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(71) Applicant: SHARP KABUSHIKI KAISHA [JP/JP]; 22-22, Nagaike-cho, Abeno-ku, Osaka-shi, Osaka, 5458522 (JP).

(72) Inventors: LU, Yuhao. WANG, Long. VAIL, Sean.

(74) Agent: HARA KENZO WORLD PATENT & TRADE-MARK; Daiwa Minamimorimachi Building, 2-6, Tenjinbashi 2-chome Kita, Kita-ku, Osaka-shi, Osaka, 5300041 (JP).

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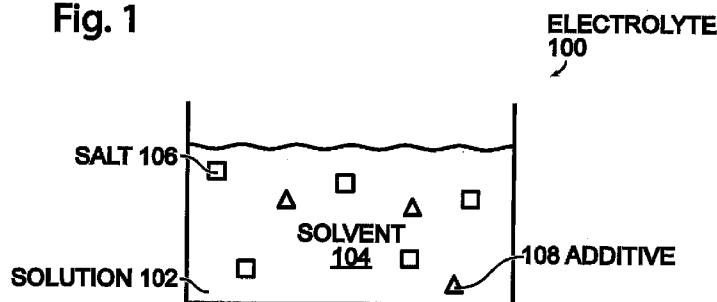
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(54) Title: ELECTROLYTE ADDITIVES FOR TRANSITION METAL CYANOMETALLATE ELECTRODE STABILIZATION

Fig. 1



(57) Abstract: A method is provided for the self-repair of a transition metal cyanometallate (TMCM) battery electrode. The battery is made from a TMCM cathode, an anode, and an electrolyte including solution formed from a solvent and an alkali or alkaline earth salt. The electrolyte includes an additive represented as G-R-g: where G and g are independently include materials with nitrogen (N) sulfur (S), oxygen (O), or combinations of the above-recited elements; and where R is an alkene or alkane group. In response to charging and discharging the battery in a plurality of cycles, the method creates vacancies in a surface of the TMCM cathode. Then, the method fills the vacancies in the surface of the TMCM cathode with the electrolyte additive. An electrolyte and TMCM battery using the above-mentioned additives are also provided.



Description

Title of Invention: ELECTROLYTE ADDITIVES FOR TRANSITION METAL CYANOMETALLATE ELECTRODE STABILIZATION

Technical Field

[0001] This invention generally relates to electrochemical cells and, more particularly, to an electrolyte containing additives useful for stabilizing transition metal cyanometallate batteries.

Background Art

[0002] Transition metal cyanometallates (TMCMs) with large interstitial spaces have been investigated as the cathode material for rechargeable lithium-ion batteries [NPL1, NPL2], sodium-ion batteries [NPL3, NPL4], and potassium-ion batteries [NPL5]. With an aqueous electrolyte containing the proper alkali-ions or ammonium-ions, copper and nickel hexacyanoferrates ((Cu,Ni)-HCFs) exhibited a very good cycling life with 83% capacity retained after 40,000 cycles at a charge/discharge current of 17C [NPL6-NPL8]. However, the materials within the aqueous electrolyte demonstrated low capacities and energy densities because: (1) just one sodium-ion can be inserted/extracted into/from per Cu-HCF or Ni-HCF formula, and (2) these transition metal cyanoferrate (TM-HCF) electrodes must be operated below 1.23 V due to the water electrochemical window. The electrochemical window of a substance is the voltage range between which the substance is neither oxidized nor reduced. This range is important for the efficiency of an electrode, and once out of this range, water becomes electrolyzed, spoiling the electrical energy intended for another electrochemical reaction.

[0003] To correct the shortcomings, manganese hexacyanoferrate (Mn-HCF) and iron hexacyanoferrate (Fe-HCF) were used as cathode materials in a non-aqueous electrolyte [NPL9, NPL10]. Assembled with a sodium-metal anode, Mn-HCF and Fe-HCF electrodes cycled between 2.0V and 4.2 V and delivered capacities of about 110 milliamp hour per gram (mAh/g).

[0004] It is worth noting that the actual capacity of a TMHCF electrode is by far smaller than the theoretical value. For instance, the theoretical capacity for Mn-HCF is 170 mAh/g, but the reported capacity was just ~120 mAh/g, as tested in a sodium-ion battery. The capacity difference could be ascribed to the structures and compositions of TMHCFs. Buser, et al. [NPL11] investigated the crystal structure of Prussian Blue (PB), $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3 \cdot x\text{H}_2\text{O}$ and found that $\text{Fe}(\text{CN})_6$ positions were only partly occupied. The vacancies led to water entering the PB interstitial space and even as-

sociating with Fe(III) in the lattice [NPL12]. In consideration of charge neutralization and interstitial space, the vacancies and water both act to reduce the concentration of mobile ions in the interstitial space of TMHCF. As an example, Matsuda, et al. [NPL9] preferred to use $A_{4x-2}M_A[M_B(CN)_6]_x \cdot zH_2O$ as a replacement to the nominal formula of $A_2M_AM_B(CN)_6$ because of the vacancies. Furthermore, the vacancies result in dense defects on the surface of TMHCFs. Without interstitial ions and supporting water, the surface easily collapses. The surface degradation can be aggravated when the interstitial ions in the vicinity of the surface are extracted out during electrochemical reactions. In a battery, such degradation leads to poor capacity retention.

- [0005] A Cu-HCF electrode with a Li^+ -ion electrolyte delivered 120 mAh/g during the first discharge, but its capacity decreased to 40 mAh/g in 10 cycles [NPL13]. By coating with Ni-HCF, the surface of the Cu-HCF electrode was modified and its stability was improved. However, the undercoordinated transition metal (UTM) on the surface retards charge transfer between the TMHCF electrode and electrolyte due to charge repulsion between the UTM and the mobile ions, which may result in poor rate performance. Park, et al. [NPL14] mentioned the surface effect on a $LiFePO_4$ electrode with undercoordinated Fe^{2+}/Fe^{3+} at the surface creating a barrier for Li^+ transport across the electrolyte/electrode interface. To improve the capacity retention, some researchers have optimized the synthesis of TMHCFs to reduce defects and vacancies on their surfaces and in the bulk of the material [NPL15, NPL16]. These defect-free TMHCFs demonstrated a longer cycle life.

Citation List

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Summary of Invention

Technical Problem

- [0007] However, defects and vacancies in TMCM electrode also likely appear during the charge and discharge cycles of a battery, and they are impossible to prevent by synthesis.
- [0008] Transition metal cyanometallate (TMCM) electrodes in metal-ion batteries have demonstrated good performance, as indicated by high energy density, high power density, and low cost. However, defects and vacancies produced in the TMCM

electrodes cause structural degradation, which limits their cycle life.

