(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
04 February 2021 (04.02.2021)

WIPO | PCT

(10) International Publication Number
WO 2021/021685 A1

(51) International Patent Classification:
H01M 4/24 (2006.01) *H01M 8/0232* (2016.01)
H01M 4/86 (2006.01) *H01M 12/08* (2006.01)
H01M 4/74 (2006.01) *H01M 8/18* (2006.01)

(21) International Application Number:
PCT/US2020/043639

(22) International Filing Date:
25 July 2020 (25.07.2020)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
62/879,126 26 July 2019 (26.07.2019) US
63/021,566 07 May 2020 (07.05.2020) US

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(54) Title: LOW COST METAL ELECTRODES

(57) Abstract: Systems and methods of the various embodiments may provide metal electrodes for electrochemical cells. In various embodiments, the electrodes may comprise iron. Various methods may enable achieving high surface area with low cost for production of metal electrodes, such as iron electrodes.

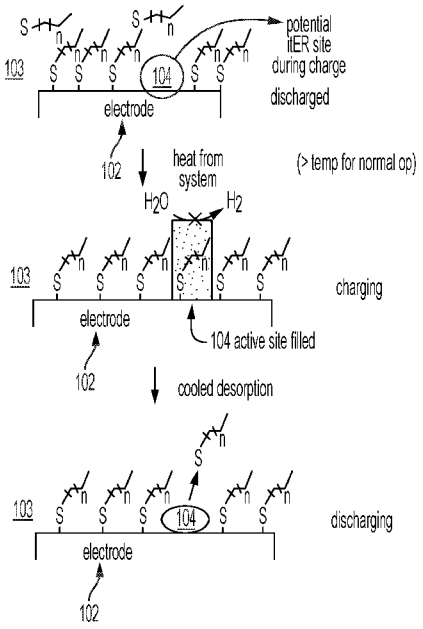


FIG. 1

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(81) **Designated States** *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, IT, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS, ZA, ZM, ZW.

(84) **Designated States** *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report (Art. 21(3))*

LOW COST METAL ELECTRODES

RELATED APPLICATIONS

[0001] This application claims the benefit of priority to U.S. Provisional Patent Application No. 62/879,126 entitled "Low Cost Metal Electrodes" filed July 26, 2019 and U.S. Provisional Patent Application No. 63/021,566 entitled "Low Cost Metal Electrodes" filed May 7, 2020 and the entire contents of both applications are hereby incorporated by reference for all purposes.

BACKGROUND

[0002] Energy storage technologies are playing an increasingly important role in electric power grids; at a most basic level, these energy storage assets provide smoothing to better match generation and demand on a grid. The services performed by energy storage devices are beneficial to electric power grids across multiple time scales, from milliseconds to years. Today, energy storage technologies exist that can support timescales from milliseconds to hours, but there is a need for long and ultra-long duration (collectively, >8h) energy storage systems.

[0003] This Background section is intended to introduce various aspects of the art, which may be associated with embodiments of the present inventions. Thus, the foregoing discussion in this section provides a framework for better understanding the present inventions, and is not to be viewed as an admission of prior art.

SUMMARY

[0004] Materials, designs, and methods of fabrication for metal electrodes for electrochemical cells are disclosed. In various embodiments, the electrode comprises iron. Various methods for achieving high surface area with low cost and high simple, highly scalable manufacturing methods are described.

[0005] Various embodiments may include a battery comprising: a first electrode; an electrolyte; and a second electrode, wherein at least one of the first electrode and the second electrode comprises atomized metal powder.

[0006] Various embodiments may include a battery comprising: a first electrode; an electrolyte; and a second electrode, wherein at least one of the first electrode and the second electrode comprises iron agglomerates.

[0007] Various embodiments may include a method of making an electrode, comprising: electrochemically producing metal powder; and forming the metal powder into an electrode.

BRIEF DESCRIPTION OF THE FIGURES

[0008] The accompanying drawings, which are incorporated herein and constitute part of this specification, illustrate example embodiments of the claims, and together with the general description given above and the detailed description given below, serve to explain the features of the claims.

[0009] FIG. 1 illustrates an example discharge method.

[0010] FIGS. 2 and 3 illustrate aspects of an electrode divided up into horizontal layers contained in a larger vessel.

[0011] FIG. 4 illustrates a metal textile with an electrode composed of direct reduced iron pellets

[0012] FIGS. 5 and 6 illustrate example porous mesh container aspects.

[0013] FIG. 7 illustrates an example backing plate.

[0014] FIG. 8 fastening rail may also serve as a bus bar

[0015] FIG. 9 illustrates a direct reduced iron (DRI) marble bed assembly.

[0016] FIG. 10 illustrates a module consisting of a rigid side walls.

[0017] FIGS. 11A and 11B show fastening techniques according to various embodiments.

[0018] FIG. 12 illustrates an expanding material contained within a rigid iron electrode containment assembly.

[0019] FIG. 13 illustrates thermal bonding.

[0020] FIG. 14 illustrates mechanical interactions of pellets.

[0021] FIG. 15 illustrates pellet beds.

[0022] FIG. 16 illustrates example current collectors.

[0023] FIG. 17 illustrates a mechanically processed pellet.

[0024] FIG. 18 compares discharge product distributions.

[0025] FIG. 19 is a temperature plot.

[0026] FIG. 20 illustrates one example method of evacuating pores.

[0027] FIG. 21 illustrates example additive holder configurations.

[0028] FIG. 22 illustrates an example additive incorporation process.

[0029] FIG. 23 illustrates an electrode formation process.

[0030] FIGS. 24-32 illustrate various example systems in which one or more aspects of the various embodiments may be used as part of bulk energy storage systems.

DETAILED DESCRIPTION

[0031] The various embodiments will be described in detail with reference to the accompanying drawings. Wherever possible, the same reference numbers will be used throughout the drawings to refer to the same or like parts. References made to particular examples and implementations are for illustrative purposes and are not intended to limit the scope of the claims. The following description of the embodiments of the invention is not intended to limit the invention to these embodiments but rather to enable a person skilled in the art to make and use this invention. Unless otherwise noted, the accompanying drawings are not drawn to scale.

[0032] As used herein, unless stated otherwise, room temperature is 25° C. And, standard temperature and pressure is 25° C and 1 atmosphere. Unless expressly stated otherwise all tests, test results, physical properties, and values that are temperature dependent, pressure dependent, or both, are provided at standard ambient temperature and pressure.

[0033] Generally, the term "about" and the symbol "~" as used herein unless specified otherwise is meant to encompass a variance or range of ±10%, the experimental or instrument error associated with obtaining the stated value, and preferably the larger of these.

[0034] As used herein unless specified otherwise, the recitation of ranges of values herein is merely intended to serve as a shorthand method of referring individually to each separate value falling within the range. Unless otherwise indicated herein, each individual value within a range is incorporated into the specification as if it were individually recited herein.

[0035] As used herein, unless specified otherwise the terms %, weight % and mass % are used interchangeably and refer to the weight of a first component as a percentage of the weight of the total, e.g., formulation, mixture, particle, pellet, agglomerate, material, structure or product. As used herein, unless specified otherwise "volume %" and "% volume" and similar such terms refer to the volume of a first component as a percentage of the volume of the total, e.g., formulation, mixture, particle, pellet, agglomerate, material, structure or product.

[0036] The following examples are provided to illustrate various embodiments of the present systems and methods of the present inventions. These examples are for illustrative purposes, may be prophetic, and should not be viewed as limiting, and do not otherwise limit the scope of the present inventions.

[0037] It is noted that there is no requirement to provide or address the theory underlying the novel and groundbreaking processes, materials, performance or other beneficial features and properties that are the subject of, or associated with, embodiments of the present inventions. Nevertheless, various theories are provided in this specification to further advance the art in this area. The theories put forth in this specification, and unless expressly stated otherwise, in no way limit, restrict or narrow the scope of protection to be afforded the claimed inventions. These theories many not be required or practiced to utilize the present inventions. It is further understood that the present inventions may lead to new, and heretofore unknown theories to explain the function-features of embodiments of the methods, articles, materials, devices and system of the present inventions; and such later developed theories shall not limit the scope of protection afforded the present inventions.

[0038] The various embodiments of systems, equipment, techniques, methods, activities and operations set forth in this specification may be used for various other activities and in other fields in addition to those set forth herein. Additionally, these embodiments, for example, may be used with: other equipment or activities that may be developed in the future; and, with existing equipment or activities which may be modified, in-part, based on the teachings of this specification. Further, the various embodiments and examples set forth in this specification may be used with each other, in whole or in part, and in different and various combinations. Thus, the configurations provided in the various embodiments of this specification may be used with each other. For example, the components of an embodiment having A, A' and B and the components of an embodiment having A'', C and D can be used with each other in various combination, e.g., A, C, D, and A. A'' C and D, etc., in accordance

with the teaching of this Specification. Thus, the scope of protection afforded the present inventions should not be limited to a particular embodiment, configuration or arrangement that is set forth in a particular embodiment, example, or in an embodiment in a particular figure.

[0039] As used herein, unless specified otherwise, the terms specific gravity, which is also called apparent density, should be given their broadest possible meanings, and generally mean weight per unit until volume of a structure, e.g., volumetric shape of material. This property would include internal porosity of a particle as part of its volume. It can be measured with a low viscosity fluid that wets the particle surface, among other techniques.

[0040] As used herein, unless specified otherwise, the terms actual density, which may also be called true density, should be given their broadest possible meanings, and general mean weight per unit volume of a material, when there are no voids present in that material. This measurement and property essentially eliminates any internal porosity from the material, e.g., it does not include any voids in the material.

[0041] Thus, a collection of porous foam balls (e.g., Nerf® balls) can be used to illustrate the relationship between the three density properties. The weight of the balls filling a container would be the bulk density for the balls:

$$Bulk\ Density = \frac{weight\ of\ balls}{volume\ of\ container\ filled}$$

[0042] The weight of a single ball per the ball's spherical volume would be its apparent density:

$$Apparent\ Density = \frac{weight\ of\ one\ ball}{volume\ of\ that\ ball}$$

[0043] The weight of the material making up the skeleton of the ball, *i.e.*, the ball with all void volume removed, per the remaining volume of that material would be the skeletal density:

$$Skeletal\ Density = \frac{weight\ of\ material}{volume\ of\ void\ free\ material}$$

[0044] As used herein, unless specified otherwise, the term agglomerate and aggregate should be given their broadest possible meanings, and in general mean assemblages of particles in a powder.

[0045] Embodiments of the present invention include apparatus, systems, and methods for long-duration, and ultra-long-duration, low-cost, energy storage. Herein, "long duration" and

"ultra-long duration" and similar such terms, unless expressly stated otherwise, should be given their broadest possible meaning and include periods of energy storage of 8 hours or longer, such as periods of energy storage of 8 hours, periods of energy storage ranging from 8 hours to 20 hours, periods of energy storage of 20 hours, periods of energy storage ranging from 20 hours to 24 hours, periods of energy storage of 24 hours, periods of energy storage ranging from 24 hours to a week, periods of energy storage ranging from a week to a year (e.g., such as from several days to several weeks to several months), etc. and would include LODES systems. Further, the terms "long duration" and "ultra-long duration", "energy storage cells" including "electrochemical cells", and similar such terms, unless expressly stated otherwise, should be given their broadest possible interpretation; and include electrochemical cells that may be configured to store energy over time spans of days, weeks, or seasons.

[0046] In general, in an embodiment, the long duration energy storage cell can be a long duration electrochemical cell. In general, this long duration electrochemical cell can store electricity generated from an electrical generation system, when: (i) the power source or fuel for that generation is available, abundant, inexpensive, and combinations and variations of these; (ii) when the power requirements or electrical needs of the electrical grid, customer or other user, are less than the amount of electricity generated by the electrical generation system, the price paid for providing such power to the grid, customer or other user, is below an economically efficient point for the generation of such power (e.g., cost of generation exceeds market price for the electricity), and combinations and variations of these; and (iii) combinations and variations of (i) and (ii) as well as other reasons. This electricity stored in the long duration electrochemical cell can then be distributed to the grid, customer or other user, at times when it is economical or otherwise needed. For example, the electrochemical cells may be configured to store energy generated by solar cells during the summer months, when sunshine is plentiful and solar power generation exceeds power grid requirements, and discharge the stored energy during the winter months, when sunshine may be insufficient to satisfy power grid requirements.

[0047] Various embodiments are discussed in relation to the use of direct reduced iron (DRI) as a material a battery (or cell), as a component of a battery (or cell) and combinations and variations of these. In various embodiments, the DRI may be produced from, or may be, material which is obtained from the reduction of natural or processed iron ores, such reduction being conducted without reaching the melting temperature of iron. In various

embodiments the iron ore may be taconite or magnetite or hematite or goethite, etc. In various embodiments, the DRI may be in the form of pellets, which may be spherical or substantially spherical. In various embodiments the DRI may be porous, containing open and/or closed internal porosity. In various embodiments the DRI may comprise materials that have been further processed by hot or cold briquetting. In various embodiments, the DRI may be produced by reducing iron ore pellets to form a more metallic (more reduced, less highly oxidized) material, such as iron metal (Fe^0), wustite (FeO), or a composite pellet comprising iron metal and residual oxide phases. In various non-limiting embodiments, the DRI may be reduced iron ore taconite, direct reduced ("DR") taconite, reduced "Blast Furnace (BF) Grade" pellets, reduced "Electric Arc Furnace (EAF)-Grade" pellets, "Cold Direct Reduced Iron (CDRI)" pellets, direct reduced iron ("DRI") pellets, Hot Briquetted Iron (HBI), or any combination thereof. In the iron and steelmaking industry, DRI is sometimes referred to as "sponge iron;" this usage is particularly common in India. Embodiments of iron materials, including for example embodiments of DRI materials, for use in various embodiments described herein, including as electrode materials, may have, one, more than one, or all of the material properties as described in Table 1 below. As used in the Specification, including Table 1, the following terms, have the following meaning, unless expressly stated otherwise: "Specific surface area" means, the total surface area of a material per unit of mass, which includes the surface area of the pores in a porous structure; "Carbon content" or "Carbon (wt%)" means the mass of total carbon as percent of total mass of DRI; "Cementite content" or "Cementite (wt%)" means the mass of Fe_3C as percent of total mass of DRI; "Total Fe (wt%)" means the mass of total iron as percent of total mass of DRI; "Metallic Fe (wt%)" means the mass of iron in the Fe^0 state as percent of total mass of DRI; and "Metallization" means the mass of iron in the Fe^0 state as percent of total iron mass. Weight and volume percentages and apparent densities as used herein are understood to exclude any electrolyte that has infiltrated porosity or fugitive additives within porosity unless otherwise stated.

Table 1

Material Property	Embodiment Range
Specific surface area*	0.01 - 25 m^2/g
Actual density**	4.6 - 7.1 g/cc
Apparent density***	2.3 - 6.5 g/cc
Minimum $d_{pore,\ 90\%\ volume}$****	10 nm - 50 μm

Minimum $d_{pore,\ 50\%\ surface\ area}$*****	1 nm - 15 μm
Total Fe (wt%)#	65 - 95 %
Metallic Fe (wt%)##	46 - 90 %
Metallization (%)###	59 - 96 %
Carbon (wt%)####	0 - 5 %
Fe^{2+} (wt%)#####	1 - 9 %
Fe^{3+} (wt%)$	0.9 - 25 %
SiO_2 (wt %)$$	1 - 15 %
Ferrite (wt%, XRD)$$$	22 - 97 %
Wustite (FeO, wt%, XRD)$$$$	0 - 13 %
Goethite (FeOOH, wt%, XRD)$$$$$	0 - 23 %
Cementite (Fe_3C, wt%, XRD)+	≪ 80 %

[0048] *Specific surface area preferably determined by the Brunauer-Emmett-Teller adsorption method ("BET"), and more preferably as the BET is set forth in ISO 9277 (the entire disclosure of which is incorporated herein by reference); recognizing that other tests, such as methylene blue (MB) staining, ethylene glycol monoethyl ether (EGME) adsorption, electrokinetic analysis of complex-ion adsorption and a Protein Retention (PR) method may be employed to provide results that can be correlated with BET results.

[0049] **Actual density preferably determined by helium (He) pycnometry, and more preferably as is set forth in ISO 12154 (the entire disclosure of which is incorporated herein by reference); recognizing that other tests may be employed to provide results that can be correlated with He pycnometry results. Actual density may also be referred to as "true density" or "skeletal density" in the art.

[0050] ***Apparent density preferably determined by immersion in water, and more preferably as is set forth in ISO 15968 (the entire disclosure of which is incorporated herein by reference); recognizing that other tests may be employed to provide results that can be correlated with He pycnometry results. Porosity may be defined as the ratio of apparent density to actual density:

$$Porosity = \frac{apparent\ density}{actual\ density}$$

[0051] ****$d_{\text{pore, 90\% volume}}$ preferably determined by mercury (Hg) intrusion porosimetry, and more preferably as is set forth in ISO 15901-1 (the entire disclosure of which is incorporated herein by reference); recognizing that other tests, such as gas adsorption, may be employed to provide results that can be correlated with Hg intrusion results. $d_{\text{pore, 90\% volume}}$ is the pore diameter above which 90% of the total pore volume exists.

[0052] *****$d_{\text{pore, 50\% surface area}}$ preferably determined by mercury (Hg) intrusion porosimetry, and more preferably as is set forth in ISO 15901-1 (the entire disclosure of which is incorporated herein by reference); recognizing that other tests, such as gas adsorption, may be employed to provide results that can be correlated with Hg intrusion results. $d_{\text{pore, 50\% surface area}}$ is the pore diameter above which 50% of free surface area exists.

[0053] #Total Fe (wt%) preferably determined by dichromate titrimetry, and more preferably as is set forth in ASTM E246-10 (the entire disclosure of which is incorporated herein by reference); recognizing that other tests, such as titrimetry after tin(II) chloride reduction, titrimetry after titanium(III) chloride reduction, inductively coupled plasma (ICP) spectrometry, may be employed to provide results that can be correlated with dichromate titrimetry.

[0054] ##Metallic Fe (wt%) preferably determined by iron(III) chloride titrimetry, and more preferably as is set forth in ISO 16878 (the entire disclosure of which is incorporated herein by reference); recognizing that other tests, such as bromine-methanol titimetry, may be employed to provide results that can be correlated with iron(III) chloride titrimetry.

[0055] ###Metallization (%) preferably determined by the ratio of metallic Fe to total Fe, each as preferably determined by the methods previously described.

[0056] #### Carbon (wt%) preferably determined by infrared absorption after combustion in an induction furnace, and more preferably as is set forth in ISO 9556 (the entire disclosure of which is incorporated herein by reference); recognizing that other tests, such as various combustion and inert gas fusion techniques, such as are described in ASTM E1019-18 may be employed to provide results that can be correlated with infrared absorption after combustion in an induction furnace.

[0057] ##### Fe^{2+} (wt%) preferably determined by titrimetry, and more preferably as is set forth in ASTM D3872-05 (the entire disclosure of which is incorporated herein by reference); recognizing that other tests, such as Mossbauer spectroscopy, X-ray absorption spectroscopy, etc., may be employed to provide results that can be correlated with titrimetry.

[0058] $ Fe^{3+} (wt%) preferably determined by the mass balance relation between and among Total Fe (wt%), Metallic Fe (wt%), Fe^{2+} (wt%) and Fe^{3+} (wt%). Specifically the equality Total Fe (wt%) = Metallic Fe (wt%) + Fe^{2+} (wt%) + Fe^{3+} (wt%) must be true by conservation of mass, so Fe^{3+} (wt%) may be calculated as Fe^{3+} (wt%) = Total Fe (wt%) - Metallic Fe (wt%) - Fe^{2+} (wt%).

[0059] $$ SiO_2 (wt %) preferably determined by gravimetric methods, and more preferably as is set forth in ISO 2598-1 (the entire disclosure of which is incorporated herein by reference); recognizing that other tests, such as reduced molybdosilicate spectrophotometric methods, x-ray diffraction (XRD), may be employed to provide results that can be correlated with gravimetric methods. In certain methods, the SiO_2 wt% is not determined directly, but rather the Si concentration (inclusive of neutral and ionic species) is measured, and the SiO_2 wt% is calculated assuming the stoichiometry of SiO_2; that is, a 1:2 molar ratio of Si:O is assumed.

[0060] $$$ Ferrite (wt%, XRD) preferably determined by x-ray diffraction (XRD).

[0061] $$$$ Wustite (FeO, wt%, XRD) preferably determined by x-ray diffraction (XRD).

[0062] $$$$$ Goethite (FeOOH, wt%, XRD) preferably determined by x-ray diffraction (XRD).

[0063] + Cementite (Fe_3C, wt%, XRD) preferably determined by x-ray diffraction (XRD).

[0064] Additionally, embodiments of iron materials, including for example embodiments of DRI materials, for use in various embodiments described herein, including as electrode materials, may have one or more of the following properties, features or characteristics, (noting that values from one row or one column may be present with values in different rows or columns) as set forth in Table 1A.

Table 1A

Fe total (wt %)[!]	> 60%	> 70%	> 80%	~83-94%
SiO_2 (wt %)[!!]	< 12%	< 7.5%	1-10%	1.5-7.5%
Al_2O_3 (wt %)[!!!]	< 10%	< 5%	0.2-5%	0.3-3%
MgO (wt %)[!!!!]	< 10%	< 5%	0.1-10%	0.25-2%
CaO (wt %)[!!!!!]	< 10%	< 5%	0.9-10%	0.75-2.5%

TiO_2 (wt %)[&]	< 10%	<2.5%	0.05-5%	0.25-1.5%
Size (largest cross-sectional distance, e.g. for a sphere the diameter)	< 200 mm	~ 50 to ~ 150 mm	~2 to ~30 mm	~4 to ~20 mm
Actual Density (g/cm^3)[&&]	~ 5	~5.8 to ~6.2	~4.0 to ~6.5	< 7.8
Apparent Density (g/cm^3)[&&&]	< 7.8	> 5	> 4	3.4 ~ 3.6
Bulk Density (kg/m^3)[&&&&]	< 7	> 1.5	~2.4 to ~3.4	~1.5 to ~2.0
Porosity (%)[&&&&&]	>15%	>50%	~ 20% to ~90%	~50% to ~70%

[0065] ! Total Fe (wt%) preferably determined by dichromate titrimetry, and more preferably as is set forth in ASTM E246-10 (the entire disclosure of which is incorporated herein by reference); recognizing that other tests, such as titrimetry after tin(II) chloride reduction, titrimetry after titanium(III) chloride reduction, inductively coupled plasma (ICP) spectrometry, may be employed to provide results that can be correlated with dichromate titrimetry.

[0066] !! SiO_2 (wt %) preferably determined by gravimetric methods, and more preferably as is set forth in ISO 2598-1 (the entire disclosure of which is incorporated herein by reference); recognizing that other tests, such as reduced molybdosilicate spectrophotometric methods, x-ray diffraction (XRD), may be employed to provide results that can be correlated with gravimetric methods. In certain methods, the SiO_2 wt% is not determined directly, but rather the Si concentration (inclusive of neutral and ionic species) is measured, and the SiO_2 wt% is calculated assuming the stoichiometry of SiO_2; that is, a 1:2 molar ratio of Si:O is assumed.

[0067] !!! Al_2O_3 (wt %) preferably determined by flame atomic absorption spectrometric method, and more preferably as is set forth in ISO 4688-1 (the entire disclosure of which is incorporated herein by reference); recognizing that other tests, such as x-ray diffraction (XRD), may be employed to provide results that can be correlated with flame atomic

absorption spectrometric method. In certain methods, the Al_2O_3 wt% is not determined directly, but rather the Al concentration (inclusive of neutral and ionic species) is measured, and the Al_2O_3 wt% is calculated assuming the stoichiometry of Al_2O_3; that is, a 2:3 molar ratio of Al:O is assumed.

[0068] !!!! MgO (wt %) preferably determined by flame atomic absorption spectrometric method, and more preferably as is set forth in ISO 10204 (the entire disclosure of which is incorporated herein by reference); recognizing that other tests, such as x-ray diffraction (XRD), may be employed to provide results that can be correlated with flame atomic absorption spectrometric method. In certain methods, the MgO wt% is not determined directly, but rather the Mg concentration (inclusive of neutral and ionic species) is measured, and the MgO wt% is calculated assuming the stoichiometry of MgO; that is, a 1:1 molar ratio of Mg:O is assumed.

[0069] !!!!! CaO (wt %) preferably determined by flame atomic absorption spectrometric method, and more preferably as is set forth in ISO 10203 (the entire disclosure of which is incorporated herein by reference); recognizing that other tests, such as x-ray diffraction (XRD), may be employed to provide results that can be correlated with flame atomic absorption spectrometric method. In certain methods, the CaO wt% is not determined directly, but rather the Ca concentration (inclusive of neutral and ionic species) is measured, and the CaO wt% is calculated assuming the stoichiometry of CaO; that is, a 1:1 molar ratio of Ca:O is assumed.

[0070] & TiO_2 (wt %) preferably determined by a diantipyrylmethane spectrophotometric method, and more preferably as is set forth in ISO 4691 (the entire disclosure of which is incorporated herein by reference); recognizing that other tests, such as x-ray diffraction (XRD), may be employed to provide results that can be correlated with the diantipyrylmethane spectrophotometric method method. In certain methods, the TiO_2 wt% is not determined directly, but rather the Ti concentration (inclusive of neutral and ionic species) is measured, and the TiO_2 wt% is calculated assuming the stoichiometry of TiO_2; that is, a 1:2 molar ratio of Ti:O is assumed.

[0071] && Actual density preferably determined by helium (He) pycnometry, and more preferably as is set forth in ISO 12154 (the entire disclosure of which is incorporated herein by reference); recognizing that other tests may be employed to provide results that can be

correlated with He pycnometry results. Actual density may also be referred to as "true density" or "skeletal density" in the art.

[0072] &&& Apparent density preferably determined by immersion in water, and more preferably as is set forth in ISO 15968 (the entire disclosure of which is incorporated herein by reference); recognizing that other tests may be employed to provide results that can be correlated with He pycnometry results.

[0073] &&&& Bulk Density (kg/m^3) preferably determined by measuring the mass of a test portion introduced into a container of known volume until its surface is level, and more preferably as is set forth in Method 2 of ISO 3852 (the entire disclosure of which is incorporated herein by reference); recognizing that other tests may be employed to provide results that can be correlated with the massing method.

[0074] &&&&& Porosity determined preferably by the ratio of the apparent density to the actual density:

$$Porosity = \frac{apparent\ density}{actual\ density}$$

[0075] The properties set forth in Table 1, may also be present in embodiments with, in addition to, or instead of the properties in Table 1A. Greater and lesser values for these properties may also be present in various embodiments.

[0076] In embodiments the specific surface area for the pellets can be from about 0.05 m^2/g to about 35 m^2/g, from about 0.1 m^2/g to about 5 m^2/g, from about 0.5 m^2/g to about 10 m^2/g, from about 0.2 m^2/g to about 5 m^2/g, from about 1 m^2/g to about 5 m^2/g, from about 1 m^2/g to about 20 m^2/g, greater than about 1 m^2/g, greater than about 2 m^2/g, less than about 5 m^2/g, less than about 15 m^2/g, less than about 20 m^2/g, and combinations and variations of these, as well as greater and smaller values.

[0077] In general, iron ore pellets are produced by crushing, grinding or milling of iron ore to a fine powdery form, which is then concentrated by removing impurity phases (so called "gangue") which are liberated by the grinding operation. In general, as the ore is ground to finer (smaller) particle sizes, the purity of the resulting concentrate is increased. The concentrate is then formed into a pellet by a pelletizing or balling process (using, for example, a drum or disk pelletizer). In general, greater energy input is required to produce higher purity ore pellets. Iron ore pellets are commonly marketed or sold under two principal categories: Blast Furnace (BF) grade pellets and Direct Reduction (DR Grade) (also

sometimes referred to as Electric Arc Furnace (EAF) Grade) with the principal distinction being the content of SiO_2 and other impurity phases being higher in the BF grade pellets relative to DR Grade pellets. Typical key specifications for a DR Grade pellet or feedstock are a total Fe content by mass percentage in the range of 63-69 wt% such as 67 wt% and a SiO_2 content by mass percentage of less than 3 wt% such as 1 wt%. Typical key specifications for a BF grade pellet or feedstock are a total Fe content by mass percentage in the range of 60-67 wt% such as 63 wt% and a SiO_2 content by mass percentage in the range of 2-8 wt% such as 4 wt%.

[0078] In certain embodiments the DRI may be produced by the reduction of a "Blast Furnace" pellet, in which case the resulting DRI may have material properties as described in Table 2 below. The use of reduced BF grade DRI may be advantageous due to the lesser input energy required to produce the pellet, which translates to a lower cost of the finished material.

Table 2

Material Property	Embodiment Range
Specific surface area*	0.21 - 25 m^2/g
Actual density**	5.5 - 6.7 g/cc
Apparent density***	3.1 - 4.8 g/cc
Minimum $d_{pore,\ 90\%\ volume}$****	50 nm - 50 μm
Minimum $d_{pore,\ 50\%\ surface\ area}$*****	1 nm - 10 μm
Total Fe (wt%)#	81.8 - 89.2 %
Metallic Fe (wt%)##	68.7 - 83.2 %
Metallization (%)###	84 - 95 %
Carbon (wt%)####	0.03 - 0.35%
Fe^{2+} (wt%)#####	2 - 8.7 %
Fe^{3+} (wt%)$	0.9 - 5.2 %
SiO_2 (wt %)$$	3 - 7 %
Ferrite (wt%, XRD)$$$	80 - 96 %
Wustite (FeO, wt%, XRD)$$$$	2 - 13 %
Goethite (FeOOH, wt%, XRD)$$$$$	0 - 11 %
Cementite (Fe_3C, wt%, XRD)+	0 - 80 %

[0079] *Specific surface area preferably determined by the Brunauer-Emmett-Teller adsorption method ("BET"), and more preferably as the BET is set forth in ISO 9277 (the entire disclosure of which is incorporated herein by reference); recognizing that other tests, such as methylene blue (MB) staining, ethylene glycol monoethyl ether (EGME) adsorption, electrokinetic analysis of complex-ion adsorption and a Protein Retention (PR) method may be employed to provide results that can be correlated with BET results.

[0080] **Actual density preferably determined by helium (He) pycnometry, and more preferably as is set forth in ISO 12154 (the entire disclosure of which is incorporated herein by reference); recognizing that other tests may be employed to provide results that can be correlated with He pycnometry results. Actual density may also be referred to as "true density" or "skeletal density" in the art.

[0081] ***Apparent density preferably determined by immersion in water, and more preferably as is set forth in ISO 15968 (the entire disclosure of which is incorporated herein by reference); recognizing that other tests may be employed to provide results that can be correlated with He pycnometry results. Porosity may be defined as the ratio of apparent density to actual density:

$$Porosity = \frac{apparent\ density}{actual\ density}$$

[0082] ****$d_{\text{pore, 90\% volume}}$ preferably determined by mercury (Hg) intrusion porosimetry, and more preferably as is set forth in ISO 15901-1 (the entire disclosure of which is incorporated herein by reference); recognizing that other tests, such as gas adsorption, may be employed to provide results that can be correlated with Hg intrusion results. $d_{\text{pore, 90\% volume}}$ is the pore diameter above which 90% of the total pore volume exists.

[0083] *****$d_{pore,\ 50\%\ \text{surface area}}$ preferably determined by mercury (Hg) intrusion porosimetry, and more preferably as is set forth in ISO 15901-1 (the entire disclosure of which is incorporated herein by reference); recognizing that other tests, such as gas adsorption, may be employed to provide results that can be correlated with Hg intrusion results. $d_{pore,\ 50\%\ \text{surface area}}$ is the pore diameter above which 50% of free surface area exists.

[0084] #Total Fe (wt%) preferably determined by dichromate titrimetry, and more preferably as is set forth in ASTM E246-10 (the entire disclosure of which is incorporated herein by reference); recognizing that other tests, such as titrimetry after tin(II) chloride reduction,

titrimetry after titanium(III) chloride reduction, inductively coupled plasma (ICP) spectrometry, may be employed to provide results that can be correlated with dichromate titrimetry.

[0085] ##Metallic Fe (wt%) preferably determined by iron(III) chloride titrimetry, and more preferably as is set forth in ISO 16878 (the entire disclosure of which is incorporated herein by reference); recognizing that other tests, such as bromine-methanol titimetry, may be employed to provide results that can be correlated with iron(III) chloride titrimetry.

[0086] ###Metallization (%) preferably determined by the ratio of metallic Fe to total Fe, each as preferably determined by the methods previously described.

[0087] #### Carbon (wt%) preferably determined by infrared absorption after combustion in an induction furnace, and more preferably as is set forth in ISO 9556 (the entire disclosure of which is incorporated herein by reference); recognizing that other tests, such as various combustion and inert gas fusion techniques, such as are described in ASTM E1019-18 may be employed to provide results that can be correlated with infrared absorption after combustion in an induction furnace.

[0088] ##### Fe^{2+} (wt%) preferably determined by titrimetry, and more preferably as is set forth in ASTM D3872-05 (the entire disclosure of which is incorporated herein by reference); recognizing that other tests, such as Mossbauer spectroscopy, X-ray absorption spectroscopy, etc., may be employed to provide results that can be correlated with titrimetry.

[0089] Fe^{3+} (wt%) preferably determined by the mass balance relation between and among Total Fe (wt%), Metallic Fe (wt%), Fe^{2+} (wt%) and Fe^{3+} (wt%). Specifically the equality Total Fe (wt%) = Metallic Fe (wt%) + Fe^{2+} (wt%) + Fe^{3+} (wt%) must be true by conservation of mass, so Fe^{3+} (wt%) may be calculated as Fe^{3+} (wt%) = Total Fe (wt%) - Metallic Fe (wt%) - Fe^{2+} (wt%).

[0090] $$ SiO_2 (wt %) preferably determined by gravimetric methods, and more preferably as is set forth in ISO 2598-1 (the entire disclosure of which is incorporated herein by reference); recognizing that other tests, such as reduced molybdosilicate spectrophotometric methods, x-ray diffraction (XRD), may be employed to provide results that can be correlated with gravimetric methods. In certain methods, the SiO_2 wt% is not determined directly, but rather the Si concentration (inclusive of neutral and ionic species) is measured, and the SiO_2 wt% is calculated assuming the stoichiometry of SiO_2; that is, a 1:2 molar ratio of Si:O is assumed.

[0091] $$$ Ferrite (wt%, XRD) preferably determined by x-ray diffraction (XRD).

[0092] $$$$ Wustite (FeO, wt%, XRD) preferably determined by x-ray diffraction (XRD).

[0093] $$$$$ Goethite (FeOOH, wt%, XRD) preferably determined by x-ray diffraction (XRD).

[0094] + Cementite (Fe_3C, wt%, XRD) preferably determined by x-ray diffraction (XRD).

[0095] The properties set forth in Table 2, may also be present in embodiments with, in addition to, or instead of the properties in Tables 1 and/or 1A. Greater and lesser values for these properties may also be present in various embodiments.

[0096] In certain embodiments the DRI may be produced by the reduction of a DR Grade pellet, in which case the resulting DRI may have material properties as described in Table 3 below. The use of reduced DR grade DRI may be advantageous due to the higher Fe content in the pellet which increases the energy density of the battery.

