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(54) Title: ANODE COMPOSITIONS FOR SODIUM-ION BATTERIES AND METHODS OF MAKING SAME

(57) Abstract: A sodium-ion battery includes a cathode comprising sodium; and an anode composition comprising a material having the formula: $A_aB_bC_cD_dO$, where A is an alkali metal, alkaline earth metal, or a combination thereof, where B is titanium, C is vanadium, D is one or more transition metal element other than titanium or vanadium, $a + b + c + d \leq 1$, $a \geq 0$, $b + c > 0$, $b \geq 0$, $c \geq 0$, $d > 0$, and where the material comprises a ilmenite structure, triclinic $VFeO_4$ structure, cubic $Ca_5Co_4(VO_4)_6$ structure, dichromate structure, orthorhombic ∀-CoV_3O_8 structure, brannerite structure, thortveitite structure, orthorhombic ∃-$CrPO_4$ structure, or the pseudo rutile structure.

ANODE COMPOSITIONS FOR SODIUM-ION BATTERIES AND METHODS OF MAKING SAME

FIELD

The present disclosure relates to compositions useful as anodes for sodium-ion batteries and methods for preparing and using the same.

BACKGROUND

Various anode compositions have been introduced for use in secondary sodium-ion batteries. Such compositions are described, for example, in Jiang Wei Wang et,al, "Microstructural Evolution of Tin Nanoparticles during In Situ Sodium Insertion and Extraction", *Nano Letters*; Yunhua Xu et. Al, "Electrochemical Performance of Porous Carbon/Tin Composite Anodes for Sodium-Ion and Lithium-Ion Batteries", *Advanced Energy Materials*; Lifen Xiao et. al, "High capacity, reversible alloying reactions in SnSb/C nanocomposites for Na-ion battery applications", *Chem. Comm.* 48 (2012) 3321; U.S. Patent. Application Publication No. 2012/0199785; Tuan T. Tran et. al, "Alloy Negative Electrodes for High Energy Density Metal-Ion Cells", *J. Electrochem. Soc.* 158 (2011) A1411; V. L. Chevrier et al., "Challenges for Na-ion Negative Electrodes", *J. Electrochem. Soc.* 158 (2011) A1011, and Shanmugan et al., "Na2/3Ni1/3Ti2/3O2: "Bi-Functional" Electrode Materials for Na-Ion Batteries", *Electrochem. Lett., 3 (2014) A23.*

SUMMARY

In some embodiments, a sodium-ion battery is provided. The sodium-ion battery includes a cathode comprising sodium; and an anode composition comprising a material having the formula:

$$A_aB_bC_cD_dO, \qquad (I)$$

where A is an alkali metal, alkaline earth metal, or a combination thereof, where B is titanium, C is vanadium, D is one or more transition metal element other than titanium or vanadium, $a + b + c + d \leq 1$, $a \geq 0$, $b + c > 0$, $b \geq 0$, $c \geq 0$, $d > 0$, and where the material comprises a ilmenite structure, triclinic $VFeO_4$ structure, cubic $Ca_5Co_4(VO_4)_6$ structure, dichromate structure, orthorhombic $\forall$-CoV_3O_8 structure, brannerite structure, thortveitite structure, orthorhombic $\exists$-$CrPO_4$ structure, or the pseudo rutile structure.

In some embodiments, a sodium-ion battery is provided. The sodium-ion battery includes a cathode comprising sodium; and an anode composition comprising a material having the formula:

$$A'_eB'_fC'_gO, \qquad (II)$$

where A' is an alkali metal, alkaline earth metal, or a combination thereof, where B' is titanium, C' is vanadium, $e + f + g \leq 1$, $e \geq 0$, $f > 0$, and $g > 0$.

In some embodiments, a method of making a sodium-ion battery is provided. The method includes providing a cathode comprising sodium and an anode. The anode includes vanadium, titanium, or a combination thereof, and optionally an alkali metal or alkaline earth metal and optionally a transition metal other than titanium or vanadium. The method further includes incorporating the cathode and anode into a battery comprising an electrolyte that includes sodium.

In some embodiments, a sodium-ion battery is provided. The sodium-ion battery includes a cathode comprising sodium; and an anode composition comprising one or more materials selected from $CoTiO_3$, $Ca_5Co_4(VO_4)_6$, CoV_3O_8, $NiTiO_3$, $Co_2V_2O_7$ or MnV_2O_6.

The above summary of the present disclosure is not intended to describe each embodiment of the present invention. The details of one or more embodiments of the disclosure are also set forth in the description below. Other features, objects, and advantages of the invention will be apparent from the description and from the claims.

BRIEF DESCRIPTION OF THE DRAWINGS

The disclosure may be more completely understood in consideration of the following detailed description of various embodiments of the disclosure in connection with the accompanying figures, in which:

Figure 1 depicts an XRD pattern of a Fe_2TiO_5 material with a pseudobrookite structure;

Figure 2 depicts the voltage capacity curve of the Fe_2TiO_5 material of Figure 1;

Figure 3 depicts an XRD pattern of a $NiTiO_3$ material with an ilmenite structure.

Figure 4 shows the voltage capacity curve of the $NiTiO_3$ material of Figure 3.

Figures 5A shows the experimental XRD pattern of Example 2, and the known peak positions of $CoTiO_3$ indicated by diamonds (Powder Diffraction File (PDF)# 00-15-

0866); and Figure 5B shows the corresponding voltage curve for a cell made with the material of Example 2.

Figure 6A shows the experimental XRD pattern of Example 3, and the known peak positions of $VFeO_4$ indicated by diamonds (PDF# 00-38-1372); and Figure 6B shows the corresponding voltage curve for a cell made with the material of Example 3.

Figure 7A shows the experimental XRD pattern of Example 4, and the known peak positions of $Ca_5Co_4(VO_4)_6$ indicated by diamonds (PDF# 00-052-1884); and Figure 7B shows the corresponding voltage curve for a cell made with the material of Example 4.

Figure 8A shows the experimental XRD pattern of Example 5, and the known peak positions $Co_2V_2O_7$ indicated by diamonds (PDF# 00-038-0193); and Figure 8B shows the corresponding voltage curve for a cell made with the material of Example 5.

Figure 9A shows the experimental XRD pattern of Example 6, and the known peak positions CoV_3O_8 indicated by diamonds (PDF# 00-022-0598); and Figure 9B shows the corresponding voltage curve for a cell made with the material of Example 6.

Figure 10A shows the experimental XRD pattern of Example 7, and the known peak positions MnV_2O_6 indicated by diamonds (PDF# 00-35-0139); and Figure 10B shows the corresponding voltage curve for a cell made with the material of Example 7.

Figure 11A shows the experimental XRD pattern of Example 8, and the known peak positions $Mn_2V_2O_7$ indicated by diamonds (PDF# 00-073-1806); and Figure 11B shows the corresponding voltage curve for a cell made with the material of Example 8.

Figure 12A shows the experimental XRD pattern of Example 9, and the known peak positions $MnTiO_3$ indicated by diamonds (PDF# 00-089-3742); and Figure 12B shows the corresponding voltage curve for a cell made with the material of Example 9.

Figure 13A shows the experimental XRD pattern of Example 10, and the known peak positions $CrVO_4$ indicated by diamonds (PDF# 00-038-1376); and Figure 13B shows the corresponding voltage curve for a cell made with the material of Example 10.

Figure 14A shows the experimental XRD pattern of Example 11, and the known peak positions $TiVO_4$ indicated by diamonds (PDF# 00-077-0332); and Figure 14B shows the corresponding voltage curve for a cell made with the material of Example 11.

DETAILED DESCRIPTION

Sodium-ion batteries are of interest as a low-cost, high energy density battery chemistry for use in, for example, electric vehicles or stationary grid storage applications. Hard carbons have been suggested as suitable negative electrode materials for use in sodium-ion batteries. However, hard carbons have volumetric capacities of only about 450 Ah/L, or about less than two-thirds the volumetric capacity of graphite in a lithium-ion cell.

It has been shown that sodium can insert into metal oxides, such as CuO, at low voltages. However, such metal oxides typically undergo displacement (or conversion) reactions of the type:

$$2Na + CuO \rightarrow Cu + Na_2O$$

While these reactions are reversible, electrodes incorporating such metal oxides as an active anode material have had low efficiency and short cycle life.

It has also been shown that sodium can insert into titanates (e.g. $Na_2Ti_3O_7$), at low voltage. The mechanism for sodiation in this material is via a reversible intercalation mechanism. However, $Na_2Ti_3O_7$ is a white insulating powder, which is typical of titanates. Such materials do not function in an electrode unless ground to a small size and combined with a large amount of carbonaceous material (e.g., carbon black). As a result, electrodes made with such materials are thought to have low volumetric capacity. Consequently, negative electrode materials for use in sodium-ion batteries that are not associated with the above-described deficiencies are desirable.

Surprisingly, it has been discovered that certain transition metal titanates and vanadium oxides can operate as efficient negative electrodes for sodium ion batteries at low voltages without the need for large amounts of carbonaceous material. Specifically, it was discovered that certain transition metal titanates and vanadium oxides sodiate via highly reversible reactions.

Definitions

In this document:

the terms "sodiate" and "sodiation" refer to a process for adding sodium to an electrode material;

the terms "desodiate " and "desodiation" refer to a process for removing sodium from an electrode material;

the terms "charge" and "charging" refer to a process for providing electrochemical energy to a cell;

the terms "discharge" and "discharging" refer to a process for removing electrochemical energy from a cell, e.g., when using the cell to perform desired work;

the term "cathode" refers to an electrode (often called the positive electrode) where electrochemical reduction and sodiation occurs during a discharging process;

the term "anode" refers to an electrode (often called the negative electrode) where electrochemical oxidation and desodiation occurs during a discharging process;

the term "alloy" refers to a substance that includes any or all of metals, metalloids, semimetals; and

the term “powder” refers to a material which exists in a particulate form comprising a plurality of particles wherein the average size of the particles is below 200 micrometers.

As used herein, PDF#s may be understood with reference to the International Centre for Diffraction Data PDF-2, Release 2002.

As used herein, the singular forms “a”, “an”, and “the” include plural referents unless the content clearly dictates otherwise. As used in this specification and the appended embodiments, the term “or” is generally employed in its sense including “and/or” unless the content clearly dictates otherwise.

As used herein, the recitation of numerical ranges by endpoints includes all numbers subsumed within that range (e.g. 1 to 5 includes 1, 1.5, 2, 2.75, 3, 3.8, 4, and 5).

Unless otherwise indicated, all numbers expressing quantities or ingredients, measurement of properties and so forth used in the specification and embodiments are to be understood as being modified in all instances by the term “about.” Accordingly, unless indicated to the contrary, the numerical parameters set forth in the foregoing specification and attached listing of embodiments can vary depending upon the desired properties sought to be obtained by those skilled in the art utilizing the teachings of the present disclosure. At the very least, and not as an attempt to limit the application of the doctrine of equivalents to the scope of the claimed embodiments, each numerical parameter should at least be construed in light of the number of reported significant digits and by applying ordinary rounding techniques.

In some embodiments, the present disclosure relates to an anode composition for a sodium ion battery. The anode composition may include a material having the formula:

$$A_aB_bC_cD_dO, \qquad (I)$$

where A is an alkali metal, alkaline earth metal, or a combination thereof, where B is titanium, C is vanadium, and D is one or more transition metal element other than titanium or vanadium, O is oxygen, $a + b + c + d \leq 1$, $a \geq 0$, $b + c > 0$, $b \geq 0$, $c \geq 0$, $d > 0$, and where the material has a ilmenite structure, triclinic $VFeO_4$ structure, cubic $Ca_5Co_4(VO_4)_6$ structure, dichromate structure, orthorhombic $\forall$-CoV_3O_8 structure, brannerite structure, thortveitite structure, orthorhombic $\exists$-$CrPO_4$ structure, or the pseudo rutile structure. In various embodiments, $(b + c)/d \geq 1$, 2, or 3; $a = 0$, or > 0.05, 0.1 or 0.2; $a + b + c + d < 1$, 0.7, 0.6, or $= 0.5$; $b + c > 0.2$, 0.3, 0.4, or $= 0.5$. In illustrative embodiments, D is nickel, cobalt, manganese, iron, chromium or a combination thereof. In some embodiments, $b > 0$ and $c = 0$. In some embodiments, $b = 0$ and $c > 0$. In some embodiments, $b > 0$ and $c > 0$. In various embodiments, A is sodium, lithium, magnesium or calcium.

The anode composition may further include a material having the formula:

$$A'_eB'_fC'_gO, \qquad (II)$$

where A' is an alkali metal, alkaline earth metal, or a combination thereof, where B' is titanium, C' is vanadium, O is oxygen, $e + f + g \leq 1$, $e \geq 0$, $f > 0$, and $g > 0$. In various embodiments, A' is sodium, lithium, magnesium or calcium. In some embodiments the material has the pseudo rutile structure.

In illustrative embodiments, specific examples of anode compositions may include those having the formulae $CoTiO_3$, $Ca_5Co_4(VO_4)_6$, CoV_3O_8, $NiTiO_3$, $Co_2V_2O_7$ or MnV_2O_6.

