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(54) Title: ELECTROCHEMICAL SYSTEMS AND METHODS FOR RECYCLING LITHIUM-ION BATTERIES

(57) Abstract: Disclosed herein are systems and methods for electrochemical recycling of lithium-ion batteries and components thereof. For example, in some embodiments, an electrochemical system is provided for the recovery of nickel, manganese, copper, lithium, and/or cobalt. In some embodiments, the system comprises one or more electrochemical cells, wherein each electrochemical cell comprises a working electrode and a counter electrode, the working electrode and counter electrode separated by a separator. In some embodiments, the systems described herein are configured for the simultaneous recovery of two or more metal (ions) for a given electrochemical cell. For example, in some embodiments, during operation of an electrochemical cell as described herein, cobalt and/or nickel may be deposited on a (working) electrode while manganese is deposited on a (counter) electrode. The systems and methods described herein may be particularly advantageous for the recovery of raw materials from spent lithium-ion batteries.



ELECTROCHEMICAL SYSTEMS AND METHODS FOR RECYCLING
LITHIUM-ION BATTERIES

RELATED APPLICATIONS

5 This application claims priority under 35 U.S.C. § 119(e) to U.S. Provisional Patent Application No. 63/386,165, filed December 5, 2022, and to U.S. Provisional Patent Application No. 63/490,302, filed March 15, 2023, each of which is hereby incorporated by reference in its entirety for all purposes.

10 **STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR
DEVELOPMENT**

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15

TECHNICAL FIELD

 Electrochemical systems, including systems for recycling components of lithium-ion batteries and related methods, are generally described.

20

BACKGROUND

 The world is quickly shifting towards an electric automotive industry; by 2030, there will be 145 million electric vehicles (EVs) on the roads, whereas in 2020 there were only 11 million. As a result, the global cathode material market size is projected to reach between \$54-110 billion by 2030. However, the extraction of raw materials for
25 lithium ion batteries (LIBs) accounts for 50-60% of the total greenhouse gas (GHG) emissions associated with LIB manufacturing, and 70% of global cobalt production occurs within the Democratic Republic of the Congo at the expense of grievous human rights violations. Moreover, future demand for critical elements, especially cobalt and nickel, will outpace the available reserves by 2035. Recycling spent LIBs could provide
30 a much-needed pathway to mitigating the environmental impact of LIB manufacturing while also reducing the cost of raw materials for the production of new batteries. Thus, it is important to develop sustainable and cost-effective recycling processes for spent LIBs,

as they represent valuable sources of critical battery materials. Accordingly, additional systems and methods are needed.

SUMMARY

5 Electrochemical systems, including systems for recycling components of lithium-ion batteries and related methods, are generally described.

In one aspect, electrochemical systems (e.g., for recovery of nickel, manganese, copper, lithium, and/or cobalt) are provided. In some embodiments, the electrochemical system comprises a first electrochemical cell in fluidic communication with the source of
10 the electrolyte, wherein the first electrochemical cell comprises a first working electrode and a first counter electrode, the first working electrode and first counter electrode separated by a first separator, and a second electrochemical cell in fluidic communication with the first electrochemical cell, wherein the second electrochemical cell comprises a second working electrode and a second counter electrode, the second working electrode
15 and second counter electrode separated by a second separator, wherein the electrolyte comprises a source of two or more ions selected from the group consisting of Co^{2+} , Cu^{2+} , Li^+ , Ni^{2+} , Fe^{2+} , Fe^{3+} and Mn^{2+} .

In some embodiments, the electrochemical system comprises an electrolyte comprising three or more metal ions selected from the group consisting of Co^{2+} , Cu^{2+} ,
20 Li^+ , Ni^{2+} , Fe^{2+} , Fe^{3+} and Mn^{2+} , a first working electrode in contact with the electrolyte and configured for the reduction of a first metal ion of the three or more metal ions, a second working electrode configured for the reduction of a second metal ion of the three or more metal ions, a counter electrode in electrical communication with the first working electrode and/or the second working electrode, the working electrode
25 configured for the oxidation of a third metal ion of the three or more metal ions, and a separator disposed between at least the first working electrode and the counter electrode.

In another aspect, methods (e.g., for recovery of nickel, cobalt, copper, lithium,
30 and/or manganese) are provided. In some embodiments, the method comprises in a reactor, neutralizing a leaching solution that comprises one or more components extracted from a lithium-ion battery in a cobalt, nickel, copper, lithium, and manganese rich solution thereby forming an electrolyte solution, flowing the electrolyte solution into

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a first electrochemical cell comprising a first working electrode and a first counter electrode, applying a first voltage across the first working electrode and the first counter electrode such that cobalt metal deposits on the first working electrode, flowing the electrolyte solution into a second electrochemical cell comprising a second working electrode and a second counter electrode, applying a second voltage across the second working electrode and the second counter electrode such that nickel metal deposits on the second working electrode, wherein, during the step of applying the first current and/or the step of applying the second current, manganese oxide is deposited on the first counter electrode and/or the second counter electrode.

In some embodiments, the method comprises providing a leaching solution of a spent lithium-ion battery, adding a buffered aqueous buffer to the leaching solution to bring the leaching solution to pH 7, immersing a working electrode (WE) and a counter electrode (CE) in the leaching solution, wherein the WE and CE are comprised of carbon paper and are in separate compartments, wherein the compartments are separated by a Li⁺ exchange membrane, reducing Co²⁺ and Ni²⁺ to Co metal and Ni metal at the WE, and oxidizing Mn²⁺ to MnO₂ at the CE via electrolysis.

In some embodiments, the method comprises flowing an electrolyte comprising three or more metal ions selected from the group consisting of Co²⁺, Cu²⁺, Li⁺, Ni²⁺, Fe²⁺, Fe³⁺ and Mn²⁺ into an electrochemical cell comprising a first working electrode and a counter electrode, applying a first current across the first working electrode and the first counter electrode such that a first metal ion reduces and deposits on the first working electrode and a second metal ion oxidizes and deposits on the counter electrode, and applying a second current across the second working electrode and the counter electrode and/or a second counter electrode such that a third metal ion reduces and deposits on the second working electrode.

Other advantages and novel features of the present invention will become apparent from the following detailed description of various non-limiting embodiments of the invention when considered in conjunction with the accompanying figures. In cases where the present specification and a document incorporated by reference include conflicting and/or inconsistent disclosure, the present specification shall control.

BRIEF DESCRIPTION OF THE DRAWINGS

Non-limiting embodiments of the present invention will be described by way of example with reference to the accompanying figures, some of which are schematic and are not intended to be drawn to scale. In the figures, each identical or nearly identical component illustrated is typically represented by a single numeral. For purposes of clarity, not every component is labeled in every figure, nor is every component of each embodiment of the invention shown where illustration is not necessary to allow those of ordinary skill in the art to understand the invention. In the figures:

FIG. 1A is schematic diagram of an exemplary electrochemical system, according to one set of embodiments.

FIG. 1B is schematic diagram of an exemplary electrochemical system, according to one set of embodiments.

FIG. 1C is schematic diagram of an exemplary electrochemical system comprising two or more electrochemical cells, according to one set of embodiments.

FIGs. 2A-2F show the characterization of redox properties of Co^{2+} , Ni^{2+} and Mn^{2+} , according to one set of embodiments, by CV measured on glassy carbon (GC) rotating disc electrode (RDE) in electrolytes at pH 7 containing 2 mM sulfate salt of Co^{2+} , Ni^{2+} and Mn^{2+} and 0.1 M Li_2SO_4 . (A) A schematic of the electrochemical cell that used for CV measurements. (B),(C) CV of 2 mM Co^{2+} at Co plating/stripping region (dark) and OER region (light). (D),(E) CV of 2 mM Ni^{2+} at Ni plating/stripping region (dark) and OER region (light). (F) CV of 2 mM Mn^{2+} at Mn plating/stripping region (dark) and electrolytic MnO_2 /OER region (light).

FIGs. 3A-3F show the design of an electrochemical process for simultaneous recovery of Ni, Mn, Co elements in spent LIBs, according to one set of embodiments.

(FIG. 3A) A schematic current-potential curves showing the reduction of Co^{2+} , to Co, the reduction of Ni^{2+} to Ni and the oxidation of Mn^{2+} to MnO_2 . (FIG. 3B) A schematic of the proposed electrochemical process where Co^{2+} and Ni^{2+} were reduced to Co and Ni at working electrode compartment (WE) while Mn^{2+} was oxidized to MnO_2 at counter electrode compartment (CE). (FIG. 3C) the evolution of the WE and CE potentials as a function of time during the electrodeposition operating at a constant current density of -10 mA cm^{-2} in electrolyte containing 0.1 M sulfate salts of Co^{2+} , Mn^{2+} and Li^+ . (FIG. 3D) X-ray diffraction (XRD) patterns of electrodeposition products at WE (Co) and CE (MnO_2). (FIG. 3E) the evolution of the WE and CE potentials as a function of time

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during the electrodeposition operating at a constant current density of -10 mA cm^{-2} in electrolyte containing 0.1 M sulfate salts of Ni^{2+} , Mn^{2+} and Li^+ . (FIG. 3F) X-ray diffraction (XRD) patterns of electrodeposition products at WE (Ni) and CE (MnO_2).

FIGs. 4A-4C show an exemplary discontinuous process, according to one set of
5 embodiments, mode for simultaneous recovery of Co, Ni and Mn elements in spent LIBs. (FIG. 4A) A schematic showing the current-potential curves of Co and Ni electroplating, (FIG. 4B) An example of potential versus time in continuous process mode for simultaneously recovering of Ni, Co and Mn elements from spent LIB, (FIG. 4C) schematic showing the solid-state synthesis of NMC active material using recovered
10 materials.

FIGs. 5A-5C show the separation of Co and Ni through electrolyte engineering, according to one set of embodiments. (FIG. 5A) Fundamental understanding of the electrolyte effect in Co^{2+}/Co and Ni^{2+}/Ni redox potential and plating/stripping kinetics, (FIG. 5B) An example of potential versus time in continuous process mode for
15 simultaneously recovering of Ni, Co and Mn elements from spent LIB, (FIG. 5C) schematic showing the solid-state synthesis of NMC active material using recovered materials.

FIG. 6 shows an exemplary flow diagram of the continuous process, according to one set of embodiments. In the acid leaching reactor, the black mass reacts with acid to
20 form a pH neutral solution containing Co^{2+} , Ni^{2+} and Mn^{2+} , stored at the storage tank. In the electrochemical cell 1, Co is deposited at WE and MnO_2 is deposition at CE. In the electrochemical cell 2, Ni is deposited at WE and electrolytic MnO_2 reactions and oxygen evolution reaction (OER) occur at CE. The outlet flow containing a Mn^{2+} rich solution is re-injected back to the storage tank. At the CE compartments of the
25 electrochemical cell 1 and 2, the electrolyte become acidic with the production of H^+ while the pH at WE remains neutral. At the electrolytic LiOH cell, where Li^+ ions go cross the Li^+ exchange Nafion membrane to form a concentrated LiOH solution with produced OH^- during hydrogen evolution reaction (HER) at WE compartment. The H^+ rich electrolyte from the CE compartment flows into is re-injected to the leaching reactor
30 as “regenerated” acid for the leaching process. The recovered materials: e.g., Co, Ni, MnO_2 and LiOH are used to regenerate NMC cathode active materials through solid-state synthesis.

FIG. 7 shows hydrogen evolution reaction (HER) measurement at near neutral pH condition, according to one set of embodiments, on Pt, Ni, Cu, Au and GC RDE electrodes in an Ar saturated aqueous solution of 0.1 M LiTFSI measured at 50 mV s⁻¹.

FIGs. 8A-8B shows Ni recovery by electrodeposition, according to one set of
5 embodiments, in electrolyte containing 0.1 M NiSO₄ and 0.1 M Li₂SO₄ operating at a
constant current density of -10 mA cm⁻². (FIG. 8A) The evolution of the WE and CE
potentials as a function of time during the electrodeposition operating at a constant
current density of -10 mA cm⁻² in electrolyte containing 0.1 M of sulfate salts of Co²⁺,
Ni²⁺, Mn²⁺ and Li⁺. (FIG. 8B) X-ray diffraction (XRD) patterns of electrodeposition
10 products at WE and CE.

DETAILED DESCRIPTION

Disclosed herein are systems and methods for electrochemical recycling of
lithium-ion batteries and components thereof. For example, in some embodiments, an
15 electrochemical system is provided for the recovery of nickel, manganese, copper,
lithium, and/or cobalt. In some embodiments, the system comprises one or more
electrochemical cells, wherein each electrochemical cell comprises a working electrode
and a counter electrode, the working electrode and counter electrode separated by a
separator. In some embodiments, the systems described herein are configured for the
20 simultaneous recovery of two or more metal (ions) for a given electrochemical cell. For
example, in some embodiments, during operation of an electrochemical cell as described
herein, cobalt and/or nickel may be deposited on a (working) electrode while manganese
dioxide is deposited on a (counter) electrode. The systems and methods described herein
may be particularly advantageous for the recovery of raw materials from spent lithium-
25 ion batteries (e.g., such that the raw materials may be used in production of new
batteries).

Advantageously, the systems and methods described herein may provide, in some
embodiments, for continuous and/or simultaneous recovery of raw materials (e.g.,
metals) from spent lithium-ion batteries, without the need for expensive, caustic, and/or
30 environmentally unfriendly reagents. Advantageously, in some embodiments, the used
electrolyte may be recycled (e.g., used as regenerated acid to promote leaching and/or
neutralization of spent lithium-ion battery components such as black mass).

In some embodiments, the electrochemical system comprises a first electrochemical cell comprising a first working electrode, a first counter electrode, and a first separator. For example, as shown schematically in FIG. 1A, system 100 comprises electrochemical cell 110. Electrochemical cell 110 comprises, in some embodiments, working electrode 112 and counter electrode 114 in electrical communication with working electrode 112. In some embodiments, working electrode 112 is at least partially submerged in an electrolyte 130. In some embodiments, electrochemical cell 110 comprises separator 116 separating (e.g., disposed between) working electrode 112 and counter electrode 114.

In some embodiments, electrochemical cell 110 comprises additional counter electrodes and/or working electrodes (e.g., configured to operate at a different potentials). For example, as shown schematically in FIG. 1B, electrochemical cell 110 further comprises optional second working electrode 122 and/or optional second counter electrode 124. While FIG. 1B shows both a second working electrode and a second counter electrode, any suitable number of working and counter electrodes may be possible. For example, in some embodiments, the electrochemical cell may comprise two working electrodes and a single counter electrode. In some embodiments, the electrochemical cell may comprise two working electrodes and two counter electrodes. Other combinations are also possible.

In some embodiments, various pairs of electrodes may be used in one or more electrochemical cells. For example, a single electrochemical cell may be operated such that a first metal ion (e.g., Co^{2+}) is reduced at a first working electrode and a second metal ion (e.g., Ni^{2+}), different than the first metal ion, is reduced at a second working electrode. In some embodiments, a metal ion (e.g., Mn^{2+}) may be oxidized at the counter electrode. In some embodiments, the reduction of the first metal ion and second metal ion occurs substantially simultaneously. In some embodiments, the reduction of the first metal ion and second metal ion occurs sequentially. For example, a first current may be applied between the first working electrode and counter electrode (e.g., a first counter electrode) such that a metal ion (e.g., Co^{2+}) is reduced at the first working electrode and a metal ion (e.g., Mn^{2+}) is oxidized at the counter electrode. In some embodiments, a second current may be applied (e.g., during the first current being applied, after the first current is applied (e.g., such that the first current is no longer being applied)) such that another metal ion (e.g., Ni^{2+}) is reduced at the first working electrode and a metal ion

(e.g., Mn^{2+}) is oxidized at the counter electrode (and/or at a second counter electrode). In some embodiments, the first working electrode and second working electrode may both be present in the electrolyte at the same time. In some embodiments, the first working electrode may be operated and then removed from the electrolyte prior to insertion (and operation) of the second working electrode. In some embodiments, two or more working electrodes are present in a single electrochemical cell. In other embodiments, a first working electrode (e.g., and associated counter electrode) is present in a first electrochemical cell and a second working electrode (e.g., and associated counter electrode) is present in a second electrochemical cell.

In some embodiments, the system comprises two or more electrochemical cells. For example, each electrochemical cell may be configured to operate at a different potential/current such that each electrochemical cell serves to recover a different metal (ion). Advantageously, the use of multiple electrochemical cells as described herein may be particularly useful for the simultaneous and/or continuous recovery of two or more metals (e.g., nickel, manganese, copper, lithium, cobalt). For example, in some embodiments, the system comprises a first electrochemical cell and a second electrochemical cell. In some embodiments, the first electrochemical cell and the second electrochemical cell are in fluidic communication. For example, as shown schematically in FIG. 1C, system 102 comprises electrochemical cell 110 and electrochemical cell 120. In some embodiments, electrochemical cell 110 comprises working electrode 112 and counter electrode 114. In some embodiments, electrochemical cell 120 comprises working electrode 122 and counter electrode 124. In some embodiments, electrochemical cell 110 comprises separator 116 (e.g., disposed between working electrode 112 and counter electrode 114). In some embodiments, electrochemical cell 120 comprises separator 126 (e.g., disposed between working electrode 122 and counter electrode 124).

