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(71) **Applicant** *(for all designated States except BB)*: **NOVONIX BATTERY TESTING SERVICES INC.** [CA/CA]; 177 Bluewater Road, Bedford, Nova Scotia B4B 1H1 (CA).

(71) **Applicant** *(for BB only)*: **BURNS, John** [US/CA]; 2723 George Dauphinee Ave., Halifax, Nova Scotia B3L 3S5 (CA).

(72) **Inventors: ZHENG, Lituo**; Dalhousie University, Dept. of Physics, Halifax, Nova Scotia B3H 4R2 (CA). **OBROVAC, Mark**; Dalhousie University, Dept. of Physics and Chemistry, Halifax, Nova Scotia B3H 4R2 (CA).

(74) **Agent: WAINWRIGHT, David**; 2585 West 1st Avenue, Vancouver, British Columbia V6K 1G8 (CA).

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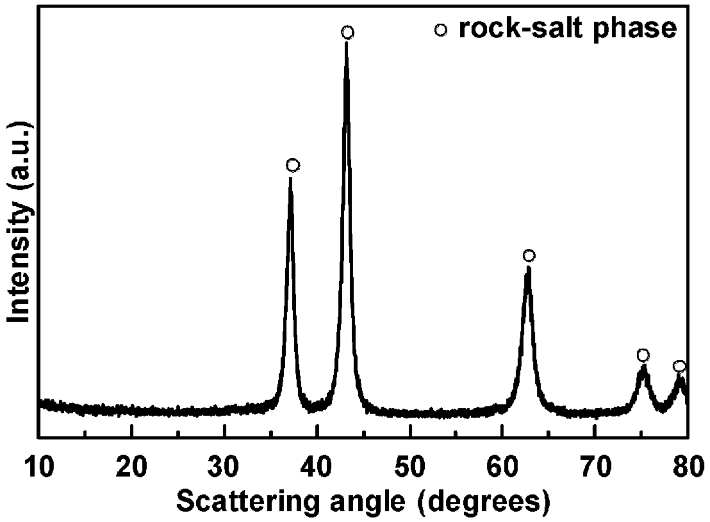

FIG. 1

(57) **Abstract:** Improved methods for preparing lithium transition metal oxide particulate such as lithium nickel metal cobalt oxide ("NMC") for use in lithium batteries and other applications are disclosed. The lithium transition metal oxide particulate is prepared from appropriate transition metal oxide and Li compound precursors mainly using dry, solid state processes including dry impact milling and heating. Further, novel precursor particulates and novel methods for preparing precursor particles for this and other applications are disclosed.

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LITHIUM TRANSITION METAL OXIDE AND PRECURSOR PARTICULATES AND METHODS

Technical Field

The present invention pertains to novel precursor particulate and improved methods for preparing lithium transition metal oxide particulate therefrom. The lithium transition metal oxide particulate is useful as an electrode material in lithium batteries and other applications.

Background

The development of rechargeable high energy density batteries, such as Li-ion batteries, is of great technological importance. Typically, commercial rechargeable Li-ion batteries use a lithium transition metal oxide cathode and a graphite anode. While batteries based on such materials are approaching their theoretical energy density limit, significant research and development continues in order to improve other important characteristics such as cycle life, efficiency, and cost. Further, significant research and development continues in order to simplify the methods of production and to reduce the complexity, material amounts, and losses involved.

Insertion compound transition metal oxide cathode materials for use in lithium rechargeable batteries typically comprise lithium, one or more first row transition metal elements, oxygen, and optional dopant elements (e.g. Mg, Al, Ti, Zr, W, Zn, Fe, Mo, K, Na, Si, Ta) and such materials can be further coated with other materials (e.g. Al_2O_3, ZrO_2, TiO_2). For ease of manufacturing, an air stable version of the transition metal oxide is usually employed. Given the substantial demand for these batteries, it is of great importance to be able to provide significant and economic supplies of such materials. At present, lithium nickel manganese cobalt oxide particulate, known as “NMC” commercially, are preferred cathode materials for commercial Li-ion batteries.

“NMC” type materials for use as cathodes in Li-ion batteries generally have an O3 layered structure and have the general actual formula $Li_{1+x}[(Ni_nMn_mCo_c)_{1-a}A_a]_{1-x}O_2$, where $-0.03 \leq x \leq 0.06$; $n + m + c = 1$; $n/(n + m + c) > 0.5$; $m \geq 0$; $c \geq 0$; A is a dopant; and $0 \leq a \leq 0.05$. Especially desirable in some applications are single crystal LiNMC lithium transition metal oxide particulate materials, abbreviated as SC-LiNMC and also known as monolithic “NMC”. In some embodiments, SC-LiNMC particles can consist of a single “NMC” grain. In some embodiments, SC-LiNMC particles can consist of multiple "NMC" grains, where the average “NMC” grain facet size is greater than 20% of the average particle size. In some embodiments of SC-LiNMC, the average particle size (D50) is between 1 μm and 30 μm.