In some embodiments, the anode compositions of the present disclosure may further include one or more additives such as binders, conductive diluents, fillers, adhesion promoters, thickening agents for coating viscosity modification such as carboxymethylcellulose, polyacrylic acid, polyvinylidene fluoride, lithium polyacrylate, carbon black, and other additives known by those skilled in the art. In some embodiments, the anode compositions of the present disclosure may further include other active anode materials, such as hard carbons (up to 10 wt.%, 20 wt.%, 50 wt. % or 70 wt.%, based on the total weight of electrode components, excluding the current collector) as described in D.A. Stevens and J.R. Dahn, J. Electrochem. Soc., 148 (2001) A803.

In some embodiments, anodes comprising the electrochemically active anode materials of the present disclosure may can have high specific capacity (mAh/g) retention (i.e., improved cycle life) when incorporated into a sodium ion battery and cycled through multiple charge/discharge cycles. For example, such anodes can have a specific capacity of greater than 50 mAh/g, greater than 100 mAh/g, greater than 500 mAh/g, or even greater than 1000 mAh/g when the battery is cycled between 0 and 2V or 5mV and 1.2V vs. Na and the temperature is maintained at about room temperature (25°C) or at 30°C or at 60°C or even higher.

The present disclosure further relates to methods of making the above-described anode compositions. Exemplary anode compositions can be prepared by any known method, for example, by heating precursor materials in a furnace, typically at temperatures above 300° C. The atmosphere during the heating process is not limited. The atmosphere can be air, an inert atmosphere, a reducing atmosphere such as one containing hydrogen gas, or a mixture of gases. The precursor materials are also not limited. Suitable precursor materials can be one or more metal oxides, metal carbonates, metal nitrates, metal sulfates, metal chlorides or combinations thereof. Such precursor materials can be combined by grinding, mechanical milling, precipitation from solution, or by other methods known in the art. The precursor material can also be in the form of a sol-gel. After firing, the oxides can be treated with further processing, such as by mechanical milling to achieve an amorphous or nanocrystalline structure, grinding and particle sizing, surface coating, and by other methods known in the art. Exemplary anode compositions can also be prepared by mechanical milling of precursor materials without firing. Suitable milling can be done by using various techniques such as vertical ball milling, horizontal ball milling, or other milling techniques known to those skilled in the art.

The present disclosure further relates to methods of making an electrode for a sodium-ion battery. In some embodiments, the method may include mixing the above-described the anode material, along with any additives such as binders, conductive diluents, fillers, adhesion promoters, thickening agents for coating viscosity modification and other additives known by those skilled in the art, in a suitable coating solvent such as water or N-methylpyrrolidinone to form a coating dispersion or coating mixture. The dispersion may be mixed thoroughly and then applied to a foil current collector by any appropriate coating technique such as knife coating, notched bar coating, dip coating, spray coating, electrospray coating, or gravure coating. The current collectors may be thin foils of conductive metals such as, for example, copper, aluminum, stainless steel, or nickel foil. The slurry may be coated onto the current collector foil and then allowed to dry in air or vacuum, and optionally by drying in a heated oven, typically at about 80° to about 300°C for about an hour to remove the solvent.

In various embodiments, the electrodes of the present disclosure may be particularly useful as negative electrodes for sodium-ion batteries. To prepare a battery, the negative electrode may be combined with an electrolyte and a cathode. Examples of suitable cathodes include sodium containing cathodes, such as sodium transition metal oxides of the formula Na_xMO_2, were M is a transition metal and x is from 0.7 to 1.2. Specific examples of suitable cathode materials include $NaCrO_2$, $NaCoO_2$, $NaNi_{0.5}Mn_{0.5}O_2$, $NaMn_{0.5}Fe_{0.5}O_2$. The electrolyte may be in the form of a liquid, solid, or gel. Electrolytes normally comprise a salt and a solvent. Examples of solid electrolyte solvents include polymers such as polyethylene oxide, polytetrafluoroethylene, fluorine-containing copolymers, and combinations thereof. Examples of liquid electrolyte solvents include ethylene carbonate, diethyl carbonate, propylene carbonate, fluoroethylene carbonate, and combinations thereof. Examples of electrolyte salts include sodium containing salts, such as $NaPF_6$ and $NaClO_4$, $Na[N(SO_2CF_3)_2]_2$, $NaCF_3SO_3$ and $NaBF_4$. A microporous separator, such as a microporous material available from Celgard LLC, Charlotte, N.C., may be incorporated into the battery and used to prevent the contact of the negative electrode directly with the positive electrode.

The disclosed electrochemical cells can be used in a variety of devices including, without limitation, portable computers, tablet displays, personal digital assistants, mobile telephones, motorized devices (e.g., personal or household appliances and vehicles), instruments, illumination devices (e.g., flashlights) and heating devices. One or more electrochemical cells of this invention can be combined to provide battery pack.

The operation of the present disclosure will be further described with regard to the following detailed examples. These examples are offered to further illustrate various specific embodiments and techniques. It should be understood, however, that many variations and modifications may be made while remaining within the scope of the present disclosure.

EXAMPLES

Comparative Example 1 – Preparation of Fe_2TiO_5 (pseudobrookite structure)

To prepare Fe_2TiO_5, 4.00 g Fe_2O_3 (5 μm, ≥99%, Sigma-Aldrich), and 2.00 g TiO_2 (puriss, 99 – 100.5 %, Sigma-Aldrich) were added to a 40 ml ball milling vial. Stoichiometric amounts of each compound were used. The precursors were ball milled for a half hour in a high energy ball mill (Spex Certiprep). The powders were then heated at 1000 °C in argon for 24 hours. After synthesis, samples were transferred directly to an argon filled glove box without air exposure.

The samples were characterized by X-ray powder diffraction (XRD) using a Rigaku Ultima IV X-Ray Diffractometer equipped with a Cu anode X-ray tube and dual detectors. A scintillation detector with a diffracted beam monochromator was used to measure XRD patterns of the powder sample.

The powder XRD sample was loaded into a gas tight X-ray sample holder (DPM Solutions, Hebbville NS) in an argon-filled glovebox. The sample holder had an aluminized Mylar window mounted in an arc such that it was perpendicular to the incident and scattered X-ray beam and did not contribute to the measured XRD patterns. The X-ray sample holder was equipped with gas fittings that allowed a continuous flow of helium gas during the XRD measurements. Rietveld refinement and profile matching of the powder diffraction data of the as prepared powders were performed using Rietica software. By this method it was determined that the prepared Fe_2TiO_5 sample had the pseudobrookite structure.

2325 type coin cells were assembled to evaluate electrochemical performance in sodium cells. Electrodes consisted of the Fe_2TiO_5 samples, carbon black (Super P, Erachem Europe), and PVDF (polyvinylidene fluoride, Kynar HSV 900) in an 8:1:1 weight ratio. These components were thoroughly mixed in N-methyl-2-pyrrolidone (Sigma Aldrich, anhydrous 99.5%) with two tungsten carbide balls in a Retsch PM200 rotary mill (100 rpm, 1 hour) to create a uniform black slurry. The slurry was then coated onto aluminum foil and dried under vacuum at 120 °C for 2 hours. Circular electrodes, 2 cm^2 in area, were punched from the resulting coatings. Coin cell preparation was carried out in an argon filled glove box. Sodium foil disk anodes were punched from thin foil (0.015 inch) that was rolled from sodium ingot (Sigma Aldrich, ACS reagent grade). The electrolyte was 1 M $NaPF_6$ (Sigma Aldrich 98%) dissolved in propylene carbonate (Novolyte Technologies). One Celgard 3501 and one BMF (blown microfiber separator, 3M Company) were used as separators. Cells were tested on a Maccor Series 4000 Automated cycler and were cycled at a constant current of C/10, calculated based on a 112 mAh/g capacity for voltage cycling from 0.005 to 4.3 V.

Figure 1 XRD pattern of Comparative Example 1 Fe_2TiO_5 material with a pseudobrookite structure.

Figure 2 shows the voltage capacity curve of Comparative Example 1 Fe_2TiO_5 material. It has very low capacity, only 45 mAh/g reversible capacity over a large voltage range.

Example 1 - Preparation of $NiTiO_3$ (ilmenite structure).

To prepare $NiTiO_3$, 2.90 g NiO (−325 mesh, 99 % Alfa Aesar), and 3.10 g TiO_2 (puriss, 99 – 100.5 %, Sigma-Aldrich) were added to a 40 ml ball milling vial. Stoichiometric amounts of each compound were used. The precursors were ball milled for a half hour in a high energy ball mill (Spex Certiprep). The powders were then heated at 1000 °C in air for 10 hours.

The sample was characterized by X-ray powder diffraction (XRD) using a Rigaku Ultima IV X-Ray Diffractometer equipped with a Cu anode X-ray tube and dual detectors. A scintillation detector with a diffracted beam monochromator was used to measure XRD patterns of powder samples.

Powder XRD samples were loaded into a gas tight X-ray sample holder (DPM Solutions, Hebbville NS) in an argon-filled glovebox. The sample holder had an aluminized Mylar window mounted in an arc such that it was perpendicular to the incident and scattered X-ray beam and did not contribute to the measured XRD patterns. The X-ray sample holder was equipped with gas fittings that allowed a continuous flow of helium gas during the XRD measurements. Rietveld refinement and profile matching of the powder diffraction data of the as prepared powders were performed using Rietica software. By this method it was determined that the prepared $NiTiO_3$ sample had the ilmenite structure.

2325 type coin cells were assembled to evaluate electrochemical performance in sodium cells. Electrodes consisted of the $NiTiO_3$ samples, carbon black (Super P, Erachem Europe), and PVDF (polyvinylidene fluoride, Kynar HSV 900) in an 8:1:1 weight ratio. These components were thoroughly mixed in N-methyl-2-pyrrolidone (Sigma Aldrich, anhydrous 99.5%) with two tungsten carbide balls in a Retsch PM200 rotary mill (100 rpm, 1 hour) to create a uniform black slurry. The slurry was then coated onto aluminum foil and dried under vacuum at 120 °C for 2 hours. Circular electrodes, 2 cm^2 in area, were punched from the resulting coatings. Coin cell preparation was carried out in an argon filled glove box. Sodium foil disk anodes were punched from thin foil (0.015 inch) that was rolled from sodium ingot (Sigma Aldrich, ACS reagent grade). The electrolyte was 1 M $NaPF_6$ (Sigma Aldrich 98%) dissolved in propylene carbonate (Novolyte Technologies). One Celgard 3501 and one BMF (blown microfiber separator, 3M Company) were used as separators. Cells were tested with a Maccor Series 4000 Automated cycler and were cycled at a constant current of C/10, calculated based on a 173 mAh/g capacity between 0.005 to 4.3 V.

Figure 3 XRD pattern of Example 1 $NiTiO_3$ material with an ilmenite structure.

Figure 4 shows the voltage capacity curve of Example 1 $NiTiO_3$ material. It displays a reversible capacity of 175 mAh/g. There is a sloping low voltage plateau below 1 volt.

Sample Preparation - Examples 2 - 11

Example	**Composition & Crystal structure**
Example 2	$CoTiO_3$ (ilmenite structure)
Example 3	$VFeO_4$ (triclinic $VFeO_4$ structure)
Example 4	$Ca_5Co_4(VO_4)_6$ (cubic $Ca_5Co_4(VO_4)_6$ structure)
Example 5	$Co_2V_2O_7$ (dichromate structure)
Example 6	CoV_3O_8 (orthorhombic ∀-CoV_3O_8 structure)
Example 7	MnV_2O_6 (brannerite structure)
Example 8	$Mn_2V_2O_7$ (thortveitite structure)
Example 9	$MnTiO_3$ (ilmenite structure)
Example 10	$CrVO_4$ (orthorhombic ∃-$CrPO_4$ structure)
Example 11	$TiVO_4$ (pseudo rutile structure)

Example 2 - Preparation of $CoTiO_3$ (ilmenite structure).

2 g of Co_3O_4 (< 10 µm, Sigma-Aldrich) and 2 g of TiO_2 (puriss, 99 – 100.5 %, Sigma-Aldrich) were added to a 40 ml ball milling vial. The precursors were ball milled for two hours in a high energy ball mill (Spex Certiprep). The powders were then heated at 800°C in air for 10 hours.

Example 3 – $VFeO_4$ (triclinic $VFeO_4$ structure).

2.13 g of V_2O_5 (> 99.6%, Sigma-Aldrich) and 1.87 g of Fe_2O_3 (< 5 µm, > 99%, Sigma-Aldrich) were added to a 40 ml ball milling vial. The precursors were ball milled for one hour in a high energy ball mill (Spex Certiprep). The powders were then heated at 550°C in air for 24 hours.

Example 4 – Preparation of $Ca_5Co_4(VO_4)_6$ (cubic $Ca_5Co_4(VO_4)_6$ structure).

0.725 g of CaO (99.9%, Sigma-Aldrich), 0.956 g of CoO (-325 mesh, Sigma-Aldrich) and 2.319 g of V_2O_5 (> 99.6%, Sigma-Aldrich) were added to a 40 ml ball milling vial. The precursors were ball milled for one hour in argon in a high energy ball mill (Spex Certiprep). The powders were then heated at 750°C in argon for 10 hours. After synthesis, the powder was transferred directly to an argon filled glove box without air exposure.

Example 5 Preparation of $Co_2V_2O_7$ (dichromate structure).