In some embodiments, an electrolyte is present in the electrochemical cell. In some embodiments, one or more electrochemical cells are in fluidic communication with a source of an electrolyte (e.g., such that the electrolyte may flow through the electrochemical cell). In some embodiments, each electrochemical cell is configured to receive and/or contain an electrolyte. For example, referring again to FIG. 1A, in some embodiments, electrochemical cell 110 comprises inlet 150 (e.g., in fluidic communication with a source of an electrolyte) and, optionally, outlet 160 (e.g., in fluidic communication with the source of the electrolyte, in fluidic communication with

another electrochemical cell). Referring again to FIG. 1C, in some embodiments, electrochemical cell 110 comprises electrolyte 130. In some embodiments, electrochemical cell 120 comprises electrolyte 132. In some embodiments, electrolyte 130 and electrolyte 132 are substantially the same. In some embodiments, electrolyte 130 and electrolyte 132 are different. For example, in some embodiments, a (first) electrolyte present in the first electrochemical cell comprises one or more metal ions in a concentration higher than a concentration of the one or more metal ions in the (second) electrolyte present in the second electrochemical cell. In some embodiments, the difference in the electrolyte between electrochemical cells is a result of the electrochemical process that occurs upstream of a particular electrochemical cell.

As described above and herein, in some embodiments, each electrochemical cell is configured such that the electrolyte flows (e.g., through the separator). Any suitable mechanism may be used to flow the electrolyte including sources of pressure, pumps, mixers, gravity, and the like. In some embodiments, the inlet and/or outlet comprises any suitable number of valves, pumps, or the like.

In some embodiments, each electrochemical cell comprises an inlet and an outlet. For example, as shown illustratively in FIG. 1C, electrochemical cell 110 comprises inlet 150 and outlet 160 and electrochemical cell 120 comprises inlet 152 and outlet 162. In some embodiments, outlet 160 and inlet 152 are in fluidic communication (e.g., such that electrolyte 130 flows through separator 116 becoming and exits outlet 162 as electrolyte 132, electrolyte 132 flows into electrochemical cell 120 via inlet 152). In some embodiments, a working electrode and counter electrode are immersed in an electrolyte. In some embodiments, one or more of Co^{2+} , Cu^{2+} , Li^+ , Ni^{2+} , Fe^{2+} , and Fe^{3+} is reduced to a corresponding metal (e.g., Co, Cu, Li, Ni, Fe) at the working electrode via electrolysis. In some embodiments, Mn^{2+} is oxidized to MnO_2 at the counter electrode via electrolysis. In some embodiments, at least a portion of the reducing and at least a portion of the oxidizing occur simultaneously. In some embodiments, the electrolyte is a neutralized leaching solution from a spent lithium-ion battery. For example, in some embodiments, a leaching solution comprising one or more components of a lithium-ion battery (e.g., black mass) is provided. In some embodiments, a buffered aqueous solution may be added to the leaching solution to neutralize the pH of the leaching solution (e.g., such that the pH of the leaching solution is greater than or equal to 6 and less than or equal to 8) thereby forming the electrolyte.

By way of example and without wishing to be limited by such, in an exemplary embodiment, the electrolyte (e.g., from a source of electrolyte) comprises Co^{2+} , Ni^{2+} and Mn^{2+} . In some embodiments, cobalt may be deposited (e.g., from the electrolyte) on a first working electrode during operation of the first electrochemical cell (e.g., as a result of reducing the Co^{2+} to Co at the working electrode). As a result, in some such
5 embodiments, the electrolyte in the second electrochemical cell (e.g., the second electrochemical cell being in fluidic communication with the first electrochemical cell) comprises less Co^{2+} than the electrolyte in the first electrochemical cell. In some embodiments, manganese may be deposited (e.g., from the electrolyte) on a first counter
10 electrode during operation of the first electrochemical cell. As a result, in some such embodiments, the electrolyte in the second electrochemical cell comprises Mn^{2+} than the electrolyte in the first electrochemical cell. In some embodiments, other metal (ions) present in the electrolyte are not deposited on the first working electrode and/or first counter electrode. For example, in this exemplary embodiment, the concentration of Ni^{2+}
15 present in the electrolyte in the first electrochemical cell and the second electrochemical cell (e.g., after operation of the first electrochemical cell and prior to operation of the second electrochemical cell) is the same. Those of ordinary skill in the art would understand that this illustrative example is intended to be non-limiting and would readily envision different combinations of electrolytes, metal (ions), working electrodes and
20 counter electrodes, based upon the teachings of this specification.

As described above and herein, in some embodiments, the leaching solution may be neutralized (e.g., in a reactor) to form the electrolyte solution. In some embodiments, the leaching solution comprises one or more components extracted from a lithium-ion battery. In some embodiments, the electrolyte is rich in one or more of cobalt, nickel,
25 copper, lithium, and manganese ions. In an exemplary set of embodiments, the electrolyte may be provided (e.g., flowed into) a first electrochemical cell comprising a first working electrode and a first counter electrode. In some embodiments, a current is applied across the first working electrode and the first counter electrode such that cobalt metal deposits on the first working electrode. In some embodiments, the electrolyte is
30 flowed into a second electrochemical cell comprising a second working electrode and a second counter electrode. In some embodiments, a current is applied across the second working electrode and the second counter electrode such that nickel metal deposits on the second working electrode. In some embodiments, during the step of applying the first

current and/or the step of applying the second current, manganese oxide is deposited on the first counter electrode and/or the second counter electrode.

Advantageously, the systems described herein may be useful for the selective recovery and/or deposition of metal (ions) on electrodes. For example, in some
5 embodiments, as a result of the operation of the electrochemical cells as described herein, at least a working electrode comprising a coating of cobalt (e.g., and substantially free of nickel), a working electrode comprising a coating of nickel (e.g., and substantially free of cobalt), and a counter electrode comprising a coating of manganese (and/or manganese oxide) (e.g., and substantially free of cobalt and nickel) are produced. In
10 some embodiments, a working electrode comprising a coating comprising a mixture of cobalt and nickel and a counter electrode comprising a coating of manganese (and/or manganese oxide) are produced. Advantageously, each electrochemical cell may be configured to deposit a single metal (ion) on a given electrode. For example, the first electrochemical cell may be configured to deposit (e.g., during operation) a first cation
15 (e.g., cobalt, nickel) on the working electrode and a second cation (e.g., manganese) on a counter electrode. Other metal (ions) and layers are also possible.

As used herein, the phrase ‘substantially free of’ a particular metal(s) generally refers to a component (e.g., a coating) having less than or equal to 10 wt%, less than or equal to 5 wt%, less than or equal to 2 wt%, less than or equal to 1 wt%, less than or
20 equal to 0.5 wt%, or less than or equal to 0.1 wt% (e.g., and greater than or equal to 0 wt%, greater than or equal to 0.1 wt%, greater than or equal to 0.5 wt%, greater than or equal to 1 wt%, greater than or equal to 2 wt%, or greater than or equal to 5 wt%) of another metal versus the total weight of the component (e.g., the coating). By way of illustrative example, in some embodiments, at least one working electrode, after
25 reducing, comprises a coating comprising cobalt, with nickel present in the coating in an amount less than or equal to 10 wt% versus the total weight of the coating. By way of illustrative example, in some embodiments, at least one working electrode, after reducing, comprises a coating comprising nickel, with cobalt present in the coating in an amount less than or equal to 10 wt% versus the total weight of the coating. By way of
30 illustrative example, in some embodiments, at least one counter electrode, after oxidizing, comprises a coating comprising manganese oxide, with cobalt and nickel each present in the coating in an amount less than or equal to 10 wt% versus the total weight of the coating.

In some embodiments, operating an electrochemical cell comprises applying current to one or more electrodes of the electrochemical cell. In some embodiments, operating the electrochemical cell results in at least one chemical reaction occurring within the reactor (e.g., such that a metal is deposited on a surface of an electrode).

5 In some embodiments, the one or more electrochemical cells are in fluidic communication with a source of an electrolyte (e.g., a reservoir containing the electrolyte). In some embodiments, the electrolyte comprises one or more of cobalt ions, copper ions, lithium ions, nickel ions, iron ions, and manganese ions. In an exemplary set of embodiments, In some embodiments, the electrolyte comprises one or more cations
10 such as metal ions. In some embodiments, the electrolyte comprises two or more (e.g., three or more, four or more, or five or more) metal ions. Non-limiting examples of suitable cations include Co^{2+} , Cu^{2+} , Li^+ , Ni^{2+} , Fe^{2+} , Fe^{3+} , and Mn^{2+} . In an exemplary set of embodiments, the electrolyte comprises at least cobalt ions, nickel ions, and manganese ions. In some embodiments, the electrolyte comprises at least cobalt ions,
15 nickel ions, manganese ions, and lithium ions. Other combinations of metal ions are also possible.

In some embodiments, the cation is present in the electrolyte as a salt. For example, in some embodiments, the cation is present in the electrolyte along with a counterion, such as when the cation is formed from solubilizing a salt containing the
20 cation and the counterion within a liquid of the electrolyte. For example, in some embodiments, the electrolyte comprises a metal hydroxide, metal chloride, metal sulfate, metal carbonate, or other metal salt (e.g., where the metal is selected from the group consisting of cobalt, copper, lithium, nickel, iron, and manganese). In some embodiments, the electrolyte comprises one or more metal salts selected from the group
25 consisting of cobalt sulfate, nickel sulfate, manganese sulfate, lithium sulfate, lithium bis(trifluoromethanesulfonyl)imide, and lithium perchlorate. Those of ordinary skill in the art would be capable of selecting additional suitable metal salts based upon the teachings of this specification. In some embodiments, cations, salts and/or metal salts not consumed during electrochemical processes described herein may be recovered (e.g.,
30 mixed with a leaching solution and/or electrolyte for further processing).

The electrolyte may comprise one or more cations and/or one or more salts at any suitable concentration. For example, in some embodiments, the electrolyte comprises a metal and/or metal salt having a concentration of greater than or equal to 0.000001 M,

greater than or equal to 0.00001 M, greater than or equal to 0.0001 M, greater than or equal to 0.001 M, greater than or equal to 0.01 M, greater than or equal to 0.1 M, greater than or equal to 0.5 M, greater than or equal to 1 M, greater than or equal to 3 M, greater than or equal to 5 M, greater than or equal to 7 M, or greater than or equal to 10 M. In certain embodiments, the electrolyte has a metal and/or metal salt concentration of less than or equal to 12 M, less than or equal to 10 M, less than or equal to 7 M, less than or equal to 5 M, less than or equal to 3 M, or less than or equal to 1 M. Combinations of the above-referenced ranges are also possible (e.g., greater than or equal to 0.000001 M and less than or equal to 12 M or greater than or equal to 0.1 M and less than or equal to 10 M). Other ranges are also possible.

For example, in an exemplary set of embodiments, the electrolyte comprises solubilized cobalt sulfate (or, for example, cobalt carbonate) at a concentration of greater than or equal to 0.01 M, greater than or equal to 0.05 M, greater than or equal to 0.1 M, greater than or equal to 0.2 M, or greater than or equal to 0.5 M. In some embodiments, the electrolyte comprises solubilized cobalt sulfate at a concentration of less than or equal to 1.0 M, less than or equal to 0.5 M, less than or equal to 0.2 M, less than or equal to 0.1 M, or less than or equal to 0.05 M. Combinations of the above-referenced ranges are also possible (e.g., greater than or equal to 0.01 M and less than or equal to 1.0 M). Other ranges are also possible.

In some embodiments, the electrolyte comprises nickel sulfate at a concentration of greater than or equal to 0.01 M, greater than or equal to 0.05 M, greater than or equal to 0.1 M, greater than or equal to 0.2 M, or greater than or equal to 0.5 M. In some embodiments, the electrolyte comprises nickel sulfate at a concentration of less than or equal to 1.0 M, less than or equal to 0.5 M, less than or equal to 0.2 M, less than or equal to 0.1 M, or less than or equal to 0.05 M. Combinations of the above-referenced ranges are also possible (e.g., greater than or equal to 0.01 M and less than or equal to 1.0 M). Other ranges are also possible.

In some embodiments, the electrolyte comprises manganese sulfate at a concentration of greater than or equal to 0.01 M, greater than or equal to 0.05 M, greater than or equal to 0.1 M, greater than or equal to 0.2 M, or greater than or equal to 0.5 M. In some embodiments, the electrolyte comprises manganese sulfate at a concentration of less than or equal to 1.0 M, less than or equal to 0.5 M, less than or equal to 0.2 M, less than or equal to 0.1 M, or less than or equal to 0.05 M. Combinations of the above-

referenced ranges are also possible (e.g., greater than or equal to 0.01 M and less than or equal to 1.0 M). Other ranges are also possible.

In some embodiments, the electrolyte comprises lithium sulfate at a concentration of greater than or equal to 0.01 M, greater than or equal to 0.05 M, greater than or equal to 0.1 M, greater than or equal to 0.2 M, or greater than or equal to 0.5 M. In some
5 embodiments, the electrolyte comprises lithium sulfate at a concentration of less than or equal to 1.0 M, less than or equal to 0.5 M, less than or equal to 0.2 M, less than or equal to 0.1 M, or less than or equal to 0.05 M. Combinations of the above-referenced ranges are also possible (e.g., greater than or equal to 0.01 M and less than or equal to 1.0 M).
10 Other ranges are also possible.

In some embodiments, the electrolyte comprises lithium perchlorate at a concentration of greater than or equal to 0.01 M, greater than or equal to 0.05 M, greater than or equal to 0.1 M, greater than or equal to 0.2 M, or greater than or equal to 0.5 M. In some
15 embodiments, the electrolyte comprises lithium perchlorate at a concentration of less than or equal to 1.0 M, less than or equal to 0.5 M, less than or equal to 0.2 M, less than or equal to 0.1 M, or less than or equal to 0.05 M. Combinations of the above-referenced ranges are also possible (e.g., greater than or equal to 0.01 M and less than or equal to 1.0 M). Other ranges are also possible.

In some embodiments, the electrolyte comprises lithium
20 bis(trifluoromethanesulfonyl)imide at a concentration of greater than or equal to 0.01 M, greater than or equal to 0.05 M, greater than or equal to 0.1 M, greater than or equal to 0.2 M, or greater than or equal to 0.5 M. In some embodiments, the electrolyte comprises lithium bis(trifluoromethanesulfonyl)imide at a concentration of less than or equal to 1.0 M, less than or equal to 0.5 M, less than or equal to 0.2 M, less than or equal to 0.1 M, or
25 less than or equal to 0.05 M. Combinations of the above-referenced ranges are also possible (e.g., greater than or equal to 0.01 M and less than or equal to 1.0 M). Other ranges are also possible.

The above-referenced ranges of metal salts are intended to be non-limiting and other concentration ranges and/or other metal salts are also possible.

30 In some embodiments, the electrolyte is derived from black mass. The phrase “black mass” is given its ordinary meaning in the art and generally refers to a mixture of shredded components from a lithium-ion battery (e.g., after the useful life of the lithium-ion battery). Black mass may be produced using any suitable methods including, for

example, pyrometallurgy techniques and/or hydrometallurgy techniques. In some embodiments, the black mass may be prepared in a leaching solution. Battery leaching solutions are generally known in the art and those of ordinary skill in the art would be capable of selecting suitable leaching solutions based upon the teachings of this

5 specification. While the description herein generally refers to black mass derived from lithium-ion batteries, the electrolytes described herein may also be derived from other sources. In some embodiments, the electrolyte comprises a metal (and/or metal ions thereof) such as alkali metals, alkaline earth metals, metals in Groups 3-13 of the Periodic Table, first-row transition metals, base metals, rare earth metals, platinum group

10 elements, noble elements, and/or post transition metals. Examples of alkali metals include Li, Na, K, Rb and Cs. Examples of alkaline earth metals include Be, Mg, Ca, Sr, and Ba. Examples of first-row transition metals include Ti, V, Cr, Mn, Fe, Co, and Ni. Example of base metals include Cu, Zn, Al, and Sn. Examples of rare earth elements include Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Pm, Sm, Sc, Tb, Tm, Yb and Y.

15 Examples of platinum group or noble elements include Ru, Rh, Pd, Re, Os, Ir, Pt, Au and Ag. Examples of post transition metals include Ga, Ge, As, Se, Cd, In, Sb, Te, Tl, Pb, Bi, Po, and Th and U.

In some embodiments, one or more metals (and/or metal ions thereof) such as alkali metals, alkaline earth metals, metals in Groups 3-13 of the Periodic Table, first-

20 row transition metals, base metals, rare earth metals, platinum group elements, noble elements, and/or post transition metals may be recovered and/or deposited on an electrode, in accordance with the embodiments described herein.

In an exemplary set of embodiments, the leaching solution is a byproduct of spent lithium-ion batteries and comprises two or more cations selected from the group

25 consisting of cobalt ions, copper ions, lithium ions, nickel ions, iron ions, and manganese ions (e.g., selected from the group consisting of Co^{2+} , Cu^{2+} , Li^{+} , Ni^{2+} , Fe^{2+} , Fe^{3+} , and Mn^{2+}).

In some embodiments, the leaching solution is neutralized thereby producing a cation-rich electrolyte. In some embodiments, the electrolyte has a pH of greater than or

30 equal to 5.8, greater than or equal to 6, greater than or equal to 6.2, greater than or equal to 6.4 greater than or equal to 6.6, greater than or equal to 6.8, greater than or equal to 7.0, greater than or equal to 7.2, greater than or equal to 7.4, greater than or equal to 7.6, or greater than or equal to 7.8. In some embodiments, the electrolyte has a pH of less

than or equal to 8.2, less than or equal to 8.0, less than or equal to 7.8, less than or equal to 7.6, less than or equal to 7.4, less than or equal to 7.2, less than or equal to 7.0, less than or equal to 6.8, less than or equal to 6.6, less than or equal to 6.4, less than or equal to 6.2, or less than or equal to 6.0. Combinations of the above-referenced ranges are also possible (e.g., greater than or equal to 5.8 and less than or equal to 8.2, greater than or equal to 6.0 and less than or equal to 8.0, greater than or equal to 6.8 and less than or equal to 7.2). Other ranges are also possible. In some embodiments, the pH of the electrolyte is relatively neutral (e.g., a pH of approximately 7.0).

