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(71) Applicant: **TECHNISCHE UNIVERSITEIT EINDHOVEN** [NL/NL]; Groene Loper 3, 5612 AE Eindhoven (NL).

(72) Inventors: **MAJID, Akmal Irfan**; Groene Loper 3, 5612 AE Eindhoven (NL). **TANG, Yali**; Groene Loper 3, 5612 AE Eindhoven (NL). **FINOTELLO, Giulia**; Groene Loper 3, 5612 AE Eindhoven (NL). **VAN DER SCHAAF, John**; Groene Loper 3, 5612 AE Eindhoven (NL). **DEEN, Niels**; Groene Loper 3, 5612 AE Eindhoven (NL).

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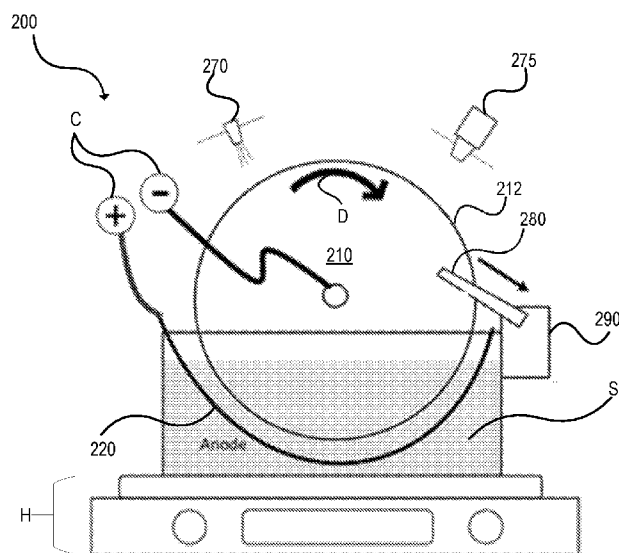


FIG. 2A

(57) Abstract: An electrochemical cell for converting metal salt or metal oxide to metal comprises: a) a mixture comprising an electrolyte and metal salt or metal oxide; b) an anode submerged in the mixture; c) a cathode partially submerged in the mixture and moveable along a closed loop path; and d) a harvester disposed at an exposed portion of the cathode outside of the mixture, wherein an electrical charge supplied to the electrochemical cell reduces the metal salt or metal oxide to metal at and disposed onto the cathode, and wherein the harvester removes the metal from the exposed portion of the cathode. Methods and systems for converting metal salt or metal oxide to metal are also disclosed including continuous methods and systems.

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SYSTEMS AND METHODS FOR CONTINUOUS ELECTROLYTIC PRODUCTION OF METALS

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This Application claims priority to U.S. Provisional Application No. 63/363,627, filed April 26, 2022, which is incorporated herein by reference.

FIELD OF INVENTION

[0002] The present invention relates to continuous electrolytic production of metals, particularly methods for converting metal salts and/or metal oxides to metals, and electrochemical cells, methods, and systems associated with same.

BACKGROUND

[0003] Available systems and methods for production of metals from metal salts and metal oxides suffer from a number of disadvantages. Examples of such disadvantages include CO₂ emission in the reduction process of metal oxides, difficulties harvesting the metal (due the solid and compact nature of the deposit as the final result), relatively low performance in terms of Faradaic efficiency and metal purity, and high energy consumption.

[0004] For example, most reduction processes of iron oxide and iron ore to metallic iron (e.g. in steel industries) are still using blast furnace, which requires a large amount of coke/coal. This method consumes a lot of energy and results in high carbon emissions.

[0005] Recently, the use of (green) hydrogen as a reducing agent is introduced for lower emission iron oxide reduction. However, this technology includes drawbacks such as the use of a high-temperature process (above 300°C) and the long duration necessary to completely reduce the iron oxide. Hence, a lot of energy is required. The sintered powders are often obtained in the final reduced powder. This process also requires a longer production chain, in which (green) hydrogen as the reducing agent, is firstly needed to be provided from other processes e.g., electrolysis by using (renewable) electrical energy; then, the produced hydrogen is used for reduction. Consequently, more energy and cost are required in this process.

[0006] Also, previous works on metal electrodeposition commonly produce compact and thick layer deposit structures which are difficult to harvest in the form of fine powders. Even when this is successful, a costly post-treatment is therefore required.

[0007] Further, the industrial-scale metal electrodeposition processes, e.g., for iron and zinc, are commonly conducted in the batch process.

[0008] Thus, the need exists for simple and efficient systems and methods of continuous electrolytic production and harvesting of metals.

SUMMARY

[0009] The present disclosure relates to the continuous production of metal powder via electrodeposition using an electrochemical cell. The embodiments of the present disclosure are advantageous for converting metal salts and metal oxides by electrochemical deposition (electrodeposition) of metals that generate dendritic metal structures. By implementing a cyclical dendritic-resulted electrodeposition together with the harvesting techniques according to the present disclosure, a continuous (electrolytic) metal powder production can be achieved. This allows shortening of production time and more effective production processes.

[0010] In the recycling of metal from the wastes, for example the metal recovery from incinerator bottom ash (IBA), may contain metal salts and/or metal oxides. Those metal salts and/or metal oxides can be also reduced to metallic form by using wet processing methods i.e. electrochemical methods, such as disclosed in embodiments of the present disclosure. This can also give future benefit in terms of production effectiveness and circularity of metal wastes.

[0011] In one aspect, an electrochemical cell for converting metal salt or metal oxide to metal, comprises: a) a mixture comprising an electrolyte and metal salt or metal oxide; b) an anode submerged in the mixture; c) a cathode partially submerged in the mixture and moveable along a closed loop path; and d) a harvester disposed at an exposed portion of the cathode outside of the mixture; wherein an electrical charge supplied to the electrochemical cell reduces the metal salt or metal oxide to metal at and disposed onto the cathode, and wherein the harvester removes the metal from the exposed portion of the cathode. In some embodiments, the metal salt or metal oxide is selected from one or more of FeCl_3 , FeSO_4 , $\text{Fe}_2(\text{SO}_4)_3$, ZnSO_4 , $\text{Zn}_2(\text{SO}_4)_3$, ZnCl_2 , CoCl_2 , CuSO_4 , Fe_2O_3 , Fe_3O_4 , FeO , ZnO , CuO , MgO , Co_3O_4 , and MnO . In some embodiments, the metal is selected from one or more of Fe, Cu, Ni, Zn, Co, Mn, Ag, Pt, Pd, Au, Ag, Mg, Li, and Pb. In some embodiments, the metal forms a plurality of dendritic structures disposed onto the cathode. The cathode may comprises a disc. In some embodiments, the cathode comprises a connected looping structure. In some embodiments, the harvester comprises a mechanical harvester, a magnetic harvester, or combinations thereof. In some embodiments, the electrochemical cell further comprises: i) a rinsing unit configured to spray cleaning fluid onto the metal; and ii) a cartridge to retain the metal removed from the cathode by the harvester. In a certain embodiment, the metal salt or metal oxide is iron oxide; the electrolyte is alkaline electrolyte; and the metal is iron.

[0012] In another aspect, a method for converting metal salt or metal oxide into metal comprises: a) providing a metal salt or oxide in an electrolyte in an electrochemical cell to form a mixture, wherein the electrochemical cell includes an anode submerged in the mixture and a cathode partially submerged in the mixture and moveable along a closed loop path; b) supplying an electrical charge in the electrochemical cell, and reducing the metal salt or metal oxide in the mixture to form the metal at and disposed onto the cathode; c) moving the cathode having the metal disposed thereon from the mixture to provide an exposed portion of the cathode outside of the mixture; and d) harvesting the metal from the exposed portion of the cathode. In some embodiments, the method is a continuous process, wherein the abovementioned steps a) to d), and, optionally, further steps mentioned below, may be repeated in a cyclical manner. In some embodiments, the method further comprises: e) rinsing the metal; and f) collecting the metal. In some embodiments, the method is a continuous process comprising repeating the steps a) to d) or a) to f). In some embodiments, the metal salt or metal oxide is selected from one or more of FeCl_3 , FeSO_4 , $\text{Fe}_2(\text{SO}_4)_3$, ZnSO_4 , $\text{Zn}_2(\text{SO}_4)_3$, ZnCl_2 , CoCl_2 , CuSO_4 , Fe_2O_3 , Fe_3O_4 , FeO , ZnO , CuO , MgO , Co_3O_4 , and MnO . In some embodiments, the metal is selected from one or more of Fe, Cu, Ni, Zn, Co, Mn, Ag, Pt, Pd, Au, Ag, Mg, Li, and Pb. In some embodiments, the metal forms a plurality of dendritic structures disposed onto the cathode.

[0013] In some embodiments, the cathode is a cathode assembly comprising a plurality of moveable cathodes. In some embodiments, the harvester is a harvester assembly comprising a plurality of harvester units positioned for harvesting metal from the plurality of movable cathodes. In a certain embodiment, the metal salt or metal oxide is iron oxide; the electrolyte is alkaline electrolyte; and the metal is iron. In some embodiments, the method further comprises heating the mixture and generating current in the electrochemical cell concurrently with heating the mixture. In some embodiments, the mixture is heated to a temperature between about 80°C to about 115°C . In some embodiments, the method further comprises stirring the mixture for a period of time to form a stirred suspension. In some embodiments, the mixture is stirred for a period of time ranging from about 10 minutes to 20 minutes or more. In some embodiments, the mixture comprises aqueous sodium hydroxide at a concentration of at least about 5 M; or wherein the metallic iron comprises a purity greater than about 90%; or wherein a mass fraction of iron oxide in the suspension is between about 5% to about 33%. In some embodiments, the method includes the electrochemical cell comprising a faradaic efficiency

greater than about 85%. In some embodiments, the electrochemical cell has an electrical energy consumption of less than 6 kWh/kg iron.