Table 3

Material Property	Embodiment Range
Specific surface area*	0.1 - 0.7 m^2/g as received or 0.19 – 25 m^2/g after performing a pre-charge formation step
Actual density**	4.6 - 7.1 g/cc
Apparent density***	2.3 - 5.7 g/cc
Minimum $d_{pore,\ 90\%\ volume}$****	50 nm - 50 µm
Minimum $d_{pore,\ 50\%\ surface\ area}$*****	1 nm - 10 µm
Total Fe (wt%)#	80 - 94 %
Metallic Fe (wt%)##	64 - 94 %
Metallization (%)###	80 - 100 %
Carbon (wt%)####	0 - 5 %
Fe^{2+} (wt%)#####	0 - 8 %
Fe^{3+} (wt%)$	0 - 10 %
SiO_2 (wt %)$$	1 - 4 %
Ferrite (wt%, XRD)$$$	22 - 80 %
Wustite (FeO, wt%, XRD)$$$$	0 - 13 %
Goethite (FeOOH, wt%, XRD)$$$$$	0 - 23 %

Cementite (Fe_3C, wt%, XRD)$^+$	$\ll$ 80 %

[0097] *Specific surface area preferably determined by the Brunauer-Emmett-Teller adsorption method ("BET"), and more preferably as the BET is set forth in ISO 9277 (the entire disclosure of which is incorporated herein by reference); recognizing that other tests, such as methylene blue (MB) staining, ethylene glycol monoethyl ether (EGME) adsorption, electrokinetic analysis of complex-ion adsorption and a Protein Retention (PR) method may be employed to provide results that can be correlated with BET results.

[0098] **Actual density preferably determined by helium (He) pycnometry, and more preferably as is set forth in ISO 12154 (the entire disclosure of which is incorporated herein by reference); recognizing that other tests may be employed to provide results that can be correlated with He pycnometry results. Actual density may also be referred to as "true density" or "skeletal density" in the art.

[0099] ***Apparent density preferably determined by immersion in water, and more preferably as is set forth in ISO 15968 (the entire disclosure of which is incorporated herein by reference); recognizing that other tests may be employed to provide results that can be correlated with He pycnometry results. Porosity may be defined as the ratio of apparent density to actual density:

$$Porosity = \frac{apparent\ density}{actual\ density}$$

[00100] ****$d_{\text{pore, 90\% volume}}$ preferably determined by mercury (Hg) intrusion porosimetry, and more preferably as is set forth in ISO 15901-1 (the entire disclosure of which is incorporated herein by reference); recognizing that other tests, such as gas adsorption, may be employed to provide results that can be correlated with Hg intrusion results. $d_{\text{pore, 90\% volume}}$ is the pore diameter above which 90% of the total pore volume exists.

[00101] *****$d_{pore,\ 50\%\ \text{surface area}}$ preferably determined by mercury (Hg) intrusion porosimetry, and more preferably as is set forth in ISO 15901-1 (the entire disclosure of which is incorporated herein by reference); recognizing that other tests, such as gas adsorption, may be employed to provide results that can be correlated with Hg intrusion results. $d_{pore,\ 50\%\ \text{surface area}}$ is the pore diameter above which 50% of free surface area exists.

[00102] #Total Fe (wt%) preferably determined by dichromate titrimetry, and more preferably as is set forth in ASTM E246-10 (the entire disclosure of which is incorporated herein by reference); recognizing that other tests, such as titrimetry after tin(II) chloride reduction, titrimetry after titanium(III) chloride reduction, inductively coupled plasma (ICP) spectrometry, may be employed to provide results that can be correlated with dichromate titrimetry.

[00103] ##Metallic Fe (wt%) preferably determined by iron(III) chloride titrimetry, and more preferably as is set forth in ISO 16878 (the entire disclosure of which is incorporated herein by reference); recognizing that other tests, such as bromine-methanol titimetry, may be employed to provide results that can be correlated with iron(III) chloride titrimetry.

[00104] ###Metallization (%) preferably determined by the ratio of metallic Fe to total Fe, each as preferably determined by the methods previously described.

[00105] #### Carbon (wt%) preferably determined by infrared absorption after combustion in an induction furnace, and more preferably as is set forth in ISO 9556 (the entire disclosure of which is incorporated herein by reference); recognizing that other tests, such as various combustion and inert gas fusion techniques, such as are described in ASTM E1019-18 may be employed to provide results that can be correlated with infrared absorption after combustion in an induction furnace.

[00106] ##### Fe^{2+} (wt%) preferably determined by titrimetry, and more preferably as is set forth in ASTM D3872-05 (the entire disclosure of which is incorporated herein by reference); recognizing that other tests, such as Mossbauer spectroscopy, X-ray absorption spectroscopy, etc., may be employed to provide results that can be correlated with titrimetry.

[00107] $ Fe^{3+} (wt%) preferably determined by the mass balance relation between and among Total Fe (wt%), Metallic Fe (wt%), Fe^{2+} (wt%) and Fe^{3+} (wt%). Specifically the equality Total Fe (wt%) = Metallic Fe (wt%) + Fe^{2+} (wt%) + Fe^{3+} (wt%) must be true by conservation of mass, so Fe^{3+} (wt%) may be calculated as Fe^{3+} (wt%) = Total Fe (wt%) - Metallic Fe (wt%) - Fe^{2+} (wt%).

[00108] $$ SiO_2 (wt %) preferably determined by gravimetric methods, and more preferably as is set forth in ISO 2598-1 (the entire disclosure of which is incorporated herein by reference); recognizing that other tests, such as reduced molybdosilicate spectrophotometric methods, x-ray diffraction (XRD), may be employed to provide results

that can be correlated with gravimetric methods. In certain methods, the SiO_2 wt% is not determined directly, but rather the Si concentration (inclusive of neutral and ionic species) is measured, and the SiO_2 wt% is calculated assuming the stoichiometry of SiO_2; that is, a 1:2 molar ratio of Si:O is assumed.

[00109] $$$ Ferrite (wt%, XRD) preferably determined by x-ray diffraction (XRD).

[00110] $$$$ Wustite (FeO, wt%, XRD) preferably determined by x-ray diffraction (XRD).

[00111] $$$$$ Goethite (FeOOH, wt%, XRD) preferably determined by x-ray diffraction (XRD).

[00112] + Cementite (Fe_3C, wt%, XRD) preferably determined by x-ray diffraction (XRD).

[00113] The properties set forth in Table 3, may also be present in embodiments with, in addition to, or instead of the properties in Tables 1, 1A, and/or 2. Greater and lesser values for these properties may also be present in various embodiments.

[00114] An electrochemical cell, such as a battery, stores electrochemical energy by using a difference in electrochemical potential generating a voltage difference between the positive and negative electrodes. This voltage difference produces an electric current if the electrodes are connected by a conductive element. In a battery, the negative electrode and positive electrode are connected by external and internal conductive elements in parallel. Generally, the external element conducts electrons, and the internal element (electrolyte) conducts ions. Because a charge imbalance cannot be sustained between the negative electrode and positive electrode, these two flow streams must supply ions and electrons at the same rate. In operation, the electronic current can be used to drive an external device. A rechargeable battery can be recharged by applying an opposing voltage difference that drives an electronic current and ionic current flowing in an opposite direction as that of a discharging battery in service.

[00115] In general, but particularly for long-duration storage applications, electrodes and electrode materials that are low-cost and simple to manufacture are desired. Manufacturing and/or fabrication processes may be evaluated and selected based on multiple criteria including capital cost, material throughput, operating costs, number of unit operations, number of material transfers, number of material handling steps, required energy input, amounts of generated waste products and/or by-products, etc.

[00116] The present invention relates to materials, electrodes and methods for electrochemical cells, including long-duration electrochemical cells for long-duration energy storage applications.

[00117] Various embodiments are discussed in relation to the use of metal agglomerates as a material in a battery (or cell), as a component of a battery (or cell), such as an electrode, and combinations and variations of these. In various embodiments, the iron material may be an iron powder such as a gas-atomized or water-atomized powder, or a sponge iron powder. In various embodiments, the iron agglomerates may be in the form of pellets, which may be spherical or substantially spherical. In various embodiments the agglomerates may be porous, containing open and/or closed internal porosity. In various embodiments the agglomerates may comprise materials that have been further processed by hot or cold briquetting. Embodiments of agglomerates materials for use in various embodiments described herein, including as electrode materials, may have, one, more than one, or all of the material properties as described in Table 4 below. As used in the Specification, including Table 4, the following terms, have the following meaning, unless expressly stated otherwise: "Specific surface area" means, the total surface area of a material per unit of mass, which includes the surface area of the pores in a porous structure; "Total Fe (wt%)" means the mass of total iron as percent of total mass of agglomerates; "Metallic Fe (wt%)" means the mass of iron in the Fe^0 state as percent of total mass of agglomerates.

Table 4

Material Property	Embodiment Range
Specific surface area*	0.01 - 25 m^2/g
Skeletal density**	4.6 - 7.8 g/cc
Apparent density***	1.5 - 6.5 g/cc
Total Fe (wt%)#	65 - 100 %
Metallic Fe (wt%)##	46 - 100 %

[00118] *Specific surface area preferably determined by the Brunauer-Emmett-Teller adsorption method ("BET"), and more preferably as the BET is set forth in ISO 9277 (the entire disclosure of which is incorporated herein by reference); recognizing that other tests, such as methylene blue (MB) staining, ethylene glycol monoethyl ether (EGME) adsorption, electrokinetic analysis of complex-ion adsorption and a Protein Retention (PR) method may be employed to provide results that can be correlated with BET results.

[00119] **Skeletal density preferably determined by helium (He) pycnometry, and more preferably as is set forth in ISO 12154 (the entire disclosure of which is incorporated herein by reference); recognizing that other tests may be employed to provide results that can be correlated with He pycnometry results. Skeletal density may also be referred to as "true density" or "actual density" in the art.

[00120] ***Apparent density preferably determined by immersion in water, and more preferably as is set forth in ISO 15968 (the entire disclosure of which is incorporated herein by reference); recognizing that other tests may be employed to provide results that can be correlated with He pycnometry results. Porosity may be defined as the ratio of apparent density to actual density:

$$Porosity = 1 - \frac{apparent\ density}{actual\ density}$$

[00121] #Total Fe (wt%) preferably determined by dichromate titrimetry, and more preferably as is set forth in ASTM E246-10 (the entire disclosure of which is incorporated herein by reference); recognizing that other tests, such as titrimetry after tin(II) chloride reduction, titrimetry after titanium(III) chloride reduction, inductively coupled plasma (ICP) spectrometry, may be employed to provide results that can be correlated with dichromate titrimetry.

[00122] ##Metallic Fe (wt%) preferably determined by iron(III) chloride titrimetry, and more preferably as is set forth in ISO 16878 (the entire disclosure of which is incorporated herein by reference); recognizing that other tests, such as bromine-methanol titimetry, may be employed to provide results that can be correlated with iron(III) chloride titrimetry.

[00123] In embodiments the specific surface area for the agglomerates can be from about 0.05 m^2/g to about 35 m^2/g, from about 0.1 m^2/g to about 5 m^2/g, from about 0.5 m^2/g to about 10 m^2/g, from about 0.2 m^2/g to about 5 m^2/g, from about 1 m^2/g to about 5 m^2/g, from about 1 m^2/g to about 20 m^2/g, greater than about 1 m^2/g, greater than about 2 m^2/g, less than about 5 m^2/g, less than about 15 m^2/g, less than about 20 m^2/g, and combinations and variations of these, as well as greater and smaller values.

[00124] The packing of agglomerates creates macro-pores, e.g., openings, spaces, channels, or voids, in between individual agglomerates. The macro-pores facilitate ion transport through electrodes that in some embodiments have a smallest dimension that is still very thick compared to some other types of battery electrodes, being multi-centimeter in

dimension. The micro-pores within the agglomerates allow the high surface area active material of the agglomerates to be in contact with electrolyte to enable high utilization of the active material. This electrode structure lends itself specifically to improving the rate capability of extremely thick electrodes for stationary long duration energy storage, where thick electrodes may be required to achieve extremely high areal capacities.

[00125] In various embodiments, a bed of conductive micro-porous agglomerates comprise an electrode in an energy storage system. In some embodiments, said agglomerates comprise agglomerates of direct reduced iron (DRI). The packing of agglomerates creates macro-pores in between individual agglomerates. The macro-pores facilitate ion transport through electrodes that in some embodiments have a smallest dimension that is still very thick as compared to some other types of battery electrodes, being of multiple centimeters in dimension. The macropores may form a pore space of low tortuosity compared to the micro-pores within the agglomerates. The micro-pores within the agglomerates allow the high surface area active material of the agglomerate to be in contact with electrolyte to enable high utilization of the active material. This electrode structure lends itself specifically to improving the rate capability of extremely thick electrodes for stationary long duration energy storage, where thick electrodes may be required to achieve extremely high areal capacities.

[00126] The agglomerates for these embodiments, and in particular for use in embodiments of electrodes for long duration energy storage systems, can be any volumetric shape, e.g., spheres, discs, pucks, beads, tablets, pills, rings, lenses, disks, panels, cones, frustoconical shapes, square blocks, rectangular blocks, trusses, angles, channels, hollow sealed chambers, hollow spheres, blocks, sheets, films, particulates, beams, rods, angles, slabs, cylinders, columns, fibers, staple fibers, tubes, cups, pipes, and combinations and various of these and other more complex shapes. The agglomerates in an electrode can be the same or different shapes. The agglomerates in an electrode that is one of several electrodes in a long duration energy storage system, can be the same as, or different from, the agglomerates in the other electrodes in that storage system.

[00127] The size of the agglomerates, unless expressly used otherwise, refers to the largest cross-sectional distance of the agglomerate, e.g., the diameter of the sphere. The agglomerates can be the same or different sizes. It is recognized that the shape and size of both the agglomerates, as well as, typically to a lesser degree, the shape and size of the container or housing holding the agglomerates, determines the nature and size of the macro-

pores in the electrode. The agglomerates can have sizes from about 0.1 mm to about 10 cm, about 5 mm to about 100 mm, 10 mm to about 50 mm, about 20 mm, about 25 mm, about 30 mm, greater than 0.1 mm, greater than 1 mm, greater than 5 mm, greater than 10 mm and greater than 25 mm, and combinations and variations of these.

[00128] In embodiments, the agglomerates as configured in an electrode can provide an electrode having a bulk density of from about 3 g/cm^3 to about 6.5 g/cm^3, about 0.1 g/cm^3 to about 5.5 g/cm^3, about 2.3 g/cm^3 to about 3.5 g/cm^3, 3.2 g/cm^3 to about 4.9 g/cm^3, greater than about 0.5 g/cm^3, greater than about 1 g/cm^3, greater than about 2 g/cm^3, greater than about 3 g/cm^3, and combinations and various of these as well as greater and lesser values.

[00129] In various embodiments, additives beneficial to electrochemical cycling, for instance, hydrogen evolution reaction (HER) suppressants may be added to the bed in solid form, for instance, as a powder, or as solid pellets.

[00130] In some embodiments, metal electrodes may have a low initial specific surface area (e.g., less than about 5 m^2/g and preferably less than about 1 m^2/g). Such electrodes tend to have low self-discharge rates in low-rate, long duration energy storage systems. One example of a low specific surface area metal electrode is a bed of agglomerates. In many typical, modern electrochemical cells, such as lithium ion batteries or nickel-metal-hydride batteries, a high specific surface area is desirable to promote high rate capability (*i.e.*, high power). In long duration systems, the rate capability requirement is significantly reduced, so low specific surface area electrodes can meet target rate-capability requirements while minimizing the rate of self-discharge.

[00131] In another embodiment, desirable impurities or additives are incorporated into the agglomerates. When these impurities are solids, they may be incorporated by ball-milling (for example, with a planetary ball mill or similar equipment) the powder additive with metal powder, the agglomerates serving as their own milling media. In this way the powder additive is mechanically introduced into the pores or surface of the agglomerate. Agglomerates may also be coated in beneficial additives, for example, by rolling or dipping in a slurry containing the additives. These desirable impurities may include alkali sulfides. Alkali sulfide salts have been demonstrated to vastly improve active material utilization in Fe anodes. Just as soluble alkali sulfides may be added to the electrolyte, insoluble alkali sulfides may be added to the agglomerates, for example, by the above method.

[00132] In various embodiments, the specific surface area of the agglomerates is increased by a factor of 3 or more, preferably a factor of 5 or more, as measured by a technique, such as the Brunauer-Emmett-Teller gas adsorption method. In some embodiments, this surface area increase is accomplished by using the agglomerates as an electrode in an electrochemical cell, and electrochemically reducing it with an applied current.

[00133] The ratio of electrolyte to iron material, for example agglomerates in a cell may be from about 0.5 $mL_{electrolyte}$: 1 $g_{iron\text{-}material}$ to about 5 $mL_{electrolyte}$: 1 $g_{iron\text{-}material}$, from about 0.6 $mL_{electrolyte}$: 1 $g_{iron\text{-}material}$ to about 3 $mL_{electrolyte}$: 1 $g_{iron\text{-}material}$, about 0.6 $mL_{electrolyte}$: 1 $g_{iron\text{-}material}$, about 0.7 $mL_{electrolyte}$: 1 $g_{iron\text{-}material}$, about 0.8 $mL_{electrolyte}$: 1 $g_{iron\text{-}material}$, about 1 $mL_{electrolyte}$: 1 $g_{iron\text{-}material}$, and combinations and variations of these as well as larger and smaller ratios.

[00134] A packed bed of agglomerates may be a desirable configuration of an iron-based electrode as it provides for an electronically conductive percolation path through the packed bed while leaving porosity available to be occupied by an electrolyte that facilitates ion transport. In certain embodiments, the ratio of electrolyte volume to agglomerate mass may be in the range of 0.5 mL/g to 20 mL/g, such as 0.5 mL/g to 5mL/g, or such as 0.6 mL/g or 1.0 mL/g. The agglomerates are generally in contact with surrounding agglomerates through a small contact area compared to the surface area of the agglomerate, and in some instances the contact can be considered a "point contact." Contacts of small cross-sectional area may be constrictions for the flow of electrical current that may result in a relatively low electrical conductivity for the agglomerate bed as a whole, which may in turn lead to high electrode overpotentials and low voltaic efficiency of the battery.

[00135] In some embodiments, additives comprising a molybdate ion are used in an alkaline battery comprising an iron anode. Without being bound by any particular scientific interpretation, such additives may aid in suppressing the hydrogen evolution reaction (HER) at the iron electrode and improving the cycling efficiency of the battery. The concentration of the additive is selected to be able to suppress HER while still enabling the desired iron charge / discharge process. As an example, a molybdate ion may be added via a molybdate compound such as $KMoO_4$. In one specific example, the electrolyte contains an additive concentration of 10 mM (mM means millimolar, 10^{-3} mol/L concentration) molybdate anion. In other embodiments, the electrolyte contains additive concentrations ranging from 1-100 mM of the molybdate anion.

[00136] In some embodiments, a surfactant is used to control wetting and bubbling during operation of a metal air battery. During charging, at least two gas evolution reactions may occur that result in bubble formation. One is hydrogen evolution at the metal anode, which is a parasitic reaction that may contribute to poor coulombic efficiency during cycling of the battery. Another is the oxygen evolution reaction, which is necessary for the functioning of the metal-air battery. A surfactant additive can mitigate undesirable effects associated with both reactions. In the case of HER, a hydrophobic surfactant additive may suppress the hydrogen evolution reaction at the metal anode by physically blocking water (a HER reactant) from the metal anode during charging. In the case of ORR, a surfactant additive may reduce electrolyte surface tension and viscosity at the oxygen evolution electrode to generate smaller, uniformly sized, controllable bubbles during charging. In one non-limiting example, 1-Octanethiol is added to the alkaline electrolyte at a concentration of 10 mM to mitigate both of these challenges.

[00137] In some embodiments, corrosion inhibitors used in the field of ferrous metallurgy to inhibit aqueous corrosion are used as components in a battery with an iron negative electrode to improve performance. In some embodiments, iron agglomerates are used as the negative electrode, and favorable performance characteristics may be achieved by using one or more corrosion inhibitors in a suitable range of concentrations. In these embodiments, the principles of corrosion science are used to prevent undesirable side reactions (e.g. hydrogen evolution) in the charge condition, mitigate the rate of spontaneous self-discharge during an electrochemical hold, and maximize the utilization of iron active material upon discharge. Generally, there are two classes of corrosion inhibitors: interface inhibitors which react with the metal surface at the metal-environment interface to prevent corrosion, and environmental scavengers that remove corrosive elements from the environment surrounding the metal surface to inhibit corrosion. Under the broad umbrella of corrosion inhibitors, appropriate concentrations of inhibitors may be added to the electrochemical cell to achieve favorable performance characteristics with respect to the efficiency and capacity of an electrochemical cell. For the iron electrode of a metal air battery, one applicable general class of inhibitors are liquid and interphase interface inhibitors. This class encompasses three major types of interface inhibitors: anodic, cathodic, and mixed inhibitors. Anodic inhibitors create a passivation layer that inhibits an anodic metal dissolution reaction. Cathodic inhibitors may decrease the rate of a reduction reaction (HER in the case of an iron electrode), or precipitate at cathodic active sites to block the same

reduction reaction. Mixed inhibitors may inhibit corrosion via one or both pathways, and include but are not limited to molecules that adsorb on the metal surface physically or chemically to form a film that may block active sites for a reduction reaction. The inhibitors can be added to a base electrolyte at any concentration.

[00138] In various embodiments, an inhibitor that forms a passivation layer on the metal surface is paired with an additive that de-passivates the iron surface. In the correct concentrations, an optimal balance of corrosion inhibition and active material utilization may be achieved. In one specific embodiment, when using direct reduced iron as the negative electrode, 10 mM molybdate anion is used as the passivator, while 10mM sulfide anion is used as the de-passivator in an alkaline electrolyte comprised of 5.5M potassium or sodium hydroxide. Specific examples of electrolyte compositions include: 5.5 M KOH + 0.5 M LiOH + 10 mM Na_2S + 10 mM 1-octanethiol; 5.95 M NaOH + 50 mM LiOH + 50mM Na_2S + 10 mM 1-octanethiol; 5.95 M NaOH + 50 mM LiOH + 50mM Na_2S + 10 mM 1-octanethiol + 10 mM K_2MoO_4; and 5.95 M NaOH + 50 mM LiOH + 50mM Na_2S + 10 mM K_2MoO_4. However, the present disclosure is not limited to any particular concentration of the above additives in the electrolyte. For example, one or more of the above additives may be included in the electrolyte at concentrations ranging from about 2mM to about 200mM, such as from about 5mM to about 50mM, or about 5mM to about 25mM.

[00139] For a physically adsorbed (chemisorbed or physisorbed) inhibitor, interaction with the metal surface is often strongly dependent on temperature.

[00140] In one embodiment, an inhibitor is used where desorption of the inhibitor from the iron surface may be favorable at lower temperatures with respect to a normal operational temperature. During charge, the inhibitor forms a film that suppresses the evolution of hydrogen at the electrode. On discharge the temperature of the cell can be increased or decreased such that the inhibitor desorbs from the metal surface and exposes active material to allow for improved electrode utilization. On the subsequent charge, the temperature of the cell may be returned to a normal operational temperature to reform the film and suppress HER. This process may be repeated to achieve high charging efficiencies and high discharge utilization of the iron electrode. In one non-limiting example, octanethiol may be used as an inhibitor that can physisorb or chemisorb on a metal anode (e.g. Fe, Ni). Upon heat treatment of an electrochemical cell up to 60°C, physisorbed octanethiol is desorbed, revealing more active sites that can be oxidized during discharge. Free octanethiol in the electrolyte then physisorbs to the anode again upon cooling. At higher temperatures (>60°C), octanethiol may

chemisorb to the electrode, forming continuous, uniform films across the surface. These chemisorbed species may be desorbed more effectively at low temperatures (<100°C).

[00141] In order to enable performance at higher temperature, organic film-forming inhibitors with oxygen, sulfur, silicon, or nitrogen functional groups can be used to form continuous chemisorbed films on the iron particulate electrode to replicate the depassivating behavior of the sulfide while resisting decomposition or oxidation.

[00142] In one embodiment, 1 to 10mM octanethiol is added to the electrolyte. During charge, the system is allowed to heat to temperatures outside of normal operating conditions (e.g., >50°C), facilitating the formation of more complete and uniform chemisorbed octanethiol films across the active sites of the iron particulate electrode and preventing hydrogen evolution at the surface. On discharge, the system is cooled and portions of the chemisorbed film desorb from the surface, revealing additional active sites for discharge. The remaining octanethiol acts to depassivate the electrode, facilitating more complete discharge. FIG. 1 illustrates an example method of facilitating such complete discharge. For example, FIG. 1 illustrates the electrode 102 in a discharge state at the top of the figures. A potential hydrogen evolution reaction (HER) site 104 was created during discharge where a octanethiol film desorbed from the electrode 102 surface. In the next step of the method as illustrated in the middle of FIG. 1, 1 to 10mM octanethiol is added to the electrolyte 103. During charge, the system is allowed to heat to temperatures outside of normal operating conditions (e.g., >50°C), facilitating the formation of more complete and uniform chemisorbed octanethiol films across the active sites of the iron particulate electrode 102 and preventing hydrogen evolution at the surface of the electrode 102 as the octanethiol film filed in the potential HER site 104. On discharge, the system is cooled and portions of the chemisorbed film desorb from the surface, revealing additional active sites for discharge, such as the HER site 104. The remaining octanethiol acts to depassivate the electrode 102, facilitating more complete discharge.

[00143] During an electrochemical rest period, it is desirable to minimize the corrosion of the metal electrode. One type of corrosive media to an iron metal electrode in an aqueous electrolyte is dissolved oxygen. During an electrochemical hold, dissolved oxygen can contact the iron electrode and corrode the active material, discharging the iron electrode.

[00144] In one embodiment, an oxygen scavenger (e.g. pyrogallol, ascorbic acid, 8-hydroxyquinoline, sodium peroxide, hydrogen peroxide) may be added to the electrolyte

during an electrochemical hold to reduce the concentration of dissolved oxygen in the electrolyte and prevent discharge of the iron electrode.

[00145] In one embodiment, an anodic corrosion inhibitor (e.g. K_2MoO_4) is added to the electrolyte at concentrations between 1 and 10mM before an electrochemical hold, creating a passive film that blocks the metal surface from corrosive media in the electrolyte to prevent self discharge. After the electrochemical hold, when the electrode must be discharged, an aggressive ion (e.g. SO_4^{2-}, CrO_4^-, NO_3^-) is added to the electrolyte to expose the active material and achieve a high utilization of active material, thus mitigating self discharge.

[00146] In certain embodiments, other corrosion inhibitors are incorporated in the electrolyte as additives (i.e., as minority constituents). Electrolyte additives may be selected from the non-limiting set of sodium thiosulfate, sodium thiocyanate, polyethylene glycol (PEG) 1000, trimethylsulfoxonium iodide, zincate (by dissolving ZnO in NaOH), hexanethiol, decanethiol, sodium chloride, sodium permanganate, lead (IV) oxide, lead (II) oxide, magnesium oxide, sodium chlorate, sodium nitrate, sodium acetate, iron phosphate, phosphoric acid, sodium phosphate, ammonium sulfate, ammonium thiosulfate, lithopone, magnesium sulfate, iron(III) acetylacetonate, hydroquinone monomethyl ether, sodium metavanadate, sodium chromate, glutaric acid, dimethyl phthalate, methyl methacrylate, methyl pentynol, adipic acid, allyl urea, citric acid, thiomalic acid, N-(2-aminoethyl)-3-aminopropyl trimethoxysilane, propylene glycol, trimethoxysilyl propyl diethylene, aminopropyl trimethoxysilane, dimethyl acetylenedicarboxylate (DMAD), 1,3-diethylthiourea, N,N'-diethylthiourea, aminomethyl propanol, methyl butynol, amino modified organosilane, succinic acid, isopropanolamine, phenoxyethanol, dipropylene glycol, benzoic acid, N-(2-aminoethyl)-3-aminopropyl, behenamide, 2-phosphonobutane tricarboxylic, mipa borate, 3-methacryloxypropyltrimethoxysilane, 2-ethylhexoic acid, isobutyl alcohol, t-butylaminoethyl methacrylate, diisopropanolamine, propylene glycol n-propyl ether, sodium benzotriazolate, pentasodium aminotrimethylene phosphonate, sodium cocoyl sarcosinate, laurylpyridinium chloride, steartrimonium chloride, stearalkonium chloride, calcium montanate, quaternium-18 chloride, sodium hexametaphosphate, dicyclohexylamine nitrite, lead stearate, calcium dinonylnaphthalene sulfonate, iron(II) sulfide, sodium bisulfide, pyrite, sodium nitrite, complex alkyl phosphate ester (e.g. RHODAFAC® RA 600 Emulsifier), 4-mercaptobenzioc acid, ethylenediaminetetraacetic acid, ethylenediaminetetraacetate (EDTA), 1,3-propylenediaminetetraacetate (PDTA),

nitrilotriacetate (NTA), ethylenediaminedisuccinate (EDDS), diethylenetriaminepentaacetate (DTPA), and other aminopolycarboxylates (APCs), diethylenetriaminepentaacetic acid, 2-methylbenzenethiol, 1-octanethiol, manganese dioxide, manganese (III) oxide, manganese (II) oxide, manganese oxyhydroxide, manganese (II) hydroxide, manganese (III) hydroxide, bismuth sulfide, bismuth oxide, antimony(III) sulfide, antimony(III) oxide, antimony(V) oxide, bismuth selenide, antimony selenide, selenium sulfide, selenium(IV) oxide, propargyl alcohol, 5-hexyn-1-ol, 1-hexyn-3-ol, N-allylthiourea, thiourea, 4-methylcatechol, trans-cinnamaldehyde, Iron(III) sulfide, calcium nitrate, hydroxylamines, benzotriazole, furfurylamine, quinoline, tin(II) chloride, ascorbic acid, 8-hydroxyquinoline, pyrogallol, tetraethylammonium hydroxide, calcium carbonate, magnesium carbonate, antimony dialkylphosphorodithioate, potassium stannate, sodium stannate, tannic acid, gelatin, saponin, agar, 8-hydroxyquinoline, bismuth stannate, potassium gluconate, lithium molybdenum oxide, potassium molybdenum oxide, hydrotreated light petroleum oil, heavy naphthenic petroleum oil (e.g. sold as Rustlick® 631), antimony sulfate, antimony acetate, bismuth acetate, hydrogen-treated heavy naphtha (e.g. sold as WD-40®), tetramethylammonium hydroxide, NaSb tartrate, urea, D-glucose, C6Na2O6, antimony potassium tartrate, hydrazine sulfate, silica gel, triethylamine, potassium antimonate trihydrate, sodium hydroxide, 1,3-di-o-tolyl-2-thiourea, 1,2-diethyl-2-thiourea, 1,2-diisopropyl-2-thiourea, N-phenylthiourea, N,N'-diphenylthiourea, sodium antimonyl L-tartrate, rhodizonic acid disodium salt, sodium selenide, potassium sulfide, and combinations thereof.

[00147] Additional additives include minerals containing SiO_2, which may have beneficial effects on electrochemical performance due to uptake of carbonate from the electrolyte or electrode. Additives which contain such functional groups may be usefully incorporated into iron electrode materials. While the specific mineralogy of ores and other factors may determine the exact SiO_2-containing material added, examples of such SiO_2-containing additives are silica, cristobalite, sodium silicates, calcium silicates, magnesium silicates, and other alkali metal silicates.

[00148] In certain embodiments, electrode agglomerates are prepared by agglomerating metal powders, such as iron containing powders, into approximately spherical agglomerates. In various embodiments the agglomeration is conducted at or about room temperature or at or about ambient outdoor temperature or at elevated temperature. In various embodiments, the agglomeration is conducted in a rotary calciner, in which the powder is simultaneously agglomerated and sintered. In certain embodiments, iron powders such as

atomized iron powder, sponge iron powder, iron filings, mill scale, carbonyl iron powder, electrolytic iron powder, and combinations or variations thereof are used as feedstocks. In various embodiments, the heat treatment process is conducted at temperatures such as about 700 °C to about 1200 °C such as about 800 °C to about 1000 °C. In various embodiments the gas environment is inert (comprising N_2 or Ar) or reducing (comprising H_2, CO_2, CO, etc) or combinations thereof. In various embodiments the heat treatment process fully or partially sinters together the powder to create agglomerates. In various embodiments the agglomerates have size ranging from 1 um (um = 10^{-6} m) to 1 cm (cm = 10^{-2} m) such as 10 um, 100 um, or 1 mm (mm = 10^{-3} m).

[00149] In certain embodiments, the feedstock materials are materials known in the art as pig iron, granulated pig iron, nodule reduced iron, scrap iron, and/or scrap steel.

[00150] In various embodiments, a fine iron powder with a substantial population of powder particles being below 44 microns (often written as -325 mesh due to the passage of such particles through a 325 mesh sieve) may be utilized as a portion of the feedstock materials or entirely comprise the feedstock materials.

[00151] In certain embodiments, electrodes are fabricated by electrochemical deposition of iron from an aqueous solution. In certain embodiments the deposition solution is acidic, with a pH less than about 4, such as pH about 3, or pH about 2. In certain embodiments, the solution is near neutral, with a pH between about 4 and about 10, such as pH about 5 or pH about 7 or pH about 9. In certain embodiments the electrolyte comprises a salt such as NaCl or LiCl or KCl. In certain embodiments the liquid electrolyte is agitated by stirring, shaking, mixing, or turbulent flow to promote an uneven deposition rate and a porous structure. In certain embodiments the liquid electrolyte is sparged or aspirated, to introduce gas bubbles into the liquid during the deposition process.

[00152] In certain embodiments, iron powders are prepared by an electrometallurgical process for making porous iron. Working from a melt, iron-comprising metal is sprayed, bubbled through, or molded onto a substrate or into a mold to produce a low-cost, high surface area iron product. In certain embodiments, these powders are subsequently agglomerated using a rotary calciner or other methods, and may be subsequently assembled into an electrode. In certain embodiments the powders are directly assembled into an electrode, with no intermediate agglomeration process. In certain embodiments, a mixture or combination of agglomerated and non-agglomerated powders are used in an electrode. In

certain embodiments, agglomerated and/or non-agglomerated powders produced by the electrometallurgical method are combined with other metals to fabricate an electrode.

[00153] Electrochemically produced metals offer a unique opportunity for production of high surface area materials, especially if the metal is in a liquid state, in which case the resulting liquid product is cooled via a variety of methods to achieve the desired properties. For example, iron produced via high temperature electrometallurgical is cooled directly in a high surface area mold, spray deposited (atomized) into particles or dispersed in a cooling media.

[00154] In certain embodiments, metal electrodes are directly prepared by electrometallurgical processes such as molten oxide electrolysis. In certain embodiments, porous electrodes are made by intentionally aspirating or sparging gas into a molten oxide electrolysis cell. In certain embodiments, the gas is an inert gas such as N_2 or Ar.

[00155] In certain embodiments, molten metal from an electrometallurgical process is sprayed, bubbled through, or molded onto a substrate or into a mold to produce a low-cost, high surface area metal electrode. In certain embodiments the metal is substantially iron.

[00156] In one non-limiting example, iron ore comprising Fe_2O_3, Fe_3O_4, and mixtures thereof, is dissolved in an electrolyte comprising SiO_2, Al_2O_3, MgO, and CaO in weight ratios of 60wt%, 20wt%, 10wt%, and 10wt%, respectively. The mixture is brought to an elevated temperature of about 1600 °C. Metallic iron is electrochemically reduced from the molten oxide mixture and pooled at the cathode. The molten metal is transferred by pipes and valves to a shot tower, and is rapidly cooled in vacuum to produce a fine iron powder with average diameter of 50 um (um $= 10^{-6}$ m). The iron powder is subsequently passed into a rotary calciner operating under a nitrogen (N_2, 100%) atmosphere at 900 °C to form aggregates with average diameter of 2 mm, which are subsequently assembled by packing into a metal electrode.

