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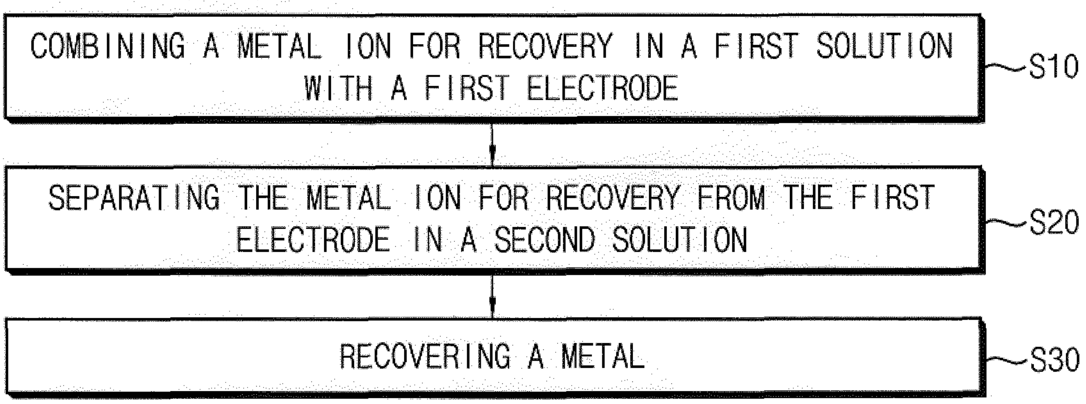
(54) METHOD FOR RECOVERING METAL FROM SOLUTION, SYSTEM FOR RECOVERING METAL FROM SOLUTION, AND SYSTEM FOR RECOVERING LITHIUM FROM SALT WATER

(57) In a method for recovering a metal from a solution, a first electrode that includes a metal for recovery and a second electrode that includes a metal different from the metal for recovery are prepared. The first electrode and the second electrode are immersed in a first solution that includes a metal ion for recovery. The metal ion for recovery in the first solution is combined with the first electrode. The first electrode and the second electrode are charged while immersing the first and second electrodes in a second solution different from the first solution so that the metal ion for recovery is separated from the first electrode. The metal for recovery is recovered from the second solution.

FIG. 1



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Description

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims priority under 35 USC § 119 to Korean Patent Application No. 10-2012-0051834 filed on May 16, 2012 in the Korean Intellectual Property Office (KIPO), the entire disclosure of which is incorporated by reference herein in its entirety.

BACKGROUND

1. Field

[0002] Example embodiments of the present invention relate to methods and systems for recovering a metal. More particularly, example embodiments of the present invention relate to methods for recovering a metal from solution, systems for recovering a metal from solution, and systems for recovering lithium from salt water.

2. Description of the Related Art

[0003] Lithium (Li) is widely utilized in various industries such as glasses, ceramics, alloys, lubricating oils, pharmaceutics, etc. Particularly, a lithium secondary battery has been recently highlighted and developed for a power supply of a hybrid vehicle and an electric vehicle. A demand for the lithium secondary battery is expected to surge up to about 100 times a demand in a compact battery market for, e.g., a cell phone, a laptop computer, etc.

[0004] Further, a demand for lithium may be increased drastically as global environmental restrictions are becoming strengthened, and an application of lithium may be expanded to various industries of 21st century including electronic, chemical and energy industries as well as the hybrid and electric vehicles industry.

[0005] A source of lithium may include a mineral, a brine or a sea water. The mineral may include spodumene, petalite and lepidolite which contain a relatively large amount of lithium in a range of about 1 % to about 1.5 %. However, an extraction of lithium from the mineral may require many complex processes such as a floatation, an annealing, a grinding, an acid mixing, an extraction, a purification, an concentration, a precipitation, etc., and thus large cost and energy may be spent during the processes. Further, an environmental pollution may be caused by an acid used in the extraction of lithium.

[0006] When lithium is recovered from the sea water, a recovery device including an adsorbent may be introduced into the sea water so that lithium may be selectively adsorbed, and then lithium may be recovered by an acid treatment. However, a concentration of lithium in the sea water is as small as about 0.17 ppm, and thus the recovery from the sea water may be limited from an economical aspect.

[0007] Considering the above problems, lithium is mainly recovered from the brine. For example, a salt lake is used as a crude source of lithium, and other salts including Mg, Ca, B, Na or K co-exist therein together with lithium.

[0008] A concentration of lithium in the brine may range from about 0.3 g/L to about 1.5 g/L, and lithium in the brine may be extracted as a form of lithium carbonate. A solubility of lithium carbonate may be about 13 g/L. Even though lithium in the brine is assumed to be completely converted into lithium carbonate, a concentration of lithium carbonate in the brine may range from about 1.59 g/L to about 7.95 g/L which is smaller than the solubility of lithium carbonate. Thus, precipitated lithium carbonate may be re-dissolved thereby to reduce a recovery ratio of lithium.

[0009] Accordingly, a conventional method for recovering lithium in the brine as the form of lithium carbonate includes pumping the brine from a natural salt lake and storing in an evaporation pond, naturally vaporizing the brine for a long period more than a year to concentrate lithium as great as several ten times, and removing impurities such as Mg, Ca or B by a precipitation so that lithium may be recovered at an amount greater than the solubility of lithium carbonate.

[0010] However, the conventional method requires much time for the vaporization and the concentration of the brine to reduce an overall productivity. Further, lithium may be precipitated together with the impurities during the vaporization and the concentration steps to cause a loss of lithium, and the method is limited in a rainy season.