[0014] In still another aspect, a continuous system for converting metal salt or metal oxide into metal comprises: an inlet to receive a mixture comprising a metal salt or metal oxide, an electrolyte, or a combination thereof, where the inlet feeds the mixture to an electrochemical cell; the electrochemical cell including the mixture, an anode submerged in the mixture, and a cathode partially submerged in the mixture and moveable along a closed loop path, wherein an electrical charge supplied to the electrochemical cell reduces the metal salt or metal oxide to the metal at and disposed onto the cathode; optionally a rinsing unit to spray cleaning fluid onto the metal disposed onto the cathode; optionally a drying unit to remove moisture from the metal; a harvester disposed at an exposed portion of the cathode outside of the mixture to remove the metal from the exposed portion of the cathode; and an outlet to discharge suspension or mixture from the system. In some embodiments, the metal salt or metal oxide is selected from one or more of FeCl_3 , FeSO_4 , $\text{Fe}_2(\text{SO}_4)_3$, ZnSO_4 , $\text{Zn}_2(\text{SO}_4)_3$, ZnCl_2 , CoCl_2 , CuSO_4 , Fe_2O_3 , Fe_3O_4 , FeO , ZnO , CuO , MgO , Co_3O_4 , and MnO . In some embodiments, the metal is selected from one or more of Fe, Cu, Ni, Zn, Co, Mn, Ag, Pt, Pd, Au, Ag, Mg, Li, and Pb. In some embodiments, the metal forms a plurality of dendritic structures disposed onto the cathode. In some embodiments, the cathode comprises a disc. In some embodiments, the cathode comprises a connected looping structure. In some embodiments, the harvester comprises a mechanical harvester, a magnetic harvester, or combinations thereof. In some embodiments, the metal salt or metal oxide is iron oxide; the electrolyte is alkaline electrolyte; and the metal is iron. In some embodiments, the system further comprises maintaining the mixture at a concentration of at least about 5M.

BRIEF DESCRIPTION OF THE DRAWINGS

[0015] FIG. 1 shows a schematic diagram of an exemplary embodiment of the continuous and integrated systems of electrolytic metal production.

[0016] FIGs. 2A-2B schematically illustrate electrochemical cells according to embodiments herein. FIG. 2A is a front view of an exemplary electrochemical cell having a rotating cathode configured to move along a closed loop path by rotating in and out of the electrolyte, a harvester for removing metal from the cathode, and a cartridge for collecting the

metal. FIG. 2B shows a top view of the electrochemical cell as in FIG. 2A illustrating an electrical motor for rotating the cathode, where the cathode is shown as a disc.

[0017] FIG. 3 illustrates a front view of another exemplary electrochemical cell showing a cathode as a moveable belt that is moveable along a closed loop path.

[0018] FIG. 4 illustrates yet another exemplary electrochemical cell showing the cathode including a plurality of rotating discs.

[0019] FIG. 5A is a photo demonstrating iron dendrite formation on a rectangular cathode under the following parameters: current supply = 2.4 A, current density = 4000 A/m², temperature = 110 °C, powder fraction: 20 wt% of Fe₂O₃ powder in aqueous NaOH (50 wt%, 18 M).

[0020] FIG. 5B is an image showing the microstructure of the metallic iron from a selected dendritic iron structure (according to FIG. 5A).

[0021] FIG. 5C is an image showing the microstructure of the metallic iron collected from crushed dendritic iron structures (according to FIG. 5A).

[0022] FIGs. 6A-6C are photos showing the growth of the metallic iron disposed on a rotating disc cathode under static conditions (disc speed = 0 rpm). FIG. 6A shows a side view of the cathode; FIG. 6B shows a front view of the cathode; and FIG. 6C shows a front view of the cathode and the dendritic iron after rinsing with distilled water.

[0023] FIG. 7A is an image showing the microstructure of dendritic structures of the metallic iron deposited on the cathode as shown in FIGs. 6A-6C.

[0024] FIG. 7B is an image showing the morphology of crushed metallic iron taken from the dendritic structures of the metallic iron deposited on the cathode as shown in FIGs. 6A-6C.

[0025] FIG. 8 shows a schematic diagram of a continuous feedstock supply (continuous system) for converting a metal salt, such as an iron oxide, to metal (here, metallic iron) according to embodiments herein.

DETAILED DESCRIPTION

[0026] The present disclosure relates to systems and methods of continuous electrolytic production of metals using an electrochemical cell. Exemplary embodiments of the present disclosure provide for such continuous processes, wherein process steps may be repeated in a cyclical manner. In one embodiment, a mixture of metal salt and/or metal oxide in electrolyte is reduced to elemental metal. The elemental metal is formed as rough and brittle dendrites on

a surface or edge of the cathode. The dendritic metal is brittle, which advantageously is easily removed from the cathode with a harvester using mechanical force (e.g., a knife or a scraper) or using magnetic force (e.g., a magnet to attract those metals). Metals that form metal dendritic structures or dendrites under the appropriate conditions include non-limiting examples Fe, Cu, Ni, Zn, Co, Mn, Ag, Pt, Pd, Au, Ag, Mg, Li, and Pb. Example references are provided in Table I, the disclosures of which are incorporated by reference herein, which describe exemplary processes and conditions used for forming metal dendritic structures with various metals.

[0027]

Table I. Literature of Dendritic Metal Structures

Metal	Authors/Link
Manganese (Mn)	Padhy et al. (2016)/DOI: 10.1016/j.hydromet.2015.10.027
Iron (Fe)	EU Commission et al. (2016)/ https://data.europa.eu/doi/10.2777/084034
Cobalt (Co)	Zheng et al. (2012)/DOI: 10.1039/C2JM30300K Zhu et al. (2004)/DOI: 10.1016/j.jcrysgro.2003.08.037
Nickel (Ni)	Li et al. (2018)/DOI: 10.1002/adfm.201705937
Copper (Cu)	Shao and Zangari (2009)/DOI: 10.1021/jp8095456 Nishikawa et al. (2013)/ DOI: 10.1149/2.087304jes
Zinc (Zn)	Banik and Akolkar (2003)/ DOI: 10.1149/2.040311jes
Palladium (Pd)	Jung-Song et al. (2008)/DOI: 10.1021/cg8007574
Silver (Ag)	Maksimovic et al. (2007)/DOI: 10.1016/j.hydromet.2006.10.004
Platinum (Pt)	Sanles-Sobrido et al. (2009)/DOI: 10.1021/cm8033214
Gold (Au)	Hsuan-Lin et al. (2011)/DOI: 10.1039/C0CC03273E
Magnesium (Mg)	Davidson et al. (2019)/DOI: 10.1021/acsenergylett.8b02470
Lithium (Li)	Nishikawa et al. (2010)/DOI: 10.1149/1.3486468
Lead (Pb)	Sun et al. (2013)/DOI: 10.1038/srep03227

[0028] The term metal dendrites, as used within the scope of the present disclosure, may be understood to refer to a characteristic three dimensional tree-like agglomerate or structure, consisting of individual metallic crystals, the crystals having the dimensions in the range of about 10 nanometers to about 100 micrometers, growing on the electrode surface, e.g., cathode surface. Such structures typically have the total length on the order of at least about 0.1 mm up to about 10 cm or more. The cathode is configured such that it or a portion thereof may move in and out of the electrolyte along a closed loop path.

[0029] FIG. 1 shows a schematic diagram of continuous systems of electrolytic metal production according to exemplary embodiments herein and outlines an exemplary method 100 for the continuous production of metal. Although the exemplary method of FIG. 1 is described

in reference to the production of metallic iron, those skilled in the art will appreciate that the exemplary or similar methods can also be used to produce other metals from their salts and/or oxides. For purposes herein, a salt is defined as a chemical compound consisting of an ionic assembly of positively charged cations and negatively charged anions, which results in a compound with no net electric charge. Metallic oxides are made of metal and oxygen. For purposes herein, an oxide is defined as a chemical compound that contains at least one oxygen atom and one other element. Non-limiting examples of metal salts suitable in the present disclosure include FeCl_3 , FeSO_4 , $\text{Fe}_2(\text{SO}_4)_3$, ZnSO_4 , $\text{Zn}_2(\text{SO}_4)_3$, ZnCl_2 , CoCl_2 , CuSO_4 , or combinations thereof. Non-limiting examples of metal oxides suitable in the present disclosure include Fe_2O_3 , Fe_3O_4 , FeO , ZnO , CuO , MgO , Co_3O_4 , MnO , or combinations thereof.

[0030] A metal salt or metal oxide (as in FIG. 1, iron oxide) 110 is added to an electrolyte (as in FIG. 1, aqueous alkaline electrolyte) 120 in an electrochemical cell as in 150. Depending on the metal salt or oxide to be reduced, the choice of electrolyte may include acidic or alkaline group(s). In the exemplary embodiment illustrated as in FIG. 1, the metal salt or metal oxide (e.g., the iron oxide) and an electrolyte (e.g., aqueous alkaline electrolyte) form a mixture or suspension that is pre-mixed 130 and heated 140. The stirring at 130 is stopped and a current is applied to the electrochemical cell at 150 to facilitate the reduction of the metal salt or metal oxide, e.g., iron oxide, to its metal (e.g., metallic iron). More generally, an electrical charge may be supplied, which may result in a voltage or current generated in the electrochemical cell 150. The conversion of the metal salt or metal oxide (e.g., iron oxide) to metallic form results in metal (e.g., metallic iron) 160 deposited on the cathode in the form of dendritic structures 170. Heating 165 can include current being applied to facilitate the reduction of metal salt or metal oxide (e.g., iron oxide) to metal (e.g., metallic iron). The cathode or a portion thereof is rotatable, moveable, or otherwise repositionable, so that at least a portion of the cathode is removed from the electrolyte for rinsing and/or drying 175. The metal (e.g., metallic iron), having been rinsed with distilled water, is then mechanically or magnetically removed or harvested from the cathode (e.g., by a mechanical force such as scraping) 180 to form metal 185 (e.g., metallic iron powder). The metal (e.g., metallic iron powder) is then collected 190. Exemplary methods can be advantageously implemented as continuous processes, wherein some or all of the steps may be repeated in a cyclical manner.

