ion cell, such as the popular 18650 lithium-ion cell, is a 3.7 or a 4.2 volt cell with up to about 8 total grams of lithium. Prior recovery methods are energy intensive and generally not economical for the recovery of lithium from spent batteries.

BREIF DESCRIPTION OF THE FIGURES

[0006] FIG. 1 is a flow diagram of an exemplary lithium recovery process; and

[0007] FIG. 2 is another flow diagram of an exemplary lithium recovery process.

SUMMARY

[0007a] In a first aspect of the present disclosure, there is provided a method of recovering graphene from a spent rechargeable lithium ion cell or battery, the method comprising:

disassembling a lithium ion cell or battery to separate an anode from a cathode to form a disassembled lithium ion cell or battery to provide an entire anode from the disassembled spent rechargeable lithium ion cell or battery as a whole component part;

mixing the entire anode as a whole component part from the disassembled lithium ion cell or battery with an acid at a temperature of about 10°C to about 100°C to form an acidic solution including graphene from the anode, lithium, and optionally one or more of soluble organics, soluble metals, and suspended solids;

wherein the acid has a pH of about 2.5 or less and includes hydrochloric acid, sulfuric acid, nitric acid, acetic acid, citric acid, or combinations thereof; and

separating the graphene from the acidic solution separate from the soluble metals.

[0007b] In another aspect of the present disclosure, there is provided an acid treated graphene obtained from a spent rechargeable lithium-ion cell or battery, the acid treated graphene obtained by disassembling a spent rechargeable lithium ion cell or battery to separate an anode from a cathode to form a disassembled lithium ion cell or battery providing an entire anode from the disassembled spent rechargeable lithium ion cell or battery as a whole component part, mixing the entire anode of the disassembled lithium ion cell or battery in an acid to form an acidic solution, the mixing at a temperature of about 10°C to about 100°C and the acidic solution including graphene from the anode, lithium, and one or more of soluble organics, soluble metals, and suspended solids and wherein the acid has a pH of about

2.5 or less and includes hydrochloric acid, sulfuric acid, nitric acid, acetic acid, citric acid, or combinations thereof, and separating the acid treated graphene from the acidic solution separate from the soluble metals.

[0007c] In another aspect of the present disclosure, there is provided a system including an acidic solution for recovery of graphene from a spent rechargeable lithium ion cell or battery, the system including a tank, an acid contained in the tank, an entire anode from a disassembled spent rechargeable lithium ion cell or battery as a whole component part directly added to the acid in the tank, graphene in the acid from a the disassembled anode of the spent lithium ion cell or battery, and one or more of soluble organics, soluble metals, and suspended solids, the acid includes hydrochloric acid, sulfuric acid, nitric acid, or combinations thereof and has an acid concentration of about 0.5 to about 30 weight percent in an aqueous solution with a pH of about 2.5 or less wherein the acid solubilizes the metals from the spent lithium ion cell or battery so that the graphene is recoverable from the acid solution separate from the metals, and wherein the graphene from the anode is recovered from the acidic solution separate from the soluble metals dissolved in the acid.

[0008] In one example, the present disclosure provides a method of recovering lithium from a lithium-containing material. The method includes mixing a lithium-containing material in an acid solution to form an acidic lithium solution. The mixing occurs at a temperature of about 10°C to about 100°C. The acidic lithium solution includes at least one or more of the acid solution, lithium, soluble organics, soluble metals, and suspended solids. After mixing, the acidic lithium solution is delivered to an ultrafiltration pretreatment membrane to retain a majority of the suspended solids and to permeate a filtered acidic lithium solution including at least one or more of the acid solution, the lithium, the soluble organics, and the soluble metals. Next, the filtered acidic lithium solution is delivered to a nanofiltration membrane to form a retentate and a permeate. The nanofiltration retentate includes one or both of the soluble organics and the soluble metals and the nanofiltration permeate forms a filtered acid and lithium solution including the acid solution and the lithium. The filtered acid and lithium solution is then delivered to a reverse osmosis membrane to form a retentate and permeate. The reverse osmosis retentate includes the lithium and the reverse osmosis permeate includes the acid solution. Lastly, the lithium is recovered as lithium salts from the reverse osmosis retentate and, the reverse osmosis permeate is optionally recycled to the mixing step.