SUMMARY

[0011] Example embodiments of the present invention provide a method for efficiently recovering various metals from a solution.

[0012] Example embodiments of the present invention provide a system for recovering various metals from a solution.

[0013] Example embodiments of the present invention provide a system for recovering various metals such as lithium from a salt water.

[0014] According to an aspect of the present inventive concepts, there is provided a method for recovering a metal from a solution. In the method, a first electrode that includes a metal for recovery and a second electrode that includes a metal different from the metal for recovery are prepared. The first electrode and the second electrode are immersed in a first solution that includes a metal ion for recovery. The metal ion for recovery in the first solution is combined with the first electrode. The first electrode and the second electrode are charged while immersing the first and second electrodes in a second solution different from the first solution so that the metal ion for recovery is separated from the first electrode. The metal for recovery is recovered from the second solution.

[0015] In example embodiments, in combining the metal ion for recovery in the first solution with the first electrode, the first electrode and the second electrode which are positively and negatively charged, respectively, may be electrically connected to induce a discharge.

[0016] In example embodiments, the metal for recovery may include lithium, the first electrode may include a lithium manganese oxide, and the second electrode may include silver, zinc, copper and/or mercury.

[0017] According to an aspect of the present inventive concepts, there is provided a system for recovering a metal from a solution. The system includes a first electrode including a first metal, a second electrode including a second metal different from the first metal, and a power source for charging the first and second electrodes. The first electrode is discharged in a first solution that includes a first metal ion to be combined with the first metal ion and is charged in a second solution different from the first solution to release the first metal ion. The second electrode is discharged in the first solution to be combined with a first anion of the first solution and is charged in the second solution to release the first anion.

[0018] In example embodiments, the first electrode may include a lithium manganese oxide, and the second electrode may include silver, zinc, copper and/or mercury.

[0019] In example embodiments, the first electrode may include $LiMn_2O_4$ having a spinel phase.

[0020] In example embodiments, the first electrode may further include a carbon electrode, and the lithium manganese oxide may be coated on a surface of the carbon electrode.

[0021] In example embodiments, the system may further include a battery capable of repeating charge and discharge processes. An electric energy generated when the first and second electrodes are discharged may be stored in the battery, and the battery may be connected to the power source to provide the stored electric energy.

[0022] According to an aspect of the present inventive concepts, there is provided a system for recovering lithium from a salt water. The system includes a first electrode including a lithium manganese oxide, a second electrode including silver, a power source for charging the first and second electrodes, and a battery capable of repeating charge and discharge processes. The first electrode is discharged in a salt water that includes a lithium ion and a chlorine ion to be combined with the lithium ion and is charged in a charging solution different from the salt water to release the lithium ion. The second electrode is discharged in the salt water to be combined with the chlorine ion and is charged in the charging solution to release the chlorine ion. The battery stores an electric energy generated when the first electrode is discharged and is connected to the power source to provide the stored electric energy.

[0023] In example embodiments, the first electrode may include $LiMn_2O_4$ having a spinel phase.

BRIEF DESCRIPTION OF THE DRAWINGS

[0024] Example embodiments will be more clearly understood from the following detailed description taken in conjunction with the accompanying drawings.

FIG. 1 is a flow chart illustrating a method for recovering a metal from a solution in accordance with example embodiments;

FIGS. 2 and 3 are schematic views illustrating a system for recovering a metal from a solution in accordance with example embodiments;

FIG. 4 is a graph showing concentration changes of a lithium ion and a sodium ion present in a discharging solution while repeating charge and discharge processes in a lithium recovery process of Example 1;

FIG. 5 is a graph showing concentration changes of a lithium ion, a calcium ion, a potassium ion, a magnesium ion and a sodium ion present in a discharging solution while repeating charge and discharge processes in a lithium recovery process of Example 2; and

FIG. 6 is a graph showing a concentration change of a lithium ion present in a charging solution while repeating charge and discharge processes in a lithium recovery process of Example 2.

DETAILED DESCRIPTION OF THE EMBODIMENTS

[0025] Various exemplary embodiments will be described more fully, in which some exemplary embodiments are shown. The present inventive concept may, however, be embodied in many different forms and should not be construed as limited to the exemplary embodiments set forth herein. Rather, these exemplary embodiments are provided so that this description will be thorough and complete, and will fully convey the scope of the present inventive concept to those skilled in the art.

[0026] The terminology used herein is for the purpose of describing particular example embodiments only and is not intended to be limiting of the present inventive concept. As used herein, the singular forms "a," "an" and "the" are intended to include the plural forms as well, unless the context clearly indicates otherwise. It will be further understood that the terms "comprises" and/or "comprising," when used in this specification, specify the presence of stated features, integers, steps, operations, elements, and/or components, but do not preclude the presence or addition of one or more other features, integers, steps, operations, elements, components, and/or groups thereof.

[0027] Example embodiments are described herein with reference to cross-sectional illustrations that are schematic illustrations of idealized example embodiments (and intermediate structures). As such, variations from the shapes of the illustrations as a result, for example, of manufacturing techniques and/or tolerances, are to be expected. Thus, example embodiments should not be construed as limited to the particular shapes of regions illustrated herein but are to include deviations in shapes that result, for example, from manufacturing. For example, an implanted region illustrated as a rectangle will, typically, have rounded or curved features and/or a gradient of implant concentration at its edges rather than a binary change from implanted to non-implanted region. Likewise, a buried region formed by implantation may result in some implantation in the region between the buried region and the surface through which the implantation takes place. Thus, the regions illustrated in the figures are schematic in nature and their shapes are not intended to illustrate the actual shape of a region of a device and are not intended to limit the scope of the present inventive concept.