[0031] In certain aspects, methods described herein, e.g., for reducing iron oxide, use low temperature (e.g., $90^\circ\text{C} \pm 5^\circ\text{C}$ to $110^\circ\text{C} \pm 5^\circ\text{C}$) electrolytic conversion to obtain a suitable form of (e.g., brittle, non-regular, and/or non-uniform) deposition of metallic iron that can be

harvested as taught in the present disclosure. Non-regular/non-uniform structure promotes deposits containing dendritic iron, especially on the side/edge/corner. This feature simplifies and facilitates harvesting the metallic deposits, thus allowing for ease of conversion and collection of metallic powder. Dendritic structures can be more easily harvested than deposits that are regular and/or uniform and/or compact in structure. The same applies to other metals capable of forming dendritic structures. Heating 140 the mixture and/or heating 165 for iron electrodeposition (wherein a heating unit may be used to heat the iron deposit and/or cathode containing the deposits thereon) preferably occurs at temperatures at $90^{\circ}\text{C} \pm 5^{\circ}\text{C}$ to $110^{\circ}\text{C} \pm 5^{\circ}\text{C}$. While dendrites were already observed forming at $80^{\circ}\text{C} \pm 5^{\circ}\text{C}$ to $90^{\circ}\text{C} \pm 5^{\circ}\text{C}$, higher temperatures may be preferred, such as below the boiling point of NaOH 50 wt% (at about 120°C , e.g., $100^{\circ}\text{C} \pm 5^{\circ}\text{C}$ to $110^{\circ}\text{C} \pm 5^{\circ}\text{C}$). Alternatively or additionally, the production and removal of metallic iron from the cathode may be performed in a continuous manner. Exemplary methods for producing other metals may include other mixture compositions, electrolytes, process steps, and temperature conditions.

[0032] Metallic iron produced using the methods described herein can achieve a purity of about 90% by weight or greater and comprises an average particle size between about 20 microns to 150 microns. The metallic iron produced can be a powder or “iron powder”. In some embodiments, the iron powder comprises greater than 90% by weight iron, where % by weight is based upon total weight of the powder. In other embodiments, the iron powder may comprise greater than 95% by weight iron, greater than 97% by weight iron, or greater than 99% by weight iron.

[0033] The average particle size of the resultant metallic iron may vary. The resultant particle size can depend on the harvesting process and/or the operating conditions that produce the dendrites prior to harvesting. For example, the iron powder may have an average particle size ranging from 20 microns to 150 microns, e.g., from 20 μm to 150 μm , from 25 μm to 125 μm , or from 30 μm to 100 μm . In terms of lower limits, the average particle size of the iron powder may be greater than 20 μm , e.g., greater than 25 μm , or greater than 30 μm . In terms of upper limits, the average particle size of the iron powder may be less than 150 μm , e.g., less than 125 μm , or less than 100 μm .

[0034] Electrochemical cells according to embodiments herein are depicted in FIGS. 2A-2B, FIG. 3, and FIG. 4. FIG. 2A illustrates a front view of electrochemical cell 200 having a cathode 210 configured to move along a closed loop path by rotating in and out of a mixture or suspension S. In this exemplary embodiment, cathode 210 is a plate-like disc that rotates in

a clockwise direction D, as shown. The direction of rotation is non-limiting, e.g., the cathode can move in reverse or a counter-clockwise direction as desired. Cathode 210 may be made of, but not limited to, stainless steel or other cathodic materials, such as graphite, nickel, and/or copper. The cathode 210 is rotatable so that the disc is partially submerged in a mixture or suspension S comprising an electrolyte (e.g., alkaline electrolyte) and a metal salt or metal oxide (e.g., iron oxide). Anode 220 is fully submerged in mixture or suspension S and is arranged to be adjacent to, and preferably parallel with, the portion of cathode 210 that is also submerged in mixture or suspension S. The anode may be made of, for example, nickel mesh/gauze plate, platinum, or other inert anodic materials. An electrical charge may be supplied between the anode 220 and the cathode 210, which may result in a voltage or current generated in the cell 200.

[0035] In an embodiment, current C is generated in cell 200 to reduce the metal salt or metal oxide in mixture or suspension S to form the metal. Cathode 210 is then rotated to provide an exposed portion 212 of cathode 210 to have the metal harvested, e.g., removed from the cathode. Exposed portion 212 of cathode 210, having been rotated out of the mixture or suspension S to another position, is no longer submerged in mixture or suspension S. Rinsing unit 270 uses a cleaning fluid, such as distilled water, to clean away excess mixture or suspension S on the exposed portion of cathode 210 leaving the deposited metal that can then be dried using dryer 275. Harvester 280 is disposed at the cathode 210 and is positioned for mechanical removal of metal from the cathode 210. One example of a suitable mechanical harvester includes a scraper. In other exemplary embodiments, the harvester can be positioned for magnetic removal of metallic iron from the cathode. Cartridge (or collector) 290 collects the harvested metal upon removal of the metal from cathode 210 of electrochemical cell 200. FIG. 2B illustrates a top view of electrochemical cell 200 as in FIG. 2A. Electrical motor M provides for moving (here, rotating) cathode 210 in direction D so that the cathode disc is moved into the mixture or suspension S, through the mixture or suspension S, and then out of the mixture or suspension S for harvesting converted metal, which can be performed in a cyclical manner.

[0036] FIG. 3 illustrates an alternative electrochemical cell 300, which is similar to cell 200 except that the cathode 310 of cell 300 is a connected looping structure, such as a belt, a strap, connected plates or a combination thereof. The connected looping structure of the cathode 310 can include discrete parts, e.g., one or more plates, so long as they are connected in such a way that the structure has a periphery capable of moving along a closed loop path for

continuous electrodeposition and harvesting of metal as taught in the present disclosure. Cathode 310 is moveable along a closed loop path P that here is defined by the belt. Motor M facilitates the cathode 310 circulating using a plurality of rollers, e.g., R1, R2, R3, R4, etc. As cathode 310 moves into the mixture or suspension S and subsequently through the mixture or suspension S adjacent to and, preferably, parallel to anode 320, a current is generated (and, optionally, heat) so that the metal salt or metal oxide in the mixture or suspension S is converted to the metal. More generally, an electrical charge may be supplied, which may result in a voltage or current generated in the cell 300. The anode 320 is preferably located underneath the cathode 310, but can also be located above the cathode 310. While FIG. 3 illustrates a horizontally oriented anode 320, it may have any suitable orientation, such as a vertical or tilted orientation. Moving further along path P, the portion of cathode 310 that is out of the mixture or suspension S is then rinsed using cleaning fluid, such as water or distilled water, provided by rinsing unit 370 (optionally dried using dryer not shown) and then mechanically or magnetically removing the metal with harvester 380. The harvester 380 may be positioned in any suitable location, such as above or below the cathode 310, or both.

[0037] In some embodiments, a system or method of the present disclosure may utilize a plurality of cathodes, as in FIG. 4. FIG. 4 illustrates yet another exemplary electrochemical cell 400 configuration. Cell 400 includes cathode assembly 410 comprising a plurality of cathodes, illustrated here as rotating discs D1 – D5. The plurality of cathodes are configured to move along a plurality of closed loop paths by rotating in and out of a mixture or suspension S (not shown) and may have any construction described in connection with other embodiments of the present disclosure. Although five cathodes are illustrated, any suitable number of cathodes is within the scope of the present disclosure. In the embodiment depicted in FIG. 4, discs D1-D5 rotate about axis A in a clockwise direction in the mixture or suspension (not shown) for removal of the metal from the cathodes by harvester assembly 480. The direction of rotation is non-limiting, e.g., the cathode can move in reverse or a counter-clockwise direction as desired. Anode assembly 420 includes one or more anode portions (not shown) submerged in the mixture or suspension S. One or more anode portions are arranged to be adjacent to, and preferably parallel with, the appropriate portions of cathode assembly 410 (such as portions of the cathodes D1-D5) that are also submerged in the mixture or suspension S.

[0038] An electrical charge is supplied, which may result in a voltage or current generated in cell 400 to reduce a metal salt or metal oxide in the mixture or suspension S to

form its metal. Cathode assembly 410 is rotated to provide exposed portions 412 of cathode discs D1-D5 to have the metal harvested, e.g., removed from the cathode discs, preferably in a continuous, cyclical process. Harvester assembly 480 is disposed at the cathode assembly 410 and is positioned for removal of the metal from the cathode assembly 410. The harvester assembly 480 includes a plurality of harvester units 481-485. Harvester units 481-485 are preferably positioned for harvesting the metal from the exposed portions 412 of cathode discs D1-D5. The harvester units 481-485 can include mechanical and/or magnetic metal removal devices. Cartridge (or collector) 490 collects the harvested metal upon removal of the metallic iron from cathode 410 of electrochemical cell 400.

[0039] FIGs. 5A-5C, 6A-6C, and 7A-B show the microstructure and the morphology of the metallic iron (iron powder) that is collected from the dendritic structures. In certain embodiments, the microstructure and the particle size of the final metallic iron depend on the electrochemical and process conditions. In some embodiments, the particle size of the metallic iron is easily varied or controlled by the duration of operation of the electrochemical cell or the rotation speed of the cathode.

[0040] FIG. 5A is a photo demonstrating iron dendrite formation on a rectangular cathode. The example as in FIG. 5A was produced using the following conditions: current supply = 2.4 A, current density = 4000 A/m^2 , temperature = 110°C , powder fraction: 20% wt of Fe_2O_3 powder in aqueous NaOH (50 wt%, 18 M). FIG. 5B shows an image of the microstructure of the metallic iron from a selected dendritic iron structure (as in FIG. 5A). FIG. 5C shows an image of the microstructure of the metallic iron collected from crushed dendritic iron structures (according to FIG. 5A) as evidence of electrolytic iron powder as a final product.

[0041] FIGs. 6A-6C show growth of the metallic iron disposed on a rotating disc cathode under static conditions (disc speed = 0 rpm). FIG. 6A shows a side view of the cathode; FIG. 6B shows a front view of the cathode; and FIG. 6C shows a front view of the cathode and the dendritic iron after rinsing with water.

[0042] FIG. 7A is an image showing the microstructure of dendritic structures of the metallic iron deposited on the cathode as shown in FIGs. 6A-6C. FIG. 7B is an image showing the morphology of crushed metallic iron taken from the dendritic structures of the metallic iron deposited on the cathode as shown in FIGs. 6A-6C.

[0043] The present disclosure provides for low electrical energy consumption, less than about 6 kWh/kg iron. Additionally, certain systems and methods herein may use renewable energy to power up the electrolytic conversion process. The electrolytic reduction process may

be conducted using electrical energy directly converted from renewable energy, thus preventing CO₂ emission.

[0044] Although certain methods and systems are described herein with specific reference to iron oxides and metallic iron, it will be appreciated that such systems and methods may be used for the production of other metals including, but not limited to, Cu, Ni, Zn, Co, Mn, Ag, Pt, Pd, Au, Ag, Mg, Li, and/or Pb .

