically conductive material and at least a group of fibers or particles filling the pores/holes of the porous layer.

[0198] NOTE: Each of the above can be: a free standing microporous or non-woven layer; or can be a coating on any of the electrodes or on another layer of the separator)

[0199] Combinations of the Multi-layer separators between anode and cathode electrodes:

[0200] At least one eNc layer and at least one eC(R) layer

[0201] At least one eNc layer and at least one eC(nR) layer

[0202] At least one eNc layer and at least one eC(R/nR) layer

[0203] Any combination of at least one eNc and at least one eC layer, such that there is no electrical conductivity between the opposite electrodes

[0204] The eC layers can have an external tab

[0205] The external tab can be used passively to monitor the voltage between the eC layer and any of the electrodes (USC paper) or can be used actively (applying voltage or current between the eC layer and any of the electrodes).

[0206] With solid electrolyte

[0207] The eC layer can be eCS

[0208] The solid electrolyte can be a free standing layer or a coating layer; or can be a component of the eC or eNc layers, e.g., particles or fibers filling the holes-pores of the eC or eNc layers

[0209] The solid electrolyte material can be any of the traditional solid electrolytes (transporting ions without any applied voltage or current at the eC layer, such as LISICON or PEO), or can be made of a nontraditional solid electrolyte, such as traditional electrode active material (transporting ions without any applied voltage or current at the eC layer, such as LiTiO₂, Silicon or Graphite); the applied voltage can be direct current or non-direct such as a sinusoidal voltage varying between the charge-discharge voltages of the nontraditional solid electrolyte.

[0210] In-situ lithiation in Li-ion batteries

[0211] Any of the eC or eNc layers may have a lithium metal coating.

[0212] Any of the eNc layers can be made of lithium (porous or not porous).

[0213] The excess lithium can be used to lithiate the electrodes (if not lithiated electrodes are used such as silicon anode and sulfur or air cathode) or can compensate for the ions loss (SEI, . . .).

[0214] Applied voltage or current to the lithium layer may be necessary via external tab, for example pulse or sinusoidal between 1 and 2.5V applied between a graphite anode and the eCS (LiTiO₂ fibers inside a copper matrix) in a li-ion cell, for example with an air or sulfur electrode.

[0215] Example of Combinations of the Multi-layer separators between anode and cathode electrodes:

[0216] eNc-eC-eNc

[0217] eNc-eC-eNc-eC

[0218] eC-eNc-eC-eNc-eC

[0219] eNc-eCS-eNc-eC

[0220] eC-eNc-eCS-eNc-eC

[0221] eC-eNc

[0222] eC-eNc-eC

[0223] eC-eNc-eCS

[0224] eCS-eNc

[0225] eCS-eNc-eCS

[0226] eCS-eNc-eC

[0227] Any electrochemical cell

[0228] Li-ion batteries

[0229] Li-metal batteries

- [0230] Metal-air batteries
- [0231] Alkaline batteries
- [0232] Zinc batteries
- [0233] Metal hydride batteries
- [0234] Lead-acid batteries
- [0235] Rechargeable or primary batteries
- [0236] Flow batteries, fuel cells, semi-solid batteries

Example 6

Exemplary Electrochemical Cells

[0237] Cell 1: A rechargeable lithium metal pouch cell containing EC: EMC (3:7 w %)-1.2M LiPF₆ electrolyte, Toda NMC (111) Cathode active wt: 0.2021 g, and lithium metal anode. The area of the cathode is about 20 cm². The separator is a multilayer film with a perforated 0.015 mm thick aluminum layer placed between two microporous polyethylene layers, each 0.007 mm thick, without adhering the layers. The aluminum layer has a periodic pattern of holes with 0.300 mm diameter and 0.300 pitch. Specific capacity at 12 mA discharge is 29.91 mAh. FIG. 11 shows the performance of the cell.

[0238] Cell 2: A rechargeable lithium-Sulfur pouch cell containing EC: EMC (3:7 w %)-1.2M LiPF₆ electrolyte, Sulfur-Carbon cathode active wt: 0.2021 g, and lithium metal anode. The area of the cathode is about 20 cm². The separator is a multilayer film with a perforated 0.007 mm thick copper layer placed between two nonwoven polyester layers, each 0.01 mm thick, without adhering the layers. The conductive layer has a periodic pattern of holes with 0.300 mm diameter and 40% porosity.

[0239] Cell 3: A rechargeable lithium ion pouch cell containing EC: EMC (3:7 w %)-1.2M LiPF₆ electrolyte, LiFePO₄ Cathode active wt: 0.2021 g, and silicon-graphite anode. The area of the cathode is about 20 cm². The separator is a multilayer film with a porous 0.01 mm thick conductive carbon/super-P layer placed between two microporous polypropylene layers, each 0.007 mm thick, with pvdf/PEO-NMP/acetone-evaporation adhering the layers. The conductive layer has 40% porosity. The glue is 50% pvdf powder, 50% PEO powder dissolved in 50% NMP, 50% acetone, which is sprayed on the corresponding sides of the separator.

[0240] Cell 4: A rechargeable Zn—Ni pouch cell containing 6 M KOH electrolyte, NiOOH cathode, and Zn—ZnO anode. The area of the cathode is about 20 cm². The separator is a multilayer film with a perforated 0.007 mm thick stainless steel layer placed between two microporous polyethylene layers, each 0.007 mm thick, without adhering the layers. The conductive layer has a periodic pattern of holes with 0.300 mm radius and 0.300 pitch.

[0241] Cell 5: A rechargeable lithium air cell containing EC: EMC (3:7 w %)-1.2M LiPF₆ electrolyte, carbon air cathode, and lithium metal anode. The area of the cathode is about 20 cm². The separator is a multilayer film with a perforated 0.003 mm thick stainless steel layer placed between two microporous polyethylene layers, each 0.007 mm thick, which were adhered by heating and pressure. The conductive layer has an arbitrary pattern of holes with 0.100 mm radius and 0.200 pitch.

[0242] Cell 6: A rechargeable lithium ion pouch cell containing EC: EMC (3:7 w %)-1.2M LiPF₆ electrolyte, LiCoO₂ Cathode active wt: 0.2021 g, and graphite anode. The area of the cathode is about 20 cm². The separator is a multilayer film with a 0.001 mm conductive PDOT-PSS-PANi based poly-

mer deposited on one side of two microporous polyethylene layers, each 0.007 mm thick, with heat-press adhering the layers. The conductive layer has 70% porosity.

[0243] Cells 7-12: Cells 1-6 where one of the microporous PE layer of the multilayer separator is removed.

[0244] Cells 13-18: Cells 1-6 where the multilayer separator has another conductive layer next to the anode.

[0245] Cells 19-24: Cells 1-6 where the multilayer separator has another conductive layer next to the cathode.

[0246] Cells 25-30: Cells 1-6 where the multilayer separator has two other conductive layers, each next to an electrode.

[0247] Cells T1-T30: Cells 1-30 where each conductive middle layer has an external tab to monitor the voltage between the conductive layer and the electrodes. After observing a voltage variation between the conductive layer and any of the electrodes, indicating an abnormality on the cell, a current is applied between the conductive layer and the said electrode such that the said voltage variation disappears.

[0248] Cells AT1-AT12: Cells 1-12 where external tabs are used to apply a voltage between each conductive layer and each electrode. The applied voltage between a conductive layer and the anode is the same as the cell voltage at any given time.