[0009] The method of the previous paragraph may be combined with one or more additional method steps or features. These additional methods steps or features include one or more of the following: wherein the acid solution includes hydrochloric acid, sulfuric acid, nitric acid, acetic acid, citric acid, and combinations thereof; wherein the acid solution has a pH of about 2.5 or less; wherein the lithium-containing material is a lithium ion battery or a lithium-containing mineral deposit; wherein one or both of the nanofiltration membrane and the reverse osmosis membrane are chlorinated; wherein the ultrafiltration pretreatment

membrane has a pore size of about 0.01 microns to about 0.5 microns and is operated at about 10 to about 100 psi; wherein the nanofiltration membrane has a pore size of about 0.0007 microns to about 0.0012 microns and is operated at about 200 to about 2000 psi; wherein the reverse osmosis membrane has a pore size of about 0.0005 microns to about 0.001 microns and is operated at about 200 to about 2000 psi; wherein the lithium-containing material is a lithium ion battery or cell including a metal oxide cathode, a carbon anode, an electrolyte, and a polymeric separator and wherein the mixing step includes placing the metal oxide cathode, the carbon anode, the electrolyte, and the polymeric separator in the acid solution; wherein the lithium-containing material is a lithium containing mineral deposit and wherein the mixing step includes a ratio of the lithium containing mineral deposit to the acid solution of about 1:2 to about 1:20 to leach the lithium from the lithium containing mineral deposit to form the acidic lithium solution; and/or wherein the mixing step of the lithium containing mineral deposit and the acid solution further includes a polymeric material selected from alkyl carbonate and mixtures of alkyl carbonates.

[0010] In another example, the present disclosure provides a method of recovering lithium from a lithium-containing material including the following method steps and features: first, a lithium-containing material is mixed in an acid solution having a pH of about 2.5 or less to form an acidic lithium solution. The mixing occurs at a temperature of about 10°C to about 100°C. The acidic lithium solution includes at least one or more of the acid solution, lithium, soluble organics, soluble metals, and suspended solids. Second, the acidic lithium solution is then filtered in a semipermeable membrane to substantially retain the suspended solids and to substantially permeate one or more of the acid solution, the lithium, the soluble organics, and the soluble metals to form a filtered acidic lithium solution. Third, the filtered acidic lithium solution is next filtered in a first chlorinated semipermeable membrane to substantially retain one or both of the soluble organics and the soluble metals and to substantially permeate the acid solution and the lithium to form a filtered acid and lithium solution. Fourth, the filtered acid and lithium solution is then filtered in a second chlorinated semipermeable membrane to substantially retain lithium and to substantially permeate the acid solution. Lastly, the lithium is recovered as lithium salts from the retained lithium and, optionally, the permeated acid solution from the second chlorinated semipermeable membrane is recycled to the mixing step.

[0011] The method of the previous paragraph may be combined with one or more additional method steps or features. These additional methods steps or features include one

WHAT IS CLAIMED IS:

1. A method of recovering graphene from a spent rechargeable lithium ion cell or battery, the method comprising:

disassembling a lithium ion cell or battery to separate an anode from a cathode to form a disassembled lithium ion cell or battery to provide an entire anode from the disassembled spent rechargeable lithium ion cell or battery as a whole component part;

mixing the entire anode as a whole component part from the disassembled lithium ion cell or battery with an acid at a temperature of about 10°C to about 100°C to form an acidic solution including graphene from the anode, lithium, and optionally one or more of soluble organics, soluble metals, and suspended solids;

wherein the acid has a pH of about 2.5 or less and includes hydrochloric acid, sulfuric acid, nitric acid, acetic acid, citric acid, or combinations thereof; and

separating the graphene from the acidic solution separate from the soluble metals.

2. The method of recovering graphene of claim 1, wherein the dissembling includes removing a shell surrounding the anode, the cathode, and an electrolyte of the lithium ion cell or battery.

3. The method of recovering graphene of claim 1, wherein the acid has an acid concentration of about 0.5 to about 30 weight percent in an aqueous solution with a pH of about 1 or less.

4. The method of recovering graphene of claim 1, wherein the mixing is for about 1 minute to about 120 minutes.

5. The method of recovering graphene of claim 1, wherein the mixing is at a temperature of about 50ºC to about 70ºC.

6. The method of recovering graphene of claim 1, further comprising delivering the acidic solution to an ultrafiltration membrane to separate a majority of the suspended solids from a permeate including at least one or more of the acid, the lithium, the soluble organics, and the soluble metals.