[0045] The electrochemical cell of the present disclosure may include an electrolyte with a mixture or suspension of metal salt or metal oxide powder, an anode, and one or more rotating disc or belt cathodes controlled by an electric motor. In some embodiments, the system comprises a plurality of moveable cathodes to improve the system's productivity. The cathode and anode are for example connected to a power supply with a constant current. The electrochemical process is for example conducted at an elevated temperature of about 110°C ± 5 °C. The electrochemical cell may be further equipped with a rinsing unit that cleans the metal disposed onto the cathode with a cleaning fluid, such as distilled water. Without wishing to limit the present disclosure to any theory or mechanism, the rinsing unit is used to remove electrolyte and metal salt or metal oxide that may still be present in the metal. As non-limiting examples, the metal may be rinsed before being mechanically or magnetically removed (e.g., scraped off) the cathode, after being harvested from the cathode, or after the metal has been collected in a cartridge. The electrochemical cell may also further comprise a cartridge to collect the metal after removing, e.g., scraping from the cathode.

[0046] The exemplary electrolyte mixture comprises aqueous sodium hydroxide (NaOH) 50 wt%, about 18 M or pH of about 15.3 (at 25°C) or at least about 5 M, and micron-sized iron oxide powder with a mass fraction between about 5% to about 33% over the total mixture. In some embodiments, the alkaline electrolyte comprises aqueous potassium hydroxide. The powders are fed into the solution and are pre-mixed for about 10-20 minutes to ensure the homogeneity of the suspension. Alternative and/or additional additive to the alkaline electrolyte include non-limiting examples ammonium and/or potassium sulphate, which can be provided in electrolyte to increase the conductivity and reduce adhesion of the converted metallic iron as fine powder.

[0047] The electrochemical process may be conducted without any agitation/stirring. As a result, metallic iron with rough dendritic structures is deposited on the cathode, particularly at sides, corners, and edges, as shown in FIG. 5A and FIGs. 6A-6C. These dendrites have a rough, solid, and brittle nature. The growth of the dendrites is a relatively slow, but

stable process depending on the duration of the process. The metallic iron produced by this method has a high purity (90% and greater), and the electrolytic conversion has a high-faradaic efficiency (greater than 85% or greater than 90%). Without wishing to limit the present disclosure to any theory or mechanism, the combination of the anode and cathode arrangement, along with the current density settings of the electrochemical cell, specifically lead to formation of dendritic, brittle, iron deposition onto the cathode of the cell.

[0048] The cathode moveable along a closed loop path according to the present disclosure allows for direct and continuous harvesting of metal powder in a cyclical manner, whereby some or all steps of the exemplary processes can be repeated. Referring again to the electrochemical cell 200 of FIGs. 2A-2B, where a harvester is coupled to the rotating disc cathode to facilitate the removal of the deposited metal from the cathode, which is collected into a cartridge. The harvester may be a knife or a scraper, and the harvester collects metal from the cathode. The harvester may include a mechanical and/or a magnetic component to facilitate collecting. In some embodiments, the harvester comprises a knife, a scraper, a magnet, or combinations thereof. An exemplary rotating disc cathode is for example partially submerged in the electrolyte and the rest of the rotating disc cathode is under contact with the knife/harvester. The cathode may be rotated at a low speed or the deposited surface and the harvesting surface may be alternated to allow for the continuous production and collection of the metal. The production cycles may be continuous or performed as multiple cycles.

[0049] Harvesters can be positioned alongside or perpendicular (or any angle there between) to any of the moveable cathodes according to embodiments herein. Mechanical harvesters work by mechanically contacting the deposit in order to remove the metal. For example, the deposited iron on the cathode can be removed by using a (mechanical) scraper. Alternatively, harvesters as in any of the embodiments herein can be magnetic for removal of the metal from the cathode. A magnetic scraper works by utilizing a magnetic field, for example, using a magnet, to attract the metal that has been deposited on the cathode. The magnetic field can be alternated (on/off system) to attract and remove the metal deposit from the magnet and place it at a desired location. In another example, the deposited iron on the cathode can be harvested by applying a magnetic field to capture the iron powder.

[0050] A system as disclosed herein may include continuous feeding of the electrolyte and discharge system of the electrolyte. The continuous system 1000 is illustrated in FIG. 8. The electrochemical cell 500 is shown schematically but can be any as described herein, e.g., cell 200, cell 300, or cell 400 having cathodes 210, 310, or 410 respectively. The system 1000

continuously converts metal salt or metal oxide (e.g., iron oxide) to metal (e.g., metallic iron) by including an inlet I for receiving a metal salt or metal oxide, an electrolyte (e.g., alkaline electrolyte), or combinations thereof to form and maintain a mixture or suspension at a desired concentration. The inlet feeds the mixture or suspension to the electrochemical cell 500 and may be connected to pump P for providing the mixture or suspension from another container 550, which is supplied with a metal salt or metal oxide, an electrolyte, or combinations thereof as needed to maintain desired concentration. Pump P may include a stirrer to mix the mixture or suspension prior to supplying to cell 500 via inlet I.

[0051] Electrochemical cell 500 includes the mixture or suspension S, an anode (included in cell 500) submerged in the mixture or suspension S, and the cathode partially submerged in the mixture or suspension and moveable along a closed loop path. A current C is applied to the electrochemical cell to reduce the metal salt or metal oxide (of the mixture or suspension S) to metal at and disposed onto the cathode in the manner as previously described for any of cell 200, cell 300, or cell 400. System 100 optionally includes a rinsing unit to spray cleaning fluid, such as distilled water, onto the metal disposed onto the cathode to remove at least some residual suspension from the metal as previously described as is optionally a drying unit to remove at least some moisture content from the metal is included in system 1000. Drying of metal can be performed, preferably before, but also after, harvesting it from the cathode of cell 500. In other words, system 1000 comprises a drying system (within cell 500) to remove moisture from the metal prior to the metal, e.g., dendritic structures, being removed. Additionally or alternatively, a drying system (within cell 500) can remove moisture post-harvesting, e.g. dried in the cartridge after the metal is harvested and removed from cell 500. The drying system may comprise hot air spray, e.g., using a heater, or other drying means.

[0052] In electrochemical cell 500, similarly as for cell 200, cell 300, or cell 400, a harvester is disposed at an exposed portion of the cathode outside of the mixture suspension S and is configured to remove the metal from the exposed portion of the cathode and to deposit it in cartridge 590 for collection. This may be performed mechanically or magnetically. System 1000 also includes an outlet O for discharging the mixture or suspension S from the system back to container 550 or away from system 1000. Outlet O helps remove the unused mixture or suspension, which can be electrolyte depleted from metal salt or metal oxide. To ensure that mixture or suspension is at a desired temperature, for example of about 105°C to 115°C for reduction of iron oxide to metallic iron, electrochemical cell 500 includes heating as previously described and/or container 550 is heated by heater H.

[0053] Clause 1. An electrochemical cell for converting metal salt or metal oxide to metal, comprising: a) a mixture comprising an electrolyte and metal salt or metal oxide; b) an anode submerged in the mixture; c) a cathode partially submerged in the mixture and moveable along a closed loop path; and d) a harvester disposed at an exposed portion of the cathode outside of the mixture; wherein an electrical charge supplied to the electrochemical cell reduces the metal salt or metal oxide to metal at and disposed onto the cathode, and wherein the harvester removes the metal from the exposed portion of the cathode.

[0054] Clause 2. The electrochemical cell of clause 1, wherein the metal salt or metal oxide is selected from one or more of FeCl_3 , FeSO_4 , $\text{Fe}_2(\text{SO}_4)_3$, ZnSO_4 , $\text{Zn}_2(\text{SO}_4)_3$, ZnCl_2 , CoCl_2 , CuSO_4 , Fe_2O_3 , Fe_3O_4 , FeO , ZnO , CuO , MgO , Co_3O_4 , and MnO .

[0055] Clause 3. The electrochemical cell of either clause 1 or 2, wherein the metal is selected from one or more of Fe, Cu, Ni, Zn, Co, Mn, Ag, Pt, Pd, Au, Ag, Mg, Li, and Pb.

[0056] Clause 4. The electrochemical cell of any of clauses 1-3, wherein the metal forms a plurality of dendritic structures disposed onto the cathode.

[0057] Clause 5. The electrochemical cell of any of clauses 1-4, wherein the cathode comprises a disc.

[0058] Clause 6. The electrochemical cell of any of clauses 1-5, wherein the cathode comprises a connected looping structure.

[0059] Clause 7. The electrochemical cell of any of clauses 1-6, wherein the harvester is a mechanical harvester.

[0060] Clause 8. The electrochemical cell of any of clauses 1-7, wherein the harvester is a magnetic harvester.

[0061] Clause 9. The electrochemical cell of any of clauses 1-8, further comprising: i) a rinsing unit configured to spray cleaning fluid onto the metal; and ii) a cartridge to retain the metal removed from the cathode by the harvester.

[0062] Clause 10. The electrochemical cell of any of clauses 1-9, wherein: the metal salt or metal oxide is iron oxide; the electrolyte is alkaline electrolyte; and the metal is iron.

[0063] Clause 11. A method for converting metal salt or metal oxide into metal, comprising: a) providing a metal salt or oxide in an electrolyte in an electrochemical cell to form a mixture, wherein the electrochemical cell includes an anode submerged in the mixture and a cathode partially submerged in the mixture and moveable along a closed loop path; b) supplying an electrical charge in the electrochemical cell, and reducing the metal salt or metal oxide in the mixture to form the metal at and disposed onto the cathode; c) moving the cathode

having the metal disposed thereon from the mixture to provide an exposed portion of the cathode outside of the mixture; and d) harvesting the metal from the exposed portion of the cathode.

[0064] Clause 12. The method of clause 11, further comprising: e) rinsing the metal; and f) collecting the metal.

[0065] Clause 13. The method of either clause 11 or 12, wherein the method is a continuous process comprising repeating the steps a) to d) or a) to f).

[0066] Clause 14. The method of any of clauses 11-13, wherein the metal salt or metal oxide is selected from one or more of FeCl_3 , FeSO_4 , $\text{Fe}_2(\text{SO}_4)_3$, ZnSO_4 , $\text{Zn}_2(\text{SO}_4)_3$, ZnCl_2 , CoCl_2 , CuSO_4 , Fe_2O_3 , Fe_3O_4 , FeO , ZnO , CuO , MgO , Co_3O_4 , and MnO .

[0067] Clause 15. The method of any of clauses 11-14, wherein the metal is selected from one or more of Fe, Cu, Ni, Zn, Co, Mn, Ag, Pt, Pd, Au, Ag, Mg, Li, and Pb.