Solution to Problem

- [0009] Disclosed herein are electrolyte additives that can interact and coordinate metal ions around these defects and vacancies to support the structures of the TMCM, enabling a longer cycle lifetime.
- [0010] Accordingly, a method is provided for the self-repair of a TMCM battery electrode. The battery is made from a TMCM cathode, an anode, and an electrolyte including a solution made up of a solvent and an alkali or alkaline earth salt. The electrolyte also includes an additive represented as G-R-g:
- [0011] where G and g are independently selected from materials that include the elements of nitrogen (N) sulfur (S), and oxygen (O), or combinations of the above-recited elements; and,
- [0012] where R is an alkene or alkane group.
- [0013] In response to charging and discharging the battery in a plurality of cycles, the method creates vacancies in a surface of the TMCM cathode. Then, the method fills the vacancies in the surface of the TMCM cathode with the electrolyte additive.
- [0014] The solvent may be water, carbonates, furan, oxane, ether, ketone, ester, amide, acetate, siloxane, or combinations thereof. Some examples of the salt include A_xCl , A_xSO_4 , A_xNO_3 , A_xPO_4 , A_xBr , A_xI , A_xAlO_2 , A_xAc (acetate), A_xPF_6 , A_xBF_6 , A_xClO_4 , A_xAsF_6 , A_xAlCl_4 , $A_xB_5Cl_5$, $A_xCF_3SO_3$, $A_x(CF_3SO_2)_2N$, and $A_x(C_2F_5SO_2)_2N$, where “A” is either an alkali or alkaline earth element. In one aspect, the R alkene/alkane may be formed with a substitution such as oxygen, silicon, fluorine, chlorine, phosphorus, aluminum, arsenic, selenium, bromine, or combinations thereof. In another aspect, G and g are independently selected from an alkene or alkane group.
- [0015] The TMCM cathode is expressed by the formula $B_nM1_pM2_q(CN)_r \cdot fH_2O$;
- [0016] where B is an alkali or alkaline earth metal;
- [0017] where M1 and M2 are independently selected from transition metals;
- [0018] where n is in a range of 0 to 2;
- [0019] where p is less than or equal to 2;
- [0020] where f is in a range of 0 to 20;
- [0021] where q is less than or equal to 2; and,
- [0022] where r is less than or equal to 6.
- [0023] The anode can be made from carbonaceous materials, alkali metals, alkaline earth metals, alloys including tin, alloys including lead, alloys including silicon, alloys including phosphorous, alloys including germanium, titanates including alkali metals, titanates including alkaline earth metals, or combinations thereof.
- [0024] Additional details of the above-described method, an electrolyte with additives, and a

battery made with the above-mentioned electrolyte are presented below.

Advantageous Effects of Invention

[0025] It would be advantageous if additives could be included in an electrolyte that would interact and coordinate with surface of TMCM electrodes, to cure and reduce the defects and undercoordinated metal-ions, and to improve the cycle lifetime.

Brief Description of Drawings

[0026] [fig.1]Fig. 1 is a partial cross-sectional view of an electrolyte for use in a battery with transition metal cyanometallate (TMCM) electrodes.

[fig.2]Fig. 2 is a partial cross-sectional view of a TMCM electrode battery.

[fig.3A]Fig. 3A depicts a fresh TMCM electrode immersed in an electrolyte containing additives.

[fig.3B]Fig. 3B depicts additives interacting or coordinating with defects on the surface of TMCM electrode to stabilize its structure.

[fig.4A]Fig. 4A is an example of a Prussian White (PW, $\text{Na}_2\text{Fe}_2(\text{CN})_6$) electrode where no electrolyte additive has been used, showing capacity vs. cycles.

[fig.4B]Fig. 4B is an example of a Prussian White (PW, $\text{Na}_2\text{Fe}_2(\text{CN})_6$) electrode where no electrolyte additive has been used, showing capacity vs. voltage.

[fig.5A]Fig. 5A is an example of the PW electrode where any electrolyte additive has been used, showing capacity vs. cycles .

[fig.5B]Fig. 5B is an example of the PW electrode where any electrolyte additive has been used, showing capacity vs. voltage.

[fig.6]Fig. 6 is a graph comparing the PW electrodes, with and without the ADN additive.

[fig.7]Fig. 7 is a flowchart illustrating a method for self-repairing a TMCM battery electrode.

Description of Embodiments

[0027] Fig. 1 is a partial cross-sectional view of an electrolyte for use in a battery with transition metal cyanometallate (TMCM) electrodes. The electrolyte 100 comprises a solution 102 including a solvent 104 and a salt that can be either an alkali or alkaline earth salt. The salt is represented using reference designator 106. The electrolyte 100 also includes an additive, represented with reference designator 108, comprising G-R-g:

[0028] where G and g are independently selected from a group of materials that include the element of nitrogen (N) sulfur (S), oxygen (O), or combinations of the above-recited elements.

[0029] Typically $G \neq g$. However, in some cases they are the same, such as is the case where $G = g = \text{adiponitrile}$.

- [0030] R is an alkene or alkane group. The term “independently selected” means that an element selected for G may, or may not be an element selected for g.
- [0031] The solvent 104 may be water, carbonates, furan, oxane, ether, ketone, ester, amide, acetate, siloxane, or combinations thereof. Some explicit examples of the salt 106 include A_xCl , A_xSO_4 , A_xNO_3 , A_xPO_4 , A_xBr , A_xI , A_xAlO_2 , A_xAc (acetate), A_xPF_6 , A_xBF_6 , A_xClO_4 , A_xAsF_6 , A_xAlCl_4 , $A_xB_5Cl_5$, $A_xCF_3SO_3$, $A_x(CF_3SO_2)_2N$, and $A_x(C_2F_5SO_2)_2N$, where “A” is an alkali or alkaline earth element.
- [0032] In one aspect, the R alkene or alkane includes a substitution such as oxygen, silicon, fluorine, chlorine, phosphorus, aluminum, arsenic, selenium, bromine, or combinations thereof. For example, if R is the alkene chain $-CH_2-CH_2-CH_2-$, in some cases, some part of R can be substituted with F to form $-CHF-CH_2-CH_2-$, with O to form $-CH_2-O-CH_2-$, or with Cl to form $-CH_2-CH_2-CCl_2-$.
- [0033] In one aspect, G and g are independently selected from an alkene or alkane group. In other words, if G is an alkene, then g may be either an alkene or an alkane. Likewise, if G is an alkane, then g may be either an alkene or an alkane. As noted above, G and g may not be the same material. However, R may be the same as either G or g. The percentage by weight (wt%) of additive 108 to solution 102 is in a range of 0.1 to 50 wt%.
- [0034] Fig. 2 is a partial cross-sectional view of a TCM electrode battery. The battery 200 comprises a TCM cathode 202 and an anode 204. In some aspects as shown, an ion-permeable barrier 206 may separate the cathode 202 from the anode 204. An electrolyte, as described above in the explanation of Fig. 1, comprises a solution 102 including a solvent 104 and either an alkali or alkaline earth metal salt 106. The electrolyte also includes additives 108, comprising G-R-g:
- [0035] where G and g are independently selected from a group of materials including the element of nitrogen (N) sulfur (S), oxygen (O), or combinations of the above-recited elements; and,
- [0036] where R is an alkene or alkane group.
- [0037] The solvent 104 may be water, carbonates, furan, oxane, ether, ketone, ester, amide, acetate, siloxane, or combinations thereof. Some explicit examples of the salt 106 include A_xCl , A_xSO_4 , A_xNO_3 , A_xPO_4 , A_xBr , A_xI , A_xAlO_2 , A_xAc (acetate), A_xPF_6 , A_xBF_6 , A_xClO_4 , A_xAsF_6 , A_xAlCl_4 , $A_xB_5Cl_5$, $A_xCF_3SO_3$, $A_x(CF_3SO_2)_2N$, and $A_x(C_2F_5SO_2)_2N$, where “A” is an alkali or alkaline earth element.
- [0038] In one aspect, the R alkene or alkane includes a substitution such as oxygen, silicon, fluorine, chlorine, phosphorus, aluminum, arsenic, selenium, bromine, or combinations thereof. In another aspect, G and g are independently selected as alkanes or alkenes. As noted above, G and g may not be the same material, but R may be the same as either G or g. The percentage by weight (wt%) of additive 108 to solution 102 is in a range of

0.1 to 50 wt%.