A common method of preparing SC-LiNMC is to first make a mixed metal hydroxide (MMH) or a mixed metal carbonate (MMC) of Ni, Mn, Co, and optional dopant A, each in proportion according to the desired final composition of $Li_{1+x}[(Ni_nMn_mCo_c)_{1-a}A_a]_{1-x}O_2$. The MMH or MMC is made by co-precipitation of metal salts in an aqueous solution, followed by filtering, drying and grinding steps. The resulting MMH or MMC is then ground together with a lithium source (e.g. LiOH, $LiOH \cdot H_2O$ or Li_2CO_3), typically in an amount that is in excess of the desired $Li_{1+x}[(Ni_nMn_mCo_c)_{1-a}A_a]_{1-x}O_2$ composition to form a mixture. The mixture is then sintered in air at temperatures in the range of 600 - 1000 °C. A description of the synthesis of SC-LiNMC by this method can be found in Journal of The Electrochemical Society, 165 (5) A1038-A1045 (2018). A two-step heating method can also be employed, as described in WO 2019/185349. However, these methods require many steps and can produce large amounts of waste water. In addition, the co-precipitation method requires that the sources of transition metals are soluble metal salts, which can be more expensive than insoluble sources of these metals, such as metal oxide, hydroxide and carbonate compounds.

An improved method for making “NMC” is described in US 7,211,237, in which cobalt-, manganese-, nickel-, and lithium containing oxides or oxide precursors are wet milled together to form a precursor. The precursor is then heated to produce an “NMC”. This method also has the disadvantage of using water, which needs to be removed by drying prior to or during the heating step.

The Journal of The Electrochemical Society, 159 (9) A1543-A1550 (2012) describes a method in which SC- $Li_{1+0.14}(Ni_{0.33}Mn_{0.33}Co_{0.33})_{0.86}O_2$ is made by ball milling $Ni(NO_3)_2 \cdot 6H_2O$, $Mn(NO_3)_2 \cdot 4H_2O$ and $Co(NO_3)_2 \cdot 6H_2O$ together, adding $LiNO_3$ and LiCl, and then heating. In this method the LiCl and KCl components are present to form a molten salt, which requires removal by rinsing after the heating step to obtain the SC LiNMC particles. This method requires many steps and can produce large amounts of waste water.

As stated in Linden's Handbook of Batteries, 4th Edition, McGraw-Hill Education (2010): "NMC and NCA materials rely on a uniform and homogeneous distribution of cations in the transition metal layers of the structure. The most common way to ensure this is to use a mixed transition metal hydroxide or carbonate precursor that has the cations perfectly mixed on the atomic scale." The most common way to synthesize such precursors is by co-precipitation. Solid-state reactions have also been proposed as an economical method to make "NMC" lithium transition metal oxide particulate materials, in which precursors are ground and sintered without the co-precipitation step. However, solid state reactions typically result in inhomogeneous element distribution and low particle size in the lithium transition metal oxide particulate, both of which are detrimental to electrochemical performance. Therefore, solid-state synthesis methods are generally thought to be unsuitable as a practical synthesis method for "NMC". For instance, regarding the solid-state synthesis of "NMC":

Nano Energy, 31 247–257 (2017): "Comparing to co-precipitation process, solid-state synthesis is expected to have a reduced cost, and reduced synthesis time. However, the major disadvantage of the solid-state synthesis is the difficulty in controlling the segregation of transition metal elements in the primary particle level, which in turn has significant impact on the electrochemical performance of the final cathode materials."

Chemistry of Materials, 29 9923−9936 (2017): "Li-rich layered compounds with different morphologies can be prepared via a wide variety of synthesis pathways including solid state, molten salts, hydrothermal, and sol−gel as well as coprecipitation in aqueous medium followed by high temperature synthesis. Among the various possible techniques, solution based coprecipitation (or aqueous sol−gel) is more viable as it can provide atomic level mixing of transition metal ions and hence homogeneity in the final oxide."

In US provisional applications 62/893787 and 62/946938 filed on August 29, 2019 and December 11, 2019 respectively, both by the same applicant and both titled “Improved Microgranulation Methods And Product Particles Therefrom”, certain NMC precursor particles were disclosed in the examples that had been prepared using an all-solid-state method. The content of these two US provisional applications are incorporated by reference herein in their entirety.

Despite this continuing and substantial global effort directed at developing improved methods of manufacture of such materials, there remain a need for further improvement. The present invention addresses these needs and provides further benefits as disclosed below.

Summary

In a first aspect of the invention, precursor particulates that are useful as an ingredient for the synthesis of lithium transition metal oxide particulates and in other applications are described. Specifically, such a precursor particulate comprises: a compound of Ni selected from the group consisting essentially of an oxide of Ni, a hydroxide of Ni, a carbonate of Ni, and mixtures thereof and a compound of Mn selected from the group consisting essentially of an oxide of Mn, a hydroxide of Mn, a carbonate of Mn, and mixtures thereof. The precursor particulate can also optionally comprise a compound of Co selected from the group consisting essentially of an oxide of Co, a hydroxide of Co, a carbonate of Co, and mixtures thereof, and/or a compound of A selected from the group consisting essentially of an oxide of A, a hydroxide of A, a carbonate of A, and mixtures thereof. Further, in such a precursor particulate, A is a metal dopant, the average grain size of each phase present in the precursor particulate is less than 50 nm, and the ratio of the total number of moles of Ni in the precursor particulate to the total number of moles of Mn in the precursor particulate to the total number of moles of optional Co in the precursor particulate to the total number of moles of optional A in the precursor particulate is equal to n:m:c:a in which n, m, c and a are numbers in which: $n + m + c = 1$; $n \geq 0.05$; $m \geq 0.05$; $c \geq 0$; and $0 \leq a \leq 0.05$.