[0068] Clause 16. The method of any of clauses 11-15, wherein the metal forms a plurality of dendritic structures disposed onto the cathode.

[0069] Clause 17. The electrochemical cell of any of clauses 1-9 or the method of any of claims 11-15, wherein the cathode is a cathode assembly comprising a plurality of moveable cathodes.

[0070] Clause 18. The electrochemical cell of any of clauses 1-9 or the method of any of claims 11-15, wherein the cathode is a cathode assembly comprising a plurality of moveable cathodes and the harvester is a harvester assembly comprising a plurality of harvester units positioned for harvesting metal from the plurality of movable cathodes.

[0071] Clause 19. The method of any of clauses 11-18, wherein: the metal salt or metal oxide is iron oxide; the electrolyte is alkaline electrolyte; and the metal is iron.

[0072] Clause 20. The method of any of clauses 11-19, further comprising heating the mixture and generating current in the electrochemical cell concurrently with heating the mixture.

[0073] Clause 21. The method of clause 20, wherein the mixture is heated to a temperature between about 80°C to about 115°C .

[0074] Clause 22. The method of any of clauses 11-21, further comprising stirring the mixture for a period of time to form a stirred suspension.

[0075] Clause 23. The method of clause 22, wherein the mixture is stirred for a period of time ranging from about 10 minutes to 20 minutes.

[0076] Clause 24. The electrochemical cell of clause 10 or the method of claim 19, wherein the mixture comprises aqueous sodium hydroxide at a concentration of at least about 5 M; or wherein the metallic iron comprises a purity greater than about 90%; or wherein a mass fraction of iron oxide in the suspension is between about 5% to about 33%.

[0077] Clause 25. The electrochemical cell of clause 10 or the method of claim 19, the electrochemical cell comprising a faradaic efficiency greater than about 85%.

[0078] Clause 26. The electrochemical cell of clause 10 or the method of claim 19, wherein the electrochemical cell has an electrical energy consumption of less than 6 kWh/kg iron.

[0079] Clause 27. A continuous system for converting metal salt or metal oxide into metal, the system comprising: an inlet to receive a mixture comprising a metal salt or metal oxide, an electrolyte, or a combination thereof, where the inlet feeds the mixture to an electrochemical cell; the electrochemical cell including the mixture, an anode submerged in the mixture, and a cathode partially submerged in the mixture and moveable along a closed loop path, wherein an electrical charge supplied to the electrochemical cell reduces the metal salt or metal oxide to the metal at and disposed onto the cathode; optionally a rinsing unit to spray cleaning fluid onto the metal disposed onto the cathode; optionally a drying unit to remove moisture from the metal; a harvester disposed at an exposed portion of the cathode outside of the mixture to remove the metal from the exposed portion of the cathode; and an outlet to discharge suspension or mixture from the system.

[0080] Clause 28. The system of clause 27, wherein the metal salt or metal oxide is selected from one or more of FeCl_3 , FeSO_4 , $\text{Fe}_2(\text{SO}_4)_3$, ZnSO_4 , $\text{Zn}_2(\text{SO}_4)_3$, ZnCl_2 , CoCl_2 , CuSO_4 , Fe_2O_3 , Fe_3O_4 , FeO , ZnO , CuO , MgO , Co_3O_4 , and MnO .

[0081] Clause 29. The system of either clause 27 or claim 28, wherein the metal is selected from one or more of Fe, Cu, Ni, Zn, Co, Mn, Ag, Pt, Pd, Au, Ag, Mg, Li, and Pb.

[0082] Clause 30. The system of any of clauses 27-29, wherein the metal forms a plurality of dendritic structures disposed onto the cathode.

[0083] Clause 31. The system of any of clauses 27-30, wherein the cathode comprises a disc.

[0084] Clause 32. The system of any of clauses 27-31, wherein the cathode comprises a connected looping structure.

[0085] Clause 33. The system of any of clauses 27-32, wherein the harvester comprises a mechanical harvester, a magnetic harvester, or combinations thereof.

[0086] Clause 34. The system of any of clauses 27-33, wherein: the metal salt or metal oxide is iron oxide; the electrolyte is alkaline electrolyte; and the metal is iron.

[0087] Clause 35. The system of clause 34, further comprising maintaining the mixture at a concentration of at least about 5M.

* * *

[0088] The present invention is not to be limited in scope by the specific embodiments described herein. Indeed various modifications of the invention in addition to those described herein will be apparent to those skilled in the art from the foregoing description and figures. Such modifications are intended to fall within the scope of the appended claims.

[0089] It is further to be understood that all values are approximate and are provided for description. All references cited and discussed in this specification are incorporated herein by reference in their entirety and to the same extent as if each reference was individually incorporated by reference.

CLAIMS

What is claimed is:

1. An electrochemical cell for converting metal salt or metal oxide to metal, comprising:
 - a) a mixture comprising an electrolyte and metal salt or metal oxide;
 - b) an anode submerged in the mixture;
 - c) a cathode partially submerged in the mixture and moveable along a closed loop path; and
 - d) a harvester disposed at an exposed portion of the cathode outside of the mixture;wherein an electrical charge supplied to the electrochemical cell reduces the metal salt or metal oxide to metal at and disposed onto the cathode, and wherein the harvester removes the metal from the exposed portion of the cathode.
2. The electrochemical cell of claim 1, wherein the metal salt or metal oxide is selected from one or more of FeCl_3 , FeSO_4 , $\text{Fe}_2(\text{SO}_4)_3$, ZnSO_4 , $\text{Zn}_2(\text{SO}_4)_3$, ZnCl_2 , CoCl_2 , CuSO_4 , Fe_2O_3 , Fe_3O_4 , FeO , ZnO , CuO , MgO , Co_3O_4 , and MnO .
3. The electrochemical cell of either claim 1 or 2, wherein the metal is selected from one or more of Fe, Cu, Ni, Zn, Co, Mn, Ag, Pt, Pd, Au, Ag, Mg, Li, and Pb.
4. The electrochemical cell of any of claims 1-3, wherein the metal forms a plurality of dendritic structures disposed onto the cathode.
5. The electrochemical cell of any of claims 1-4, wherein the cathode comprises a disc.
6. The electrochemical cell of any of claims 1-5, wherein the cathode comprises a connected looping structure.
7. The electrochemical cell of any of claims 1-6, wherein the harvester is a mechanical harvester.

8. The electrochemical cell of any of claims 1-7, wherein the harvester is a magnetic harvester.
9. The electrochemical cell of any of claims 1-8, further comprising:
 - i) a rinsing unit configured to spray cleaning fluid onto the metal; and
 - ii) a cartridge to retain the metal removed from the cathode by the harvester.
10. The electrochemical cell of any of claims 1-9, wherein: the metal salt or metal oxide is iron oxide; the electrolyte is alkaline electrolyte; and the metal is iron.
11. A method for converting metal salt or metal oxide into metal, comprising:
 - a) providing a metal salt or oxide in an electrolyte in an electrochemical cell to form a mixture, wherein the electrochemical cell includes an anode submerged in the mixture and a cathode partially submerged in the mixture and moveable along a closed loop path;
 - b) supplying an electrical charge in the electrochemical cell, and reducing the metal salt or metal oxide in the mixture to form the metal at and disposed onto the cathode;
 - c) moving the cathode having the metal disposed thereon from the mixture to provide an exposed portion of the cathode outside of the mixture; and
 - d) harvesting the metal from the exposed portion of the cathode.
12. The method of claim 11, further comprising:
 - e) rinsing the metal; and
 - f) collecting the metal.
13. The method of either claim 11 or 12, wherein the method is a continuous process comprising repeating the steps a) to d) or a) to f).
14. The method of any of claims 11-13, wherein the metal salt or metal oxide is selected from one or more of FeCl_3 , FeSO_4 , $\text{Fe}_2(\text{SO}_4)_3$, ZnSO_4 , $\text{Zn}_2(\text{SO}_4)_3$, ZnCl_2 , CoCl_2 , CuSO_4 , Fe_2O_3 , Fe_3O_4 , FeO , ZnO , CuO , MgO , Co_3O_4 , and MnO .
15. The method of any of claims 11-14, wherein the metal is selected from one or more of Fe, Cu, Ni, Zn, Co, Mn, Ag, Pt, Pd, Au, Ag, Mg, Li, and Pb.

16. The method of any of claims 11-15, wherein the metal forms a plurality of dendritic structures disposed onto the cathode.
17. The electrochemical cell of any of claims 1-9 or the method of any of claims 11-15, wherein the cathode is a cathode assembly comprising a plurality of moveable cathodes.
18. The electrochemical cell of any of claims 1-9 or the method of any of claims 11-15, wherein the cathode is a cathode assembly comprising a plurality of moveable cathodes and the harvester is a harvester assembly comprising a plurality of harvester units positioned for harvesting metal from the plurality of movable cathodes.
19. The method of any of claims 11-18, wherein: the metal salt or metal oxide is iron oxide; the electrolyte is alkaline electrolyte; and the metal is iron.
20. The method of any of claims 11-19, further comprising heating the mixture and generating current in the electrochemical cell concurrently with heating the mixture.
21. The method of claim 20, wherein the mixture is heated to a temperature between about 80°C to about 115°C.
22. The method of any of claims 11-21, further comprising stirring the mixture for a period of time to form a stirred suspension.
23. The method of claim 22, wherein the mixture is stirred for a period of time ranging from about 10 minutes to 20 minutes.
24. The electrochemical cell of claim 10 or the method of claim 19, wherein the mixture comprises aqueous sodium hydroxide at a concentration of at least about 5 M; or wherein the metallic iron comprises a purity greater than about 90%; or wherein a mass fraction of iron oxide in the suspension is between about 5% to about 33%.