[0039] The TMCM cathode 202 is expressed by the formula $B_nM1_pM2_q(CN)_r \cdot fH_2O$;

[0040] where B is a first group of metals that may, for example, be an alkali or alkaline earth metal;

[0041] where M1 and M2 are independently selected from a second group of transition metals;

[0042] where n is in a range of 0 to 2;

[0043] where p is less than or equal to 2;

[0044] where f is in a range of 0 to 20;

[0045] where q is less than or equal to 2; and,

[0046] where r is less than or equal to 6.

[0047] Some examples from the first group of metals include lithium (Li), sodium (Na), potassium (K), rubidium (Rb), cesium (Cs), calcium (Ca), strontium (Sr), barium (Ba), silver (Ag), aluminum (Al), magnesium (Mg), and combinations thereof.

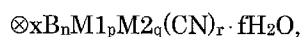
[0048] M1 and M2 are each independently selected from the second group of metals that includes titanium (Ti), vanadium (V), chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), niobium (Nb), ruthenium (Ru), tin (Sn), indium (In), cadmium (Cd), calcium (Ca), magnesium (Mg), strontium (Sr), and barium (Ba). M1 and M2 may, or may not be the same metal.

[0049] The anode 204 can be made from carbonaceous materials, alkali metals, alkaline earth metals, alloys including tin, alloys including lead, alloys including silicon, alloys including phosphorous, alloys including germanium, titanates including alkali metals, titanates including alkaline earth metals, or combinations thereof.

[0050] Fig. 3A depicts a fresh TMCM electrode immersed in an electrolyte containing additives. Fig. 3B depicts additives interacting or coordinating with defects on the surface of TMCM electrode to stabilize its structure. During charge and discharge of the battery, mobile ions 300

($\otimes$)

can “rock” back and forth between TMCM electrode 202, depicted as



and the counter electrode (not shown). Metal cyanide vacancies or transition metal defects 302 occur, and undercoordinated metal ions 306 appear in TMCM, especially near the surface, making the cathode unstable. In its charged state the B-ions are completely removed from the TMCM and its framework may collapse, starting from the surface, due to the lack of supporting B-ions. Consequently, the cycle life becomes an issue in rechargeable batteries with a TMCM electrode. In addition, undercoordinated metal ions can impede the charge transfer across the interface between the

electrode and electrolyte because of charge repulsion between undercoordinated metal ions and B-ions.

- [0051] In order to stabilize the TMCM electrode 202 and reduce defects/vacancies 302 on its surface, an additive 108, G-R-g, is added into the electrolyte 100. G and g represent groups containing nitorogen (N), and/or sulfur (S), and/or oxygen (O). R is an alkene or alkane group that may be fluoridized. G and g interact or coordinate with transition-metal ions near the cathode surface 304 to stabilize the structure of TMCM electrode 202. The groups also can connect with the undercoordinated metal ions on the surface to reduce their repulsion to B-ions. Fig. 3B depicts the surface modification of TMCM electrode 202 with additives 108 in the electrolyte 100.
- [0052] Figs. 4A and 4B are an example of a Prussian White (PW, $\text{Na}_2\text{Fe}_2(\text{CN})_6$) electrode where no electrolyte additive has been used, respectively showing capacity vs. cycles, and capacity vs. voltage. With an electrolyte of ethylene carbonate (EC) / diethyl carbonate (DEC) containing NaClO_4 , the performance of PW electrode with a sodium-metal counter electrode is shown. In the first cycle PW electrode delivered a capacity of ~ 120 mAh/g, and then it faded to 84 mAh/g in 90 cycles.
- [0053] Figs. 5A and 5B are an example of the PW electrode where any electrolyte additive has been used, respectively showing capacity vs. cycles, and capacity vs. voltage. To improve performance, adiponitrile (ADN) was used as an additive in the electrolyte of EC/DEC and NaCl_4 . The lone pair electrons in nitrogen interact with d-orbitals of Fe so that the ADN chains can fill up the defects/vacancies to stabilize the PW structure. The ADN additive did not cause a significant difference in the PW electrode charge/discharge profiles and its initial capacity, but improved its cycling performance remarkably as shown.
- [0054] Fig. 6 is a graph comparing the PW electrodes, with and without the ADN additive. In 90 cycles, the PW electrode with ADN additive retained 92.6% of its initial capacity. Under the same conditions, just 70.1% of initial capacity was retained in PW electrode without ADN. In conclusion, ADN stabilized the structure of PW electrode and improved its cycle life.
- [0055] Fig. 7 is a flowchart illustrating a method for self-repairing a TMCM battery electrode. Although the method is depicted as a sequence of numbered steps for clarity, the numbering does not necessarily dictate the order of the steps. It should be understood that some of these steps may be skipped, performed in parallel, or performed without the requirement of maintaining a strict order of sequence. Generally however, the method follows the numeric order of the depicted steps. The method starts at Step 700.
- [0056] Step 702 provides a battery comprising a TMCM cathode, an anode, and an electrolyte. The electrolyte includes a solution comprising a solvent, an alkali or

alkaline earth salt, and an additive comprising G-R-g:

[0057] where G and g are independently selected from a group of materials including the element of nitrogen (N) sulfur (S), oxygen (O), and combinations of the above-recited elements; and,

[0058] where R is an alkene or alkane group.

[0059] As is well known in the art, an alkene is an unsaturated, aliphatic hydrocarbon with one or more carbon-carbon double bonds. An alkane is a saturated hydrocarbon, consisting of only hydrogen and carbon atoms, with single bonds. In one aspect, the percentage by weight of additive to solution is in the range of 0.1 to 50 wt%. Generally, the battery provided in Step 702 is as described above in the explanation of Fig. 2, above. In response to charging and discharging the battery in a plurality of cycles, Step 704 creates vacancies and defects in a surface of the TMCM cathode. Typically, the battery is discharged by connecting an external load between the anode and cathode. Likewise, the battery is charged by interposing an external power supply between the anode and cathode, to reverse the direction of current flow exhibited during the discharge cycle. Step 706 fills the vacancies and defects in the surface of the TMCM cathode with the electrolyte additive.

[0060] Some examples of solvents include water, carbonates, furan, oxane, ether, ketone, ester, amide, acetate, siloxane, and combinations thereof. Some examples of salts include A_xCl , A_xSO_4 , A_xNO_3 , A_xPO_4 , A_xBr , A_xI , A_xAlO_2 , A_xAc (acetate), A_xPF_6 , A_xBF_6 , A_xClO_4 , A_xAsF_6 , A_xAlCl_4 , $A_xB_5Cl_5$, $A_xCF_3SO_3$, $A_x(CF_3SO_2)_2N$, and $A_x(C_2F_5SO_2)_2N$, where "A" is either an alkali or alkaline earth elements.

[0061] In one aspect, the R alkene may include one of the following substitutions: oxygen, silicon, fluorine, chlorine, phosphorus, aluminum, arsenic, selenium, bromine, and combinations thereof. In another aspect, G and g are independently either an alkene or alkane. Note: the examples listed above are not an exhaustive list of materials.

[0062] An electrolyte has been provided with an additive useful in the self-repair of TMCM battery electrodes. Examples of particular materials have been presented to illustrate the invention. However, the invention is not limited to merely these examples. Other variations and embodiments of the invention will occur to those skilled in the art.