The precursor particulate of the invention can be further characterized by having grains of a rock-salt phase with an average grain size less than 50 nm. Further, the lattice constant of the rock-salt phase grains can be greater than 4.18 Å. In some embodiments, the precursor particulate can consist essentially of grains of a rock-salt phase, e.g. is almost entirely rock-salt phase. In some embodiments of the invention, suitable oxygen containing compounds of Ni, Mn, Co or A are oxides, hydroxides, carbonates, and mixtures thereof. In some embodiments of the invention the precursor particulates comprise oxide compounds of Ni, Mn, Co or A. In some embodiments of the invention the precursor particulates consist essentially of oxide compounds. Metal oxide compounds can be especially suitable oxygen containing compounds, since they are often inexpensive. They can also be advantageous to use during the milling process, compared to metal carbonate and hydroxide compounds, that can be more prone to decomposition reactions that resulting in the production of gas during milling.

The aforementioned precursor particulate can be made by a method comprising obtaining an amount of the compound of Ni, obtaining an amount of the compound of Mn, preparing a precursor mixture comprising the amounts of the compound of Ni and the compound of Mn together, and dry impact milling the precursor mixture sufficiently to produce a precursor particulate comprising grains of at least one phase wherein the average grain size of each phase present in the precursor particulate is less than 50 nm. In the method, the precursor mixture can consist essentially of compounds selected from the group consisting of oxides, hydroxides, carbonates and mixtures thereof. Further, in the method, the ratio of the total number of moles of Ni in the precursor mixture to the total number of moles of Mn in the precursor mixture to the total number of moles of optional Co in the precursor mixture to the total number of moles of optional A in the precursor mixture is equal to n:m:c:a.

The precursor particulate may optionally contain lithium. Compounds of lithium, including LiOH, Li_2O, and Li_2CO_3, may be used as sources of lithium in the preparation of the precursor particulate. Precursor particulates containing lithium can be made by a method comprising obtaining an amount of the compound of lithium, obtaining an amount of the compound of Ni, obtaining an amount of the compound of Mn, preparing a precursor mixture comprising the amounts of the compound of Li, the compound of Ni and the compound of Mn, and dry impact milling the precursor mixture sufficiently to produce a precursor particulate comprising grains of at least one phase wherein the average grain size of each phase present in the precursor particulate is less than 50 nm.

As mentioned above, desirable lithium transition metal oxide particulate with an O3 crystal structure and having the formula $Li_{1+x}[(Ni_nMn_mCo_c)_{1-a}A_a]_{1-x}O_2$ with the aforementioned limitations on A, x, m, n, m, c, and a can then be prepared using this novel precursor particulate. An aspect of the invention thus comprises the discovery of improved methods for preparing lithium transition metal oxide particulate, such as lithium nickel metal cobalt oxide ("NMC") for use in lithium batteries and other applications. The methods can especially be used to prepare larger lithium transition metal oxide particulate suitable for such applications, e.g. having an average particle size > 1 μm. The lithium transition metal oxide particulate can be prepared from appropriate oxygen containing transition metal compounds and lithium and oxygen containing compound powders solely using dry, solid state processes including dry impact milling and heating.

In some embodiments, the novel precursor particulates are especially suitable for making SC-LiNMC. For instance, in one embodiment, novel precursor particulate prepared by any suitable method is initially obtained. Then, a final mixture comprising an amount of the precursor particulate and an amount of a Li compound selected from the group consisting essentially of Li oxide, Li hydroxide, Li carbonate and mixtures thereof is prepared, and then heated to react the Li compound with the precursor particulate and thereby produce the lithium transition metal oxide particulate with the O3 crystal structure. In another general embodiment, novel precursor particulate can initially be prepared according to the method described above. Then, a final mixture comprising an amount of the precursor particulate and an amount of a Li compound selected from the group consisting essentially of Li oxide, Li hydroxide, Li carbonate and mixtures thereof is prepared, and then heated to react the Li compound with the precursor particulate and thereby produce the lithium transition metal oxide particulate with the O3 crystal structure.