Referring again to FIG. 1C, while FIG. 1C depicts two electrochemical cells in series, those of ordinary skill in the art would understand that three or more, four or more, five or more, six or more, or seven or more electrochemical cells may be fluidically connected (e.g., in series and/or in parallel). In some embodiments, the systems described herein are substantively closed loop such that unused components (e.g., electrolyte) may be recovered and/or reused. For example, in some embodiments, the system comprises at least a third electrochemical cell (e.g., in fluidic communication with the first and/or second electrochemical cells), the third electrochemical cell comprising a third working electrode and a third counter electrode, the third working electrode and third counter electrode separated by a third separator.

As described above and herein, in some embodiments, each electrochemical cell comprises a separator. In some embodiments, the separator comprises a cation exchange membrane (e.g., selectively permeable to a cation(s)). Non-limiting examples of suitable separators include separators comprising Nafion®, Fumatech (e.g., fumasep ion exchange membranes, fumapem ion exchange membranes), Aquivion®, Xion Composites, other perfluorosulfonic acid polymer membranes, polystyrene, glass wool, divinylbenzene, and combinations thereof.

The separator may have any suitable thickness. In some embodiments, the separator has a thickness of greater than or equal to 15 microns, greater than or equal to 20 microns, greater than or equal to 30 microns, greater than or equal to 50 microns, greater than or equal to 100 microns, greater than or equal to 150 microns, greater than or equal to 200 microns, greater than or equal to 300 microns, or greater than or equal to 400 microns. In some embodiments, the separator has a thickness of less than or equal to 500 microns, less than or equal to 400 microns, less than or equal to 300 microns, less than or equal to 200 microns, less than or equal to 150 microns, less than or equal to 100

microns, less than or equal to 50 microns, less than or equal to 30 microns, or less than or equal to 20 microns. Combinations of the above-referenced ranges are also possible (e.g., greater than or equal to 15 microns and less than or equal to 500 microns). Other ranges are also possible.

5 In some embodiments, the separator comprises a reinforcement layer. Any of a variety of suitable reinforcement layer can be used. In some embodiments, the reinforcement layer comprises a polymer. Non-limiting examples of suitable polymers for the reinforcement layer include poly ether ether ketone, polyethylene terephthalate, polypropylene, perfluorinated perfluoroalkoxyl polymers, polytetrafluoroethylene
10 (PTFE), microporous expanded PTFE, and combinations thereof.

Any of a variety of suitable electrode materials may be used in accordance with the embodiments described herein. In some embodiments, the working electrode and/or the counter electrode is a carbon-based electrode. For example, in some embodiments, the carbon-based electrode comprises carbon paper, carbon cloth, carbon felt, or
15 combinations thereof. In some embodiments, the working and/or the counter electrode may be selected according to the target metal to be deposited. For example, in some embodiments, the working and/or counter electrode comprises carbon paper, carbon cloth, carbon felt, cobalt foil, cobalt foam, cobalt mesh, nickel foil, nickel foam, nickel mesh, copper foil, copper foam, copper mesh, titanium foil, titanium screens e.g.,
20 platinized titanium screens), titanium frit, titanium fiber felt (e.g., porous titanium fiber felt), platinized titanium fiber felt, alloys thereof, and combinations thereof. In some embodiments, the working electrode and/or the counter electrode comprises one or more coatings. For example, in some embodiments, the working electrode and/or counter electrode comprises a coating comprising platinum nanoparticles, iridium-based (e.g., Ir,
25 IrO₂) nanoparticles, ruthenium-based (e.g., Ru, RuO₂) nanoparticles, and combinations thereof.

In some embodiments, one or more working electrodes is configured for the reduction of cobalt ions and comprises carbon paper, carbon cloth, carbon felt, cobalt foil, cobalt foam, cobalt mesh, and/or combinations thereof.

30 In some embodiments, one or more working electrodes is configured for the reduction of nickel ions and comprises carbon paper, carbon cloth, carbon felt, nickel foil, nickel foam, nickel mesh, alloys thereof, and/or combinations thereof.

In some embodiments, one or more working electrodes is configured for the reduction of copper ions and comprises carbon paper, carbon cloth, carbon felt, copper foil, copper foam, copper mesh, alloys thereof, and/or combinations thereof.

5 In some embodiments, one or more working electrodes is configured for the reduction of lithium ions and comprises platinum nanoparticles deposited on carbon cloth and/or carbon paper, nickel foil, nickel foam, nickel mesh, alloys thereof (e.g., a nickel alloy alkaline water electrode), and combinations thereof.

10 In some embodiments, one or more counter electrodes is configured for the oxidation of lithium ions and comprises iridium and/or iridium oxide nanoparticles on titanium (e.g., mesh/frit/foam/screen/fiber felt), ruthenium and/or ruthenium oxide nanoparticles on titanium (e.g., mesh/frit/foam/screen/fiber felt), nickel foil, nickel foam, nickel mesh, and/or combinations thereof.

15 In some embodiments, one or more counter electrodes is configured for the oxidation of manganese ions and comprises carbon paper, carbon cloth, carbon felt, titanium foil, platinized titanium screen, titanium frit, titanium fiber felt, platinized titanium fiber felt, and/or combinations thereof.

20 Other combinations of working electrodes and counter electrodes are also possible. Other working electrodes and counter electrodes are also possible. Those of ordinary skill in the art would be capable of selecting appropriate working electrodes and counter electrodes based upon the teachings of this specification.

Referring again to FIG. 1C, in some embodiments, working electrode 112 and working electrode 122 may be the same type of electrode (e.g., carbon paper, carbon cloth, carbon felt, etc.). In some embodiments, working electrode 112 and working electrode 122 are different types of electrodes. In some embodiments, counter electrode 114 and working electrode 124 may be the same type of electrode (e.g., carbon paper, carbon cloth, carbon felt, etc.). In some embodiments, counter electrode 114 and working electrode 124 are different types of electrodes. In some embodiments, separator 116 and separator 126 may comprise the same type of material. In some embodiments, separator 116 and separator 126 comprise different types of materials.

30 One or more portions of each electrochemical cell may be maintained under inert gas, such as argon gas.

As described above, in some embodiments, the system comprises a reactor. For example, as shown illustratively in FIG. 6, in some embodiments an electrochemical

system comprises an acid leaching reactor (e.g., for leaching and/or neutralization). In some embodiments, the reactor is configured to receive and/or leach lithium-ion battery components thereby forming a leaching solution. In some other embodiments, the reactor comprises an electrolyte (e.g., comprising neutralized leaching solution, comprising an ion-rich solution). In some embodiments, the system comprises two or more reactors (e.g., a first reactor for leaching/neutralizing black mass and a second reactor for storing electrolyte). In some embodiments, the reactor comprises an aqueous buffer. In some embodiments, one or more reactors are in fluidic communication with at least the first electrochemical cell. In some embodiments, the system does not comprise a separate reactor (e.g., the electrolyte is added directly to one or more electrochemical cells).

In some embodiments, the system uses a continuous process. For example, as shown schematically in FIG. 6, in an exemplary embodiment, the system comprises a first electrochemical cell (e.g., for simultaneous recovery of cobalt and manganese oxide), a second electrochemical cell (e.g., for simultaneous recovery of nickel and manganese oxide), and a third electrochemical cell (e.g., for recovery of lithium (e.g., as LiOH) from lithium ions). Advantageously, in some embodiments, the electrochemical cells are in fluidic communication such that remaining ions in the electrolyte in each cell can be recycled and/or regenerated into additional electrolyte for use in future electrolysis processes. Advantageously, the system may be configured to produce LiOH.

In an exemplary set of embodiments, the system may be configured to simultaneously and/or continuously reduce and/or oxidize two or more metal ions (e.g., such that the metal is deposited on an electrode) and/or produce LiOH. Advantageously, the metal layers and/or LiOH produced by the system may be used to generate new battery-grade materials.

Advantageously, in some embodiments, each electrochemical cell does not require the use of a sacrificial (e.g., galvanic) electrode.

As described above and elsewhere herein, in some embodiments, methods are provided. In an exemplary set of embodiments, the method comprises in a reactor, neutralizing a leaching solution that comprises one or more components extracted from a lithium-ion battery in a cobalt, nickel, copper, lithium, and manganese rich solution thereby forming an electrolyte solution. In some embodiments, the method comprises extracting one or more components from a lithium-ion battery, wherein the one or more components comprise two or more metal ions selected from the group consisting of

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nickel, cobalt, copper, lithium, and manganese, to form a leaching solution. In some embodiments, the method comprises, in a reactor, neutralizing the leaching solution that comprises the one or more components from the lithium-ion battery in a metal ion rich solution thereby forming an electrolyte solution. In some embodiments, the metal ion
5 rich solution comprises two or more metal ions selected from the group consisting of cobalt, nickel, manganese, copper, and lithium. In some embodiments, the method comprises exposing a component of the lithium-ion battery, the component comprising one or more of cobalt, nickel, manganese, and lithium, to the leaching solution.

In some embodiments, the method comprises flowing the electrolyte solution into
10 a first electrochemical cell comprising a first working electrode and a first counter electrode. In some embodiments, the method comprises applying a first current across the first working electrode and the first counter electrode such that cobalt metal deposits on the first working electrode. In some embodiments, the method comprises flowing the electrolyte solution into a second electrochemical cell comprising a second working
15 electrode and a second counter electrode. In some embodiments, the method comprises applying a second current across the second working electrode and the second counter electrode such that nickel metal deposits on the second working electrode. In some embodiments, during the step of applying the first current and/or the step of applying the second current, manganese oxide is deposited on the first counter electrode and/or the
20 second counter electrode.

In some embodiments, the first current and the second current are different. In some embodiments, one or more electrochemical cells are operated at a particular current density. In some embodiments, an electrochemical cell is operated at a current density of less than or equal to -10 mA/cm^2 , less than or equal to -20 mA/cm^2 , or less than or equal
25 to -30 mA/cm^2 . In some embodiments, an electrochemical cell is operated at a current density of greater than or equal to -40 mA/cm^2 , greater than or equal to -30 mA/cm^2 , greater than or equal to -20 mA/cm^2 , or greater than or equal to -15 mA/cm^2 . Combinations of the above-referenced values are possible (e.g., less than or equal to -10 mA/cm^2 and greater than or equal to -40 mA/cm^2). Other ranges are also possible.

30 According to certain embodiments, the method further comprises applying an electrical potential (within a given electrochemical cell) of greater than or equal to -5 V , greater than or equal to -4 V , greater than or equal to -3 V , greater than or equal to -2 V , greater than or equal to -1 V , greater than or equal to -0.75 V , greater than or equal to -

0.5 V, greater than or equal to -0.25 V, or greater than or equal to 0 V vs the reversible hydrogen electrode. In some embodiments, the method comprises applying an electrical potential (within a given electrochemical cell) of less than or equal to 2 V, less than or equal to 1 V, less than or equal to 0 V, less than or equal to -0.25 V, less than or equal to -0.5 V, less than or equal to -0.75 V, less than or equal to -1 V, or less than or equal to -2 V vs the reversible hydrogen electrode. Combinations of these ranges are also possible (e.g., greater than or equal to -5 V and less than or equal to 2 V or greater than or equal to -3 V and less than or equal to 2 V).

In accordance with some embodiments, applying an electrical potential comprises applying a constant potential. In certain embodiments, applying an electrical potential comprises applying a varying potential (e.g., a time-varying potential, a sequence of potential pulses, or a stepwise increasing or decreasing sequence of potentials).

In some embodiments, one or more electrochemical cells is a flow-by design, by which it is meant that the electrolyte flows at least in some portion of the electrochemical cell in a direction parallel to the plane of an electrode, while the electric field provided by the electrodes is at least in some portion of the electrochemical cell normal to the direction of flow. In some embodiments, each electrochemical cell comprises one or more electrodes held at positive potential, and one or more electrodes held at negative potential, through which the electrolyte is flowed. When more than one electrode is used, the electrodes are each held at the same, or different, electrical potential.

In some embodiments, the method is a flow-through design, by which it is meant that at least an electrode of the electrochemical cell is porous (non-limiting examples being a mesh, foam, weave, and/or mat of fibers, as described above), and the electrolyte flows at least in some portion of the electrochemical cell in a direction normal to the plane of said electrode (e.g., including through the porous electrode), while the electric field provided by the electrodes is at least in some portion of the electrochemical cell parallel to the direction of flow. In some embodiments, each electrochemical cell comprises one or more electrodes held at positive potential, and one or more electrodes held at negative potential, past which the electrolyte is flowed. When more than one electrode is used, the electrodes are each held at the same, or different, electrical potential.

In some embodiments, the system comprises a single electrochemical cell containing one or more electrodes held at positive potential and one or more electrodes

held at negative potential. In some embodiments, the system comprises more than one electrochemical cell (e.g., 2-6, or 2-5, or 2-4, or 2-3, or 1-5, or 1-4, or 1-3 electrochemical cell(s)), each of which contains one or more electrodes held at positive potential and one or more electrodes held at negative potential. In some embodiments, the system comprises one or more reference electrodes relative to which the electrical potential of a positive electrode and/or a negative electrode is measured. In some embodiments, the electrolyte is flowed once through said electrochemical cell or electrochemical cells. In some embodiments, the electrolyte is recirculated and flowed two or more times through said electrochemical cell or electrochemical cells. In some embodiments, flow of the electrolyte through said electrochemical cell or electrochemical cells is continuous, and in other embodiments, said flow is interrupted, to allow a longer residence time of the electrolyte within said electrochemical cell or electrochemical cells than in the instance of continuous flow.

According to certain embodiments, the time for one or more of the steps (e.g., oxidation, reduction, leaching) may each independently be greater than or equal to 1 minute, greater than or equal to 5 minutes, greater than or equal to 10 minutes, greater than or equal to 15 minutes, greater than or equal to 30 minutes, greater than or equal to 1 hour, greater than or equal to 6 hours, greater than or equal to 12 hours, or greater than or equal to 24 hours. In some embodiments, the time for one or more of the steps (e.g., oxidation, reduction, leaching) may each independently be less than or equal to 48 hours, less than or equal to 36 hours, less than or equal to 24 hours, less than or equal to 12 hours, less than or equal to 6 hours, less than or equal to 1 hour, less than or equal to 30 minutes, less than or equal to 15 minutes, or less than or equal to 5 minutes. Combinations of these ranges are also possible (e.g., greater than or equal to 1 minute and less than or equal to 48 hours, or greater than or equal to 5 minutes and less than or equal to 30 minutes).

In some embodiments, the recycled battery component(s) (e.g., from which the black mass is produced) comprises components, such as silicon and/or metals (e.g., alkali metals, alkaline earth metals, metals in Groups 3-13 of the Periodic Table, first-row transition metals, base metals, rare earth metals, platinum group elements, noble elements, and/or post transition metals). Examples of alkali metals include Li, Na, K, Rb and Cs. Examples of alkaline earth metals include Be, Mg, Ca, Sr, and Ba. Examples of first-row transition metals include Ti, V, Cr, Mn, Fe, Co, and Ni. Example of base

metals include Cu, Zn, Al, and Sn. Examples of rare earth elements include Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Pm, Sm, Sc, Tb, Tm, Yb and Y. Examples of platinum group or noble elements include Ru, Rh, Pd, Re, Os, Ir, Pt, Au and Ag. Examples of post transition metals include Ga, Ge, As, Se, Cd, In, Sb, Te, Tl, Pb, Bi, Po, Th and U.

5 In some embodiments, an aqueous buffer disclosed herein has a pH of less than 7, less than or equal to 6, less than or equal to 5, less than or equal to 4, less than or equal to 3, less than or equal to 2, less than or equal to 1, or less than or equal to 0. In some
10 embodiments, an aqueous buffer disclosed herein has a pH of greater than or equal to -5, greater than or equal to -2, greater than or equal to 0, greater than or equal to 1, greater
15 than or equal to 2, greater than or equal to 3, greater than or equal to 4, or greater than or equal to 5. In certain cases, an aqueous buffer disclosed herein has a pH of 0.
 Combinations of these ranges are also possible (e.g., greater than or equal to -5 and less than 7, greater than or equal to -2 and less than or equal to 1, greater than or equal to 0
 and less than 7, or greater than or equal to 0 and less than or equal to 5).

15 In certain embodiments, a reactor (e.g., reactor containing leaching solution, reactor containing electrolyte) disclosed herein is stirred at an appropriate rate. For
 example, in some embodiments, a reactor disclosed herein is stirred at a rate of greater than or equal to 0 rpm, greater than or equal to 50 rpm, greater than or equal to 100 rpm,
 greater than or equal to 200 rpm, greater than or equal to 300 rpm, or greater than or
20 equal to 400 rpm. In certain instances, a reactor disclosed herein is stirred at a rate of less than or equal to 500 rpm, less than or equal to 400 rpm, less than or equal to 300
 rpm, less than or equal to 200 rpm, or less than or equal to 100 rpm. Combinations of
 these ranges are also possible (e.g., greater than or equal to 0 rpm and less than or equal to 500 rpm or greater than or equal to 50 rpm and less than or equal to 500 rpm). In
25 some cases, a vessel, substance, and/or component disclosed herein is not stirred.

 In some embodiments, the systems and/or methods described herein have one or more advantages, such as excellent selectivity, high efficiency, reduced need for
 chemical inputs, operation viability using existing infrastructure, and cost-effectiveness. For example, in some embodiments, the electrochemical deposition methods and systems
30 described herein have a greater than or equal to 80%, greater than or equal to 85%,
 greater than or equal to 90%, greater than or equal to 95%, greater than or equal to 98%,
 or greater than or equal to 99% efficiency at the reduction electrode. In some
 embodiments, the electrochemical deposition methods and system described herein have

a less than or equal to 100%, less than or equal to 98%, less than or equal to 95%, less than or equal to 90%, or less than or equal to 85% efficiency at the reduction electrode. Combinations of the above-referenced values are also possible (e.g., greater than or equal to 80% and less than or equal to 100%). Other ranges are also possible.