1.88 g of Co_3O_4 (< 10 µm, Sigma-Aldrich) and 2.12 g of V_2O_5 (> 99.6%, Sigma-Aldrich) were added to a 40 ml ball milling vial. The precursors were ball milled for one hour in a high energy ball mill (Spex Certiprep). The powders were then heated at 600°C in air for 30 hours.

Example 6 – Preparation of CoV_3O_8 (orthorhombic $\forall$-CoV_3O_8 structure).

0.88 g of CoO (-325 mesh, Sigma-Aldrich), 0.98 g of V_2O_4 (99.9% trace metals basis) and 2.14 g of V2O5 (> 99.6%, Sigma-Aldrich) were added to a 40 ml ball milling vial. The precursors were ball milled for one hour in argon a high energy ball mill (Spex Certiprep). The powders were then heated at 600°C in argon for 12 hours. After synthesis, the powder was transferred directly to an argon filled glove box without air exposure.

Example 7 – Preparation of MnV_2O_6 (brannerite structure).

1.21 g of Mn_2O_3 (-325 mesh, 99%, Sigma-Aldrich) and 2.79 g of V_2O_5 (> 99.6%, Sigma-Aldrich) were added to a 40 ml ball milling vial. The precursors were ball milled for one hour in a high energy ball mill (Spex Certiprep). The powders were then heated at 600°C in air for 30 hours.

Example 8 – Preparation of $Mn_2V_2O_7$ (thortveitite structure).

1.75 g of MnO (-60 mesh, 99%, Sigma-Aldrich) and 2.25 g of V_2O_5 (> 99.6%, Sigma-Aldrich) were added to a 40 ml ball milling vial. The precursors were ball milled for one hour in a high energy ball mill (Spex Certiprep). The powders were then heated at 800°C in air for 30 hours.

Example 9 – Preparation of $MnTiO_3$ (ilmenite structure).

3.13 g of MnO_2 (60 - 230 mesh, > 99%, Sigma-Aldrich) and 2.87 g of TiO_2 (puriss, 99 – 100.5 %, Sigma-Aldrich) were added to a 40 ml ball milling vial. The precursors were ball milled for one hour in argon in a high energy ball mill (Spex Certiprep). The powders were then heated at 1100°C in argon for 10 hours. After synthesis, the powder was transferred directly to an argon filled glove box without air exposure.

Example 10 – Preparation of $CrVO_4$ (orthorhombic ∃-$CrPO_4$ structure).

1.82 g of Cr_2O_3 (50 µm, > 98%, Sigma-Aldrich) and 2.18 g of V_2O_5 (> 99.6%, Sigma-Aldrich) were added to a 40 ml ball milling vial. The precursors were ball milled for one hour in a high energy ball mill (Spex Certiprep). The powders were then heated at 800°C in air for 30 hours.

Example 11 – Preparation of $TiVO_4$ (pseudo rutile structure).

2.94 g of TiO_2 (puriss, 99 – 100.5 %, Sigma-Aldrich) and 3.06 g of V_2O_5 (> 99.6%, Sigma-Aldrich) were added to a 40 ml ball milling vial. The precursors were ball milled for 30 minutes in argon in a high energy ball mill (Spex Certiprep). The powders were then heated at 1000°C in argon for 16 hours. After synthesis, the powder was transferred directly to an argon filled glove box without air exposure.

Characterization and Evaluation - Examples 2-11

Examples 2 - 11 were characterized by X-ray powder diffraction (XRD) using a Rigaku Ultima IV X-Ray Diffractometer equipped with a Cu anode X-ray tube and dual detectors. A scintillation detector with a diffracted beam monochromator was used to measure XRD patterns of powder samples.

Using the materials prepared in Examples 2-11, 2325 type coin cells were assembled to evaluate electrochemical performance in sodium cells. Electrodes consisted of the sample, carbon black (Super P, Erachem Europe), and PVDF (polyvinylidene fluoride, Kynar HSV 900) in an 8:1:1 weight ratio. These components were thoroughly mixed in N-methyl-2-pyrrolidone (Sigma Aldrich, anhydrous 99.5%) with two tungsten carbide balls in a Retsch PM200 rotary mill (100 rpm, 1 hour) to create a uniform black slurry. The slurry was then coated onto aluminum or copper foil and dried under vacuum at 120 °C for 2 hours. Circular electrodes, 2 cm^2 in area, were punched from the resulting coatings. Coin cell preparation was carried out in an argon filled glove box. Sodium foil disk anodes were punched from thin foil (0.015 inch) that was rolled from sodium ingot (Sigma Aldrich, ACS reagent grade). The electrolyte was 1 M $NaPF_6$ (Sigma Aldrich 98%) dissolved in 3/6/1 ethylene carbonate/diethyl carbonate/monofluoroethylene carbonate (all from Novolyte Technologies). Two Celgard 2300 and one BMF (blown microfiber separator, 3M Company) were used as separators. Cells were tested on a Maccor Series 4000 Automated cycler and were cycled at constant current rates of C/10 and C/40 with a trickle discharge to C/20 and C/80, respectively, calculated based on capacities between 100 – 200 mAh/g for cycling from 0.005 to 2.5 V and/or 0.005 to 4.5 V.

Experimental Results – Examples 2-11

Figure 5 shows the experimental XRD pattern of Example 2 compared with the literature pattern of $CoTiO_3$ (top) and the corresponding voltage curve for cell made with Example 2 material (bottom). Example 2 is phase pure $CoTiO_3$ with the R-3 (148) space group (ilmenite structure). This material has reversible low average voltage capacity showing potential for use as a negative electrode material in sodium ion batteries.

Figure 6 shows the experimental XRD pattern of Example 3 compared with the literature pattern of $VFeO_4$ (top) and the corresponding voltage curve for cell made with

Example 3 material (bottom). Example 3 is phase pure $VFeO_4$ with the P-1 (2) space group (triclinic $VFeO_4$ structure). This material has reversible low average voltage capacity showing potential for use as a negative electrode material in sodium ion batteries.

Figure 7 shows the experimental XRD pattern of Example 4 compared with the literature pattern of $Ca_5Co_4(VO_4)_6$ (top) and the corresponding voltage curve for cell made with Example 4 material (bottom). A phase pure was not obtained; the $Ca_5Co_4(VO_4)_6$ phase with the Ia-3d (230) space group (cubic $Ca_5Co_4(VO_4)_6$ structure) is present with a minor $Co_3V_2O_8$ impurity. This material has reversible low average voltage capacity showing potential for use as a negative electrode material in sodium ion batteries.

Figure 8 shows the experimental XRD pattern of Example 5 compared with the literature pattern of $Co_2V_2O_7$ (top) and the corresponding voltage curve for cell made with Example 5 material (bottom). Example 5 is phase pure $Co_2V_2O_7$ with the P21/c (14) space group (dichromate structure). This material has reversible low average voltage capacity showing potential for use as a negative electrode material in sodium ion batteries.

Figure 9 shows the experimental XRD pattern of Example 6 compared with the literature pattern of CoV_3O_8 (top) and the corresponding voltage curve for cell made with Example 6 material (bottom). A phase pure was not obtained; the CoV_3O_8 phase with the Cmce (64) space group (orthorhombic ∀-CoV_3O_8 structure) is present with minor cobalt/vanadium oxide impurities. This material has reversible low average voltage capacity showing potential for use as a negative electrode material in sodium ion batteries.

Figure 10 shows the experimental XRD pattern of Example 7 compared with the literature pattern of MnV_2O_6 (top) and the corresponding voltage curve for cell made with Example 7 material (bottom). Example 7 is phase pure MnV_2O_6 with the C2/m (12) space group (brannerite structure). This material has reversible low average voltage capacity showing potential for use as a negative electrode material in sodium ion batteries.

Figure 11 shows the experimental XRD pattern of Example 8 compared with the literature pattern of $Mn_2V_2O_7$ (top) and the corresponding voltage curve for cell made with Example 8 material (bottom). Example 8 is phase pure $Mn_2V_2O_7$ with the C2/m (12) space group (thortveitite structure). This material has reversible low average voltage capacity showing potential for use as a negative electrode material in sodium ion batteries.

Figure 12 shows the experimental XRD pattern of Example 9 compared with the literature pattern of $MnTiO_3$ (top) and the corresponding voltage curve for cell made with

Example 9 material (bottom). Example 9 is phase pure $MnTiO_3$ with the R-3 (148) space group (ilmenite structure). This material has reversible low average voltage capacity showing potential for use as a negative electrode material in sodium ion batteries.

Figure 13 shows the experimental XRD pattern of Example 10 compared with the literature pattern of $CrVO_4$ (top) and the corresponding voltage curve for cell made with Example 10 material (bottom). Example 10 is phase pure $CrVO_4$ with the Cmcm (63) space group (orthorhombic ∃-CrPO4 structure) is present with a minor unidentified impurity. This material has reversible low average voltage capacity showing potential for use as a negative electrode material in sodium ion batteries.

Figure 14 shows the experimental XRD pattern of Example 11 compared with the literature pattern of $TiVO_4$ (top) and the corresponding voltage curve for cell made with Example 11 material (bottom). Example 11 is phase pure $TiVO_4$ with the P42/mmm (136) space group (pseudo rutile structure). This material has reversible low average voltage capacity showing potential for use as a negative electrode material in sodium ion batteries.

WHAT IS CLAIMED IS:

1. A sodium-ion battery comprising:

a cathode comprising sodium; and

an anode composition comprising a material having the formula:

$$A_aB_bC_cD_dO, \qquad (I)$$

where A is an alkali metal, alkaline earth metal, or a combination thereof, where B is titanium, C is vanadium, D is one or more transition metal element other than titanium or vanadium, $a + b + c + d \leq 1$, $a \geq 0$, $b + c > 0$, $b \geq 0$, $c \geq 0$, $d > 0$, and where the material comprises a ilmenite structure, triclinic $VFeO_4$ structure, cubic $Ca_5Co_4(VO_4)_6$ structure, dichromate structure, orthorhombic $\forall$-CoV_3O_8 structure, brannerite structure, thortveitite structure, orthorhombic $\exists$-$CrPO_4$ structure, or the pseudo rutile structure.

2. The sodium-ion battery of claim 1, wherein $(b + c)/d \geq 1$.

3. The sodium-ion battery of any one of claims 1-2, wherein $b = 0$.

4. The sodium-ion battery of any one of claims 1-2, wherein $c = 0$.

5 The sodium-ion battery of any one of claims 1-2, wherein $b > 0$ and $c > 0$.

6. The sodium-ion battery according to any one of the preceding claims, wherein $a > 0.05$.

7. The sodium-ion battery according to any one of the preceding claims, wherein D is iron, nickel, cobalt, manganese, chromium, or combinations thereof.

8. A sodium-ion battery comprising:

a cathode comprising sodium; and

an anode composition comprising a material having the formula:

$$A'_eB'_fC'_gO, \qquad (II)$$

where A' is an alkali metal, alkaline earth metal, or a combination thereof, where B' is titanium, C' is vanadium, $e + f + g \leq 1$, $e \geq 0$, $f > 0$, and $g > 0$.

9. The sodium-ion battery according to any one of the preceding claims, wherein A or A' is sodium, lithium, magnesium, calcium, or combinations thereof.

10. The sodium-ion battery according to any one of the preceding claims, wherein the sodium-ion battery further comprises an electrolyte comprising sodium.

11. An electronic device comprising a sodium-ion battery according to any one of the preceding claims.

12. A method of making a sodium-ion battery, the method comprising:

providing a cathode comprising sodium;

providing an anode comprising vanadium, titanium or a combination thereof, and optionally an alkali metal or alkaline earth metal and optionally a transition metal other than titanium or vanadium; and

incorporating the cathode and anode into a battery comprising an electrolyte, wherein the electrolyte comprises sodium.

13. A sodium-ion battery comprising:

a cathode comprising sodium; and

an anode composition comprising one or more materials selected from $CoTiO_3$, $Ca_5Co_4(VO_4)_6$, CoV_3O_8, $NiTiO_3$, $Co_2V_2O_7$ or MnV_2O_6.