[0028] Unless otherwise defined, all terms (including technical and scientific terms) used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this inventive concept belongs. It will be further understood that terms, such as those defined in commonly used dictionaries, should be interpreted as having a meaning that is consistent with their meaning in the context of the relevant art and will not be interpreted in an idealized or overly formal sense unless expressly so defined herein.

Methods for Recovering a Metal from a Solution

[0029] FIG. 1 is a flow chart illustrating a method for recovering a metal from a solution in accordance with example embodiments.

[0030] Referring to FIG. 1, in step S10, a first electrode and a second electrode may be immersed in a first solution containing a metal ion for recovery, and the metal ion in the first solution may be combined with the first electrode. In example embodiments, the first electrode and the second electrode may be positively and negatively charged, respectively, and the first and second electrodes may be electrically connected to cause a discharge so that the metal ion for recovery in the first solution may be combined with the first electrode.

[0031] Preferably, before electrically connecting the first and second electrodes, the first electrode may be positively charged and the second electrode may be negatively charged.

[0032] A metal for recovery may not be specifically limited, however, may include, e.g., lithium, sodium, potassium, magnesium, calcium, strontium, manganese, etc.

[0033] The first solution may be obtained, e.g., a sea water or a highly concentrated brine (or a salt water). The first solution may further include other metal ions and anions in addition to the metal ion for recovery. For example, if the metal for recovery is lithium, the first solution may include cations of lithium, sodium, potassium, magnesium, calcium, strontium, manganese, etc., and a chlorine anion (Cl^-).

[0034] The first electrode may include the metal for recovery. For example, if the metal for recovery is lithium, the first electrode may also include lithium. Preferably, the first electrode may have a selectivity for the metal for recovery. For example, if the metal for recovery is lithium, the first electrode may include a lithium manganese oxide (LMO). Specifically, the LMO may include $LiMn_2O_4$, $LiMnO_6$, etc., and these may be used alone or in a combination thereof. The selectivity for a lithium ion of the LMO may vary according to a phase of the LMO. Preferably, the LMO may have a spinel phase.

[0035] Preferably, the second electrode may include a metal different from the metal for recovery. Further, the metal of the second electrode may have an ionization tendency greater than that of the metal for recovery. Thus, when the first and second electrodes are electrically connected to each other, the first electrode may serve as an anode (positive electrode) and the second electrode may serve as a cathode (negative electrode). Preferably, the metal of the second electrode may be selected in consideration of the ionization tendency of the metal for recovery, for example, may include silver, zinc, copper, mercury, etc. The second electrode may preferably include the metal that may be combined with and separated from an anion reversibly and repeatedly in charge and discharge processes. Thus, silver may be used as the metal of the second electrode in consideration of the reversibility and an environmental aspect.

[0036] When the first and second electrodes are electrically connected to each other, the discharge may occur. In the discharge, electrons may be moved from the first electrode to the second electrode. The metal ion for recovery in the first solution may accept the electron to be combined with the first electrode, and the metal of the second electrode may lose the electron to be combined with an anion in the first solution. In an embodiment, the first electrode may include

$LiMn_2O_4$, the second electrode may include silver, and the first solution may include the lithium cation and the chlorine anion. In this case, a reaction represented by Chemical Equation 1 may occur in the first electrode, and a reaction represented by Chemical Equation 2 may occur in the second electrode.

[Chemical Equation 1] $Li_{1-x}Mn_2O_4 + xLi+ + xe^- \rightarrow LiMn_2O_4$

[Chemical Equation 2] $xAg + xCl^- \rightarrow xAgCl + xe^-$

[0037] As indicated in the above equations, the lithium ion in the first solution may be combined with the LMO of the first electrode, and the chlorine ion in the first solution may be combined with silver of the second electrode to generate silver chloride. As a result, concentrations of the lithium and chlorine ions in the first solution may be reduced.

[0038] In example embodiments, the LMO included in the first electrode may have the selectivity for lithium, and thus lithium may be selectively separated from the first solution containing the different metal ions.

[0039] In example embodiments, the positively charged first electrode and the negatively charged second electrode may be electrically connected to each other for discharging the first and second electrodes. However, alternatively, a power source may be connected to the first and second electrodes, the first electrode may be negatively charged (electrons may be provided), and the second electrode may be positively charged so that the lithium ion in the first solution may be combined with the first electrode.

[0040] Subsequently, in step S20, the first and second electrodes may be immersed in a second solution different from the first solution and may be charged so that the metal ion for recovery may be separated from the first electrode. The second solution may be an aqueous solution including suitable electrolytes.

[0041] In a case that the first electrode includes $LiMn_2O_4$ and the second electrode includes silver chloride, the first and second electrodes may be charged such that the first electrode may be positively charged and the second electrode may be negatively charged to cause a reaction represented by Chemical Equation 3 in the first electrode and a reaction represented by Chemical Equation 4 in the second electrode.

[Chemical Equation 3] $LiMn_2O_4 \rightarrow Li_{1-x}Mn_2O_4 + xLi+ + xe^-$

[Chemical Equation 4] $xAgCl + xe^- \rightarrow xAg + xCl^-$

[0042] As a result, the LMO of the first electrode may lose the lithium ion, and silver chloride of the second electrode may lose the chlorine ion to be reduced into silver. Accordingly, the second solution may include the lithium cation and the chlorine anion.

[0043] Subsequently, in step S30, the metal for recovery may be recovered from the second solution. Various conventional methods may be implemented for recovering the metal.