5 In some embodiments, the electrochemical deposition methods and systems described herein have a greater than or equal to 80%, greater than or equal to 85%, greater than or equal to 90%, greater than or equal to 95%, greater than or equal to 98%, or greater than or equal to 99% efficiency at the oxidation electrode. In some embodiments, the electrochemical deposition methods and system described herein have
10 a less than or equal to 100%, less than or equal to 98%, less than or equal to 95%, less than or equal to 90%, or less than or equal to 85% efficiency at the oxidation electrode. Combinations of the above-referenced values are also possible (e.g., greater than or equal to 80% and less than or equal to 100%). Other ranges are also possible. Efficiency, as described herein, may be determined by measuring the mass of deposited products on
15 each electrode by measuring the mass of the electrode before and after the electrodeposition. The efficiency (η) of oxidation and reduction reaction can be calculated via $\eta = \frac{Q_{deposit}}{Q_{tot}} * 100$, expressed as a percentage, where Q_{tot} is total charge provided during the electrochemical conversion, that can be calculated by the product of current, I , and time, t , $Q_{tot} = It$; and $Q_{deposit}$ corresponds to the charge involved to
20 form the product (e.g., Co, Ni on the working electrode and MnO_2 on the counter electrode), that can be calculated as following equation: $Q_{deposit} = \frac{\Delta m}{M} n \mathcal{N}_A e$, with Δm is the mass of deposited product, M is the molar mass of the deposited product, n is the number of charges involved in the electrochemical reaction, $\mathcal{N}_A$ is the Avogadro number, e is the elementary charge.

25 In some embodiments, a single metal ion can be reduced onto a single electrode. In some embodiments, two or more metal ions can be reduced onto a single electrode. For example, in one set of embodiments, a working electrode may comprise a first layer of metal (e.g., cobalt) and a second layer of metal (e.g., nickel). In other embodiments, each electrochemical cell may be operated such that only one metal ion is reduced at a
30 given working electrode. For example, in some such embodiments, the system produces a first working electrode comprising a layer of a first metal (e.g., cobalt, wherein the layer comprises substantially no other metals) and a second working electrode

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comprising a layer of a second metal (e.g., nickel, wherein the layer comprises substantially no other metals). In some embodiments, the counter electrode may comprise a layer of oxidized metal (e.g., manganese oxide), wherein the layer comprises substantially no other metals. That is to say, advantageously, the systems and methods described herein are capable, in some embodiments, of depositing cobalt metal and nickel metal on separate electrodes, despite their relatively similar reduction potentials. In some embodiments, deposition of cobalt metal and nickel metal on separate electrodes occurs simultaneously (e.g., in different electrochemical cells). The recovered materials may be used, advantageously, to regenerate nickel-manganese-cobalt cathode active materials e.g., through solid-state synthesis.

EXAMPLES

The following examples are intended to illustrate certain embodiments of the present invention, but do not exemplify the full scope of the invention.

15

The recycling of EV LIBs generally faces more challenges than that of lead acid and nickel-metal hydride batteries due to the complexities related to the multiplicity of material chemistries used in today's EV LIBs. For instance, at least five different cathode chemistries, e.g., LiCoO_2 (LCO), $\text{LiNi}_x\text{Mn}_y\text{Co}_z\text{O}_2$ (NMC), LiFePO_4 (LFP), LiMn_2O_4 (LMO), and $\text{LiNi}_x\text{Co}_y\text{Al}_z\text{O}_2$ (NCA) are being widely used in commercial LIBs, with many EV batteries also using a mixture of two or three cathode materials in a single cell. Among major battery recycling technologies at industrial scale, hydrometallurgical processes offer the recovery of high purity products and operate at low temperature with less energy consumption comparing to pyrometallurgical methods. Although chemical-based hydrometallurgy enables selective metal recovery, its development and scaling-up are impeded by consumption of large volumes of chemicals, secondary pollution generation and complicated product separation processes. Recently, electrochemistry-assisted approaches have attracted considerable attention for the recycling of spent LIBs because of their excellent selectivity, high efficiency, environmental compatibility and adoptability, operation viability, and cost-effectiveness.

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To achieve selective metal electrodeposition processes for recycling spent LIBs, the standard reduction potentials of metals are important. For example, the individual metals contained in LCO, LMO and LFP materials, such as Co ($E_0 = -0.28 \text{ V}_{\text{NHE}}$), Mn ($E_0 =$

–1.18 V_{NHE}), Fe ($E_0 = -0.44$ V_{NHE}), Li ($E_0 = -3.05$ V_{NHE}) and Cu ($E_0 = +0.34$ V_{NHE}) can be easily separated by electrodeposition due to their distinct standard reduction potentials. However, the separation of Co and Ni from NMC, NCA or their mixture can be challenging due to their similar standard reduction potentials: Co ($E_0 = -0.28$ V_{NHE}) and Ni ($E_0 = -0.26$ V_{NHE}), which can cause impurities of the deposited metal layer.

To overcome the difficulty in separating Co and Ni, a low-cost and eco-friendly recycling technology was developed, assisted by electrochemistry and electrolyte engineering. In this work, a two-electrode electrochemical cell has been designed to simultaneously recover Co, Ni and Mn from spent LIBs by electrodeposition, which significantly simplifies the separation process, and reduces the energy consumption and greenhouse gas emissions comparing to the pyrometallurgical and hydrometallurgical (e.g., co-precipitation) processes. At the cathode, Co²⁺ and Ni²⁺ cations are reduced to Co and Ni metals, while at the anode, Mn²⁺ cation was oxidized to MnO₂. The test was performed in an H-cell with a Li⁺ exchange Nafion membrane as separator, where the electrolyte contained 0.1 M sulfate salts of Co²⁺, Ni²⁺ and Mn²⁺ and 0.1 M Li₂SO₄. The electrochemical deposition process showed an efficiency of 85% for reduction reaction (Co deposition) and 81.4% for oxidation reaction (MnO₂ deposition). The proposed electrochemical process offers great opportunities in LIB cathode active material recycling for clean energy transition.

Methods

A simple electrochemical process for simultaneously recovering of Ni, Co and Mn using carbon paper electrodes has been proposed to recycle NMC cathode active materials from spent LIB. The proposed recovering process has been carried in an H-cell, where carbon paper electrodes are used as cathode and anode. A lithium-ion exchange membrane (Nafion 117) was employed as the separator, where Li⁺ ions migrate from anodic compartment to cathodic compartment during the electrochemical deposition processes. A Biologic SP-300 potentiostat was employed for all electrochemical measurements. Potentials were recorded versus a saturated calomel reference electrode (SCE). All potentials were converted to the RHE scale. The redox properties of Co²⁺/Co, Ni²⁺/Ni and Mn²⁺/MnO₂ redox pairs were probed by cyclic voltammetry (CV). The electrochemical deposition processes were examined by chronoamperometry (CA) measurements at a current density of -10 or -20 mA cm⁻² in

Ar saturated electrolyte at room temperature. To identify the deposited products, powder X-ray diffraction was carried out with a Bruker D2 phaser Gen II X-ray powder diffractometer equipped with a Cu sealed-tube X-ray source (wavelength, $\lambda = 1.5418 \text{ \AA}$) at 40 kV and 40 mA. The electrolyte containing 0.1 M Ni^{2+} , 0.1 M Co^{2+} and 0.2 M Mn^{2+} cations (simulating leaching solution of spent LIB) was prepared from deionized water (Millipore, $>18.2 \text{ M}\Omega\cdot\text{cm}$) and nickel sulfate (Sigma-Aldrich 99.9%), cobalt sulfate (Sigma-Aldrich 99.9%) and manganese sulfate (Sigma-Aldrich 99.9%). 0.1 M lithium sulfate (Sigma-Aldrich 99.9%) was added as supporting electrolyte.

10 Results and discussions

Characterization of redox features of Co^{2+}/Co , Ni^{2+}/Ni and $\text{Mn}^{2+}/\text{MnO}_2$ on glassy carbon (GC) rotating disc electrode (RDE) in electrolytes at pH7. CV measurements in electrolyte at pH 7 containing an individual cation (Co^{2+} , Ni^{2+} or Mn^{2+}) have been performed in a three-electrode electrochemical cell (**Fig. 2A**) to characterize the redox features of Co^{2+}/Co , Ni^{2+}/Ni and $\text{Mn}^{2+}/\text{MnO}_2$ and estimate the redox potential. The CV of 2 mM CoSO_4 in 0.1 M LiClO_4 electrolyte (**FIG. 2B**) showed four features: hydrogen evolution ($E < -0.5 \text{ V}_{\text{RHE}}$), Co plating ($-0.5 \text{ V}_{\text{RHE}} < E < 0 \text{ V}_{\text{RHE}}$), Co stripping ($0 \text{ V}_{\text{RHE}} < E < 0.8 \text{ V}_{\text{RHE}}$) and oxygen evolution ($(E > 1.8 \text{ V}_{\text{RHE}})$). Co stripping (positive current density) and plating (negative current density) features were shown to be rotation-dependent (**FIG. 2C**), indicating that the Co oxidation and Co^{2+} reduction can be partially limited by mass transport of Co^{2+} ions. The similar electrochemical features for 2 mM NiSO_4 electrolyte have been observed (**FIGs. 2D-2E**), where Ni stripping was shown to be rotation-independent (**FIG. 2E**), suggesting that Ni stripping reaction rates was governed by kinetic rather than mass transport. In addition, nickel plating process was found rotation-dependent with an onset potential at $-0.2 \text{ V}_{\text{RHE}}$, lower than that of Co plating at 0 V_{RHE} (**FIGs. 2B-2C**). The observed redox features of Co, Ni and Mn indicate that Co and Ni can be electrochemically reduced to metal form without significant HER.

The CVs of 2 mM MnSO_4 in 0.1 M LiClO_4 electrolyte (**FIG. 2F**) showed that the redox feature of Mn^{2+}/Mn took place at potential range of -0.7 to $-0.3 \text{ V}_{\text{RHE}}$. Mn stripping only occurred at the 1st cycle, then HER became major reaction at negative potential ($\sim -1 \text{ V}_{\text{RHE}}$). This observation could arise from the combination of Mn^{2+} and OH^- formed during HER, which leads to the formation of $\text{Mn}(\text{OH})_2$ passivation layer on

the electrode surface, thus an irreversibility of Mn plating/stripping. Furthermore, manganese oxide formation/reduction peaks (at potential range of 0.5-2 V_{RHE}) and OER (at potential > 2 V_{RHE}) can be observed at positive potential region. The observation indicates that it could be easier to extract Mn by electrolytic MnO₂ rather than the
5 reduction of Mn²⁺ to Mn metal.

Designing an electrochemical process for simultaneous recovery of Ni, Mn, Co by electro-reduction of Co and Ni, and electrolytic of MnO₂. Based on the redox features of Co²⁺, Mn²⁺ and Ni²⁺ in electrolytes at pH7 on GC RDE (**FIGs. 2A-2F**), a simple electrochemical process has been developed for the simultaneous recovery of Co, Mn
10 and Ni elements from the cathode active material leaching solution of spent LIBs using carbon paper as electrodes. At the working electrode (WE), Co²⁺ and Ni²⁺ are reduced to metal form whereas Mn²⁺ is oxidized to MnO₂ on the counter electrode (CE) via electrolytic MnO₂ process (**FIG. 3A**). A schematic of the electrochemical cell is shown in **FIG. 3B**, where a Li⁺ exchange Nafion membrane is used as the separator and carbon
15 paper is employed as electrodes. Carbon materials exhibits lower HER onset potential (-0.7 V_{RHE}) at pH7 than metal catalyst (e.g., Pt, Cu, Ni and Au), as shown in **FIG. 7**, which provide a potential range for Co and Ni deposition (-0.5 to 0 V_{RHE} and -0.5 to -0.2 V_{RHE}, respectively) without significant HER current (**FIG. 2C and FIG. 2E**). In addition, Co, Ni and MnO₂ deposited on carbon paper are then expected to be used in
20 solid-state synthesis without further separation to form NMC active materials, where carbon material could be transformed to gas phase CO₂ and separated from the solid phase product.

The performance of the disclosed electrochemical process of simultaneous Co²⁺, Mn²⁺ and Ni²⁺ recovery by operating at a constant current density of -10 mA cm⁻² for
25 two-hour operation is shown in **FIG. 3C**. The potential of reduction process (Co and Ni deposition at WE) stabilized around -0.25 V_{RHE} whereas the potential of oxidation process (MnO₂ deposition at CE) increased from 2.5 to 3.1 V_{RHE} for the first 10 min from the beginning and then stabilized around 3.1 V_{RHE}. The increase in electrode potential at oxidation compartment (CE) could be attributed to the decrease of pH caused
30 by the production of H⁺ during the process, which could increase the equilibrium potential of Mn²⁺/MnO₂ in RHE scale. The pH measurements of the electrolyte at both compartments before and after the electrochemical recovering process showed that the electrolyte pH at oxidation compartment (CE) decreased from 7 to 0, where H⁺ was

formed during MnO_2 formation ($\text{Mn}^{2+} + 2\text{H}_2\text{O} = \text{MnO}_2 + 4\text{H}^+ + 2\text{e}^-$) and OER ($2\text{H}_2\text{O} = \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$). The inevitable production of H^+ opens opportunities for the regeneration of acid that can be used for leaching process in this technology. To avoid of potential change associated with pH variation at reduction compartment (WE), a Li^+ exchange Nafion membrane as separator was intentionally employed to prevent the transport of H^+ from oxidation compartment (CE) to reduction compartment (WE). Consequently, the electrolyte pH at reduction compartment (WE) remained neutral (~ 7).

X-ray diffraction (XRD) was further performed to identify the chemical composition of deposited products on each electrode. XRD patterns (**FIG. 3D**) shows that reduction electrode (WE) exhibits four peaks at 42.2° , 45° , 47.9° and 76.8° , that correspond to $\text{Co}(100)$, $\text{Co}(111)$, $\text{Co}(101)$ and $\text{Co}(110)$, respectively, indicating that Co metal was deposited on carbon paper electrode. XRD patterns (**FIG. 3F**) shows that reduction electrode (WE) exhibits three peaks at 44.5° , 51.9° and 76.4° , that correspond to $\text{Ni}(111)$, $\text{Ni}(200)$ and $\text{Ni}(220)$, respectively, indicating that Ni metal was deposited on carbon paper electrode. For oxidation electrode (**FIGS. 3D and 3F**) two peaks were observed at 38° for $\text{MnO}_2(211)$ and 67° for $\text{MnO}_2(002)$, indicating that MnO_2 was formed and deposited on carbon paper electrode.

To further estimate the efficiency of the electrochemical process, the mass of deposited products on each electrode were measured by determining the mass of the electrode before and after the electrodeposition (**Table 1**). The efficiency (η) of oxidation and reduction reaction can be calculated via $\eta = \frac{Q_{\text{deposit}}}{Q_{\text{tot}}} * 100$, where Q_{tot} is total charge provided during the electrochemical conversion, that can be calculated by the product of current, I , and time, t , $Q_{\text{tot}} = It$; and Q_{deposit} correspond to the charge involved to form the product (Co, Ni on WE and MnO_2 on WE), that can be calculated as following equation: $Q_{\text{deposit}} = \frac{\Delta m}{M} n \mathcal{N}_A e$, with Δm is the mass of deposited product, M is the molar mass of the deposited product, n is the number of charges involved in the electrochemical reaction, $\mathcal{N}_A$ is the Avogadro number, e is the elementary charge. For the test at -10 mA cm^{-2} current density for two-hour operation, 18.8 mg of Co metal and 26.4 mg of MnO_2 are recovered, which yield an efficiency of 85% and 81.4% at reduction and oxidation electrodes, respectively (**Table 1**). For the Ni/ MnO_2 test at -10 mA cm^{-2} current density for one-hour operation, 9.34 mg of Ni metal and 16.8 mg of MnO_2 are recovered, which yield an efficiency of $85 \pm 2\%$ and $103.4 \pm 4\%$ at reduction

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and oxidation electrodes, respectively (**Tables 1 and 2**). (Efficiency over 100% may be due to uncertainty of measurement or additional water present with the MnO₂ which was not quantified in this particular test).

5 **Table 1. Estimation of the efficiency of the proposed electrochemical process and the estimation of the mass of the deposited products on WE (Co) and CE (MnO₂)..**

	m_{initial} (mg)	m_{final} (mg)	Δm (mg)	Q (C)	Efficiency (%)
WE (Co)	13.8	24.23	10.43	36	94.9
CE (MnO₂)	13.6	29.72	16.12		99.4

10 **Table 2. Estimation of the efficiency of the proposed electrochemical process and the estimation of the mass of the deposited products on WE (Ni) and CE (MnO₂).**

	m_{initial} (mg)	m_{final} (mg)	Δm (mg)	Q (C)	Efficiency (%)
WE (Ni)	14.0	23.34	9.34	36	85.0
CE (MnO₂)	13.5	30.3	16.8		103.6

In some cases, only Co was deposited on carbon paper at WE compartment due to the short duration of the tests (~2 hours), where only 2.4% of Co²⁺ in the electrolyte was recovered. Co²⁺/Co redox couple exhibits higher onset potential than Ni²⁺/Ni redox pair (**FIGs. 2A-F**), which offers the opportunity of the extraction of Co and Ni individually via electrochemical process. For example, only Co metal was detected at WE in the test shown in **FIGs. 3A-3D**, that can be attributed to the short duration of the test (2 hours) and large access of the Co and Ni cations (0.1 M). To further demonstrate the electrodeposition of Ni metal, the test was performed in an electrolyte of 0.1 M NiSO₄ (**FIGs. 8A-8B**), where XRD patterns showed peaks at 44.5°, 51.9° and 76.4°, correspond to Ni(111), Ni(200) and Ni(220), indicating that Ni metal was deposited on carbon paper during the electrodeposition.