7. The method of recovering graphene of claim 6, wherein the ultrafiltration membrane has a pore size of about 0.01 microns to about 0.5 microns and is operated at about 10 to about 100 psi.

8. The method of recovering graphene of claim 1, wherein the spent rechargeable lithium ion cell or battery includes a metal oxide cathode, a metal foil anode, an electrolyte, and a polymeric separator.

9. The method of recovering graphene of claim 8, wherein the metal oxide cathode is an aluminum foil having a coating of cobalt nickel alloy, lithium cobalt oxide, lithium iron phosphate, lithium manganese oxides, lithium fluoride phosphate, lithium moly oxide, nickel cobalt oxide, or combinations thereof.

10. The method of recovering graphene of claim 8, wherein the electrolyte is a polymeric organic, organic solvent, phosphate, fluoride, a lithium salt, phosphate fluoride, or combinations thereof.

11. The method of recovering graphene of claim 8, wherein the polymeric separator is polypropylene, polyethylene, or combinations thereof.

12. An acid treated graphene obtained from a spent rechargeable lithium-ion cell or battery, the acid treated graphene obtained by disassembling a spent rechargeable lithium ion cell or battery to separate an anode from a cathode to form a disassembled lithium ion cell or battery providing an entire anode from the disassembled spent rechargeable lithium ion cell or battery as a whole component part, mixing the entire anode of the disassembled lithium ion cell or battery in an acid to form an acidic solution, the mixing at a temperature of about 10°C to about 100°C and the acidic solution including graphene from the anode, lithium, and one or more of soluble organics, soluble metals, and suspended solids and wherein the acid has a pH of about 2.5 or less and includes hydrochloric acid, sulfuric acid, nitric acid, acetic acid, citric acid, or combinations thereof, and separating the acid treated graphene from the acidic solution separate from the soluble metals.

13. The acid treated graphene of claim 12, wherein the acid has an acid concentration of about 0.5 to about 30 weight percent in an aqueous solution with a pH of about 1 or less.

14. The acid treated graphene of claim 12, wherein the spent rechargeable lithium ion cell or battery includes a metal oxide cathode, a metal foil anode, an electrolyte, and a polymeric separator.

15. A system including an acidic solution for recovery of graphene from a spent rechargeable lithium ion cell or battery, the system including a tank, an acid contained in the tank, an entire anode from a disassembled spent rechargeable lithium ion cell or battery as a whole component part directly added to the acid in the tank, graphene in the acid from a the disassembled anode of the spent lithium ion cell or battery, and one or more of soluble organics, soluble metals, and suspended solids, the acid includes hydrochloric acid, sulfuric acid, nitric acid, or combinations thereof and has an acid concentration of about 0.5 to about 30 weight percent in an aqueous solution with a pH of about 2.5 or less wherein the acid solubilizes the metals from the spent lithium ion cell or battery so that the graphene is recoverable from the acid solution separate from the metals, and wherein the graphene from the anode is recovered from the acidic solution separate from the soluble metals dissolved in the acid.

16. The system of claim 15, further including the soluble metals selected from the group consisting of calcium, magnesium, zinc, copper, aluminum, iron, rare earth metals, cobalt, nickel, or combinations thereof.

17. The system of claim 15, wherein a temperature of acidic solution is about 50°C to about 70°C.

18. The system of claim 15, wherein the acid is sulfuric acid.

19. The system of claim 18, wherein the acidic solution includes one or more of a copper foil anode covered with the graphene; and optionally one or more of an aluminum foil cathode covered with one or more of a cobalt nickel alloy, lithium cobalt oxide, lithium iron phosphate, lithium manganese oxides, lithium fluoride phosphate, lithium moly oxide, or

nickel cobalt oxide; an electrolyte including one or more of polymeric organics, organic solvents, phosphates, fluorides, lithium salts, organic solvents, lithium, or phosphate fluoride; a polymeric separator including polypropylene or polyethylene; or a battery case of a metal or polymeric laminate.

20. The system of claim 18, wherein the acidic solution includes about 100 to about 5000 ppm of lithium.