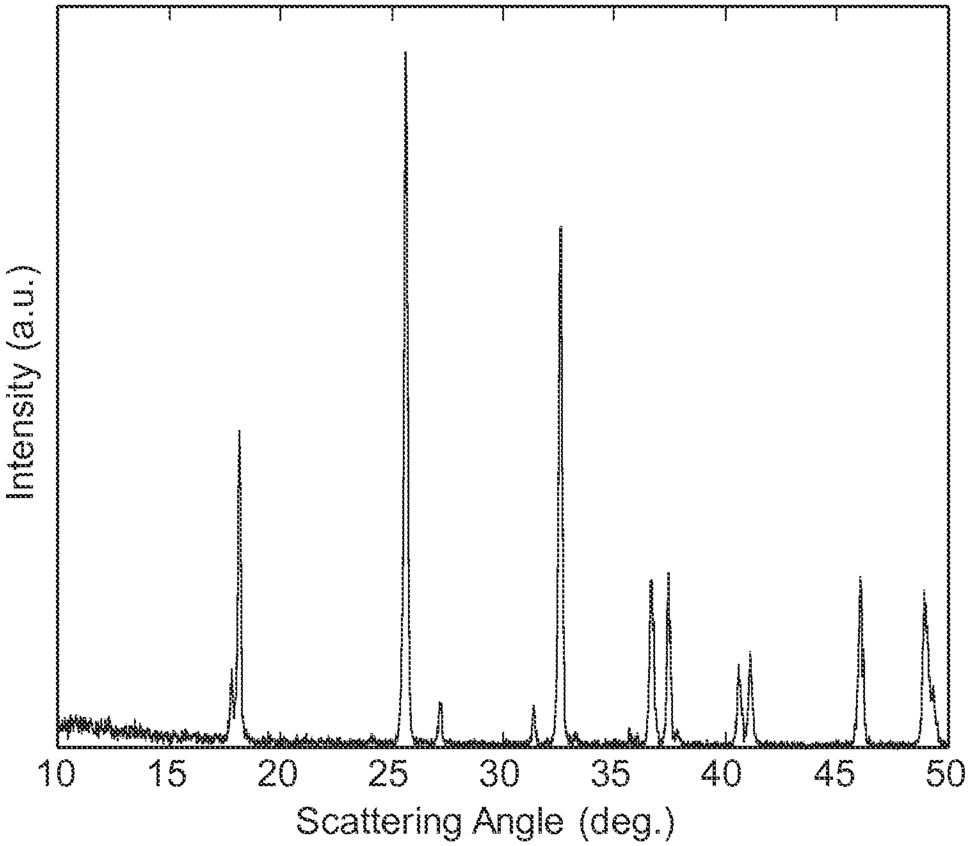

Intensity (a.u.)
10
15
20
25
30
35
40
45
50
Scattering Angle (deg.)

FIG. 1

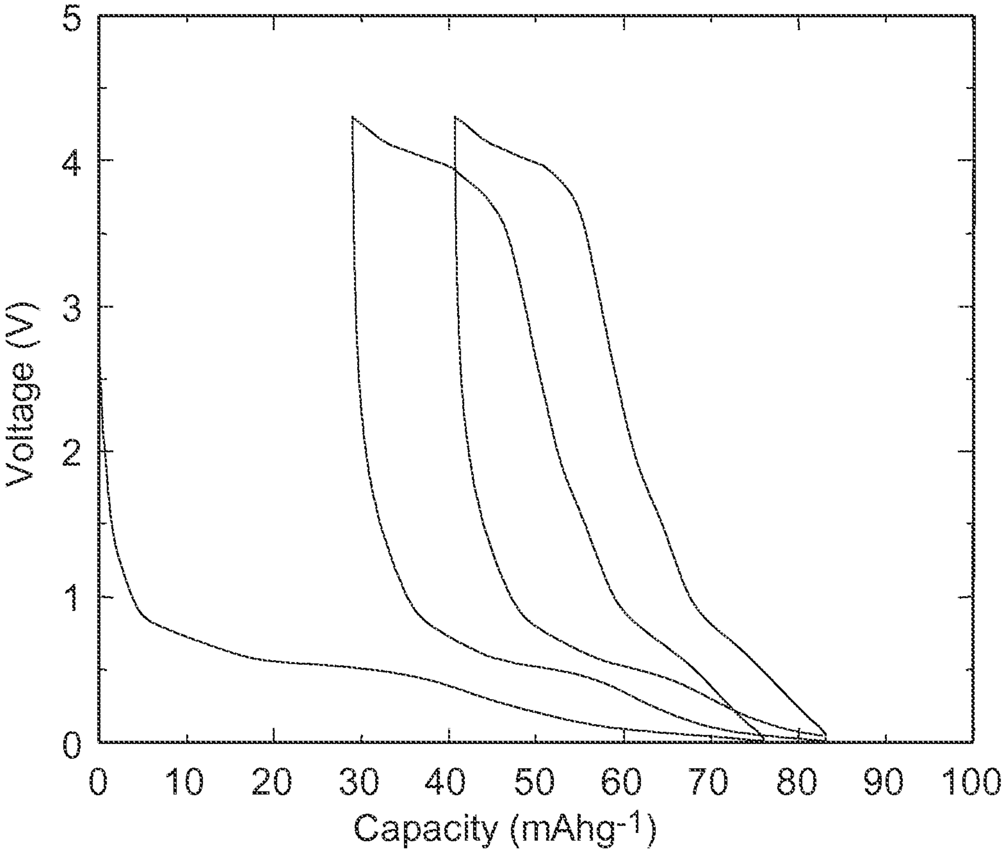
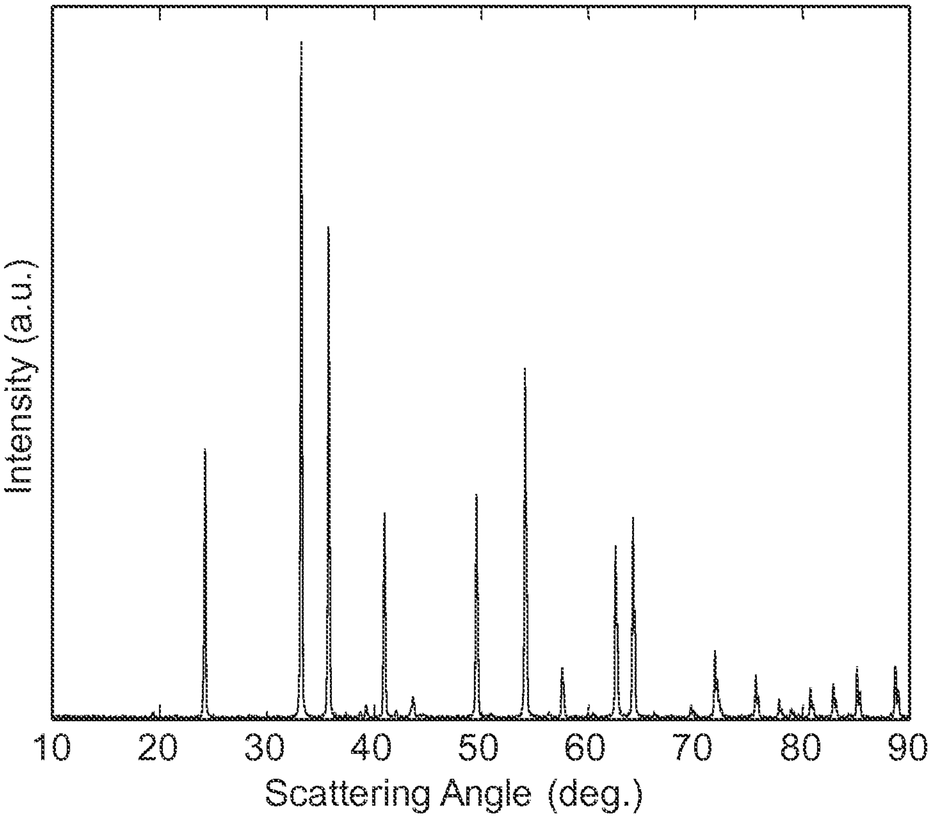

5
4
3
2
1
0
Voltage (V)
0
10
20
30
40
50
60
70
80
90
100
Capacity (mAhg-1)

FIG. 2


Intensity (a.u.)
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20
30
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50
60
70
80
90
Scattering Angle (deg.)

FIG. 3

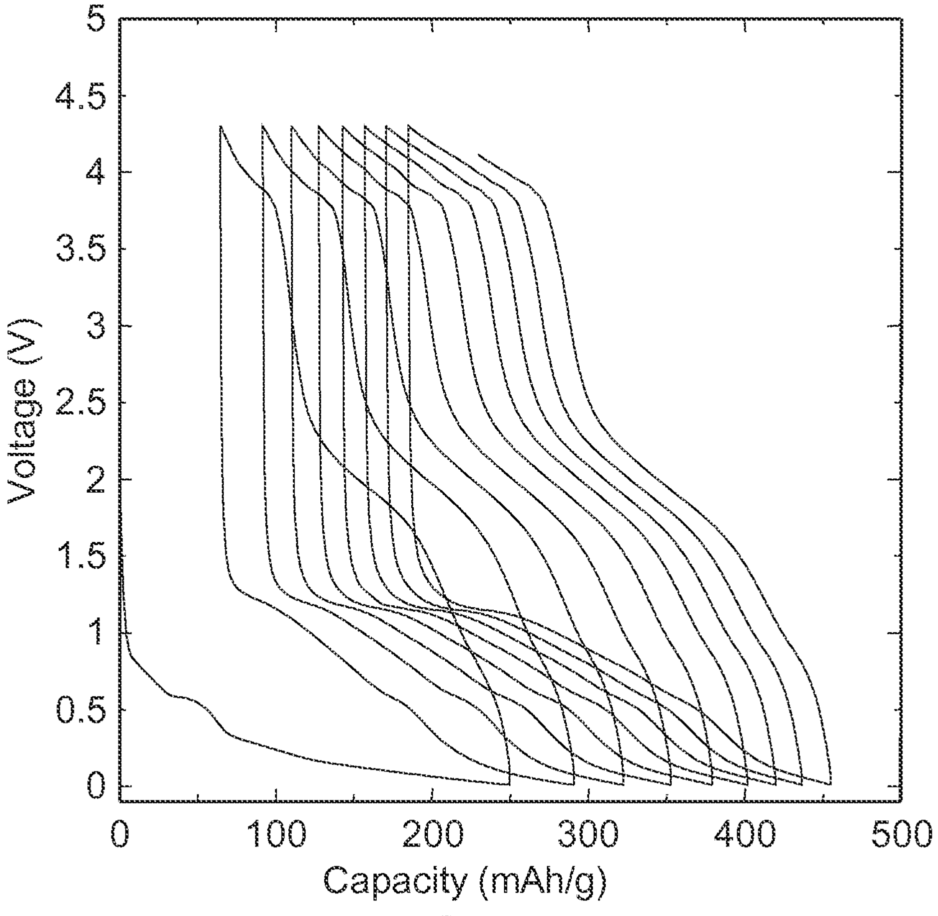
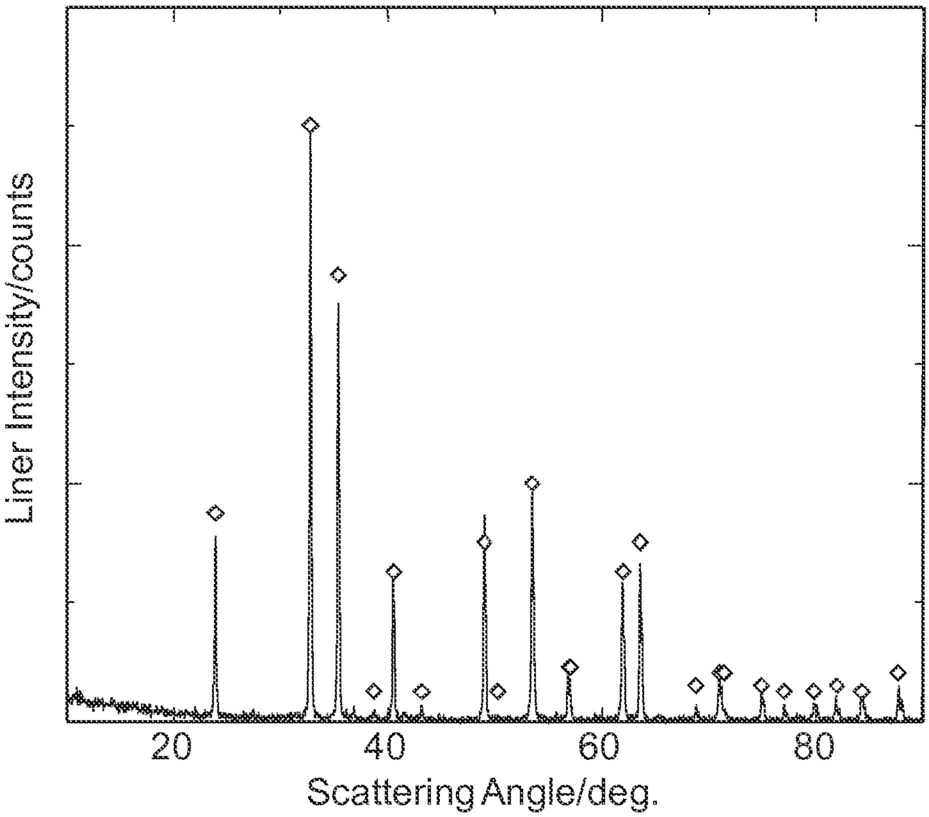

5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
Voltage (V)
0
100
200
300
400
500
Capacity (mAh/g)

FIG. 4


Liner Intensity/counts
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80
Scattering Angle/deg.