For the discontinuous process, the separation of Co and Ni is not necessary, in some cases. The desired ratio of Co, Ni and Mn can be adjusted (e.g., 1:1:1 for NMC111 and 8:1:1 for NMC811 synthesis) in leaching solution and then recover Co, Ni metal on

WE and MnO₂ on CE by electrodeposition. The recovered Co, Ni and MnO₂ on carbon paper could be used for the solid-state synthesis of NMC materials.

For the continuous process, the separation of Co and Ni is useful for gaining accurate control of the ratio of Co, Ni and Mn solid-state synthesis of NMC materials.

5 To enhance the selective extraction of Co and Ni, there are few potential approaches:

Electrolyte engineering

To maximize the difference in redox potential of Co²⁺/Co and Ni²⁺/Ni (**FIG. 4A**) tuning electrolyte composition via modulation of the supporting electrolyte, concentration and pH may be used. In previous work separating Co and Ni by electrodeposition, only thermodynamic approaches from the Pourbaix diagram have been considered, where the standard redox potentials of the Co²⁺/Co and Ni²⁺/Ni redox couples are similar. However, thermodynamics does not consider the non-covalent interactions associated with redox centers, inert ions, and solvent molecules. The physical chemistry of electrolytes was shown to alter the redox potential by altering the solvation environment of the redox center via non-covalent interactions. Understanding the dependence of the redox potentials of Co²⁺/Co and Ni²⁺/Ni on the electrolyte composition provides insights in finding the conditions where the potential difference between Co²⁺/Co and Ni²⁺/Ni is maximum, at which point the selectivity of Co and Ni extraction can be improved.

Second, the correlation between metal plating kinetics and local solvation environments was investigated at electrified interfaces (**FIG. 2A**). Although the redox potentials of Co²⁺/Co and Ni²⁺/Ni redox couples are similar from thermodynamics point of view, thermodynamics cannot necessarily accurately predict the kinetic barrier. For example, preliminary results showed that the exchange current density of Co plating/stripping (~0.1 mA cm⁻²) is 2 orders of magnitude larger than that of Ni plating/stripping (~0.001 mA cm⁻²) by rotating disc electrode (RDE) measurements. The local solvation environment can be tailored at electrified interfaces through electrolyte engineering to alter the kinetic barrier of the electrochemical process, thus tuning the kinetics of metal deposition. Achieving such kinetic control may enhance the selectivity of Co and Ni extraction and may also improve the efficiency of the electrodeposition processes.

Selective Co^{2+} and Ni^{2+} transport by cation exchange Nafion

The selectivity can be further tuned through tailoring the specific cation exchange property of Nafion membrane. As shown in **FIG. 6**, Co can be selectively deposited at the WE compartment in electrochemical cell 1 where Co^{2+} exchange Nafion membrane is used a separator. The outlet flow of the WE compartment of electrochemical cell 1 containing Ni^{2+} and Mn^{2+} rich electrolyte was injected in the WE compartment of the electrochemical cell 2 for Ni deposition with Ni^{2+} exchange Nafion membrane. Then, the outlet flow of the WE compartment of electrochemical cell 1 containing Ni^{2+} rich electrolyte was re-injected into storage tank of electrolyte at neutral pH.

Electrolytic MnO_2 and OER reactions produce H^+ as by-product, which can be used for the acid leaching process of NMC materials. As shown in **FIG. 6**, the outlet flow containing H^+ rich stream of CE compartment of the electrochemical cell 2 is re-injected to the acid leaching reactor. The H^+ in the flow can react with the “black mass” to release Co^{2+} , Ni^{2+} and Mn^{2+} and neutralize the solution, leading to a Co^{2+} , Ni^{2+} and Mn^{2+} rich solution at neutral pH (storage tank).

To increase the efficiency of the process, the electrolyte engineering and electrode material functionalization may be adjusted to inhibit HER and OER, and facilitate Co, Ni and MnO_2 electrodeposition.

Recovery/concentration of LiOH using electrochemical process (**FIG. 6**) Closed-loop acid regeneration for leaching process.

Conclusion

An electrochemical process, which allows to recover Co, Ni and Mn elements from the leaching solution of spent lithium-ion batteries has been developed. Co and Ni are generally deposited in metal form on carbon paper at reduction compartment while MnO_2 was deposited on carbon paper at oxidation compartment. The test performed in an H-cell in 0.1 M MSO_4 ($\text{M}=\text{Co}$, Ni and Mn) and 0.1 M Li_2SO_4 with a Li^+ exchange Nafion membrane as separator showed an efficiency of 85% for reduction reaction (Co deposition) and 81.4% for oxidation reaction (MnO_2 deposition). The proposed electrochemical process offers the opportunity in LIB cathode active material recycling at lower cost and lower pollutions/emissions comparing to pyrometallurgical technology and hydrometallurgy via co-precipitation.

Advantages and improvements over existing methods, device or materials

The recycling of EV LIBs faces more challenges than that of lead acid and nickel-metal hydride batteries due to the multiplicity of materials used in today's EV LIBs. For instance, at least five different cathode materials are widely used in commercial LIBs, with many EV batteries using a mixture of cathode materials in a single cell. Among major LIB battery recycling technologies at industrial scale, hydrometallurgical processes can recover high purity products with less energy consumption compared to pyrometallurgical methods. However, the scaling of hydrometallurgical recycling is impeded by its consumption of large volumes of chemicals, secondary pollution generation and complicated product separation processes, which drive up costs for this recycling process (\$20,000/metric ton of lithiated nickel manganese cobalt oxide (NMC) produced). In contrast, the electrochemistry-assisted approach described herein is more apt for the recycling of spent LIBs because of its excellent selectivity, high efficiency, reduced need for chemical inputs, operation viability using existing infrastructure, and cost-effectiveness. The key to this technology rests on selective metal electrodeposition for the recycling of spent LIBs, where the standard reduction potentials of metals are important. Copper, cobalt, iron, manganese, and lithium can be easily extracted by electrodeposition due to their distinct standard reduction potentials. However, the separation of cobalt and nickel is challenging due to their similar standard reduction potentials. To overcome this difficulty, recycling technologies assisted by electrochemistry and electrolyte engineering as described herein will enable highly-controlled metal electrodeposition for each metal in a LIB. Furthermore, this process may advantageously use carbon paper as electrode materials, where the recovered material deposited on carbon paper can be used directly in the solid-state synthesis of NMC materials without further separation. Previous studies employed metal electrodes, e.g., Pt, Al, Ti, stainless steel, etc., which generally require the separation between the deposit and the electrode substrate. Through this novel method of recycling, it is expected to outcompete current pyro- and hydrometallurgical recycling methods in terms of environmental impact, energy usage, cost, and efficiency of material recovery and separation.

Commercial applications (economic potential, etc.)

Social Impact. LIB recycling could decrease battery costs, mitigate the environmental impacts of battery manufacturing, and reduce reliance on imported materials. This technology can directly contribute to lower EV prices for consumers, making the transition to a net-zero emissions economy faster, more affordable, and more equitable. LIB recycling is imperative for decarbonization of the global energy system for EVs, which in turn is crucial to the global effort to slow climate change. Furthermore, by building a domestic supply chain for battery manufacturing, jobs for communities in the U.S. may be provided.

Prophetic Market Viability. This innovative approach seeks to play roles in the market similar to those of mining and battery material manufacturing companies by providing battery-grade active materials, with the distinction that such raw materials will originate from spent batteries, rather than from natural resources. The innovations in the electrochemical recycling of battery materials described herein can be applied using currently existing technologies already employed in industry. A pilot plant based on the invention described herein can purchase and refine the raw ‘black mass’ that can be recovered from spent EV batteries, and capital costs can resemble a mixture of capital costs seen in industrial electroplating facilities and commercial battery material manufacturing. Based on technoeconomic analyses of these types of plants, the estimated capital costs of a plant capable of producing ~1,200 metric tons of NMC per year (enough NMC for ~11,000 EV batteries) to be around \$6.5 M USD. The operating costs of a plant, including utilities, the purchase and shipment black mass, labor, and reagent costs (like lithium carbonate) to be ~\$11.4 M/year if assuming the initial capital cost is spread over a 20-year operating lifetime. Thus, the cost per metric ton of NMC produced per year from recycling would be about \$9,500, whereas the current market price of NMC is roughly \$35,600/metric ton. Recycled NMC could be sold directly to battery manufacturers for implementation into new EV batteries, for a profit of \$33 M/year given a hypothetical 1,200 metric ton/year scale and the current market price of NMC.

The low cost of the process described compared to the cost of commercial NMC or hydro/pyrometallurgical recycling stems, for example, from not needing to use large amounts of harsh chemical reagents to process the raw black mass, and the ability to recover the metals with high efficiency and without need for costly separation processes,

and because the materials in a spent battery are already enriched sources of nickel, manganese, and cobalt, which is not the case for the natural ores of these metals.

While several embodiments of the present invention have been described and
5 illustrated herein, those of ordinary skill in the art will readily envision a variety of other means and/or structures for performing the functions and/or obtaining the results and/or one or more of the advantages described herein, and each of such variations and/or modifications is deemed to be within the scope of the present invention. More generally, those skilled in the art will readily appreciate that all parameters, dimensions, materials,
10 and configurations described herein are meant to be exemplary and that the actual parameters, dimensions, materials, and/or configurations will depend upon the specific application or applications for which the teachings of the present invention is/are used. Those skilled in the art will recognize, or be able to ascertain using no more than routine experimentation, many equivalents to the specific embodiments of the invention
15 described herein. It is, therefore, to be understood that the foregoing embodiments are presented by way of example only and that, within the scope of the appended claims and equivalents thereto, the invention may be practiced otherwise than as specifically described and claimed. The present invention is directed to each individual feature, system, article, material, and/or method described herein. In addition, any combination
20 of two or more such features, systems, articles, materials, and/or methods, if such features, systems, articles, materials, and/or methods are not mutually inconsistent, is included within the scope of the present invention.

The indefinite articles “a” and “an,” as used herein in the specification and in the claims, unless clearly indicated to the contrary, should be understood to mean “at least
25 one.”

The phrase “and/or,” as used herein in the specification and in the claims, should be understood to mean “either or both” of the elements so conjoined, i.e., elements that are conjunctively present in some cases and disjunctively present in other cases. Other elements may optionally be present other than the elements specifically identified by the
30 “and/or” clause, whether related or unrelated to those elements specifically identified unless clearly indicated to the contrary. Thus, as a non-limiting example, a reference to “A and/or B,” when used in conjunction with open-ended language such as “comprising” can refer, in one embodiment, to A without B (optionally including elements other than

B); in another embodiment, to B without A (optionally including elements other than A); in yet another embodiment, to both A and B (optionally including other elements); etc.

As used herein in the specification and in the claims, “or” should be understood to have the same meaning as “and/or” as defined above. For example, when separating
5 items in a list, “or” or “and/or” shall be interpreted as being inclusive, i.e., the inclusion of at least one, but also including more than one, of a number or list of elements, and, optionally, additional unlisted items. Only terms clearly indicated to the contrary, such as “only one of” or “exactly one of,” or, when used in the claims, “consisting of,” will refer to the inclusion of exactly one element of a number or list of elements. In general,
10 the term “or” as used herein shall only be interpreted as indicating exclusive alternatives (i.e. “one or the other but not both”) when preceded by terms of exclusivity, such as “either,” “one of,” “only one of,” or “exactly one of.” “Consisting essentially of,” when used in the claims, shall have its ordinary meaning as used in the field of patent law.

As used herein in the specification and in the claims, the phrase “at least one,” in
15 reference to a list of one or more elements, should be understood to mean at least one element selected from any one or more of the elements in the list of elements, but not necessarily including at least one of each and every element specifically listed within the list of elements and not excluding any combinations of elements in the list of elements. This definition also allows that elements may optionally be present other than the
20 elements specifically identified within the list of elements to which the phrase “at least one” refers, whether related or unrelated to those elements specifically identified. Thus, as a non-limiting example, “at least one of A and B” (or, equivalently, “at least one of A or B,” or, equivalently “at least one of A and/or B”) can refer, in one embodiment, to at least one, optionally including more than one, A, with no B present (and optionally
25 including elements other than B); in another embodiment, to at least one, optionally including more than one, B, with no A present (and optionally including elements other than A); in yet another embodiment, to at least one, optionally including more than one, A, and at least one, optionally including more than one, B (and optionally including other elements); etc.

30 In the claims, as well as in the specification above, all transitional phrases such as “comprising,” “including,” “carrying,” “having,” “containing,” “involving,” “holding,” and the like are to be understood to be open-ended, i.e., to mean including but not limited to. Only the transitional phrases “consisting of” and “consisting essentially of” shall be

closed or semi-closed transitional phrases, respectively, as set forth in the United States Patent Office Manual of Patent Examining Procedures, Section 2111.03.

CLAIMS

What is claimed is:

1. An electrochemical system for recovery of nickel, manganese, copper, lithium,
5 and/or cobalt, the system comprising:
a first electrochemical cell comprising an electrolyte, wherein the first
electrochemical cell comprises a first working electrode and a first counter electrode, the
first working electrode and first counter electrode separated by a first separator; and
a second electrochemical cell in fluidic communication with the first
10 electrochemical cell, wherein the second electrochemical cell comprises a second
working electrode and a second counter electrode, the second working electrode and
second counter electrode separated by a second separator,
wherein the electrolyte comprises a source of two or more ions selected from the
group consisting of Co^{2+} , Cu^{2+} , Li^{+} , Ni^{2+} , $^{+}$, Fe^{2+} , Fe^{3+} and Mn^{2+} .
15
2. The electrochemical system of claim 1, wherein at least one of the first working
electrode, first counter electrode, second working electrode, and second counter
electrode is a carbon-based electrode.
- 20 3. The electrochemical system of claim 1, further comprising a source of the
electrolyte in fluidic communication with the first electrochemical cell and/or the second
electrochemical cell.
4. The electrochemical system of claim 1, further comprising a third
25 electrochemical cell in fluidic communication with the first and/or second
electrochemical cell, wherein the third electrochemical cell comprises a third working
electrode and a third counter electrode, the third working electrode and third counter
electrode separated by a third separator.
- 30 5. The electrochemical system of any preceding claim, further comprising a reactor
configured to receive and/or leach lithium-ion battery materials, the reactor in fluidic
communication with at least the first electrochemical cell.

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6. The electrochemical system of any preceding claim, wherein the reactor comprises an aqueous buffer.
7. The electrochemical system of any preceding claim, wherein the separator
5 comprises an ion-exchange membrane.
8. The electrochemical system of any preceding claim, wherein the first electrochemical cell and/or the second electrochemical cell does not comprise a sacrificial electrode.
- 10
9. The electrochemical system of any preceding claim, wherein the ion-exchange membrane comprises a cation-exchange membrane.
10. The electrochemical system of any preceding claim, wherein the systems is
15 configured such that, during operation of the system, one or more of the following occurs:
- 1) cobalt metal is deposited directly on the first working electrode,
 - 2) nickel metal is deposited directly on the second working electrode, and
 - 3) manganese dioxide is deposited directly on the first counter electrode and/or
20 the second counter electrode.
11. The electrochemical system of any preceding claim, wherein, during operation of the system, LiOH is recovered from the electrolyte.
- 25
12. The electrochemical system of any preceding claim, wherein the reactor and/or source of electrolyte are in fluidic communication with the third electrochemical cell, thereby forming a continuous system.
13. The electrochemical system of any preceding claim, wherein the electrolyte
30 comprises one or more of cobalt sulfate, nickel sulfate, manganese sulfate, lithium sulfate, and lithium perchlorate.

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14. A method for simultaneous recovery of nickel, cobalt, copper, lithium, and/or manganese from a lithium-ion battery, the method comprising:
in a reactor, neutralizing a leaching solution that comprises one or more components extracted from a lithium-ion battery thereby forming an electrolyte solution;
5 flowing the electrolyte solution into a first electrochemical cell comprising a first working electrode and a first counter electrode;
applying a first current across the first working electrode and the first counter electrode such that cobalt metal deposits on the first working electrode;
flowing the electrolyte solution into a second electrochemical cell comprising a
10 second working electrode and a second counter electrode;
applying a second current across the second working electrode and the second counter electrode such that nickel metal deposits on the second working electrode,
wherein, during the step of applying the first current and/or the step of applying the second current, manganese oxide is deposited on the first counter electrode and/or the
15 second counter electrode.
15. The method of claim 14, further comprising extracting one or more components from a lithium-ion battery, wherein the one or more components comprise two or more metal ions selected from the group consisting of nickel, cobalt, copper, lithium, and
20 manganese, to form a leaching solution.
16. The method of claim 15, further comprising, in a reactor, neutralizing the leaching solution that comprises the one or more components from the lithium-ion battery in a metal ion rich solution thereby forming an electrolyte solution.
25
17. The method of claim 16, wherein the metal ion rich solution comprises two or more metal ions selected from the group consisting of cobalt, nickel, manganese, copper, and lithium.
- 30 18. The method of claim 14, further comprising exposing a component of the lithium-ion battery, the component comprising one or more of cobalt, nickel, manganese, and lithium, to the leaching solution.