[0063] All applications described below are incorporated herein by reference: (1) hard carbon composite for alkali metal-ion batteries, invented by Yuhao Lu et al, Serial No. 62/009,069, filed June 6, 2014, attorney docket No. SLA3416P; (2) METAL CYANOMETALLATE synthesis method, invented by Long Wang et al, Serial No. 62/008,869, filed June 6, 2014, attorney docket No. SLA3430P; (3) RECHARGEABLE METAL-ION BATTERY WITH NON-AQUEOUS HYBRID ION ELECTROLYTE, invented by Long Wang et al, Serial No. 14/271,498, filed May 7, 2014, attorney docket No. SLA3388; (4) REACTIVE SEPARATOR FOR A

METAL-ION BATTERY, invented by Long Wang et al, Serial No. 14/230,882, filed March 31, 2014, attorney docket No. SLA3370; (5) NASICON-POLYMER ELECTROLYTE STRUCTURE, invented by Long Wang et al, Serial No. 14/198,755, filed March 6, 2014, attorney docket No. SLA3367; (6) BATTERY WITH an anode preloaded with consumable metals, invented by Yuhao Lu et al, Serial No. 14/198,702, filed March 6, 2014, attorney docket No. SLA3364; (7) BATTERY ANODE WITH PRELOADED METALS, invented by Long Wang et al, Serial No. 14/198,663, filed March 6, 2014, attorney docket No. SLA3363; (8) METAL BATTERY ELECTRODE WITH PYROLYZED COATING, invented by Yuhao Lu et al, Serial No. 14/193,782, filed February 28, 2014, attorney docket No. SLA3353; (9) METAL HEXA-CYANOMETALLATE ELECTRODE WITH SHIELD STRUCTURE, invented by Yuhao Lu et al, Serial No. 14/193,501, filed February 28, 2014, attorney docket No. SLA3352; (10) Cyanometallate Cathode Battery and Method for Fabrication, invented by Yuhao Lu et al, Serial No. 14/174,171, filed February 6, 2014, attorney docket No. SLA3351; (11) SODIUM IRON(II)-HEXACYANOFERRATE(II) BATTERY ELECTRODE AND SYNTHESIS METHOD, invented by Yuhao Lu et al, Serial No. 14/067,038, filed October 30, 2013, attorney docket No. SLA3315; (12) TRANSITION Metal HexacyanoMETALLATE-CONDUCTIVE POLYMER COMPOSITE, invented by Sean Vail et al., Serial No. 14/059,599, filed October 22, 2013, attorney docket No. SLA3336; (13) Metal-Doped Transition Metal Hexacyanoferrate (TMHCF) Battery Electrode, invented by Yuhao Lu et al., Serial No. 13/907,892, filed June 1, 2013, attorney docket No. SLA3287; (14) HEXA-CYANOFERRATE BATTERY ELECTRODE MODIFIED WITH FERRO-CYANIDES OR FERRICYANIDES, invented by Yuhao Lu et al., Serial No. 13/897,492, filed May 20, 2013, attorney docket No. SLA3286; (15) PROTECTED TRANSITION METAL HEXACYANOFERRATE BATTERY ELECTRODE, invented by Yuhao Lu et al., Serial No. 13/872,673, filed April 29, 2013, attorney docket No. SLA3285; (16) TRANSITION METAL HEXACYANOFERRATE BATTERY CATHODE WITH SINGLE PLATEAU CHARGE/DISCHARGE CURVE, invented by Yuhao Lu et al., Serial No. 13/752,930, filed January 29, 2013, attorney docket No. SLA3265; (17) SUPERCAPACITOR WITH HEXA-CYANOMETALLATE CATHODE, ACTIVATED CARBON ANODE, AND AQUEOUS ELECTROLYTE, invented by Yuhao Lu et al., Serial No. 13/603,322, filed September 4, 2012, attorney docket No. SLA3212; (18) IMPROVEMENT OF ELECTRON TRANSPORT IN HEXACYANOMETALLATE ELECTRODE FOR ELECTROCHEMICAL APPLICATIONS, invented by Yuhao Lu et al., Serial No. 13/523,694, filed June 14, 2012, attorney docket No. SLA3152; (19) ALKALI AND ALKALINE-EARTH ION BATTERIES WITH HEXACYANOMETALLATE

CATHODE AND NON-METAL ANODE, invented by Yuhao Lu et al., Serial No. 13/449,195, filed April 17, 2012, attorney docket no. SLA3151; (20) Electrode Forming Process for Metal-Ion Battery with Hexacyanometallate Electrode, invented by Yuhao Lu et al., Serial No. 13/432,993, filed March 28, 2012, attorney docket no. SLA3146. All these applications are incorporated herein by reference.

Claims

- [Claim 1] An electrolyte for use in a battery with transition metal cyanometallate (TMCM) electrodes, the electrolyte comprising:
a solution including a solvent and a salt selected from a group consisting of alkali and alkaline earth salts;
an additive comprising G-R-g;
where G and g are independently selected from a group of materials including an element of nitrogen (N) sulfur (S), oxygen (O), and combinations of the above-recited elements; and,
where R is selected from a group consisting of an alkene and an alkane.
- [Claim 2] The electrolyte of claim 1 wherein the solvent is selected from a group consisting of water, carbonates, furan, oxane, ether, ketone, ester, amide, acetate, siloxane, and combinations thereof.
- [Claim 3] The electrolyte according to one of claims 1 or 2 wherein the salt is selected from a group consisting of A_xCl , A_xSO_4 , A_xNO_3 , A_xPO_4 , A_xBr , A_xI , A_xAlO_2 , A_xAc (acetate), A_xPF_6 , A_xBF_6 , A_xClO_4 , A_xAsF_6 , A_xAlCl_4 , $A_xB_5Cl_5$, $A_xCF_3SO_3$, $A_x(CF_3SO_2)_2N$, and $A_x(C_2F_5SO_2)_2N$, where “A” is selected a group consisting of alkali and alkaline earth elements.
- [Claim 4] The electrolyte according to one of claims 1 to 3 wherein R includes substitutions selected from a group consisting of oxygen, silicon, fluorine, chlorine, phosphorus, aluminum, arsenic, selenium, bromine, and combinations thereof.
- [Claim 5] The electrolyte according to any one of claims 1 to 4 wherein G and g independently selected from a group consisting of an alkane and an alkene.
- [Claim 6] The electrolyte according to any one of claims 1 to 5 wherein the percentage by weight (wt%) of additive to solution is in a range of 0.1 to 50 wt%.
- [Claim 7] A transition metal cyanometallate (TMCM) electrode battery comprising:
a TMCM cathode;
an anode;
an electrolyte comprising:
a solution including a solvent and a salt selected from a group consisting of alkali and alkaline earth metals;
an additive comprising G-R-g;
where G and g are independently selected from a group of materials