FIG. 5A

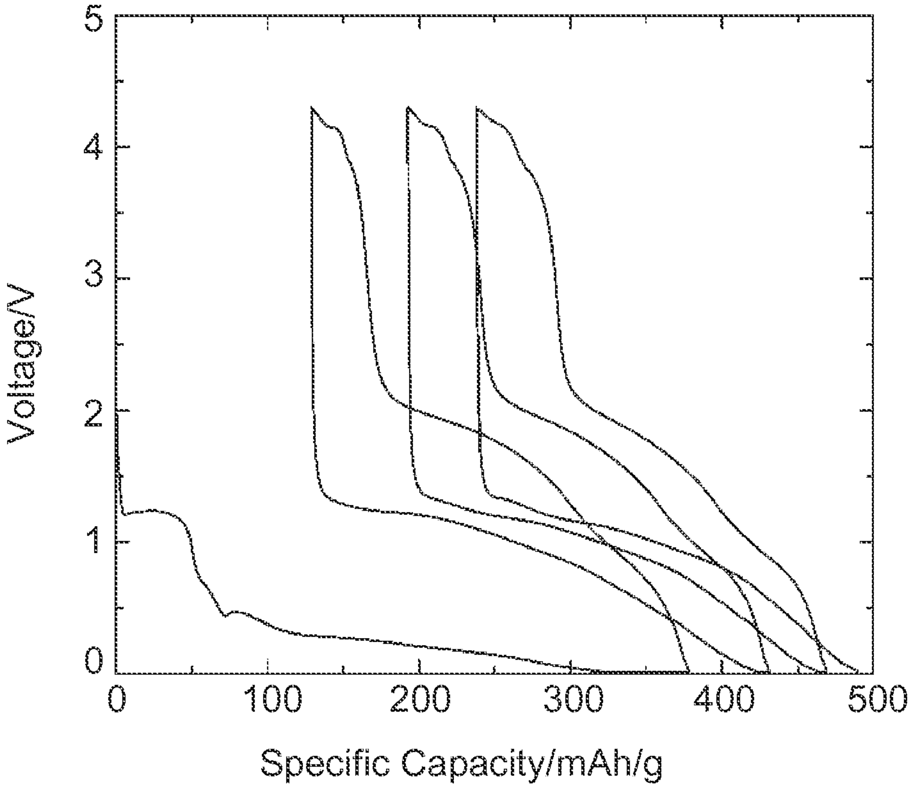
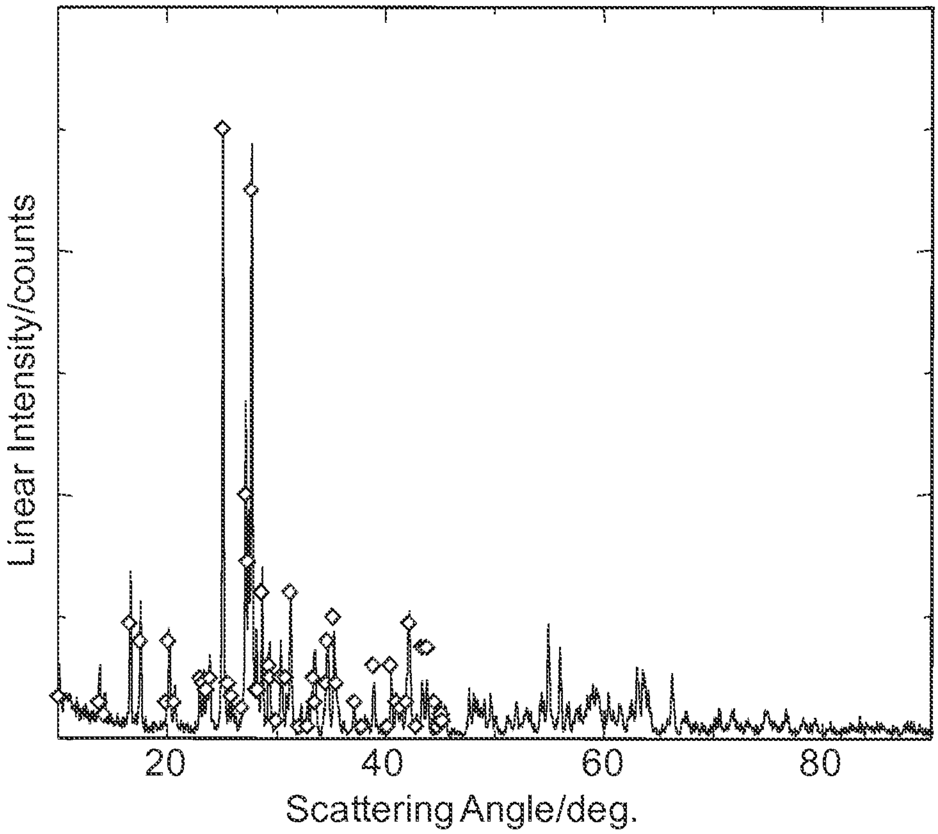

5
4
3
2
1
0
Voltage/V
0
100
200
300
400
500
Specific Capacity/mAh/g

FIG. 5B


Linear Intensity/counts
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40
60
80
Scattering Angle/deg.

FIG. 6A

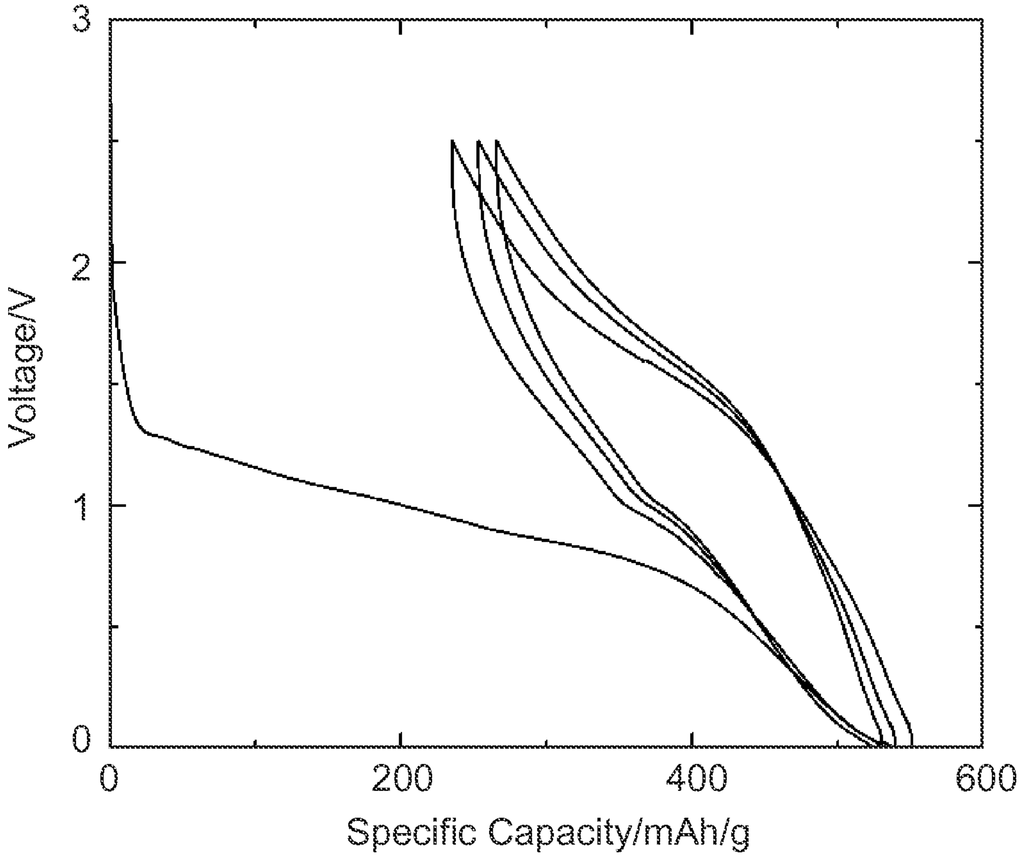
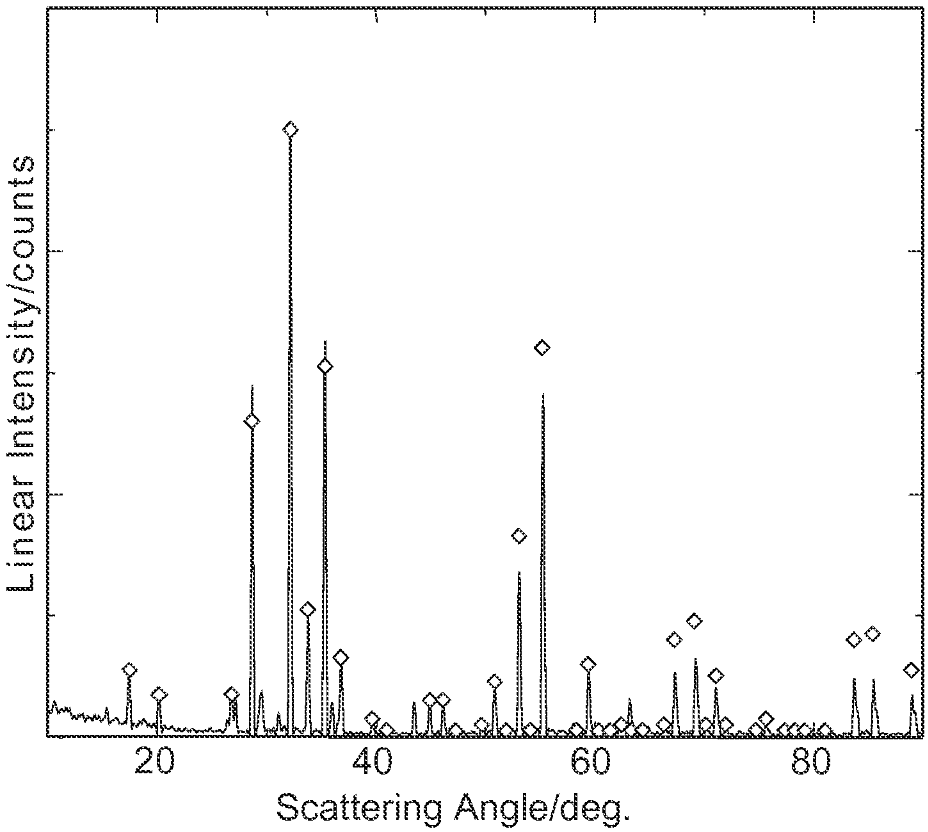

3
2
1
0
Voltage/V
0
200
400
600
Specific Capacity/mAh/g

FIG. 6B


Linear Intensity/counts
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40
60
80
Scattering Angle/deg.

FIG. 7A

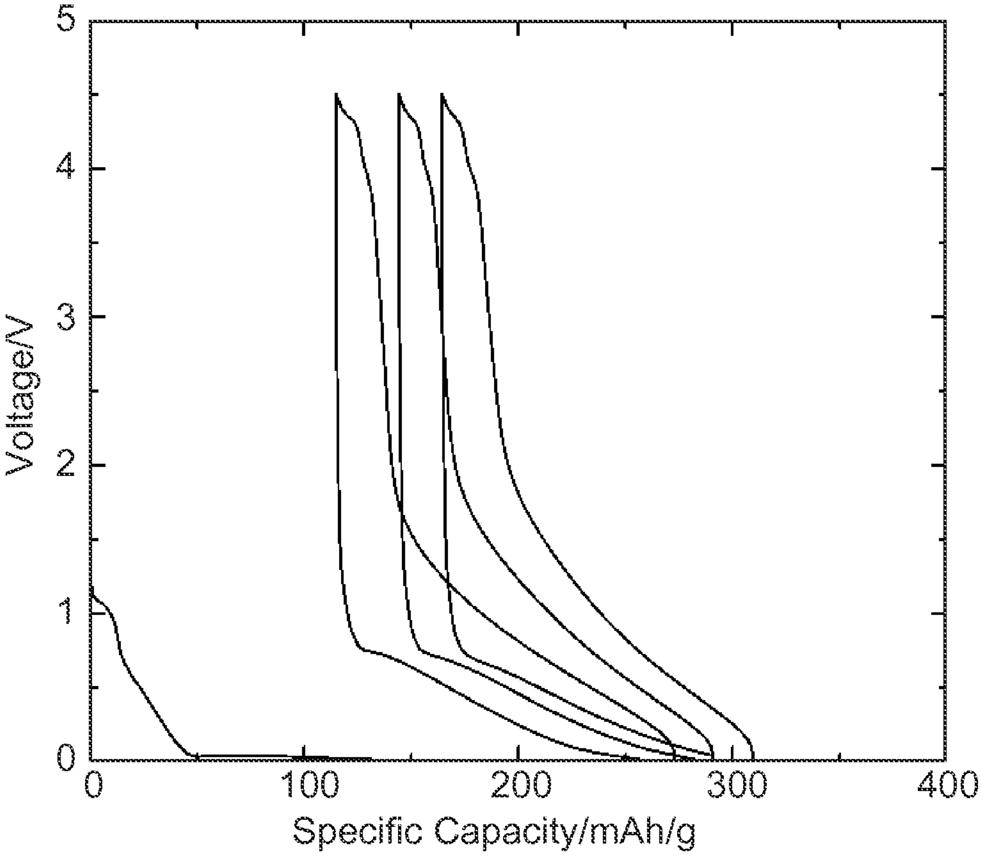
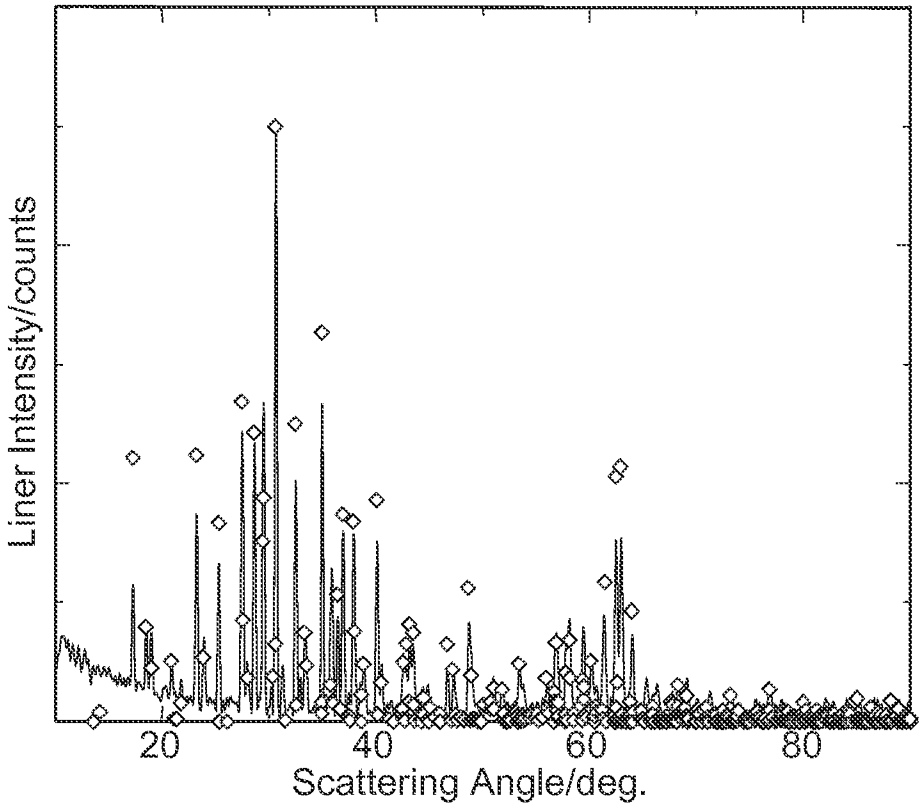

5
4
3
2
1
0
Voltage/V
0
100
200
300
400
Specific Capacity/mAh/g

FIG. 7B


Liner Intensity/counts
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60
80
Scattering Angle/deg.