[00157] In certain embodiments, the electrodes may be fabricated from the thermochemical reduction of iron oxides. In some embodiments, the reduction may proceed almost to complete reduction of the iron oxides to metallic iron. Nearly complete reduction of the iron oxide to metallic iron is the goal of many industrial thermochemical reduction processes for iron. However, there are many potential reasons why incomplete reductions of iron oxides to metallic iron would make such incompletely-reduced products particularly useful for the creation of iron batteries. First, several of the oxide phases created during the

reduction of iron are semiconducting, and thus may usefully serve as electronic conductors in an iron electrode material. For example, magnetite is fairly conductive close to room temperature. Wüstite, while less conductive than magnetite, is still highly conductive relative to most oxides. In some embodiments, one may take advantage of the semiconducting nature of wustite and magnetite to form a battery electrode which is possibly a composite with metallic iron. Partially reduced products may also be more electrochemically active. The inventors have observed that wüstite may in some circumstances be more electrochemically active than even metallic iron. Wüstite may be less expensive to thermochemically reduce due to its higher oxidation state than metallic iron Wüstite may therefore be less expensive and higher performance than iron as a component of a battery electrode. In one aspect, a positive electrode for an alkaline iron battery may be produced from indurated pellets composed of hematite traditionally fed to direct reduction or blast furnace processes. The pellets may be reduced in a vertical shaft furnace via appropriate mixtures of hydrocarbons and other reducing gases known in the art of the direct reduction of iron. The reduction process may terminate by way when a metallization of at most 95% is achieved (metallization is a term used in the art of direct reduction of iron to describe the fraction of iron atoms which are fully metallic in their oxidation state). In some instances, a lower metallization may be preferred, with metallizations as low as 0% yielding large quantities of magnetite and wüstite as alternative input materials for a battery. The resulting partially reduced pellets, lump, fragment or other particulate may be packed into a bed of particles in order to serve as an iron electrode material. The electrode material may consist entirely of iron oxides, and comprise primarily a mixture of magnetite and wustite.

[00158] **Current Collection, Compression, and other means of enhancing charge transfer**

[00159] In some instances, porous iron electrode materials may suffer from high electrical resistance when assembled into a bed. As such, the performance of iron electrode materials inside a battery may be enhanced by methods for decreasing the resistance to charge transfer between and among the particulate materials, and enhanced methods for current collection from the electrode active materials. This section describes methods for enhancing the charge transfer within the packed bed through to the current collectors.

[00160] The inventors have discovered through experiment that the performance of porous iron electrodes may be enhanced by applying a compressive force to the anode bed during the course of battery cycling. For example, the contact resistance between porous

particulate materials may be decreased by over one order of magnitude by application of a uniaxial compressive stress of 0.01 MPa or more. Too high of compressive stresses may lead to local failure of the electrode material via cracking of the material (and therefore potential local decreases in electrical conduction), densification due to deformation of the porous iron electrode material without cracking (which may in turn lead to a reduction in the pore space available for the formation of discharge product or a decrease in the mass transport through the pore space), or other mechanical failure modes. The application of compressive stresses that do not lead to material failure but are above the stresses needed for reduction of contact resistance may lead to increases in the performance of the porous iron electrode material during electrochemical cycling. Within this regime, further increases in compressive stresses and different configurations of compressive stresses may be used to increase the conductivity of the bed, with stresses on the order of 0.1-10 MPa yielding enhanced performance in some systems. As the applied stresses (and therefore forces) increase, the requirements for the mechanical enclosure which may successfully apply such stresses become more stringent, and generally the costs of the enclosure increases. Thus, in one aspect, a mechanical structure which permits simultaneous current collection and compression of a porous iron electrode material with stresses between 0.1 and 10 MPa is an especially useful means of containing the iron electrode materials within an electrochemical cell.

[00161] In various embodiments, it may be useful for a current collector to serve multiple functions in the cell, including serving as a structural member. In one example, the current collector may provide structural support to the electrode by running through a middle of the packed bed of particulate material. In some embodiments, the packed bed may have current collectors on both sides in addition to a central current collector. In some embodiments, the current collector in the middle of the packed bed may be fabricated from a sheet without perforations, whereas the current collectors on the external faces may be perforated or otherwise containing holes to facilitate transport of ions to the electrode active materials. In various embodiments, air electrodes or other positive electrode materials may be placed adjacent to the iron electrode material on both sides such that ions do not need to flow through the electrode material across a given depth in the electrode, this may be due to e.g. a plane of symmetry for the transport. As such, a lack of perforations in the current collector included in the middle of the bed may usefully reduce costs for the center current collecting sheet while having little to no impact on the transport within the system. The iron electrode materials may be mounted to or compressed against a combined structural support and

current collector included in the middle of the packed bed. Additional functions performed by a current collecting component in an iron electrode may include: anode locating/mounting, enhanced current collection, adjacent cell separation, and voltage stacking.

[00162] The degree to which the resistivity of a porous electrode must be reduced to reach a given level of electrochemical performance is a function of the current collection method, as well as the material properties. If current is being collected from more sides, or with shorter total path lengths to the current collector, a battery may be able to operate efficiently with a higher resistivity path, as the ultimate voltage drop is lower. As such, the compression strategies and the current collection strategies for porous iron electrodes may be usefully co-optimized to yield systems with the lowest total cost for a given level of performance. Below, a set of techniques and designs for current collection from, and compression of, porous electrode beds which may be used in combination or separately in order to yield high performance porous battery electrodes with low price.

[00163] The current collecting materials may be any of those used in the art to collect current in alkaline batteries at the potentials that anodes in alkaline iron-based batteries may be exposed to. The composition of the electrolyte, the specific potentials used during battery cycling, and other process variables (e.g. temperature) will determine the degree to which various current collecting materials are stable. These materials may include nickel, nickel-plated stainless steel, copper, copper plated stainless steel, iron of sufficient thickness, carbon fiber and other carbon-based materials, and iron coated with cobalt ferrite.

[00164] In one aspect, a reactor containing a porous iron electrode may be divided up into horizontal layers contained in a larger vessel. FIGS. 2 and 3 illustrate example aspects of such an embodiment in which a larger vessel 202 is divided into horizontal layers 203-207. With reference to FIGS. 2 and 3, these horizontal layers (e.g., 203-207) may be referred to as packets. In each of these horizontal layers (e.g., 203-207), the anode, such as particulate anode material 212, may be compressed via any of the methods applicable for compressing and containing particulate materials. In doing so, a current-collecting divider 210 between the packet may be inserted into the larger vessel 202 holding the packets (e.g., 203-207). Tabs 215 on the divider 210 or other compliant, conductive mechanisms may be used to hold the compressive forcer (e.g., divider 210) for the packet (e.g., 203-207) in place while also serving as a means of current collection. This is shown in FIGS. 2 and 3. The divider 210 may also include an optional catch lip 216 on the side.

[00165] In an aspect, the current collector may be a metallic or other conductive textile. Examples include meshes woven of nickel, copper, or graphite fibers. The current collector may surround or be layered into the electrode materials. The current collecting textile may surround a Direct Reduced Iron (DRI) pellet bed as an electrode shown below. The textile may be tightened, cinched, or otherwise brought into close mechanical contact with the electrode material in order to promote sufficient electrical contact with electrode material. An illustrative example is shown in FIG. 4 for the case of a metal textile 402 with an electrode composed of direct reduced iron pellets 403. The metal textile 402 may be a mesh or screen encasing the DRI pellets 403 and providing a compressive force or load 404 on the DRI pellets 403 to press the DRI pellets 403 together within the metal textile 402 mesh and to establish close contact between the metal textile 402 and the DRI pellets 403. The current 405 may be collected by the metal textile 402.

[00166] In another aspect, a conductive mesh pouch or bag may be used as a means of simultaneously compressing and current-collecting from an electrode material. More specifically, a mesh pouch or bag may be filled with particulate iron electrode material, the bag may be cinched or otherwise reduced in volume via a belt, string, wire or other cinching mechanism in order to apply compression to the anode material. A conductive mesh tube or similar may be filled with particulate iron electrode material, and the electrode material may be compressed via application of axial tension to the conductive mesh tube. In such a case, the weave of the mesh may be optimized such that the mesh tube undergoes substantial compression upon application of axial tension. One may understand this in analogy to the Chinese finger trap, wherein axial extension of a woven tube causes the diameter of the tube to narrow. The amount of compression applied to the particulate iron material may be adjusted by the thickness of the strands in the weave, the density of the strands in the weave, and the amount of axial force/extension applied to the weave. In some instances, the porous iron electrode material may be composed of direct reduced iron pellets. In some instances, the porous iron electrode material may be composed of crushed direct reduced iron pellets. A binder may usefully be included in the particulate iron material in some cases to aid in adhesion of the pellet.

[00167] In some aspects, a porous mesh container and the particulate active materials may be disposed in a similar geometric manner to a teabag and tea leaves, for example as illustrated in FIGS. 5 and 6. FIG. 5 illustrates a single cinch configuration 500 in which the porous mesh bag 501 is tied at a single cinch point 503 by the current collector 502. FIG. 6

illustrates a double cinch configuration 600 in which the porous mesh bag 501 is tied at a first cinch point 503 by the current collector 502 and a second cinching point 602. This tea bag container (e.g., 501) may be conducting and serve as a current collector. In some aspects, the tea bag container (e.g., 501) may have a current collector placed inside of the tea bag container's envelope. The tea bag container (e.g., 501) may have ties to aid in compression, including ties that are not at the top of the tea bag container (e.g., 501), such as a second cinch tie 602 or other placed cinch ties. The tea bag container (e.g., 501) may also have ties at the top of the container to maintain active material within the container. In another aspect, the tea bag container (e.g., 501) may be non-conductive and the current collective may be performed solely through a current collector placed inside of the tea bag container's envelope.

[00168] In another aspect, a loose, flexible, conducting sheet may loosely attached at the edges to a backing plate, which may or may not be rigid, forming a pouch. Cinches, such as wires, inserted through the flexible sheet and the back, are opened to allow filling the pouch with a pellet or powder anode material. The cinches are pulled shut to compress the anode, and may be used for current collection. The cinching wires may be conductive and serve as added current collectors distributed throughout the pouch. The pouch may also be attached in a rigid manner (by e.g. welds), or by connections which are rigid with respect to some forms of motion and flexible with respect to others (e.g. a hinged connection). In some instances, the current collection may take place from one side such that either the backing plate or the pouch are not current-collecting, whereas in other instances it may be advantageous to collect current from both sides of the pouch construction. An example of such a cinched construction 700 with a backing plate 702 is shown by way of non-limiting example in FIG. 7. In some embodiments, the backing plate 702 may be used to rigidly support pouches 705 on both sides as illustrated in FIG. 7 with cinching wires 704 running across the backing plate 702 and pouches 705. Electrode material may be poured into the pouches 705 through an opening that may be then cinched or welded closed to form a closure 703.

[00169] In another embodiment, a particulate electrode material may be compressed within perforated sheets. The sheets may be conductive such that they serve as both a means of compressing the electrode material and a means of collecting current from the electrode material. The perforations in the sheet may be selected such that they are smaller than a

characteristic size of the particulate material, and thus that the particulate material may not easily escape from the cage formed by the perforated sheet.

[00170] In various embodiments, the electrode material may be a particulate material. The desire for facile transport of ions between the positive and negative electrodes may necessitate that the materials surrounding the electrode materials are porous or otherwise perforated. In some instances, a particulate material with a particle size finer than the porosity or perforations may be desired due to e.g. the difficulties of making very fine perforations. In instances where particles finer than the porosity or perforations are desired, the electrode material may be agglomerated via a binder such that a secondary particle forms which is composed of many primary particles. The primary particle sizes thus may be finer than the perforations, but the secondary particle size may be coarser than the perforations. Such coarser particles will be less susceptible to egress through the porosity or perforations of the current collectors and other compressing materials, and may be more effectively compressed as a result. In one aspect, a polymer stable in alkaline conditions may be used to bind an agglomerate together such as poly(ethylene) or poly(tetrafluoroethylene). In another aspect, a polymer may be introduced onto the surface of the primary particles and subsequently pyrolyzed to form a conducting binder on the surface of the primary particles, thereby binding them together. In yet another aspect, a polymeric binder that is only partially stable in the conditions appropriate to the electrode may be introduced between the primary particles. The binder may permit the electrode to be cycled a sufficient amount via e.g. several electrochemical charge and discharge cycles such that a bond forms electrochemically between the various primary particles prior to the disintegration or degradation of the polymer. In another aspect, the shape of the porosity or perforations in the structure compressing the electrode materials may be engineered to retain the electrode materials within the structure, but to maximize the ionic transport through the perforations or porosity. By way of non limiting example, long slits may be introduced into a perforated sheet such that the particles may not exit through the slits, but the amount of area open to mass transport is increased relative to the amount present if the perforations were equiaxed. In one aspect, the particulate electrode material may be composed of direct reduced iron, and the perforated sheet may be composed of stainless steel. In another aspect, the particulate electrode material may be composed of crushed direct reduced iron to a particle size several times smaller than the native pellet size, and the perforations in a current collector may be sized such that the crushed fragments do not escape from the compressing cage.

[00171] In one aspect, a bed of particulates is vibrated, shaken, stirred, or moved so particulates settle closer together than when initially filled. This method may also be used periodically during the life of the system to help encourage new contact angles or arrangements between particulates as they change shape or size. In the case of a container which provides pockets for particulates, its orientation may be changed, such as spinning in the case of a wheel-shaped containment.

[00172] In another aspect, additives may be included or added to the bed of the electrode material to enhance conduction through the electrode between current collectors. The additives may be usefully concentrated at key points in the electrode structure. In one aspect, a particulate anode material is stuck to a current collector, which may take any shape, including rounded, or a hollow sphere, and may have particulate on both sides, using a conductive glue. The conductive glue may comprise a binder stable in the intended environment, such as alkaline electrolyte, and a conductive particle, such as metal, such as iron, filings or powder, including steel mill dust. The binder may, for example, comprise poly(ethylene) or poly(tetrafluoroethylene). The conductive glue may additionally contain additives useful to battery performance, such as sulfide salt additives, or additives intended to bond with carbonate ions in solution, such as calcium hydroxide. Creating a conductive bond between the electrode particulate materials and the current collector may usefully enhance battery performance at low added cost when the interface resistance between the particulate material and the current collector is one of the larger resistances in the electrochemical system. The composition of the conductive glue may be between 10-80 vol.% of the conductive additive, with the remainder comprising a binder, any additives, and a possible cosolvent or tackifier.

[00173] In another aspect, current collection may occur by creating a bond between each of the particulate materials and a conductive rod. If the particulate materials are attached by a conductive bond to a current collector, the compressive stresses need not be applied. The particulate materials may be attached to a rod along its length. The mass of anode material may extend past the end of the rod. The anode mass may be attached via sintering, welding, or other metal bonding techniques, by attachment with wire, or by deposition onto the rod from solution or slurry, which may take place via magnetism or evaporation of the solvent. The rod may be used for current collection from the anode. Anodes of this rod format may be snap-fit into a flexible ring-with-a-slit-like fastening mechanism for easy assembly of a compound anode. This fastening rail may also serve as a bus bar. This is schematically shown

in FIG. 8 in which rods 802 with attached iron particulate material 805 are fitted to a bus bar 803. The rod 802 may have any cross section, including circular or linear, and need not be straight, but may rather assume a coil or some other shape to enhance packing and limit the bus bar 803 volume needed.

[00174] In another aspect, simultaneous current collection and compression may take place via a pouch, open at the top, which may be fabricated, for instance, from crimped or welded sheet metal. The pouch may be filled with a particulate iron electrode material and the top may be rolled down to provide compression of the particulate materials. The compression may make use of a horizontal rod inside the rolled portion to perform the rolling. The pouch may be made of conductive materials suitable to be current collectors in alkaline battery environments, and specifically at iron positive electrodes. Current may be collected from the end(s) of the rod. The pouch may be porous or perforated to permit ionic transport through the pouch, as in a metallic mesh made of nickel.

[00175] In another aspect, a rigid container may be formed. The rigid container may have at least one conductive wall, and may be constructed of materials suitable for use in an alkaline electrolyte, and further may be suitable to serve in the current collector of an iron positive electrode. The rigid container may be filled with particulate electrode material, and compressed via a piston or plunger mechanism. In one exemplary embodiment, a welded can with a bottom and wrap-around outside is filled with anode pellets (or powder) and compressed from the top using a plunger mechanism. The faces of the rigid container may be constructed of rigid, but ion permeable material such as perforated sheet metal or expanded sheet. In one aspect, an expanded sheet metal comprised the sidewalls of the rigid container. The platen or face used by the plunger may contain tabs or other compliant mechanisms which may mechanically engage with features in the sidewalls of the rigid container such that the plunger may only be needed to provide a compressive force for assembly. The mechanically engaging features thus enable the piston to be used for initial compression but subsequently removed. Compressive load in this and other embodiments may be applied via any of the means common in the art for applying compressive loads, including but not limited to bolts, hydraulics, weight, threaded rods, zip ties, and rivets. FIG. 9 shows an exemplary embodiment wherein a perforated press 902 is used to compress the iron electrode material 903 within a rigid anode container 905. In this case, the iron electrode material 903 may be direct reduced iron pellets, referred to as a DRI marble bed. FIG. 9 shows an exploded view on the left and an assembled view on the right.

[00176] In another aspect, iron particulate materials may be sandwiched between two sheets of conductive, compliant material, such as a metal textile, and riveted to be fastened around the edges to provide compression. In some instances, the conductive compliant material may be riveted, cinched, or otherwise reduced in volume intermittently throughout the area of the electrode to provide more uniform compression.

[00177] In another aspect, a compliant sheet or mesh may be used in combination with a rigid side wall to provide simultaneous compression, current collection, and containment. More specifically, in one exemplary embodiment, such as illustrated in FIG. 10, a module 1002 consisting of a rigid side walls 1004 may be slightly overfilled with iron electrode material 1005 with metal mesh top and bottom plates 1003, all enclosed with fasteners 1006 (e.g., bolts, threaded rods, zip ties, rivets etc). The mesh 1003 applies a compressive load to the iron electrode material 1005 when the fasteners 1006 are tightened as the side walls 1004 may be slightly overfilled with marbles (e.g., DRI marbles as the iron electrode material 1005). The mesh 1003 may serve as a current collector. The mesh 1003 may allow for good electrolyte circulation or diffusion to the iron electrode material 1005. The fasteners 1006, in combination with the other elements, may keep the iron electrode material 1005 contained and may apply a clamping load. In some embodiment, the fasteners 1006 may also serve as a current collector. The mesh 1003 may be wire mesh, perforated plate, resistive to corrosion i.e. nickel, stainless steel etc. The side walls 1004 may be any rigid material suitably stable in the electrochemical environment of the iron electrodes 1005, i.e. plastic, some metals, etc. The resulting assembly of iron electrode material 1005 and the current collecting apparatus may be a modular component or may be permanently connected to an electrochemical energy storage system entirely.

[00178] In another aspect, a compliant material, gasket-like material is used to contain the iron particulate electrode material on several faces. The compliant material permits variable displacement of the force-applying elements of the design according to the local compliance and/or packing of the bed. In one example, a compliant gasket borders a cylindrical cell and conducive, current collecting, perforated plates form the ends of the cylindrical cell. The plates are forced together at various points along the circumference of the cell via, e.g. bolts penetrating through the silicon gasket. The gasket may be made of a compliant, alkaline resistant material, such as an Ethylene propylene diene monomer (EPDM) rubber or related material. In some instances, the gasket may need to be highly

compliant, in which case a foam of a polymeric material, such as an EPDM foam, may be useful.

[00179] In another aspect, a current collector may contain divots or other locating or contacting features on its surface. These features may serve to enhance the contact area between the current collector and the particulate iron material and/or to locate a particulate material such that it packs efficiently as a result of the templating provided by the surface of the current collector. In one example, a current collector may contain a series of divots sized and placed such that a spherical set of particles, such as those from a direct reduction process, may pack in a close-packed manner adjacent to the surface. Other templates, such as a body-centered cubic template are possible. For particulate materials with an axis of symmetry, such as rods, the templating may have an axis of symmetry like a divot that is a cylindrical trough. The divots may be introduced through machining, sheet metal dimpling or other deformation processing, or may include suitably-sized perforations or through-holes in the current collector. The current collector may be shaped so as to compress the particulate materials most optimally against each other, for example, in the case of rod-shaped particulate material, the current collector may comprise a sheet rolled into a cylinder around the cylindrical aggregates and compressed to constrain the cylinder diameter.

[00180] In order to reduce electrical resistance due to current collection, current collectors may be engineered to allow current collection to occur more homogeneously throughout the packed bed electrode by introducing current collecting components throughout the thickness of the electrode, or which penetrate a reasonable way through the thickness of the electrode.

[00181] In certain embodiments, a current collector may feature spikes, rods, tabs, or other high aspect ratio features that may project out into the electrode bed from a current collecting sheet or other boundary of the packed bed electrode. These high aspect ratio features may be configured in size and shape such that they contact many electrode material particles in the bed which would not be contacted by a simple, flat sheet current collectors. In certain embodiments, a sheet metal current collector with tabs that project into the space filled with particulate material is used as a current collector. In another aspect, an expanded sheet metal sheet is used as a current collector, and some struts within the sheet are cut and bent inward to serve as tabs projecting into the space filled with active material.

[00182] In certain embodiments, a conductive brush or series of wires are attached to a current collector. The wires flexibly project into the space filled by an iron electrode material. The wires are put in contact with the material due to their spring constants, and the contact may be improved by use of a compressive pressure.

[00183] In many embodiments, fasteners or other compression-providing elements are desired to retain current collectors in compressed position relative to one another. In what follows, the term fastener shall be understood to mean any element of a mechanical assembly that provides a fastening or compressive function through the use of an additional part that mechanically engages with other portions of the assembly. The performance of an iron positive electrode comprised of individual pellets increases when a sustained compressive load is applied to it before operating the cell. However, using metal fasteners such as stainless steel bolts to sustain the load is disadvantageous because of both added part count and assembly time, and because the bolts likely need to be electrically isolated from current collectors to mitigate the hydrogen evolution reaction (an undesired parasitic side reaction that lowers coulombic efficiency) occurring on the bolts, which adds more complexity to the design and likely adds to part count. Thus, while fasteners are desirable from a mechanical perspective, metallic fasteners are disadvantageous. Several methods of replacing metallic fasteners with other methods are considered below.

[00184] In some embodiments, non-metallic fasteners may be used in place of metallic fasteners. In one example embodiment, two sandwiching current collector plates may surround the iron electrode bed. The current collector plates could be made to apply a compressive force on the anode bed via fasteners made from an electrically insulating, non-metallic material that is resistant to degradation in the alkaline environment of the electrolyte. The electrically insulating and non-metallic nature of the fasteners would result in a lack of electron transport to the electrolyte-exposed surfaces of the fasteners, which would prevent the undesired hydrogen evolution reaction from occurring on the exposed surfaces of the fasteners. Reducing the HER rate means that more electrons participate in the desired anode reduction reaction, that is, a higher coulombic efficiency. In certain embodiments, the fasteners are bolts and nuts. In certain embodiments, the fasteners are made of one or more of acrylic, polytetrafluoroethylene, polyethylene, low density polyethylene, high density polyethylene, ultra high molecular weight polyethylene, polypropylene, or polyether ether ketone. In another exemplary embodiment, two sandwiching current collector plates that surround the anode bed could be made to apply a compressive force on the anode bed via

fasteners that save assembly time by the use of a "snap-in" mechanism rather than a screw mechanism that requires rotation of a fastener. In certain embodiments, the fasteners are dual-locking snap-in supports of the appropriate length. Any combination of the above fastening techniques may be used to provide compression while avoiding the use of metallic fasteners. Some fastening techniques are illustrated in FIGS. 11A and 11B. The illustration in FIG. 11A shows an electrically insulating nut 1103 sandwiching two current collecting sheets 1105 against an iron electrode material 1100 and labeled as an 'anode active material' in FIG. 11A. The nut 1103 tightens on the bolt 1102 to draw the sheets 1105 together, thereby compressing the anode active material 1100. A second example of snap-in compressive features, such as snap in support 1110 is shown in FIG. 11B replacing, and operating in a similar manner to, the bolt 1102 and nut 1103 of FIG. 11A.

[00185] In some embodiments, it may be useful to use a compliant mechanism capable of applying a large, distributed load to a current collector or compressive platen. In one example, the last face dimension of a rectangular prism box for containing the anode is a leaf-spring mechanism that springs back after anode loading to compress and contain the pellet anode. The current collector itself may be a compliant mechanism such that applying load on relatively few points (as occurs with a leaf spring), may result in a distributed load across the system.

[00186] Application of a compressive stress may be applied by alternative means from compression applied via mechanical fastening of the structure. In certain cases, iron electrode material may be contained by a rigid body (for example, a prismatic cell with current collectors or other mechanical supports on all faces), but the need for applying a compressive load during assembly may be eliminated by the use of an expanding material lining one face of the anode containment body. The expanding material may expand after assembly of the cell, thus providing a compressive load on the anode bed after filling the cell with electrolyte. In certain embodiments, the expanding material may be placed in between the iron electrode material and one of the small faces of the iron electrode material containment body. In certain embodiments, the expanding material is an expanding hydrogel that swells when in contact with the aqueous electrolyte, thus providing a compressive load on the anode active material upon filling with electrolyte. In certain embodiments, the expanding material is an inflatable plastic balloon with a port for pumping in air, thus providing a compressive load on the anode active material once pumped with air. The plastic balloon may be composed of poly(ethylene), poly(propylene) or similar polymers that are flexible and resistant to

degradation in alkaline solution. FIG. 12 illustrates an example of an embodiment of an expanding material 1200 contained within a rigid iron electrode containment assembly 1202. The unexpanded state is illustrated in the left hand of FIG. 12 and the expanded state of the expanding material 1200 compressing the anode active material 1202 within the anode containment assembly 1202 is illustrated on the right-hand side of FIG. 12.

[00187] In another embodiment, the container for the iron electrode material is not rigid, but still conserves its volume or has a maximal volume to within a reasonable approximation over stress ranges below ~10 MPa, as with some metal textiles - this may be termed a flexible cage. In such a case, an expandable material may be placed within the flexible cage, and compression provided by the expansion of expandable material within the flexible cage. The expandable materials from above may be used, as well. The flexible cage may be conducting and serve as both a current collector and as a means of providing compression to the iron electrode material with which it is filled.

[00188] In another embodiment, the iron electrode material may exhibit a substantial magnetic moment in the presence of a magnetic field. The iron electrode material may be ferromagnetic, as is the case for iron. Thus, a magnetic field set up by one or more permanent magnets or electromagnets may be used to induce a magnetic force on the iron electrode material toward a rigid wall, thereby providing a compressive load to the anode active material.

[00189] In another embodiment, pumps existing within the system, for instance, those intended to move electrolyte, are used to provide suction on the particulate bed. The suction provided by the pump pulls the particulate bed together, and the particulates into contact with one another. Particulates are prevented from being sucked into the pump by means of a screen or mesh with openings smaller than the smallest expected particulate.

[00190] In another aspect, phosphates (including iron phosphate), phosphoric acid, or similar phosphor-containing additives may be usefully incorporated into a particulate iron electrode material in order to promote mechanical contact and bonding between particulate materials. The phosphate groups may form phosphate bridges between the metal oxide groups, thereby cementing the particulate materials of the electrode bed together, and forming an electrode that is better mechanically and electrically connected. The oxides of irons may serve as useful conductors because several of them (especially magnetite and wüstite) are semiconducting. In the case where the bonded oxides are electrochemically reduced to

metallic species, such metallic species may electrochemically sinter or otherwise bond. Thus, the bonding of such oxides, even transiently may lead to enhanced electrochemical performance over many cycles. The electrode materials may be pre-treated with a phosphorus-containing solution before entering the electrolyte, or a phosphorus-containing compound may be introduced into the electrolyte for the purpose of forming such phosphate bonds. Phosphate bonds may occur across a variety of metal-oxide systems including in cadmium, magnesium, aluminum, and zinc. Phosphate additives may be particularly beneficial in iron electrodes as they may reduce the tendency for hydrogen evolution at the iron surface during charging as well.

[00191] In some embodiments, one may desire to create a conductive path between the particles of the iron electrode material via metallurgically bonding the particles of the iron electrode material prior to insertion into the electrolyte. Such a metallurgical bond may lead to sufficient conduction through the iron electrode material that compression is not needed to achieve satisfactory electrochemical performance. Below, a variety of methods for eliminating the need for compression of the iron electrode material are described.

[00192] In one embodiment, the iron electrode materials are thermally assembled via a high temperature process including sintering or brazing. A thermal step for bonding the iron electrode material to a current collector may decrease the contact resistance between particulate materials by fusing similar metals to one another for a more robust electrical connection. While sintering has been considered for the manufacturing of iron electrode materials, the sintering of some particulate iron materials has not been considered to date due to their unique particulate structure. In one example, direct reduced iron is an attractive feedstock for an iron electrode material, but due to its coarse particle size, it is not an obvious candidate for thermal bonding via a sintering process. Direct reduced iron may be used in a sintering process directly, or it may be used in combination with another bonding material at the surface of the direct reduced iron such that a suitable metallurgical bond is formed. The bonding material may be painted, sprayed or otherwise introduced onto the direct reduced iron or other particulate iron material in order to permit it to bond to other direct reduced iron particles during a thermal treatment process. The bonding material may be usefully concentrated at the contact points between the direct reduced iron or other particulate material as a means of gaining the most electrical contact with the smallest added cost. An example of a bonding material is a material with a low sintering temperature which may cause a metallurgical bond during a sintering process, such as a suspension of carbonyl iron

that is painted or sprayed onto the direct reduced iron or other particulate material. In a second example, a bonding material may melt, or cause a fusion weld or braze upon exposure to heat. In a second example, a nickel brazing compound may be coated onto an iron electrode material, and the material may then be heated to the appropriate temperature for a metallurgical bond to form. The thermal bonding method is illustrated in FIG. 13. FIG. 13 illustrates that a plurality of metal pellets 1300 are provided on an anode current collector 1302. Heat is applied to the pellets 1300 and anode current collector 1302 resulting in the pellets 1300 being fused to the current collector as illustrated in FIG. 13.

[00193] A possible manufacturing technique for a thermally bonded particulate bed system may feature a rolled sheet of steel which may act as the furnace belt. This belt would unroll from a coil and straighten to become a horizontally translating surface inside of a continuous hydrogen furnace. At the inlet of the furnace, iron electrode material (such as direct reduced iron) would accumulate on the belt via a hopper. This iron electrode material and belt sheet would travel through the furnace rising to a maximum temperature bonding the iron electrode material and the belt. This iron electrode material and current collector sheet could then be cut into small sections to be used as an anode in reactors.

[00194] In various embodiments, the particulate materials for iron electrodes achieve excellent contact with each other via creation of 'flats' due to the stress concentration at a contact point. In some instances, the electrode material may not need to be held at high force throughout life, but rather the particulate materials may be pressed against one another during fabrication, the flat spots created, and then held with a smaller force throughout life. To accomplish this, an electrode cage may be supported during the high-load stress application to form the flats on the particulate materials and lower the inter-particle contact resistance. The force may then be partially released, the cage may be removed from the supporting structure, and then the electrode cage may be put into the reactor under this lower compressive force, but with the contact resistance that was lowered due to the application of the higher compressive force. If, at any point during life, the cage gets jumbled or the cell gets too resistive, the cage may be removed, put into the supporting structure, recompressed, and the force could be released again, the cage could be put back into the cell.

[00195] In various embodiments, the solubility of iron intermediates in alkaline media may be utilized to form necks between particulate material in an iron electrode material comprising a packed bed. The iron electrode may be held at appropriate pH, temperature, and optionally voltage ranges such that the $HFeO_2^-$ soluble intermediate may form in high enough

concentrations that the bonds between particles within the packed bed grow due to solution-precipitation reactions mediated by the soluble species, as shown in the diagram below, wherein the particles are referred to as marbles. The bond between the particles may be referred to as a neck. The formation of such necks may be a preprocessing step or may happen in-situ in an electrochemical cell for energy storage. The coarsening may form necks between pellets to enhance inter-pellet conductivity, reducing overpotential at the anode. In one aspect of neck formation, the process involves soaking the pellet bed in an alkaline solution for >3 days, such that the soluble species coarsens the bed at the micron to millimeter scale and enhances inter-pellet contact. In another embodiment, electrochemical cycling is employed to enhance deposition of the soluble intermediate species. In a third embodiment, the pellets are coated in iron powder, such as atomized or sponge iron powder, to promote the formation of "necks" and reduce contact resistance between DRI pellets. As cycling continues, the powder particles can "sinter" to the host DRI pellet. Mechanistically this can occur due to the mass transfer of the soluble intermediate Fe species ($HFeO_2^-$) favoring deposition of discharge product at the interfaces of small and large particles, for example as illustrated in FIG. 14. Specifically, FIG. 14 illustrates that a bed 1400 of individual DRI pieces 1402 (e.g., DRI marbles) may be provided. An electrochemical and/or chemical reaction may result in the bed 1400 being formed into a necked together bed 1405 of DRI pieces 1402 (e.g., marbles) joined together by necks 1406 therebetween. In this manner, the bed 1405 may be a solid mass of joined DRI pieces as opposed to the original starting bed 1400 of separate pieces.

[00196] In various embodiments, the particulate materials may be bonded by techniques common for the welding of metallic materials. In one aspect, the particulate materials may be resistance welded by passage of a high current through the packed bed. The current may be applied by a compacting roller assembly such that the particles are brought into contact prior to or concurrently with a resistance welding process. In various embodiments, the particles may be mechanically deformed at high temperature such that a metallurgical bond forms at the contact points between the particles. In one example, a hot briquetting machine for the hot briquetting or direct reduced iron may be run at low compacting pressures such that the particulate material deforms at the contact points to form metallurgical bonds. For particulate materials with internal porosity (such as direct reduced iron) compacting may take advantage of the stress concentration at the contact points between particles such that metallurgical bonds form between particles, but the internal

porosity of the particulate material may be largely unchanged away from the contact points. In various embodiments, the creation of the metallurgical bonds may take place in inert atmosphere to prevent oxidation of the iron electrode material. In various embodiments, the bed of particulate material may be ultrasonically consolidated or consolidated by other vibratory means. The ultrasonic or vibratory compaction may be accompanied by an axial pressure. In various embodiments, the particulate materials may be fusion welded together via any of the fusion welding techniques common in the art, including but not limited to tungsten inert gas welding, metal inert gas welding, and gas metal arc welding. In another aspect, the material may be explosively welded.

[00197] In various embodiments, a conducting metallic solder may be placed at the contact points between the particulate materials such that a metallic bond may be formed between the materials. In one example, tin or a may be dip coated onto a particulate material bed. In another example, copper may be dip coated onto the particulate material. In an additional embodiment, the conducting liquid is coated onto the particulate by means of passing both through a tube or nozzle and depositing the coated particulate. Precise control of the nozzle allows precision placement of individual particulates, which may aid in achieving optimized electrode geometries. Particulates deposited in this manner may be stacked to produce three-dimensional structures.