- including an element of nitrogen (N) sulfur (S), oxygen (O), and combinations of the above-recited elements; and,
 where R is selected from a group consisting of an alkene and an alkane.
- [Claim 8] The battery of claim 7 wherein the solvent is selected from a group consisting of water, carbonates, furan, oxane, ether, ketone, ester, amide, acetate, siloxane, and combinations thereof.
- [Claim 9] The battery according to one of claims 7 or 8 wherein the salt is selected from a group consisting of A_xCl , A_xSO_4 , A_xNO_3 , A_xPO_4 , A_xBr , A_xI , A_xAlO_2 , A_xAc (acetate), A_xPF_6 , A_xBF_6 , A_xClO_4 , A_xAsF_6 , A_xAlCl_4 , $A_xB_5Cl_5$, $A_xCF_3SO_3$, $A_x(CF_3SO_2)_2N$, and $A_x(C_2F_5SO_2)_2N$, where “A” is selected a group consisting of alkali and alkaline earth elements.
- [Claim 10] The battery according to any one of claims 7 to 9 wherein R includes substitutions selected from a group consisting of oxygen, silicon, fluorine, chlorine, phosphorus, aluminum, arsenic, selenium, bromine, and combinations thereof.
- [Claim 11] The battery according to any one of claims 7 to 10 wherein G and g independently selected from a group consisting of an alkane and an alkene.
- [Claim 12] The battery according to any one of claims 7 to 11 wherein the percentage by weight (wt%) of additive to solution is in a range of 0.1 to 50 wt%.
- [Claim 13] The battery according to any one of claims 7 to 12 wherein the TMCM cathode is expressed by the formula $B_nM1_pM2_q(CN)_r \cdot fH_2O$;
 where B is selected from a first group of metals selected from a group including alkali and alkaline earth metals;
 where M1 and M2 are independently selected from a second group of transition metals;
 where n is in a range of 0 to 2;
 where p is less than or equal to 2;
 where f is in a range of 0 to 20;
 where q is less than or equal to 2; and,
 where r is less than or equal to 6.
- [Claim 14] The battery of claim 13 wherein the first group of metals includes lithium (Li), sodium (Na), potassium (K), rubidium (Rb), cesium (Cs), calcium (Ca), strontium (Sr), barium (Ba), silver (Ag), aluminum (Al), magnesium (Mg), and combinations thereof.
- [Claim 15] The battery according to one of claims 13 or 14 wherein M1 and M2 are each independently selected from the second group of metals

consisting of titanium (Ti), vanadium (V), chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), niobium (Nb), ruthenium (Ru), tin (Sn), indium (In), cadmium (Cd), calcium (Ca), magnesium (Mg), strontium (Sr), and barium (Ba).

[Claim 16] The battery according to any one of claim 7 to 15 wherein the anode is made from a material selected from a group consisting of carbonaceous materials, alkali metals, alkaline earth metals, alloys including tin, alloys including lead, alloys including silicon, alloys including phosphorous, alloys including germanium, titanates including alkali metals, titanates including alkaline earth metals, and combinations thereof.

[Claim 17] A method for self-repairing a transition metal cyanometallate (TMCM) battery electrode, the method comprising:
 providing a battery comprising a TMCM cathode, an anode, and an electrolyte including solution comprising a solvent, a salt selected from a group consisting of alkali and alkaline earth salts, and an additive comprising G-R-g;
 where G and g are independently selected from a group of materials including an element of nitrogen (N) sulfur (S), oxygen (O), and combinations of the above-recited elements;
 where R is selected from a group consisting of an alkene and an alkane;
 in response to charging and discharging the battery in a plurality of cycles, creating vacancies in a surface of the TMCM cathode; and,
 filling the vacancies in the surface of the TMCM cathode with the electrolyte additive.

[Claim 18] The method of claim 17 wherein the solvent is selected from a group consisting of water, carbonates, furan, oxane, ether, ketone, ester, amide, acetate, siloxane, and combinations thereof.

[Claim 19] The method according to one of claims 17 or 18 wherein the salt is selected from a group consisting of A_xCl , A_xSO_4 , A_xNO_3 , A_xPO_4 , A_xBr , A_xI , A_xAlO_2 , A_xAc (acetate), A_xPF_6 , A_xBF_6 , A_xClO_4 , A_xAsF_6 , A_xAlCl_4 , $A_xB_5Cl_5$, $A_xCF_3SO_3$, $A_x(CF_3SO_2)_2N$, and $A_x(C_2F_5SO_2)_2N$, where “A” is selected a group consisting of alkali and alkaline earth elements.

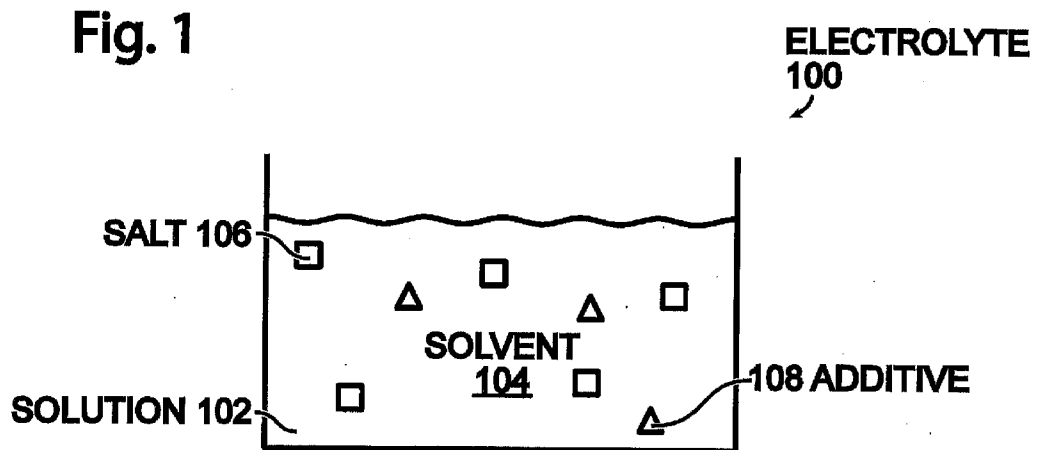
[Claim 20] The method according to any one of claims 17 to 19 wherein R includes substitutions selected from a group consisting of oxygen, silicon, fluorine, chlorine, phosphorus, aluminum, arsenic, selenium, bromine, and combinations thereof.

[Claim 21] The method according to any one of claims 17 to 20 wherein G and g

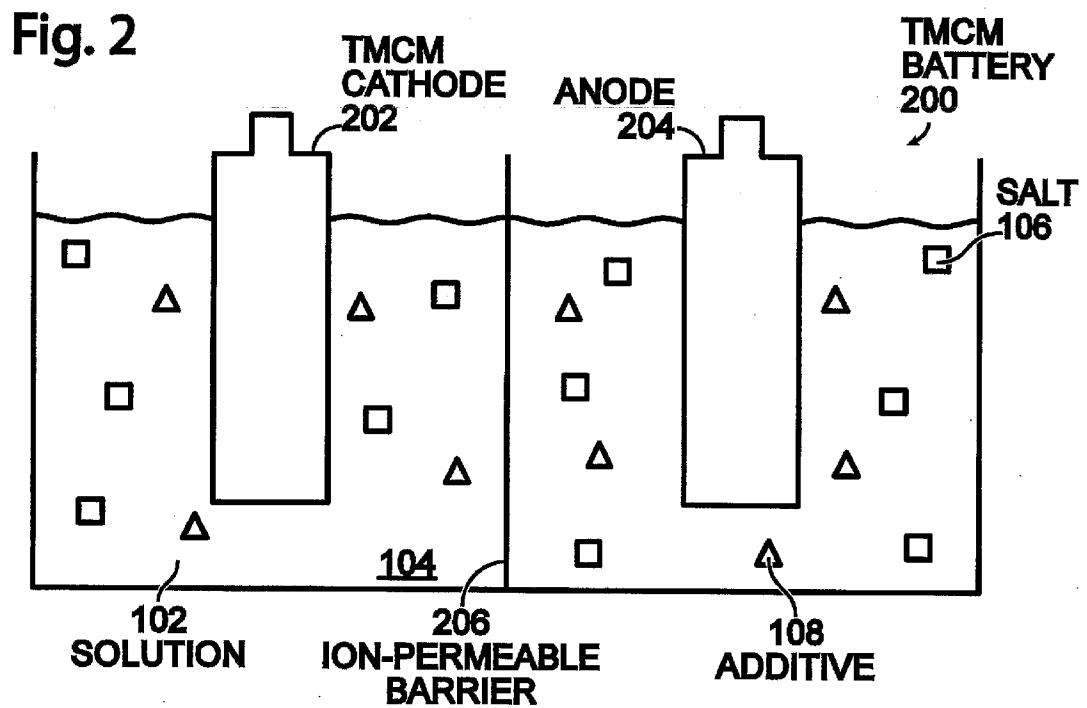
[Claim 22]

independently selected from a group consisting of alkanes and alkenes.
The method according to any one of claims 17 to 21 wherein the percentage by weight (wt%) of additive to solution is in a range of 0.1 to 50 wt%.