FIG. 8A

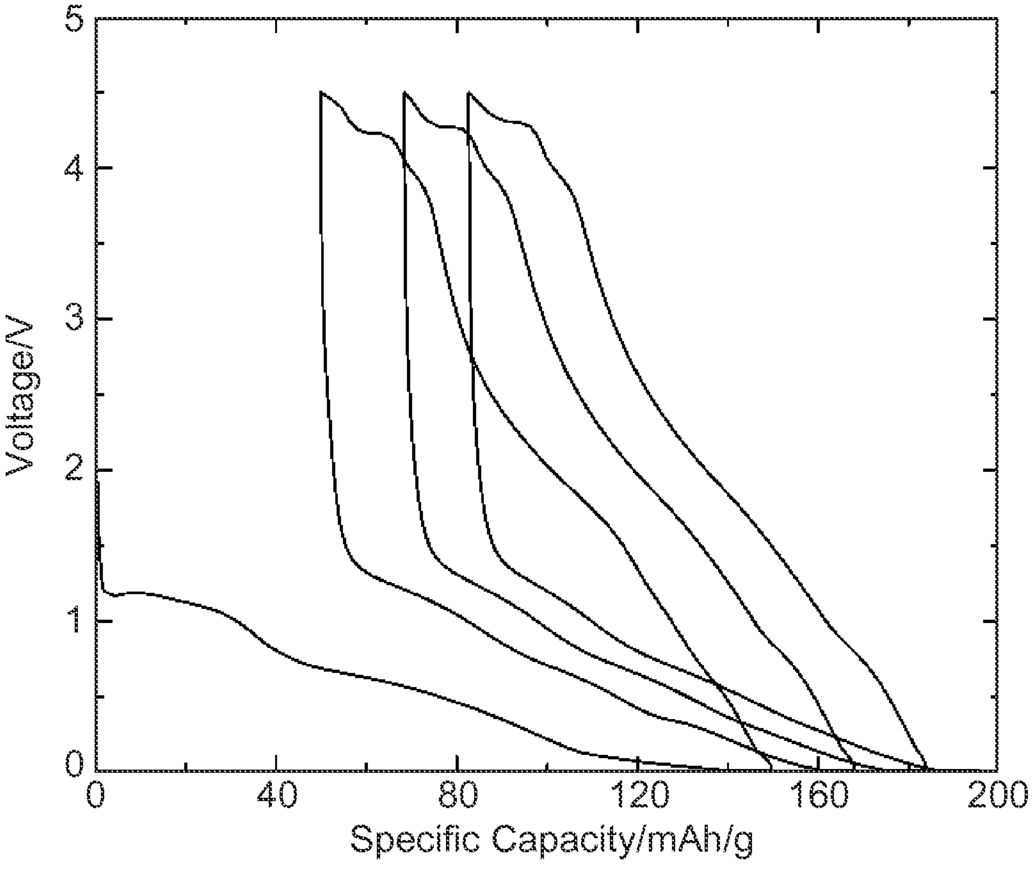
5
4
3
2
1
0
Voltage/V
0
40
80
120
160
200
Specific Capacity/mAh/g

FIG. 8B

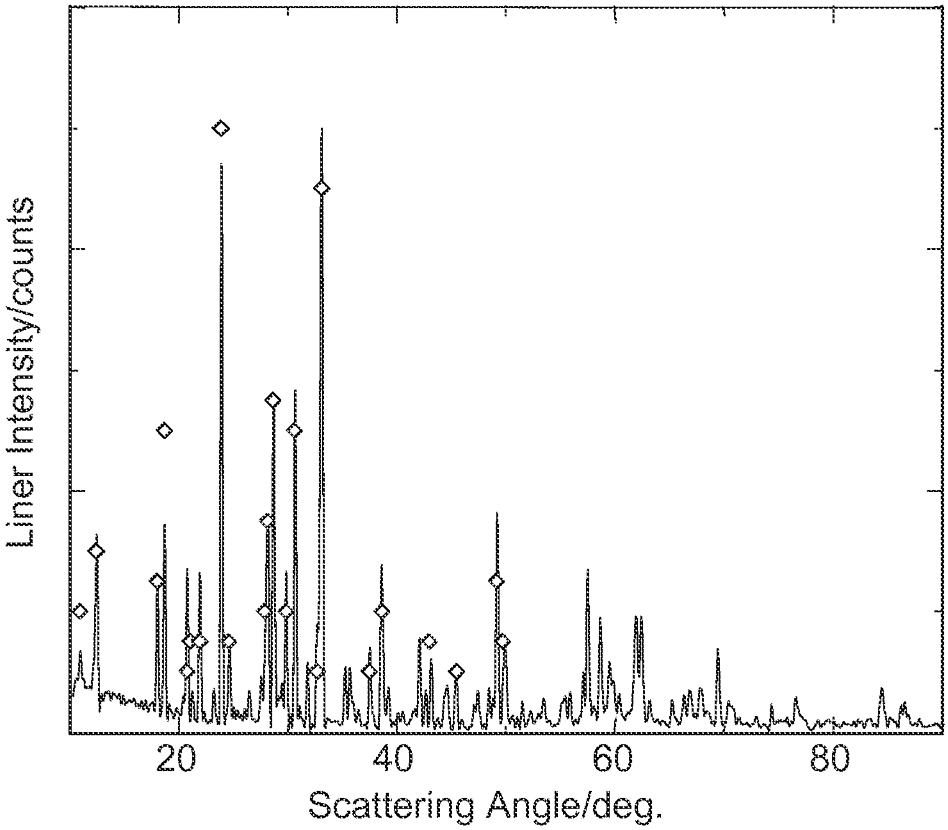
Liner Intensity/counts
20
40
60
80
Scattering Angle/deg.

FIG. 9A

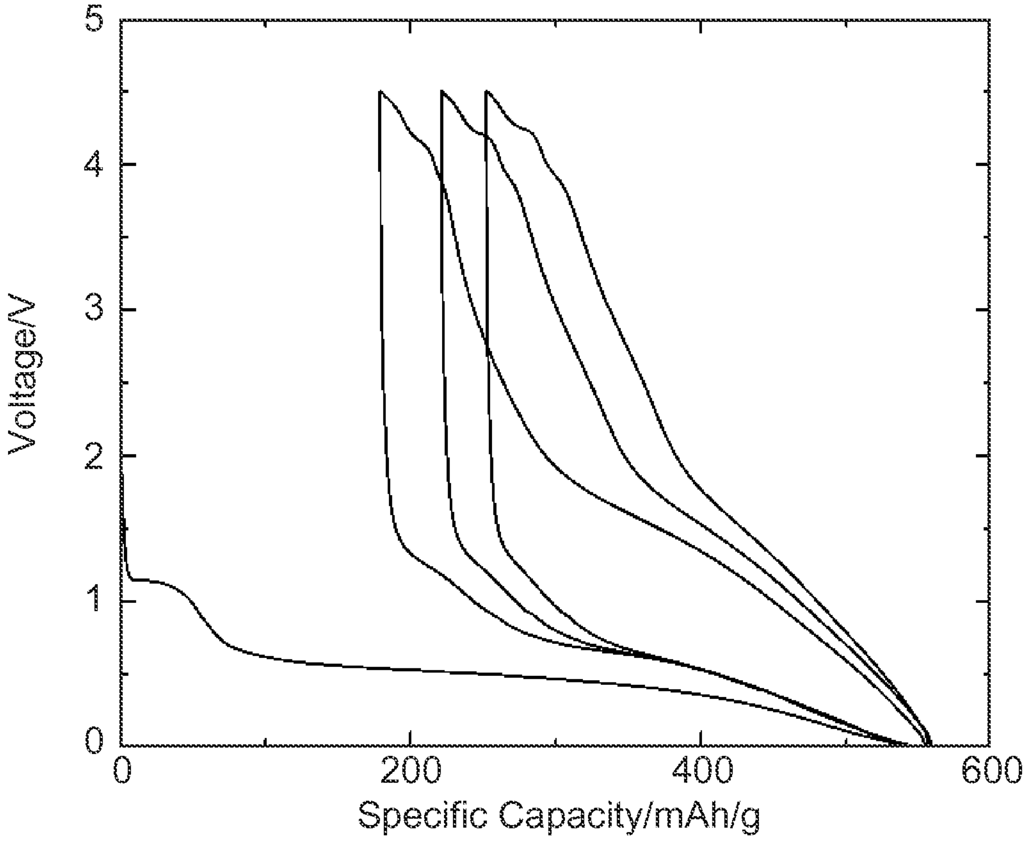
5
4
3
2
1
0
Voltage/V
0
200
400
600
Specific Capacity/mAh/g