25. The electrochemical cell of claim 10 or the method of claim 19, the electrochemical cell comprising a faradaic efficiency greater than about 85%.
26. The electrochemical cell of claim 10 or the method of claim 19, wherein the electrochemical cell has an electrical energy consumption of less than 6 kWh/kg iron.
27. A continuous system for converting metal salt or metal oxide into metal, the system comprising:
- an inlet to receive a mixture comprising a metal salt or metal oxide, an electrolyte, or a combination thereof, where the inlet feeds the mixture to an electrochemical cell;
 - the electrochemical cell including the mixture, an anode submerged in the mixture, and a cathode partially submerged in the mixture and moveable along a closed loop path, wherein an electrical charge supplied to the electrochemical cell reduces the metal salt or metal oxide to the metal at and disposed onto the cathode;
 - optionally a rinsing unit to spray cleaning fluid onto the metal disposed onto the cathode;
 - optionally a drying unit to remove moisture from the metal;
 - a harvester disposed at an exposed portion of the cathode outside of the mixture to remove the metal from the exposed portion of the cathode; and
 - an outlet to discharge suspension or mixture from the system.
28. The system of claim 27, wherein the metal salt or metal oxide is selected from one or more of FeCl_3 , FeSO_4 , $\text{Fe}_2(\text{SO}_4)_3$, ZnSO_4 , $\text{Zn}_2(\text{SO}_4)_3$, ZnCl_2 , CoCl_2 , CuSO_4 , Fe_2O_3 , Fe_3O_4 , FeO , ZnO , CuO , MgO , Co_3O_4 , and MnO .
29. The system of either claim 27 or claim 28, wherein the metal is selected from one or more of Fe, Cu, Ni, Zn, Co, Mn, Ag, Pt, Pd, Au, Ag, Mg, Li, and Pb.
30. The system of any of claims 27-29, wherein the metal forms a plurality of dendritic structures disposed onto the cathode.
31. The system of any of claims 27-30, wherein the cathode comprises a disc.

32. The system of any of claims 27-31, wherein the cathode comprises a connected looping structure.
33. The system of any of claims 27-32, wherein the harvester comprises a mechanical harvester, a magnetic harvester, or combinations thereof.
34. The system of any of claims 27-33, wherein: the metal salt or metal oxide is iron oxide; the electrolyte is alkaline electrolyte; and the metal is iron.
35. The system of claim 34, further comprising maintaining the mixture at a concentration of at least about 5M.

