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McNally; Joshua S. et al.

Methods of recovering active materials from rechargeable batteries, and related apparatuses

Abstract

A method of recovering active materials from a rechargeable battery comprises placing an active material of a rechargeable battery in a cathode chamber comprising a cathode of an electrochemical cell comprising the cathode chamber, an anode chamber comprising an anode, and a membrane separating the cathode chamber from the anode chamber, contacting the active material in the cathode chamber with an electrolyte comprising an acid, ferric ions, and ferrous ions, and dissolving at least one of lithium and cobalt from the active material into the electrolyte. Related apparatuses for recovering metals from active materials of rechargeable batteries are also disclosed.

Inventors: McNally; Joshua S. (Idaho Falls, ID), Diaz Aldana; Luis A. (Idaho Falls, ID), Klaehn; John R. (Idaho Falls, ID), Lister; Tedd E. (Bangor, ME), Reed; David W. (Idaho Falls, ID)

Applicant: Battelle Energy Alliance, LLC (Idaho Falls, ID)

Family ID: 1000008750520

Assignee: Battelle Energy Alliance, LLC (Idaho Falls, ID)

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Primary Examiner: Apicella; Karie O'Neill

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Background/Summary

CROSS-REFERENCE TO RELATED APPLICATIONS (1) This application is a national phase entry under 35 U.S.C. § 371 of International Patent Application PCT/US2020/070081, filed May 28, 2020, designating the United States of America and published as International Patent Publication WO 2020/252495 A1 on Dec. 17, 2020, which claims the benefit under Article 8 of the Patent Cooperation Treaty to U.S. Provisional Patent Application Ser. No. 62/861,672, filed Jun. 14, 2019.

TECHNICAL FIELD

(1) Embodiments of the disclosure relate generally to methods of dissolving one or more active materials from waste rechargeable battery materials. More particularly, embodiments of the disclosure relate to methods of recovering active materials from rechargeable batteries, such as lithium-ion batteries and metal hydride batteries, using an electrochemical cell, and to related apparatuses for recovering the active materials.

BACKGROUND

(2) Lithium-ion batteries (LIBs) are one of the most often used rechargeable batteries in consumer electronic devices, such as cellular phones, laptop computers, and video cameras. Lithium-ion batteries are known for their relatively light weight and associated high energy density, low self-discharge rate, high battery voltage, wide operating temperature range, and no memory effect, among other things, making them desirable candidates for use in such electronic devices. In addition to electronic devices, lithium-ion batteries are used in transportation, such as in hybrid and fully electric vehicles, portable tools, and in various military and aerospace applications. Lithium-ion batteries are also used to store electrical energy for later use within an electrical power grid. In addition to lithium-ion batteries, other types of rechargeable batteries, such as metal hydride batteries, are used in various electronic devices and equipment. Due to the increasing demand for electronic devices and equipment incorporating rechargeable batteries, the global production and consumption of rechargeable batteries have been rising.

(3) A lithium-ion battery includes an anode, a cathode, electrolytes, a separator between the anode and the cathode, and an outer shell. The separator is made from polymeric materials and the outer shell is conventionally a steel or plastic material. The anode typically includes a composite of carbon powder and a binder (polymer), which is coated with copper foil. The cathode may include an active material comprising lithium cobalt oxide (LiCoO₂). Other lithium-ion batteries include active materials including other transition metals, such as one or both of nickel and manganese, to partially or completely substitute traditional cobalt to form different types of cathode materials. Thus, active cathode materials may include carbon powder, a polymer binder, and lithium transition metal oxides LiCoO₂, LiMnO₂, LiNiO₂, LiNi_xCo_yMn_zO₂ (LNCM) (LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂), and NiCoAlO.

(4) Other forms of rechargeable batteries include, for example, metal hydride batteries (e.g., nickel-metal hydride batteries). Metal hydride batteries include active materials comprising, for example, nickel oxide hydroxide (NiOOH) (also referred to as nickel oxyhydroxide), nickel oxide (NiO), nickel hydroxide (Ni(OH)₂), manganese tetraoxide (Mn₂O₃), magnesium oxide-hydroxide (MgO(OH)) (also referred to as manganite), cobalt oxide (CoO), or other materials.

(5) After lithium-ion batteries and metal hydride batteries reach the end of their useful life (i.e., after the batteries are spent), they are disposed of. Often, the batteries are disposed of by sending them to a landfill. However, disposal of such batteries in landfills leads to soil and groundwater contamination due to the presence of various materials present in the batteries. Since the batteries include metals, including

cobalt, lithium, nickel, and manganese, various processes have been developed for the separation and subsequent recovery of the metals from spent batteries. Various methods include hydrometallurgical methods or pyrometallurgical methods. Pyrometallurgical methods require smelting the battery materials in a furnace to obtain a metal alloy. However, the smelting process generates and emits harmful gases. (6) Hydrometallurgical processes include dissolving the cathode materials of the batteries in an acid, such as citric acid, ascorbic acid, hydrochloric acid, sulfuric acid, or nitric acid. After the cathode materials are dissolved in the acid (leachate), dissolved metals in the leachate may be recovered. However, leaching of metals using such methods is difficult due to the inherent insolubility of cathode materials (e.g., Co(III)) in such solutions. Therefore, the methods require significant quantities of and strength of acid, which generate significant quantities of waste acid. In addition, some methods of leaching metals in lithium-ion batteries result in hazardous gas emissions (Cl.sub.2, SO.sub.2).

BRIEF SUMMARY

(7) In accordance with one embodiment described herein, methods and apparatuses for recovering metals from active materials of rechargeable batteries, such as lithium-ion batteries or metal hydride batteries. For example, in some embodiments, a method of recovering active materials from a rechargeable battery comprises placing an active material of a rechargeable battery in a cathode chamber comprising a cathode of an electrochemical cell comprising the cathode chamber, an anode chamber comprising an anode, and a membrane separating the cathode chamber from the anode chamber, contacting the active material in the cathode chamber with an electrolyte comprising an acid, ferric ions, and ferrous ions, applying a potential between the anode and the cathode, and dissolving at least one of lithium and cobalt from the active material into the electrolyte.

(8) In additional embodiments, an apparatus for recovering metals from active materials of rechargeable batteries comprises an electrochemical cell comprising an anode, a cathode, a membrane between the anode and the cathode, and an electrolyte. The electrolyte comprises an acid, ferric ions, ferrous ions, and an active material of a rechargeable battery. The apparatus further comprises a system for recovering at least one of lithium and cobalt from the electrolyte in operable communication with the electrochemical cell.

Description

BRIEF DESCRIPTION OF THE DRAWINGS

(1) FIG. 1A is a simplified schematic of an electrochemical cell for removing active materials from rechargeable batteries, in accordance with embodiments of the disclosure;

(2) FIG. 1B is a simplified schematic of a system for removing active materials from rechargeable batteries, in accordance with other embodiments of the disclosure;

(3) FIG. 1C is a simplified schematic of an electrochemical cell for removing active materials from rechargeable batteries, in accordance with other embodiments of the disclosure; and

(4) FIG. 2 is a simplified flow diagram of a system for recovering metals from active materials, in accordance with embodiments of the disclosure.