[0044] For example, when the second solution includes the lithium cation and the chlorine anion, the second solution may be heated to obtain a solid-state lithium chloride. Lithium chloride may be non-toxic and chemically stable, and thus easily stored and managed. Additionally, lithium chloride may be directly used as an electrolyte of a lithium secondary battery.

[0045] In other examples, the second solution including the lithium cation and the chlorine anion may be treated by an electrolysis to collect lithium.

[0046] Before recovering the metal, the discharge process in the first solution and the charge process in the second solution described above may be repeated so that a concentration of the metal for recovery in the second solution may be increased. The first electrode may be positively charged and the second electrode may be negatively charged by the charge process in the second solution. The first and second electrodes may be taken out from the second solution, and immersed and electrically connected to each other again in the first solution so that the lithium ion in the first solution may be combined again with the first electrode by the discharge process. If the concentration of the metal for recovery in the second direction becomes increased, a recovery efficiency of the metal may be improved.

[0047] According to example embodiments of the present invention, a metal may be efficiently recovered from a solution. Specifically, highly concentrated lithium may be obtained in a short time compared to conventional methods using vaporization/concentration of brine and adsorption from a sea water. Further, the method in accordance with example embodiments may include simple processes and may be relatively free from an environmental pollution. Additionally, an electric energy generated from the discharge process may be stored and reused to minimize an energy consumption.

[0048] The method in accordance with example embodiments may be used for recovering a metal from a sea water or a highly concentrated brine, and may be also used for recovering a metal from an industrial wastewater.

[0049] Hereinafter, a system for implementing the method for recovering a metal from a solution, and a system for recovering lithium from a brine are described in detail with reference to accompanying drawings.

Systems for Recovering a Metal from a Solution and Systems for Recovering Lithium from a Brine

[0050] A system for recovering a metal from a solution according to example embodiments may comprise a first electrode including a first metal and a second electrode including a second metal different from the first metal. The first and second electrodes may be electrically connected to each other. The first electrode may be discharged in a first solution including a first metal ion to be combined with the first metal ion, and may be charged in a second solution different from the first solution to release the first metal ion. The second electrode may be discharged in the first solution to be combined with a first anion of the first solution, and may be charged in the second solution to release the first anion. The system may include a power source for charging the first and second electrodes.

[0051] FIGS. 2 and 3 are schematic views illustrating a system for recovering a metal from a solution in accordance with example embodiments.

[0052] Referring to FIG. 2, a first solution 30 may be accommodated in a first bath 40. A first electrode 10 and a second electrode 20 may be immersed in the first solution 30. For example, the first electrode 10 and the second electrode 20 may be partially immersed in the first solution 30 such that upper portions thereof may be exposed from the first solution 30. In some embodiments, the first and second electrodes 10 and 20 may be entirely immersed in the first solution 30.

[0053] The first solution 30 may include a metal ion for recovery. In example embodiments, a metal for recovery may be lithium. The first solution 30 may be a sea water or a highly concentrated brine (or salt water), and may further include sodium, potassium, magnesium, calcium, strontium, manganese, etc., in addition to lithium. The first solution 30 may also include an anion. If the first solution 30 is the sea water or the highly concentrated brine, the first solution may mainly include a chlorine anion (Cl^-).

[0054] The first electrode 10 may include the metal for recovery. For example, if the metal for recovery is lithium, the first electrode 10 may also include lithium. Preferably, the first electrode 10 may have a selectivity for the metal for recovery. For example, if the metal for recovery is lithium, the first electrode 10 may include a lithium manganese oxide (LMO). Specifically, the LMO may include $LiMn_2O_4$, $LiMnO_6$, etc., and these may be used alone or in a combination thereof. The selectivity for a lithium ion of the LMO may vary according to a phase of the LMO. Preferably, the LMO may have a spinel phase.

[0055] The LMO may have a relatively low conductivity. Thus, the first electrode 10 may further include an additional material having a relatively strong conductivity. For example, the first electrode 10 may include a carbon electrode containing graphite, carbon nanotube, graphene, etc., and the LMO may be at least partially coated on a surface of the carbon electrode. A wire for electrically connecting the first electrode 10 and the second electrode 20 may be connected to the carbon electrode.

[0056] Specifically, the first electrode 10 may include a mixture of powders of the LMO and graphite, and the mixture may be at least partially coated on the surface of the carbon electrode. For example, a positive electrode material composition including the LMO, the powder of graphite, a binding agent and a solvent may be coated on the carbon electrode, and dried to obtain the first electrode 10. For example, the binding agent may include polyvinyliden fluoride (PVDF), polyvinyl alcohol (PVA), polyurethane (PU), etc. These may be used alone or in a combination thereof. For example, the solvent may include an alcohol such as methanol, ethanol, propanol, butanol, etc. These may be used alone or in a combination thereof.

[0057] The second electrode 20 may include a metal different from the metal for recovery. Further, the metal of the second electrode 20 may have an ionization tendency greater than that of the metal for recovery. Thus, when the first and second electrodes 10 and 20 are electrically connected to each other, the first electrode 10 and the second electrode 20 may serve as an anode and a cathode, respectively. Preferably, the metal of the second electrode 20 may include silver, zinc, copper, mercury, etc. In example embodiments, the second electrode 20 may include silver.

[0058] The first and second electrodes 10 and 20 may be electrically connected to each other through the wire for a discharge process. Preferably, before electrically connecting the first and second electrodes 10 and 20, the first electrode 10 may be positively charged, and the second electrode 20 may be negatively charged to result in the discharge process of the first and second electrodes 10 and 20.