[00198] In various embodiments, the particulate material may be etched via any one of a variety of acids and subsequently mechanically deformed prior to insertion into an electrochemical cell. The etching action may remove any surface oxides impeding bonding, and may permit electrical contact between the anode materials. Acids such as hydrochloric acid, nitric acid, or any other asides used to strip iron oxides off of metallic iron surfaces may be used. In some instances, the compression may be done while the particulate material is in the acid.

[00199] In various embodiments, a particulate material for an iron electrode may comprise a direct reduced iron material. The direct reduced iron material may be fabricated without the cement coating used to decrease sticking during the reduction processing. These cements may inhibit charge transfer across the interfaces between pellets. In such a manner, the direct reduced iron materials may exhibit enhanced charge transfer properties for electrochemical cycling. In one example, a fluidized bed reduction process is used in order to enable the use of direct reduction iron materials which do not require cement coatings.

[00200] In various embodiments, particulate material to comprise an iron electrode material may be compressed around a current collector mesh. The current collecting mesh may then be heated (e.g. by electrical resistance) such that the chicken wire welds to the particulate material surrounding it. The pellets are then interconnected by the mesh, and may be welded to each other. The mesh may be comparatively thick and open, like a chicken-wire fence material.

[00201] **Pellet size and shape modification before battery assembly**

[00202] During operation of the battery with a pellet bed electrode, intra-pellet mass and electronic transfer may be difficult due to the size of pellets, resulting in polarization that can reduce the energy efficiency of the battery via (1) Voltage drops on charge and discharge resulting in lower voltaic efficiency and (2) Coulombic inefficiency due to insufficient competition with the hydrogen evolution reaction during charge. As a result of insufficient charging, the specific capacity of resultant iron electrodes is also reduced. For example, in certain cases the polarization is dominated by mass transport of hydroxide ions through pellet pores from the outside of a pellet to iron reaction sites at the center of the pellet. In other cases, the polarization is dominated by electronic transport through the intra-pellet network of iron material from an electrical point of contact on the outside of a pellet to the center of the pellet. Either of these sources of polarization may result in local electrochemical potential within the pellet that favors the hydrogen evolution reaction during charge more than the desired reduction reaction of iron oxide species, which reduces coulombic efficiency.

[00203] In one aspect, the size of the particulates may be chosen to promote better packing. For one non-limiting example, a bed may be comprised of 50% particles over 5 mm in diameter, 25% particles between 5 mm and 1 mm in diameter, and 25% particles under 1 mm diameter, in order for the smaller particles to fill space between the larger particles. Particles of smaller sizes than the native DRI size may be made from DRI by the methods detailed below. These particles may be added to their containment in a specific order in order to ensure optimal packing, for one non-limiting example, a layer of larger particles may first be added, followed by an addition of smaller particles to fill spaces, followed by another layer of larger particles and another addition of smaller particles.

[00204] Size reduction of iron pellets before battery assembly is disclosed as a method of addressing one or more of the energy efficiency and specific capacity losses due to the size of the pellets. Reducing the size of pellets reduces the characteristic length of intra-pellet

mass and electrical transport, which reduces polarization and may enhance one or more of energy efficiency and specific capacity.

[00205] Reducing the size of pellets by means of a comminution process, such as a jaw crusher ("crushing") before assembling into a pellet bed has been shown to result in higher voltaic efficiency. However, the crushing of the pellets should result in both less particle-to-particle contacts on a per-particle basis (irregular particles achieve fewer contacts than spherical particles), and more interface resistances per particle in a bed of a given thickness. Further, 'rattlers,' wherein a particle is not in electrical contact with its neighbors due to the geometric packing of the bed are more likely for polydisperse, irregular shapes than for relatively monodisperse spheres. As a result, it is inferred that the gains in voltaic efficiency due to enhanced intra-pellet mass and electrical transport partially mask increases in electronic resistance-based voltage drops and a lack of electrically accessed material (and therefore lower capacity) due to an increased rattler fraction.

[00206] In certain embodiments, the size of pellets is reduced to half or less of its original size through crushing, which results in a reduction of the overpotential of the iron electrode by more than 10 mV (mV = millivolts = 10-3 V).

[00207] Crushing of the pellets could lead to substantial performance gains if a secondary conductive additive were to be added to the pellet bed to enhance one more of inter-pellet electrical conductivity or pellet-to-current-collector electrical conductivity. The additive would increase conductivity by increasing the conductive surface area in contact with pellets, mitigating the added interface resistance in a pellet bed of crushed pellets. An additive is desired which does not inhibit mass transfer and results in substantially higher electrical conductivity of the bed. The optimal additive percolates at low volume fractions and is highly conductive.

[00208] In certain embodiments, the additive is one or more of carbon black or graphite that is added to the crushed pellet bed in greater than 1% volume fraction, such that the carbon black or graphite bridges crushed pellets together. In certain other embodiments, activated carbon or biochar or low to modest conductivity is used as a low-cost alternative to graphite.

[00209] In certain embodiments, the additives are pieces of conductive mesh such as stainless steel wire mesh.

[00210] In certain embodiments, the additives are conductive rods such as stainless steel rods of a diameter less than the average pellet size.

[00211] Before nominal operation of the battery, additives that improve iron electrode performance may be chemically incorporated into the iron electrode via various processes that rely on intra-pellet mass transport of chemical species in an electrolyte to active iron sites within the porous structure of the pellet. Homogeneous permeation of the additives into the pellets is often necessary to achieve the maximum desired performance-enhancing effect of the additive. However, it is often difficult to get homogeneous permeation of certain liquid-soluble and solid-state additives into pellets that are typically output from direct reduction processes, especially for those additives with low solubility that react with the direct reduced iron.

[00212] Size reduction of iron pellets before battery assembly is disclosed as a method of achieving more homogenous permeation of liquid-soluble and solid-state additives into the pellets during the additive incorporation process. Reducing the size of pellets reduces the characteristic length of intra-pellet mass transport, which reduces gradients in concentration of the additive, thus enabling a more homogeneous permeation and incorporation of the additive into the electrode.

[00213] In certain embodiments, the additive incorporation process is one or more of soaking in an electrolyte, electrochemical plating, and electrochemical cycling.

[00214] In certain embodiments, the additive is an initially liquid-soluble hydrogen evolution inhibitor that incorporates into the solid-state electrode via an electrochemical or spontaneous chemical reaction.

[00215] In certain embodiments, the additive is an initially solid-state hydrogen evolution inhibitor that is further incorporated into the solid-state electrode via an electrochemical or chemical dissolution-reprecipitation reaction.

[00216] In certain embodiments, additives include one or more of sodium thiosulfate, sodium thiocyanate, polyethylene glycol (PEG) 1000, trimethylsulfoxonium iodide, zincate (by dissolving ZnO in NaOH), hexanethiol, decanethiol, sodium chloride, sodium permanganate, lead (IV) oxide, lead (II) oxide, magnesium oxide, sodium chlorate, sodium nitrate, sodium acetate, iron phosphate, phosphoric acid, sodium phosphate, ammonium sulfate, ammonium thiosulfate, lithopone, magnesium sulfate, iron(III) acetylacetonate, hydroquinone monomethyl ether, sodium metavanadate, sodium chromate, glutaric acid,

dimethyl phthalate, methyl methacrylate, methyl pentynol, adipic acid, allyl urea, citric acid, thiomalic acid, N-(2-aminoethyl)-3-aminopropyl trimethoxysilane, propylene glycol, trimethoxysilyl propyl diethylene, aminopropyl trimethoxysilane, dimethyl acetylenedicarboxylate (DMAD), 1,3-diethylthiourea, N,N'-diethylthiourea, aminomethyl propanol, methyl butynol, amino modified organosilane, succinic acid, isopropanolamine, phenoxyethanol, dipropylene glycol, benzoic acid, N-(2-aminoethyl)-3-aminopropyl, behenamide, 2-phosphonobutane tricarboxylic, mipa borate, 3-methacryloxypropyltrimethoxysilane, 2-ethylhexoic acid, isobutyl alcohol, t-butylaminoethyl methacrylate, diisopropanolamine, propylene glycol n-propyl ether, sodium benzotriazolate, pentasodium aminotrimethylene phosphonate, sodium cocoyl sarcosinate, laurylpyridinium chloride, steartrimonium chloride, stearalkonium chloride, calcium montanate, quaternium-18 chloride, sodium hexametaphosphate, dicyclohexylamine nitrite, lead stearate, calcium dinonylnaphthalene sulfonate, iron(II) sulfide, sodium bisulfide, pyrite, sodium nitrite, complex alkyl phosphate ester (e.g. RHODAFAC® RA 600 Emulsifier), 4-mercaptobenzioc acid, ethylenediaminetetraacetic acid, ethylenediaminetetraacetate (EDTA), 1,3-propylenediaminetetraacetate (PDTA), nitrilotriacetate (NTA), ethylenediaminedisuccinate (EDDS), diethylenetriaminepentaacetate (DTPA), and other aminopolycarboxylates (APCs), diethylenetriaminepentaacetic acid, 2-methylbenzenethiol, 1-octanethiol, bismuth sulfide, bismuth oxide, antimony(III) sulfide, antimony(III) oxide, antimony(V) oxide, bismuth selenide, antimony selenide, selenium sulfide, selenium(IV) oxide, propargyl alcohol, 5-hexyn-1-ol, 1-hexyn-3-ol, N-allylthiourea, thiourea, 4-methylcatechol, trans-cinnamaldehyde, Iron(III) sulfide, calcium nitrate, hydroxylamines, benzotriazole, furfurylamine, quinoline, tin(II) chloride, ascorbic acid, tetraethylammonium hydroxide, calcium carbonate, magnesium carbonate, antimony dialkylphosphorodithioate, potassium stannate, sodium stannate, tannic acid, gelatin, saponin, agar, 8-hydroxyquinoline, bismuth stannate, potassium gluconate, lithium molybdenum oxide, potassium molybdenum oxide, hydrotreated light petroleum oil, heavy naphthenic petroleum oil (e.g. sold as Rustlick® 631), antimony sulfate, antimony acetate, bismuth acetate, hydrogen-treated heavy naphtha (e.g. sold as WD-40®), tetramethylammonium hydroxide, NaSb tartrate, urea, D-glucose, C6Na2O6, antimony potassium tartrate, hydrazine sulfate, silica gel, triethylamine, potassium antimonate trihydrate, sodium hydroxide, 1,3-di-o-tolyl-2-thiourea, 1,2-diethyl-2-thiourea, 1,2-diisopropyl-2-thiourea, N-phenylthiourea, N,N'-diphenylthiourea, sodium antimonyl L-tartrate, rhodizonic acid disodium salt, sodium selenide, potassium sulfide, and combinations thereof.

[00217] FIG. 15 illustrates example pellet beds 1501 and 1502 according to various embodiments. During operation of the battery with a pellet bed electrode, mass and electronic transfer through the pellet bed may be difficult due to the total thickness of the pellet bed, resulting in polarization that can reduce the energy efficiency of the battery via (1) voltage drops on charge and discharge resulting in lower voltaic efficiency and (2) coulombic inefficiency due to insufficient competition with the hydrogen evolution reaction during charge. As a result of insufficient charging, the specific capacity of resultant iron electrodes is also reduced. For example, in certain cases the polarization is partially due to mass transport of hydroxide ions from outside of the pellet bed to the center of the pellet bed. In other cases, the polarization is partially due to electronic transport through the network of iron pellets. Either of these sources of polarization may result in local electrochemical potential within the pellet that favors the hydrogen evolution reaction during charge more than the desired reduction reaction of iron oxide species, which reduces coulombic efficiency.

[00218] Increasing the volumetric packing density of pellets is one way to address one or more of the energy efficiency and specific capacity losses due to the total thickness of the pellet bed. By increasing the volumetric packing density, the thickness of the pellet bed for a given electrode capacity decreases, thereby reducing through-bed polarization and enhancing one or more of energy efficiency or specific capacity. For example, FIG. 15 illustrates a pellet bed 1501 with porous pellets 1503 that are formed as spheres or marbles and pellet bed 1502 with porous pellet pieces 1505 that may be formed by crushing spheres, marbles, or other shapes into pieces. The intra-pellet transport length t1 of the pellet bed 1501 may be greater than the intra-pellet piece length t2 of the pellet bed 1502.

[00219] Processing the pellets by means of a jaw crusher ("crushing") before assembling into a pellet bed is disclosed as a method to increase volumetric packing density and reduce polarization. In this manner, the crushing may result in a pellet bed 1502 rather than the pellet bed 1501. Before crushing, the pellets may be roughly spherical and may have a narrow size range. The crushing operation may break the pellets into multiple pieces with non-spherical shapes and a broader size distribution that result in a higher volumetric packing density. The resulting higher volumetric packing density reduces the thickness of the pellet bed for a fixed projected area and mass of electrode material, thus reducing through-bed polarization and enhancing one or more of energy efficiency or specific capacity (for example when comparing pellet bed 1502 to pellet bed 1501 such that pellet bed 1502 has reduced through-bed polarization and enhanced one or more of energy efficiency or specific

capacity in comparison to pellet bed 1502 when the material composition of the porous pellets 1503 and porous pellet pieces 1505 may be the same). FIG. 16 illustrates the pellet beds 1501 and 1502 with current collectors 1601 attached. The height of the pellet bed 1501 without crushing, h1, may be greater than the height, h2, of the pellet bed with crushing 1502 even though the same amount of pellet material may be present in pellet bed 1501 and 1502. As such, crushing may compact the size of the electrode.

[00220] In certain embodiments, the pellets after a crushing operation break into pieces with jagged edges and with a polydisperse size distribution such that smaller pieces fall within the interstices between larger pellets, thus increasing packing density.

[00221] **Methods of regaining performance after performance decay**

[00222] Certain performance attributes of a pellet bed electrode may worsen due to time-dependent or charge-throughput dependent mechanisms during battery operation. Performance attributes that worsen may include but are not limited to specific capacity (mAh/g), electrode overpotential (mV), self-discharge rate (mAh/mo.), and coulombic efficiency (%). Several methods of regaining iron electrode performance by treatments to the battery after beginning of life are disclosed here.

[00223] In certain cases, the specific capacity of the electrode may decrease with battery cycling because of a cycle-dependent change in microstructure of the electrode that hinders mass or electronic transport, thereby reducing the accessible capacity at a given polarization. More specifically, pores within the pellets may become increasingly constricted with cycling as they are filled with remnant electrochemical discharge products that have a larger molar volume (per mol iron) than metallic iron. The progressive pore filling results in a hindered mass transport to the iron within those pores, which may render the iron within pores less and less accessible for the electrochemical reaction to occur, which reduces specific capacity. In other cases, the electrical resistance to certain iron sites may increase because of a constriction of the conductive pathways provided by the metallic network within a pellet. In other cases, there may be a core of unreacted metallic iron within each pellet that is completely covered by a passivating layer.

[00224] The loss of accessible capacity due to battery use may be regained by ex-situ treatments that are performed on the pellets after the electrode capacity has decayed to a minimum threshold. Various embodiments include processing the used pellets with mechanical, chemical, electrochemical, and/or thermal processes before re-introducing the

pellets into the electrochemical cell (i.e., processing the pellets ex-situ) to return the electrode to a state with better chemical and physical properties. Better chemical and physical properties may include higher content of desirable impurities (e.g., hydrogen evolution reaction (HER) suppressants), lower content of undesirable impurities (e.g., HER catalysts), higher specific surface area, higher total porosity, different pore size distribution (e.g. multimodal to reduce mass transport resistance), different pellet size distribution (e.g. multimodal to enhance bed packing), different aspect ratio (e.g. to enhance bed packing), etc. Mechanical processes that may be applied to the pellets ex-situ may include crushing, pulverizing, and/or powderizing that include but are not limited to size reduction. A mechanical size reduction re-exposes passivated metallic iron at the core of pellets, which makes the previously inaccessible iron accessible, thus increasing capacity. Note that mechanical processes that expose initially passivated iron at the core of pellets may not be desirable to be done before battery use, because more exposed metallic iron provides more sites at which the hydrogen evolution reaction might occur, either via the Faradaic parasitic reaction during charging, or via the spontaneous self-discharge reaction. However, mechanical processes done ex-situ may be desirable as a method to regain and/or improve capacity electrical resistance that have decayed due to battery usage, at which point a larger fraction of iron is passivated and inaccessible as illustrated for example in FIG. 17. Specifically, FIG. 17 shows a pellet 1702 after battery usage that is processed ex-situ, such as by crushing, pulverizing, etc., to expose the iron core 1703 in the pellet 1702. FIG. 17 shows the passivation layer 1705 which may make the core 1703 inaccessible until after processing.

[00225] Thermal processes that may be applied to the pellets ex-situ may include processing the pellets in at elevated temperature in reducing (e.g., hydrogen), oxidizing, and/or carburizing (e.g., carbon monoxide and/or carbon dioxide) atmosphere. In certain embodiments, the reducing condition is a gas mixture is 10% nitrogen, 30% carbon monoxide, 15% carbon dioxide, and 45% hydrogen at 800°C for 90 minutes. Electrochemical processes that may be applied to the pellets ex-situ may include reverse electroplating, electrochemical dissolution, etc. Chemical processes that may be applied to the pellets ex-situ may include acid etching, etc. In various embodiments, to increase accessible capacity of the pellets during the discharge reaction, the pellets may be pretreated by soaking in an acid bath (e.g., concentrated HCl) that will etch the iron and enlarge pores in the pellets, increasing the total porosity of the pellets in comparison to used pellets. In various embodiments, to increase the accessible capacity of the pellets during the discharge reaction, the pellets may be

pretreated by soaking in a neutral or slightly basic bath that removes excess discharge product from the electrode. For example, one of the expected discharge products, iron (II) hydroxide, is typically unstable at pH < 8. By soaking in a bath at pH < 8, the iron (II) hydroxide is preferentially removed while the metallic iron is preserved in the electrode. In the pH range pH > 7 and pH < 8, the bath may be a diluted form of the electrolyte used during electrochemical operation of the battery. After pretreatment, the etched and now more porous pellets may be re-assembled into the negative electrode. The chemical process time may be optimized to increase the usable capacity of the pellets, without losing too much active material to the acid etching solution. Any of the aforementioned processes may be optimized to preferentially make small pores in the pellets larger. In certain embodiments, an electrochemical process utilizes one or more large current pulses that result in a non-uniform current distribution within the pellet such that current is concentrated at sharp and small physical features within the pellet, which preferentially drives the electrochemical dissolution at small physical features and thus makes initially small pores larger. Any of the above processes may also be done before battery operation to make the chemical and physical properties of the pellets better relative to their unmodified, unused state.

[00226] **Electrolyte additives for controlling discharge product morphology**

[00227] The shape and size of discharge product within the pores of the iron pellets can affect performance in a variety of ways. For example, a thin, uniform layer of discharge product may avoid clogging pores, which may improve capacity retention. On the other hand, a thin uniform layer of discharge product that is not porous may passivate underlying metallic iron such that mass transport of hydroxide ions through the discharge product layer during discharge becomes hindered, thus reducing accessible capacity of the electrode. In another example, an uneven, high-surface-area, porous discharge product may facilitate mass transport through the discharge layer while increasing the active surface area for the next discharge, both of which may increase total accessible capacity. FIG. 18 compares discharge product distributions. The left side of FIG. 18 shows discharge product 1803 unevenly distributed on a surface of an anode 1802. The right side of FIG. 18 shows discharge product 1804 in an even layer on the surface of the anode 1802. The discharge product formation may be mediated by the electrolyte additives, anode additives, and/or surface coatings of the anode 1802. Various methods of controlling discharge product morphology in iron electrodes are disclosed.

[00228] Additives and counterions in the electrolyte and/or in the electrode may be used to control the discharge product morphology. Additives and counterions may change the porosity of the discharge layer and accessibility electrochemically active sites by way of the following mechanism: Fe forms a two-layer discharge product with a relatively static inner layer of Fe_3O_4 and a very porous outer layer, which is affected strongly by electrolyte composition. Bivalent cations tend to inhibit uniform discharge and help produce a more porous outer layer. Monovalent cations inhibit uniform discharge and produce a more porous outer layer when they are not well-matched in size with the Fe cations in the outer layer of discharge product. For example, lithium and cesium cations tend to produce a more porous outer layer than sodium and potassium cations because lithium and cesium are less matched in size with the iron cation. Additives and counterions to control discharge product morphology include but are not limited to sulfide (S_2-), hydrosulfide (HS-), lithium cation (Li+), sodium cation (Na+), calcium cation (Ca_2+), selenide (Se_2-), cesium cation (Cs+), and barium cation (Ba_2+). In certain embodiments, sodium sulfide, lithium hydroxide, sodium hydroxide, calcium hydroxide, sodium selenide, and/or barium hydroxide are added into the electrolyte at various concentrations to provide the soluble additives and counterions that act to control discharge product morphology.

[00229] In certain embodiments, the additives to control discharge product morphology are initially contained within the solid-state electrode. The solid-state additives may be in the form of solid-state metal oxides and/or metal sulfides introduced as solids to an iron electrode. Metal sulfides and oxides of interest include: FeS, FeS_2, MnS, Bi_2S_3, Bi_2O_3, Sb_2S_3, FeAsS, PbS, SnS, HgS, AsS, $Pb_4FeSb_6S_{14}$, $Pb_3Sn_4FeSb_2S_{14}$, SeS_2, among others.

[00230] In certain embodiments, additives to control discharge product morphology include one or more of sodium thiosulfate, sodium thiocyanate, polyethylene glycol (PEG) 1000, trimethylsulfoxonium iodide, zincate (by dissolving ZnO in NaOH), hexanethiol, decanethiol, sodium chloride, sodium permanganate, lead (IV) oxide, lead (II) oxide, magnesium oxide, sodium chlorate, sodium nitrate, sodium acetate, iron phosphate, phosphoric acid, sodium phosphate, ammonium sulfate, ammonium thiosulfate, lithopone, magnesium sulfate, iron(III) acetylacetonate, hydroquinone monomethyl ether, sodium metavanadate, sodium chromate, glutaric acid, dimethyl phthalate, methyl methacrylate, methyl pentynol, adipic acid, allyl urea, citric acid, thiomalic acid, N-(2-aminoethyl)-3-aminopropyl trimethoxysilane, propylene glycol, trimethoxysilyl propyl diethylene, aminopropyl trimethoxysilane, dimethyl acetylenedicarboxylate (DMAD), 1,3-

diethylthiourea, N,N'-diethylthiourea, aminomethyl propanol, methyl butynol, amino modified organosilane, succinic acid, isopropanolamine, phenoxyethanol, dipropylene glycol, benzoic acid, N-(2-aminoethyl)-3-aminopropyl, behenamide, 2-phosphonobutane tricarboxylic, mipa borate, 3-methacryloxypropyltrimethoxysilane, 2-ethylhexoic acid, isobutyl alcohol, t-butylaminoethyl methacrylate, diisopropanolamine, propylene glycol n-propyl ether, sodium benzotriazolate, pentasodium aminotrimethylene phosphonate, sodium cocoyl sarcosinate, laurylpyridinium chloride, steartrimonium chloride, stearalkonium chloride, calcium montanate, quaternium-18 chloride, sodium hexametaphosphate, dicyclohexylamine nitrite, lead stearate, calcium dinonylnaphthalene sulfonate, iron(II) sulfide, sodium bisulfide, pyrite, sodium nitrite, complex alkyl phosphate ester (e.g. RHODAFAC® RA 600 Emulsifier), 4-mercaptobenzioc acid, ethylenediaminetetraacetic acid, ethylenediaminetetraacetate (EDTA), 1,3-propylenediaminetetraacetate (PDTA), nitrilotriacetate (NTA), ethylenediaminedisuccinate (EDDS), diethylenetriaminepentaacetate (DTPA), and other aminopolycarboxylates (APCs), diethylenetriaminepentaacetic acid, 2-methylbenzenethiol, 1-octanethiol, bismuth sulfide, bismuth oxide, antimony(III) sulfide, antimony(III) oxide, antimony(V) oxide, bismuth selenide, antimony selenide, selenium sulfide, selenium(IV) oxide, propargyl alcohol, 5-hexyn-1-ol, 1-hexyn-3-ol, N-allylthiourea, thiourea, 4-methylcatechol, trans-cinnamaldehyde, Iron(III) sulfide, calcium nitrate, hydroxylamines, benzotriazole, furfurylamine, quinoline, tin(II) chloride, ascorbic acid, tetraethylammonium hydroxide, calcium carbonate, magnesium carbonate, antimony dialkylphosphorodithioate, potassium stannate, sodium stannate, tannic acid, gelatin, saponin, agar, 8-hydroxyquinoline, bismuth stannate, potassium gluconate, lithium molybdenum oxide, potassium molybdenum oxide, hydrotreated light petroleum oil, heavy naphthenic petroleum oil (e.g. sold as Rustlick® 631), antimony sulfate, antimony acetate, bismuth acetate, hydrogen-treated heavy naphtha (e.g. sold as WD-40®), tetramethylammonium hydroxide, NaSb tartrate, urea, D-glucose, C6Na2O6, antimony potassium tartrate, hydrazine sulfate, silica gel, triethylamine, potassium antimonate trihydrate, sodium hydroxide, 1,3-di-o-tolyl-2-thiourea, 1,2-diethyl-2-thiourea, 1,2-diisopropyl-2-thiourea, N-phenylthiourea, N,N'-diphenylthiourea, sodium antimonyl L-tartrate, rhodizonic acid disodium salt, sodium selenide, potassium sulfide, and combinations thereof

[00231] A pretreatment involving electrochemical cycling may also serve to control the morphology of discharge products for an iron electrode. For example, the inventors have observed that the compactness of the discharge product changes with temperature and current

density. A pretreatment involving electrochemical cycling at a temperature and current density that is not necessarily the nominal operating condition of the battery may be used to form a discharge product morphology that is conducive to high accessible capacity, and is sustained when the operating conditions are set to nominal values after the pretreatment. In various embodiments, the pretreatment consists of deep electrochemical charge and discharge cycling at 10°C at a gravimetric current density of 25 mA/gFe for 100 cycles.

[00232] **Using temperature as a means of improving performance**

[00233] The inventors have found that decreasing the operating temperature of the iron electrode to below 30°C improves various performance attributes, such as specific capacity, the retention of specific capacity over many electrochemical cycles, and Coulombic efficiency of the electrode. Various mechanisms may be at play simultaneously to result in these effects. For example, specific capacity may be improved at lower temperatures due to an increase in electrical conductivity of the electrode material, including but not limited to iron and iron oxide discharge products. The increase in electrical conductivity of the electrode material would enhance electrical transport to electrochemical reaction sites, which would result in an increase in specific capacity at a given polarization limit of the electrode. In another example, reducing temperature may slow the kinetics of undesirable electrolyte degradation or poisoning reactions that take place during the lifetime of the battery, such as carbonate formation due to carbon dioxide from the atmosphere. For example, carbonate formation consumes OH- ions, decreasing the conductivity of the electrolyte, which decreases the pH of the solution and leads to a decrease in specific capacity. Decreasing the temperature slows these undesirable reactions and result in better specific capacity retention at the iron electrode over the lifetime of the battery. In another example, the decrease in temperature may slow the kinetics of the undesirable hydrogen evolution reaction more so than the desired iron reduction reaction during charging of the battery, thus resulting in a higher coulombic efficiency during charging. In various embodiments, the iron electrode is maintained at 20°C ± 5°C to improve electrode performance. In other embodiments, the iron electrode is maintained at 10°C ± 5°C to improve electrode performance. FIG. 19 is a temperature plot of specific capacity and Coulombic efficiency versus cycle number. .

[00234] **Redox mediator to improve performance**

[00235] Better electrochemical kinetics of the charging (reduction) and discharging (oxidation) reactions at the iron-based electrode would improve both voltaic efficiency and

coulombic efficiency of the cell. A redox mediator can be used to improve the electrochemical kinetics of the iron-based electrode. A redox mediator is a chemical compound that acts as an electron "shuttle" to mediate a reduction or oxidation reaction. Though typically used in the field of biocatalysis, redox mediators can also be used to facilitate the desired oxidation and reduction reactions at the iron-based electrode. Requirements of the redox mediator include (1) fast and reversible redox kinetics; (2) similar redox potential to that of the reaction it facilitates (including but not limited to $Fe \rightleftarrows Fe(OH)_2$ and/or $Fe(OH)_2 \rightleftarrows Fe_3O_4$); (3) stable in the presence of the electrolyte of interest. The redox mediator can be either soluble or insoluble in the electrolyte of interest. In some embodiments, the redox mediator contains one or more unsaturated base groups, saturated base groups, or combinations thereof. In some embodiments, the base groups contain electron-withdrawing functional groups, electron-donating functional groups, or combinations thereof. In certain embodiments, the unsaturated base groups include but are not limited to cyclopenta-1,3-diene, benzene, 1H-pyrrole, pyridine, pyrazine, furan, 4H-pyran, 1,4-dioxine, thiophene, 4H-thiopyran, 1,4-dithiine, 1-methyl-1H-pyrrole, or combinations thereof. In certain embodiments, the saturated base groups include but are not limited to cyclopentane, cyclohexane, 1,4-dioxane, tetrahydrofuran, tetrahydro-2H-pyran, 1,4-dithiane, tetrahydrothiophene, tetrahydro-2H-thiopyran, 1,4-dimethylpiperazine, 1,3,5-troxane, 1,3,5-trithiane, or combinations thereof. In certain embodiments, the electron-withdrawing functional groups include but are not limited to nitro, trichloro, cyano, carboxyl, fluoro, hydroxyl, or combinations thereof. In certain embodiments, the electron-donating functional groups include but are not limited to primary amine, secondary amine, tertiary amine, amide, methoxy, methyl, alkyl, alkenyl, alkynyl, phenyl, or combinations thereof. In one embodiment, the redox mediator for the iron-based negative electrode are viologen-based compounds. In certain embodiments, the viologen-based compounds include but are not limited to methyl viologen, propyl viologen, hexyl viologen, octyl viologen or combinations thereof.

[00236] **Sulfide incorporation to the iron electrode via electrolyte**

[00237] In an electrochemical cell with an iron electrode, sulfur addition to the cell unlocks utilization of the iron electrode. However, sulfur is a known catalyst poison, so in electrochemical cell embodiment with a catalyst positive electrode, it may be optimal for the sulfur concentration around the iron electrode is high, while sulfur concentration at the catalyst electrode is low.

[00238] In one embodiment, sulfur may be concentrated at the iron electrode by submerging the iron electrode in a highly concentrated sulfur solution before it enters the electrochemical cell. Furthermore, if the iron electrode undergoes a single formation cycle of charge, then discharge, sulfur will be electrochemically added to the structure of the iron electrode. Then upon addition to the desired electrochemical cell it will remain concentrated near the anode.

[00239] In certain embodiments, the iron electrode is soaked in an electrolyte with a high sulfide concentration (i.e., >50 mM) prior to cycling in an electrolyte with a lower sulfide concentration (ie 50 mM).

[00240] In certain embodiments, the porous iron electrode is soaked in an electrolyte bath with any alkali or transition metal sulfide (Na_2S, K_2S, Bi_2S_3, SbS_3, etc.) to increase the presence of sulfide.

[00241] In certain embodiments, sulfide is incorporated through a high sulfide concentration electrolyte soak prior to cycling, after which the positive electrodes are inserted into the full cell wherein the initial sulfide concentration can be in the range of 10-250 mM (1.4-33.8 mgS/gFe) or higher.

[00242] In one non-limiting example, the porous iron electrode described above comprises a bed of DRI pellets.

[00243] Uniform or controlled incorporation of sulfide or other beneficial additives into a porous iron electrode is difficult. One method to uniformly incorporate additives into a porous material is vacuum infiltration, where a substrate is exposed to vacuum (<1 atm) to evacuate the pores and then exposed to a liquid or molten additive to infill any vacancies in the material.

[00244] In various embodiments, a substrate is exposed to vacuum sufficient to evacuate pores. FIG. 20 illustrates one example method of evacuating pores. The substrate 2000 is in a first step exposed to a high vacuum to empty the pores 2001.

[00245] In one embodiment, the evacuated substrate is then exposed in a second step to an aqueous electrolyte formulation containing additives as specified previously at temperatures between 0 and 250°C resulting in pores fully or partially filled with additive 2002. After specified time, such as less than 48 hours, the substrate 2000 may be rinsed or centrifuged to remove excess electrolyte in a third step.

[00246] In one embodiment, the evacuated substrate is then exposed to a liquid or molten form of additive, where additives are those specified previously in section ## that someone skilled in the art could identify as being compatible with melt processes (e.g. octanethiol, FeS), at temperatures between 25 to 250°C or 250 and 2000°C. After a specified time less than 48 hours, substrate may be rinsed or centrifuged to remove excess liquid or molten material.

[00247] In one embodiment, the evacuated substrate is then exposed to a gaseous additive (e.g. H_2S, H_2Se, CS_2 above 50°C, PH_3). After a specified time, such as less than 48 hours, substrate may be purged with an inert gas or under vacuum to remove excess of the gaseous additive.

[00248] In a non-limiting example, a solution containing sodium sulfide is vacuum infiltrated into the pores of a porous iron electrode 2000 prior to cycling to improve the penetration. Better penetration of sulfide into the anode may improve overall performance capacity.

[00249] In a non-limiting example, sodium thiosulfate is heated until melted (>45°C) and vacuum infiltrated into the pores of a porous iron electrode prior to cycling.

[00250] Additional methods to localize the sulfide to the iron particulate material electrode include sequestering the sulfide additive in a holder of variable permeability within or adjacent to the electrode. In this way, controlled amounts of sulfide could be added to the iron particulate electrode through passive or active electrochemical or chemical dissolution.

[00251] In one embodiment, the additive may be contained in a fully or semipermeable holder, where the holder is made of a plastic stable in an alkaline solution (e.g., polypropylene, polyethylene).

[00252] In one embodiment, the additive may be contained in the holder behind an ion-selective membrane, which permits flow of electrolyte into the holder and the slow diffusion of additive into solution.

[00253] In one embodiment, the additive may be contained in an electrically conductive material (e.g., conducting polymer mesh, metallic wire mesh).

[00254] In one embodiment, the holder may be made of a layer of porous oxide (e.g. silica).

[00255] In one embodiment, the additive holder may be in physical, electrical, or physical and electrical contact with the iron particulate material electrode.

[00256] In one embodiment, the additive holder may be in contact with the electrolyte and only in contact with the iron particulate material electrode through ionic transport in the electrolyte.

[00257] In one embodiment, the additive holder may be submerged in a separate container of electrolyte to provide a constant source of sulfide. The electrolyte in contact with the iron particulate material electrode is then replaced with the electrolyte in contact with the additive holder.

[00258] In one embodiment, the additive holder may be in electrical contact with a potentiostat or system, which maintains the holder at potentials that prevent the dissolution of the additive in the holder. FIG. 21 illustrates example additive holder configurations. In the configuration shown in the top portion of FIG. 21, the bag containing additive 2104 may be in contact with the iron particulate material 2103 disposed in the electrolyte 2100 between the current collectors 2102 along with the iron particulate material 2103. In the configuration shown in the bottom portion of FIG. 21, the bag containing additive 2104 may be suspended in the electrolyte 2100 separated from the iron particulate material 2103 and current collector 2102, such as by an optional electrical connection 2110.