In more detail, such methods are for making lithium transition metal oxide particulate with an O3 crystal structure and having the formula $Li_{1+x}[(Ni_nMn_mCo_c)_{1-a}A_a]_{1-x}O_2$ in which A is a metal dopant (e.g. Mg, Al, Ti, Zr, W, Zn, Fe, Mo, K, Na, Si, Ta, or combinations thereof), and x, n, m, c and a are numbers in which:

$-0.03 \leq x \leq 0.06$;
$n + m + c = 1$;
$n \geq 0.05$;
$m \geq 0.05$;
$c \geq 0$; and
$0 \leq a \leq 0.05$;

At its most basic, the method comprises the following simple dry process steps of:

obtaining an amount of a compound of Ni selected from the group consisting essentially of an oxide of Ni, a hydroxide of Ni, a carbonate of Ni, and mixtures thereof;

obtaining an amount of a compound of Mn selected from the group consisting essentially of an oxide of Mn, a hydroxide of Mn, a carbonate of Mn, and mixtures thereof;

preparing a precursor mixture comprising the amounts of the compound of Ni and the compound of Mn together;

dry impact milling the precursor mixture sufficiently to produce a precursor particulate comprising grains of at least one phase wherein the average grain size of each phase present in the precursor particulate is less than 50 nm;

preparing a final mixture comprising an amount of the precursor particulate and an amount of a Li compound selected from the group consisting essentially of Li oxide, Li hydroxide, Li carbonate and mixtures thereof; and

heating the final mixture to react the Li compound with the precursor particulate and thereby produce the crystal lithium transition metal oxide particulate with the O3 crystal structure.

Optionally however, additional steps involving liquids may be employed. For instance, if an excess of Li compound is employed in the final mixture, the method can additionally comprise washing away excess unreacted Li compound from the produced lithium transition metal oxide particulate. Additionally, a liquid based coating method could be used to apply a particle coating (e.g. Al_2O_3, ZrO_2, TiO_2) to improve the performance.

In certain embodiments, the precursor mixture can consist solely of oxides, hydroxides, carbonates and mixtures thereof. That is, the precursor mixture can consist essentially of compounds selected from the group consisting of oxides, hydroxides, carbonates and mixtures thereof.

In the method, the ratio of the total number of moles of Ni in the precursor mixture to the total number of moles of Mn in the precursor mixture to the total number of moles of Co in the precursor mixture to the total number of moles of A in the precursor mixture can be equal to n:m:c:a.

In exemplary embodiments in which "NMC" materials are produced, the method additionally comprises the steps of obtaining an amount of a source of Co selected from the group consisting essentially of an oxide of Co, a hydroxide of Co, a carbonate of Co, and mixtures thereof, and preparing the precursor mixture comprising the amounts of the compound of Ni, the compound of Mn, and the compound of Co together. In particular, the compound of Ni can be NiO, the compound of Mn can be MnO, and the compound of Co can be Co_3O_4.

To avoid iron contamination, it can be preferred for the dry impact milling to be conducted using non-ferrous milling apparatus. For instance, ball milling using a non-ferrous mill and non-ferrous milling media can be preferred.

In preparing the lithium transition metal oxide particulate, the Li compound employed can be Li_2CO_3, Li_2O, Li_2O_2, LiOH or combinations thereof. Further, the step of heating the final mixture can comprise heating in oxygen and/or air. It can be particularly advantageous to obtain certain characteristics in the lithium transition metal oxide particulate however to heat the final mixture first in oxygen and then afterwards in air. In exemplary embodiments, the heating step can be conducted at temperatures greater than 600° C, greater than 700° C, greater than 800° C or greater than 900° C for sintering times greater than 1 hour, greater than 4 hours, greater than 8 hours or for greater than or about 12 hours. Additional sintering steps with additional Li compound may also be employed.

The method of the invention is particularly suitable for producing larger lithium transition metal oxide particulate, e.g. having an average particle size greater than 1 μm. Further, the lithium transition metal oxide particulate produced can be characterized by an average facet size of greater than 1 μm. 17. Further still, the average facet size of the single crystal lithium transition metal oxide particulate produced can be greater than 20% of the average particle size. And further still, the O3 crystal structure of the lithium transition metal oxide particulate produced can have a c/a ratio of greater than 4.95.

The lithium transition metal oxide particulate made according to the inventive method may be considered for use in numerous commercial applications including as a rechargeable battery electrode. It can be particularly suitable for use in cathode electrodes in rechargeable lithium batteries, e.g. lithium ion batteries.

Brief Description of the Drawings

Figure 1 shows the XRD pattern of NMC622 precursor particulate prepared in accordance with the invention and referred to as PM1 in the Examples.

Figure 2 shows the XRD pattern of NMC622 precursor particulate prepared in accordance with the invention and referred to as PM2 in the Examples.

Figure 3 shows the XRD pattern of NMC622 precursor particulate prepared in a comparative manner and referred to as PM3 in the Examples.

Figures 4a and 4b show SEM images of SC-LiNMC-1 lithium transition metal oxide particulate of Inventive Example 1 at different magnifications.

Figure 4c shows the XRD pattern of the SC-LiNMC-1 lithium transition metal oxide particulate.

Figure 4d shows the expanded XRD pattern of the SC-LiNMC-1 lithium transition metal oxide particulate between 20° and 30°.

Figure 4e shows the Cu $K_{\alpha1}/K_{\alpha2}$ splitting of the (104) peak of the SC-LiNMC-1 lithium transition metal oxide particulate.

Figure 4f shows the (003) peak of the SC-LiNMC-1 lithium transition metal oxide particulate.

Figure 4g shows the first cycle potential profile of the laboratory test cell made with SC-LiNMC-1 lithium transition metal oxide particulate.

Figures 5a and 5b show SEM images of SC-LiNMC-2 lithium transition metal oxide particulate of Inventive Example 2 at different magnifications.