[0059] In example embodiments, the first electrode 10 may include $LiMn_2O_4$, the second electrode 20 may include silver, and the first solution 30 may include the lithium cation and the chlorine anion. Therefore, when the first and second electrodes 10 and 20 are electrically connected to each other, the lithium cation of the first solution 30 may be combined with the LMO of the first electrode 10, and the chlorine anion of the first solution 30 may be combined with silver of the second electrode 20 to generate silver chloride. As a result, concentrations of the lithium and chorine ions may be reduced in the first solution 30.

[0060] The first and second electrodes 10 and 20 may be connected to a battery 50. An electric energy generated from the discharge process may be stored in the battery 50. The battery 50 may be also used as a power source in a charge process described below. The battery 50 may include any conventional battery capable of repeating charge and discharge processes of an electric energy. For example, a lead storage battery, a mercury battery, a lithium ion battery, a lithium polymer battery, etc., may be used as the battery 50.

[0061] Referring to FIG. 3, the first and second electrodes 10 and 20 after the discharge process may be immersed in a second solution 60 accommodated in a second bath 70.

[0062] When the first and second electrodes 10 and 20 are positively and negatively charged, respectively, by charging the first and second electrodes 10 and 20, the LMO of the first electrode 10 may lose the lithium ion and silver chloride of the second electrode 20 may lose the chlorine ion to be reduced into silver. Accordingly, the second solution 60 may include the lithium cation and the chlorine anion.

[0063] The first and second electrodes 10 and 20 may be connected to a suitable power source for charging the first and second electrode 10 and 20. The power source may be connected to the battery 50, and the electric energy stored in the battery may be utilized so that an energy efficiency may be improved.

[0064] By repeating the charge and discharge processes illustrated in FIGS. 2 and 3, a highly concentrated lithium ion may be achieved, and lithium may be recovered as a form of, e.g., a lithium salt from the lithium ion solution.

[0065] In example embodiments, the first and second bath 40 and 70 may be separated from each other. However, the discharge process may be performed in the first solution, and then the first solution may be replaced with the second solution to perform the charge process continuously in a single container.

[0066] According to example embodiments, highly concentrated lithium may be obtained in a short time compared to conventional methods using vaporization/concentration of brine and adsorption from a sea water. Further, the method or the system in accordance with example embodiments may include simple processes and may be relatively free from an environmental pollution. Additionally, an electric energy generated from the discharge process may be stored and reused to minimize an energy consumption.

[0067] Hereinafter, a method for recovering a metal from a solution, a system for implementing the method, and a system for recovering lithium from a brine are described in detail with reference to specific Examples.

Example 1

[0068] A silver electrode of 3x3 cm^2, and a graphite electrode of the same size were prepared. A powder of $LiMn_2O_4$, Super-P (manufactured by Timcal, Swiss) as a graphite powder, and PVDF as a binder resin were mixed in a mixing ratio of about 80:10:8 to form a mixture. The mixture was dispersed in ethanol, coated on the graphite electrode and dried to prepare an electrode for lithium recovery.

[0069] The electrode for lithium recovery and the silver electrode were immersed with a distance of about 1 cm therebetween in a charging solution of about 90 ml including lithium chloride of about 25 mM. A power source was connected to the electrodes to provide a charging voltage of about 1.2 V for about 20 minutes. Accordingly, the electrode for lithium recovery was positively charged, and the silver electrode was negatively charged.

[0070] Subsequently, the electrode for lithium recovery and the silver electrode were immersed in a discharging solution of about 90 ml including lithium chloride of about 25 mM and sodium chloride of about 25 mM. The electrode for lithium recovery and the silver electrode were connected through a wire to be discharged for about 30 minutes.

[0071] The charge and discharge processes were repeatedly performed three times. On completion of each cycle (including one charge process and one discharge process), a sample of about 1 ml was extracted from the discharging solution, and concentration changes of lithium and sodium ions were measured using a ion-chromatography apparatus, DX-120 (manufactured by DIONEX). The results are shown in FIG. 4.

Example 2

[0072] A silver electrode of 3x3 cm^2, and a graphite electrode of the same size were prepared. A powder of $LiMn_2O_4$, Super-P (manufactured by Timcal, Swiss) as a graphite powder, and PVDF (weight average molecular weight: ~ 534,000, glass transition temperature: -38 °C, density at 25 °C: 1.74 g/ml, manufactured by Sigma Aldrich, USA) as a binder resin were mixed in a mixing ratio of about 80:10:8 to form a mixture. The mixture was dispersed in ethanol, coated on the graphite electrode and dried to prepare an electrode for lithium recovery.

[0073] The electrode for lithium recovery and the silver electrode were immersed with a distance of about 1 cm therebetween in a charging solution of about 80 ml including lithium chloride of about 30 mM. A power source was connected to the electrodes to provide a charging voltage of about 1.2 V for about 20 minutes. Accordingly, the electrode for lithium recovery was positively charged, and the silver electrode was negatively charged.

[0074] Subsequently, the electrode for lithium recovery and the silver electrode were immersed in a discharging solution of about 80 ml including lithium chloride of about 30 mM, sodium chloride of about 30 mM, potassium chloride of about 30 mM and magnesium chloride of about 30 mM. The electrode for lithium recovery and the silver electrode were connected through a wire to be discharged for about 40 minutes.