[00259] ***Solid sulfur containing additives***

[00260] Sulfide ions in the electrolyte solution have been proven to increase accessible capacity and cyclability of iron electrodes in alkaline secondary batteries. Sulfide ions, however, have been shown to reduce in concentration in the electrolyte due to ageing with cycle number and time, which may reduce the positive impacts of the dissolved sulfide on anode performance. One method to enable improved performance throughout lifetime is to incorporate sulfur containing species directly into the iron electrode material.

[00261] In one embodiment, elemental sulfur is introduced directly into porous iron anodes by melt diffusing the sulfur into the porous metal. The sulfur will then be introduced to the anode as a solid and be in intimate contact with the active metal anode material, promoting positive interactions that improve accessible capacity and cycle life.

[00262] In another embodiment, metal sulfides are introduced as solids to an iron anode. Metal sulfides of interest include: FeS, FeS_2, MnS, Bi_2S_3, Sb_2S_3, FeAsS, PbS, SnS, HgS, AsS, $Pb_4FeSb_6S_{14}$, $Pb_3Sn_4FeSb_2S_{14}$, SeS_2, among others. The cation in the metal sulfide

may contribute to the battery's capacity (i.e., Fe), be inert to the charge/discharge reaction (i.e., Mn), or retard the hydrogen evolution reaction (i.e., Pb, Sb, Hg, As, Bi).

[00263] In one non-limiting example, the metal sulfides are incorporated into a bed of direct reduced iron (DRI) pellets.

[00264] Methods for incorporation of sulfur containing species into iron electrodes include, but are not limited to: (1) Incorporation of bulk solid particles, powders, or agglomerates into voids between material in the electrode bed; (2) Incorporation via melt diffusion into the electrode pores for metal sulfides with melting points below the melting point of iron metal (i.e., Bi_2S_3); (3) Incorporation of metal sulfide powders by mixing into oxidized ore pellets (i.e., taconite pellets) during the pelletization process (In such an embodiment, the metal sulfide would remain in the pellet through the reduction process, producing a pellet with metallic iron, metal sulfide, and impurities.); (4) Incorporation of metal sulfides into pellets containing only the metal sulfide and a binder. In one non-binding example, these pellets could be directly incorporated into a pellet bed of DRI in a specific ratio with DRI pellets; and (5) Incorporation of metal sulfide powder using a mixing, milling, or rolling apparatus, such as a ball mill.

[00265] In another embodiment, the above-mentioned incorporation methods are used with sulfur containing additives including, but not limited to, metal sulfides.

[00266] In another embodiment, sulfur containing additives including, but not limited to, metal sulfides, are incorporated into the iron anode material via the Trommel screening process step of DRI production, such as illustrated in FIG. 22 in which DRI pellets 2200 in a mesh cylinder are infused with sulfur additives during production to result in DRI with sulfur additive pellets 2202.

[00267] **Incorporation of sulfide or other anionic species into an Fe anode**

[00268] Uniform or controlled incorporation of additives into a preformed metal electrode is difficult and limits effectiveness of additives.

[00269] Various embodiments include selective precipitation with reactive counterions. In various embodiments, a metal is incorporated into the particulate iron material electrode in the neutral or oxidized state and subsequently reacted with a counterion of choice. The concentration of the metal additive is determined by the solubility of the source compound or final desired concentration of the reactive counterion in the electrode. In certain embodiments, this electrode is exposed to an electrolyte containing a source of a

reactive counterion (e.g. Na_2S, K_2S, Na_2Se, Na_2Te) to form a compound (e.g. CdS, Bi_2S_3, Bi_2Se_3) in situ where the localization and concentration may be determined by the presence, concentration, and solubility of the additive metal, reactive counterion, or resulting compound. In certain embodiments, accessibility of these additives may be further adjusted by use of fugitive pore-formers. In certain embodiments this electrode is cycled electrochemically before or after exposure to an electrolyte containing the reactive counterion in a specified concentration to control the uptake of the reactive counterion.

[00270] In a non-binding example, 0.5 to 10 wt% Bi_2O_3 is incorporated into the electrode before being cycled electrochemically to potentials sufficiently reducing to form Bi(s). Exposure to an electrolyte containing 250mM Na_2S may form Bi_2S3 distributed throughout the electrode in the reactions shown below:

$$Bi_2O_3 + 3\ H_2O \rightarrow 2\ Bi\ (s) + 6\ OH^-$$

$$2\ Bi(s) + 3\ S_2^- \rightarrow Bi_2S_3\ .$$

[00271] In various embodiments, an additive of interest that is a source of sulfur, selenium, tellurium, nitrogen, or phosphorus (e.g. Na_2S, Na_2Se, Na_3PO_4) is incorporated into the electrode at a concentration determined by the solubility of the source compound or final desired concentration of the final compound in the electrode.

[00272] In certain embodiments, this electrode is exposed to an electrolyte containing a source of a reactive metal (e.g. Fe, Bi, Hg, As, Cd, Cu, Ni, In, Tl, Zn, Mn, Ag) or metal-containing ion (e.g. , $Bi(NO_3)_3$, $NaAsO_4$, $Cd(NO_3)_2$, $CuSO_4{\cdot}xH_2O$ (where x = 0 to 12)) to form a compound (e.g. CdS, Bi_2S_3, Bi_2Se_3) in situ where the localization and concentration may be determined by the presence, concentration, and solubility of the additive metal, reactive counterion, or resulting compound. The solubility of the non-metallic additive may allow for the creation of local concentration gradients in the electrolyte, leading to regions where precipitation is more favored. In certain embodiments, accessibility of these additives may be further adjusted by use of fugitive pore-formers. In certain embodiments this electrode is cycled electrochemically before or after exposure to an electrolyte containing the metal or metal-containing ion in a specified concentration to control the uptake of the metal or metal-containing ion.

[00273] In a non-binding example, Na_2S may be incorporated into the metal electrode. Exposure to an electrolyte containing $Bi(NO_3)_3$ may form Bi_2S_3 distributed throughout the electrode in the reaction shown below:

$$2\ Bi(NO_3)_3\ (aq) + 3\ Na_2S \rightarrow 6\ NaNO_3 + Bi_2S_3\ (s)$$

[00274] In various embodiments, an additive of interest that is a source of sulfur, selenium, tellurium, nitrogen, or phosphorus but may be not itself be ionic (e.g. S or Se metal) is incorporated into the electrode at a concentration determined by the solubility of the source compound or final desired concentration of the final compound in the electrode.

[00275] In various embodiments, this electrode containing a non-reactive additive may be exposed to an electrolyte, which in one embodiment contains NaOH or KOH, and, in one embodiment, is electrochemically cycled to generate anionic species on the anode or in the electrolyte (e.g. S_2^-, S_2^{2-}, polysulfides). The species may react to form Bi_2S_3 on the surface or sequestered in the anode as illustrated in FIG. 23. The exposure of the anode to this electrolyte may increase the overall porosity as the counterion reacts, which may be beneficial to overall accessible capacity.

[00276] **Improve longevity of sulfide in electrolyte**

[00277] Water and air sensitive additives can rapidly degrade in aqueous alkaline electrolyte. For example, compounds containing sulfide (S^{2-}) and bisulfide (HS^-) such as Na_2S or NaSH degrade on exposure to oxygen by forming sulfate or other sulfur-containing compounds (e.g. sulfite, thiosulfate, sulfur, polysulfides):

2 $HS^- + 3\ O_2 \rightarrow SO_3^{2-} + 2\ H^+$

3 $2\ HS^- + 3\ O_2 + 2\ OH^- \rightarrow SO_3^{2-} + 2\ H_2O$

2 $SO_3^{2-} + O_2 \rightarrow 2\ SO_4^{2-}$

3 $2\ SO_3^{2-} + 2HS^- + O_2 \rightarrow 2\ S_2O_3^{2-} + 2\ OH^-$

[00278] It is favorable to maintain sulfur species in the electrode or electrolyte as sulfide or bisulfide as the reduction of sulfate or other oxidized sulfur-containing compounds back to sulfide, bisulfide, or hydrogen sulfide is difficult.

[00279] In one embodiment, oxidized sulfur-containing species (e.g., Na_2SO_4, $Na_2S_2O_3$, Na_2SO_3, S metal) are added to the electrolyte in sufficient quantity to reduce or completely suppress formation of oxidized sulfur species by shifting the equilibrium in favor of the reduced sulfur species, in accordance with Le Chatelier's principle.

[00280] In one embodiment, oxidized sulfur-containing species (e.g., Na_2SO_4, $Na_2S_2O_3$, Na_2SO_3, S metal) are added to the electrode. Upon exposure to the electrolyte, these

soluble additives may dissolve in the electrolyte, increasing the porosity of the electrode and reducing or suppressing the formation of oxidized sulfur species in solution.

[00281] In one embodiment, oxidized sulfur-containing species that also contain a metallic cation (e.g. $FeSO_4$, FeS_2O_3, $FeSO_3$) is added to suppress the oxidation of reduced sulfur species as well as suppress the dissolution of metallic species from the iron electrode.

[00282] **High sulfide compatibility of DRI-based iron-air batteries**

[00283] DRI-based iron negative electrodes exhibit compatibility over a wide range of initial sulfide concentrations within the electrolyte. In addition, it has been shown that the initial sulfide concentration on a gS/gFe is the driving factor, not sulfide concentration in the electrolyte.

[00284] In certain embodiments, an initial sulfide concentration of 1mM Na_2S (0.1 mgS/gFe) is sufficient for stable capacity performance.

[00285] In certain embodiments, an initial sulfide concentration of 10mM Na_2S (1.4 mgS/gFe) is sufficient for stable capacity performance.

[00286] In certain embodiments, an initial sulfide concentration of 50 mM Na_2S (6.8 mgS/gFe) is sufficient for stable capacity performance.

[00287] In certain embodiments, an initial sulfide concentration of 175 mM Na_2S (23.6 gS/gFe) is sufficient for stable capacity performance.

[00288] In certain embodiments, an initial sulfide concentration of >=250 mM Na_2S (33.8 gS/gFe) is sufficient for stable capacity performance.

[00289] Further, the method of sulfide incorporation into the iron negative electrode can be achieved with a variety of techniques.

[00290] In certain embodiments, sulfide is incorporated through a high sulfide concentration electrolyte within the full cell.

[00291] In certain embodiments, sulfide is incorporated through a high sulfide concentration electrolyte soak prior to cycling, which can be completed in a non-sulfide containing electrolyte (may be beneficial for the positive electrodes).

[00292] In certain embodiments, sulfide is incorporated through a high sulfide concentration electrolyte soak prior to cycling, after which the positive electrodes are inserted

into the full cell wherein the sulfide concentration can be in the range of 10-250 mM (1.4-33.8 mgS/gFe) or higher.

[00293] Optimal sulfide incorporation may also be achieved via maintenance methods including, but not limited to: 1) periodic addition of high sulfide concentration solution or in solid form; and 2) continual addition of sulfide in solid or solution form, wherein the sulfide concentration can be in the range of 10-250 mM (1.4-33.8 mgS/gFe) or higher

[00294] In an embodiment, -325 mesh iron sponge powders with open porosity internal to the particles are thermally bonded via sintering to comprise the base for an iron electrode material. Bismuth oxide and iron sulfide are incorporated throughout the sintered electrode material, and the materials are thermally bonded to a current collecting, perforated sheet, and the sintered connections to the current collectors and between the powder particles obviate the need for compression to attain conduction. An alkaline electrolyte is comprised of a mixture of 80% potassium hydroxide, 15% sodium hydroxide, and 5% lithium hydroxide on a molar basis, with a total hydroxide concentration of 6 molar (mol/L) in an aqueous solution.

[00295] In one embodiment, the iron electrode material may comprise direct reduced iron pellets, with an electrolyte comprising six molar potassium hydroxide, 0.1 molar lithium hydroxide, 0.05 molar sodium sulfide. The iron electrode may further comprise 1 wt.% bismuth sulfide distributed finely among the direct reduced iron pellets. The electrode materials may be compressed in a rigid cage comprising nickel-plated current collecting stainless steel plates applying uniaxial pressure to compress the pellets within a rigid wall structure comprised of poly(methylmethacrylate), the current collecting plates held in place by stainless steel bolts which are electrically isolated from the current collectors. The bed thicknesses of such an embodiment may range from one to ten centimeters thick.

[00296] In an embodiment, the iron electrode material may comprise a carbonyl iron powder, lead oxide, and iron sulfide. The lead oxide is added at 0.1 wt.%, and the iron sulfide is included as 1.5 wt.%, both of the total weight of solids in the electrode. The solids are lightly sintered such that they bond and agglomerate, and are subsequently compressed in a nickel mesh textile which is compressed by inflation of a polyethylene balloon. The electrolyte is five molar sodium hydroxide with additives of 0.005 molar sodium sulfide and 0.01 molar octanethiol.

[00297] In another embodiment, direct reduced iron pellets are crushed to form particle sizes in the range of 1-6 mm. The particles are mixed with natural flake graphite with a

particle size of 200 microns at 1 wt.% of the solids mix and 100 micron particle size iron sulfide at 0.05 wt.%. The electrolyte is aqueous with 6.5 molar potassium hydroxide, 0.5 molar lithium hydroxide, and 0.25 molar sodium sulfide, and 0.001 molar octanethiol. The solids mix is loaded into a nickel mesh bag with a mesh size around 0.5 mm, and the bag is compressed via a cinching mechanism to compress the solids material lightly.

[00298] Various embodiments may provide devices and/or methods for use in bulk energy storage systems, such as long duration energy storage (LODES) systems, short duration energy storage (SDES) systems, etc. As an example, various embodiments may provide batteries for bulk energy storage systems, such as batteries for LODES systems. Renewable power sources are becoming more prevalent and cost effective. However, many renewable power sources face an intermittency problem that is hindering renewable power source adoption. The impact of the intermittent tendencies of renewable power sources may be mitigated by pairing renewable power sources with bulk energy storage systems, such as LODES systems, SDES systems, etc. To support the adoption of combined power generation, transmission, and storage systems (e.g., a power plant having a renewable power generation source paired with a bulk energy storage system and transmission facilities at any of the power plant and/or the bulk energy storage system) devices and methods to support the design and operation of such combined power generation, transmission, and storage systems, such as the various embodiment devices and methods described herein, are needed.

[00299] A combined power generation, transmission, and storage system may be a power plant including one or more power generation sources (e.g., one or more renewable power generation sources, one or more non-renewable power generations sources, combinations of renewable and non-renewable power generation sources, etc.), one or more transmission facilities, and one or more bulk energy storage systems. Transmission facilities at any of the power plant and/or the bulk energy storage systems may be co-optimized with the power generation and storage system or may impose constraints on the power generation and storage system design and operation. The combined power generation, transmission, and storage systems may be configured to meet various output goals, under various design and operating constraints.

[00300] FIGS. 24-102 illustrate various example systems in which one or more aspects of the various embodiments may be used as part of bulk energy storage systems, such as LODES systems, SDES systems, etc. For example, various embodiments described herein with reference to FIGS. 1A-93 may be used as batteries for bulk energy storage systems, such

as LODES systems, SDES systems, etc. and/or various electrodes as described herein may be used as components for bulk energy storage systems. As used herein, the term "LODES system" may mean a bulk energy storage system configured to may have a rated duration (energy/power ratio) of 24 hours (h) or greater, such as a duration of 24 h, a duration of 24 h to 50 h, a duration of greater than 50 h, a duration of 24 h to 150 h, a duration of greater than 150 h, a duration of 24 h to 200 h, a duration greater than 200 h, a duration of 24 h to 500 h, a duration greater than 500 h, etc.

[00301] FIG. 24 illustrates an example system in which one or more aspects of the various embodiments may be used as part of bulk energy storage system. As a specific example, the bulk energy storage system incorporating one or more aspects of the various embodiments may be a LODES system 2404. As an example, the LODES system 2404 may include various embodiment batteries described herein, various electrodes described herein, etc. The LODES system 2404 may be electrically connected to a wind farm 2402 and one or more transmission facilities 2406. The wind farm 2402 may be electrically connected to the transmission facilities 2406. The transmission facilities 2406 may be electrically connected to the grid 2408. The wind farm 2402 may generate power and the wind farm 2402 may output generated power to the LODES system 2404 and/or the transmission facilities 2406. The LODES system 2404 may store power received from the wind farm 2402 and/or the transmission facilities 2406. The LODES system 2404 may output stored power to the transmission facilities 2406. The transmission facilities 2406 may output power received from one or both of the wind farm 2402 and LODES system 2404 to the grid 2408 and/or may receive power from the grid 2408 and output that power to the LODES system 2404. Together the wind farm 2402, the LODES system 2404, and the transmission facilities 2406 may constitute a power plant 2400 that may be a combined power generation, transmission, and storage system. The power generated by the wind farm 2402 may be directly fed to the grid 2408 through the transmission facilities 2406, or may be first stored in the LODES system 2404. In certain cases the power supplied to the grid 2408 may come entirely from the wind farm 2402, entirely from the LODES system 2404, or from a combination of the wind farm 2402 and the LODES system 2404. The dispatch of power from the combined wind farm 2402 and LODES system 2404 power plant 2400 may be controlled according to a determined long-range (multi-day or even multi-year) schedule, or may be controlled according to a day-ahead (24 hour advance notice) market, or may be controlled according to an hour-ahead market, or may be controlled in response to real time pricing signals.

[00302] As one example of operation of the power plant 2400, the LODES system 2404 may be used to reshape and "firm" the power produced by the wind farm 2402. In one such example, the wind farm 2402 may have a peak generation output (capacity) of 260 megawatts (MW) and a capacity factor (CF) of 41%. The LODES system 2404 may have a power rating (capacity) of 106 MW, a rated duration (energy/power ratio) of 150 hours (h), and an energy rating of 15,900 megawatt hours (MWh). In another such example, the wind farm 2402 may have a peak generation output (capacity) of 300 MW and a capacity factor (CF) of 41%. The LODES system 2404 may have a power rating of 106 MW, a rated duration (energy/power ratio) of 200 h and an energy rating of 21,200 MWh. In another such example, the wind farm 2402 may have a peak generation output (capacity) of 176 MW and a capacity factor (CF) of 53%. The LODES system 2404 may have a power rating (capacity) of 88 MW, a rated duration (energy/power ratio) of 150 h and an energy rating of 13,200 MWh. In another such example, the wind farm 2402 may have a peak generation output (capacity) of 277 MW and a capacity factor (CF) of 41%. The LODES system 2404 may have a power rating (capacity) of 97 MW, a rated duration (energy/power ratio) of 50 h and an energy rating of 4,850 MWh. In another such example, the wind farm 2402 may have a peak generation output (capacity) of 315 MW and a capacity factor (CF) of 41%. The LODES system 2404 may have a power rating (capacity) of 110 MW, a rated duration (energy/power ratio) of 25 h and an energy rating of 2,750 MWh.

[00303] FIG. 25 illustrates an example system in which one or more aspects of the various embodiments may be used as part of bulk energy storage system. As a specific example, the bulk energy storage system incorporating one or more aspects of the various embodiments may be a LODES system 2404. As an example, the LODES system 2404 may include various embodiment batteries described herein, various electrodes described herein, etc. The system of FIG. 25 may be similar to the system of FIG. 24, except a photovoltaic (PV) farm 2502 may be substituted for the wind farm 2402. The LODES system 2404 may be electrically connected to the PV farm 2502 and one or more transmission facilities 2406. The PV farm 2502 may be electrically connected to the transmission facilities 2406. The transmission facilities 2406 may be electrically connected to the grid 2408. The PV farm 2502 may generate power and the PV farm 2502 may output generated power to the LODES system 2404 and/or the transmission facilities 2406. The LODES system 2404 may store power received from the PV farm 2502 and/or the transmission facilities 2406. The LODES system 2404 may output stored power to the transmission facilities 2406. The transmission

facilities 2406 may output power received from one or both of the PV farm 2502 and LODES system 2404 to the grid 2408 and/or may receive power from the grid 2408 and output that power to the LODES system 2404. Together the PV farm 2502, the LODES system 2404, and the transmission facilities 2406 may constitute a power plant 2500 that may be a combined power generation, transmission, and storage system. The power generated by the PV farm 2502 may be directly fed to the grid 2408 through the transmission facilities 2406, or may be first stored in the LODES system 2404. In certain cases the power supplied to the grid 2408 may come entirely from the PV farm 2502, entirely from the LODES system 2404, or from a combination of the PV farm 2502 and the LODES system 2404. The dispatch of power from the combined PV farm 2502 and LODES system 2404 power plant 2500 may be controlled according to a determined long-range (multi-day or even multi-year) schedule, or may be controlled according to a day-ahead (24 hour advance notice) market, or may be controlled according to an hour-ahead market, or may be controlled in response to real time pricing signals.

[00304] As one example of operation of the power plant 2500, the LODES system 2404 may be used to reshape and "firm" the power produced by the PV farm 2502. In one such example, the PV farm 2502 may have a peak generation output (capacity) of 490 MW and a capacity factor (CF) of 24%. The LODES system 2404 may have a power rating (capacity) of 340 MW, a rated duration (energy/power ratio) of 150 h and an energy rating of 51,000 MWh. In another such example, the PV farm 2502 may have a peak generation output (capacity) of 680 MW and a capacity factor (CF) of 24%. The LODES system 2404 may have a power rating (capacity) of 410 MW, a rated duration (energy/power ratio) of 200 h, and an energy rating of 82,000 MWh. In another such example, the PV farm 2502 may have a peak generation output (capacity) of 330 MW and a capacity factor (CF) of 31%. The LODES system 2404 may have a power rating (capacity) of 215 MW, a rated duration (energy/power ratio) of 150 h, and an energy rating of 32,250 MWh. In another such example, the PV farm 2502 may have a peak generation output (capacity) of 510 MW and a capacity factor (CF) of 24%. The LODES system 2404 may have a power rating (capacity) of 380 MW, a rated duration (energy/power ratio) of 50 h, and an energy rating of 19,000 MWh. In another such example, the PV farm 2502 may have a peak generation output (capacity) of 630 MW and a capacity factor (CF) of 24%. The LODES system 2404 may have a power rating (capacity) of 380 MW, a rated duration (energy/power ratio) of 25 h, and an energy rating of 9,500 MWh.

[00305] FIG. 26 illustrates an example system in which one or more aspects of the various embodiments may be used as part of bulk energy storage system. As a specific example, the bulk energy storage system incorporating one or more aspects of the various embodiments may be a LODES system 2404. As an example, the LODES system 2404 may include various embodiment batteries described herein, various electrodes described herein, etc. The system of FIG. 26 may be similar to the systems of FIGS. 24 and 25, except the wind farm 2402 and the photovoltaic (PV) farm 2502 may both be power generators working together in the power plant 2600. Together the PV farm 2502, wind farm 2402, the LODES system 2404, and the transmission facilities 2406 may constitute the power plant 2600 that may be a combined power generation, transmission, and storage system. The power generated by the PV farm 2502 and/or the wind farm 2402 may be directly fed to the grid 2408 through the transmission facilities 2406, or may be first stored in the LODES system 2404. In certain cases the power supplied to the grid 2408 may come entirely from the PV farm 2502, entirely from the wind farm 2402, entirely from the LODES system 2404, or from a combination of the PV farm 2502, the wind farm 2402, and the LODES system 2404. The dispatch of power from the combined wind farm 2402, PV farm 2502, and LODES system 2404 power plant 2600 may be controlled according to a determined long-range (multi-day or even multi-year) schedule, or may be controlled according to a day-ahead (24 hour advance notice) market, or may be controlled according to an hour-ahead market, or may be controlled in response to real time pricing signals.

[00306] As one example of operation of the power plant 2600, the LODES system 2404 may be used to reshape and "firm" the power produced by the wind farm 2402 and the PV farm 2502. In one such example, the wind farm 2402 may have a peak generation output (capacity) of 126 MW and a capacity factor (CF) of 41% and the PV farm 2502 may have a peak generation output (capacity) of 126 MW and a capacity factor (CF) of 24%. The LODES system 2404 may have a power rating (capacity) of 63 MW, a rated duration (energy/power ratio) of 150 h, and an energy rating of 9,450 MWh. In another such example, the wind farm 2402 may have a peak generation output (capacity) of 170 MW and a capacity factor (CF) of 41% and the PV farm 2502 may have a peak generation output (capacity) of 110 MW and a capacity factor (CF) of 24%. The LODES system 2404 may have a power rating (capacity) of 57 MW, a rated duration (energy/power ratio) of 200 h, and an energy rating of 11,400 MWh. In another such example, the wind farm 2402 may have a peak generation output (capacity) of 105 MW and a capacity factor (CF) of 51% and the PV farm

2502 may have a peak generation output (capacity) of 70 MW and a capacity factor (CF) of 31 The LODES system 2404 may have a power rating (capacity) of 61 MW, a rated duration (energy/power ratio) of 150 h, and an energy rating of 9,150 MWh. In another such example, the wind farm 2402 may have a peak generation output (capacity) of 135 MW and a capacity factor (CF) of 41% and the PV farm 2502 may have a peak generation output (capacity) of 90 MW and a capacity factor (CF) of 24%. The LODES system 2404 may have a power rating (capacity) of 68 MW, a rated duration (energy/power ratio) of 50 h, and an energy rating of 3,400 MWh. In another such example, the wind farm 2402 may have a peak generation output (capacity) of 144 MW and a capacity factor (CF) of 41% and the PV farm 2502 may have a peak generation output (capacity) of 96 MW and a capacity factor (CF) of 24%. The LODES system 2404 may have a power rating (capacity) of 72 MW, a rated duration (energy/power ratio) of 25 h, and an energy rating of 1,800 MWh.

[00307] FIG. 27 illustrates an example system in which one or more aspects of the various embodiments may be used as part of bulk energy storage system. As a specific example, the bulk energy storage system incorporating one or more aspects of the various embodiments may be a LODES system 2404. As an example, the LODES system 2404 may include various embodiment batteries described herein, various electrodes described herein, etc. The LODES system 2404 may be electrically connected to one or more transmission facilities 2406. In this manner, the LODES system 2404 may operate in a "stand-alone" manner to arbiter energy around market prices and/or to avoid transmission constraints. The LODES system 2404 may be electrically connected to one or more transmission facilities 2406. The transmission facilities 2406 may be electrically connected to the grid 2408. The LODES system 2404 may store power received from the transmission facilities 2406. The LODES system 2404 may output stored power to the transmission facilities 2406. The transmission facilities 2406 may output power received from the LODES system 2404 to the grid 2408 and/or may receive power from the grid 2408 and output that power to the LODES system 2404.

[00308] Together the LODES system 2404 and the transmission facilities 2406 may constitute a power plant 900. As an example, the power plant 900 may be situated downstream of a transmission constraint, close to electrical consumption. In such an example downstream situated power plant 2700, the LODES system 2404 may have a duration of 24h to 500h and may undergo one or more full discharges a year to support peak electrical consumptions at times when the transmission capacity is not sufficient to serve customers.

Additionally in such an example downstream situated power plant 2700, the LODES system 2404 may undergo several shallow discharges (daily or at higher frequency) to arbiter the difference between nighttime and daytime electricity prices and reduce the overall cost of electrical service to customer. As a further example, the power plant 2700 may be situated upstream of a transmission constraint, close to electrical generation. In such an example upstream situated power plant 2700, the LODES system 2404 may have a duration of 24h to 500h and may undergo one or more full charges a year to absorb excess generation at times when the transmission capacity is not sufficient to distribute the electricity to customers. Additionally in such an example upstream situated power plant 2700, the LODES system 2404 may undergo several shallow charges and discharges (daily or at higher frequency) to arbiter the difference between nighttime and daytime electricity prices and maximize the value of the output of the generation facilities.

[00309] FIG. 28 illustrates an example system in which one or more aspects of the various embodiments may be used as part of bulk energy storage system. As a specific example, the bulk energy storage system incorporating one or more aspects of the various embodiments may be a LODES system 2404. As an example, the LODES system 2404 may include various embodiment batteries described herein, various electrodes described herein, etc. The LODES system 2404 may be electrically connected to a commercial and industrial (C&I) customer 2802, such as a data center, factory, etc. The LODES system 2404 may be electrically connected to one or more transmission facilities 2406. The transmission facilities 2406 may be electrically connected to the grid 2408. The transmission facilities 2406 may receive power from the grid 2408 and output that power to the LODES system 2404. The LODES system 2404 may store power received from the transmission facilities 2406. The LODES system 2404 may output stored power to the C&I customer 2802. In this manner, the LODES system 2404 may operate to reshape electricity purchased from the grid 2408 to match the consumption pattern of the C&I customer 2802.

[00310] Together, the LODES system 2404 and transmission facilities 2406 may constitute a power plant 2800. As an example, the power plant 2800 may be situated close to electrical consumption, i.e., close to the C&I customer 2802, such as between the grid 2408 and the C&I customer 2802. In such an example, the LODES system 2404 may have a duration of 24h to 500h and may buy electricity from the markets and thereby charge the LODES system 2404 at times when the electricity is cheaper. The LODES system 2404 may then discharge to provide the C&I customer 2802 with electricity at times when the market

price is expensive, therefore offsetting the market purchases of the C&I customer 2802. As an alternative configuration, rather than being situated between the grid 2408 and the C&I customer 2802, the power plant 2800 may be situated between a renewable source, such as a PV farm, wind farm, etc., and the transmission facilities 2406 may connect to the renewable source. In such an alternative example, the LODES system 2404 may have a duration of 24h to 500h, and the LODES system 2404 may charge at times when renewable output may be available. The LODES system 2404 may then discharge to provide the C&I customer 2802 with renewable generated electricity so as to cover a portion, or the entirety, of the C&I customer 2802 electricity needs.

[00311] FIG. 29 illustrates an example system in which one or more aspects of the various embodiments may be used as part of bulk energy storage system. As a specific example, the bulk energy storage system incorporating one or more aspects of the various embodiments may be a LODES system 2404. As an example, the LODES system 2404 may include various embodiment batteries described herein, various electrodes described herein, etc. The LODES system 2404 may be electrically connected to a wind farm 2402 and one or more transmission facilities 2406. The wind farm 2402 may be electrically connected to the transmission facilities 2406. The transmission facilities 2406 may be electrically connected to a C&I customer 2802. The wind farm 2402 may generate power and the wind farm 2402 may output generated power to the LODES system 2404 and/or the transmission facilities 2406. The LODES system 2404 may store power received from the wind farm 2402.

[00312] The LODES system 2404 may output stored power to the transmission facilities 2406. The transmission facilities 2406 may output power received from one or both of the wind farm 2402 and LODES system 2404 to the C&I customer 2802. Together the wind farm 2402, the LODES system 2404, and the transmission facilities 2406 may constitute a power plant 2900 that may be a combined power generation, transmission, and storage system. The power generated by the wind farm 2402 may be directly fed to the C&I customer 2802 through the transmission facilities 2406, or may be first stored in the LODES system 2404. In certain cases, the power supplied to the C&I customer 2802 may come entirely from the wind farm 2402, entirely from the LODES system 2404, or from a combination of the wind farm 2402 and the LODES system 2404. The LODES system 2404 may be used to reshape the electricity generated by the wind farm 2402 to match the consumption pattern of the C&I customer 2802. In one such example, the LODES system 2404 may have a duration of 24h to 500h and may charge when renewable generation by the

wind farm 2402 exceeds the C&I customer 2802 load. The LODES system 2404 may then discharge when renewable generation by the wind farm 2402 falls short of C&I customer 2802 load so as to provide the C&I customer 2802 with a firm renewable profile that offsets a fraction, or all of, the C&I customer 2802 electrical consumption.

[00313] FIG. 30 illustrates an example system in which one or more aspects of the various embodiments may be used as part of bulk energy storage system. As a specific example, the bulk energy storage system incorporating one or more aspects of the various embodiments may be a LODES system 2404. As an example, the LODES system 2404 may include various embodiment batteries described herein, various electrodes described herein, etc. The LODES system 2404 may be part of a power plant 3000 that is used to integrate large amounts of renewable generation in microgrids and harmonize the output of renewable generation by, for example a PV farm 2502 and wind farm 2402, with existing thermal generation by, for example a thermal power plant 3002 (e.g., a gas plant, a coal plant, a diesel generator set, etc., or a combination of thermal generation methods), while renewable generation and thermal generation supply the C&I customer 2802 load at high availability. Microgrids, such as the microgrid constituted by the power plant 3000 and the thermal power plant 3002, may provide availability that is 90% or higher. The power generated by the PV farm 2502 and/or the wind farm 2402 may be directly fed to the C&I customer 2802, or may be first stored in the LODES system 2404.

[00314] In certain cases the power supplied to the C&I customer 2802 may come entirely from the PV farm 2502, entirely from the wind farm 2402, entirely from the LODES system 2404, entirely from the thermal power plant 3002, or from any combination of the PV farm 2502, the wind farm 2402, the LODES system 2404, and/or the thermal power plant 3002. As examples, the LODES system 2404 of the power plant 3000 may have a duration of 24h to 500h. As a specific example, the C&I customer 2802 load may have a peak of 100 MW, the LODES system 2404 may have a power rating of 14 MW and duration of 150 h, natural gas may cost $6/million British thermal units (MMBTU), and the renewable penetration may be 58%. As another specific example, the C&I customer 2802 load may have a peak of 100 MW, the LODES system 2404 may have a power rating of 25 MW and duration of 150 h, natural gas may cost $8/MMBTU, and the renewable penetration may be 65%.

[00315] FIG. 31 illustrates an example system in which one or more aspects of the various embodiments may be used as part of bulk energy storage system. As a specific

example, the bulk energy storage system incorporating one or more aspects of the various embodiments may be a LODES system 2404. As an example, the LODES system 2404 may include various embodiment batteries described herein, various electrodes described herein, etc. The LODES system 2404 may be used to augment a nuclear plant 3102 (or other inflexible generation facility, such as a thermal, a biomass, etc., and/or any other type plant having a ramp-rate lower than 50% of rated power in one hour and a high capacity factor of 80% or higher) to add flexibility to the combined output of the power plant 3100 constituted by the combined LODES system 2404 and nuclear plant 3102. The nuclear plant 3102 may operate at high capacity factor and at the highest efficiency point, while the LODES system 2404 may charge and discharge to effectively reshape the output of the nuclear plant 3102 to match a customer electrical consumption and/or a market price of electricity. As examples, the LODES system 2404 of the power plant 3100 may have a duration of 24h to 500h. In one specific example, the nuclear plant 3102 may have 1,000 MW of rated output and the nuclear plant 3102 may be forced into prolonged periods of minimum stable generation or even shutdowns because of depressed market pricing of electricity. The LODES system 2404 may avoid facility shutdowns and charge at times of depressed market pricing; and the LODES system 2404 may subsequently discharge and boost total output generation at times of inflated market pricing.

[00316] FIG. 32 illustrates an example system in which one or more aspects of the various embodiments may be used as part of bulk energy storage system. As a specific example, the bulk energy storage system incorporating one or more aspects of the various embodiments may be a LODES system 2404. As an example, the LODES system 2404 may include various embodiment batteries described herein, various electrodes described herein, etc. The LODES system 2404 may operate in tandem with a SDES system 3202. Together the LODES system 2404 and SDES system 3202 may constitute a power plant 3200. As an example, the LODES system 2404 and SDES system 3202 may be co-optimized whereby the LODES system 2404 may provide various services, including long-duration back-up and/or bridging through multi-day fluctuations (e.g., multi-day fluctuations in market pricing, renewable generation, electrical consumption, etc.), and the SDES system 3202 may provide various services, including fast ancillary services (e.g. voltage control, frequency regulation, etc.) and/or bridging through intra-day fluctuations (e.g., intra-day fluctuations in market pricing, renewable generation, electrical consumption, etc.). The SDES system 3202 may have durations of less than 10 hours and round-trip efficiencies of greater than 80%. The

LODES system 2404 may have durations of 24h to 500h and round-trip efficiencies of greater than 40%. In one such example, the LODES system 2404 may have a duration of 150 hours and support customer electrical consumption for up to a week of renewable under-generation. The LODES system 2404 may also support customer electrical consumption during intra-day under-generation events, augmenting the capabilities of the SDES system 3202. Further, the SDES system 3202 may supply customers during intra-day under-generation events and provide power conditioning and quality services such as voltage control and frequency regulation.