[0249] Cells AT13-AT24: Cells 1-12 where external tabs are used to apply a voltage between each conductive layer and each electrode. The applied voltage between a conductive layer and the cathode is the same as the cell voltage at any given time.

[0250] Cells ATH1-ATH12: Cells 1-12 where external tabs are used to apply a voltage between each conductive layer and each electrode. The applied voltage between a conductive layer and the anode is half of the cell voltage at any given time.

[0251] Cells ATH13-ATH24: Cells 1-12 where external tabs are used to apply a voltage between each conductive layer and each electrode. The applied voltage between a conductive layer and the anode varies between zero and cell voltage at a frequency of 1 kHz.

[0252] Cells ATH25-ATH36: Cells 1-12 where external tabs are used to apply a voltage between each conductive layer and each electrode. The applied voltage between a conductive layer and the anode varies between zero and cell voltage at a frequency of 100 Hz.

[0253] Cells ATH37-ATH48: Cells 1-12 where external tabs are used to apply a voltage between each conductive layer and each electrode. The applied voltage between a conductive layer and the anode varies between zero and cell voltage at a frequency of 10 kHz.

[0254] Cells ATH49-ATH60: Cells 1-12 where external tabs are used to apply a voltage between each conductive layer and each electrode. The applied voltage between a conductive layer and the anode varies between zero and cell voltage in pulses with 1 minute duration at zero, one minute at rest (no applied voltage) and one minute at cell voltage.

[0255] Cells B1-B6: Cells 25-30 where each conductive layer has an external tab and the applied voltage between each conductive layer and the electrode closer to it is zero.

[0256] Cells B7-B12: Cells 25-30 where each conductive layer has an external tab and the applied voltage between each conductive layer and the electrode further away from it to it is zero.

[0257] Cells B13-B18: Cells 25-30 where each conductive layer has an external tab and the applied voltage between the two conductive layers is zero.

[0258] Cells B19-B24: Cells 25-30 where each conductive layer has an external tab and the applied voltage between the two conductive layers is half the cell voltage, such that the direction of the generated electric field is the same as the cell internal electric field.

[0259] Cells B25-B30: Cells 25-30 where each conductive layer has an external tab and the applied voltage between the two conductive layers is half the cell voltage, such that the direction of the generated electric field is opposite the cell internal electric field.

[0260] Cells B31-B36: Cells 25-30 where each conductive layer has an external tab and the applied voltage between the two conductive layers varies between zero and the cell voltage with 10 kHz frequency.

[0261] Cells B37-B42: Cells 25-30 where each conductive layer has an external tab and the applied voltage between the two conductive layers varies between zero and the cell voltage with a pulse pattern of 1 minute with a 2 minute rest in between.

[0262] Cells S1-S12: Cells 1-12 where the porosity of the conductive layer is fully filled with a polymer solid electrolyte, here PEO-LIPON based, such that the electrolytes on the opposite sides of the conductive/PEO-LIPON layer would not mix. In cell S5, the electrolyte on the air cathode side is replaced with an aqueous electrolyte, based on 3M LiOH salt.

[0263] Cells S13-S24: Cells 1-12 where the porosity of the conductive layer is filled with a ceramic/glass solid electrolyte, here LISICON based, such that the electrolytes on the opposite sides of the conductive/LISICON layer would not mix.

[0264] Cells S25-S36: Cells 1-12 where the porosity of the conductive layer is filled with 100 nm Li_3N , such that the electrolytes on the opposite sides of the conductive/ Li_3N layer would not mix.

[0265] Cells S27-S48: Cells 1-12 where the porosity of the conductive layer is filled with a catalyst, here MnO_2 and platinum based, that assists the cycling of the cell.

[0266] Cells S49-S60: Cells 1-12 where the porosity of the conductive layer is filled with an ion-selective filler, here Nafion based including sodium p-styrenesulfonate, lithium stearate and polydipamine, that only allows the transportation of negative ions through.

[0267] Cells S61-S72: Cells 1-12 where the porosity of the conductive layer is filled with TiO_2 /LTO filler such that the electrolytes on the opposite sides of the conductive/ TiO_2 /LTO layer would not mix.

[0268] Cells RS1-RS12: Cells 1-12 where the porosity of the conductive layer is filled with a redox shuffle filler, here perfluoro aryl boronic esters/fluorinated 1,3,2-benzodioxaborole/2,5-di-tert-butyl-1,3-dimethoxy-benzane/TEMPO, such that the cell is protected by the redox shuttle agent in the event of an overvoltage.

[0269] FIG. 8 provides a plot of capacity (mAh) versus cycles for a LiTiO_2 , Toray, Al, lithium cell of the present invention having a composite separator with an electronically conductive layer. FIG. 9 provides a plot of capacity (mAh) versus cycles for a LiTiO_2 , Celgard, Cu, lithium cell of the present invention having a composite separator with an electronically conductive layer. FIG. 10 provides a plot of capacity (mAh) versus cycles for a LiTiO_2 , Celgard, Ni, lithium cell of the present invention having a composite separator with an electronically conductive layer. The plots shown in FIGS. 8-10 show a variety of sharp peaks (e.g., at about 200 cycles in FIG. 8, about 65 cycles in FIG. 9, about 80 cycles in FIG.

10) that are believed to correspond to the formation of a short in the electrochemical cell. As shown in the plots, however, these peaks are followed by a return to normal capacities for subsequent cycles. In some embodiments, it is believed that the formation of the short results in an alloy reaction, for example, involving the lithium dendrite and the aluminum electronically conductive layer of the composite electrode that results in the consumption and/or dissipation of energy. In some embodiments, the peak is most pronounced during charging, which is believed to correspond to an electrical short being burned out during the charge cycle.

[0270] FIG. 11 provides a plot of capacity (mAh) versus cycles for a pouch cell containing EC: EMC (3:7 wt %)-1.2M LiPF_6 , Toda NMC(111) vs. Li. Cathode active wt: 0.2021 g and having a composite separator with an electronically conductive layer. The results shown in FIG. 11 show a specific capacity at 12 mA discharge equal to 148 mAh/g. The cycling behavior shown in FIG. 11 is consistent with an avoidance of a short, for example, due to the electrical field provided by the electronically conductive layer of the composite separator of this embodiment.

Example 7

Electrodes, Separators, Membranes, Current Collectors and Electrochemical Cells

[0271] The electrochemical cells in this disclosure include, but are not limited to, batteries, fuel cells, flow batteries and semi-solid batteries. Any of the electrode active materials can be solid, liquid, gas, flowable semi-solid or condensed liquid composition. A flowable anodic semi-solid (also referred to herein as “anolyte”) and/or a flowable cathodic semi-solid (also referred to herein as “catholyte”) are/is comprised of a suspension of electrochemically-active agents (anode particulates and/or cathode particulates) and, optionally, electronically conductive particles (e.g., carbon). The cathodic particles and conductive particles are co-suspended in an electrolyte to produce a catholyte semi-solid. The anodic particles and conductive particles are co-suspended in an electrolyte to produce an anolyte semi-solid. All voltages are wrt Li_+/Li .

[0272] Composite Separators and Functionally Graded Separators

[0273] Several novel separators and membranes for electrochemical cells and electrochemical cells employing such separators-membranes are introduced. In an embodiment, use of these separators results in batteries (primary or rechargeable) with better performance than state of the art as an example rechargeable lithium metal based batteries, rechargeable zinc metal based batteries and longer life cycle silicon based lithium ion batteries are possible, also are fast charge, high power li-ion batteries and long life alkaline and lead-acid batteries. For example, the performance of the battery may be improved over those including separators and membranes made in a symmetric form such that the porosity and structure of the separator is the same at any depth through the thickness of the separator.