DETAILED DESCRIPTION

(5) The following description provides specific details, such as material types, dimensions, and processing conditions in order to provide a thorough description of embodiments of the disclosure. However, a person of ordinary skill in the art will understand that the embodiments of the disclosure may be practiced without employing these specific details. Indeed, the embodiments of the disclosure may be practiced in conjunction with conventional fabrication techniques employed in the industry. In addition, the description provided below does not form a complete process flow, apparatus, or system for recovering metals from a lithium-ion battery or from a metal hydride battery or of a reactor (e.g., a bioreactor) for forming gluconic acid. Only those process acts and structures necessary to understand the embodiments of the disclosure are described in detail below. Additional acts to remove metals from a lithium-ion battery or a metal hydride battery and recover the metals described herein may be performed by conventional techniques. Also note, any drawings accompanying the present application are for illustrative purposes only, and are thus not drawn to scale. Additionally, elements common between figures may retain the same numerical designation.

(6) As used herein, a “battery active material” refers to materials within a battery (e.g., a rechargeable battery), such as a lithium-ion battery or a metal hydride battery, which materials are used to provide power. For example, a battery active material of a lithium-ion battery may include a compound formulated and configured to provide one or more of lithium ions, compounds including lithium, or ions including lithium within the lithium-ion battery. A battery active material of a metal hydride battery may include a component of the metal hydride battery formulated and configured to provide power such as, for example, one or more of a metal oxide hydroxide, a metal hydride, a metal oxide (e.g., a transition metal oxide), or a metal hydroxide (e.g., a transition metal hydroxide). The term “active material” is also used herein to refer to such materials and is used interchangeably with the term “battery active material.” Active materials may include, for example, one or more of lithium cobalt (LiCoO.sub.2), lithium manganese oxide (LiMn.sub.2O.sub.3), lithium nickel oxide (LiNiO.sub.2), LiNi.sub.xCo.sub.yMn.sub.zO.sub.2 (LNCM), lithium-nickel-manganese-cobalt-aluminum oxide ((Li(NiCoAl)O.sub.2) (NCA)), nickel oxyhydroxide, nickel hydroxide, manganese tetroxide, manganite (MnO(OH)), cobalt oxide, or another material. In some embodiments, active materials may also include rare earth-containing materials (e.g., rare earth ores, rare earth tailings, rare earth magnets), cobalt-containing magnets (e.g., samarium cobalt, aluminum-nickel-cobalt (AlNiCo) magnets), nickel cadmium (NiCd) batteries, fluid catalytic cracking (FCC) catalysts, phosphors, phosphogypsum (e.g., CaSO.sub.4.2H.sub.2O), phosphate clays, neodymium magnets, coal fly ash, materials of photovoltaic cells (e.g., indium, gallium, tellurium), or other materials including one or more metals.

(7) According to embodiments described herein, a method of recovering metals (e.g., active materials) from a rechargeable battery (e.g., a lithium-ion battery, a metal hydride battery) includes leaching (e.g., by reductive leaching) the metals from the active battery material in an electrochemical cell. The electrochemical cell includes an anode chamber, a cathode chamber, and a membrane between the anode chamber and the cathode chamber. The cathode chamber may include an electrolyte comprising an acid and iron sulfate (FeSO.sub.4) dissolved therein. The iron sulfate generates ferrous ions (Fe.sup.2+) in the cathode chamber. The ferrous ions act as a reducing agent to reduce metals from the active battery materials, such as one or more of cobalt, nickel, and manganese from the active battery material (e.g., one or more of LiCoO.sub.2, LiMn.sub.2O.sub.3, LiNiO.sub.2, or LiNi.sub.xCo.sub.yMn.sub.zO.sub.2, Li(NiCoAl)O.sub.2, nickel oxyhydroxide, nickel hydroxide, manganese tetroxide, manganite (MnO(OH)), or cobalt oxide). The ferrous ions are, in turn, oxidized to ferric (Fe.sup.3+). The metals from the active battery material are reduced by the ferrous ions, increasing the solubility of the metals in the electrolyte and generating a loaded electrolyte comprising dissolved active materials therein. The ferric ions are regenerated to ferrous ions at the cathode, facilitating continued reductive leaching of the metals of the active battery materials without requiring additional reducing agents. The membrane between the anode chamber and the cathode chamber facilitates transfer of protons (H.sup.+) to the cathode chamber and transfer of hydroxide ions (OH.sup.-) to the anode chamber. Hydroxide ions in the anode chamber react to generate water and electrons.

(8) The metals dissolved in the electrolyte may be selectively recovered by flowing the loaded electrolyte through one or more metal recovery

apparatuses formulated and configured to selectively recover one or more of the dissolved metals. For example, the loaded electrolyte may be flowed through one or more extraction stages to separate cobalt and manganese from nickel and lithium, such as with a solvent (e.g., an organic solvent). The cobalt may be separated from the manganese to selectively recover the cobalt and the manganese. The nickel may be separated from the lithium to selectively recover the nickel and the lithium. In some embodiments, aluminum, copper, or both may be recovered from the electrolyte. In some embodiments, one or more of the metals (e.g., cobalt, manganese, nickel, lithium) may be recovered by flowing the loaded electrolyte through an ion exchange resin formulated and configured to selectively adsorb the one or more metals. The electrolyte from which the dissolved metals have been substantially recovered may be recycled to the cathode chamber of the electrochemical cell where the electrolyte may be loaded with dissolved metals from the active material and the process may continue. Accordingly, one or more metals may be recovered from lithium-ion battery materials with the electrochemical cell.

(9) In some embodiments, the acid of the electrolyte is generated organically and is, thus, renewable. For example, the acid of the electrolyte may be formed by an acid-generating bacteria that may produce one or more of gluconic acid, xylonic acid, citric acid, succinic acid, and acetic acid. The acid generating bacteria may metabolically generate the acid (e.g., gluconic acid) using glucose, corn stover, or another organic material as a feed material. The generated gluconic acid may be used in the electrochemical cell to dissolve the metals from the active battery materials. Thus, the metals may be removed from the active battery material with a renewable acid. Generation of the gluconic acid with the bacteria may reduce the environmental impact of the method of recovering the metals from the active battery materials. For example, since the acid (e.g., gluconic acid, xylonic acid, citric acid, succinic acid, and acetic acid) is an organic acid, the environmental impact of the acid may be reduced relative to leaching processes using a mineral acid.

(10) FIG. 1A is a simplified schematic of an electrochemical cell **100** for removing active materials from rechargeable batteries, such as lithium ion batteries, metal hydride batteries, or both, in accordance with embodiments of the disclosure. The electrochemical cell **100** may be used for recovering at least some metals from which the cathode portion of lithium-ion batteries are formed, or from which the anode or cathode of metal hydride batteries are formed. The electrochemical cell **100** may include an anode chamber **110**, a cathode chamber **120**, and a membrane **130** between the anode chamber **110** and the cathode chamber **120**.