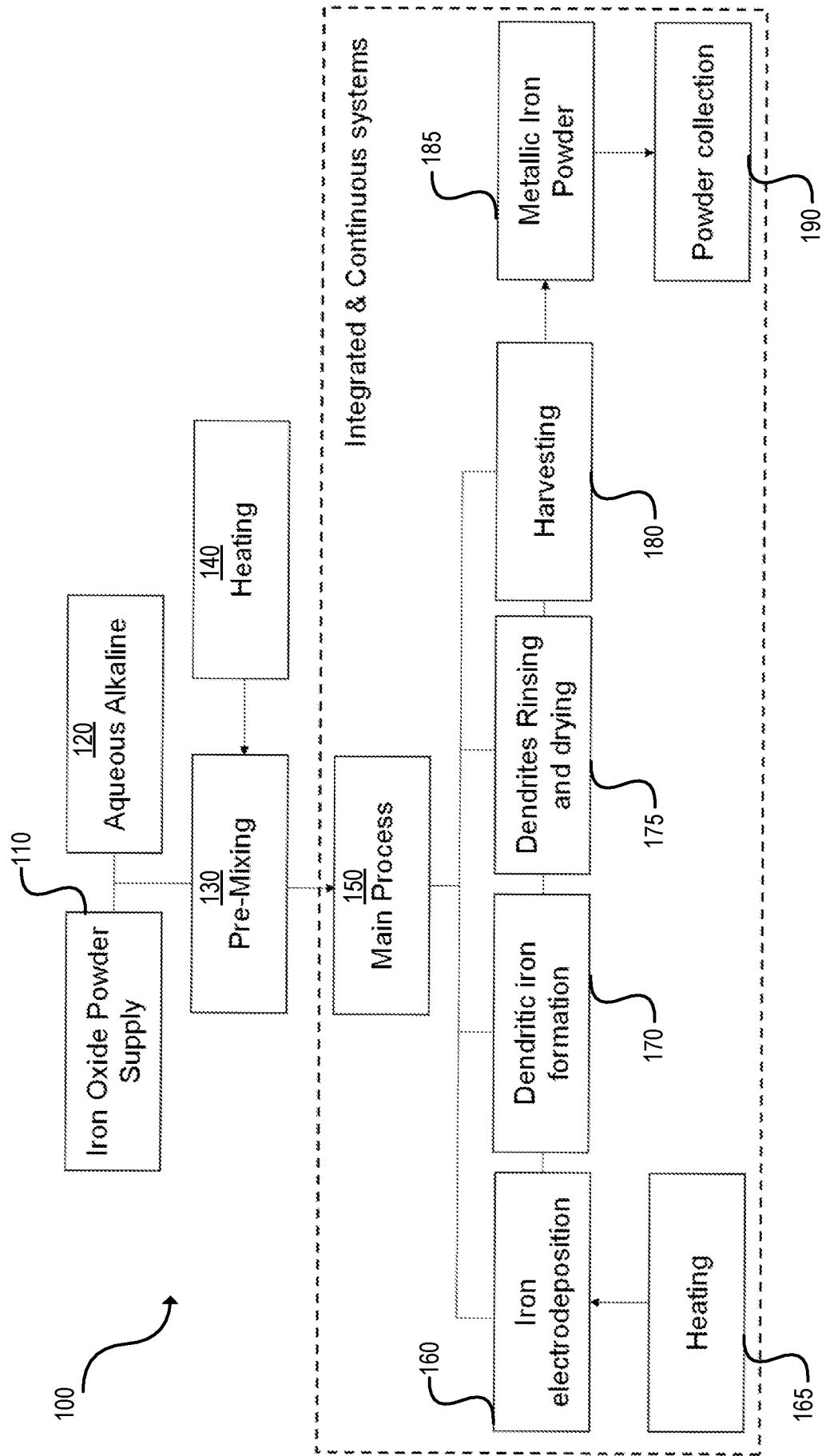


FIG. 1

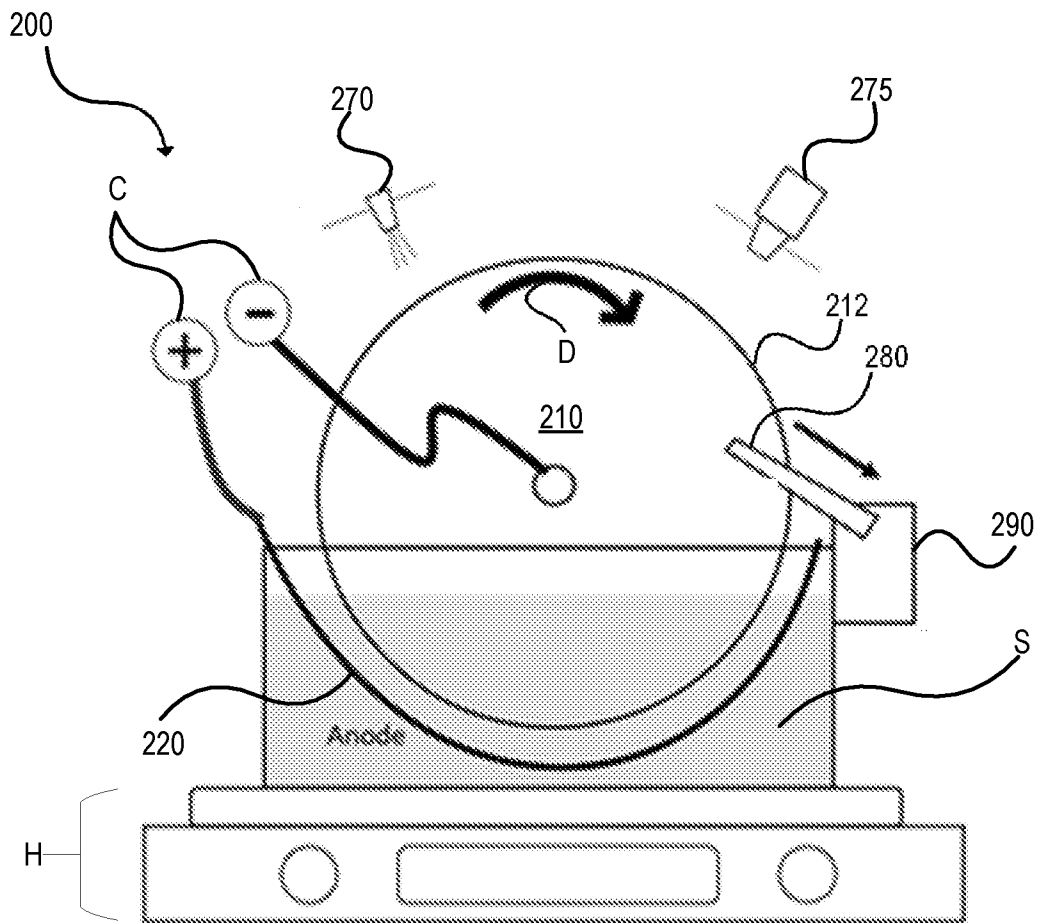


FIG. 2A

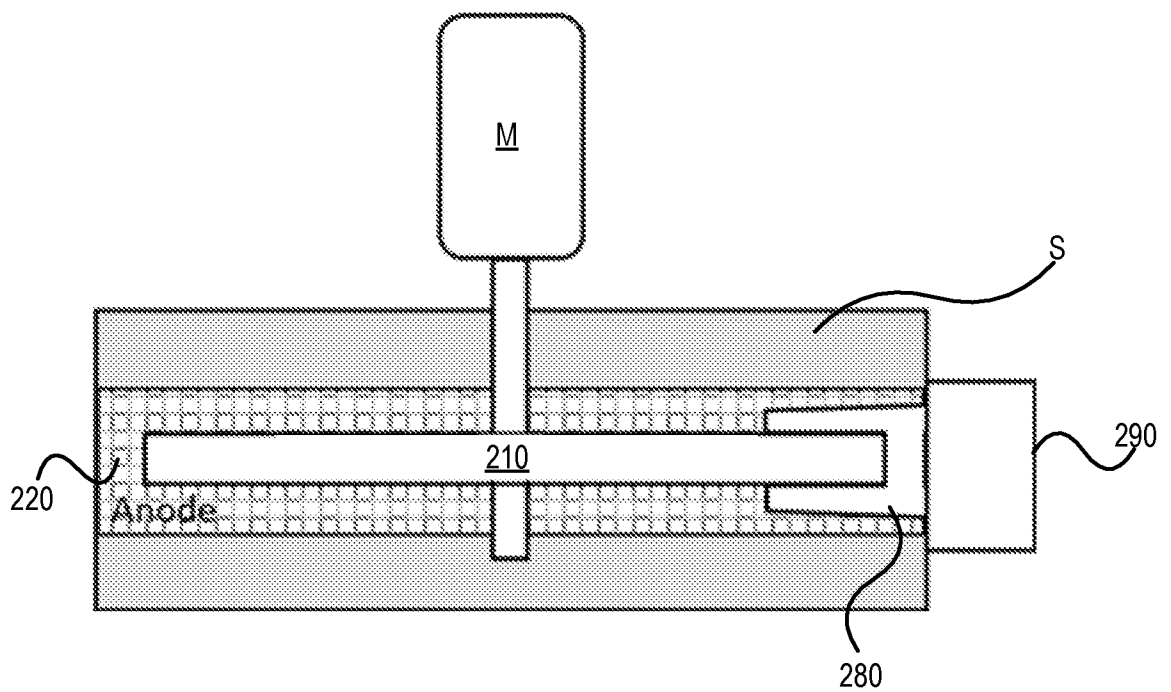


FIG. 2B

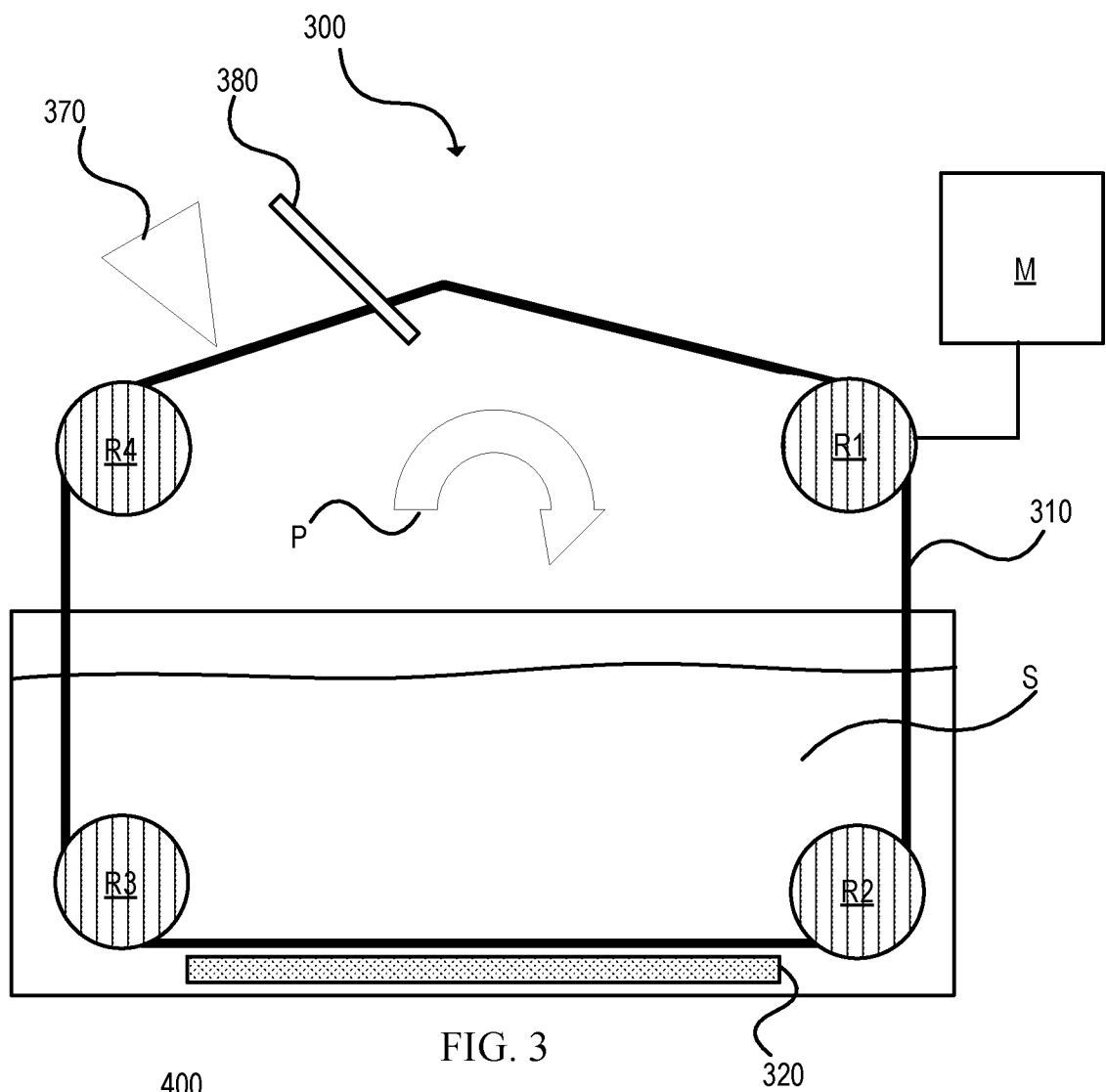


FIG. 3

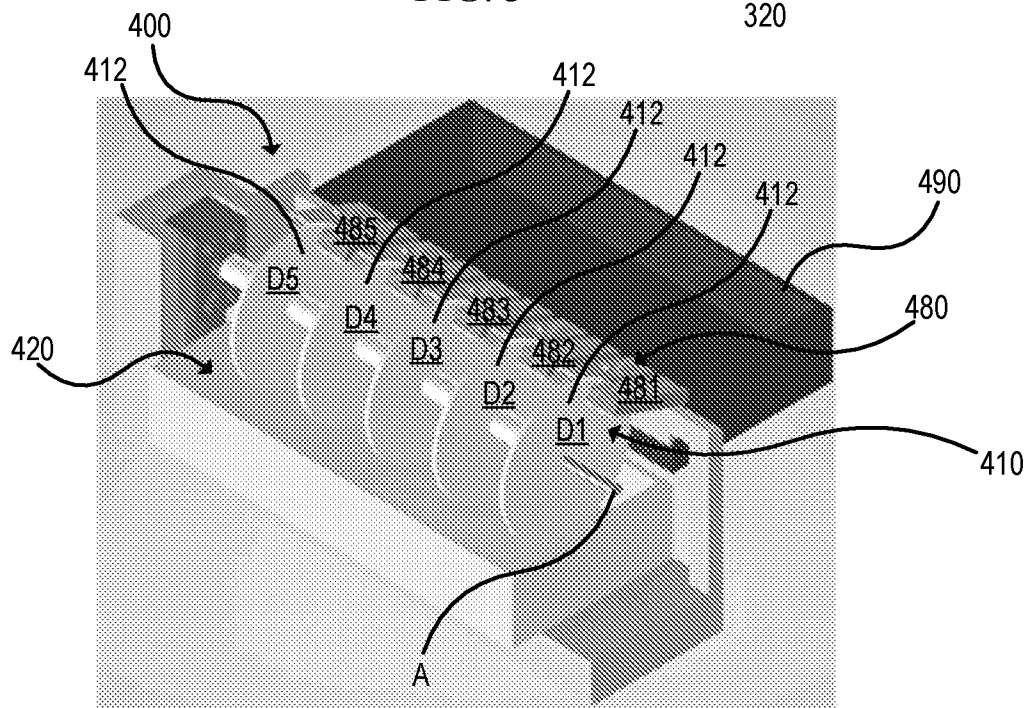


FIG. 4

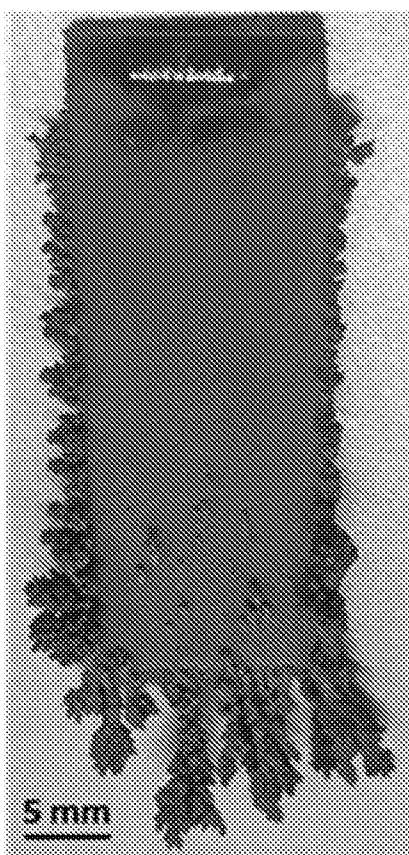


FIG. 5A

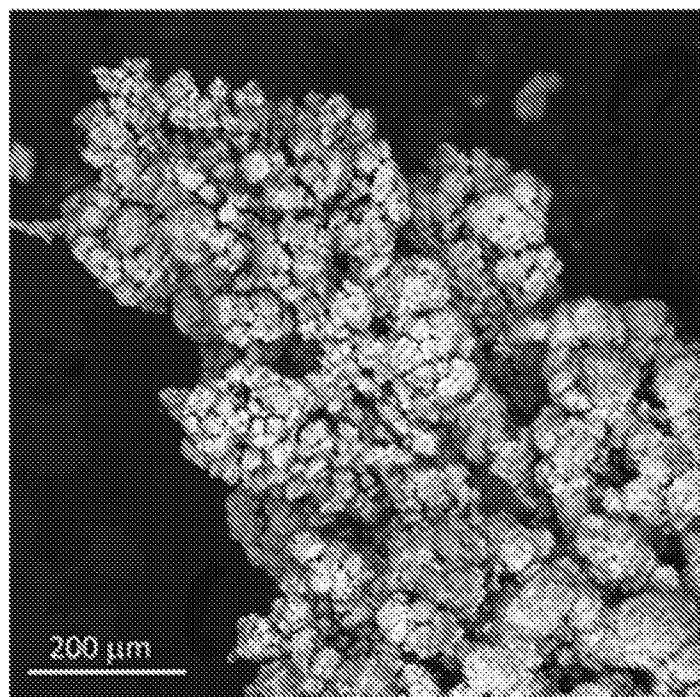


FIG. 5B

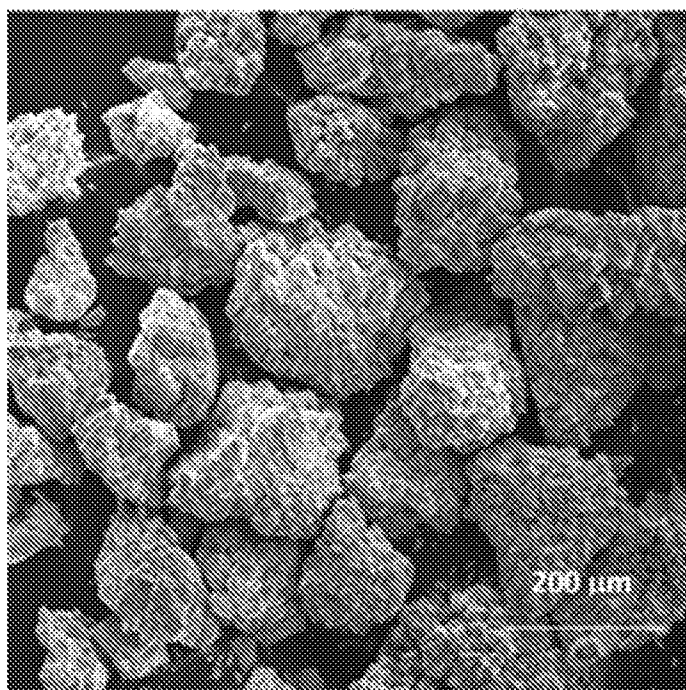


FIG. 5C

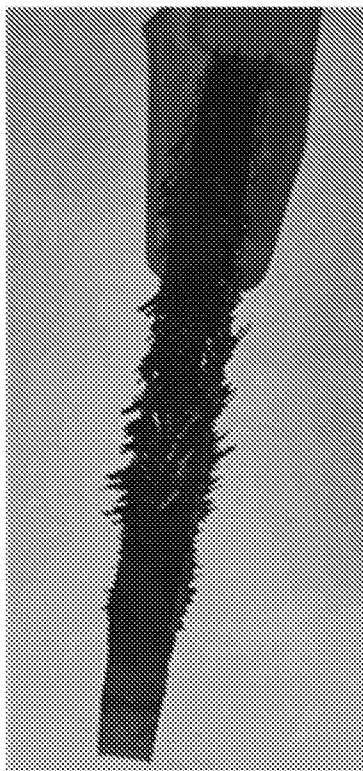


FIG. 6A



FIG. 6B



FIG. 6C

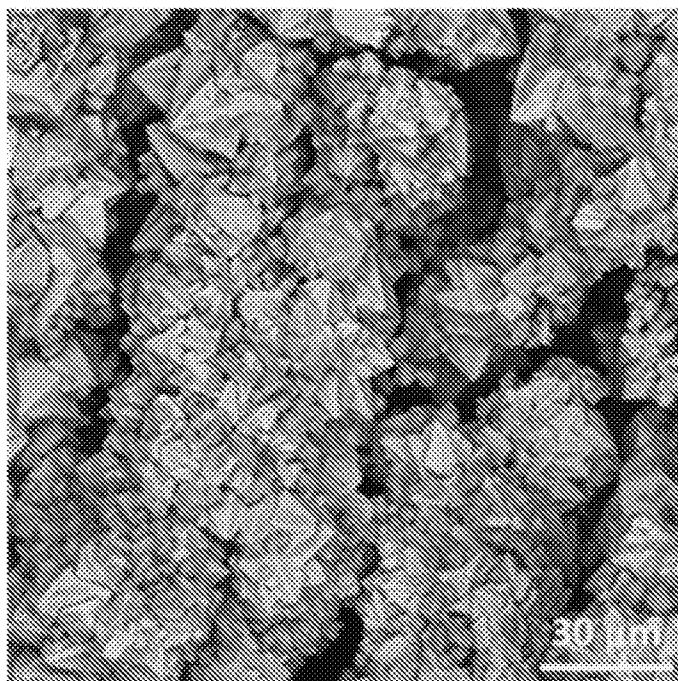


FIG. 7A

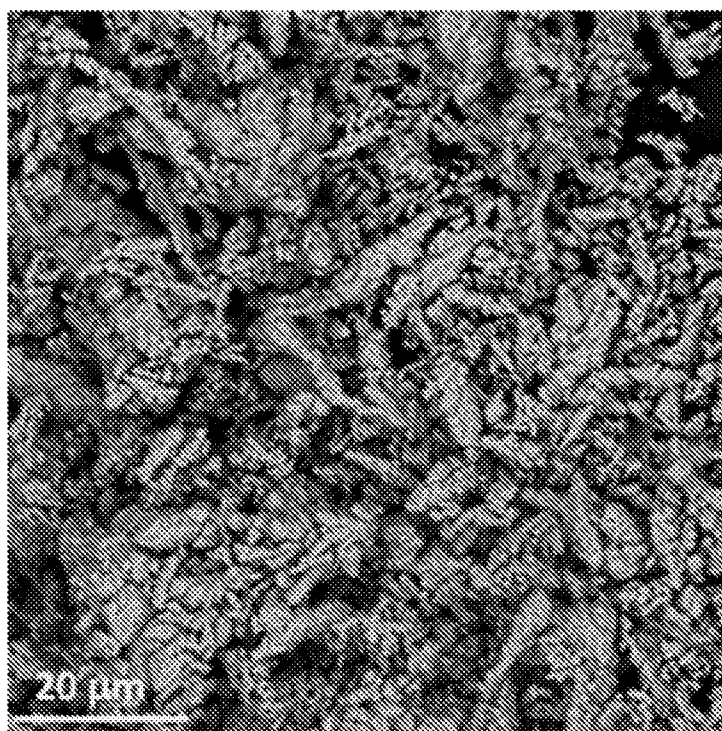


FIG. 7B

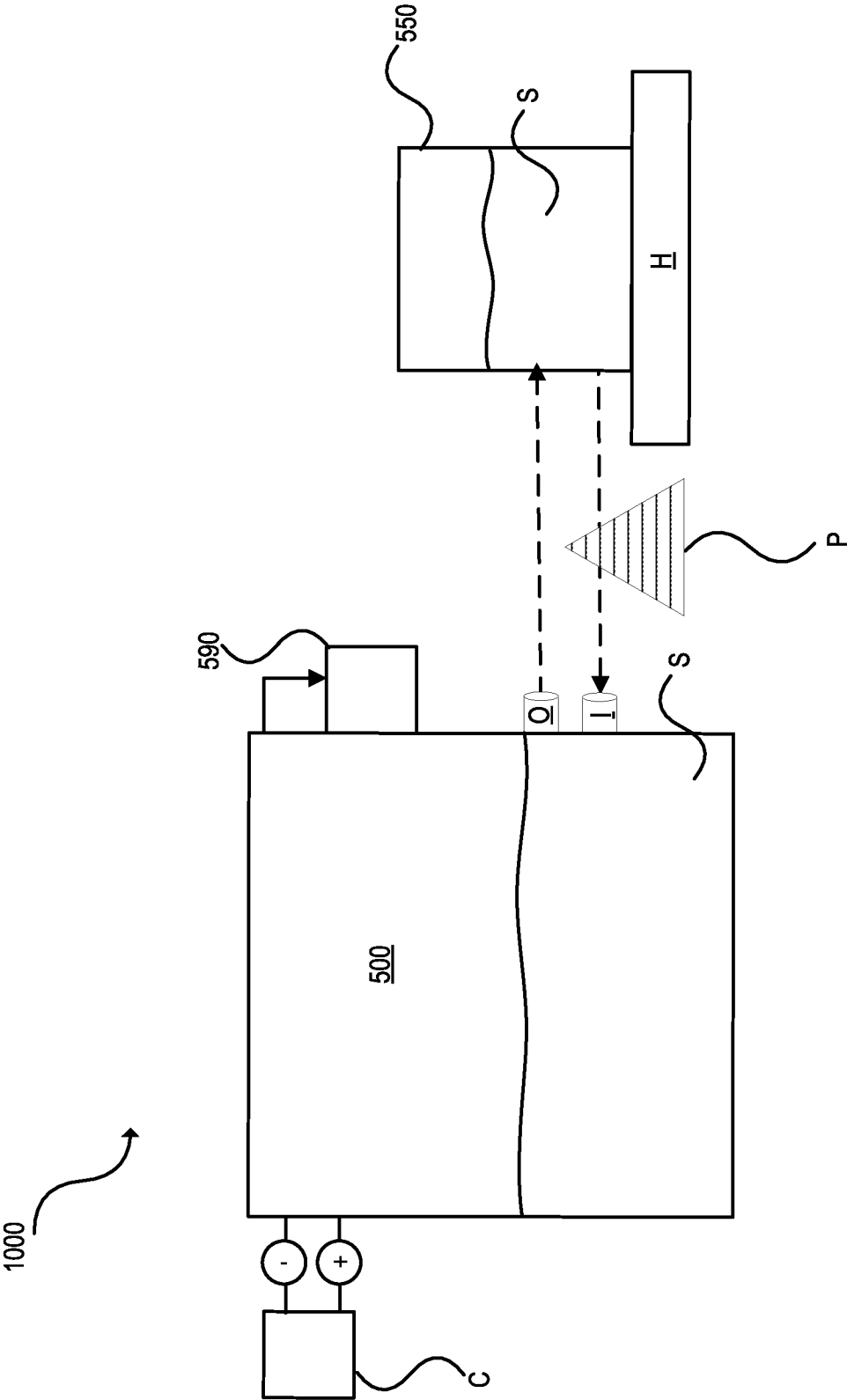


FIG. 8

INTERNATIONAL SEARCH REPORT

International application No
PCT/IB2023/054198

A. CLASSIFICATION OF SUBJECT MATTER

INV. C25C1/00 C25C7/00 C25C7/08 C25C1/06 C25C5/02
ADD.

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)
C25C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, COMPENDEX, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 860 509 A (EMMETT JR ROBERT CLARENCE) 14 January 1975 (1975-01-14) the whole document -----	1-35
X	WO 2017/191605 A1 (UNIV PRETORIA [ZA]) 9 November 2017 (2017-11-09) the whole document -----	1-35
X	WO 2016/081030 A1 (AQUA METALS INC [US]) 26 May 2016 (2016-05-26) the whole document -----	1-35
X	SU 956 628 A1 (SHOSTKINSKIY VGNI PI KHIM FOTO [SU]) 7 September 1982 (1982-09-07) the whole document -----	1-6, 8, 10-35
X	SU 377 211 A1 (NOVOCHERKASSK PERMANENT M) 17 April 1973 (1973-04-17) the whole document -----	1-6, 8, 10-35

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

☒ See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"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

22 August 2023

Date of mailing of the international search report

29/08/2023

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Juhart, Matjaz

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/IB2023/054198

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
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