[0274] Composite separators include separators that have different amounts or forms of openings through the thickness, for example the two sides are different from each other or/and the sides are different from the interior. The different amount of porosity and the structure of the porosity (e.g., size of the holes) are designed such that they match the requirements of the adjacent electrode. This is expected to result in better

performance of the electrodes and electrochemical cells as the separator-electrode interface plays a role in the performance (such as rate needed for fast charging and high power and cycle life) of the electrochemical cell. Some electrodes (e.g., lithium battery cathode materials, such as lithium metal oxides) need more electrolyte in their vicinity to keep the surface homogeneously wet (this can be due to dependence of the ionic conductivity of the electrode on the charge state, e.g. $\text{Li}_{1-x}\text{FePO}_4$ or $\text{Li}_{1-x}\text{CoO}_2$ have different ionic conductivities depending on the values of x) thus require a very porous interface with the electrolyte (at least 40% porosity on the separator interface). An example can be a nonwoven separator or a ceramic coated separator. On the other hand some electrodes (such as metals e.g. lithium, silicon, zinc, Mg, lead, aluminum) perform better (e.g. better recharging and cycle life) when there is a confining force on their surface (the out of plane pressure on the surface or tension in the plane from the sides can result in a smoother deposition during electroplating the ions); thus here a stronger and less porous separator interface is preferred, an example can be a micro-porous separator, elastomer-material separator or the separator as described in US Patent Application Publication 2013/0224632. As the result a non-symmetric separator with different properties on each of the sides is of great interest. The separator can be a multilayer separator in which each layer has a different property, as an example an electrochemical cell with lithium metal anode and lithium metal oxide cathode can be made in which the separator is a two layer separator consisting of a nonwoven layer (e.g. 0.01 mm thick) on the cathode side and a mechanically strong layer (e.g. 0.01 mm thick micro-porous or a polymer electrolyte or a solid electrolyte.) on the anode side. The layers can be laminated to each other by the methods known in the art such as using binders and/or applying heat-pressure. Any electrolyte such as non-aqueous, organic electrolyte, aqueous electrolyte, polymer electrolyte or solid (such as ceramic) electrolyte can also be used.

[0275] As another example, an electrochemical cell may have electrodes that prefer less resistance, for example more porosity in the electrode and in the separator, at the interface with the separator. However, to keep the mechanical integrity of the separator and/or preventing any shorts between the opposite electrodes, a stronger and/or less porous layer is needed to be placed in the interior; thus a multilayer separator can be formed. The exterior layers can be highly porous nonwoven layers and the interior can be a micro-porous layer or a polymer electrolyte or a solid electrolyte. The layers can be laminated to each other by the methods known in the art, such as using binders and/or applying heat-pressure. Any electrolyte can be used. For a multilayer separator such as those introduced here or the conventional multi-layer separators known in the art, the change in the layers' properties of the separator can be designed such that the interface resistance is minimized, this can be done for example by designing functionally graded multi-layer separator where the porosity and structure of the pores vary gradually to minimize the ionic resistance of the separator which itself increases the rate and cycle life performance of the electrochemical cell.

[0276] Composite separators also include those described in US Patent Application Publications 2013/0017432 (Roumi) and US 2013/0224632 (Roumi).

[0277] Buffer Separators:

[0278] An electrochemical cell may perform better if out of plane pressure is applied on the surface of at least one of the

electrodes (such as lithium, silicon, zinc, Mg, lead, Aluminum). One example is metallic lithium anode which gets thinner during dissolution (discharge); however on the recharging lithium metal is known to deposit non-smoothly which results in electrolyte loss (due to repetitive SEI formation-destruction) and possible dendritic growth of the metal. Mechanical pressure is shown to mitigate or even prevent this non-uniformity. However, current state of the art such as micro-porous separators may not be able to apply the desired pressure after the electrode thickness (and thus the cell thickness) is decreased significantly due to discharging, due cycling for example because of the created gaps between the electrode and the separator at least one location; examples are cells made with lithium, zinc-oxide or lithiated silicon electrodes when they get smaller due to losing material. Thus, a separator that can act as an elastomer is of interest. Another example is a silicon electrode which undergoes large deformation in electrochemical cycling which results in electrolyte loss (due to repetitive SEI formation-destruction) and active material capacity loss (electronic isolation). Here a separator is introduced which can also act as an elastomer or buffer such that the surface of the electrode is under pressure. An example of such a separator is a multilayer made with a mechanically strong layer on the electrode side (such as the lithium anode or silicon anode) and a deformable, elastic, or spongy layer making the rest of the separator or making the interior of the separator. The deformable, elastic or spongy layer can be for example a porous or perforated layer or foam sheet. It can be made of for example silicone, rubber, PP, PE, polyurethanes, polyesters or other materials known in the arts of membranes and elastomers. It can also be made of metallic materials or alloys such as metal foams (e.g., Ni-foam or titanium foam) that may also be coated by electronically insulating layers.

[0279] Elastomeric Current Collectors:

[0280] Several novel current collectors for electrochemical cells and electrochemical cells employing such current collectors are introduced. It is expected that this results in batteries (primary or rechargeable) with better performance than state of the art, as an example rechargeable lithium metal based batteries, rechargeable zinc metal based batteries and longer life cycle silicon based lithium ion batteries are possible, also are fast charge, high power li-ion batteries and long life alkaline and lead-acid batteries. State of the art current collectors for batteries including alkaline batteries and li-ion batteries are made of very thin (0.01 mm thick) sheets of metals such as copper and aluminum. The main functionality of the current collector is transporting electrons between the inside and outside of the cell. However, current collectors occupy volume and add to the weight of the cell so it is beneficial to use them for other advantages. As an example, an electrochemical cell may perform better if out of plane pressure is applied on the surface of at least one of the electrodes (such as lithium, silicon, zinc, Mg, lead, Aluminum). One example is metallic lithium anode which gets thinner during dissolution (discharge); however on the recharging lithium metal is known to deposit back non-smoothly which results in electrolyte loss (due to repetitive SEI formation-destruction) and possible dendritic growth of the metal. Mechanical pressure is shown to mitigate or even prevent this non-uniformity. However, current separators, due to the created gaps between the cell components, may not be able to apply the desired pressure after the electrode thickness (and thus the cell thickness) is decreased significantly during different steps of cycling. Thus, a current collector that can act as an elastomer

is of interest. Another example is a silicon anode in a li-ion battery which undergoes large deformation in electrochemical cycling which results in electrolyte loss (due to repetitive SEI formation-destruction) and active material capacity loss (electronic isolation).

[0281] New current collectors are introduced which can act as elastomers or buffers and keep the surface of the electrode under pressure during cycling to improve the performance and cycle life. An example of such a current collector is a multilayer made with a high electronically conductive layer on the electrode side (such as the lithium anode or silicon anode) [or the exterior sides of the current collector] and a deformable, elastic, or spongy layer making the interior [or back] of the current collector. The deformable, elastic or spongy layer can be for example a porous, perforated layer or foam sheet. It can be made of for example silicone, rubber, PP, PE, polyesters, polyurethanes or other materials known in the arts of membranes and elastomers. It can also be made of metallic materials or alloys such as metal foams (e.g., Ni-foam or titanium foam) that may be coated by corrosion protective layers. The thickness of the new current collector in the compressed state (for example in the full charge state in lithium batteries) is preferred to be comparable to the state of the art current collectors (e.g., 0.01 mm in lithium batteries). The thickness in the decompressed state (e.g., after discharge in lithium batteries) can be bigger (for example 10% to 1000% strain in the out of plane direction) such that necessary out of plane pressure can be applied on the electrode materials (for example a few KPa to hundreds of MPa). [“Plane” is defined as parallel to the electrode surface.]