Figure 5c shows the XRD pattern of the SC-LiNMC-2 lithium transition metal oxide particulate.

Figure 5d shows the expanded XRD pattern of the SC-LiNMC-2 lithium transition metal oxide particulate between 20° and 30°.

Figure 5e shows the Cu $K_{\alpha1}/K_{\alpha2}$ splitting of the (104) peak of the SC-LiNMC-2 lithium transition metal oxide particulate.

Figure 5f shows the (003) peak of the SC-LiNMC-2 lithium transition metal oxide particulate.

Figure 5g shows the first cycle potential profile of the laboratory test cell made with SC-LiNMC-2 lithium transition metal oxide particulate.

Figures 6a and 6b show SEM images of SC-LiNMC-3 lithium transition metal oxide particulate of Inventive Example 3 at different magnifications.

Figure 6c shows the XRD pattern of the SC-LiNMC-3 lithium transition metal oxide particulate.

Figure 6d shows the expanded XRD pattern of the SC-LiNMC-3 lithium transition metal oxide particulate between 20° and 30°.

Figure 6e shows the Cu $K_{\alpha 1}/K_{\alpha 2}$ splitting of the (104) peak of the SC-LiNMC-3 lithium transition metal oxide particulate.

Figure 6f shows the (003) peak of the SC-LiNMC-3 lithium transition metal oxide particulate.

Figure 6g shows EDS mapping of the SC-LiNMC-3 lithium transition metal oxide particulate.

Figure 6h shows the first cycle potential profile of the laboratory test cell made with SC-LiNMC-3 lithium transition metal oxide particulate.

Figures 7a and 7b show SEM images of SC-LiNMC-4 lithium transition metal oxide particulate of Inventive Example 4 at different magnifications.

Figure 7c shows the XRD pattern of the SC-LiNMC-4 lithium transition metal oxide particulate.

Figure 7d shows the expanded XRD pattern of the SC-LiNMC-4 lithium transition metal oxide particulate between 20° and 30°.

Figure 7e shows the Cu $K_{\alpha 1}/K_{\alpha 2}$ splitting of the (104) peak of the SC-LiNMC-4lithium transition metal oxide particulate.

Figure 7f shows the (003) peak of the SC-LiNMC-4 lithium transition metal oxide particulate.

Figure 7h shows the first cycle potential profile of the laboratory test cell made with SC-LiNMC-4 lithium transition metal oxide particulate.

Figures 8a and 8b show SEM images of SC-LiNMC-5 lithium transition metal oxide particulate of Inventive Example 5 at different magnifications.

Figure 8c shows the XRD pattern of the SC-LiNMC-5 lithium transition metal oxide particulate.

Figure 8d shows the expanded XRD pattern of the SC-LiNMC-5 lithium transition metal oxide particulate between 20° and 30°.

Figure 8e shows the Cu $K_{\alpha1}/K_{\alpha2}$ splitting of the (104) peak of the SC-LiNMC-5 lithium transition metal oxide particulate.

Figure 8f shows the (003) peak of the SC-LiNMC-5 lithium transition metal oxide particulate.

Figure 8g shows the first cycle potential profile of the laboratory test cell made with SC-LiNMC-5 lithium transition metal oxide particulate.

Figures 9a and 9b show SEM images of SC-LiNMC-6 lithium transition metal oxide particulate of Inventive Example 6 at different magnifications.

Figure 9c shows the XRD pattern of the SC-LiNMC-6 lithium transition metal oxide particulate.

Figure 9d shows the expanded XRD pattern of the SC-LiNMC-6 lithium transition metal oxide particulate between 20° and 30°.

Figure 9e shows the Cu $K_{\alpha1}/K_{\alpha2}$ splitting of the (104) peak of the SC-LiNMC-6 lithium transition metal oxide particulate.

Figure 9f shows the (003) peak of the SC-LiNMC-6 lithium transition metal oxide particulate.

Figure 9g shows EDS mapping of the SC-LiNMC-6 lithium transition metal oxide particulate.

Figure 9h shows the first cycle potential profile of the laboratory test cell made with SC-LiNMC-6 lithium transition metal oxide particulate.

Figure 10a shows the XRD pattern of CE-LiNMC-1 lithium transition metal oxide particulate of Comparative Example 1.

Figure 10b shows the expanded XRD pattern of the CE-LiNMC-1 lithium transition metal oxide particulate between 20° and 30°.

Figure 10c shows the Cu $K_{\alpha1}/K_{\alpha2}$ splitting of the (104) peak of the CE-LiNMC-1 lithium transition metal oxide particulate.

Figure 10d shows EDS mapping of the CE-LiNMC-1 lithium transition metal oxide particulate.

Detailed Description

Unless the context requires otherwise, throughout this specification and claims, the words "comprise", “comprising” and the like are to be construed in an open, inclusive sense. The words “a”, “an”, and the like are to be considered as meaning at least one and are not limited to just one.

The phrases “consisting essentially of” or “consists essentially of” are to be interpreted as limiting to the specified materials or steps involved (depending on context) but also to include – and not to exclude – any materials or steps that do not materially affect the basic and novel characteristics of the materials or steps involved.

In a quantitative context, the term “about” should be construed as being in the range up to plus 10% and down to minus 10%.