(11) The anode chamber **110** may include a first liquid **112** and an anode **114** at least partially submerged by the first liquid **112**. In some embodiments, the first liquid **112** comprises water and includes one or more ions dissolved therein. The first liquid **112** may include hydroxide ions. The anode **114** may comprise a material suitable for conducting electricity and exhibiting a tolerance to aqueous solutions (e.g., water, hydroxide ions, etc.). In some embodiments, the anode **114** comprises one or more of carbon, stainless steel, and nickel. However, the disclosure is not so limited and the anode **114** may comprise one or more materials other than, or in addition to, those described. The cathode **124** may include a material suitable for conducting electricity and exhibiting a tolerance to the electrolyte **122**. In some embodiments, the cathode **124** comprises stainless steel.

(12) The membrane **130** may comprise a bipolar membrane, a proton-exchange membrane (PEM), or another membrane formulated and configured to allow passage of protons therefrom while substantially electrically insulating the anode chamber **110** from the cathode chamber **120**. In some embodiments, the membrane **130** is substantially impermeable to ferric ions, ferrous ions, and metal cations such as ions of one or more of lithium, cobalt, manganese, nickel, aluminum, copper, or another metal. In some embodiments, the membrane **130** comprises a bipolar membrane. In some such embodiments, the membrane **130** comprises an anion exchange layer **131** on the side of the anode chamber **110** and a cation exchange layer **133** on the side of the cathode chamber **120**.

(13) The cathode chamber **120** may include an electrolyte **122** and a cathode **124** at least partially submerged within the electrolyte **122**. The electrolyte **122** may include active materials **126** collected from lithium-ion batteries, metal hydride batteries, or active materials from other rechargeable batteries. The active materials **126** may include one or more of lithium, cobalt, nickel, manganese, or aluminum. For example, the active materials **126** may comprise one or more of LiCoO_2 , LiMn_2O_4 , LiNiO_2 , or $\text{LiNi}_x\text{Co}_y\text{Mn}_z\text{O}_2$, $\text{Li}(\text{NiCoAl})\text{O}_2$, nickel oxyhydroxide, nickel hydroxide, manganese tetroxide, manganese oxide-hydroxide (manganite; $\text{MnO}(\text{OH})$), or cobalt oxide. In some embodiments, the active materials **126** comprise LiCoO_2 . In some embodiments, the active material **126** further includes one or more of aluminum, nickel, and manganese. The active material **126** may comprise a composite material including battery active materials from lithium-ion batteries, metal hydride batteries, or other rechargeable batteries. In some embodiments, the active material **126** may be substantially free of polymer materials, binder materials, graphite, battery electrolytes, or other components that may comprise a portion of rechargeable batteries but do not constitute the active materials. In other embodiments, the active material **126** comprises a cake or powder including the active battery materials and further including, for example, graphite powder. In some embodiments, the active material **126** includes a composite material comprising graphite and one or more of lithium, cobalt, nickel, manganese, aluminum, or copper (which may be present in the current collector of the anode materials of lithium-ion batteries).

(14) In addition to the active materials **126**, the electrolyte **122** may include ferric ions and ferrous ions dissolved therein. By way of nonlimiting example, iron sulfate (FeSO_4) may be dissolved within the electrolyte **122** to provide ferrous ions. As will be described herein, the ferric ions may reduce at least some of the metals of the active material **126** to solubilize the metals of the active material **126** and to generate ferric ions. A concentration of the ferric ions and the ferrous ions within the electrolyte **122** may be within a range from about 0.005 M to about 0.10 M, such as from about 0.005 M to about 0.01 M, from about 0.01 M to about 0.02 M, from about 0.02 M to about 0.03 M, from about 0.03 M to about 0.05 M, from about 0.05 M to about 0.075 M, or from about 0.075 M to about 0.10 M. However, the disclosure is not so limited, and the concentration of the iron sulfate in the electrolyte **122** may be different.

(15) The electrolyte **122** may comprise an acid in which the ferric ions and the ferrous ions are dissolved to form an aqueous solution. In some embodiments, electrolyte **122** may comprise a mineral acid, such as one or more of sulfuric acid, hydrochloric acid, phosphoric acid, nitric acid, gluconic acid ($\text{C}_6\text{H}_{12}\text{O}_7$), and an organic acid (e.g., one or more of xylonic acid ($\text{C}_5\text{H}_8\text{O}_6$), citric acid ($\text{C}_6\text{H}_8\text{O}_7$), succinic acid ($\text{C}_4\text{H}_6\text{O}_4$), and acetic acid (CH_3COOH)). In some embodiments, the electrolyte **122** comprises sulfuric acid. In some embodiments, the electrolyte **122** comprises an organic acid, such as gluconic acid. In some embodiments, the electrolyte **122** comprises gluconic acid and xylonic acid. In some embodiments, the electrolyte **122** comprises gluconic acid, xylonic acid, citric acid, succinic acid, and acetic acid. The acid may have a concentration within a range from about 0.1 M to about 5.0 M, such as from about 0.1 M to about 0.2 M, from about 0.2 M to about 0.5 M, from about 0.5 M to about 1.0 M, from about 1.0 M to about 2.0 M, from about 2.0 M to about 3.0 M, from about 3.0 M to about 4.0 M, or from about 4.0 M to about 5.0 M. The pH of the electrolyte **122** may be within a range from about less than about 0.0 to about 4.0, such as from about 0.0 to about 0.5, from about 0.5 to about 1.0, from about 1.0 to about 1.5, from about 1.5 to about 2.0, from about 2.0 to about 2.5, from about 2.5 to about 3.0, from about 3.0 to about 3.5, or from about 3.5 to about 4.0. In some embodiments, the pH of the electrolyte **122** is within a range from about 2.0 to about 2.3.

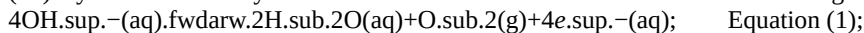
(16) In some embodiments, the electrolyte **122** is formed by dissolving iron sulfate in a solution comprising one or both of sulfuric acid and gluconic acid. The active materials **126** are added to the electrolyte **122**. In some embodiments, the pH of the electrolyte **122** is maintained by addition of the active materials **126** to the electrolyte **122**. For example, in some embodiments, addition of the active materials **126** may increase the pH of the electrolyte **122**. In use and operation, protons are consumed during dissolution of the metals from the active material **126**. Accordingly, the pH of the electrolyte **122** may increase during use and operation. A pH of the electrolyte **122** may be maintained less than

about 4.0, or less than about 3.0, or between about 2.0. In some embodiments, the pH of the electrolyte **122** may be decreased by addition of the acid. For example, a pump and a pH controller may be coupled to the electrochemical cell **100** to control the pH of the electrolyte **122**.