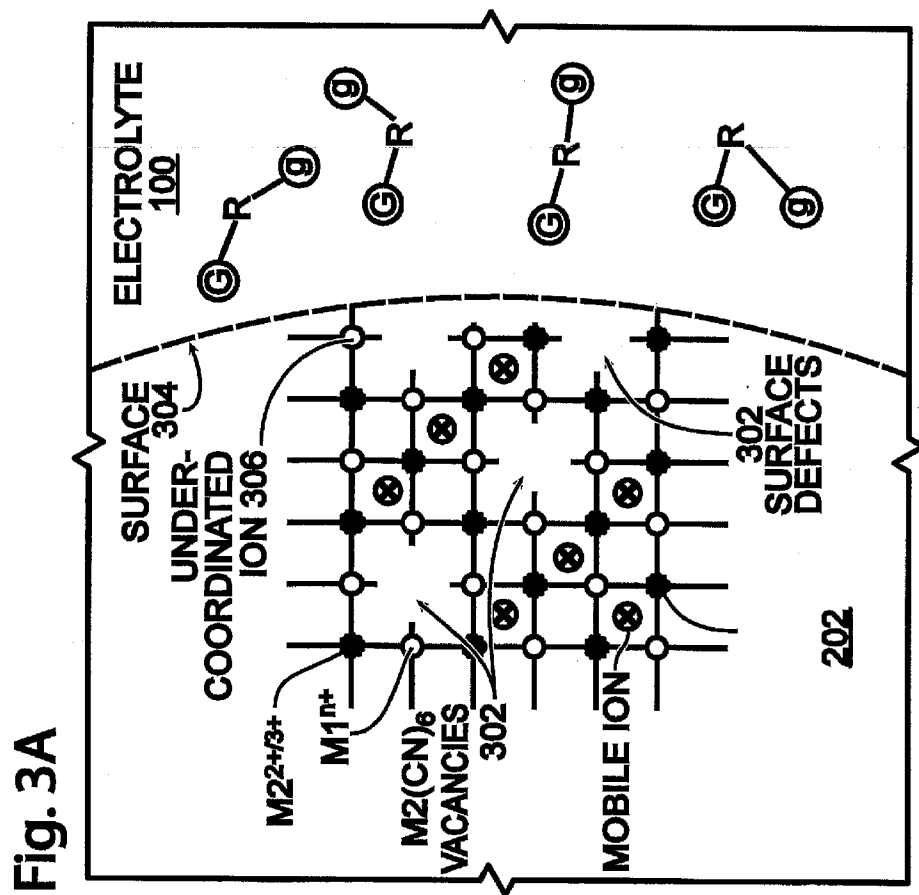
[Fig. 1]



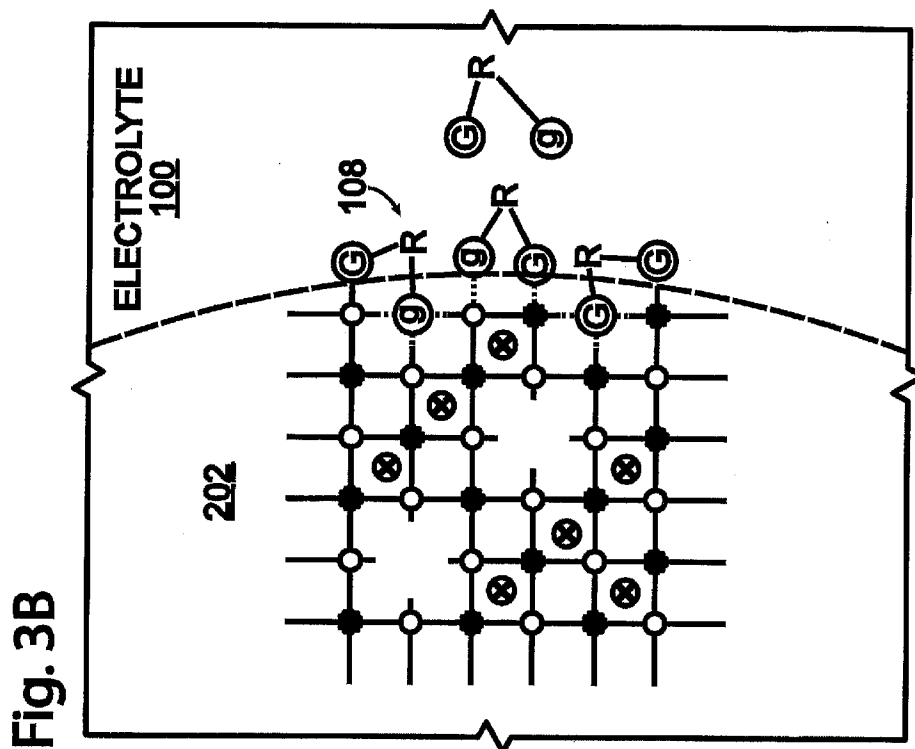
[Fig. 2]



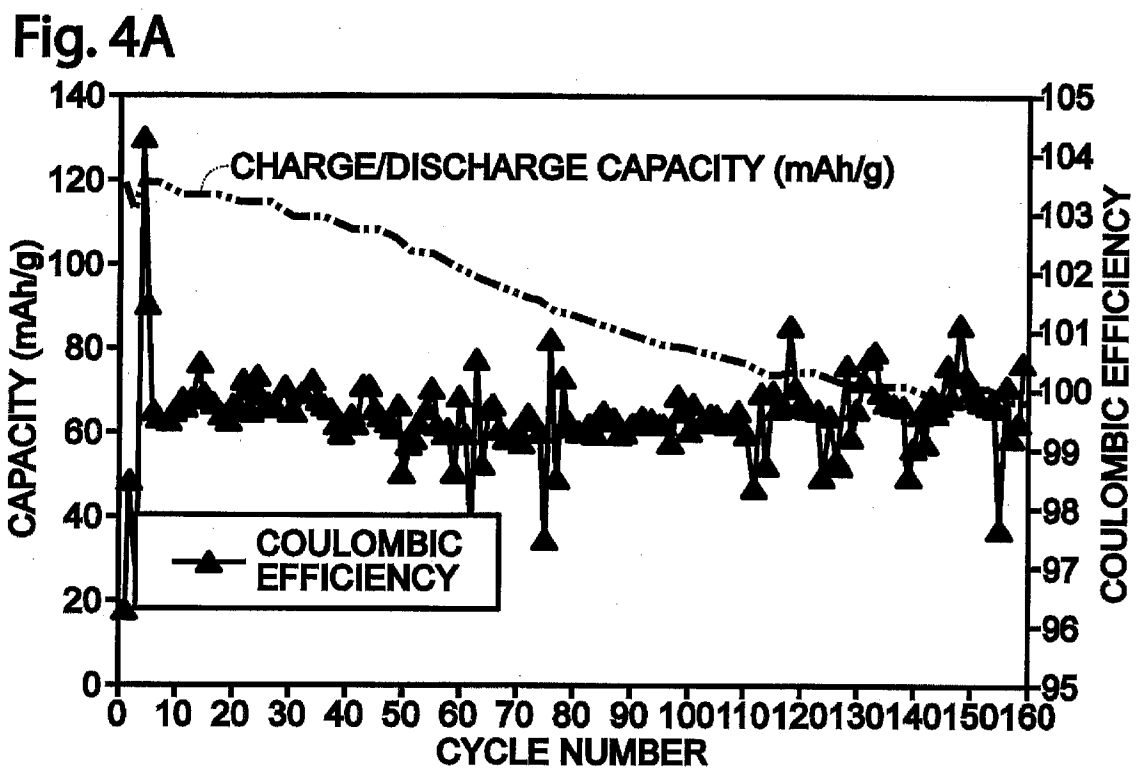
[Fig. 3A]