In addition, the following definitions are to be applied throughout the specification:

“Particulate” refers to a plurality of “particles” in which the “particles” are composed of one or more “grains” (also known in the art as crystallites).

The term “average particle size” refers to the average of the greatest dimension of at least 20 random particles as directly observed by SEM.

The term “average grain size” refers to the average grain size of a phase as determined by the Scherrer grain size determination method.

A "facet" is a plane section of a grain that corresponds to the emergence to the surface of a crystal face with definite Miller indices. The term “average facet size” herein refers to the average of at least 20 random grain facets as directly observed by SEM.

The term “single crystal lithium transition metal oxide particulate” refers to a lithium transition metal oxide particulate material in which its constituent particles are composed of grains having an average facet size that is greater than 20% of the average particle size.

The term "O3" refers to phases having a α-$NaFeO_2$ type structure, as described in C. Delmas, C. Fouassier, and P. Hagenmuller, Physica, 99B (1980) 81-85.

The term "rock-salt phase" refers to a phase having a cubic rock-salt crystal structure that is absent of cation layering order.

"Metal dopant" refers to the group of metals capable of serving as a dopant in a lithium transition metal oxide, and includes but is not limited to the metals Mg, Al, Ti, Zr, W, Zn, Fe, Mo, K, Na, Si, and Ta.

The term "phase" has its conventional general meaning, namely being a distinct and homogeneous form of matter separated at its surface from other forms of matter.

The term "dry impact milling" refers to a dry milling process that principally uses repeated impacts upon a sample to result in a grain size reduction and/or a chemical change in the sample. Suitable dry impact milling methods include ball milling, SPEX milling, pebble milling, rod milling, high energy ball milling, attritor milling, Sweco milling, vibratory milling, planetary milling and low energy ball milling as described in U.S. Patent No. 8,287,772 (Le et al).

The term "metal-ion cell" or "metal-ion battery" refers to alkali metal ion cells, including for instance lithium ion cells.

The term "cathode" refers to the electrode at which reduction occurs when a metal-ion is discharged. In a lithium ion cell, the cathode is the electrode that is lithiated during discharge and delithiated during charge.

The term "anode" refers to the electrode at which oxidation occurs when a metal-ion cell is discharged. In a lithium ion cell, the anode is the electrode that is delithiated during discharge and lithiated during charge.

The term "half-cell" refers to a cell that has a working electrode and a metal counter/reference electrode. A lithium half-cell has a working electrode and a lithium metal counter/reference electrode.

In one aspect of the invention, dry, solid state processes can be used to prepare certain lithium transition metal oxide particulate that hitherto were believed to necessarily require more complex, liquid processing steps (e.g. steps requiring large amounts of water). Relevant lithium transition metal oxide particulate includes single phase, lithium transition metal oxide particulate with an O3 crystal structure. Such materials are characterized with low cation mixing (i.e. no transition metal in the lithium layer) and are desirable for good kinetics and low irreversible capacity for use in rechargeable lithium batteries.

Relevant lithium transition metal oxide particulate having the O3 structure is further characterized by the chemical formula $Li_{1+x}[(Ni_nMn_mCo_c)_{1-a}A_a]_{1-x}O_2$ in which A is a metal dopant, and x, n, m, c and a are numbers in which

$-0.03 \le x \le 0.06$;

$n + m + c = 1$;

$n \ge 0.05$;

$m \ge 0.05$;

$c \ge 0$; and

$0 \le a \le 0.05$.

Thus, relevant lithium transition metal oxide particulate includes the transition metals Ni and Mn with Co being optional. Further, the optional dopant A can be any of those commonly considered for use with such materials, including but not limited to Mg, Al, Ti, Zr, W, Zn, Fe, Mo, K, Na, Si, Ta or combinations thereof.

In the method, a precursor particulate is prepared from a precursor mixture comprising stoichiometrically appropriate amounts of oxygen containing transition metal compounds. The precursor mixture may also contain stoichiometrically appropriate amounts of oxygen containing compounds of the dopant A. The precursor mixture is then subjected to dry impact milling to produce a precursor particulate. Appropriate transition metal oxygen containing compounds include Ni, Mn, and optionally Co compounds selected from the group consisting of oxides, hydroxides, carbonates, and mixtures thereof. Appropriate sources of the dopant A include oxygen containing compounds of A selected from the group consisting of oxides, hydroxides, carbonates, and mixtures thereof. Any of various known dry impact mechanical milling techniques may be employed, including ball or jar milling (as in the Examples following), hammer milling, planetary milling, vibratory milling, and so on. Such dry milling of precursors typically produce multiphase polycrystalline particles. Importantly, the dry impact milling is performed to a sufficient extent so as to produce precursor particulate comprising grains of at least one phase in which the average grain size of each phase present is less than 50 nm.

After sufficient dry impact milling has been performed, a final mixture is prepared comprising appropriate amounts of the prepared precursor particulate and a Li compound. Thereafter, a heating is used to react the Li compound with the precursor particulate to produce the desired lithium transition metal oxide particulate. Suitable Li compounds include a Li oxide, Li hydroxide, Li carbonate and/or a mixture thereof. In some embodiments, the amounts of each may be chosen based on the final desired stoichiometry of the lithium transition metal oxide particulate. In other embodiments, it may be preferred to use an excess of the Li compound, in which case an additional step (e.g. a water washing step) is required to remove excess unreacted Li compound from the desired lithium transition metal oxide particulate.