[0282] Another example of elastomeric current collector is a composite current collector made of a chemically inert polymer as the middle layer and metallic layers on the sides; the polymer layer can further increase the tensile strength of the current collector which is necessary for winding and fabrication. One major benefit of such a current collector is lower weight and ease of fabrication in contrast to conventional current collectors (e.g., 0.005 mm thick PP or silicone film with a double side coating of 0.001 mm copper can serve as an anode current collector for lithium batteries, especially rechargeable li-ion with silicon anode); Further the polymer can have elastomeric behavior either due to the material (e.g., rubber, silicone, etc.) or due to the design, such as a polymer layer that has a homogeneous distribution of trapped voids inside (e.g., in the above example, the PP or silicone layer can have a distribution of microvoids, the microvoids can be filled with an inert gas such as argon. The microvoids in this example are compressible and thus provide the necessary elastic deformation during charge-discharge or due to external forces).

[0283] The current collector can further be pre-stressed to improve the charge-discharge performance of the electrochemical cell for example current collectors which have undergone pretension in out-plane or compression in-plane will apply out-plane compressive or in-plane tensile force on the electrodes which improves the performance of the electrode.

[0284] Electrodes with Elastomeric Frames or with Mechanically Strong Frame:

[0285] A novel electrode structure and electrochemical cells (e.g., rechargeable lithium batteries, alkaline batteries) implementing such electrode structures are introduced. The electrode structure implements a frame structure that helps mechanically holding the electrode active materials (e.g.

Lithium, silicon, Sn, zinc or zinc oxide). The current collector is at least partially disposed within the suspension such that the suspension substantially encapsulates the said current collector. The structure can be in the form of a mesh, such as a metallic mesh made of materials and/or coatings that do not fail (i.e., dissolution, corrode) during the operation of the electrochemical cell (e.g., made of Ti, TiO₂, Al₂O₃, PE, PP, Ni, Sn, Fe, Stainless steel, etc.). The frame structure not only reduces the weight and cost of the inactive materials (such as electrode binders) but also increases the cycle life and performance. The frame can be pre-stressed before cell assembly to apply in-plane or out-of-plane forces on the active material; for example a frame that has been pre-stressed under compressive in-plane forces during the poring/coating of active materials will apply in-plane tensions to the electrode and thus mechanically (e.g., with the assistance of positive Poisson’s ratio) holds the active materials in place even during the operation of the electrochemical cell (many electrodes undergo deformations due to discharging/recharging the cell); further this helps with reducing the damage to the electrodes due to operations (e.g., silicon anode undergoes very large deformations that shorten the cycle life of the li-ion battery). In some embodiments, the mentioned frame can be made of mechanically strong materials (such as metals or alloys, e.g., stainless steel, copper, aluminum, titanium or nickels, or such as ceramics, e.g., Al₂O₃, TiO₂, SiO₂, Al₂O₃, glass, or such as plastics, e.g., PVC, polyurethanes, PP, PE, or any combinations of them) that can be further useful in protection of the cell in the event of an applied external force that would otherwise cause the active materials penetrate the separator and short the cell. In some embodiments, at least one part of the mentioned frame is made of materials that are very deformable such as elastomers (e.g., rubber, silicone) that can act as a buffer for deformations due to the cycling of active electrode materials; this is especially useful to prolong the cycle life of the electrodes, e.g., silicon and tin undergo very large deformations upon lithiation that can significantly shorten the cycle life; the elastomer frame can mitigate this problem. In some embodiments the frame is made of electronically conductive materials (e.g. PAN, Cu, Al, Ti) that can help with decreasing the electronic resistivity of the electrode which can also help with enabling thicker electrodes and thus higher energy density electrochemical cells. In order to have thicker electrodes ionic conductivity and electronic conductivity of the electrode should be maintained through the thickness. One way of doing this is by making connected pores in the electrode, while preventing clogging by binder and conductive carbon particles which reduces the ionic conductivity through the thickness (e.g., the work by Yet Ming Chiang). The frame structure can also increase the thermal and/or electric field homogeneity of the electrode and thus improves the performance of the electrochemical cell. It is noted that although some basic structure is used for lead acid batteries, the current invention is far beyond that and also is applicable to not only lead acid batteries but also lithium batteries and other alkaline batteries; e.g., the lead acid frame is rigid and not pre-stressed, but our frame can be very deformable acting as an elastomer or buffer for operational or external caused deformations of the electrode. Another example is a lithium battery with lithium metal anode pressed into a metallic grid such as stainless steel, Titanium, nickel or copper grid such that in the winding of the wound cells such as 18650 cells, there is no need for sputtering lithium on the current collector to enable strength for tensions during winding; as the grid

itself may be exposed at the two ends, during the winding, which can carry the tension load of winding without breaking apart the lithium; this greatly reduces the cost of the lithium metal anode fabrication.

[0286] Electrodes with Patterns:

[0287] It is known that mechanical energy (stress and strain) plays a role in the performance (e.g. cycling rate and lifetime) of electrochemical cells (Farshid Roumi, PhD thesis 2010 Caltech). It is also known that the mechanical energy (including elastic energy) can be reduced by designing the optimized geometry for example by specific patterns of the electrode. An example is a periodic pattern (straight, staggered, etc.) in which the electrode has two different thicknesses, e.g., a metal lithium anode (or Zn, ZnO, Lead, lead oxide or Si) with a periodic array of circles (e.g., 0.5 mm diameter) with the thickness of 0.025 mm inside the circles and 0.02 mm anywhere else. Further, in some embodiments, the cell can have a multilayer separator such that it matches the electrode in a way that there is always good physical contact between the electrode and the separator; for example for our periodic electrode layer, the separator can consist of several layers such that the layer next to the electrode can be 0.005 mm with a periodic hole structure that matches the electrode structure such that the total thickness of the electrode and this separator layer is uniformly 0.025 mm. The separator can further have another layer complementary to the first said layer (see US Patent Publication no. 2013/0224632) such that the electrode surface is completely in contact with the two separator layers (the 0.02 mm parts in contact with the first said separator layer and the 0.025 mm parts with the second said separator layer); The separator can further have other layers, for example a nonwoven layer next to LCO cathode is preferred. In some embodiments, the current collector can also have a pattern such that the pattern matches the electrode layer such that the total thickness of current collector and electrode stays uniformly the same, e.g., for the above electrode pattern, the current collector can be 0.005 mm with a periodic hole or trench structure that matches the electrode structure such that the total thickness of the electrode and current collector is uniformly the same everywhere. Either of the patterned current collector or separator layer can further have some elastomeric parts, e.g., the current collector can be a composite material made of both electronically conductive metallic materials and elastomer materials.

[0288] Electrodes with Elastomer Particles:

[0289] Such as argon bubbles, polymers or voids trapped in the electrode. The volume of the argon bubbles, polymers or voids around 5% of the total volume. The argon bubbles, polymers or voids acting as cushions to accommodate the shape changes during the cycling.