FIG. 9B

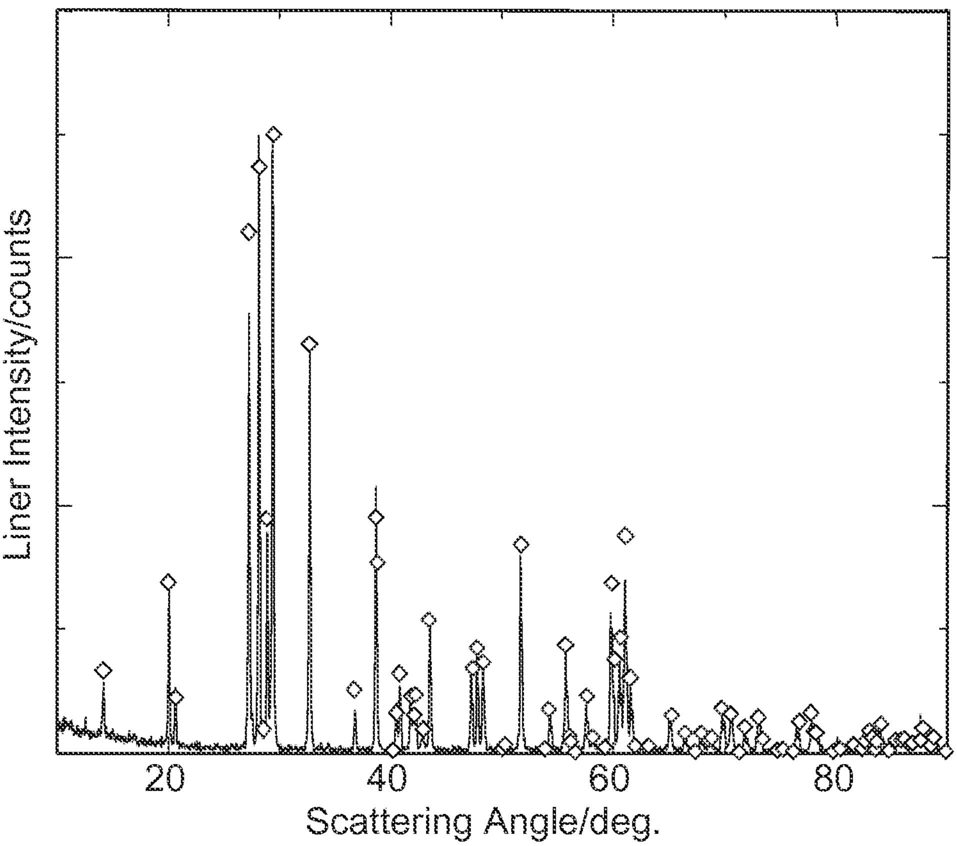

FIG. 10A

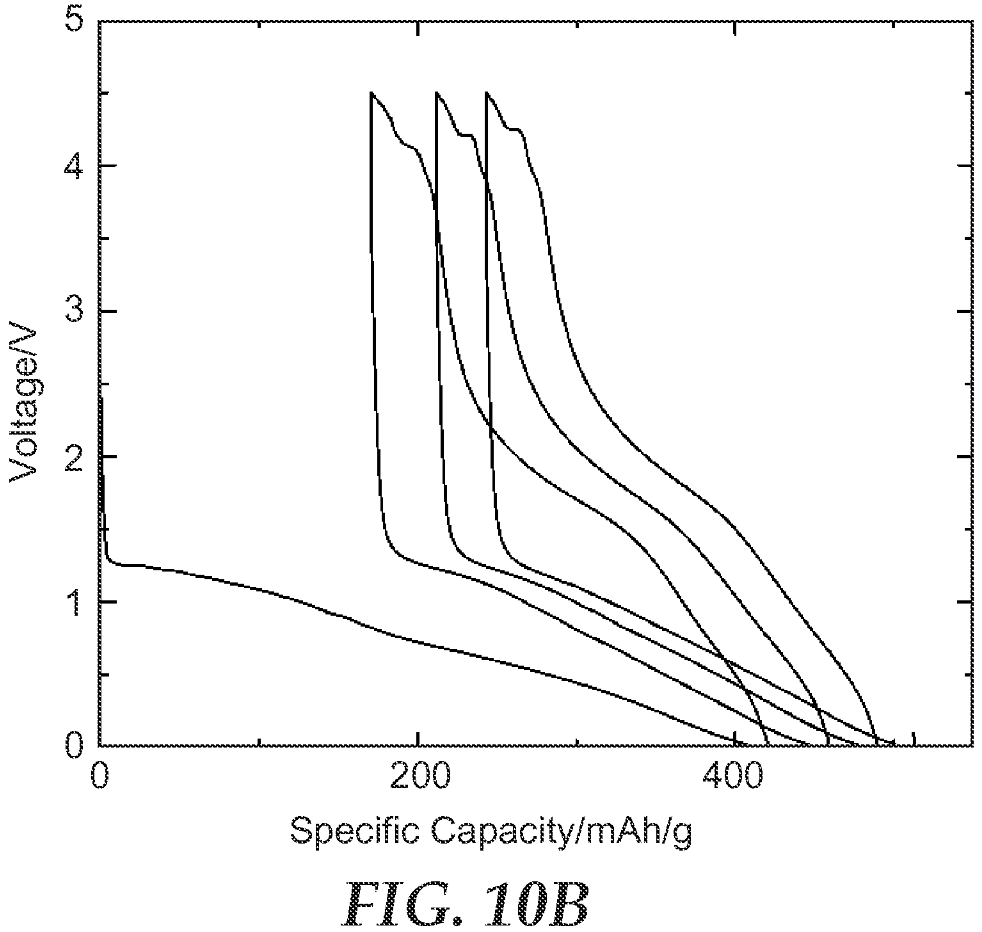

FIG. 10B

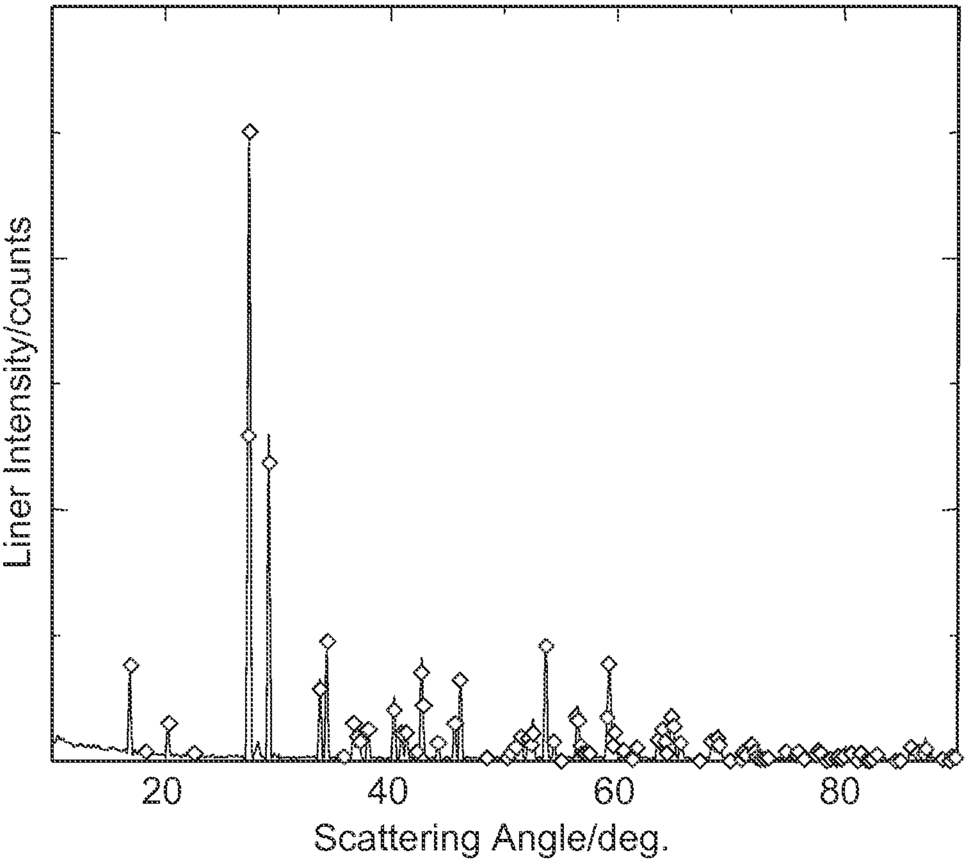

FIG. 11A

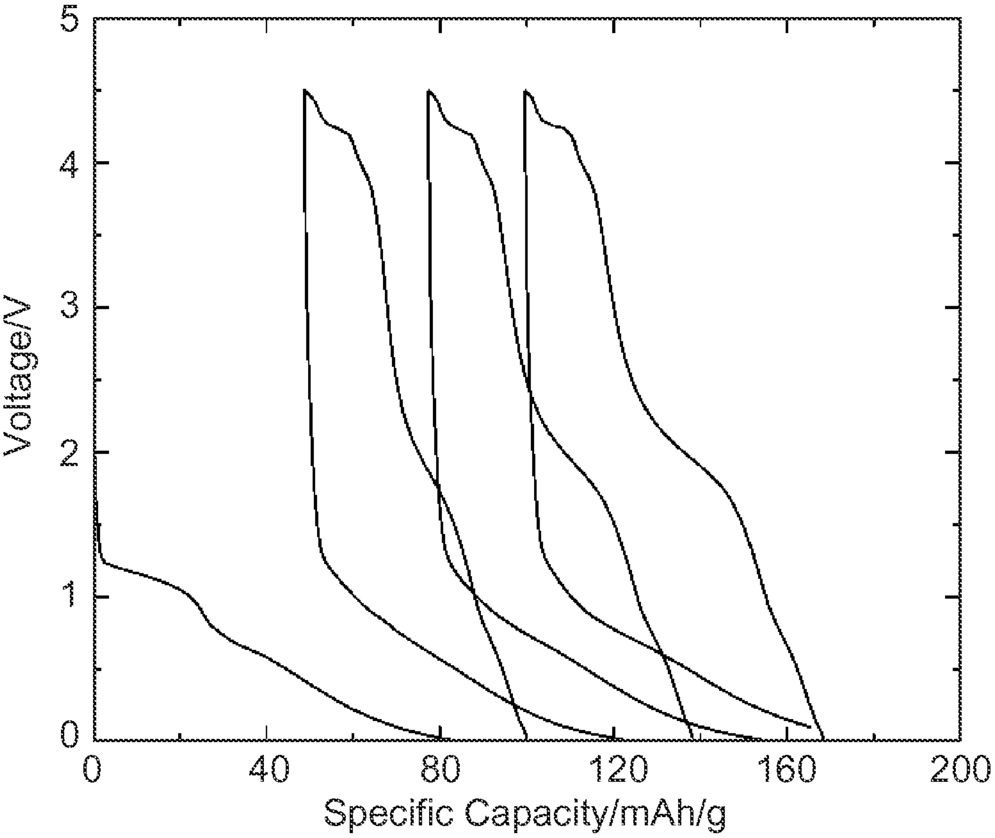

FIG. 11B

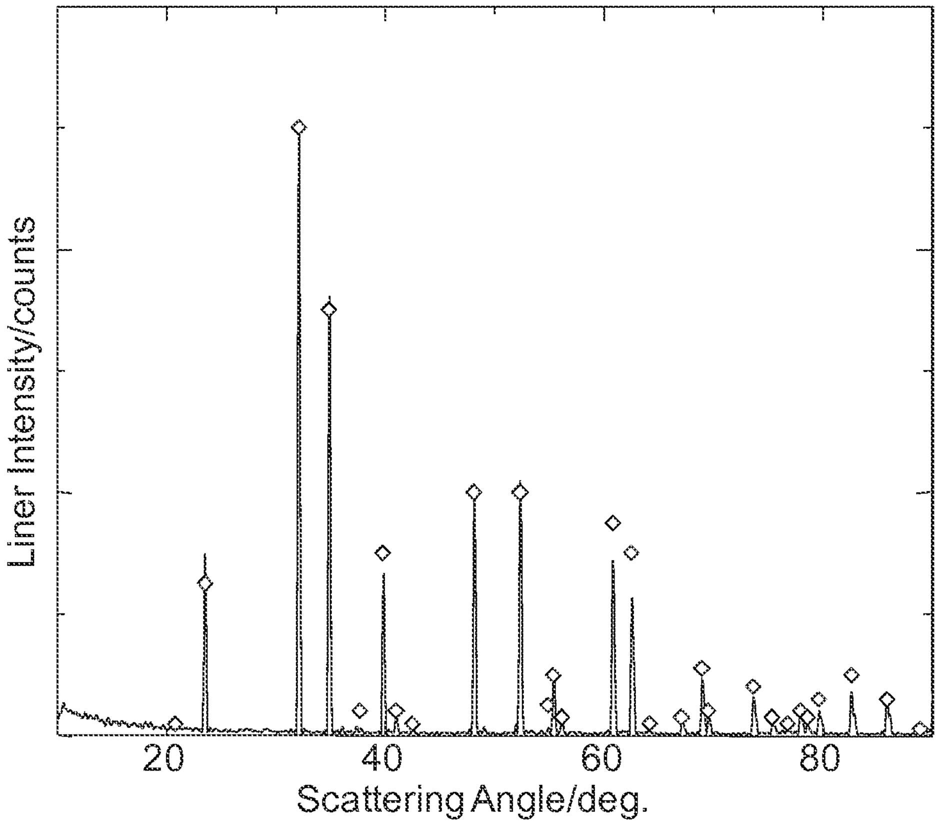

FIG. 12A

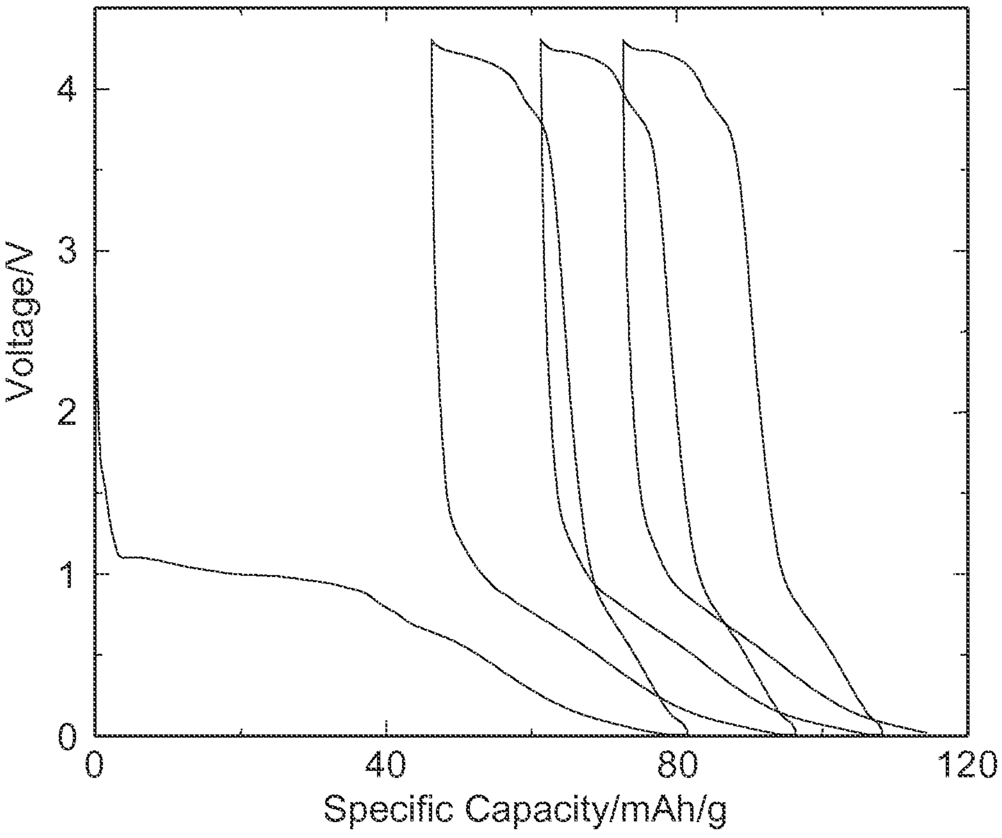

FIG. 12B

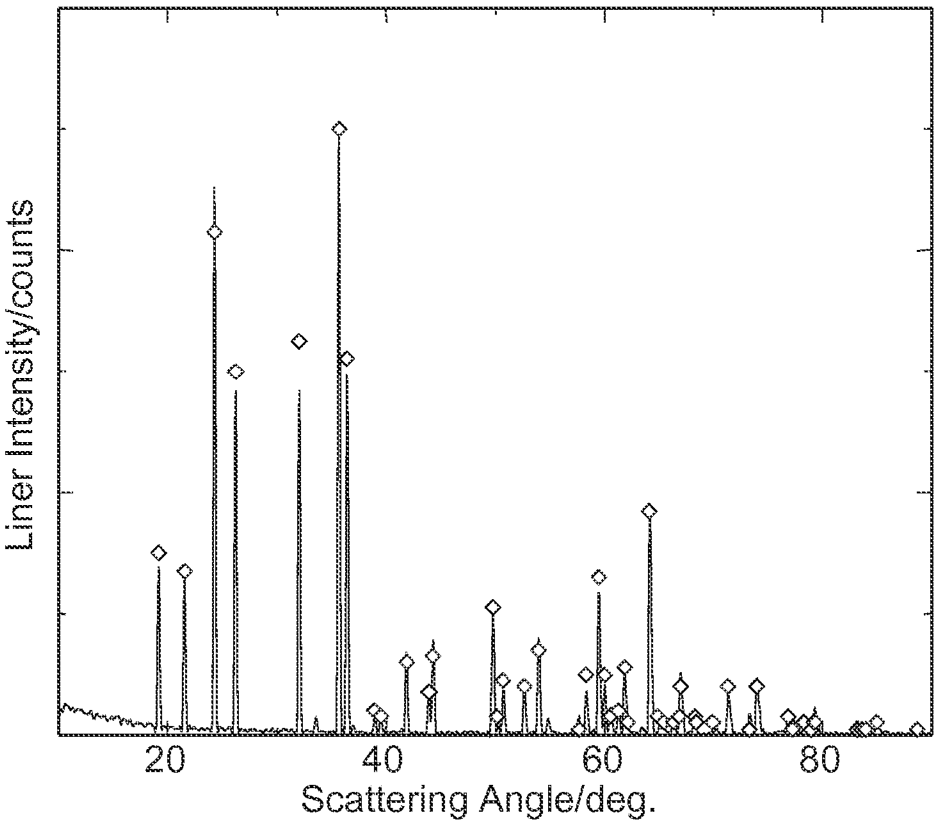

FIG. 13A

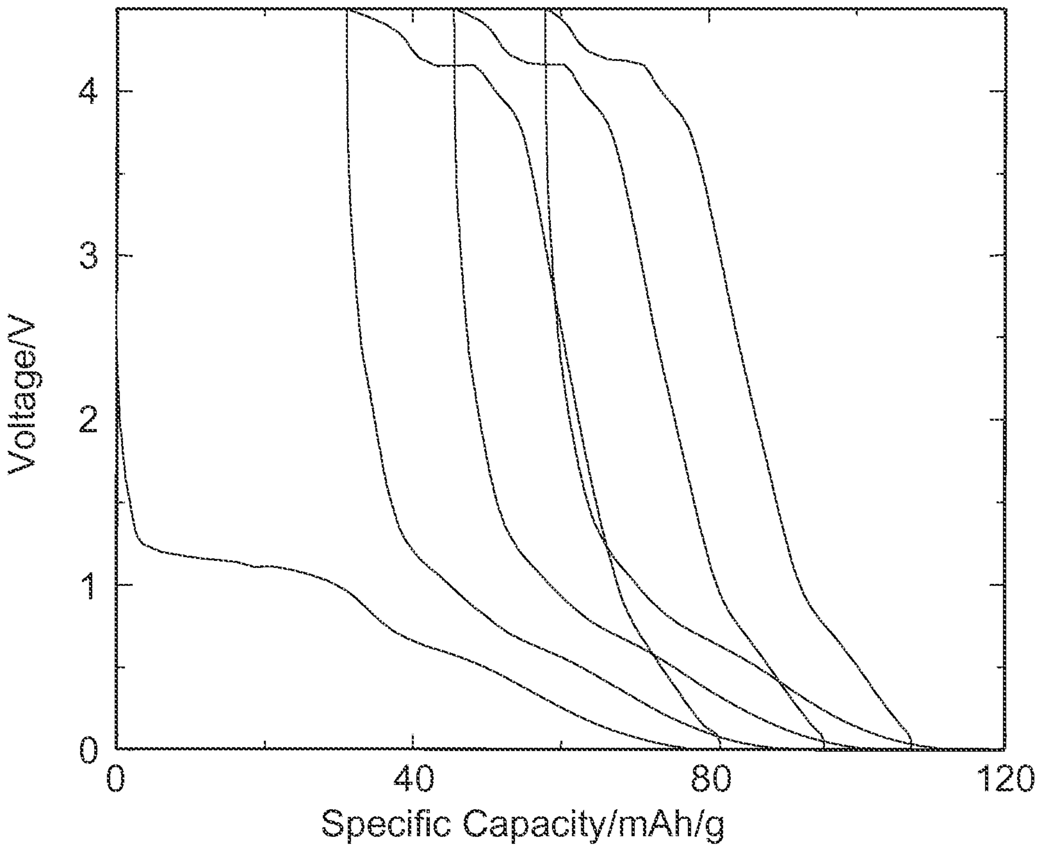

FIG. 13B

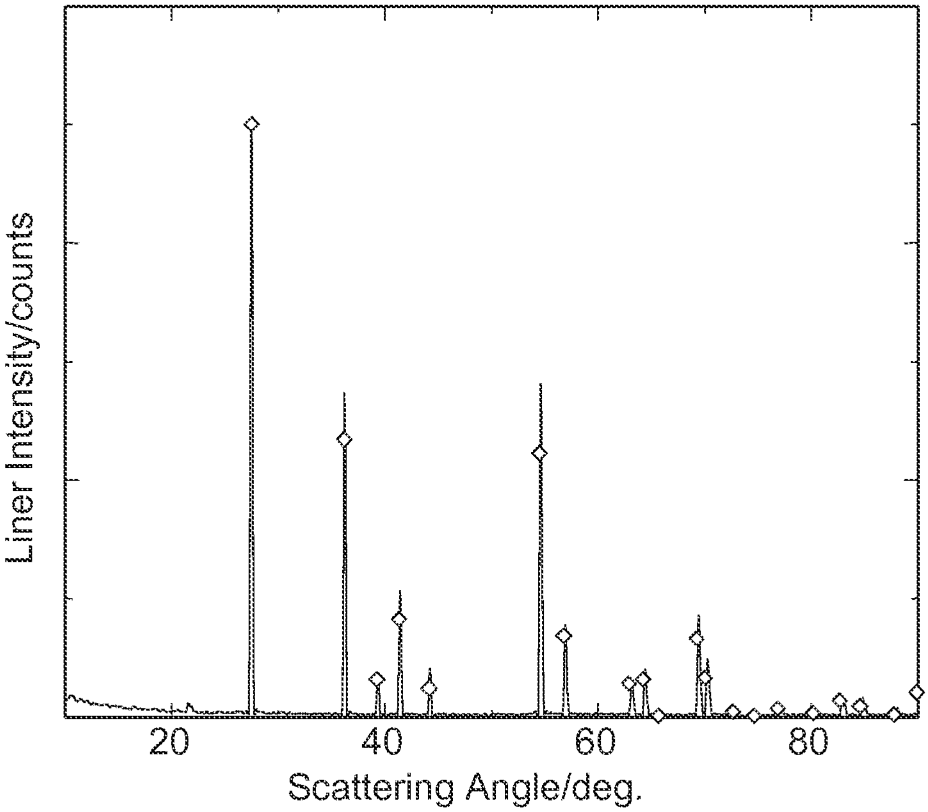

FIG. 14A

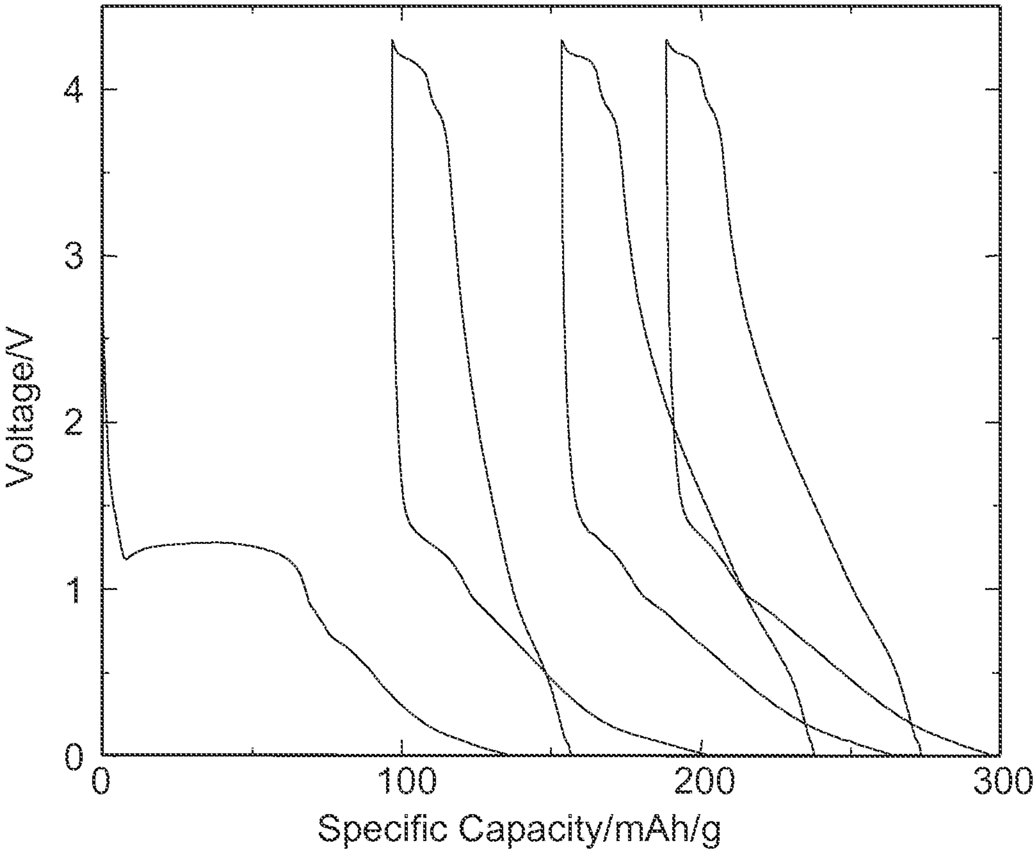

FIG. 14B

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US15/28121

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - H01M 4/02, 4/583 (2015.01)
CPC - H01M 4/02, 4/583
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(8): H01M 4/02, 4/583 (2015.01)
CPC: H01M 4/02, 4/583

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)
PatSeer (US, EP, WO, JP, DE, GB, CN, FR, KR, ES, AU, IN, CA, INPADOC Data); ProQuest; Scifinder; Google/Google Scholar; KEYWORDS: sodium, ion, battery, cathode, anode, alkali, alkaline, transition, titanium, vanadium, ilmenite, pseudo, rutile, orthorhombic, bannerite, triclinic

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2005/0238961 A1 (BARKER, J et al.) 27 October 2005; abstract; paragraphs [0006], [0008]-[0014], [0085], [0176]-[0181], [0196]	12