[0075] The charge and discharge processes were repeatedly performed four times. On completion of each cycle (including one charge process and one discharge process), a sample of about 1 ml was extracted from the discharging solution, and concentration changes of lithium, potassium, calcium, magnesium and sodium ions were measured using a ion-chromatography apparatus, DX-120 (manufactured by DIONEX). The same amount of a sample was extracted from the charging solution, and a concentration change of a lithium ion was measured. The results are shown in FIGS. 5 and 6.

[0076] FIG. 4 is a graph showing concentration changes of the lithium ion and the sodium ion present in the discharging solution while repeating the charge and discharge processes in Example 1. FIG. 5 is a graph showing concentration changes of the lithium ion, the calcium ion, the potassium ion, the magnesium ion and the sodium ion present in the discharging solution while repeating the charge and discharge processes in Example 2. FIG. 6 is a graph showing a concentration change of the lithium ion present in the charging solution while repeating the charge and discharge processes in Example 2.

[0077] Referring to FIG. 4, the concentration of the lithium ion was continuously decreased while repeating the charge and discharge processes in Example 1, however, the concentration of the sodium ion was substantially maintained without a reduction. Therefore, it can be acknowledged that the lithium ion may be selectively recovered from a mixture with the sodium ion using the method and the system for recovering a metal from a solution according to example embodiments.

[0078] Referring to FIG. 5, the concentration of the lithium ion was continuously decreased while repeating the charge and discharge processes in Example 2, however, the concentrations of the calcium ion, the potassium ion and the sodium ion were substantially maintained without a reduction. The concentration of the magnesium ion was decreased in a first cycle, and then substantially maintained without a reduction in the subsequent cycles. Referring to FIG. 6, the concentration of the lithium ion was continuously increased in the charging solution while repeating the charge and discharge processes. Therefore, it can be acknowledged that the lithium ion may be selectively recovered from a mixture with the sodium ion, the potassium ion, the calcium ion and the magnesium ion using the method and the system for recovering a metal from a solution according to example embodiments.

[0079] The sodium and magnesium ions are significantly present in the sea water and the highly concentrated brine which may be sources of lithium. Particularly, magnesium may have a solubility similar to that of lithium, and thus may not be easily separated by a vaporization method. The presence of these ions may be a main factor reducing an efficiency in a lithium recovery process. Therefore, the method and the system for recovering a metal from a solution according to example embodiments may be implemented to efficiently recover lithium from the sea water and the highly concentrated brine.

[0080] The foregoing is illustrative of example embodiments and is not to be construed as limiting thereof. Although a few example embodiments have been described, those skilled in the art will readily appreciate that many modifications are possible in the example embodiments without materially departing from the novel teachings and advantages of the present inventive concept. Accordingly, all such modifications are intended to be included within the scope of the present inventive concept as defined in the claims. Therefore, it is to be understood that the foregoing is illustrative of various example embodiments and is not to be construed as limited to the specific example embodiments disclosed, and that modifications to the disclosed example embodiments, as well as other example embodiments, are intended to be included within the scope of the appended claims.

Claims

1. A method for recovering a metal from a solution, comprising:

preparing a first electrode that includes a metal for recovery and a second electrode that includes a metal different from the metal for recovery;
immersing the first electrode and the second electrode in a first solution that includes a metal ion for recovery;
combining the metal ion for recovery in the first solution with the first electrode;
charging the first electrode and the second electrode while immersing the first and second electrodes in a second solution different from the first solution so that the metal ion for recovery is separated from the first electrode; and
recovering the metal for recovery from the second solution.

2. The method of claim 1, wherein combining the metal ion for recovery in the first solution with the first electrode includes:

electrically connecting the first electrode and the second electrode which are positively and negatively charged, respectively, to induce a discharge.

3. The method of claim 1, wherein the metal for recovery includes lithium, the first electrode includes a lithium manganese oxide, and the second electrode includes at least one selected from the group consisting of silver, zinc, copper and mercury.

4. A system for recovering a metal from solution, comprising:

a first electrode including a first metal, the first electrode being discharged in a first solution that includes a first metal ion to be combined with the first metal ion and being charged in a second solution different from the first solution to release the first metal ion;
a second electrode including a second metal different from the first metal, the second electrode being discharged in the first solution to be combined with a first anion of the first solution and being charged in the second solution to release the first anion; and
a power source for charging the first and second electrodes.

5. The system of claim 4, wherein the first electrode includes a lithium manganese oxide, and the second electrode includes at least one selected from the group consisting of silver, zinc, copper and mercury.

6. The system of claim 5, wherein the first electrode includes $LiMn_2O_4$ having a spinel phase.

7. The system of claim 5, wherein the first electrode further includes a carbon electrode, and the lithium manganese oxide is coated on a surface of the carbon electrode.

8. The system of claim 4, further comprising a battery capable of repeating charge and discharge processes, wherein an electric energy generated when the first and second electrodes are discharged is stored in the battery, and the battery is connected to the power source to provide the stored electric energy.

9. A system for recovering lithium from a salt water, comprising:

a first electrode including a lithium manganese oxide, the first electrode being discharged in a salt water that includes a lithium ion and a chlorine ion to be combined with the lithium ion and being charged in a charging solution different from the salt water to release the lithium ion;
a second electrode including silver, the second electrode being discharged in the salt water to be combined with the chlorine ion and being charged in the charging solution to release the chlorine ion;
a power source for charging the first and second electrodes; and
a battery capable of repeating charge and discharge processes, the battery storing an electric energy generated when the first electrode is discharged and being connected to the power source to provide the stored electric energy.