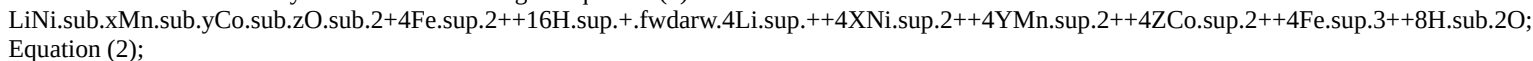
(17) In use and operation, a voltage may be applied between the anode **114** and the cathode **124**. In some embodiments, a controlled potential may be applied over the cathode **124** using a reference electrode, such as, for example, Ag/AgCl at -0.3 V. The voltage may be within a range from about 1.0 V to about 5.0 V, such as from about 1.0 V to about 1.5 V, from about 1.5 V to about 2.0 V, from about 2.0 V to about 2.5 V, from about 2.5 V to about 3.0 V, from about 3.0 V to about 3.5 V, from about 3.5 V to about 4.0 V, from about 4.0 V to about 4.5 V, or from about 4.5 V to about 5.0 V. However, the disclosure is not so limited and different potentials may be applied between the anode **114** and the cathode **124**. In some embodiments, the potential between the anode **114** and the cathode **124** is maintained substantially constant to reduce evolution of hydrogen gas from the electrochemical cell **100**. In some embodiments, the potential between the anode **114** and the cathode **124** may be below a range at which copper would be removed from the active materials **126**. In some such embodiments, copper may be separated from other metals located within the active materials **126**.

(18) A current between the anode **114** and the cathode **124** may be between about 0.5 A and about 1.0 A. However, the disclosure is not so limited and the current between the anode **114** and the cathode **124** may be different than that described above. The maximum current may depend, at least in part, on the size of the anode **114** and the cathode **124**. The current may decrease during extraction of the metals from the active materials **126**.

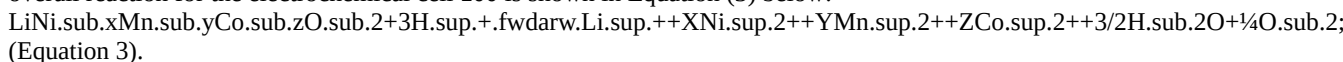
(19) Hydroxide ions may react to form water in the anode chamber **110** according to Equation (1) below:



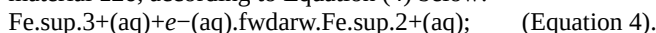
(20) The electrons generated in the anode chamber **110** may be transferred to the cathode chamber **120**. In the cathode chamber **120**, metals of the active materials **126** may be reduced according to Equation (2) below:



wherein $X+Y+Z$ is equal to about 1.0 and the ions are in the aqueous phase and the $\text{LiNi}.\text{sub}.\text{xMn}.\text{sub}.\text{yCo}.\text{sub}.\text{zO}.\text{sub}.2$ is a solid. In some embodiments, one or more of X, Y, or Z is equal to 0 and the active material **126** comprises, for example, $\text{LiCoO}.\text{sub}.2$, $\text{LiMn}.\text{sub}.2\text{O}.\text{sub}.3$, or $\text{LiNiO}.\text{sub}.2$. Of course, where the active material **126** has a different composition, Equation (2) may be different than described above. The overall reaction for the electrochemical cell **100** is shown in Equation (3) below:

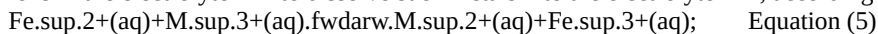


(21) The generated ferric ions may be reduced at the cathode **124** to regenerate the ferrous ions that are used to reduce the metals of the active material **126**, according to Equation (4) below:



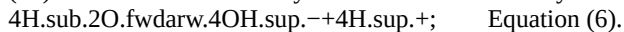
(22) Accordingly, in some embodiments, the ferrous ions are regenerated within the cathode chamber **120** and are not substantially consumed by the electrochemical cell **100**. By way of comparison, conventional methods of recovering metals from lithium-ion batteries require dissolving the metals in an acid to dissolve the metals and recovering the metals from the acid. Dissolution of the metals may require significant amounts of one or more reducing agents, which reducing agents are generally consumed during the process. Such methods often require significant amounts of make-up acid and reducing agent to maintain a desired strength of the acid and continue to dissolve metals from the lithium-ion battery materials. Since the electrolyte **122** includes ferric ions that are regenerated within the cathode chamber **120**, the method does not require significant amounts of makeup materials (e.g., reducing agents ($\text{Fe}2.\text{sup}+.$)) to continue the dissolution of the metals from the active materials **126**.

(23) In use and operation, a potential is applied between the cathode **124** and a reference electrode (e.g., a silver chloride reference electrode, a stainless steel reference electrode). The reference electrode may be located in the anode chamber **110**, for example. In other embodiments, the reference electrode may be located in the cathode chamber **120**. Metals from the active material **126** are reduced by interaction with ferrous ions in the electrolyte **122** to dissolve such metals into the electrolyte **122**, according to the simplified Equation below:



wherein M is one or more of Ni, Mn, Co, or Al.

(24) The membrane **130** may facilitate formation of hydroxide ions and hydrogen ions according to Equation (6) below:



(25) After the metals are dissolved from the active materials **126** into the electrolyte **122**, the metals may be selectively recovered from the electrolyte **122**. The cathode chamber **120** may be in fluid communication with one or more metal recovery processes that may be formulated and configured to recover the dissolved metals from the electrolyte **122**. After the dissolved metals are recovered, the electrolyte **122** may be recycled back to the cathode chamber **120** and the process may continue.

(26) Accordingly, in some embodiments, metals from the active materials **126** may be recovered using ferric ions. By way of comparison, in conventional metal recovery processes, ferrous ions and ferric ions are considered to be contaminants and are removed from solutions including dissolved metals from active material metals. The ferrous and ferric ions are used in the electrochemical cell **100** to reduce consumption of chemicals since they are regenerated during operation of the electrochemical cell **100**. In other words, since the ferrous ions are regenerated by the cathode **124**, significant quantities of a reducing agent are not required to disproportionate the metals of the active material **126**.

(27) In some embodiments, the electrolyte **122** may be generated with an organism that metabolically generates one or more organic acids (e.g., one or more of gluconic acid, xylonic acid, citric acid, succinic acid, and acetic acid). The organic acid (e.g., gluconic acid) generated by the organism may be introduced (e.g., fed) to the electrochemical cell **100**, such as to the cathode chamber **120** of the electrochemical cell **100**. FIG. 1B is a simplified schematic of a system **150** for recovering metals from active battery materials, in accordance with embodiments of the disclosure.

(28) With reference to FIG. 1B, the system **150** may include the electrochemical cell **100** of FIG. 1A. The system **150** may include a vessel **140** in fluid communication with the electrochemical cell **100**. The vessel **140** may include, for example, a bioreactor, such as a continuous stirred-tank reactor (CSTR). The vessel **140** may be in fluid communication with a feed material **142** and may generate an acid **144** that may be in fluid communication with the electrochemical cell **100**. The acid may also be referred to herein as a lixiviant or a biolixiviant.

(29) The vessel **140** may include one or more organisms configured to generate the acid **144**. The organisms may comprise bacteria that generate the acid **144** metabolically. By way of nonlimiting example, the organisms may comprise one or more of *Gluconobacter oxydans*, *Aspergillus niger*, and *Ceriporiopsis subvermispura*. In some embodiments, the *Gluconobacter oxydans* comprises a NRRL B 58 strain bacteria and produces gluconic acid. In some embodiments, the *Aspergillus niger* comprises a NRRL326 strain bacteria and produces at least citric acid. In some embodiments, *Ceriporiopsis subvermispura* produces at least succinic acid. The acid **144** may comprise one or more organic acids (e.g., one or more of gluconic acid, xylonic acid, citric acid, succinic acid, and acetic acid). In some embodiments, the acid **144** has a pH within a range from about 2.0 to about 3.0, such as from about 2.0 to about 2.5 or from about 2.5 to about 3.0.