[00317] Various embodiments may include a battery comprising: a first electrode; an electrolyte; and a second electrode, wherein at least one of the first electrode and the second electrode comprises iron agglomerates. In some embodiments, the electrolyte comprises a soluble sulfide. In some embodiments, at least one of the first electrode and the second electrode further comprises a solid sulfide. In some embodiments, at least one of the first electrode or the second electrode is subjected to a compressive load. In some embodiments, the compressive load is applied on one side of at least one of the first electrode or second electrode by a current collecting member. In some embodiments, the iron agglomerates comprise at least one of magnetite, hematite, or wustite. In some embodiments, the electrolyte comprises a corrosion inhibitor. In some embodiments, the iron agglomerates have an average length ranging from about 50 um to about 50 mm. In some embodiments, the iron agglomerates have an average internal porosity ranging from about 10% to about 90% by volume. In some embodiments, the iron agglomerates have an average specific surface area ranging from about 0.1 m^2/g to about 25 m^2/g. In some embodiments, the electrolyte is infiltrated between the iron agglomerates. In some embodiments, the electrolyte comprises 1-octanethiol. In some embodiments, the electrolyte comprises a molybdate anion and a sulfide anion. In some embodiments, the iron agglomerates are supported within a metal textile mesh providing compressive force and current collection for the iron agglomerates. In some embodiments, the iron agglomerates are bonded to one another and bonded to a current collector.

[00318] Various embodiments may include a battery comprising: a first electrode; an electrolyte; and a second electrode, wherein at least one of the first electrode and the second electrode comprises atomized metal powder. In some embodiments, the electrolyte comprises a soluble sulfide. In some embodiments, at least one of the first electrode and the second electrode further comprises a solid sulfide. In some embodiments, at least one of the

first electrode or the second electrode is subjected to a compressive load. In some embodiments, the compressive load is applied on one side of at least one of the first electrode or second electrode by a current collecting member. In some embodiments, the atomized metal powder comprise at least one of magnetite, hematite, or wustite. In some embodiments, the electrolyte comprises a corrosion inhibitor. In some embodiments, the electrolyte is infiltrated between the atomized metal powder. In some embodiments, the electrolyte comprises 1-octanethiol. In some embodiments, the electrolyte comprises a molybdate anion and a sulfide anion. In some embodiments, the atomized metal powder is supported within a metal textile mesh providing compressive force and current collection for the atomized metal powder. In some embodiments, the atomized metal powder is bonded together and bonded to a current collector.

[00319] Various embodiments include a method of making an electrode, comprising: electrochemically producing metal powder; and forming the metal powder into an electrode. In some embodiments, electrochemically producing the metal powder comprises electrochemically producing the metal powder at least in part using a molten salt electrochemistry. In some embodiments, electrochemically producing the metal powder comprises electrochemically producing the metal powder at least in part using gas atomization. In some embodiments, electrochemically producing the metal powder comprises electrochemically producing the metal powder at least in part using water atomization.

[00320] Various embodiments may include a bulk energy storage system, comprising: one or more batteries, wherein at least one of the one or more batteries comprises: a first electrode; an electrolyte; and a second electrode, wherein at least one of the first electrode and the second electrode comprises iron agglomerates. In some embodiments, the bulk energy storage system is a long duration energy storage (LODES) system. In some embodiments, the electrolyte comprises a soluble sulfide. In some embodiments, at least one of the first electrode and the second electrode further comprises a solid sulfide. In some embodiments, at least one of the first electrode or the second electrode is subjected to a compressive load. In some embodiments, the compressive load is applied on one side of at least one of the first electrode or second electrode by a current collecting member. In some embodiments, the iron agglomerates comprise at least one of magnetite, hematite, or wustite. In some embodiments, the electrolyte comprises a corrosion inhibitor. In some embodiments, the iron agglomerates have an average length ranging from about 50 um to about 50 mm. In

some embodiments, the iron agglomerates have an average internal porosity ranging from about 10% to about 90% by volume. In some embodiments, the iron agglomerates have an average specific surface area ranging from about 0.1 m^2/g to about 25 m^2/g. In some embodiments, the electrolyte is infiltrated between the iron agglomerates. In some embodiments, the electrolyte comprises 1-octanethiol. In some embodiments, the electrolyte comprises a molybdate anion and a sulfide anion. In some embodiments, the iron agglomerates are supported within a metal textile mesh providing compressive force and current collection for the iron agglomerates. In some embodiments, the iron agglomerates are bonded to one another and bonded to a current collector.

[00321] Various embodiments may include a bulk energy storage system, comprising: one or more batteries, wherein at least one of the one or more batteries comprises: a first electrode; an electrolyte; and a second electrode, wherein at least one of the first electrode and the second electrode comprises atomized metal powder. In some embodiments, the bulk energy storage system is a long duration energy storage (LODES) system. In some embodiments, the electrolyte comprises a soluble sulfide. In some embodiments, at least one of the first electrode and the second electrode further comprises a solid sulfide. In some embodiments, at least one of the first electrode or the second electrode is subjected to a compressive load. In some embodiments, the compressive load is applied on one side of at least one of the first electrode or second electrode by a current collecting member. In some embodiments, the atomized metal powder comprise at least one of magnetite, hematite, or wustite. In some embodiments, the electrolyte comprises a corrosion inhibitor. In some embodiments, the electrolyte is infiltrated between the atomized metal powder. In some embodiments, the electrolyte comprises 1-octanethiol. In some embodiments, the electrolyte comprises a molybdate anion and a sulfide anion. In some embodiments, the atomized metal powder is supported within a metal textile mesh providing compressive force and current collection for the atomized metal powder. In some embodiments, the atomized metal powder is bonded together and bonded to a current collector.

[00322] The foregoing method descriptions are provided merely as illustrative examples and are not intended to require or imply that the steps of the various embodiments must be performed in the order presented. As will be appreciated by one of skill in the art the order of steps in the foregoing embodiments may be performed in any order. Words such as "thereafter," "then," "next," etc. are not necessarily intended to limit the order of the steps; these words may be used to guide the reader through the description of the methods. Further,

any reference to claim elements in the singular, for example, using the articles "a," "an" or "the" is not to be construed as limiting the element to the singular. Further, any step of any embodiment described herein can be used in any other embodiment.

[00323] The preceding description of the disclosed aspects is provided to enable any person skilled in the art to make or use the present invention. Various modifications to these aspects will be readily apparent to those skilled in the art, and the generic principles defined herein may be applied to other aspects without departing from the scope of the invention. Thus, the present invention is not intended to be limited to the aspects shown herein but is to be accorded the widest scope consistent with the principles and novel features disclosed herein.

WHAT IS CLAIMED IS:

1. A battery comprising:

a first electrode;

an electrolyte; and

a second electrode,

wherein at least one of the first electrode and the second electrode comprises iron agglomerates.

2. The battery of claim 1, wherein the electrolyte comprises a soluble sulfide.

3. The battery of claim 1, wherein at least one of the first electrode and the second electrode further comprises a solid sulfide.

4. The battery of claim 1, wherein at least one of the first electrode or the second electrode is subjected to a compressive load.

5. The battery of claim 4, wherein the compressive load is applied on one side of at least one of the first electrode or second electrode by a current collecting member.

6. The battery of claim 1, wherein the iron agglomerates comprise at least one of magnetite, hematite, or wustite.

7. The battery of claim 1, wherein the electrolyte comprises a corrosion inhibitor.

8. The battery of claim 1, wherein the iron agglomerates have an average length ranging from about 50 um to about 50 mm.

9. The battery of claim 1, wherein the iron agglomerates have an average internal porosity ranging from about 10% to about 90% by volume.

10. The battery of claim 1, wherein the iron agglomerates have an average specific surface area ranging from about 0.1 m^2/g to about 25 m^2/g.

11. The battery of claim 1, wherein the electrolyte is infiltrated between the iron agglomerates.

12. The battery of claim 11, wherein the electrolyte comprises 1-octanethiol.

13. The battery of claim 11, wherein the electrolyte comprises a molybdate anion and a sulfide anion.

14. The battery of claim 11, wherein the iron agglomerates are supported within a metal textile mesh providing compressive force and current collection for the iron agglomerates.

15. The battery of claim 11, wherein the iron agglomerates are bonded to one another and bonded to a current collector.

16. A battery comprising:

a first electrode;

an electrolyte; and

a second electrode,

wherein at least one of the first electrode and the second electrode comprises atomized metal powder.

17. A method of making an electrode, comprising:

electrochemically producing metal powder; and

forming the metal powder into an electrode.

18. The method of claim 17, wherein electrochemically producing the metal powder comprises electrochemically producing the metal powder at least in part using a molten salt electrochemistry.

19. The method of claim 17, wherein electrochemically producing the metal powder comprises electrochemically producing the metal powder at least in part using gas atomization.

20. The method of claim 17, wherein electrochemically producing the metal powder comprises electrochemically producing the metal powder at least in part using water atomization.

21. A bulk energy storage system, comprising:

one or more batteries, wherein at least one of the one or more batteries comprises:

a first electrode;

an electrolyte; and

a second electrode,

wherein at least one of the first electrode and the second electrode comprises iron agglomerates.

22. The bulk energy storage system of claim 21, wherein the bulk energy storage system is a long duration energy storage (LODES) system.

23. The bulk energy storage system of claim 21, wherein the electrolyte comprises a soluble sulfide.

24. The bulk energy storage system of claim 21, wherein at least one of the first electrode and the second electrode further comprises a solid sulfide.

25. The bulk energy storage system of claim 21, wherein at least one of the first electrode or the second electrode is subjected to a compressive load.

26. The bulk energy storage system of claim 25, wherein the compressive load is applied on one side of at least one of the first electrode or second electrode by a current collecting member.

27. The bulk energy storage system of claim 21, wherein the iron agglomerates comprise at least one of magnetite, hematite, or wustite.

28. The bulk energy storage system of claim 21, wherein the electrolyte comprises a corrosion inhibitor.

29. The bulk energy storage system of claim 21, wherein the iron agglomerates have an average length ranging from about 50 um to about 50 mm.

30. The bulk energy storage system of claim 21, wherein the iron agglomerates have an average internal porosity ranging from about 10% to about 90% by volume.

31. The bulk energy storage system of claim 21, wherein the iron agglomerates have an average specific surface area ranging from about 0.1 m^2/g to about 25 m^2/g.

32. The bulk energy storage system of claim 21, wherein the electrolyte is infiltrated between the iron agglomerates.

33. The bulk energy storage system of claim 32, wherein the electrolyte comprises 1-octanethiol.

34. The bulk energy storage system of claim 33, wherein the electrolyte comprises a molybdate anion and a sulfide anion.

35. The bulk energy storage system of claim 33, wherein the iron agglomerates are supported within a metal textile mesh providing compressive force and current collection for the iron agglomerates.

36. The bulk energy storage system of claim 33, wherein the iron agglomerates are bonded to one another and bonded to a current collector.

37. A bulk energy storage system, comprising:

one or more batteries, wherein at least one of the one or more batteries comprises:

a first electrode;

an electrolyte; and

a second electrode,

wherein at least one of the first electrode and the second electrode comprises atomized metal powder.

38. The bulk energy storage system of claim 15, wherein the bulk energy storage system is a long duration energy storage (LODES) system.

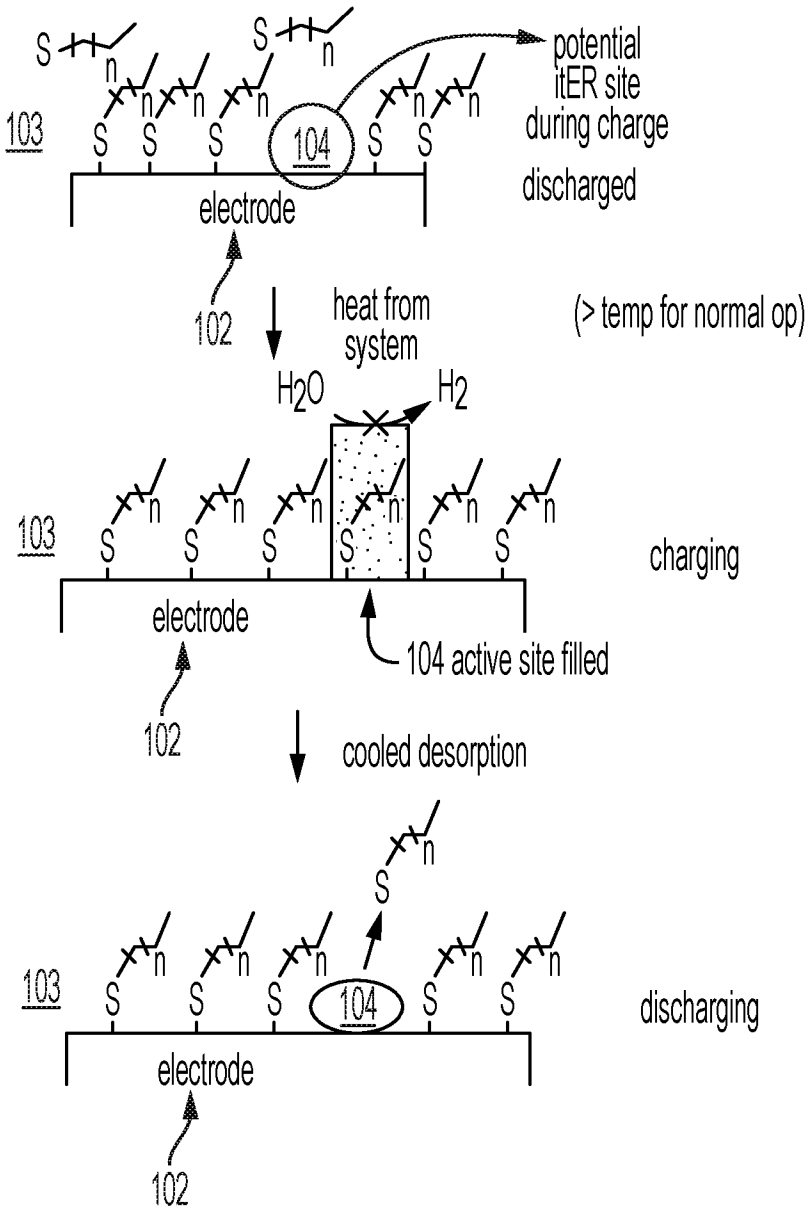

potential
itER site
during charge
discharged
103
104
electrode
102
heat from
system
(> temp for normal op)
H_2O
H_2
charging
104 active site filled
cooled desorption
discharging

FIG. 1

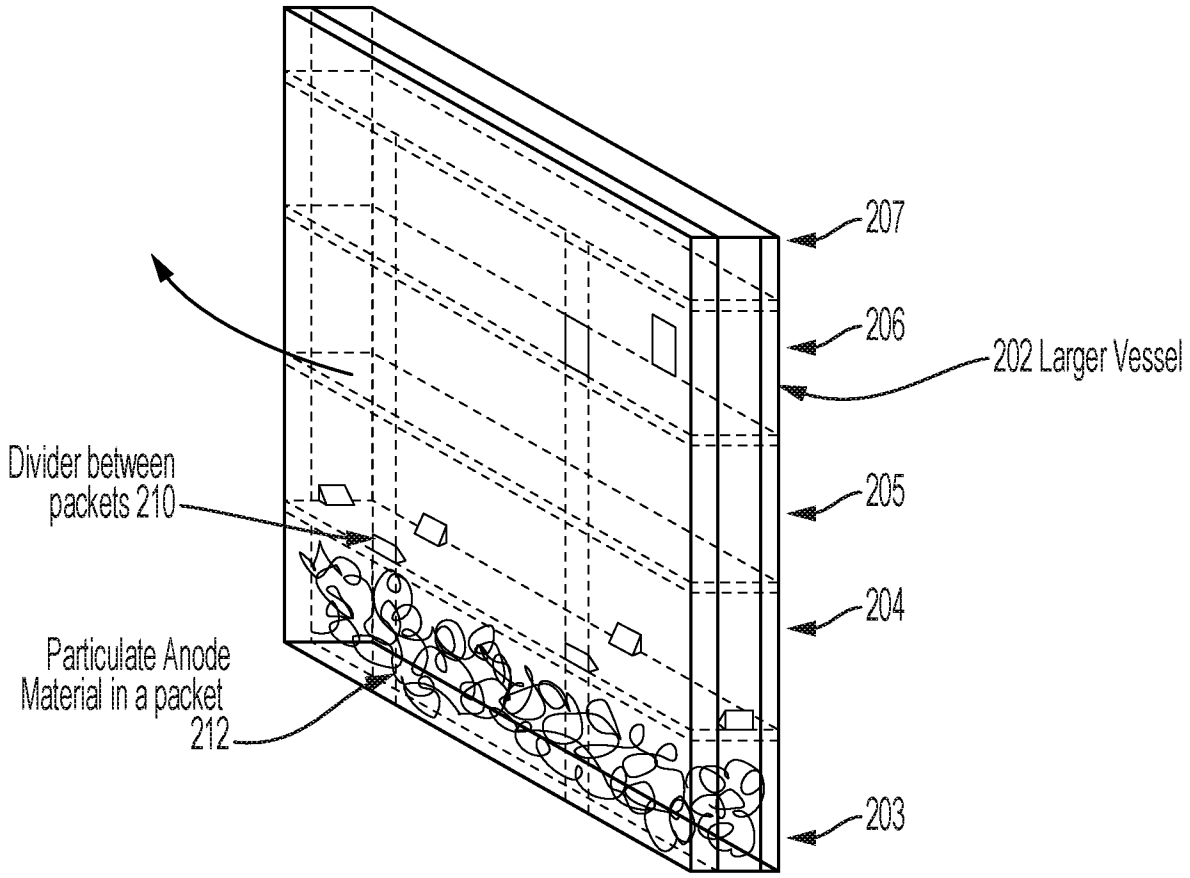

207
206
202 Larger Vessel
205
204
203
Divider between packets 210
Particulate Anode Material in a packet 212

FIG. 2

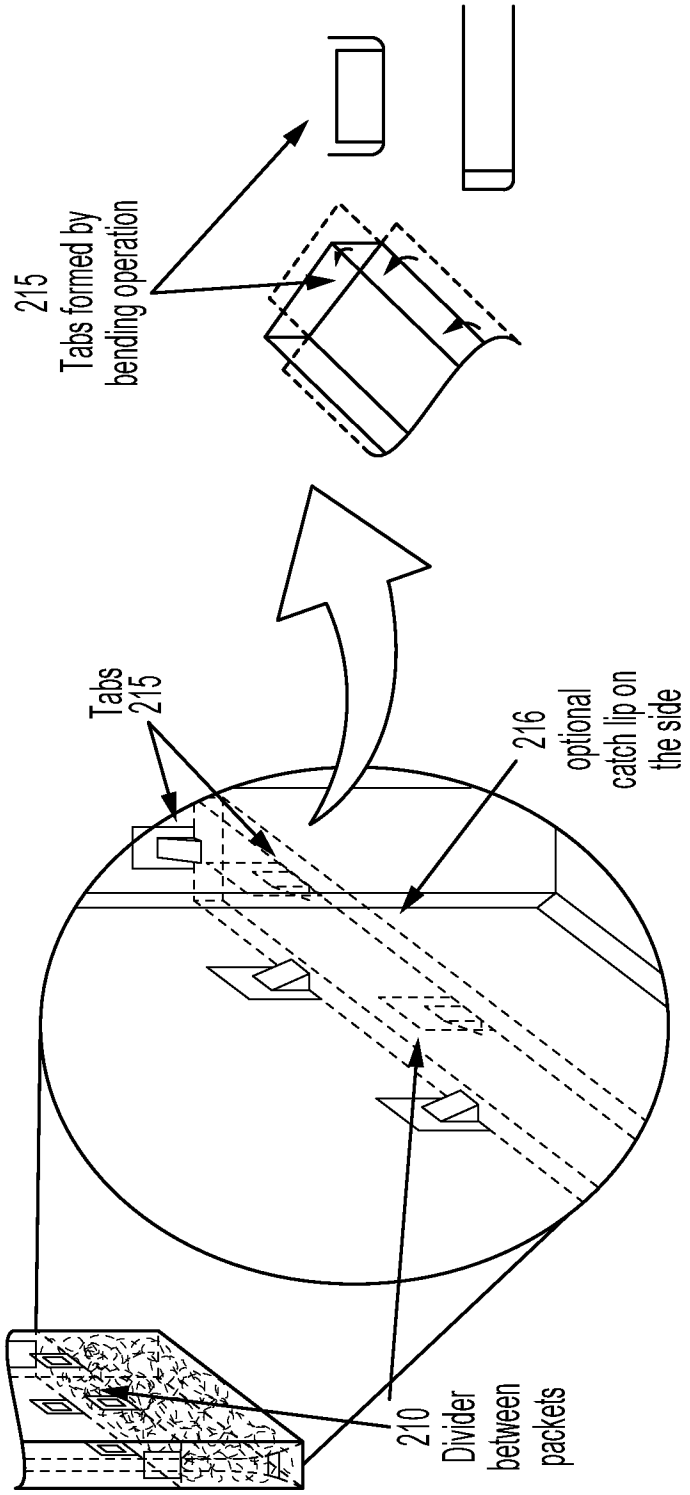

215
Tabs formed by
bending operation
Tabs
215
216
optional
catch lip on
the side
210
Divider
between
packets

FIG. 3

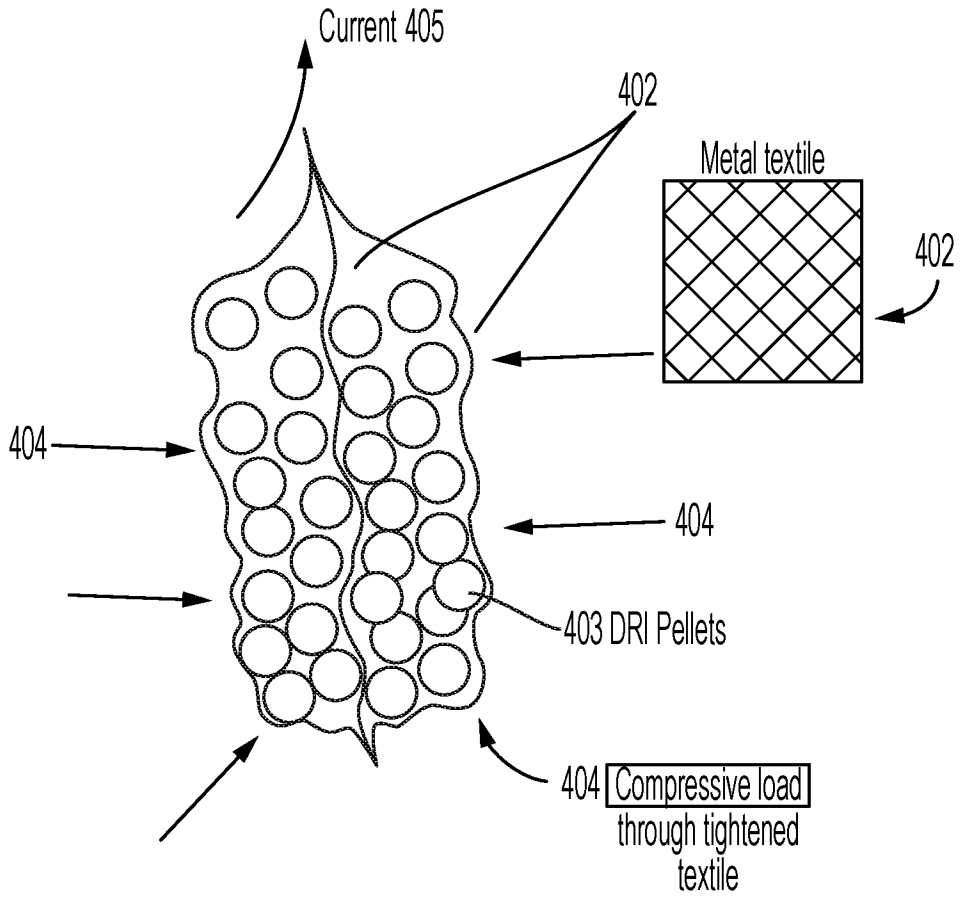

Current 405
402
Metal textile
402
404
404
403 DRI Pellets
404
Compressive load
through tightened
textile

FIG. 4

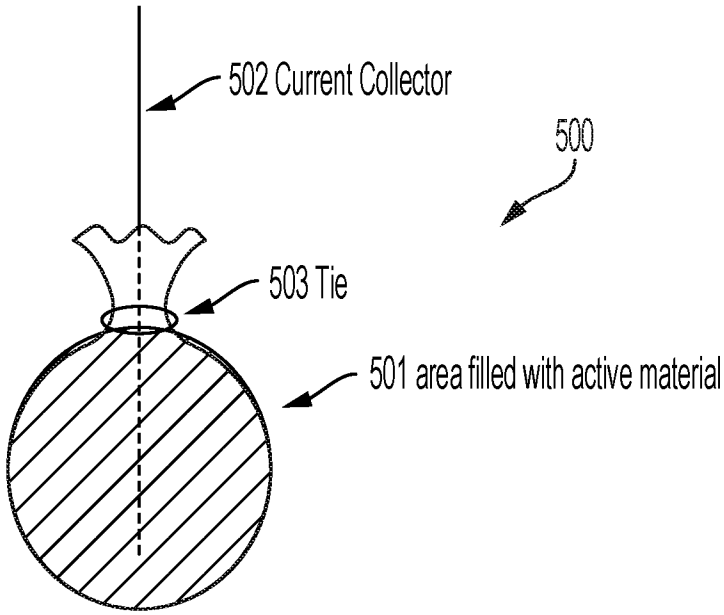

502 Current Collector
500
503 Tie
501 area filled with active material

FIG. 5

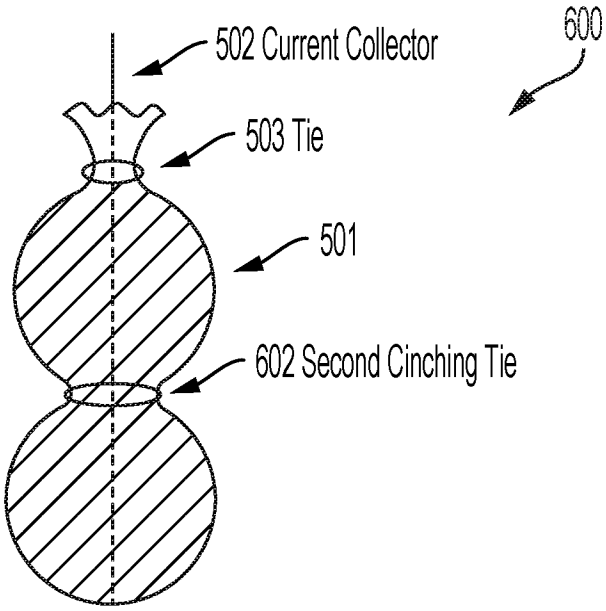

502 Current Collector
600
503 Tie
501
602 Second Cinching Tie

FIG. 6

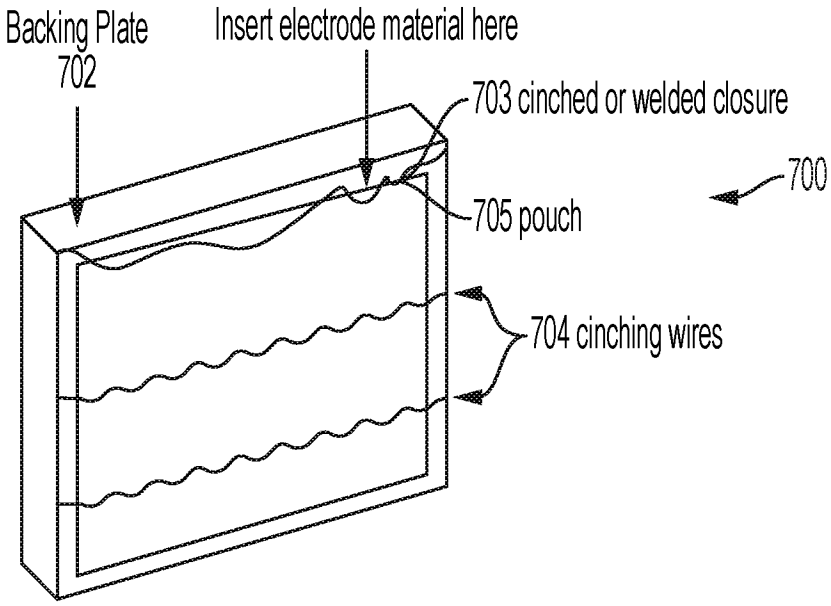
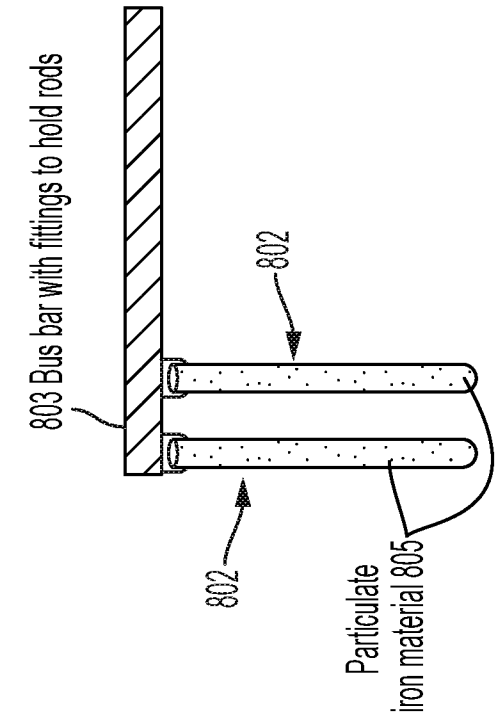

Backing Plate
702
Insert electrode material here
703 cinched or welded closure
700
705 pouch
704 cinching wires

FIG. 7


803 Bus bar with fittings to hold rods
802
802
Particulate
iron material 805

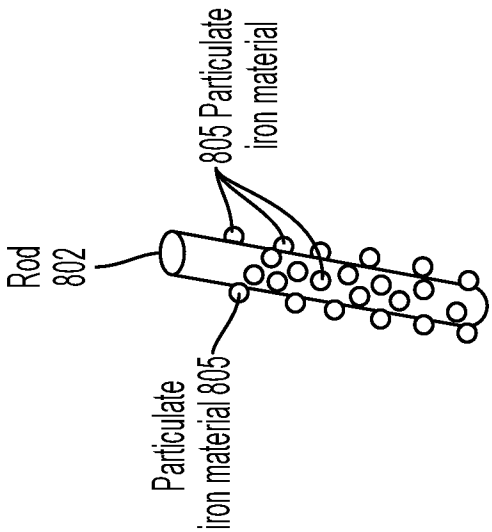

805 Particulate
iron material
Rod
802
Particulate
iron material 805

FIG. 8

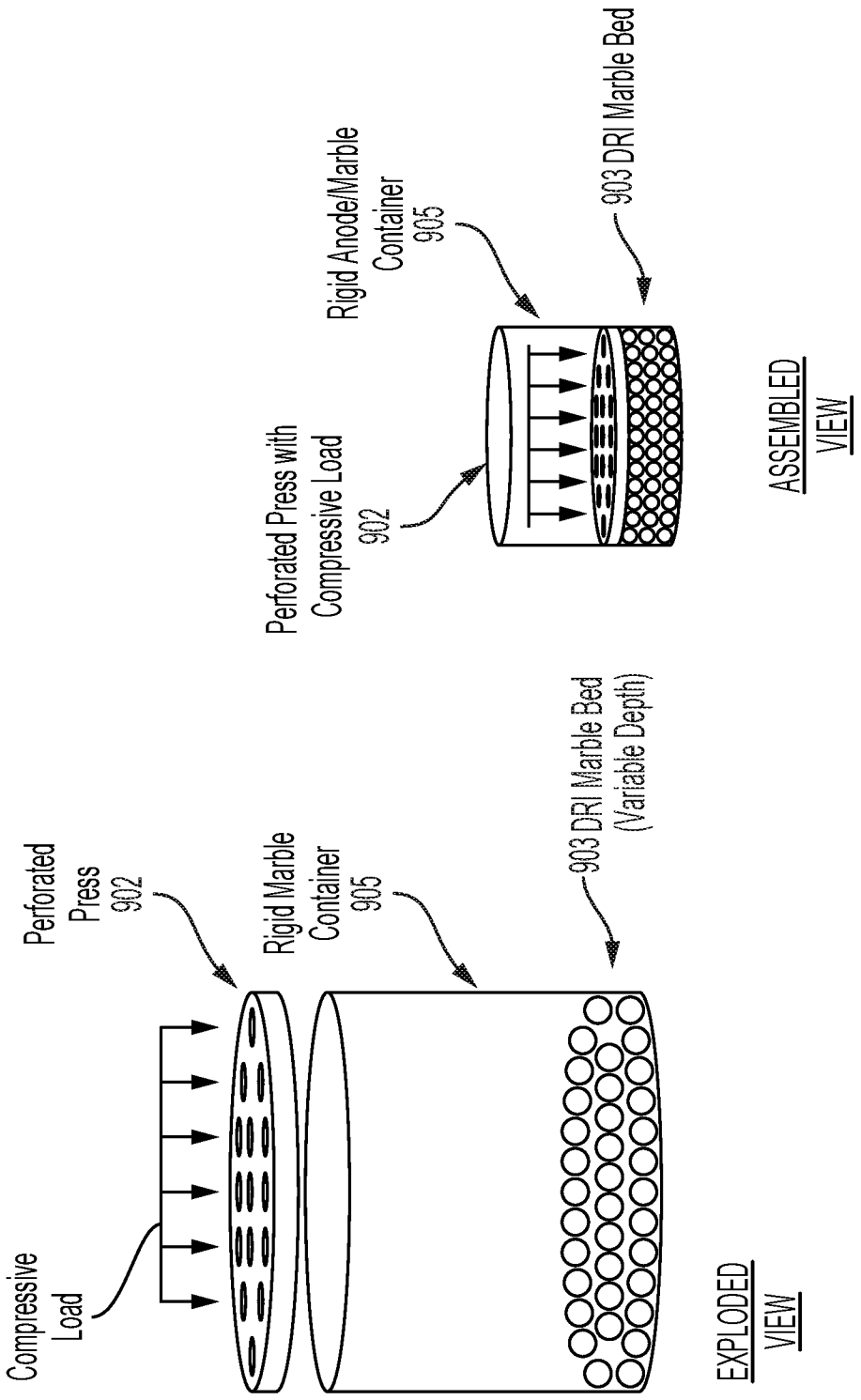

Perforated Press with Compressive Load
902
Rigid Anode/Marble Container
905
903 DRI Marble Bed
ASSEMBLED VIEW
Perforated Press
902
Rigid Marble Container
905
903 DRI Marble Bed (Variable Depth)
Compressive Load
EXPLODED VIEW