10. The system of claim 9, wherein the first electrode includes $LiMn_2O_4$ having a spinel phase.

FIG. 1

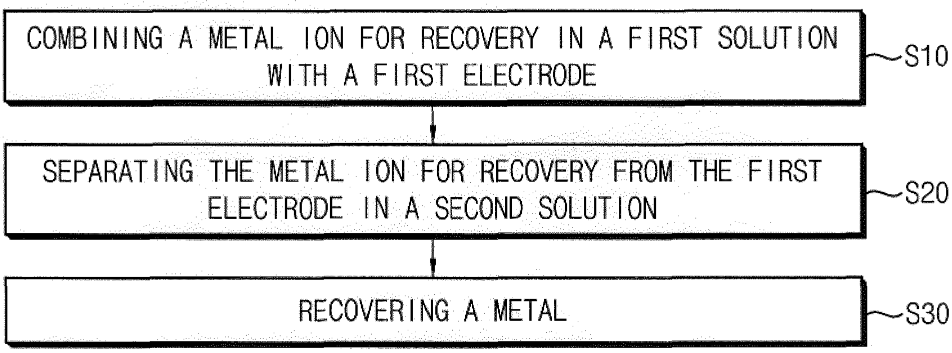


FIG. 2

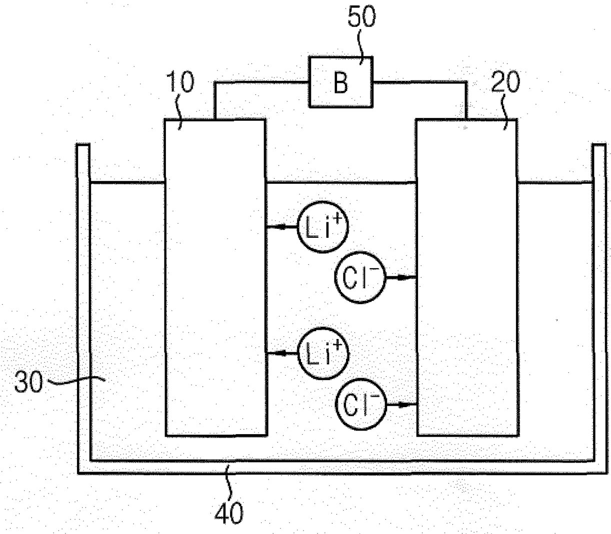


FIG. 3

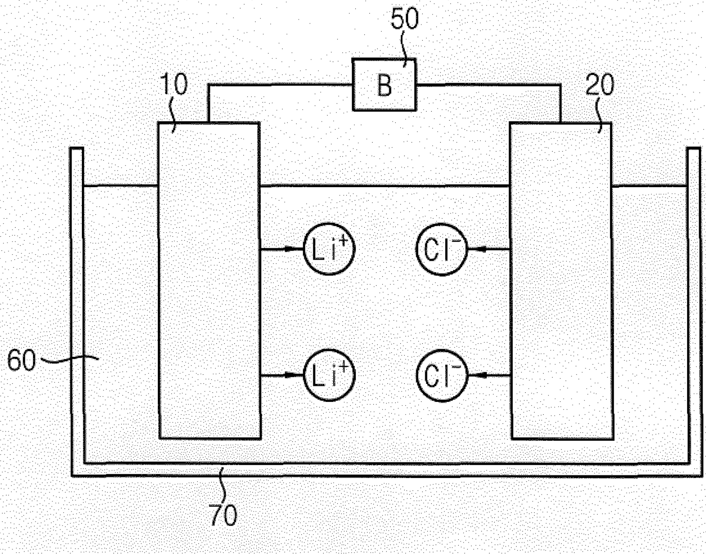
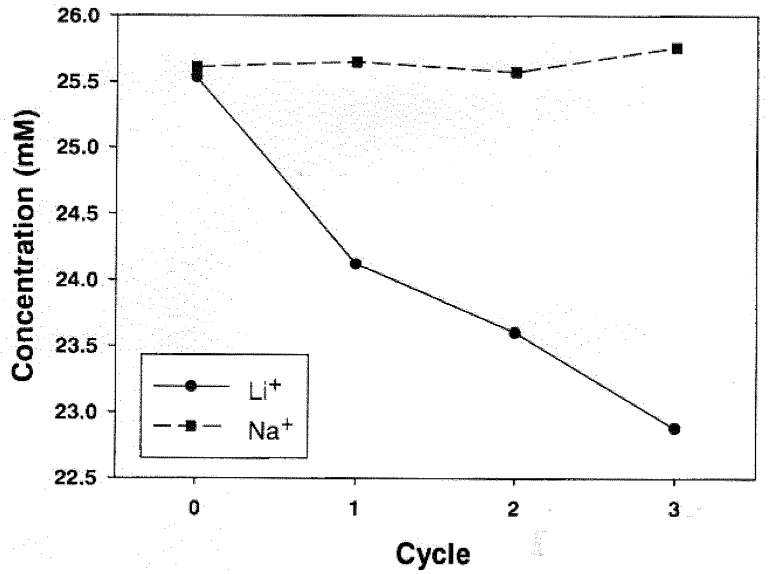