In particular, the method can be used to prepare single crystal lithium nickel metal cobalt oxide lithium transition metal oxide particulate or SC-LiNMC, which is a preferred electrode material for use in lithium rechargeable batteries and other applications. SC-LiNMC is desirable in such applications in part because of its excellent lithiation/delithiation kinetics.

In prior art techniques, co-precipitation was conventionally used to initially prepare hydroxide or carbonate precursors which were then subsequently heated to produce SC-LiNMC. This is because the slow diffusion of the transition metals requires them to be intimately mixed, so that they can form single-phase materials when heated. It was also thought that the size of the precursor governs the size of SC-LiNMC.

We have found that precursors of oxides, carbonates, and/or hydroxides that are dry impact milled sufficiently, namely such that the resulting precursor particulate contains no phase having a grain size greater than 50 nm, are suitable for forming SC-LiNMC during heating with a Li compound. Further, the size of the SC-LiNMC thus formed is not related to the size of the precursor particulate. Instead, without being bound by theory, it is believed that the particle size of the SC-LiNMC is determined by the heating time in air of the final mixture. For instance, it has been found that heating in air promotes grain growth, while heating in oxygen promotes more perfect ion ordering in the lithium transition metal oxide O3 structure. However, heating in oxygen only results in smaller grains. Therefore, in some embodiments, it can be desirable to first heat the final mixture in air for a time necessary to obtain the desired grain size and then heat the resulting material in oxygen to obtain more perfect ion ordering. As a result of such a two-step heating method, SC-LiNMC with large facets and good O3 ordering may be obtained.

It has also been found that sufficient dry impact milling can result in the milled precursors forming a precursor particulate consisting essentially of a single rock-salt phase having a grain size less than 50 nm. Without being bound by theory, it is believed that a single rock-salt phase formation is indicative of atomic-scale mixing and that such precursor particulate can have superior lithium transition metal oxide particulate forming ability during heating because of the resulting shortened diffusion lengths. The lattice constant of rock-salt phase grains produced in this way can be greater than 4.18 Å.

Using the method of the invention, lithium transition metal oxide particulate can be produced with an average particle size greater than 1 μm and less than 40 μm, and comprising facets in which the average facet size is >1 μm, more preferably >4 μm, and even more even preferably >8 μm. The average facet size of the lithium transition metal oxide particulate may be greater than 20%, greater than 30%, greater than 50%, greater than 60% or even greater than 70% of the lithium transition metal oxide particulate average particle size. The average particle size of the lithium transition metal oxide particulate may be greater than 1 μm, greater than 5 μm, greater than 7 μm or even greater than 9 μm. The c/a ratio of the crystal structure (as obtained via XRD), which is indicative of O3 ordering, can preferably be greater than 4.95, and more preferably greater than 4.96. Further a pronounced Cu $K_{\alpha 1}/K_{\alpha 2}$ splitting of the (104) peak can be obtained, which is another indication of good ordering in the O3 structure.

As disclosed in more detail in the following Examples, it has further been found that in preparing the precursor particulate, dry impact milling using non-ferrous mills and milling media can avoid iron contamination in the lithium transition metal oxide particulate prepared from the precursor particulate and thereby improve the quality of lithium transition metal oxide particulate produced for battery applications by this method. This is because Fe is known to migrate into the Li layer during battery cycling, resulting in increased polarization and capacity fade in such batteries. Thus, use of iron-free materials in the milling apparatus is desirable.

As those skilled in the art will appreciate, appropriate operating parameters for the dry impact milling and heating processes required to obtain good lithium transition metal oxide particulate can be expected to vary according to the type and size of precursors employed, the milling technique and apparatus employed, and the like. It is expected that those of ordinary skill will readily be able to determine appropriate operating parameters for a given situation based on guidance provided in the Examples below.

Once prepared as in the preceding manner, the lithium transition metal oxide particulate is generally ready for conventional use in its intended application. In battery applications, electrodes and electrochemical devices employing lithium transition metal oxide particulate may be prepared in numerous manners known to those in the art. For instance, there are numerous optional designs and methods for making cathode electrodes for rechargeable lithium ion batteries as well as for making the batteries themselves and these have been documented extensively in the art.

In another aspect of the invention, novel precursor particulates have been developed that are useful as an ingredient for the synthesis of the aforementioned lithium transition metal oxide particulates and for other potential applications. These precursor particulates comprise: a compound of Ni selected from the group consisting essentially of an oxide of Ni, a hydroxide of Ni, a carbonate of Ni, and mixtures thereof and a compound of Mn selected from the group consisting essentially of an oxide of Mn, a hydroxide of Mn, a carbonate of Mn, and mixtures thereof. The precursor particulate can also optionally comprise a compound of Co selected from the group consisting essentially of an oxide of Co, a hydroxide of Co, a carbonate of Co, and mixtures thereof, and/or a compound of A selected from the group consisting essentially of an oxide of A, a hydroxide of A, a carbonate of A, and mixtures thereof. Further, in such a precursor particulate, A is a metal dopant, the average grain size of each phase present in the precursor particulate is less than 50 nm, and the ratio of the total number of moles of Ni in the precursor particulate to the total number of moles of Mn in the precursor particulate to the total number of moles of optional Co in the precursor particulate to the total number of moles of optional A in the precursor particulate is equal to n:m:c:a in which n, m, c and a are numbers in which: $n + m + c = 1$; $n \geq 0.05$; $m \geq 0.05$; $c \geq 0$; and $0 \leq a \leq 0.05$.