– 41 –

19. The method of any preceding claim, wherein the electrolyte solution has a pH of greater than 6 and less than or equal to 8.
20. The method of any preceding claim, wherein the first current is greater than or
5 equal to the second current.
21. The method of any preceding claim, further comprising recovering lithium hydroxide from the electrolyte solution.
- 10 22. The method of any preceding claim, wherein each working electrode and counter electrode are separated by a separator.
23. The method of claim 22, wherein the separator is an ion-exchange separator.
- 15 24. The method of any preceding claim, further comprising flowing the electrolyte solution, after the step of applying the second current, to the reactor thereby forming a continuous process.
25. A method, comprising:
20 providing a leaching solution of a spent lithium-ion battery;
adding a buffered aqueous buffer to the leaching solution to bring the leaching solution to pH 7;
immersing a working electrode (WE) and a counter electrode (CE) in the leaching solution, wherein the WE and CE are comprised of carbon paper and are in separate
25 compartments, wherein the compartments are separated by a Li⁺ exchange membrane;
reducing Co²⁺ and Ni²⁺ to Co metal and Ni metal at the WE; and
oxidizing Mn²⁺ to MnO₂ at the CE via electrolysis.
26. The method of claim 25, further comprising:
30 immersing a saturated calomel reference electrode (SCE) in the WE compartment using the SCE to record potentials.
27. The method of claim 25, wherein the Li⁺ exchange membrane comprises Nafion.

28. The method of claim 26, wherein the solution in the WE compartment is maintained under an argon (Ar) atmosphere.

5 29. The method of claim 27, wherein the current is at 10 mA/cm².

30. An electrochemical system for recovery of nickel, manganese, copper, lithium, and/or cobalt, the system comprising:

an electrolyte comprising three or more metal ions selected from the group
10 consisting of Co²⁺, Cu²⁺, Li⁺, Ni²⁺, Fe²⁺, Fe³⁺ and Mn²⁺.
a first working electrode in contact with the electrolyte and configured for the reduction of a first metal ion of the three or more metal ions;
a second working electrode configured for the reduction of a second metal ion of the three or more metal ions;
15 a counter electrode in electrical communication with the first working electrode and/or the second working electrode, the working electrode configured for the oxidation of a third metal ion of the three or more metal ions; and
a separator disposed between at least the first working electrode and the counter electrode.

20

31. A method for simultaneous recovery of nickel, cobalt, copper, lithium, and/or manganese from a lithium-ion battery, the method comprising:

flowing an electrolyte comprising three or more metal ions selected from the group consisting of Co²⁺, Cu²⁺, Li⁺, Ni²⁺, Fe²⁺, Fe³⁺ and Mn²⁺ into an electrochemical
25 cell comprising a first working electrode and a counter electrode;

applying a first current across the first working electrode and the first counter electrode such that a first metal ion reduces and deposits on the first working electrode and a second metal ion oxidizes and deposits on the counter electrode; and

applying a second current across the second working electrode and the counter
30 electrode and/or a second counter electrode such that a third metal ion reduces and deposits on the second working electrode.

100 ↗

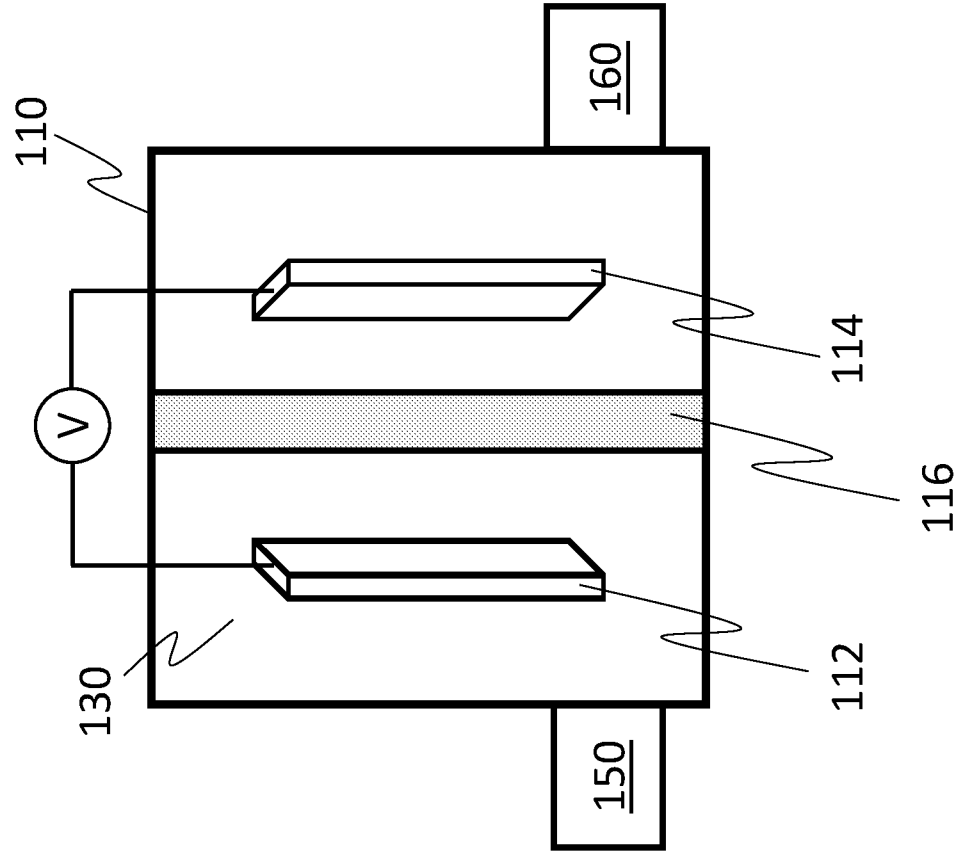
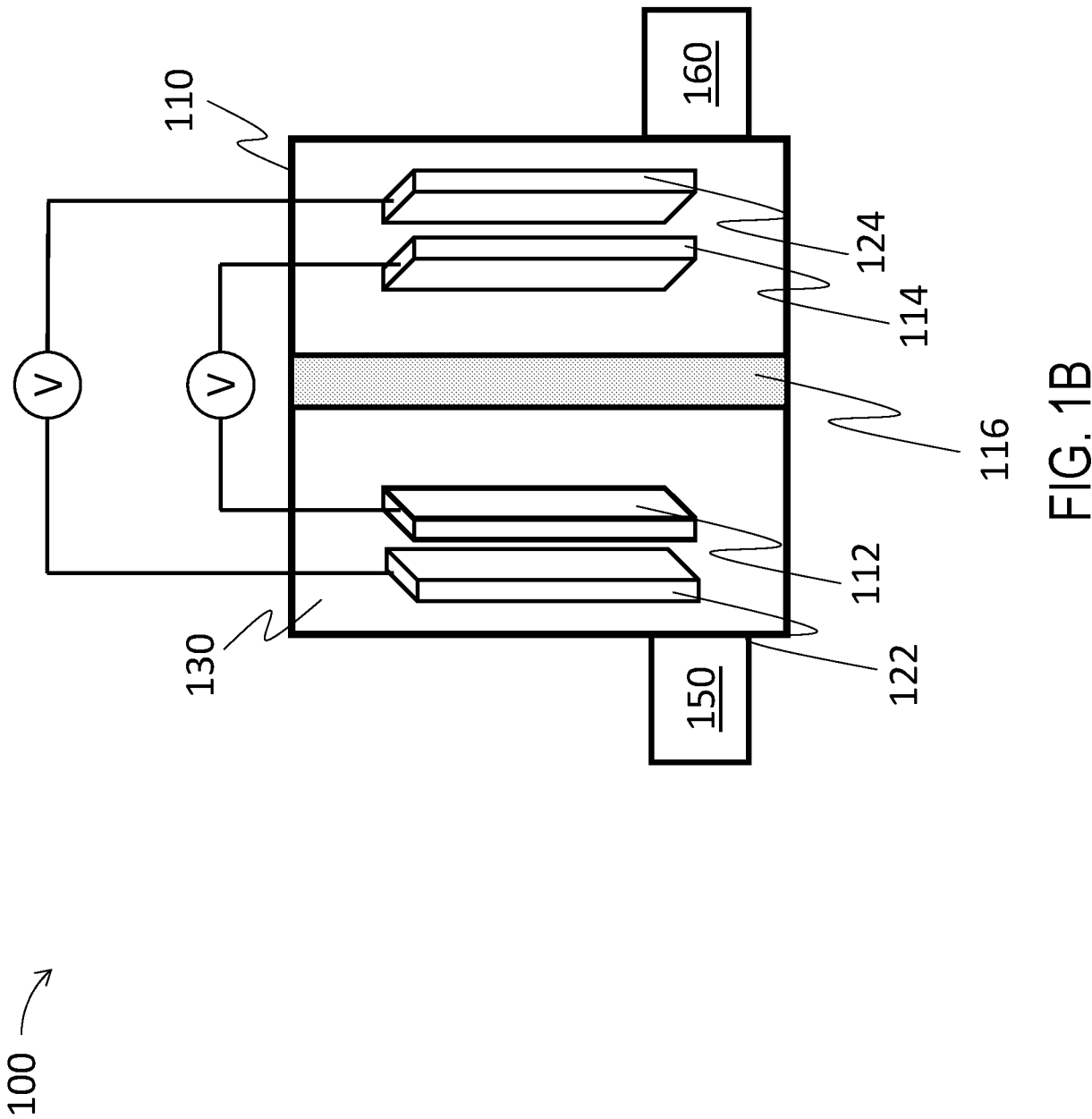


FIG. 1A



102 ↗

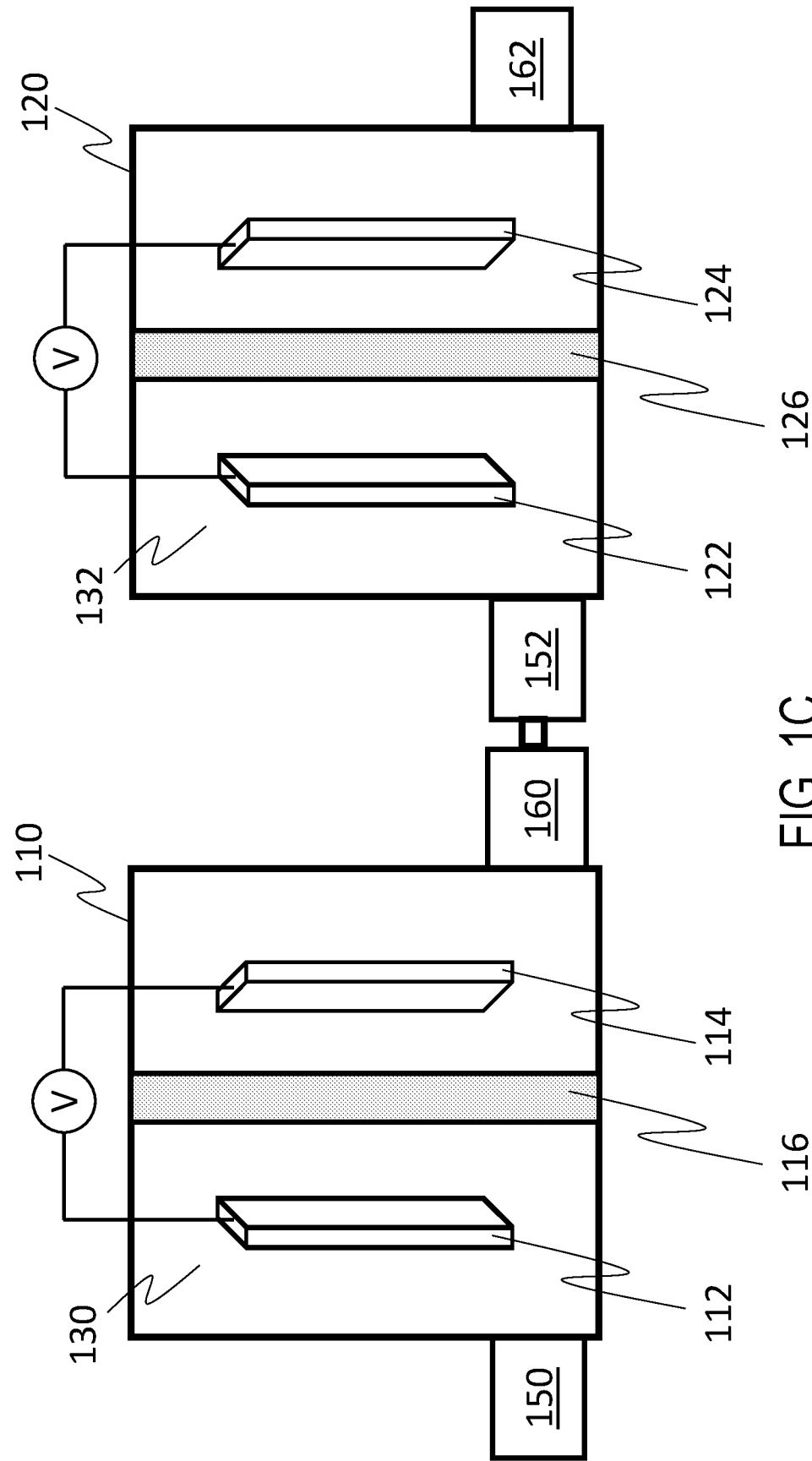


FIG. 1C

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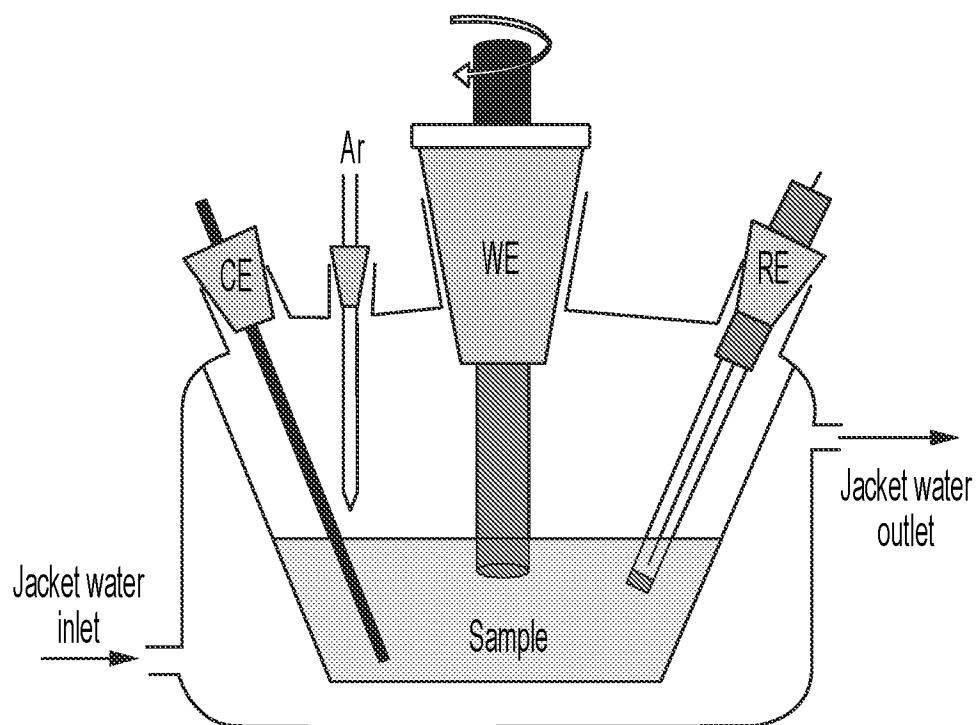