[0290] Safer Batteries:

[0291] Overvoltage protection and Safe-short separators and electrochemical cells implement them: Instability of cathode and anode due to overcharge can result in a thermal event. Currently, Overcharge protection is provided by the battery management system (BMS) Electronics add weight, volume, and cost to the pack. Redox shuttle compounds could eventually replace or reduce the role of the BMS Redox shuttle (RS) compounds have a reduction-oxidation reaction at the potential where overvoltage protection is desired. When this overpotential voltage is reached during cell charging, the extra charge is used to oxidize the RS additive at the positive electrode instead of further charging the cell; the cell voltage

is pegged. The oxidized form of the redox shuttle additive migrates to the anode, where it is reduced. This process could occur indefinitely for a species that exhibits completely reversible electrochemical behavior and has chemically stable oxidized and reduced forms; however current electrochemical cells which use redox shuttle compounds as additives to electrolyte suffer from negative effects on the normal operational performance; in addition the shuttle process is not fully reversible; thus there is a major challenge in the optimum amount of the RS additive that doesn't affect the normal performance negatively but can perform well in the event of an overvoltage. In an embodiment, using the RS is used not as an additive to the electrolyte but as one of the components of the separator material; e.g. a thin layer of coating on at least one perforated layer of a multilayer separator, in which the separator has at least one perforated layer with minimum of 30% porosity or as a thin layer of coating on a nonwoven separator or micro-porous separator, the adhesion can be made by methods known in the art such as, but not limited to, dip-coating, heat sealing and adhering (e.g. with pvdf, ptfe or PEO). One advantage is that due to the possibility of using much larger amount of RS compared to the conventional electrolyte-additive method (which are current-density limited), the performance of the RS in the event of overvoltage is significantly improved; especially the RS performance can last for many cycles, in contrast to current state of the art RS additives that provide protection only for a few cycles. An example of RS materials is Perfluoro Aryl Boronic Esters, A fluorinated 1,3,2-benzodioxaborole (BDB). Redox voltage is about 4.43 V. Good redox shuttle candidate for NMC cathodes which operate at 4.1 to 4.2 V. Another RS material is 2,5-Di-tert-butyl-1,3-dimethoxy-benzene (DDB) is a well-known, well-characterized redox shuttle compound. Its E0 of about 3.9 V is too low for NMC cathodes but well-suited for LFP cathodes. Some other examples are TEMPO, MPT, 1,4-di-tert-butyl-2,5-bis(2,2,2-trifluoroethoxy)benzene, lithium borate cluster salt, Li2B12H12-xFx (x=9 and 12) and other known RS materials in the art. It should be emphasized that our approach is chemistry-agnostic (chemistry-indifferent) and can be used with any of the known electrochemical systems (electrolyte, electrodes and RS materials) once the suitable voltages are identified.

[0292] This layer or coating can be selected such that it reacts with the materials inside the cell such as the electrolyte, upon activation (for example due to overvoltage or excess heat or pressure). This reaction consumes energy and reduces the failure severity and chance for example by the disappearance of the insulating layer or by uncovering the underneath metallic layer that can further change the nature of the failure. Other additives to the electrolyte can also be introduced in the form of coating or layers of the separator.

[0293] Ionic Diodes as Separators or Electrolytes

[0294] in electrochemical cells such as batteries (e.g., li batteries, alkaline batteries, air batteries etc.), fuel cells, flow batteries or semisolid batteries are introduced here. Ionic diodes are well known in biology, especially cell membranes, however has never been used in electrochemical cells. In the present disclosure ionic diodes, in the form of a pair of one directional ion channels with opposite directions, are used as components of the separator and/or electrolyte. Each ionic diode has a minimum required concentration or voltage that ions less than that certain minimum concentration or voltage can't enter the channel. Only one set of the channels is active at any time. One set is active during the charge transporting

the ions from the cathode to the anode, and the other set of channels is active during the discharge. The ionic diode can be designed based on concentration or voltage gradients between the opposite ends. Also see FIG. 11.

[0295] An electrochemical cell (preferably rechargeable) is introduced in which more than two active materials (conventional electrochemical cell have one anode active material and one cathode active material) are used in a layered format such that at least one active material layer is placed between the anode primary active material and cathode primary active material; primary active material is defined as the active material that is in direct physical and electronic contact with a current collector. As an example, consider a rechargeable lithium battery consisting of (in order of placement) anode current collector (such as a foil or mesh made of copper, stainless steel, iron, Ti, Ni, or any other highly electronically conductive material), first active anode (such as lithium metal anode or a silicon anode that may have conductive carbon added), separator and electrolyte (such as aqueous electrolyte or non-aqueous electrolyte and micro-porous or nonwoven PE-PP separator, or solid polymer electrolyte, or gel polymer electrolyte, or solid ceramic electrolyte) and first cathode active material and finally cathode current collector (such as mesh or foil made of materials with very high electronic conductivity such as aluminum, Ni, Ti, stainless steel); this is how a battery is made today, now if we place a second active layer of anode (cathode) between the said first active anode (cathode) layer and the said separator then we have made the novel battery introduced here. It is noted that the second active material does not need to be physically connected to the said current collector directly; and it doesn't need to be in complete physical contact with the said first active material at all times.

[0296] The benefits of the novel design by the example that was introduced are explained. As an example of the second anode layer consider LTO (lithium titanate) which is a known anode active material with very good cyclability; however with the voltage of about 1.5 the energy density of any cell with only LTO as anode is much less than that of with conventional graphite anode. On the other any battery with lithium metal anode is known to have very high energy density but can only last very few cycles due to lithium dendrite formation and electrolyte depletion (corrosion of lithium metal). It is also known that physical pressure on the surface of lithium metal can significantly increase the cycle life of lithium metal anode batteries; however this is not practical in wound cells, cylindrical cells or any conventional format of batteries other than very small coin cells that implement a spring but has a very low ratio of active material to inactive material. Similar problem happens with alloy anodes such as silicon, aluminum, Sn or other high capacity anode materials as they undergo large deformations when lithiated such that active material and electrolyte may be lost and thus the cycle life is very low. In an embodiment, the second layer of the anode active material helps with confining the first anode active material in place by applying pressure on its surface. during lithiation; during discharge the anode loses lithium which can result in creation of free space between the current anode collector and the separator, this gap then can result in poor lithium deposition during the charging of the battery as there is no pressure to keep the surface of the lithium uniform during lithium deposition or to keep the electric contact in place, especially useful for silicon or Sn anode. By introducing the second layer of active material such as LTO (lithium

titanate), this helps in maintaining the pressure on the first active electrode material (Li, Si, Sn, etc.) by possibly at least one mechanism including 1—(Mechanical) the second active material layer such as LTO has higher elastic modulus than electrolyte (many polymer electrolytes such as PEO, Balsa-ra's group polymer, etc. are developed but none can have high elastic modulus and high ionic conductivity at the same time) and is mechanically stronger than separator so dendrites can't get thicker after penetrating it by making the pores bigger; this means that the second layer is mechanically strong to apply pressure on the first electrode surface and thus help with better performance and cycling 2—(electrochemical) the second active layer such as LTO may show a different electrochemical behavior (e.g., LTO is at about 1.5 v wrt Li_+/ Li) this means that any dendrite that may form on the lithium layer or anode current collector has to stop growing once it reaches the LTO layer and gives priority to LTO lithiation; even after the LTO lithiation stops the dendrite may prefer not to grow as the lithiated LTO provides not only the physical barrier (mentioned earlier) but also it can change the electric field and also the electric conductivity at the lithium-LTO interface, thus more uniform lithium deposition is possible.