Y		1-2, 3/1-2, 4/1-2, 5/1-2, 8, 13
Y	US 2013/0224583 A1 (GREEN, M) 29 August 2013; abstract; paragraph [0053]	1-2, 3/1-2, 4/1-2, 5/1-2, 8, 13
Y	US 2010/0266907 A1 (YAZAMI, R) 21 October 2010; paragraphs [0108]-[0109], [0124]	1-2, 3/1-2, 4/1-2, 5/1-2
A	US 2011/0052986 A1 (BARKER, J et al.) 03 March 2011; entire document	1-2, 3/1-2, 4/1-2, 5/1-2, 8, 12-13
A	US 2006/0046144 A1 (OBROVAC, MN et al.) 02 March 2006; entire document	1-2, 3/1-2, 4/1-2, 5/1-2, 8, 12-13
A	US 2007/0218361 A1 (INOUE, T et al.) 20 September 2007; entire document	1-2, 3/1-2, 4/1-2, 5/1-2, 8, 12-13
A	US 2007/0218354 A1 (RYU, JH et al.) 20 September 2007; entire document	1-2, 3/1-2, 4/1-2, 5/1-2, 8, 12-13

☐ 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 14 July 2015 (14.07.2015)	Date of mailing of the international search report 31 JUL 2015
Name and mailing address of the ISA/ Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-8300	Authorized officer Shane Thomas PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US15/28121

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☒ Claims Nos.: 6-7, 9-11
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.