FIG. 2A

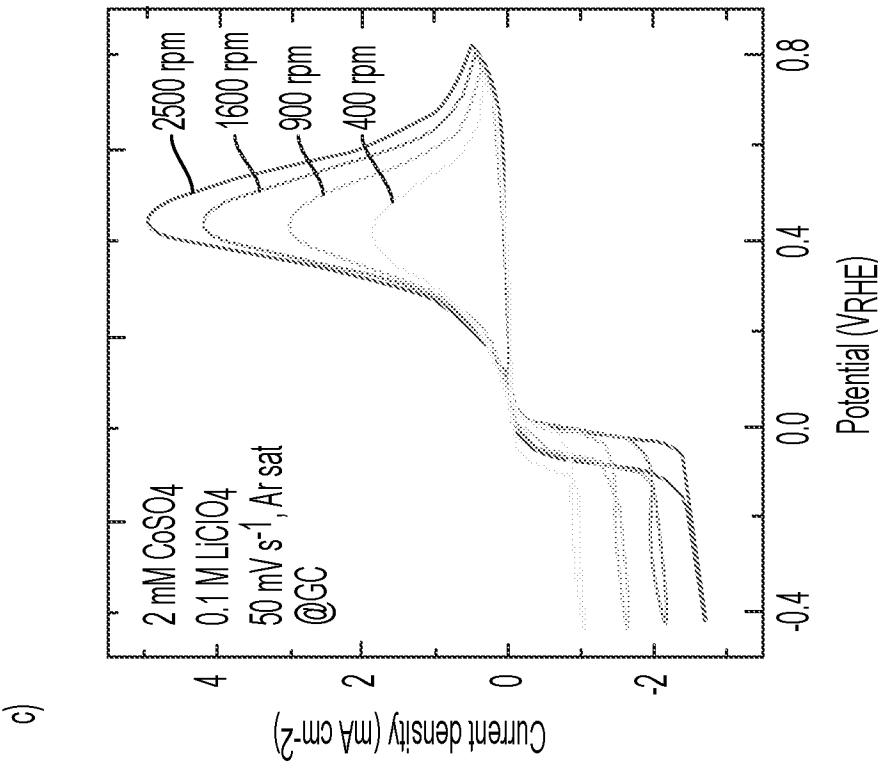


FIG. 2B

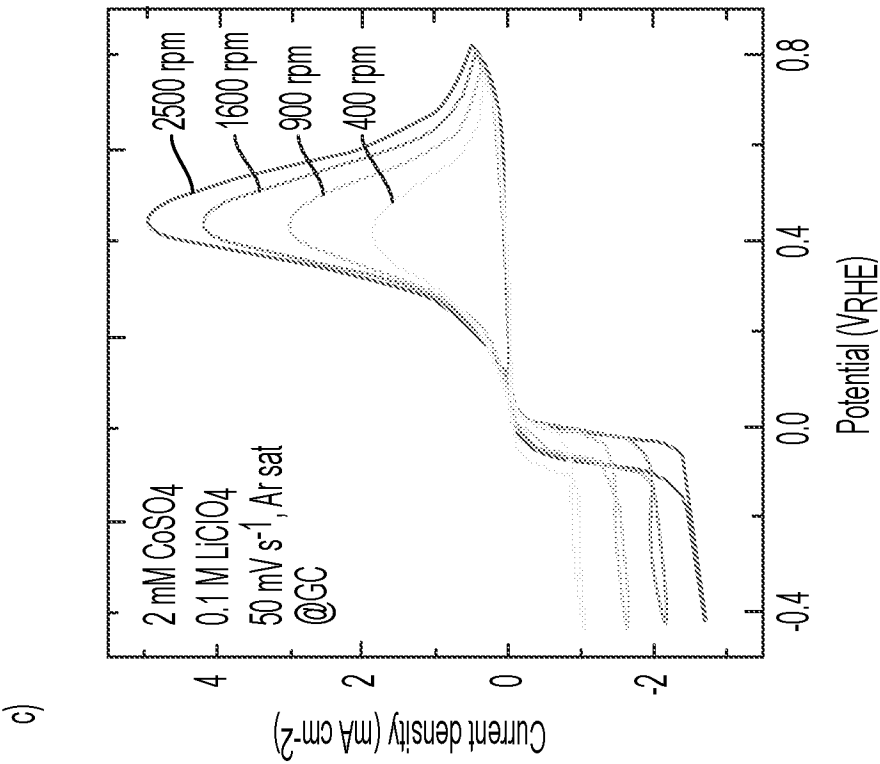


FIG. 2C

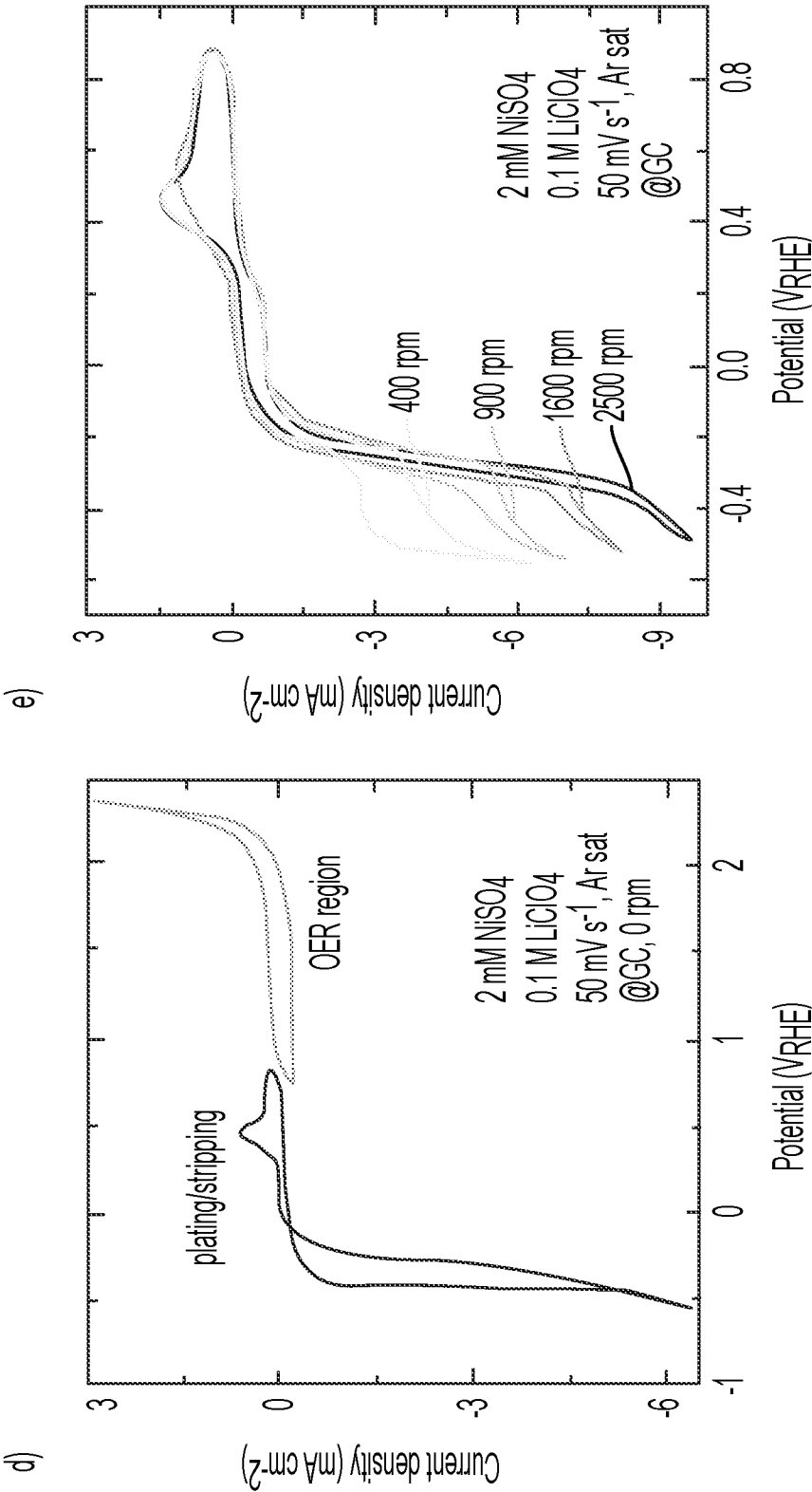


FIG. 2E

FIG. 2D

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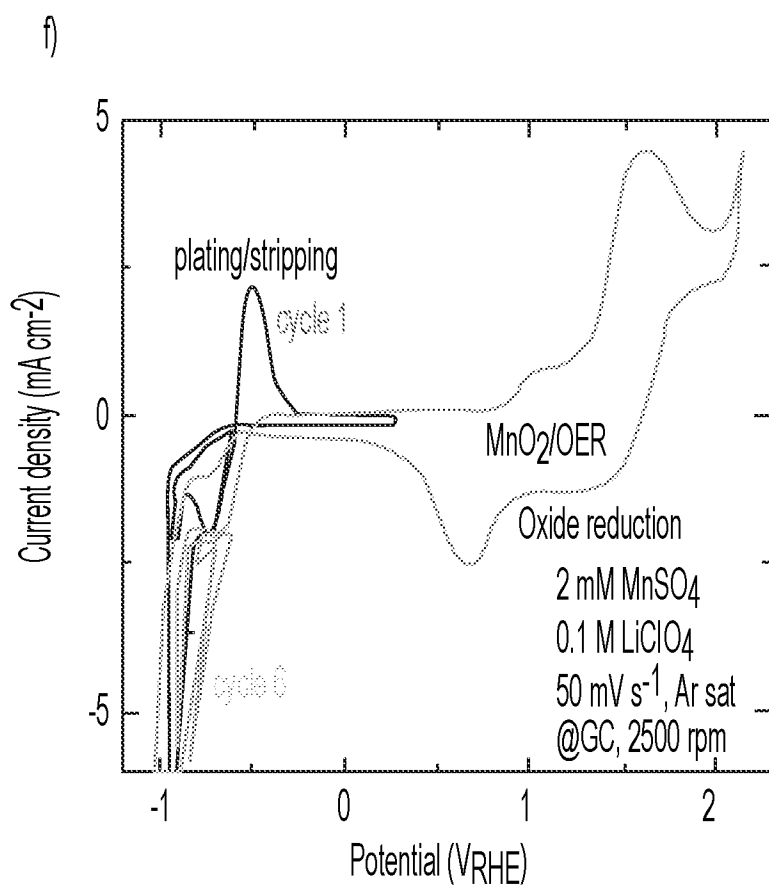


FIG. 2F

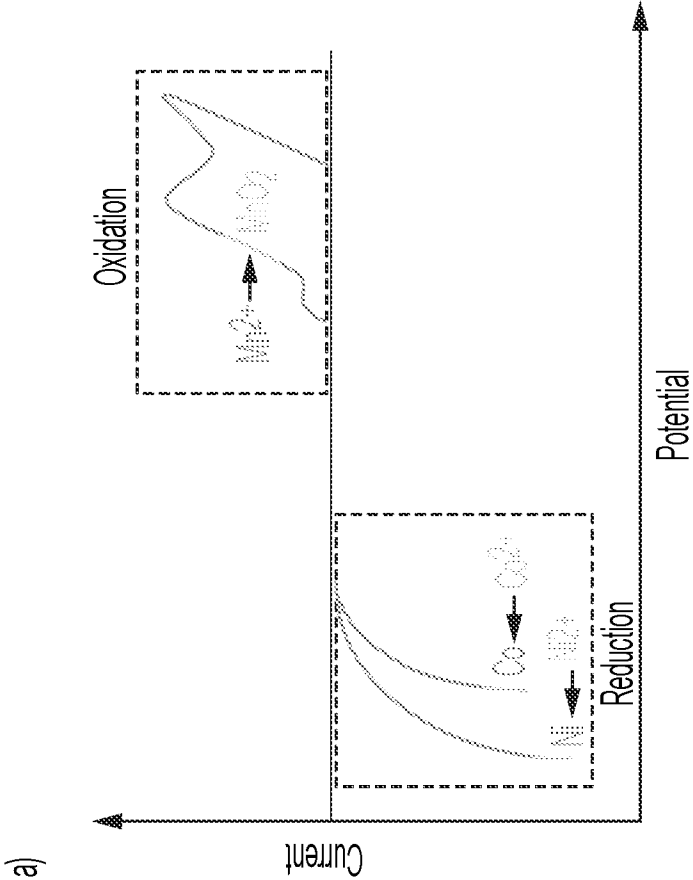


FIG. 3A

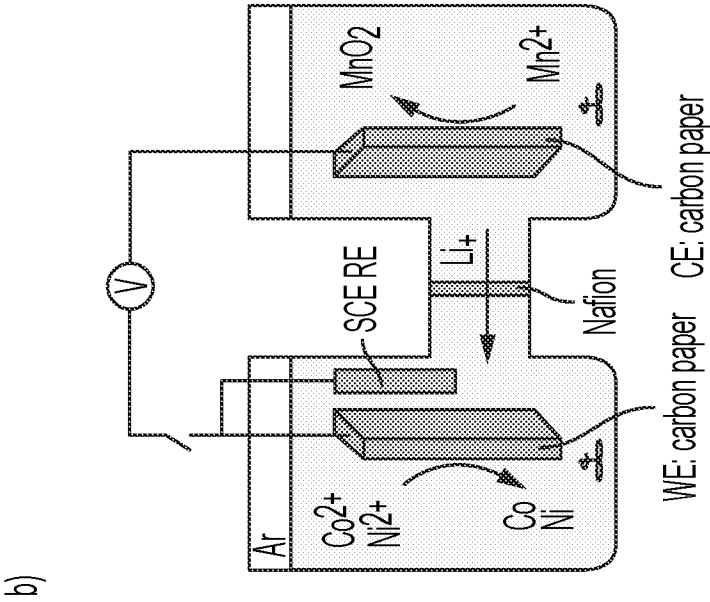


FIG. 3B

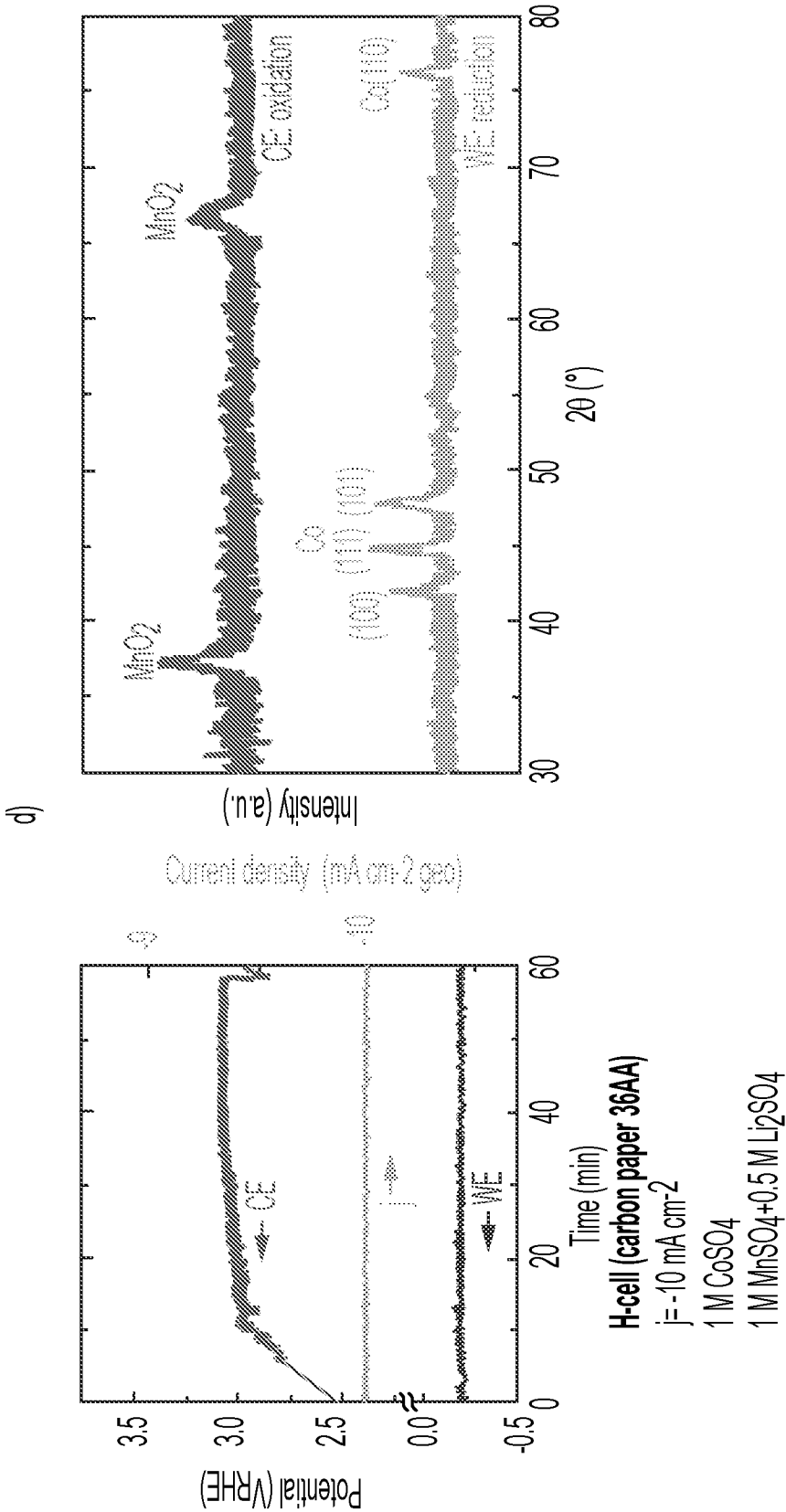
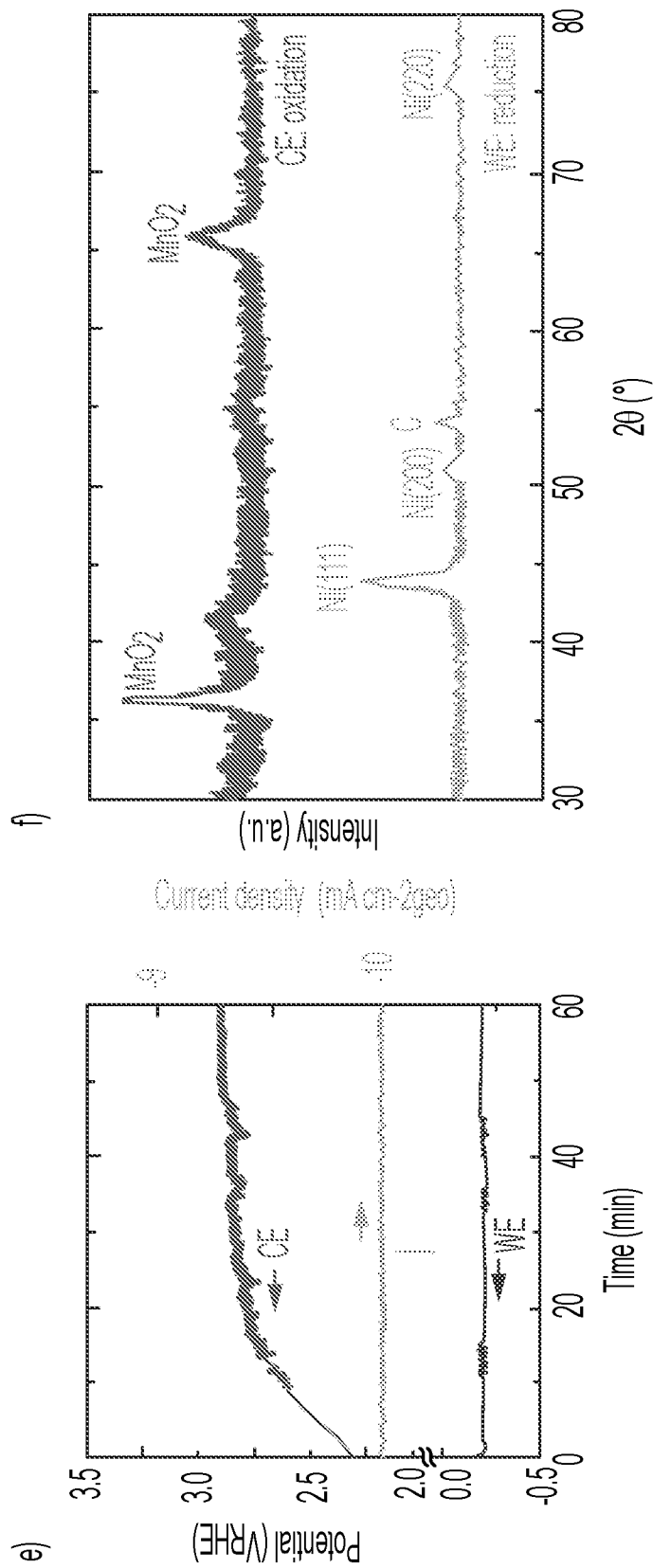