[0297] The second electrode active material mentioned here can be a free standing layer, can be a coating on the first active material layer or can be a coating on the separator layer (separator includes polymer and solid electrolytes). The said second active layer can be as thick as the first one, but preferably thinner (as the first one is the one with high energy density and the second one is there to increase the safety and cycle life); it can be a few micrometers or tens of micrometers thick or even tens or hundreds of nanometers thick). The second active layer further may have electronic conductivity or not, for example it can have about 10% conductive carbon or may not. As an example it can be a few micrometers thick with no electronic conductivity. In some embodiments the first and second layers can be separated by a thin layer (e.g., 0.007 mm porous, woven, non-woven or perforated layer made of inert materials such as PE, PP, polyester, polyimide, TiO_2 , etc.). In some embodiments the secondary electrode layer has higher porosity than the first one. In some embodiments the secondary electrode (internal layer that is closer to the opposite electrode) layer has lower electric conductivity than the primary electrode layer (external layer that is further from the opposite electrode), for example it has less conductive carbon added.

[0298] Another example is a composite anode that is made of at least two different anode active materials that may have different voltages and capacities. For example an anode that is made of lithium metal and LTO anode (lithiated or delithiated). The two different materials can make a fibrous composite (e.g., LTO matrix and Lithium fibers), a laminated composite (e.g., lithium layer on the current collector side and LTO layer on the electrolyte side) or a coated-shell composite (e.g., LTO coated on lithium), or lithium used as one of the binders-conductors of the other cathode (e.g. LTO powders made with addition-deposition of lithium metal). Upon recharging for example in an electrochemical cell with LCO cathode and non-aqueous electrolyte, the LTO helps with maintaining the structure of the anode and thus helps with the uniform deposition of lithium metal (a known problem with conventional lithium metal anode is that the structure is lost after discharging and the lithium metal may not deposit back uniformly leading to capacity loss and even shorting). Note that porous metal oxides such as LTO have good lithium ion

conductivity and allow the lithium ion to reach to the back of the current collector; it can also mechanically prevent lithium dendrite shorting. Also note that, in the above example, upon recharging the cell may be charged in more than one step: first at about 1.5 volts corresponding to LTO lithiation and then lithium deposition at 0 volt; on the other hand on discharge the LTO may delithate first before lithium dissolution; this greatly enhances the cycle life of the battery by mitigating dendrite formation and electrolyte consumption (SEI formation at about 0.7v); especially that in many applications only part of the energy of the battery is needed and thus the time at near 0 voltage (wrt Li_+/Li) is reduced; it is known that less time at 0 voltage increases the

[0299] LTO-Air Battery:

[0300] An air battery consisting of LTO anode and conventional air cathode is disclosed. The electrolyte can be non-aqueous or can be aqueous. The aqueous electrolyte has the advantage of easier handling and fabrication. The voltage is about 1.5 v and the capacity can be 100 mAh/g of total weight of the battery, including oxygen. This gives energy density of about 150 Wh/kg. The battery can be charged discharged thousands of cycles.

[0301] Porous Metal Structure Anode:

[0302] An electrochemical cell (lithium battery, alkaline battery, lead battery, air battery, flow battery, semisolid battery or fuel cell) with porous metal (such as silicon wool, aluminum wool or titanium wool) as anode is disclosed; conductive carbon can further be added to the porous silicon to form an electronic conductive path of coating that is needed for ionic (such as lithium ions and electrons forming lithium metal-silicon anode) deposition (dissolution) inside the silicon pores during the charging (discharging) of the cell. The electrochemical cell can be a rechargeable lithium ion battery. The benefit of porous silicon (such as those known in the art of porous silicon with at least 25% porosity, preferably closer but less than 75% porosity) is that porous silicon structure acts as the host for the lithium during lithiation (charging the cell). The rationale for preferring about 75% porosity is that silicon is known to undergo very large deformations upon lithiation that increases its volume by a factor of 3, thus 75% porosity can act as a buffer and enable good cycle life by preventing the anode failure. Nano silicon has been tried by many different researchers and better cyclability is observed but it is very expensive; it is also preferred to grow the silicon nano-rods in a preferable crystallographic orientation such that the large deformation due to lithiation happens mostly in the free space between the nano-rods (that is deformation happens in the plane with the rod orientation as the axis); and even doing so still the conductive carbon path may be lost after some cycles; also the electrolyte loss is unavoidable (the silicon shape change still occurs). On the other hand porous silicon with about 70% porosity can avoid the electrolyte loss and conductive carbon path loss because porous silicon doesn't need to change its shape and undergo large deformations during cycling of the cell. The porous silicon can be prepared by methods known in the art of silicon use such as by stain etching or anodization. Note that this is different from conventional electrode making in which particles of the active material are adhered to each other by a binder (such as pvdf). There is no need for a binder in our electrode. Another problem with silicon nanorods is that it is not flexible enough even at very low thicknesses of electrodes (e.g. 0.100 mm) and thus making a wound or cylindrical cell is not practical, on the other hand the porous silicon can be easily deformed into a

wound format for a cylindrical cell and thus has a cost advantage. See FIG. 12 for two perforated aluminum foils with complementary hole patterns.

[0303] Example of rechargeable battery with lithium metal anode and conventional li-ion cathode (such as LiFePO_4 , NMC, NCA and LiCoO_2), especially useful for high power applications. Example: rechargeable battery with lithium metal anode, two perforated aluminum foils with complementary hole patterns (0.007 mm thickness, and 0.5 mm hole diameter and 1 mm pitch), the two perforated aluminum foils

[0304] Another example is a rechargeable lithium metal battery with lithiated cathode. The lithium metal anode is separated from the cathode with a porous-perforated elastomer (such as silicone, rubber or elastic electrode binder materials known in the art, e.g., styrene-butadiene (ST-BD) copolymer and 2-ethylhexyl acrylate-acrylonitrile (2EHA-AN) copolymer, acryloxy perfluoropolyether, alginate, polyurethane) and is made in the discharged mode that has the minimum thickness (e.g., current collector thickness and possibly a thin layer of lithium that performs as the substrate for lithium deposition during charging). This way upon charging the lithium deposition results in compressive stress in the porous-perforated elastomer which itself applies pressure on the newly deposited lithium and thus improves the performance of the electrode and electrochemical cell. The cell also has an electrolyte and can further have a separator (conventional separators or those introduced by US Patent Publication no. 2013/0224632); the electrolyte can be aqueous, non-aqueous, polymer or solid electrolyte such as those known in the art; electrolyte (liquid, gel, polymer or solid occupies the pores-apertures of the said elastomer layer.

[0305] Notes: the effect of pressure in these designs allows a smoother surface with fewer irregularities, on the electrodes. The effect of pressure may be due to the change of the free energy; however, as too much pressure may reduce the ionic conductivity of the pores in the separator layers or even electrodes, thus, there exist an optimum pressure range in which the best cell performance (smooth deposition on electrodes in addition to cycle life and rate capability) can be obtained. It is noteworthy to mention that very high pressure can result in a non-working condition, for example by hindering the electrolyte from covering the entire surface of any of the electrodes. Any of the mentioned methods or devices can further be combined with one or more of the other methods or devices described here such as the separator bag to enhance the cyclic performance of an electrochemical cell. The methods mentioned here can be used for batteries, fuel cells, flow batteries, supercapacitors, ultracapacitors, or even as membranes in filtration industries such as food, medical, oil, gas, water, etc.