FIG. 9

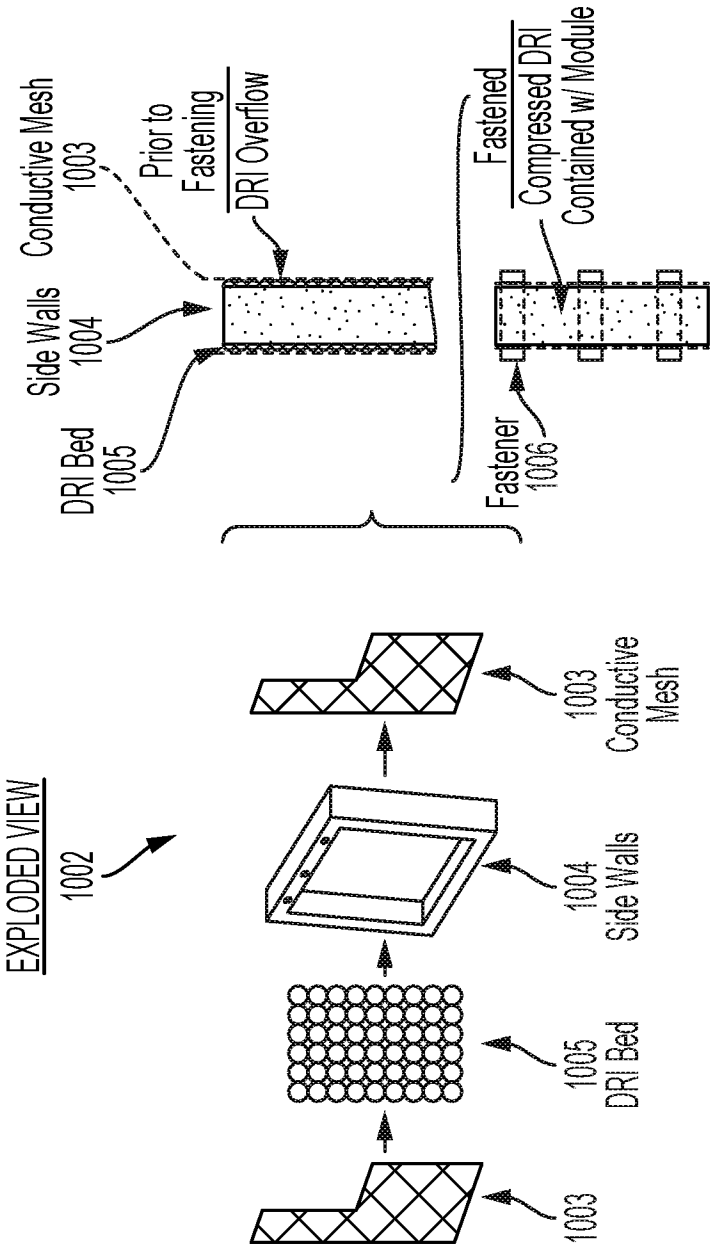

Conductive Mesh
1003
Prior to
Fastening
DRI Overflow
Side Walls
1004
DRI Bed
1005
Fastened
Compressed DRI
Contained w/ Module
Fastener
1006
EXPLODED VIEW
1002
1003
Conductive
Mesh
1004
Side Walls
1005
DRI Bed
1003

FIG. 10

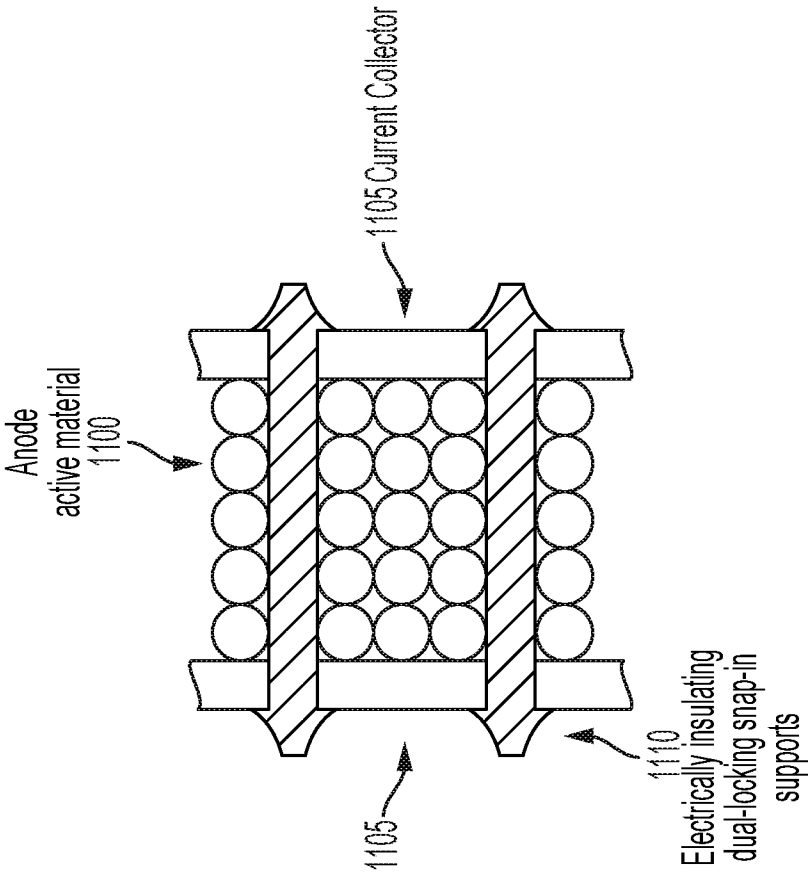


FIG. 11B

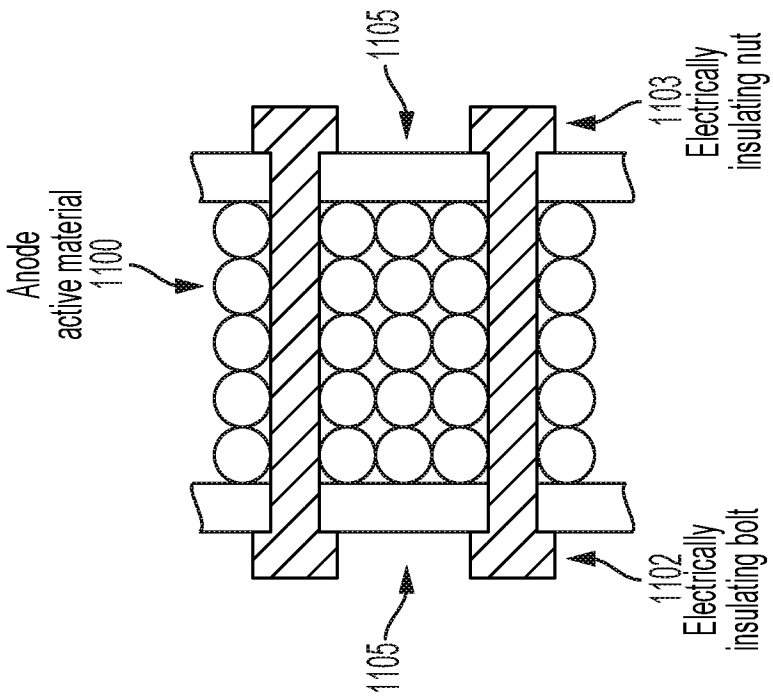


FIG. 11A

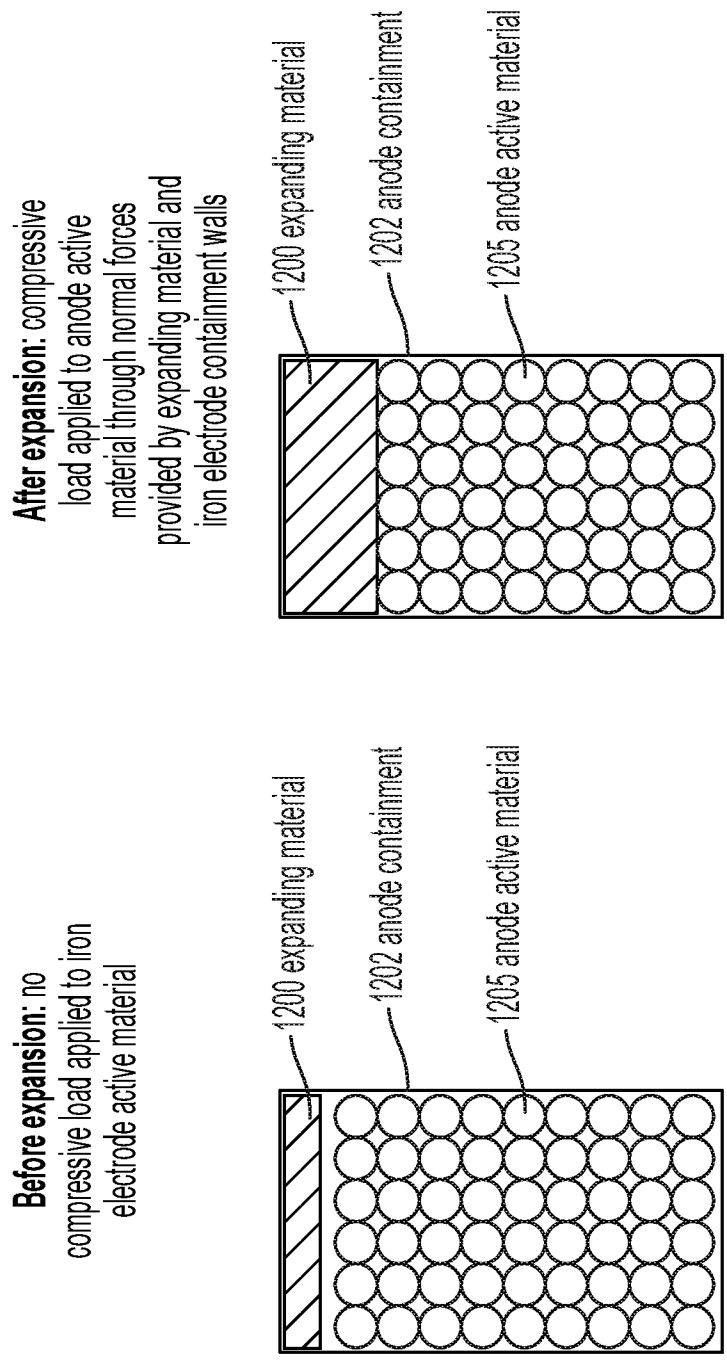

After expansion: compressive load applied to anode active material through normal forces provided by expanding material and iron electrode containment walls
1200 expanding material
1202 anode containment
1205 anode active material
Before expansion: no compressive load applied to iron electrode active material
1200 expanding material
1202 anode containment
1205 anode active material

FIG. 12

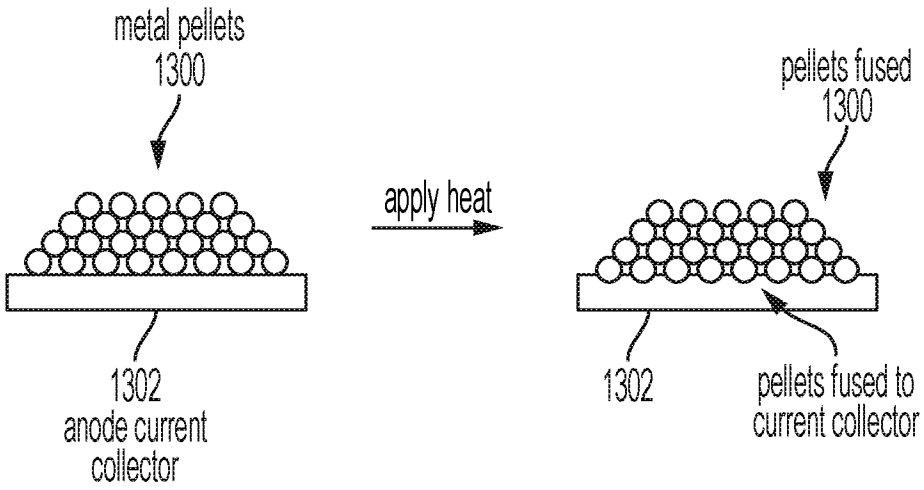

metal pellets
1300
apply heat
pellets fused
1300
1302
anode current
collector
1302
pellets fused to
current collector

FIG. 13

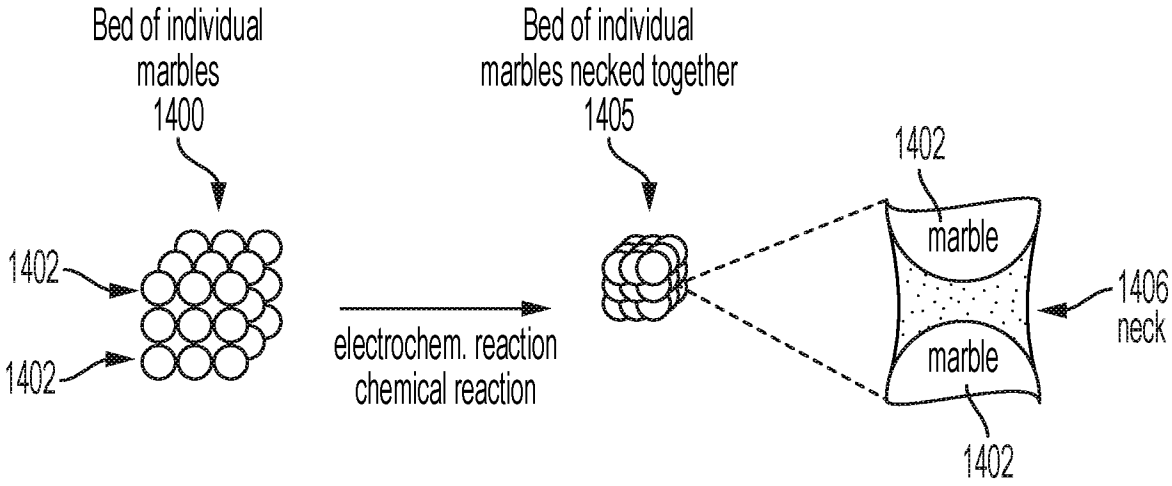

Bed of individual
marbles
1400
Bed of individual
marbles necked together
1405
1402
1402
1402
electrochem. reaction
chemical reaction
1402
marble
marble
1406
neck
1402

FIG. 14

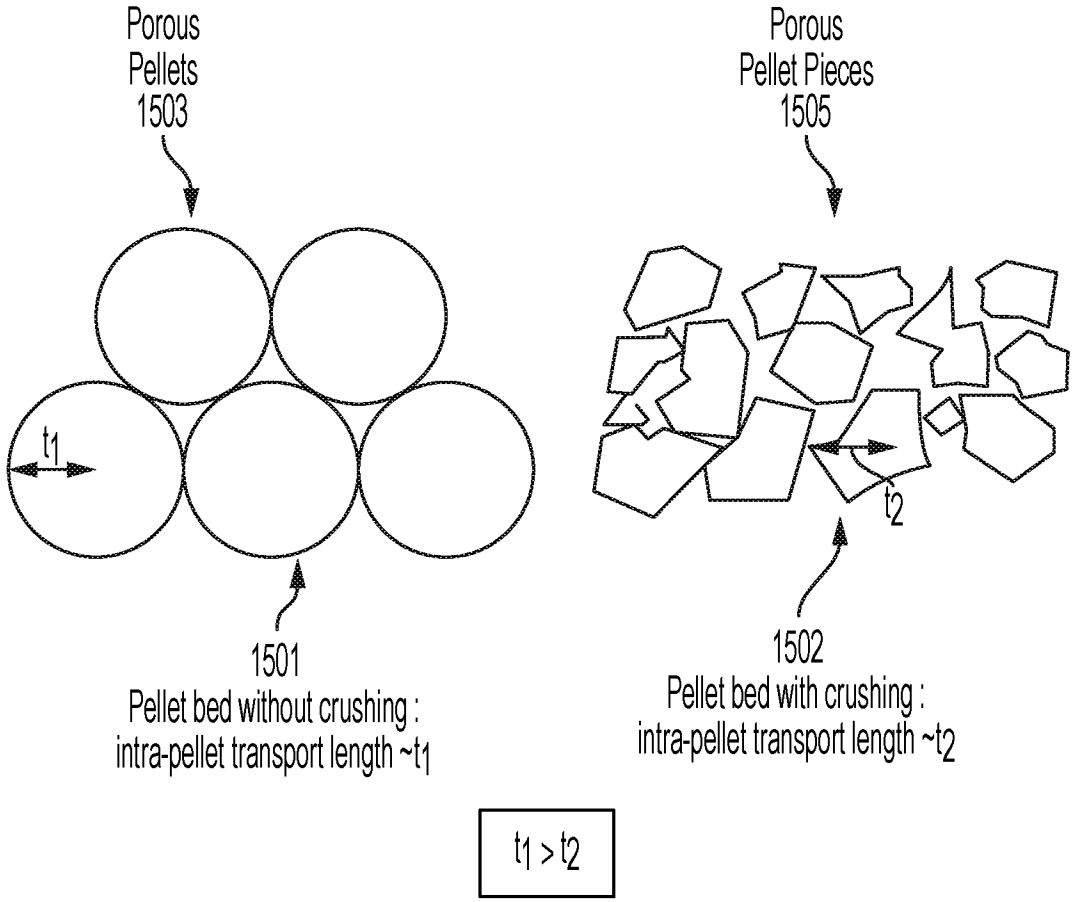

Porous
Pellets
1503
Porous
Pellet Pieces
1505
t1
t2
1501
Pellet bed without crushing :
intra-pellet transport length ~t1
1502
Pellet bed with crushing :
intra-pellet transport length ~t2
t1 > t2

FIG. 15

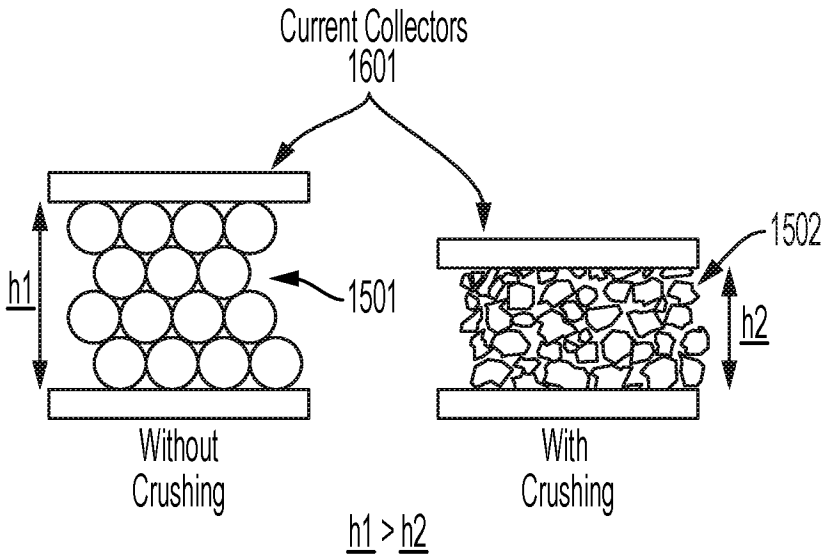

Current Collectors
1601
h1
1501
1502
h2
Without
Crushing
With
Crushing
h1 > h2

FIG. 16

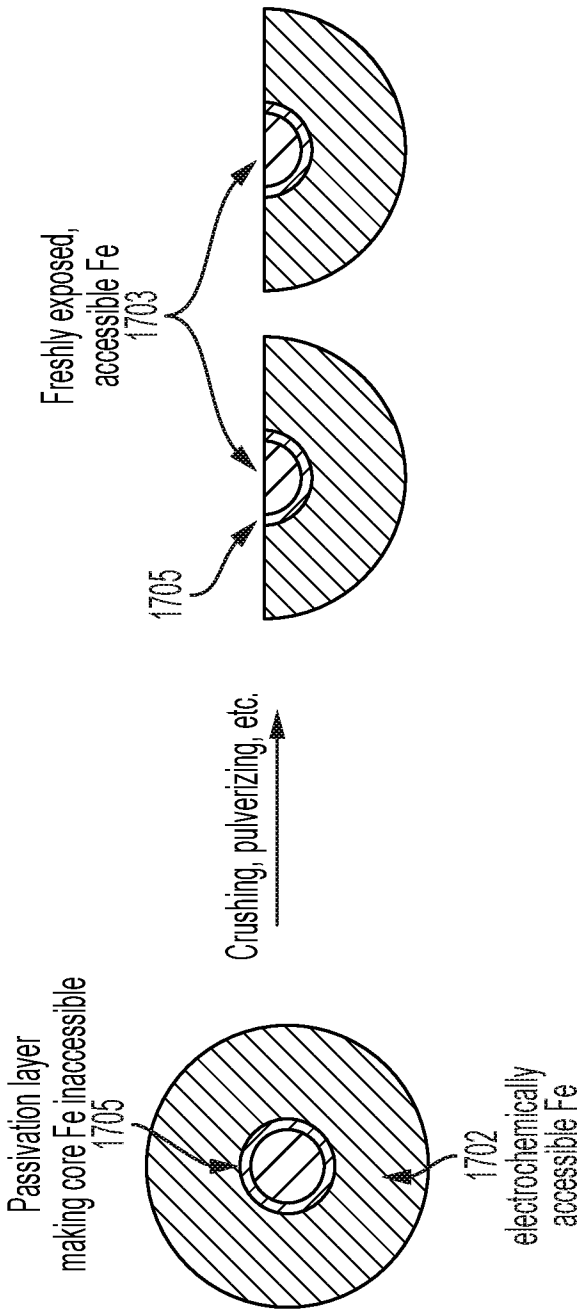

Passivation layer
making core Fe inaccessible
1705
1702
electrochemically
accessible Fe
Crushing, pulverizing, etc.
1705
Freshly exposed,
accessible Fe
1703

FIG. 17

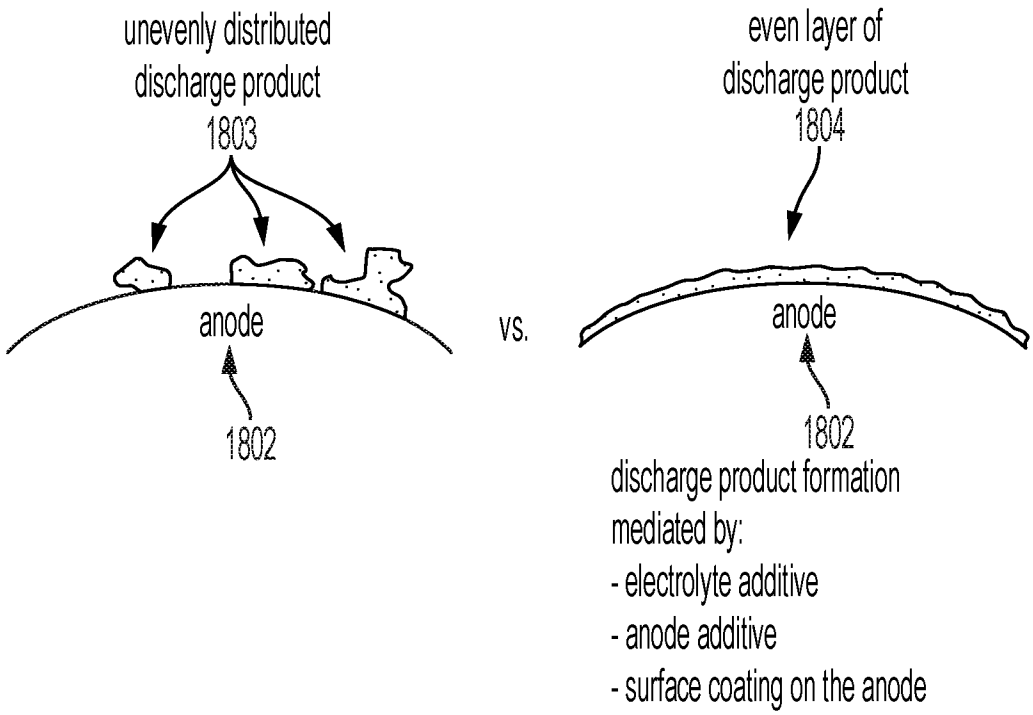

unevenly distributed
discharge product
1803
anode
1802
vs.
even layer of
discharge product
1804
anode
1802
discharge product formation
mediated by:
- electrolyte additive
- anode additive
- surface coating on the anode

FIG. 18

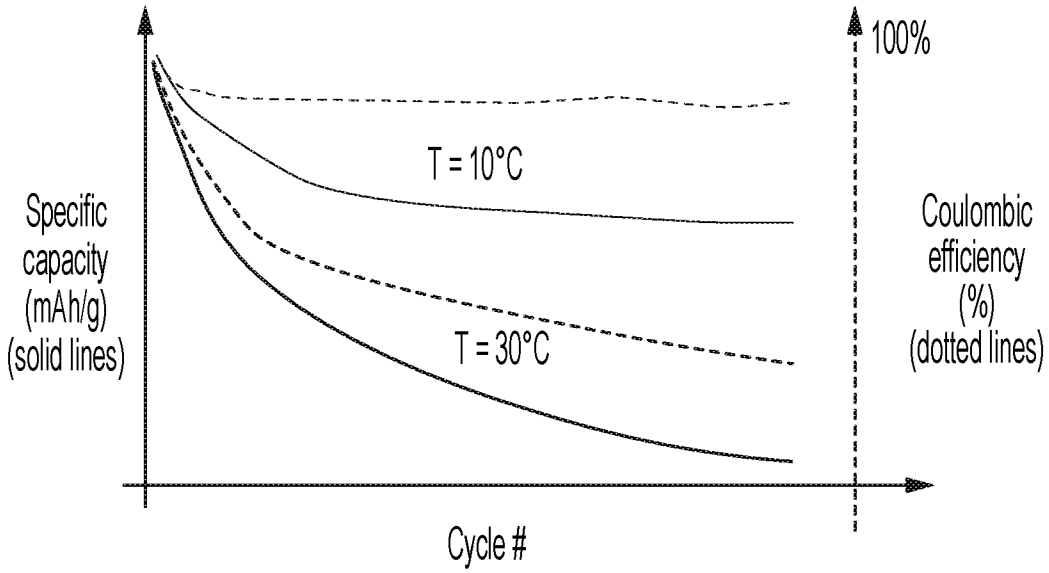

100%
T = 10°C
T = 30°C
Specific capacity (mAh/g) (solid lines)
Coulombic efficiency (%) (dotted lines)
Cycle #

FIG. 19

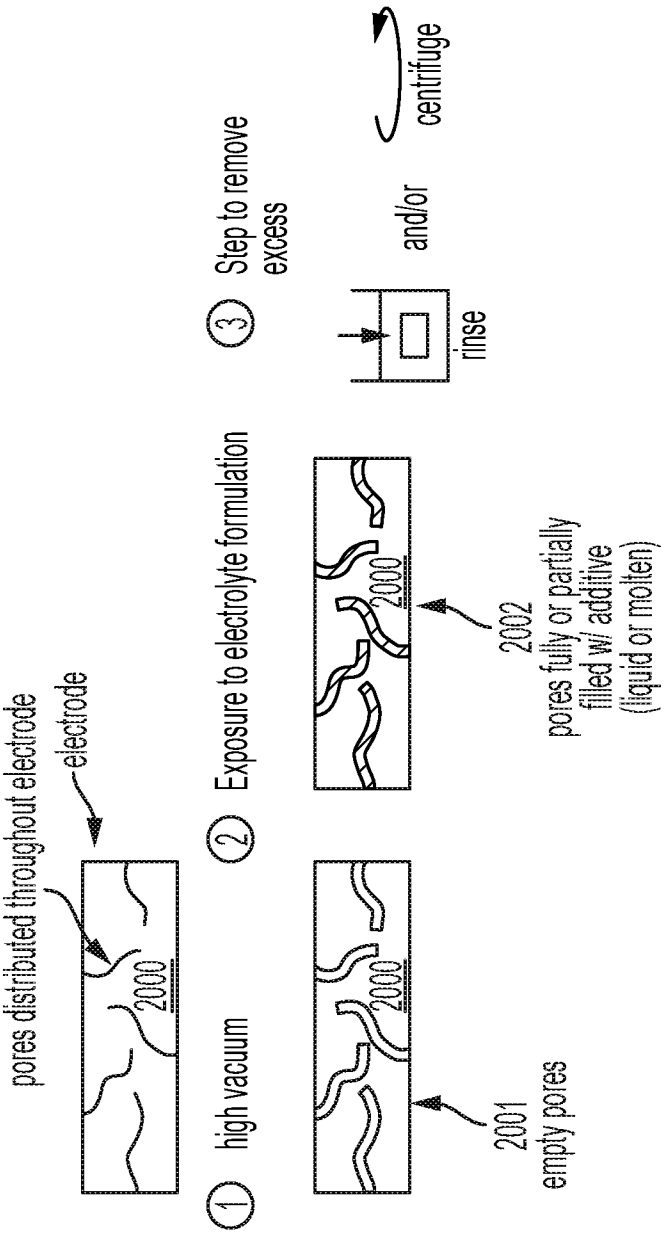
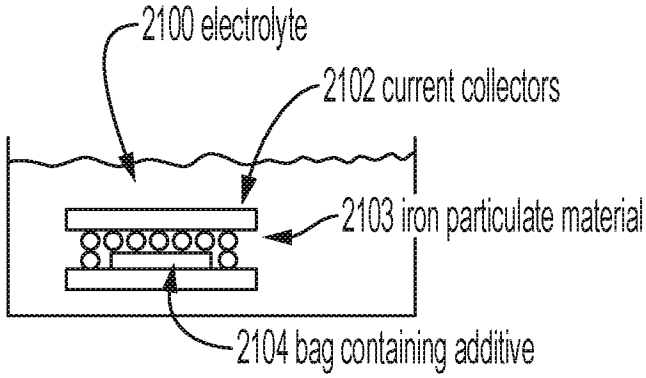

pores distributed throughout electrode
electrode
2000
① high vacuum
2001
empty pores
② Exposure to electrolyte formulation
2000
2002
pores fully or partially
filled w/ additive
(liquid or molten)
③ Step to remove
excess
and/or
centrifuge
rinse

FIG. 20


2100 electrolyte
2102 current collectors
2103 iron particulate material
2104 bag containing additive

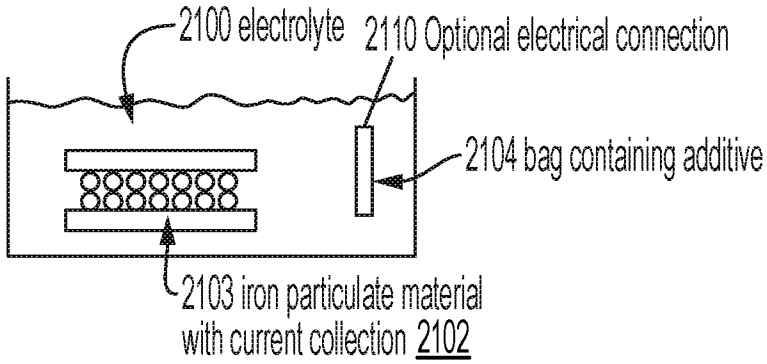

2100 electrolyte
2110 Optional electrical connection
2104 bag containing additive
2103 iron particulate material
with current collection 2102

FIG. 21

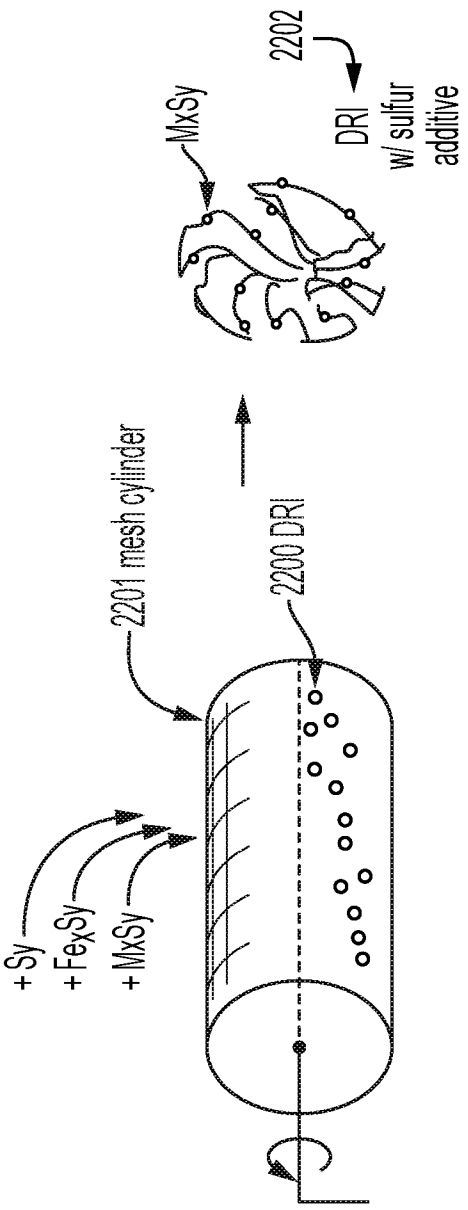

2202
DRI
w/ sulfur
additive
MxSy
2201 mesh cylinder
2200 DRI
+Sy
+FexSy
+MxSy

FIG. 22

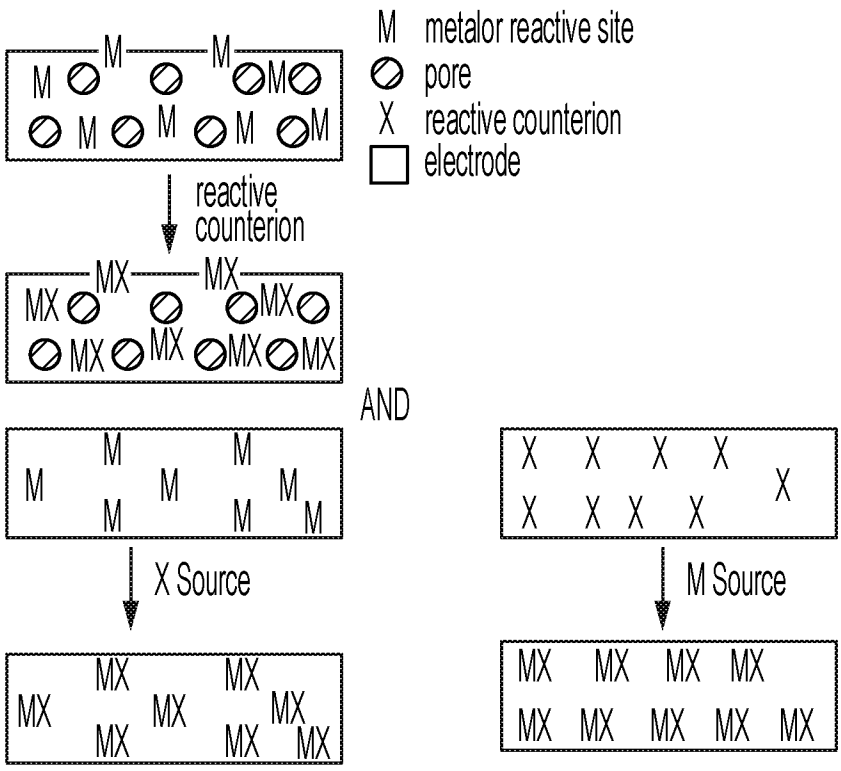

M metalor reactive site
pore
X reactive counterion
electrode
reactive counterion
AND
X Source
M Source