FIG. 3D

FIG. 3C



H-cell (carbon paper 36AA)
 $j = -10 \text{ mA cm}^{-2}$
1 M NiSO₄
1 M MnSO₄+0.5 M Li₂SO₄

FIG. 3E

FIG. 3F

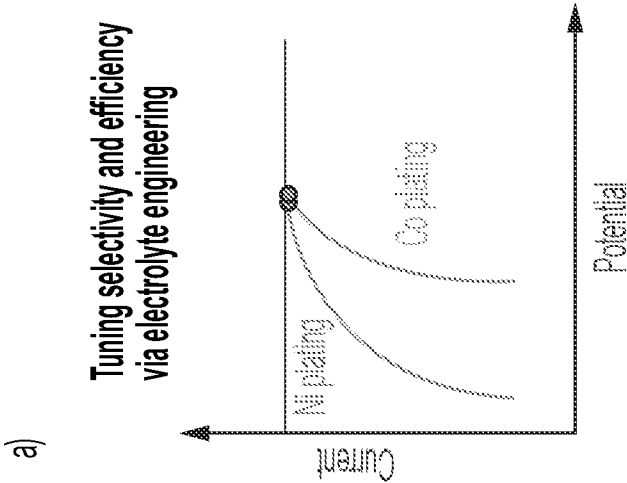


FIG. 4A

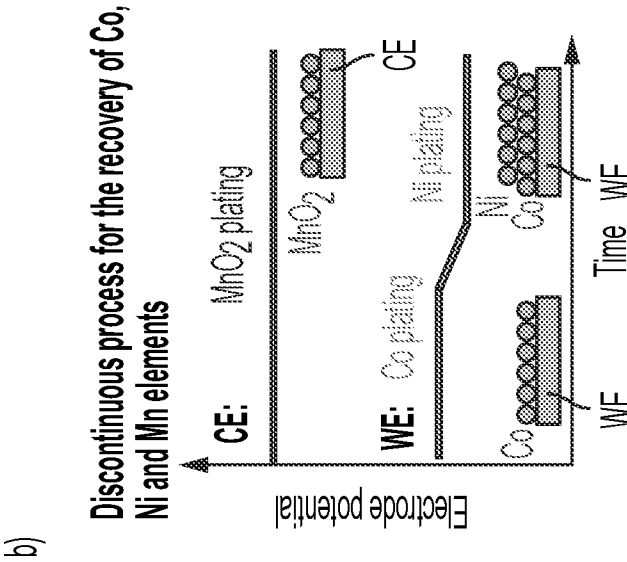


FIG. 4B

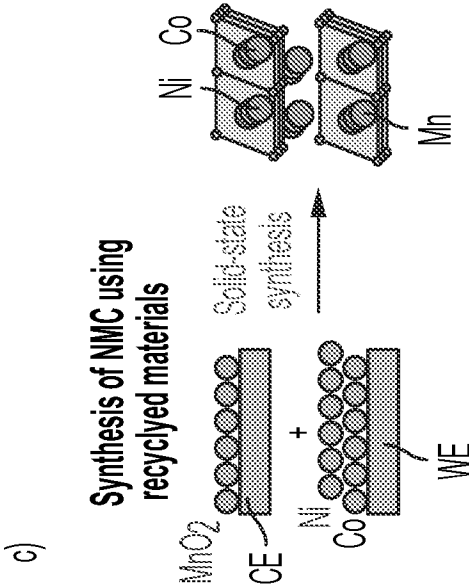


FIG. 4C

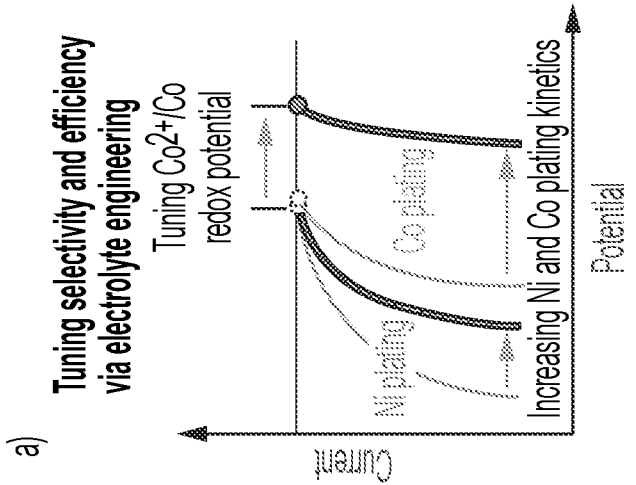


FIG. 5A

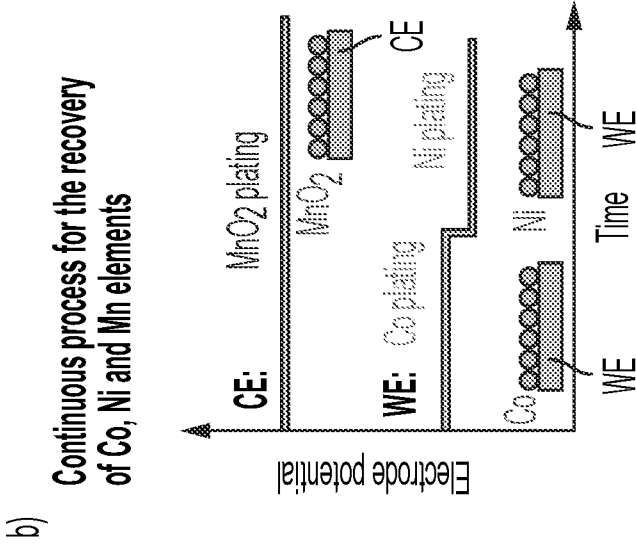


FIG. 5B

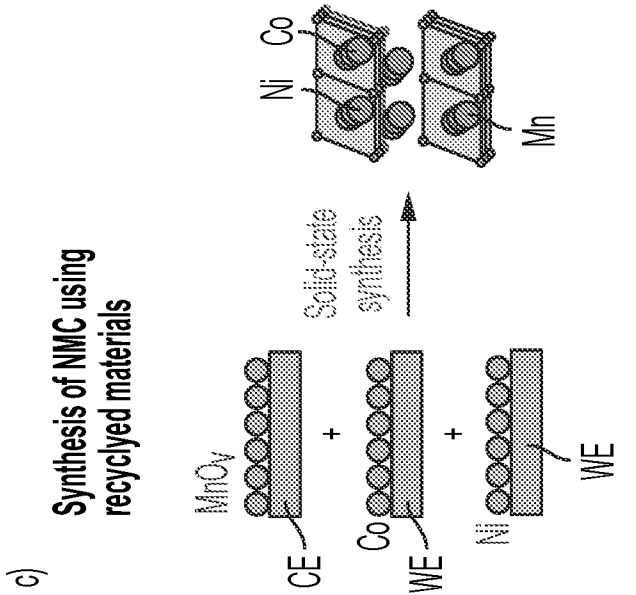


FIG. 5C

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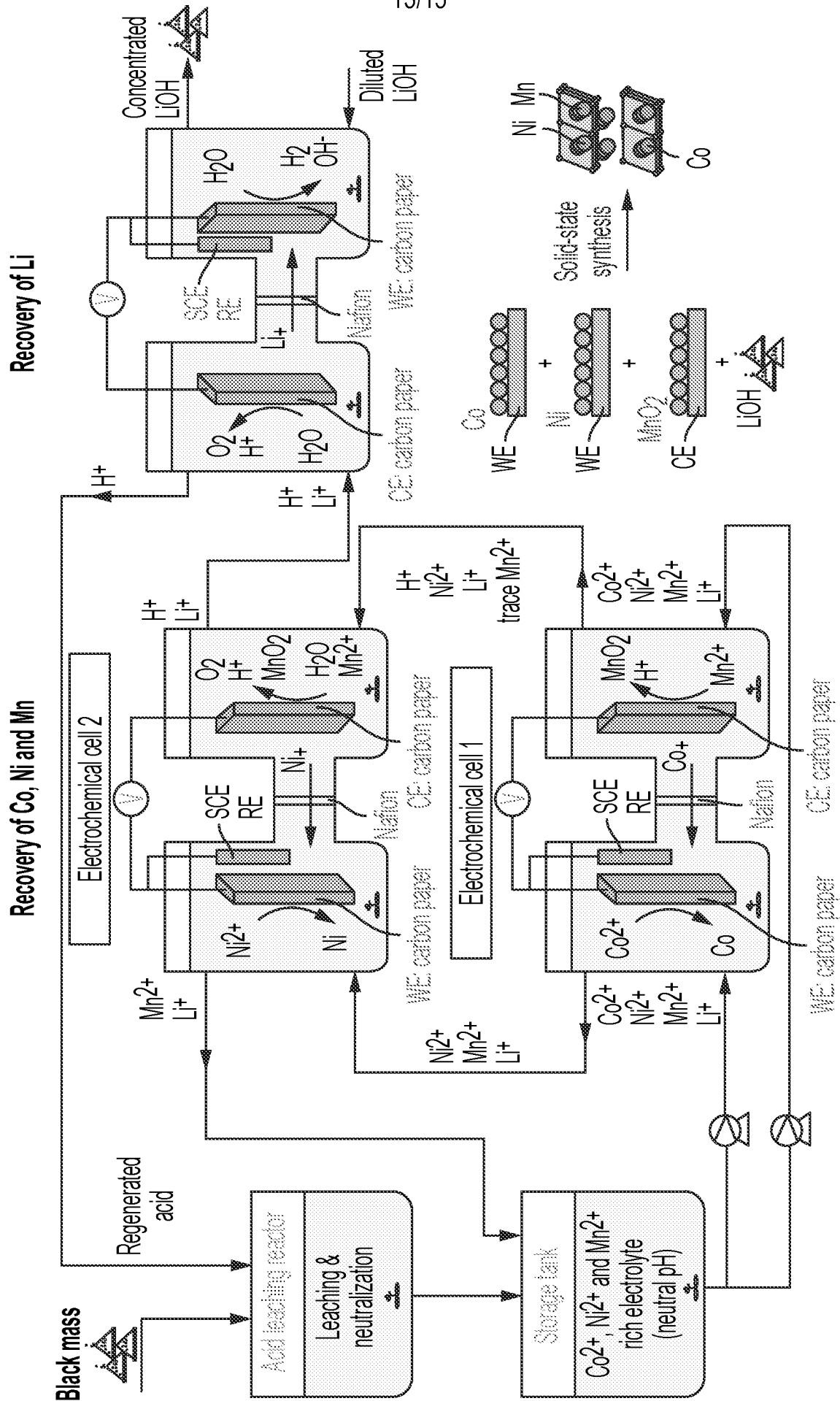


FIG. 6

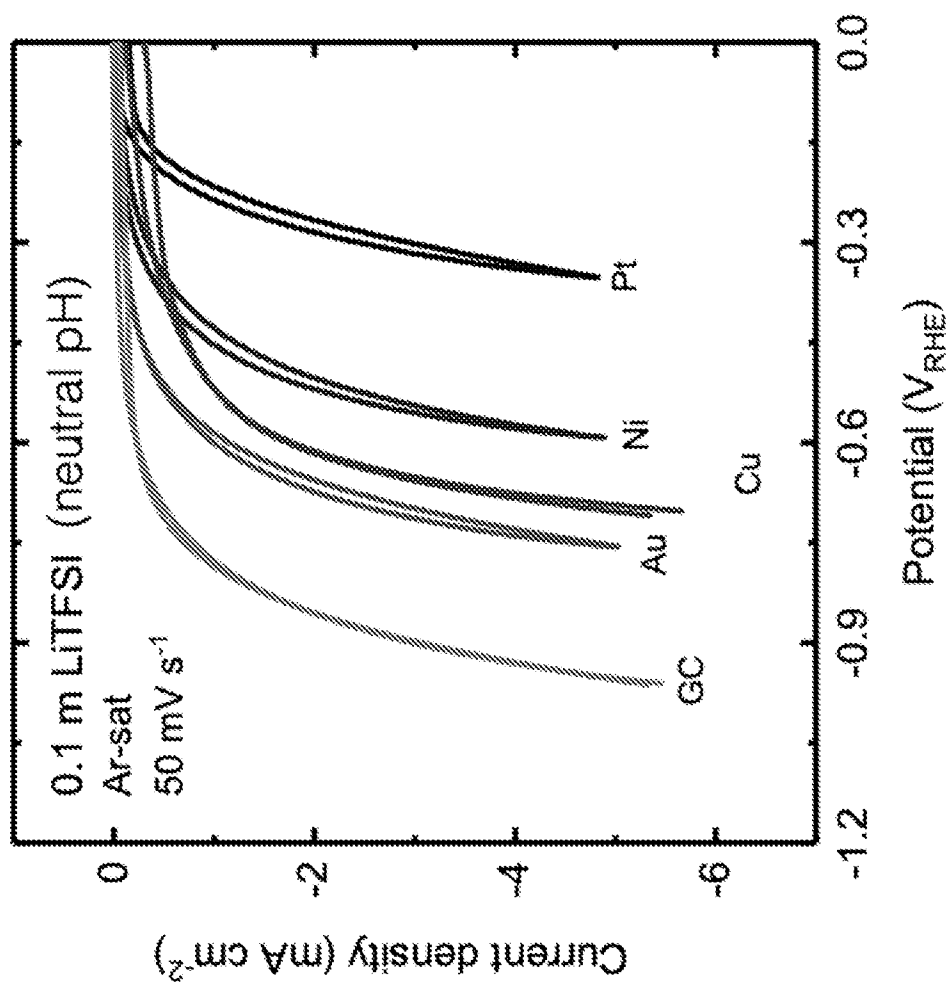


FIG. 7

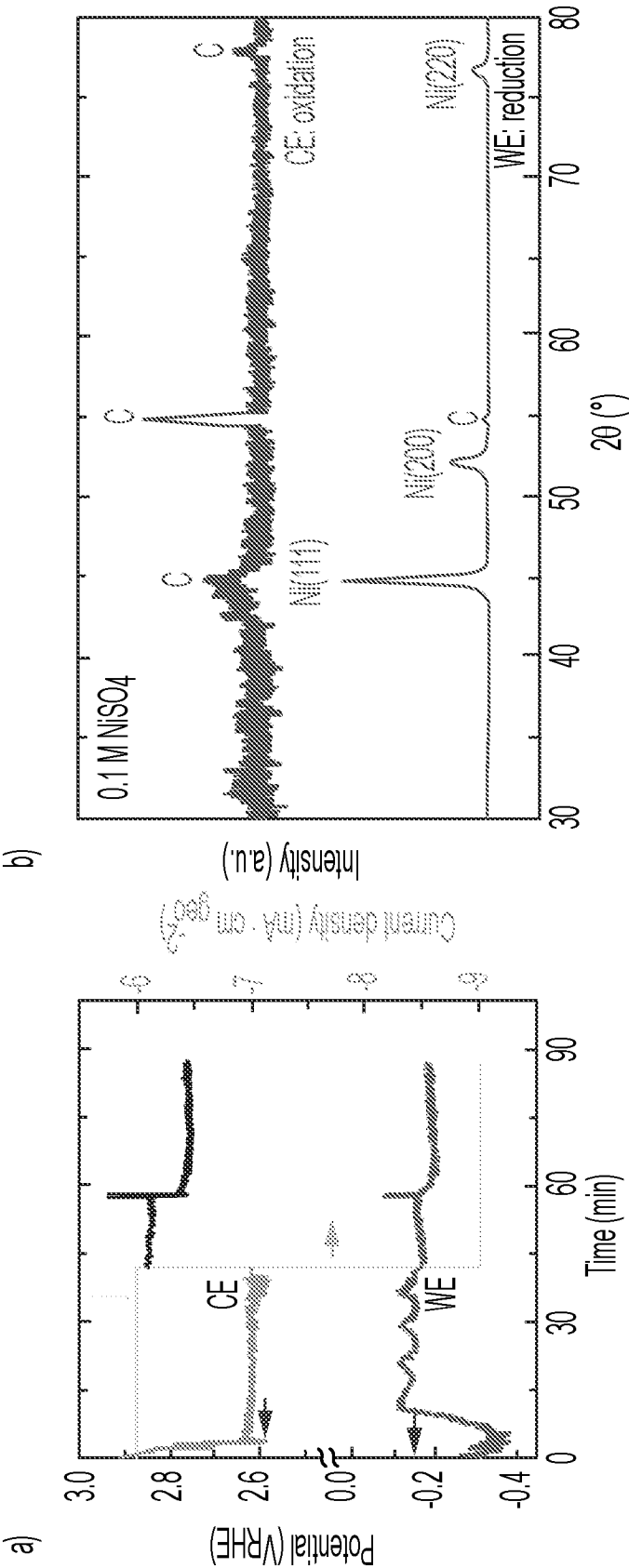


FIG. 8A

FIG. 8B