[0306] Solid Electrolytes and Electrochemical Cells in which the Solid Electrolyte Powders (Such as NASICON, LISICON Type Ceramic Electrolytes) are Adhered to Each, Other Using a Binder.

[0307] The use of binders (such as pvdf, ptfе or other binders known in the art) provides flexible, long-life, no-hole and low cost solid electrolytes without the need of high temperature fabrication. Current solid electrolytes are made with powders treated at very high temperatures which results in very expensive solid electrolytes which have to be thick to avoid pinholes and fragility. The high thickness results in higher ionic conductivity and no-deformability which makes them impractical in industrial applications. Further our novel method allows using different new materials such as LTO

powder as components of the solid electrolyte. The amount of the binder can be about 5-10%. A solvent (organic based or water based or any other solvent) can be used to glue the powders to each other. Electrochemical cells suitable for use with this embodiment, include lithium batteries, aluminum batteries, air batteries, alkaline batteries, fuel cells, flow batteries, semisolid batteries and so on.

STATEMENTS REGARDING INCORPORATION BY REFERENCE AND VARIATIONS

[0308] All references cited throughout this application, for example patent documents including issued or granted patents or equivalents; patent application publications; and non-patent literature documents or other source material; are hereby incorporated by reference herein in their entireties, as though individually incorporated by reference, to the extent each reference is at least partially not inconsistent with the disclosure in this application (for example, a reference that is partially inconsistent is incorporated by reference except for the partially inconsistent portion of the reference).

[0309] The terms and expressions which have been employed herein are used as terms of description and not of limitation, and there is no intention in the use of such terms and expressions of excluding any equivalents of the features shown and described or portions thereof, but it is recognized that various modifications are possible within the scope of the invention claimed. Thus, it should be understood that although the present invention has been specifically disclosed by preferred embodiments, exemplary embodiments and optional features, modification and variation of the concepts herein disclosed may be resorted to by those skilled in the art, and that such modifications and variations are considered to be within the scope of this invention as defined by the appended claims. The specific embodiments provided herein are examples of useful embodiments of the present invention and it will be apparent to one skilled in the art that the present invention may be carried out using a large number of variations of the devices, device components, methods steps set forth in the present description. As will be obvious to one of skill in the art, methods and devices useful for the present methods can include a large number of optional composition and processing elements and steps.

[0310] When a group of substituents is disclosed herein, it is understood that all individual members of that group and all subgroups, including any isomers, enantiomers, and diastereomers of the group members, are disclosed separately. When a Markush group or other grouping is used herein, all individual members of the group and all combinations and subcombinations possible of the group are intended to be individually included in the disclosure. When a compound is described herein such that a particular isomer, enantiomer or diastereomer of the compound is not specified, for example, in a formula or in a chemical name, that description is intended to include each isomers and enantiomer of the compound described individual or in any combination. Additionally, unless otherwise specified, all isotopic variants of compounds disclosed herein are intended to be encompassed by the disclosure. For example, it will be understood that any one or more hydrogens in a molecule disclosed can be replaced with deuterium or tritium. Isotopic variants of a molecule are generally useful as standards in assays for the molecule and in chemical and biological research related to the molecule or its use. Methods for making such isotopic variants are known in the art. Specific names of compounds are intended to be

exemplary, as it is known that one of ordinary skill in the art can name the same compounds differently.

[0311] It must be noted that as used herein and in the appended claims, the singular forms “a”, “an”, and “the” include plural reference unless the context clearly dictates otherwise. Thus, for example, reference to “a cell” includes a plurality of such cells and equivalents thereof known to those skilled in the art, and so forth. As well, the terms “a” (or “an”), “one or more” and “at least one” can be used interchangeably herein. It is also to be noted that the terms “comprising”, “including”, and “having” can be used interchangeably. The expression “of any of claims XX-YY” (wherein XX and YY refer to claim numbers) is intended to provide a multiple dependent claim in the alternative form, and in some embodiments is interchangeable with the expression “as in any one of claims XX-YY.”

[0312] Unless defined otherwise, all technical and scientific terms used herein have the same meanings as commonly understood by one of ordinary skill in the art to which this invention belongs. Although any methods and materials similar or equivalent to those described herein can be used in the practice or testing of the present invention, the preferred methods and materials are now described. Nothing herein is to be construed as an admission that the invention is not entitled to antedate such disclosure by virtue of prior invention.

[0313] Every formulation or combination of components described or exemplified herein can be used to practice the invention, unless otherwise stated.

[0314] Whenever a range is given in the specification, for example, a temperature range, a time range, or a composition or concentration range, all intermediate ranges and sub-ranges, as well as all individual values included in the ranges given are intended to be included in the disclosure. As used herein, ranges specifically include the values provided as endpoint values of the range. For example, a range of 1 to 100 specifically includes the end point values of 1 and 100. It will be understood that any subranges or individual values in a range or subrange that are included in the description herein can be excluded from the claims herein.

[0315] As used herein, “comprising” is synonymous with “including,” “containing,” or “characterized by,” and is inclusive or open-ended and does not exclude additional, unrecited elements or method steps. As used herein, “consisting of” excludes any element, step, or ingredient not specified in the claim element. As used herein, “consisting essentially of” does not exclude materials or steps that do not materially affect the basic and novel characteristics of the claim. In each instance herein any of the terms “comprising”, “consisting essentially of” and “consisting of” may be replaced with either of the other two terms. The invention illustratively described herein suitably may be practiced in the absence of any element or elements, limitation or limitations which is not specifically disclosed herein.

[0316] One of ordinary skill in the art will appreciate that starting materials, biological materials, reagents, synthetic methods, purification methods, analytical methods, assay methods, and biological methods other than those specifically exemplified can be employed in the practice of the invention without resort to undue experimentation. All art-known functional equivalents, of any such materials and methods are intended to be included in this invention. The terms and expressions which have been employed are used as terms of description and not of limitation, and there is no intention that

in the use of such terms and expressions of excluding any equivalents of the features shown and described or portions thereof, but it is recognized that various modifications are possible within the scope of the invention claimed. Thus, it should be understood that although the present invention has been specifically disclosed by preferred embodiments and optional features, modification and variation of the concepts herein disclosed may be resorted to by those skilled in the art, and that such modifications and variations are considered to be within the scope of this invention as defined by the appended claims.

1. An electrochemical cell comprising:
 - a positive electrode;
 - a negative electrode;
 - one or more ionically conductive electrolytes positioned between said positive electrode and said negative electrode; and
 - a composite separator comprising at least one electronically insulating layer and at least one electronically conductive layer; said composite separator being positioned between said positive electrode and said negative electrode and being permeable to ionic charge carriers, but not electronically conductive across the composite separator;
 wherein said electronically conductive layer undergoes deposition or electroplating of ionic charge carriers or chemical reaction with a dendrite structure or an internal defect upon formation of an internal short between the negative or the positive electrode and said electronically conductive layer, the short formed by contact of the dendrite structure or the internal defect with said electronically conductive layer.
2. The electrochemical cell of claim 1, wherein the electronically conductive layer is chemically reactive with the dendrite structure.
3. The electrochemical cell of claim 2, wherein the chemical reaction is an alloying reaction.
4. The electrochemical cell of claim 1, wherein the dendrite structure is a lithium or zinc dendrite.
- 5.-7. (canceled)
8. The electrochemical cell of claim 1, wherein said positive electrode comprises a positive electrode active material, said negative electrode comprises a negative electrode active material and said electronically conductive layer is provided between said insulating layer and said positive electrode or said negative electrode, thereby providing an additional electronic path for the positive electrode active material or the negative electrode active material.
9. The electrochemical cell of claim 1 further comprising a second insulating layer, wherein said electronically conductive layer is provided between the two insulating layers.
- 10.-14. (canceled)
15. The electrochemical cell of claim 1, wherein said electronically conductive layer is a perforated or porous layer having a porosity greater than or equal to 30% and less than or equal to 90%.
- 16.-17. (canceled)
18. An electrochemical cell comprising:
 - a positive electrode comprising a positive electrode active material and a first current collector in electronic communication with the positive electrode active material, the first current collection further comprising a first external connection tab;