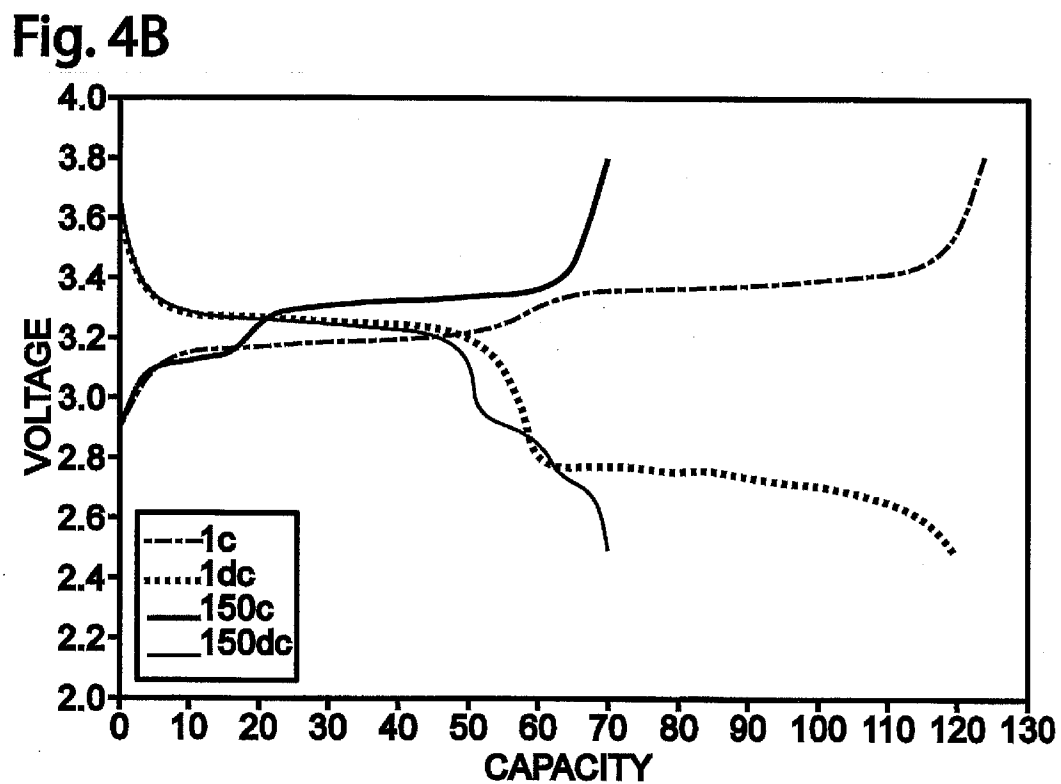
[Fig. 3B]



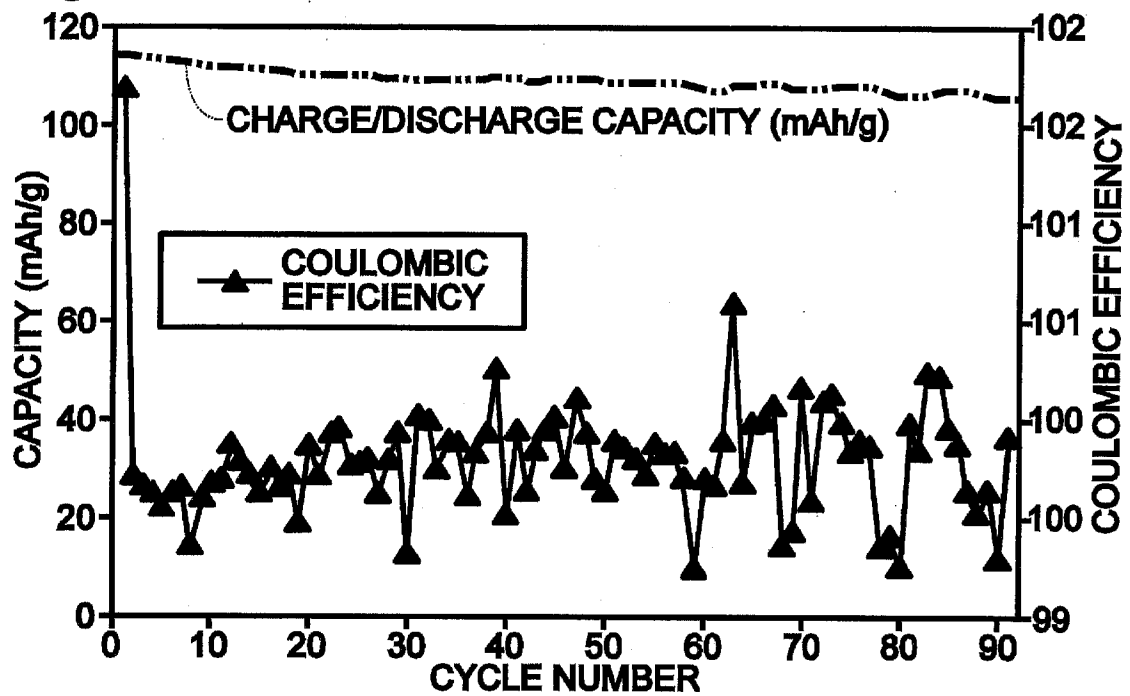
[Fig. 4A]



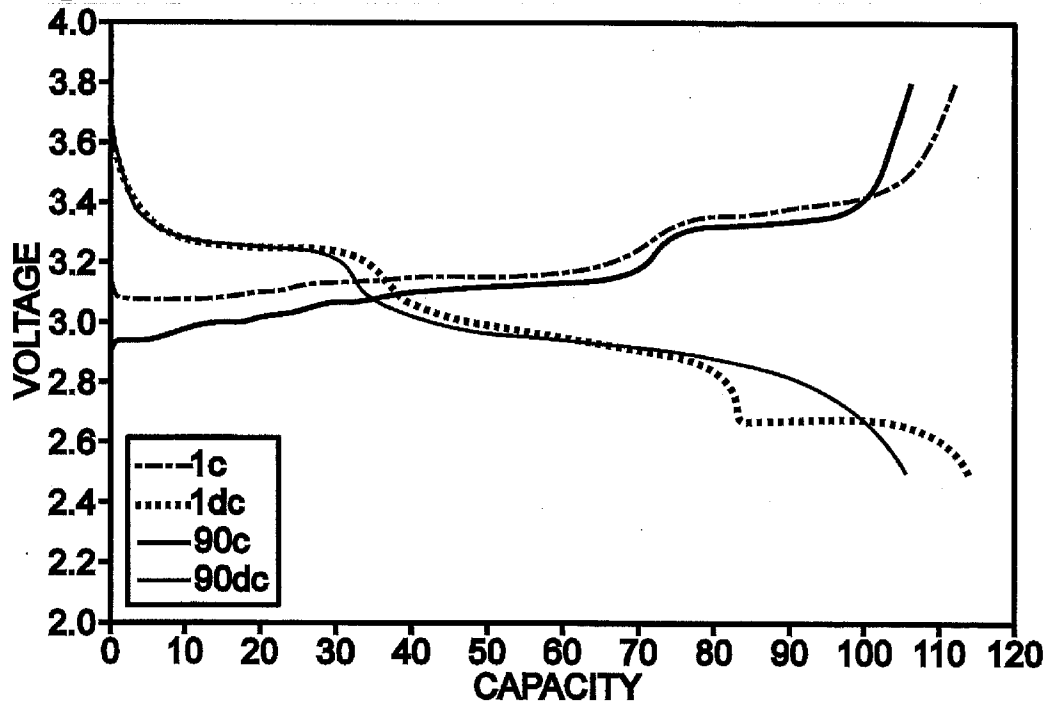
[Fig. 4B]