(30) The feed material **142** may include one or more materials that may be used by the organisms in the vessel **140** to metabolically generate the acid **144**. In some embodiments, the feed material **142** includes one or both of glucose or corn stover (e.g., the leaves stacks, and cobs of corn).

(31) The acid **144** may be provided to the electrochemical cell **100**. In some embodiments, the acid **144** is provided to the cathode chamber **120** of the electrochemical cell **100**. In some embodiments, the acid **144** is generated based on the amount of acid **144** required by the electrochemical cell **100** to dissolve the metals of the active material **126**.

(32) Although FIG. 1A and FIG. 1B have been described and illustrated as including the electrochemical cell **100** having a particular structure, the disclosure is not so limited. FIG. 1C is a simplified schematic of an electrochemical cell **160** for removing active materials from rechargeable batteries, in accordance with other embodiments of the disclosure. The electrochemical cell **160** may be substantially similar to the electrochemical cell **100** of FIG. 1A, except that the electrochemical cell **160** may include a reference electrode **162** in the cathode chamber **120**. Each of the reference electrode **162**, the anode **114**, and the cathode **124** may be coupled to a potentiostat **164** configured to control a voltage difference between the reference electrode **162** and one of the anode **114** and the cathode **124**. The electrochemical cell **160** may further include a mixer **166** configured to combine (e.g., mix, stir) the electrolyte **122**. Although FIG. 1C illustrates that the mixer **166** comprises a blades, in other embodiments, the mixer **166** comprises a magnetic stirrer (e.g., a stir magnet).

(33) FIG. 2 is a simplified flow diagram of a system **200** for recovering metals from active materials **126** (FIG. 1A, FIG. 1B), in accordance with embodiments of the disclosure. The system **200** includes the electrochemical cell **100** of FIG. 1A and FIG. 1B or the electrochemical cell **160** of FIG. 1C, which is in fluid communication with a liquid-liquid extraction cell **202**. In some embodiments, such as embodiments described with reference to FIG. 1B, the electrochemical cell **100**, **160** may be in fluid communication with the vessel **140**. The acid **144** may flow from the vessel **140** to the electrochemical cell **100**, **160**. In some such embodiments, the feed material **142** may be provided to the vessel **140**. In some embodiments, a material **152** may exit the electrochemical cell **100**, **160**. The material **152** may include graphite and other components located within the active material **126** (FIG. 1A, FIG. 1B) that are not dissolved by the electrolyte **122**.

(34) The liquid-liquid extraction cell **202** may be in fluid communication with a solvent **204**, which may be mixed with the electrolyte **122** in the liquid-liquid extraction cell **202**. In some embodiments, the solvent **204** comprises an organic solvent. In some embodiments, the pH of liquid-liquid extraction cell **202** may be maintained within a range from about 3.0 to about 6.0.

(35) The solvent **204** may contact the electrolyte **122** in the liquid-liquid extraction cell **202**. The solvent **204** may be substantially immiscible with the electrolyte **122** but may absorb at least some of the metals dissolved in the electrolyte **122**. In other words, at least some of the metals dissolved in the electrolyte **122** may be more soluble in the solvent **204** than in the aqueous solution of the electrolyte **122**. Accordingly, a loaded solvent **205** including one or more metals absorbed from the electrolyte **122** may be formed in the liquid-liquid extraction cell **202**. An aqueous solution **207** exiting the liquid-liquid extraction cell **202** may comprise the solution of the electrolyte **122** including one or more dissolved metals therein (e.g., metals that are not dissolved in the loaded solvent **205**).

(36) The loaded solvent **205** may include, for example, one or both of cobalt and manganese, which may be absorbed from the electrolyte **122** into the solvent **204** in the liquid-liquid extraction cell **202**. Accordingly, the one or both of the cobalt and manganese may be substantially removed from the electrolyte **122** and absorbed by the solvent of the loaded solvent **205**. In some embodiments, one or more of dissolved lithium and dissolved nickel remain in the electrolyte **122** and are not substantially absorbed by the solvent **204** in the liquid-liquid extraction cell **202**. The one or more of dissolved lithium and dissolved nickel may remain in the aqueous solution **207**.

(37) The solvent **204** may include one or more materials formulated and configured to selectively absorb at least one of the metals dissolved in the electrolyte **122**. By way of nonlimiting example, the solvent **204** may include thenoyltrifluoroacetone (TTA), a dialkyl phosphinic acid extractant (such as CYANEX®, commercially available from Solvay of Houston, Texas). In some embodiments, the solvent **204** comprises thenoyltrifluoroacetone. In other embodiments, the solvent **204** comprises a dialkyl phosphinic acid extractant, an alkane (e.g., kerosene, isoparaffinic hydrocarbons (such as ISOPAR™ series materials commercially available from Brenntag of the United Kingdom), branched or linear alkanes having from about 5 carbon atoms to about 20 carbon atoms (C5-C20 alkanes), halogen-containing alkanes (e.g., branched or linear alkanes having from about 5 carbon atoms to about 20 carbon atoms and including at least one halogen atom)), unsaturated alkenes, aromatics (e.g., toluene, xylenes), halogen-containing aromatics, ethers, esters, and sulfones. In other embodiments, such as where the solvent **204** includes thenoyltrifluoroacetone, the solvent **204** may further include an alcohol.

(38) By way of nonlimiting example, where the active material **126** (FIG. 1A, FIG. 1B, FIG. 1C) comprises LiCoO.sub.2, lithium may remain in the aqueous solution **207** while cobalt is substantially removed from the electrolyte **122** and absorbed in the loaded solvent **205**. In embodiments where the active material **126** comprises LiMn.sub.2O.sub.3, lithium may remain in the aqueous solution **207** while manganese is substantially removed from the aqueous solution **207** and absorbed in the loaded solvent **205**. In embodiments where the active material **126** comprises LiNi.sub.xCo.sub.yMn.sub.zO.sub.2, the lithium and nickel may remain in the aqueous solution **207**, while cobalt and manganese are substantially removed from the aqueous solution **207** and absorbed in the loaded solvent **205**. Where the active material **126** comprises LiNiO.sub.2, the system **200** may not include the liquid-liquid extraction cell **202** and may include a component for separating the lithium from the nickel, as will be described herein.

(39) With continued reference to FIG. 2, the aqueous solution **207** may exit the liquid-liquid extraction cell **202** and enter a nickel separation vessel **206** while the loaded solvent **205** exits the liquid-liquid extraction cell **202** and enters a second separation vessel **208**. The nickel separation vessel **206** may be configured to separate, for example, nickel from lithium in embodiments where the aqueous solution **207** includes both nickel and lithium. In other embodiments, such as where the aqueous solution **207** does not include dissolved nickel, the system **200** may not include the nickel separation vessel **206**.