- a negative electrode comprising a negative electrode active material and a second current collector in electronic communication with the negative electrode active material, the second current collector further comprising a second external connection tab;
 - one or more ionically conductive electrolytes positioned between said positive electrode and said negative electrode; and
 - a composite separator comprising at least one electronically insulating layer and at least one electronically conductive layer; said composite separator being positioned between said positive electrode and said negative electrode and being permeable to ionic charge carriers, but not electronically conductive across the composite separator;
- wherein said electronically conductive layer further comprises a third external connection tab and is not provided in electrical contact with said positive electrode or said negative electrode in the absence of said electrical short.
19. The electrochemical cell of claim 18, further comprising a voltage or current monitoring circuit or voltage or current applying circuit connected between said electronically conductive layer and the negative or positive electrode.
 - 20.-21. (canceled)
 22. The electrochemical cell of claim 18, wherein said positive electrode comprises a positive electrode active material, said negative electrode comprises a negative electrode active material and said electronically conductive layer is provided between said insulating layer and said positive electrode or said negative electrode, thereby providing an additional electronic path for the positive electrode active material or the negative electrode active material.
 23. The electrochemical cell of claim 18, further comprising a second insulating layer, wherein said electronically conductive layer is provided between the two insulating layers.
 - 24.-29. (canceled)
 30. The electrochemical cell of claim 18, further comprising a solid electrolyte, wherein said electronically conductive layer is provided between the solid electrolyte and the insulating layer.
 31. The electrochemical cell of claim 18, further comprising a solid electrolyte, wherein the electronically conducting layer is porous and the solid electrolyte is provided in the pores of the electronically conducting layer.
 - 32.-57. (canceled)
 58. An electrochemical system comprising the electrochemical cell of claim 18 and further comprising a device for assessing state of charge or state of health of the electrochemical cell, thereby allowing application of voltage or current through voltage or current applying circuit as a function of state of charge and state of health of the cell, during each cycle.
 59. A method of detecting the onset of a short in an electrochemical cell;
 - said method comprising the steps of:
 - providing said electrochemical cell comprising:
 - a positive electrode;
 - a negative electrode;
 - one or more ionically conducting electrolytes positioned between said positive electrode and said negative electrode; and
 - a composite separator comprising an electronically insulating and an electronically conductive layer; said

separator positioned between said positive electrode and said negative electrode such that said charge carriers are able to be transported between said positive electrode and said negative electrode; and

monitoring the voltage, current, capacity or a combination thereof of said electrochemical cell, wherein said electrochemical cell undergoes an observable change in voltage, current, capacity or a combination thereof between any two of the positive electrode, the negative electrode and the electronically conductive layer upon formation of an electrical short between the electronically conductive layer and said positive electrode or said negative electrode.

60. The method of claim **59**, wherein the positive electrode comprises a positive electrode active material and a first current collector in electronic communication with the positive electrode active material, the first current collection further comprising a first external connection tab, the negative electrode comprises a positive electrode active material and a second current collector in electronic communication with the negative electrode active material, the second current collection further comprising a second external connection tab, said electronically conductive layer further comprises a third external connection tab, and the voltage monitored is the voltage between the electronically conductive layer and the positive electrode or the negative electrode.

61. The method of claim **59**, further comprising the step of changing at least one operating condition of said electrochemical cell in the event of detection of said observable change in voltage, current, capacity or a combination thereof, wherein said operating condition is selected from the group consisting of a discharge rate, a load on said electrochemical cell, an voltage between the positive electrode and the negative electrode, and a temperature of said electrochemical cell.

62. A method of reducing dendrite growth in an electrochemical cell; said method comprising the steps of:

- a) providing said electrochemical cell comprising:
 - a positive electrode;
 - a negative electrode;
 - one or more electrolytes positioned between said positive electrode and said negative electrode; said one or more ionically conductive electrolytes; and
 - a composite separator comprising an electronically insulating and an electronically conductive layer; said separator positioned between said positive electrode and said negative electrode such that said charge carriers are able to be transported between said positive electrode and said negative electrode; and

charging said electrochemical cell, wherein said electronically conductive layer undergoes deposition, electrochemical plating or alloy reaction with a dendrite structure formed during charge between the electronically conductive layer and said positive electrode, negative electrode or both.

63. The method of claim **62**, wherein said deposition, electrochemical plating or alloy reaction stops or decrease the rate of growth of said dendrite structure or internal defect.

64. A method of operating an electrochemical cell, the method comprising the steps of:

- providing said electrochemical cell comprising:
 - a positive electrode;
 - a negative electrode;

one or more ionically conductive electrolytes positioned between said positive electrode and said negative electrode; and

a composite separator comprising at least one electronically insulating layer and at least one electronically conductive layer; said composite separator being positioned between said positive electrode and said negative electrode and being permeable to ionic charge carriers, but not electronically conductive across the composite separator;

charging, discharging or charging and discharging the electrochemical cell, thereby inducing a surface charge on the surface of the electronically conductive layer.

65. The method of claim **64**, wherein said electronically conductive layer provides an electric field adjacent to and within said positive electrode, said negative electrode or both, thereby providing uniform ion deposition into said positive electrode, said negative electrode or both during charging or discharging of said electrochemical cell.

66. (canceled)

67. The method of claim **64**, further comprising changing at least one operating condition of said electrochemical cell in the event of detection of said observable change in voltage.

68.-70. (canceled)

71. The electrochemical cell of claim **18**, further comprising a voltage or current applying circuit connected between each of said electrochemically conductive layers and one of the positive or the negative electrode, thereby allowing modification of the electric field and the performance of the electrochemical cell.

72. The method of claim **64**, wherein

the positive electrode comprises a positive electrode active material and a first current collector in electronic communication with the positive electrode active material, the first current collection further comprising a first external connection tab;

the negative electrode comprises a negative electrode active material and a second current collector in electronic communication with the negative electrode active material, the second current collector further comprising a second external connection tab;

electronically conductive layer further comprises a third external connection tab and is not provided in electrical contact with said positive electrode or said negative electrode;

and the method further comprises the step of applying a voltage or current between the third external connection tab and one of the first or the second external connection tab, thereby redistributing active material in the cell.

73. The method of claim **64**, wherein

the positive electrode comprises a positive electrode active material and a first current collector in electronic communication with the positive electrode active material, the first current collection further comprising a first external connection tab;

a negative electrode comprises a negative electrode active material and a second current collector in electronic communication with the negative electrode active material, the second current collector further comprising a second external connection tab;

the cell further comprises a layer of electrolyte additive attached to said electronically conductive layer; and

the method further comprises the step of applying a voltage or current between the third external connection tab and one of the first or the second external connection tabs, thereby releasing electrolyte additive into the electrolyte of the cell.

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