FIG. 23

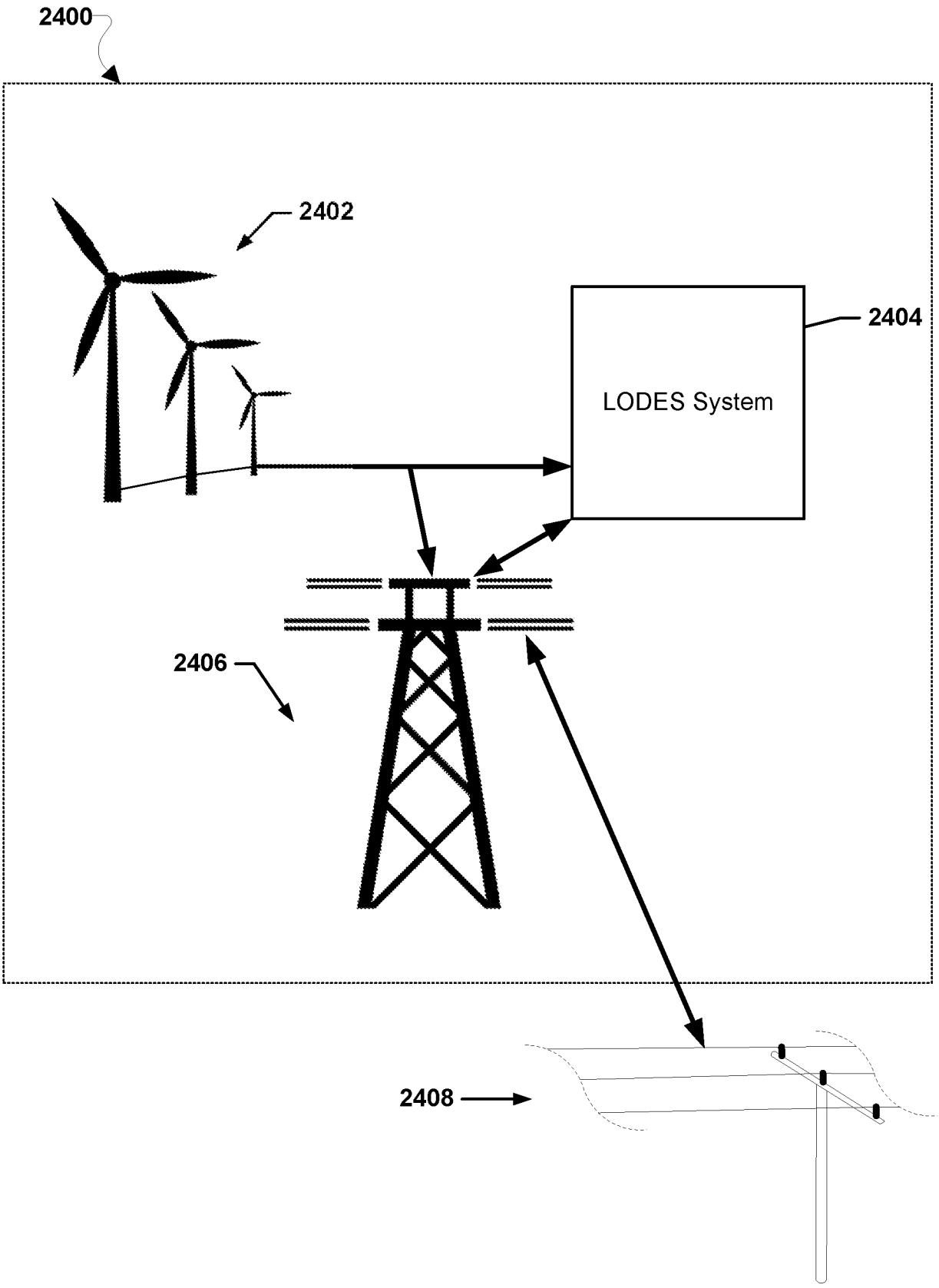


FIG. 24

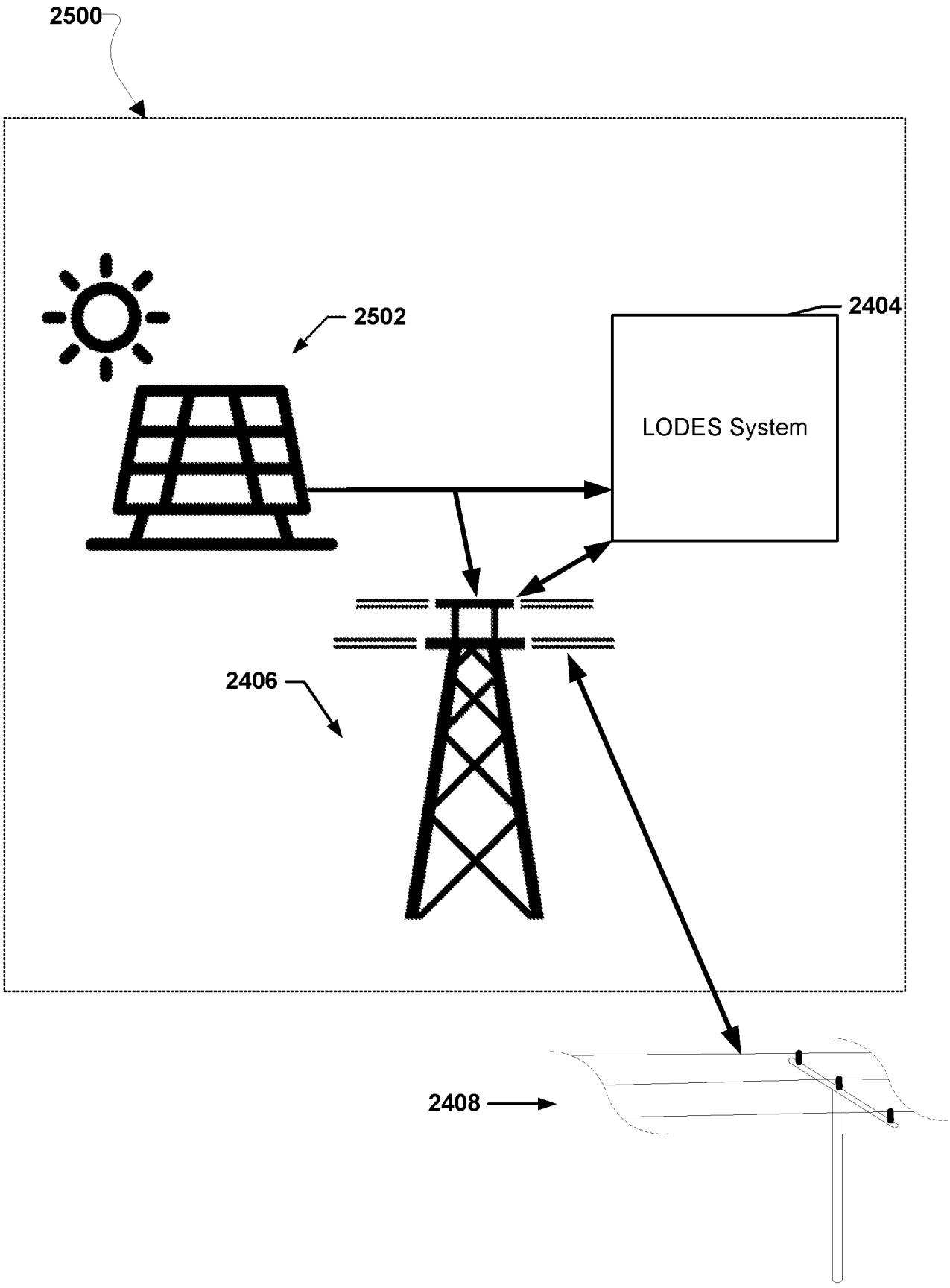


FIG. 25

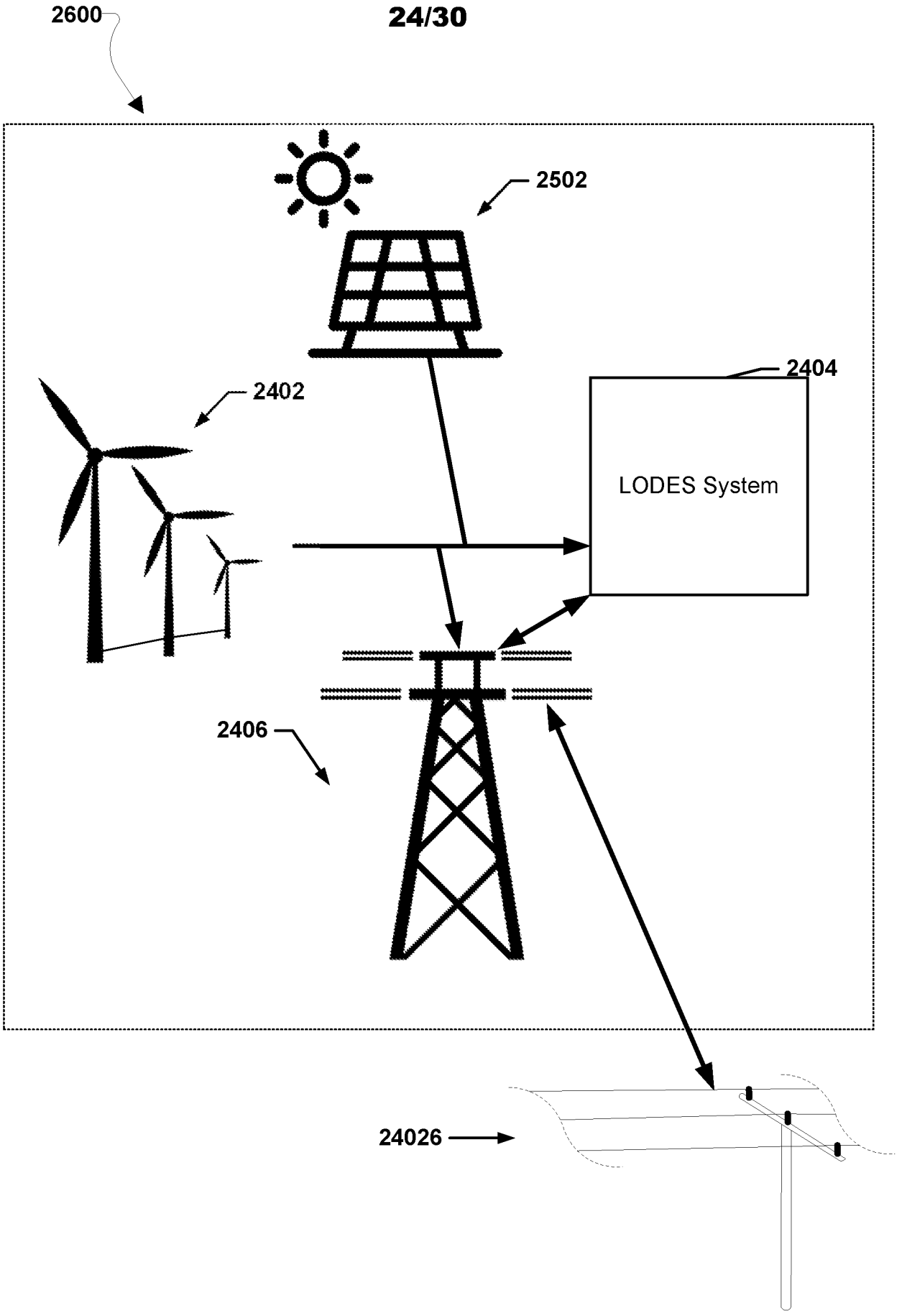


FIG. 26

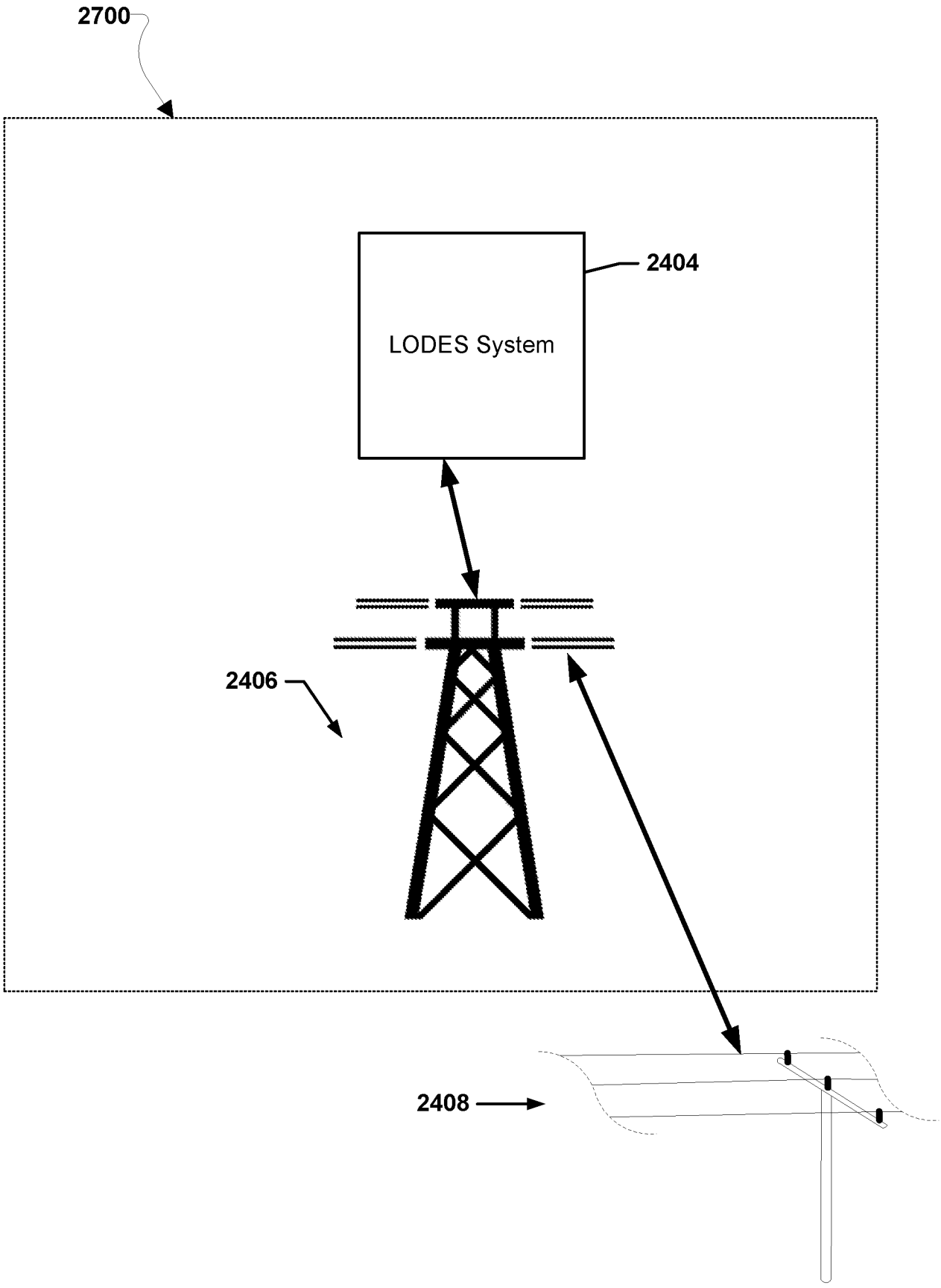


FIG. 27

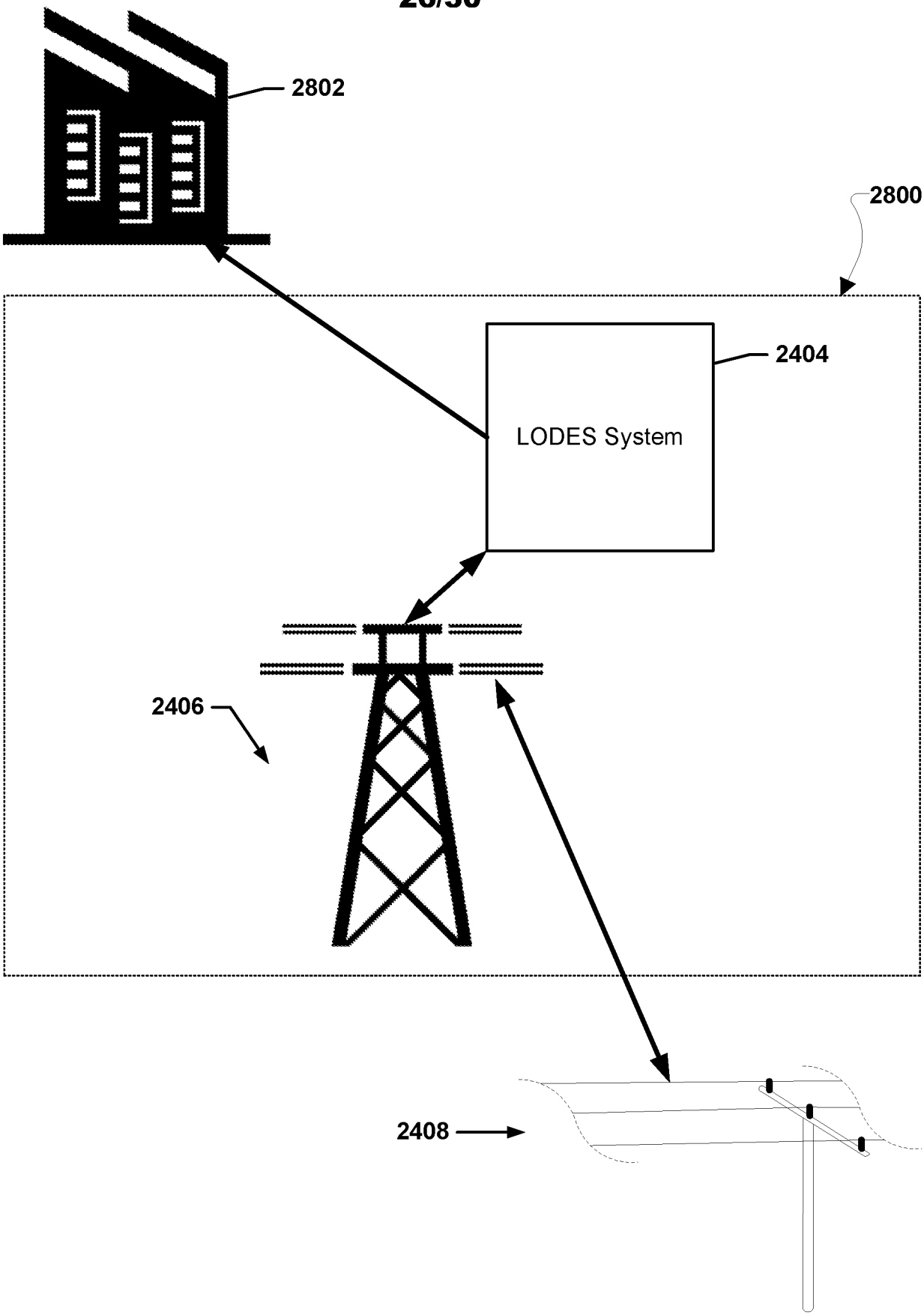


FIG. 28

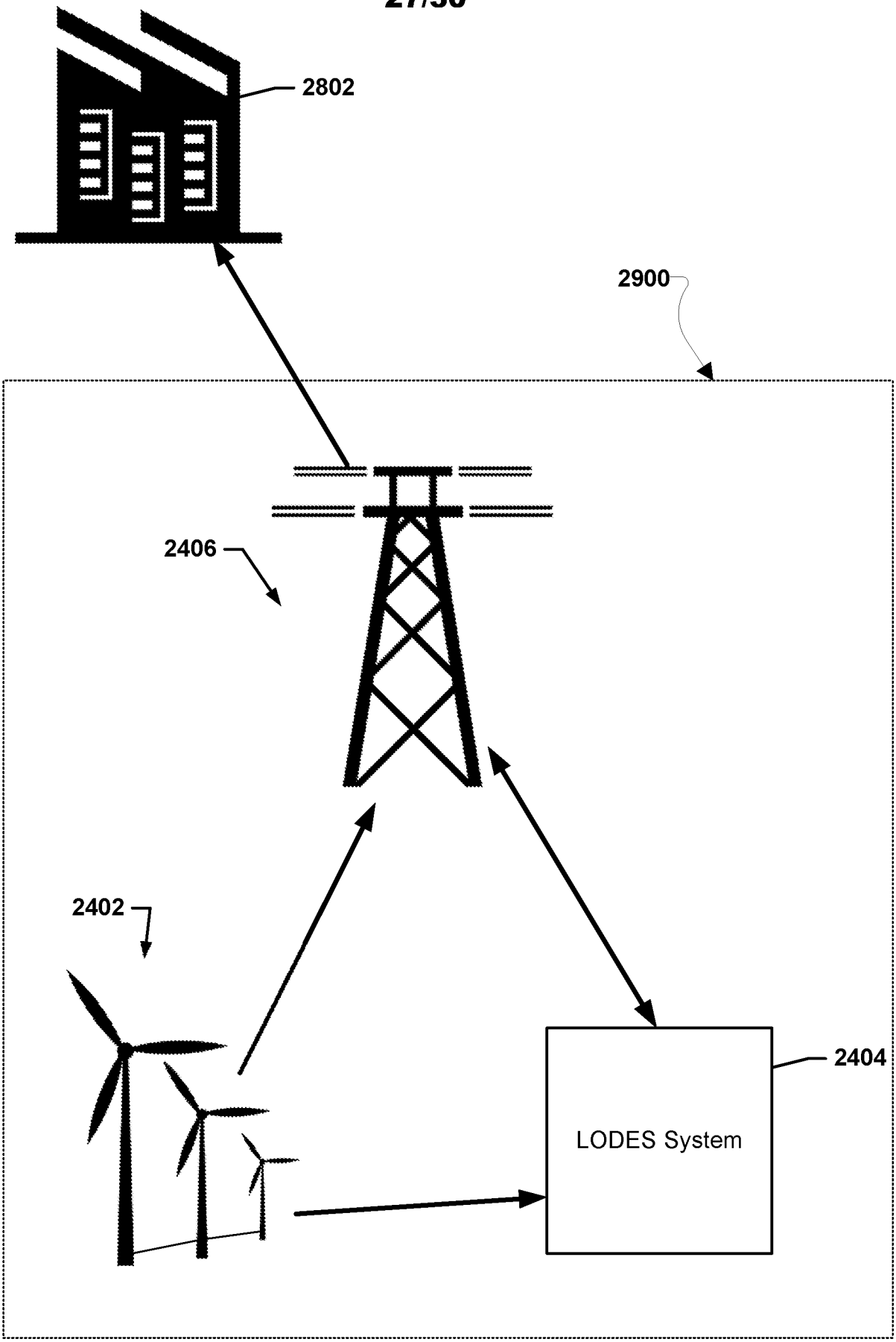


FIG. 29

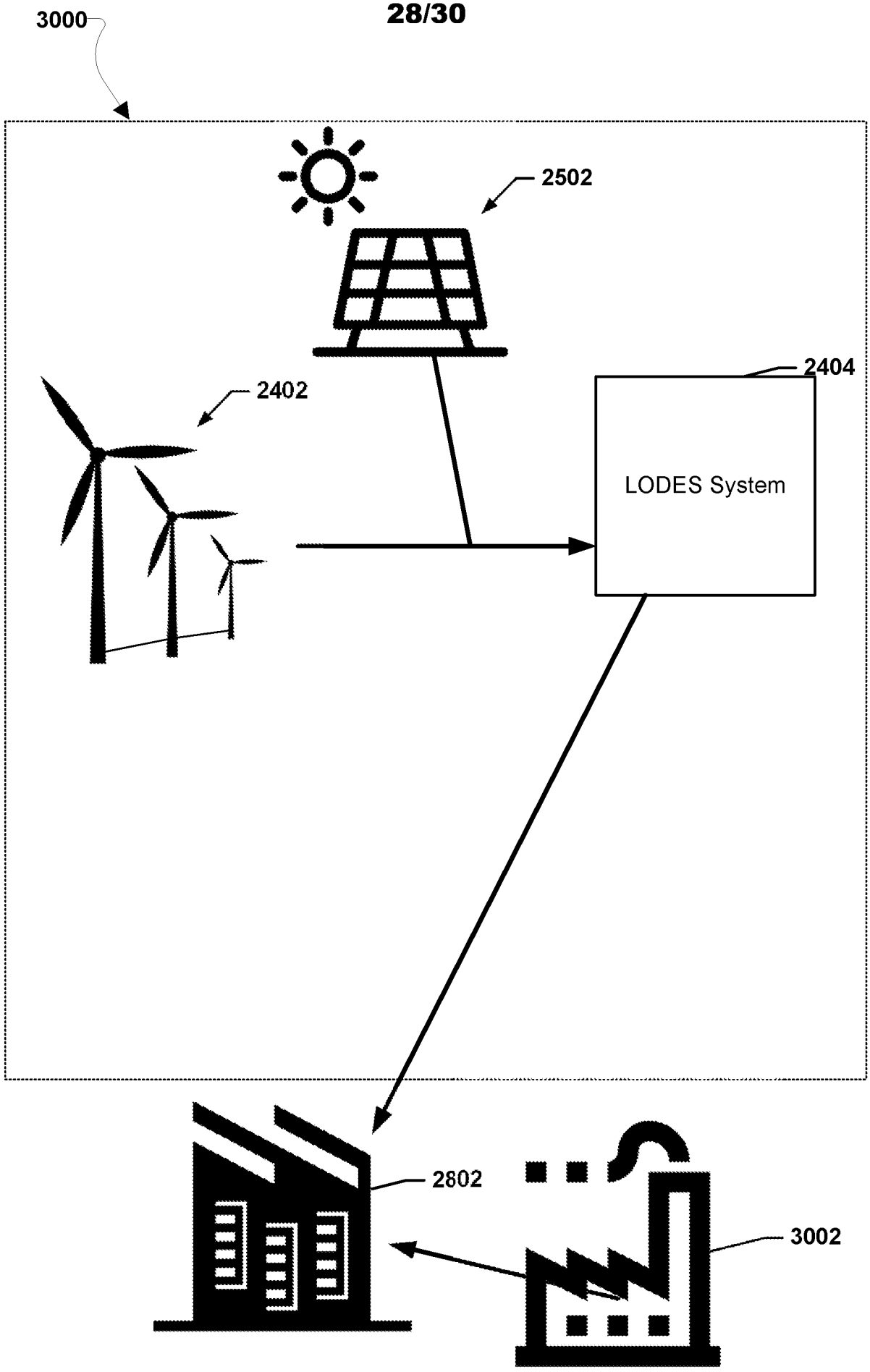


FIG. 30

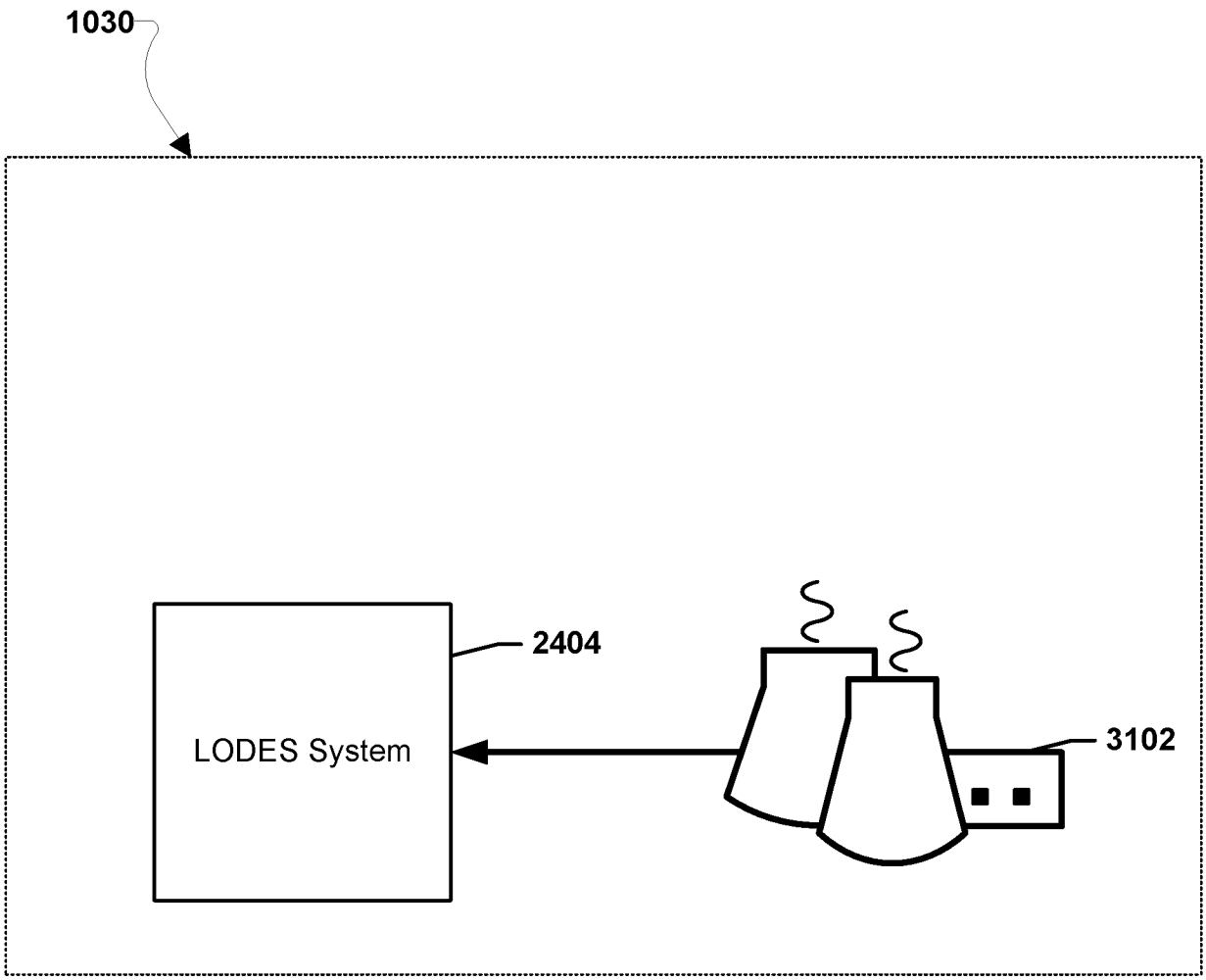


FIG. 31

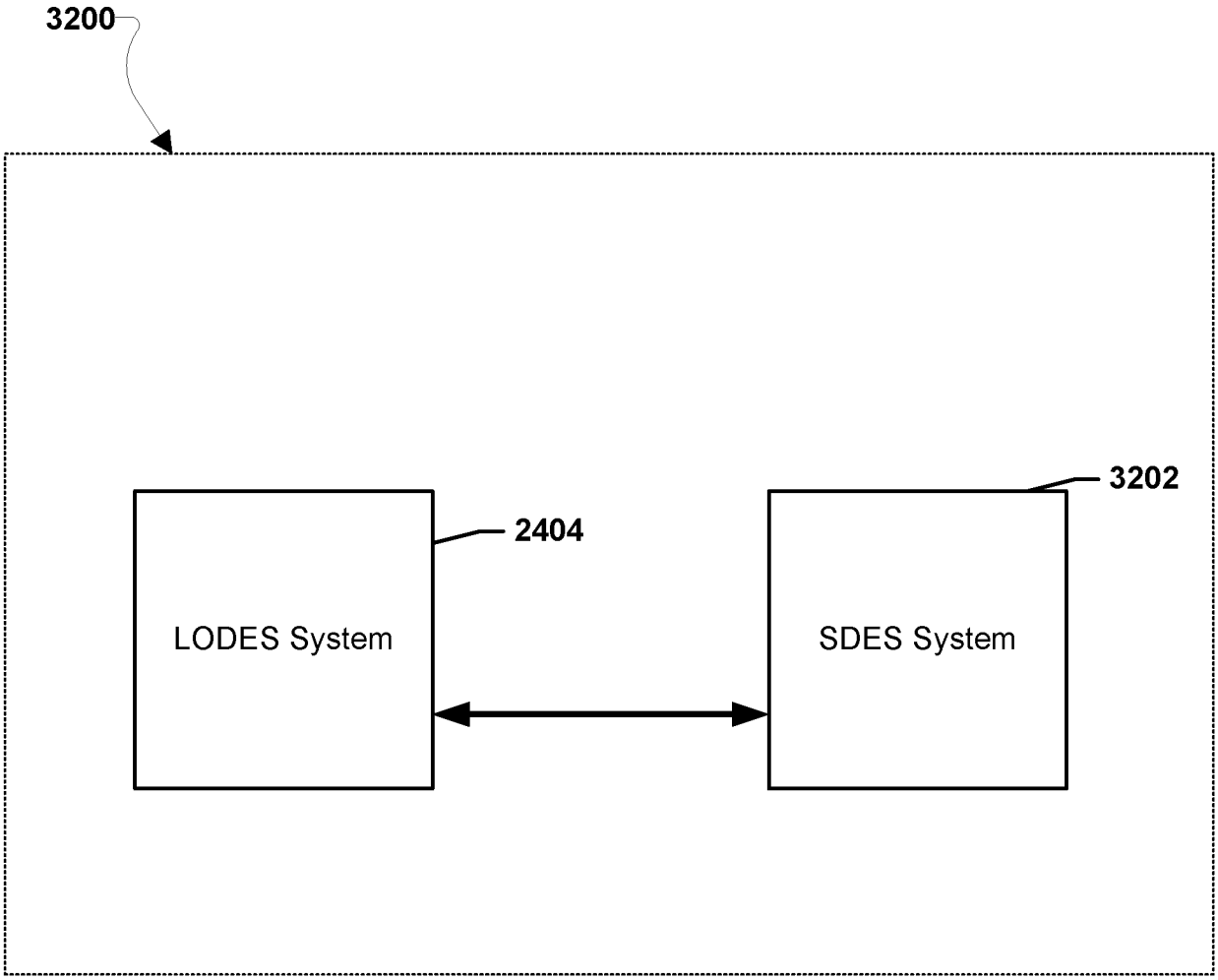


FIG. 32

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2020/043639

A. CLASSIFICATION OF SUBJECT MATTER

H01M 4/24(2006.01)i, H01M 4/86(2006.01)i, H01M 4/74(2006.01)i, H01M 8/0232(2016.01)i, H01M 12/08(2006.01)i, H01M 8/18(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
H01M 4/24; B01J 002/00; C23C 8/18; H01M 10/26; H01M 12/06; H01M 12/08; H01M 4/04; H01M 4/36; H01M 4/38; H01M 4/62; H01M 4/86; H01M 4/74; H01M 8/0232; H01M 8/18

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models
Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & keywords: electrode, iron, electrolyte, sulfide, atomize metal powder

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2014-0220460 A1 (ENCELL TECHNOLOGY, INC.) 07 August 2014 claims 1, 4; paragraphs [0035], [0039]	1-15,21-36
X	US 2018-0219220 A1 (KABUSHIKI KAISHA KOBE SEIKO SHO (KOBE STEEL, LTD.) et al.) 02 August 2018 claims 1, 7; paragraph [0002]	16-20,37,38
X	KR 10-2014-0068850 A (UNIVERSITY OF SOUTHERN CALIFORNIA) 09 June 2014 claims 1-29	1-15,21-36
A	US 2018-0010228 A1 (ENCELL TECHNOLOGY, INC.) 11 January 2018 claims 1-15	1-38
A	US 2004-0221426 A1 (IGAWA, Y. et al.) 11 November 2004 claims 1-12	1-38
A	US 2014-0162129 A1 (SAMSUNG SDI CO., LTD.) 12 June 2014 claims 1-20	1-38

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents:
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"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents,such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
12 November 2020 (12.11.2020)	**13 November 2020 (13.11.2020)**

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/US2020/043639

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