(40) A nickel separation agent **210** may be added to the aqueous solution **207** in the second separation vessel **208**. The nickel separation agent **210** may be formulated and configured to selectively interact (e.g., chemically react, bind to, etc.) with nickel dissolved in the aqueous solution **207** and substantially not interact with at least another metal dissolved in the aqueous solution **207**. In some embodiments, addition of the nickel separation agent **210** to the nickel separation vessel **206** may form a nickel-containing material **212**. The nickel separation agent **210** may include a precipitating agent, a chelating agent, or both. In some embodiments, the nickel separation agent **210** includes a precipitating agent formulated and configured to react with dissolved nickel in the aqueous solution **207** and form a nickel-containing material **212** comprising a solid precipitate. By way of nonlimiting example, the nickel separation agent **210** may comprise sodium carbonate (Na.sub.2CO.sub.3) and the nickel-containing material **212** may comprise nickel carbonate (NiCO.sub.3). In other embodiments, the nickel separation agent **210** includes one or more chelating agents formulated and configured to interact with dissolved nickel in the aqueous solution **207**. By way of nonlimiting example, the nickel separation agent **210** may include one or more of ethylenediamine, ethylenediaminetetraacetic acid (EDTA), or another chelating agent. The nickel from the nickel-containing material **212** may be removed as a solid, such as solid nickel.

(41) Although the nickel separation vessel **206** has been described as being in fluid communication with the nickel separation agent **210**, the disclosure is not so limited. In some embodiments, the nickel separation vessel **206** comprises an ion exchange resin formulated and configured to selectively adsorb the dissolved nickel from the aqueous solution **207**. The adsorbed nickel in the nickel separation vessel **206** may be recovered by passing a stripping agent through the ion exchange resin.

(42) With continued reference to FIG. 2, a lithium-containing aqueous solution **213** may exit the nickel separation vessel **206**. The lithium-containing aqueous solution **213** may include an aqueous solution comprising the composition of the electrolyte **122** and including lithium dissolved therein. In some embodiments, the lithium-containing aqueous solution **213** further includes the ferric and ferrous ions that were dissolved in the electrolyte **122**. The lithium-containing aqueous solution **213** may be flowed from the nickel separation vessel **206** to a lithium separation vessel **214**.

(43) In the lithium separation vessel **214**, lithium dissolved in the lithium-containing aqueous solution **213** may be removed from the aqueous solution. For example, a lithium separation agent **219** may be added to the lithium-containing aqueous solution **213** in the lithium separation vessel **214** to form a lithium-containing material **216** and an aqueous solution **218** substantially free of dissolved active material **126** (FIG. 1A, FIG. 1B) metals. In some embodiments, the lithium separation agent **219** comprises a precipitating agent formulated and configured to precipitate lithium. In some embodiments, the lithium separation agent **219** comprises sodium carbonate and the lithium-containing material **216** comprises lithium carbonate (Li.sub.2CO.sub.3).

(44) With continued reference to FIG. 2, the loaded solvent **205** may be flowed from the liquid-liquid extraction cell **202** to the second separation vessel **208**. The second separation vessel **208** may be configured to facilitate removal of dissolved metals (e.g., cobalt, manganese, or both) from the loaded solvent **205** into an aqueous acid solution **220** to form regenerated solvent **223** and a loaded aqueous acid solution **221**. The regenerated solvent **223** may be substantially free of dissolved metals in some embodiments. In some embodiments, the regenerated solvent **223** is protonated. The regenerated solvent **223** may be recycled and mixed with the solvent **204** or mixed directly into the liquid-liquid extraction cell **202**.

(45) The aqueous acid solution **220** may be formulated and configured to selectively remove one or both of cobalt and manganese from the loaded solvent **205**. The aqueous acid solution **220** may comprise, for example, one or more of nitric acid, phosphoric acid, sulfuric acid, or hydrochloric acid.

(46) The loaded aqueous acid solution **221** may include one or both of dissolved cobalt and dissolved manganese. The loaded aqueous acid solution **221** may be flowed to a manganese separation vessel **222** where the loaded aqueous acid solution **221** may be mixed with a manganese separation agent **224**. The manganese separation agent **224** may be formulated and configured to selectively interact with the manganese in the loaded aqueous acid solution **221** to form a manganese-containing material **226** and a cobalt-containing aqueous solution **225**.

(47) The manganese separation agent **224** may not substantially interact with cobalt. The manganese separation agent **224** may include a precipitating agent, a chelating agent, or both. In some embodiments, the manganese separation agent **224** includes a precipitating agent formulated and configured to react with dissolved manganese in the loaded aqueous acid solution **221** and form a manganese-containing precipitate. By way of nonlimiting example, the precipitating agent may comprise sodium carbonate and the manganese-containing precipitate may comprise manganese carbonate (MnCO.sub.3).

(48) In other embodiments, the manganese separation agent **224** includes one or more chelating agents formulated and configured to interact with dissolved manganese in the loaded aqueous acid solution **221** to form the manganese-containing material **226**. By way of nonlimiting example, the chelating agent may comprise para-aminosalicylic acid (PAS) or ethylenediamine disuccinic acid (EDDS), for example. However, the disclosure is not so limited and other chelating agents formulated and configured to chelate with manganese may be used. Manganese may be recovered from the manganese-containing material by conventional methods of removing manganese from a manganese-containing material.

(49) In some embodiments, the manganese separation vessel **222** comprises an ion exchange resin. In some such embodiments, the loaded aqueous acid solution **221** is flowed through the ion exchange resin, which may be formulated and configured to selectively adsorb manganese from the loaded aqueous acid solution **221**. The adsorbed manganese may be recovered from the loaded ion exchange resin by passing a stripping agent through the ion exchange resin.

(50) With continued reference to FIG. 2, the cobalt-containing aqueous solution **225** may enter a cobalt separation vessel **228**. A cobalt separation agent **229** may mix with the cobalt-containing aqueous solution **225** to form a cobalt-containing material **230** and an aqueous solution **231** substantially free of dissolved metals such as cobalt, manganese, nickel, and lithium. However, the aqueous solution **231** may include, for example, ferric ions and ferrous ions.

(51) The cobalt separation agent **229** may include a material formulated and configured to interact with dissolved cobalt in the cobalt-containing aqueous solution **225**. The cobalt separation agent **229** may include a precipitating agent, a chelating agent, or both. In some embodiments, the cobalt separation agent **229** comprises a precipitating agent such as an oxalate (e.g., ammonium oxalate ((NH.sub.4).sub.2C.sub.2O.sub.4)), a hydroxide (e.g., sodium hydroxide (NaOH)), or another precipitating agent. In some such embodiments, the cobalt-containing material **230** may comprise, for example, cobalt oxalate (Co(C.sub.2O.sub.4).sub.2), also written as CoC.sub.2O.sub.4*2H2O) or cobalt hydroxide (Co(OH).sub.2).

(52) In other embodiments, the cobalt separation agent **229** comprises a chelating agent. By way of nonlimiting example, the chelating agent may include one or more of ethylenediaminetetraacetic acid, dimercaptosuccinic acid (DMFS), or another chelating agent. However, the disclosure is not so limited and other chelating agents formulated and configured to chelate with cobalt may be used.

(53) In some embodiments, the cobalt separation vessel **228** comprises an ion exchange resin. In some such embodiments, the cobalt-containing material **230** is flowed through the ion exchange resin, which may be formulated and configured to selectively adsorb cobalt from the cobalt-containing material **230**. The adsorbed cobalt may be recovered from the loaded ion exchange resin by passing a stripping agent through the ion exchange resin.