FIG. 4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25.0
24.5
24.0
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23.0
22.5
Concentration (mM)
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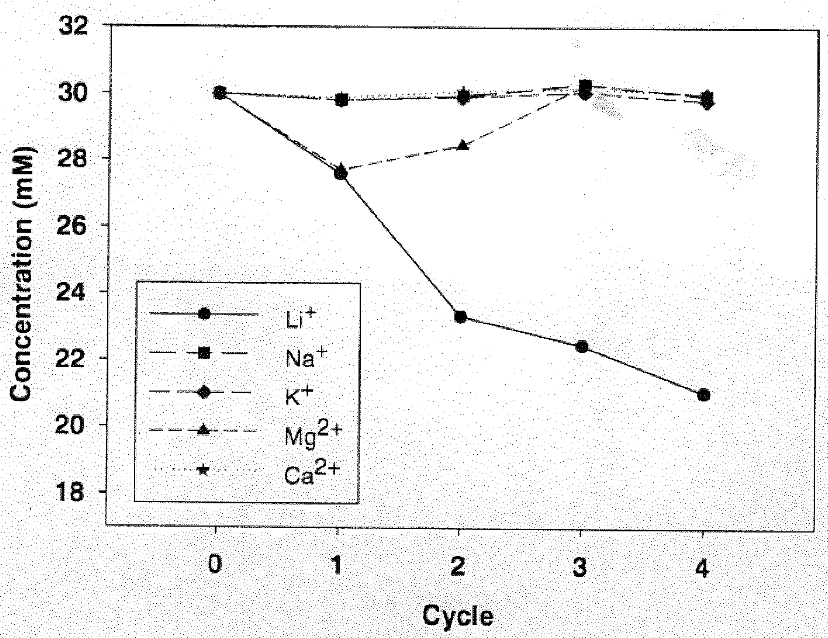
1
2
3
Cycle
Li+
Na+

FIG. 5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30
28
26
24
22
20
18
Concentration (mM)
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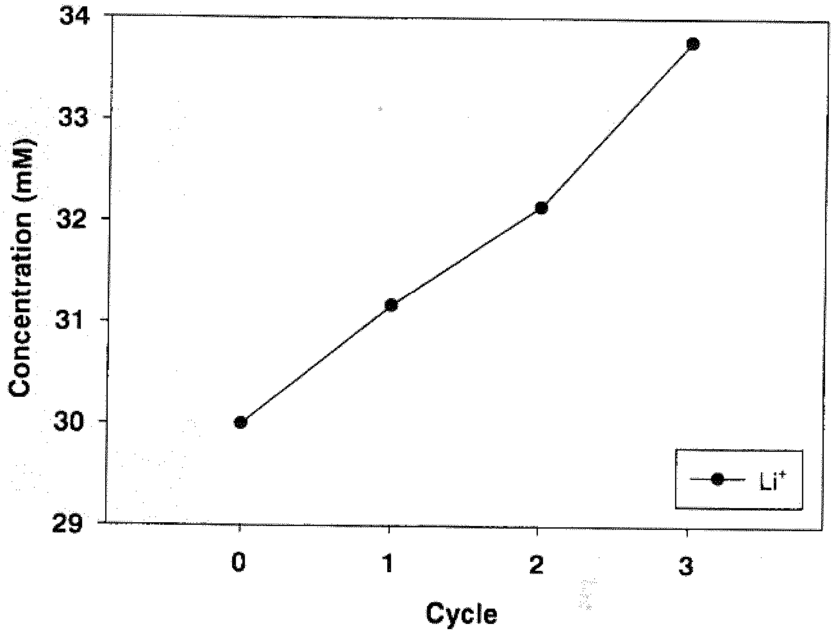
1
2
3
4
Cycle
Li+
Na+
K+
Mg2+
Ca2+

FIG. 6



INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR2013/000353

A. CLASSIFICATION OF SUBJECT MATTER

C25C 3/02(2006.01)i, C22B 26/12(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)

IPC: C25C 3/02; C25C 7/00; C22B 3/24; H01M 10/40; C25C 1/20; H01M 4/134; C25C 7/02; C22B 26/12; H01M 10/54

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: IPC as above
Japanese Utility models and applications for Utility models: IPC as above

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

eKOMPASS (KIPO internal) & Keywords: lithium, collection, brine, discharge, charge, electrode, Lithium manganese oxide, spinel

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2009-235552 A (I'MSEP CO., LTD.) 15 October 2009 See abstract, paragraphs [0011]-[0013], [0019], claims 1, 8 and figure 1.	1-10
A	KR 10-2012-0024423 A (JAPAN ATOMIC ENERGY AGENCY) 14 March 2012 See abstract, paragraphs [0029], [0037], claims 1, 13 and figure 1.	1-10
A	JP 2005-011698 A (KAWASAKI HEAVY IND. LTD. et al.) 13 January 2005 See paragraphs [0024], [0030] and figure 2.	1-10
A	KR 10-2012-0015658 A (RESEARCH INSTITUTE OF INDUSTRIAL SCIENCE & TECHNOLOGY) 22 February 2012 See paragraphs [0035]-[0044] and figure 3.	1-10
A	US 3980538 A (HIGGINS, David L.) 14 September 1976 See column 3, lines 41-62, claims 1, 5 and figure 1.	1-10

☐ 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
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"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 18 APRIL 2013 (18.04.2013)	Date of mailing of the international search report **24 APRIL 2013 (24.04.2013)**
Name and mailing address of the ISA/KR Korean Intellectual Property Office Government Complex-Daejeon, 189 Seonsa-ro, Daejeon 302-701, Republic of Korea Facsimile No. 82-42-472-7140	Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (July 2009)

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/KR2013/000353

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		US 7713396 B2	11.05.2010
KR 10-2012-0015658 A	22.02.2012	KR 10-1238898 B1	04.03.2013
US 3980538 A	14.09.1976	NONE	

Form PCT/ISA/210 (patent family annex) (July 2009)

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- KR 1020120051834 **[0001]**