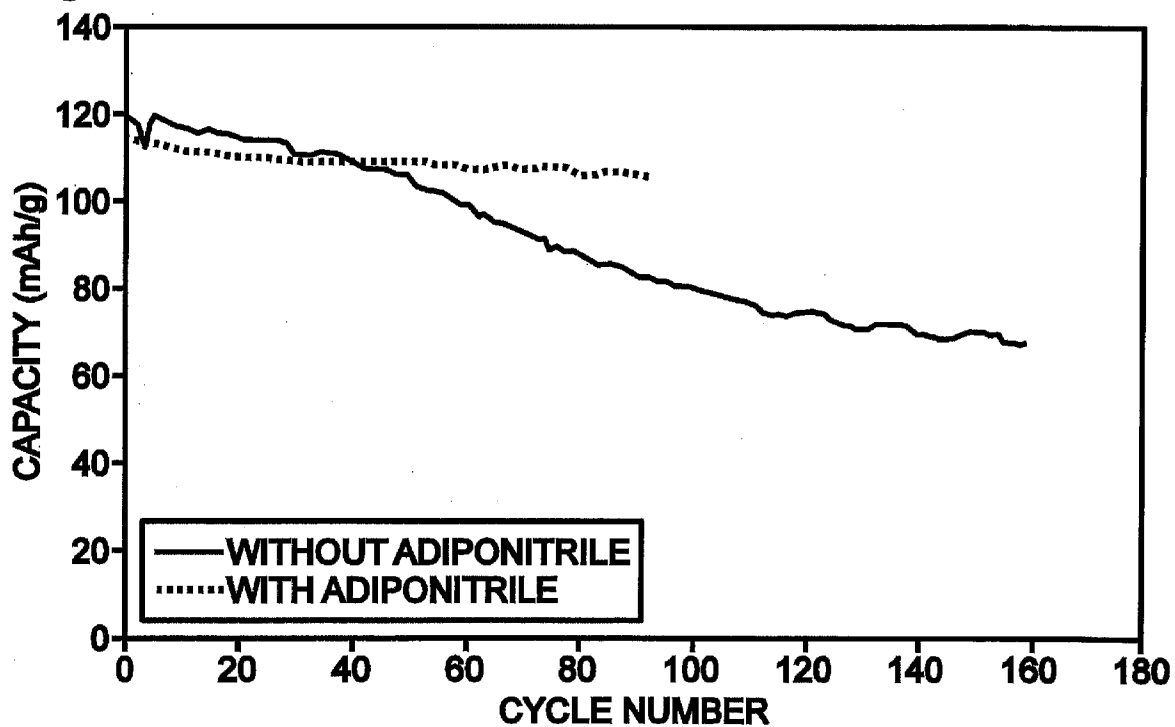
[Fig. 5A]

Fig. 5A

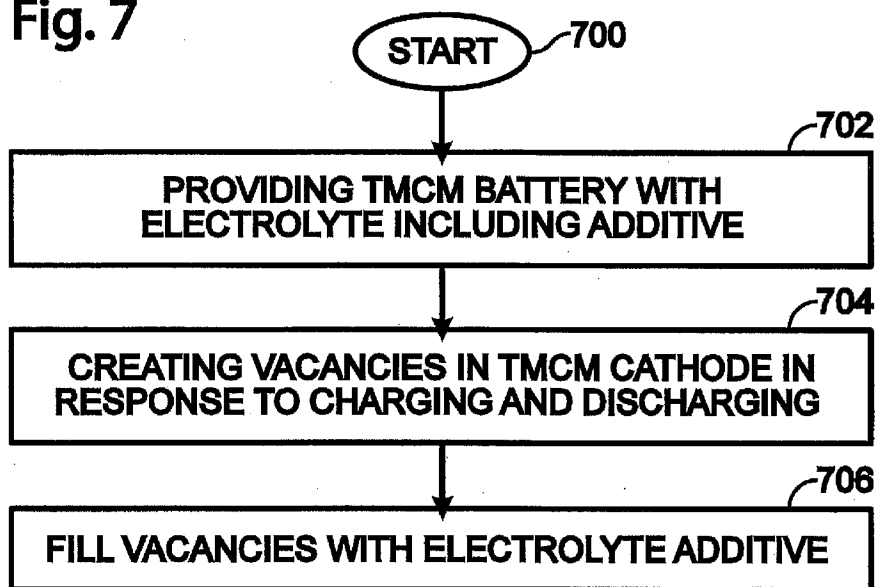
[Fig. 5B]

Fig. 5B

[Fig. 6]

Fig. 6

[Fig. 7]

Fig. 7

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2015/003261

A. CLASSIFICATION OF SUBJECT MATTER			
Int.Cl. H01M10/0567 (2010.01)i, H01M4/58 (2010.01)i, H01M10/054 (2010.01)i, H01M10/0568 (2010.01)i, H01M10/0569 (2010.01)i, H01M10/36 (2010.01)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)			
Int.Cl. H01M10/0567, H01M4/58, H01M10/054, H01M10/0568, H01M10/0569, H01M10/36			
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched			
Published examined utility model applications of Japan 1922-1996 Published unexamined utility model applications of Japan 1971-2015 Registered utility model specifications of Japan 1996-2015 Published registered utility model applications of Japan 1994-2015			
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)			
JSTPlus/JSTChina/JST7580 (JDreamIII), Science Direct			
C. DOCUMENTS CONSIDERED TO BE RELEVANT			
Category*	Citation of document, with indication, where appropriate, of the relevant passages		Relevant to claim No.
A	WO 2013/157660 A1 (SHARP KABUSHIKI KAISHA) 2013.10.24, WHOLE DOCUMENTS & JP 2015-515081 A & US 2013/0260222 A1 & CN 104247131 A		1-22
A	JP 2008-108586 A (HITACHI MAXELL, LTD.) 2008.05.08, WHOLE DOCUMENTS & US 2008/0102369 A1 & CN 102723526 A & KR 10-2014-0026591 A		1-22
☐ 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		Date of mailing of the international search report	
14.09.2015		29.09.2015	
Name and mailing address of the ISA/JP		Authorized officer	
Japan Patent Office		Chikako AOKI	
3-4-3, Kasumigaseki, Chiyoda-ku, Tokyo 100-8915, Japan		4X 9351	
		Telephone No. +81-3-3581-1101 Ext. 3477	