(54) Although FIG. 2 has been illustrated and described as including the cobalt separation vessel **228** configured to receive the cobalt separation agent **229** and form the cobalt-containing material **230**, the disclosure is not so limited. In some embodiments, the cobalt separation vessel **228** comprises an ion exchange column. In some such embodiments, the cobalt-containing aqueous solution **225** may be fed to the ion exchange column, which may include one or more materials (e.g., resins) formulated and configured to selectively remove (e.g., strip) dissolved cobalt from the cobalt-containing aqueous solution **225** and form the aqueous solution **231**.

(55) Referring again to FIG. 2, the aqueous solution **231** may be mixed with the aqueous solution **218** to form a recycle solution **232**. The recycle solution **232** may comprise the same acid as found in the electrolyte **122**. The recycle solution **232** may be recycled to the electrochemical cell **100** and reused in the process of dissolution of metals from the active material **126** (FIG. 1A, FIG. 1B) in the cathode chamber **120** (FIG. 1A, FIG. 1B).

(56) Accordingly, the system **200** and electrochemical cell **100**, **160** may be used for dissolving metals within active battery materials in an electrolyte, and for selectively recovering the dissolved metals from the electrolyte. The system **200** does not require significant acid strengths or significant amounts of makeup reducing agents since the metals are removed from the active materials **126** (FIG. 1A, FIG. 1B, FIG. 1C) in the electrochemical cell **100**, **160** with ferrous ions that are regenerated within the cathode chamber **120** (FIG. 1A, FIG. 1B, FIG. 1C) of the electrochemical cell **100**, **160**. In some embodiments, the electrolyte **122** may be continuously generated from a renewable source, such as from the bacteria in the vessel **140**. In some such embodiments, the electrolyte **122** may include an organic acid that may reduce the

environmental impact of the acid of the electrolyte **122** relative to where the electrolyte **122** includes, for example, mineral acids such as sulfuric acid, hydrochloric acid, phosphoric acid, or nitric acid.

(57) Although FIG. **2** has been described and illustrated as comprising a particular system **200** for recovering the dissolved metals from the electrolyte **122**, the disclosure is not so limited. In other embodiments, the electrolyte **122** including the dissolved metals (e.g., one or more of dissolved lithium, nickel, cobalt, and manganese) may be flowed through a first ion exchange resin cell comprising a first ion exchange resin formulated and configured to selectively adsorb nickel, cobalt, and manganese. In some such embodiments, the electrolyte **122** may pass through the ion exchange resin bed and may include dissolved lithium. The lithium remaining in the electrolyte **122** may be recovered by passing the electrolyte **122** through a second ion exchange resin cell including an ion exchange resin formulated and configured to adsorb lithium. In other embodiments, the lithium may be recovered by contacting the electrolyte **122** with a lithium separation agent (e.g., the lithium separation agent **219**). The nickel, cobalt, and manganese adsorbed on the first ion exchange resin may be recovered by, for example, passing, over the first ion exchange resin, a first extractant formulated and configured to selectively absorb at least one of the nickel, cobalt, and manganese from the ion exchange resin. A second extractant may be passed over the first ion exchange resin to selectively absorb another of the nickel, cobalt, and manganese from the first ion exchange resin. A third extractant may be passed over the first ion exchange resin to selectively absorb the remaining of the nickel, cobalt, and manganese from the first ion exchange resin. In other embodiments, the adsorbed nickel, cobalt, and manganese may be removed from the first ion exchange resin with an extractant and may be recovered from solution, such as with one or more of a nickel separation agent, a manganese separation agent, and a cobalt separation agent.

EXAMPLE

(58) 24.0 grams of an active battery material was placed in an electrochemical cell such as the electrochemical cell **100** of FIG. **1A**. The active battery material had a chemical composition illustrated in Table I below when placed in the electrochemical cell.

(59) TABLE-US-00001 TABLE I Component Weight Percent (%) Li 2.31 Co 14.16 Ni 4.27 Mn 3.31 Fe 0.16 Cu 0.16 Zn 0.09 Sn 0.17 Al 0.48

(60) With reference to Table I, the remaining composition of the active battery material was carbon in the form of graphite. The active battery material was placed in 200 ml of a 1.0 M sulfuric acid solution to form an electrolyte. Iron sulfate was added to the electrolyte to a concentration of about 0.01 M. A current was applied between the anode and the cathode of the electrochemical cell so that metals of the active battery material were dissolved. An elemental analysis of the remaining active battery material is shown in Table II. Over 98% of the nickel, cobalt, and manganese were dissolved from the active battery material.

(61) TABLE-US-00002 TABLE II Component Extraction Efficiency (%) Li 99% Co 98% Ni 99% Mn 99% Fe 48% Cu 80% Zn 76% Sn — Al 82%

(62) Non-limiting example embodiments of the disclosure are described below.

(63) Embodiment 1: A method of recovering active materials from a rechargeable battery, the method comprising: placing an active material of a rechargeable battery in a cathode chamber comprising a cathode of an electrochemical cell comprising the cathode chamber, an anode chamber comprising an anode, and a membrane separating the cathode chamber from the anode chamber; contacting the active material in the cathode chamber with an electrolyte comprising an acid, ferric ions, and ferrous ions; applying a potential between the anode and the cathode; and dissolving at least one of lithium and cobalt from the active material into the electrolyte.

(64) Embodiment 2: The method of Embodiment 1, further comprising reducing ferrous ions to ferric ions at the cathode.

(65) Embodiment 3: The method of Embodiment 1 or Embodiment 2, wherein contacting the active material in the cathode chamber with an electrolyte comprising an acid, ferric ions, and ferrous ions comprises contacting the lithium-ion battery material with an electrolyte having a concentration within a range from about 0.005 M to about 0.10 M.

(66) Embodiment 4: The method of any one of Embodiments 1 through 3, wherein placing an active material of a rechargeable battery in a cathode chamber comprising a cathode of an electrochemical cell comprises placing the active material in an electrochemical cell comprising the anode chamber separated from the cathode chamber by a bipolar membrane.

(67) Embodiment 5: The method of any one of Embodiments 1 through 4, further comprising generating water and electrons from hydroxide ions in the anode chamber.

(68) Embodiment 6: The method of any one of Embodiments 1 through 5, wherein contacting the active material in the cathode chamber with an electrolyte comprising an acid, ferric ions, and ferrous ions comprises contacting the active material with an electrolyte comprising sulfuric acid.

(69) Embodiment 7: The method of Embodiment 6, wherein contacting the active material with an electrolyte comprising sulfuric acid comprises contacting the active material with sulfuric acid having a within a range 0.5 M to about 5.0 M.

(70) Embodiment 8: The method of any one of Embodiments 1 through 7, wherein applying a potential between the anode and the cathode comprises applying a potential within a range from about 1.0 V to about 5.0 V between the anode and the cathode.

(71) Embodiment 9: The method of any one of Embodiments 1 through 8, wherein dissolving at least one of lithium and cobalt from the active material into the electrolyte comprises dissolving lithium and cobalt from the active material into the electrolyte.

(72) Embodiment 10: The method of any one of Embodiments 1 through 9, wherein dissolving at least one of lithium and cobalt from the active material into the electrolyte further comprises dissolving at least one of manganese and nickel into the electrolyte.

(73) Embodiment 11: The method of Embodiment 10, further comprising separating the at least one of nickel and lithium from the at least one of manganese and cobalt.

(74) Embodiment 12: The method of Embodiment 11, wherein separating the at least one of nickel and lithium from the at least one of manganese and cobalt comprises contacting the electrolyte with an organic solvent to absorb the at least one of manganese and cobalt in the organic solvent.

(75) Embodiment 13: The method of any one of Embodiments 1 through 12, further comprising one of: contacting the electrolyte with a nickel separation agent to form a nickel-containing material and separate the nickel from the lithium; or passing the electrolyte through an ion exchange resin formulated and configured to selectively adsorb at least one of the nickel, manganese, or cobalt from the electrolyte.

(76) Embodiment 14: The method of any one of Embodiments 1 through 13, further comprising recycling the electrolyte to the electrochemical cell after removing substantially all of the at least one of lithium and cobalt from the electrolyte.

(77) Embodiment 15: The method of any one of Embodiments 1 through 14, wherein contacting the active material in the cathode chamber with an electrolyte comprising an acid, ferric ions, and ferrous ions comprises contacting the active material with an electrolyte comprising at least one organic acid.

(78) Embodiment 16: The method of Embodiment 15, further comprising forming, in a vessel, the at least one organic acid with an organism comprising one or more of *Gluconobacter oxydans*, *Aspergillus niger*, and *Ceriporiopsis subvermispora*.

(79) Embodiment 17: The method of Embodiment 16, further comprising providing the at least one organic acid from the vessel to the electrochemical cell.

(80) Embodiment 18: The method of Embodiment 16, wherein forming, in a vessel, the at least one organic acid comprises forming gluconic acid in the vessel.

(81) Embodiment 19: An apparatus for recovering metals from active materials of rechargeable batteries, the apparatus comprising: an electrochemical cell comprising an anode, a cathode, a membrane between the anode and the cathode, and an electrolyte, the electrolyte comprising: an acid; ferric ions; ferrous ions; and an active material of a rechargeable battery; and a system for recovering at least one of lithium and cobalt from the electrolyte in operable communication with the electrochemical cell.

(82) Embodiment 20: The apparatus of Embodiment 19, further comprising a vessel including bacteria that metabolically generates gluconic acid.

(83) Embodiment 21: The apparatus of Embodiment 19 or Embodiment 20, wherein the vessel is in fluid communication with the electrochemical cell.

(84) While embodiments of the disclosure may be susceptible to various modifications and alternative forms, specific embodiments have been shown by way of example in the drawings and have been described in detail herein. However, it should be understood that the disclosure is not limited to the particular forms disclosed. Rather, the disclosure encompasses all modifications, variations, combinations, and alternatives falling within the scope of the disclosure as defined by the following accompanying claims and their legal equivalents.

Claims

1. A method of recovering active materials from a rechargeable battery, the method comprising: placing an active material of a rechargeable battery in a cathode chamber comprising a cathode of an electrochemical cell comprising the cathode chamber, an anode chamber comprising an anode, and a membrane separating the cathode chamber from the anode chamber; contacting the active material in the cathode chamber with an electrolyte comprising an acid, ferric ions, and ferrous ions; applying a potential between the anode and the cathode; and dissolving at least one of lithium and cobalt from the active material into the electrolyte.
 2. The method of claim 1, further comprising reducing ferric ions to ferrous ions at the cathode.
 3. The method of claim 1, wherein contacting the active material in the cathode chamber with an electrolyte comprising an acid, ferric ions, and ferrous ions comprises contacting a lithium-ion battery material with an electrolyte having a concentration within a range from about 0.005 M to about 0.10 M.
 4. The method of claim 1, wherein placing an active material of a rechargeable battery in a cathode chamber comprising a cathode of an electrochemical cell comprises placing the active material in an electrochemical cell comprising the anode chamber separated from the cathode chamber by a bipolar membrane.
 5. The method of claim 1, further comprising generating water and electrons from hydroxide ions in the anode chamber.
 6. The method of claim 1, wherein contacting the active material in the cathode chamber with an electrolyte comprising an acid, ferric ions, and ferrous ions comprises contacting the active material with an electrolyte comprising sulfuric acid.
 7. The method of claim 6, wherein contacting the active material with an electrolyte comprising sulfuric acid comprises contacting the active material with sulfuric acid having a concentration within a range of from about 0.5 M to about 5.0 M.
 8. The method of claim 1, wherein applying a potential between the anode and the cathode comprises applying a potential within a range from about 1.0 V to about 5.0 V between the anode and the cathode.
 9. The method of claim 1, wherein dissolving at least one of lithium and cobalt from the active material into the electrolyte comprises dissolving lithium and cobalt from the active material into the electrolyte.
 10. The method of claim 1, wherein dissolving at least one of lithium and cobalt from the active material into the electrolyte further comprises dissolving at least one of manganese and nickel into the electrolyte.
 11. The method of claim 10, further comprising separating at least one of nickel and lithium from at least one of manganese and cobalt.
 12. The method of claim 11, wherein separating at least one of nickel and lithium from at least one of manganese and cobalt comprises contacting the electrolyte with an organic solvent to absorb the at least one of manganese and cobalt in the organic solvent.
 13. The method of claim 11, further comprising one of: contacting the electrolyte with a nickel separation agent to form a nickel-containing material and separate the nickel from the lithium; or passing the electrolyte through an ion exchange resin formulated and configured to selectively adsorb at least one of nickel, manganese, or cobalt from the electrolyte.
 14. The method of claim 1, further comprising recycling the electrolyte to the electrochemical cell after removing substantially all of the at least one of lithium and cobalt from the electrolyte.
 15. The method of claim 1, wherein contacting the active material in the cathode chamber with an electrolyte comprising an acid, ferric ions, and ferrous ions comprises contacting the active material with an electrolyte comprising at least one organic acid.
 16. The method of claim 15, further comprising forming, in a vessel, the at least one organic acid with an organism comprising one or more of *Gluconobacter oxydans*, *Aspergillus niger*, and *Ceriporiopsis subvermispota*.
 17. The method of claim 16, further comprising providing the at least one organic acid from the vessel to the electrochemical cell.
 18. The method of claim 16, wherein forming, in a vessel, the at least one organic acid comprises forming gluconic acid in the vessel.
 19. An apparatus for recovering metals from active materials of rechargeable batteries, the apparatus comprising: an electrochemical cell comprising an anode, a cathode, a membrane between the anode and the cathode, and an electrolyte, the electrolyte comprising: an acid; ferric ions; ferrous ions; and an active material of a rechargeable battery; and a system for recovering at least one of lithium and cobalt from the electrolyte in operable communication with the electrochemical cell.
 20. The apparatus of claim 19, wherein the acid comprises gluconic acid, the apparatus further comprising a vessel including bacteria that metabolically generates the gluconic acid.
 21. The apparatus of claim 20, wherein the vessel is in fluid communication with the electrochemical cell.
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