The novel precursor particulate can be further characterized by having grains of a rock-salt phase with an average grain size less than 50 nm. Further, the lattice constant of the rock-salt phase grains can be greater than 4.18 Å. In some embodiments, the precursor particulate can consist essentially of grains of a rock-salt phase, e.g. is almost entirely rock-salt phase. In some embodiments of the invention, suitable oxygen containing compounds of Ni, Mn, Co or A are oxides, hydroxides, carbonates, and mixtures thereof. In some embodiments of the invention the precursor particulates comprise oxide compounds of Ni, Mn, Co or A. In some embodiments of the invention the precursor particulates consist essentially of oxide compounds.

Novel precursor particulate can be made by a method comprising obtaining an amount of the compound of Ni, obtaining an amount of the compound of Mn, preparing a precursor mixture comprising the amounts of the compound of Ni and the compound of Mn together, and dry impact milling the precursor mixture sufficiently to produce a precursor particulate comprising grains of at least one phase wherein the average grain size of each phase present in the precursor particulate is less than 50 nm. In the method, the precursor mixture can consists essentially of compounds selected from the group consisting of oxides, hydroxides, carbonates and mixtures thereof. Further, in the method, the ratio of the total number of moles of Ni in the precursor mixture to the total number of moles of Mn in the precursor mixture to the total number of moles of optional Co in the precursor mixture to the total number of moles of optional A in the precursor mixture is equal to n:m:c:a.

The precursor particulate may optionally contain lithium. Compounds of lithium, including LiOH, Li_2O, and Li_2CO_3, may be used as sources of lithium in the preparation of the precursor particulate. Precursor particulates containing lithium can be made by a method comprising obtaining an amount of the compound of lithium, obtaining an amount of the compound of Ni, obtaining an amount of the compound of Mn, preparing a precursor mixture comprising the amounts of the compound of Li, the compound of Ni and the compound of Mn, and dry impact milling the precursor mixture sufficiently to produce a precursor particulate comprising grains of at least one phase wherein the average grain size of each phase present in the precursor particulate is less than 50 nm.

As disclosed earlier, desirable lithium transition metal oxide particulate with an O3 crystal structure and having the aforementioned formula $Li_{1+x}[(Ni_nMn_mCo_c)_{1-a}A_a]_{1-x}O_2$ can be prepared using this novel precursor particulate. For instance, in one embodiment, novel precursor particulate can initially be prepared according to the method described above. Then, a final mixture comprising an amount of the precursor particulate and an amount of a Li compound selected from the group consisting essentially of Li oxide, Li hydroxide, Li carbonate and mixtures thereof is prepared, and then heated to react the Li compound with the precursor particulate and thereby produce the lithium transition metal oxide particulate with the O3 crystal structure. In another general embodiment, novel precursor particulate prepared by any suitable method is initially obtained. Then, a final mixture comprising an amount of the precursor particulate and an amount of a Li compound selected from the group consisting essentially of Li oxide, Li hydroxide, Li carbonate and mixtures thereof is prepared, and then heated to react the Li compound with the precursor particulate and thereby produce the lithium transition metal oxide particulate with the O3 crystal structure.

The following examples are illustrative of certain aspects of the invention but should not be construed as limiting the invention in any way. Those skilled in the art will readily appreciate that other variants are possible for the methods used and materials produced herein.

Examples

Exemplary lithium transition metal oxide and precursor particulates were prepared using the dry processing methods in accordance with the invention. Other lithium transition metal oxide and precursor particulates were also prepared for comparison purposes. Various characteristics of these particulates were determined and presented below. In addition, electrodes and electrochemical cells were prepared using some of these lithium transition metal oxide particulates. The cell performance results obtained from the electrochemical cells are also presented below.

Material characterization

Specific surface area was determined by the single-point Brunauer-Emmett-Teller (BET) method using a Micromeritics Flowsorb II2300 surface area analyzer.

X-ray diffraction (XRD) patterns were collected using a Rigaku Ultima IV diffractometer equipped with a Cu Kα X-ray source, a diffracted beam graphite monochromator and a scintillation detector. Average grain size was determined from XRD patterns using the Scherrer grain size determination method.

Scanning electron microscope (SEM) images were obtained using a JEOL 840-SEM. Energy dispersive x-ray spectroscopy (EDS) mapping images were obtained using a MIRA-3 TESCAN variable pressure Schottky Field Emission Scanning Electron Microscope or FESEM.

Average facet size was determined as the average of at least 20 random grain facets as directly observed by SEM.

Average particle size was determined as the average of the greatest dimension of at least 20 random particles as directly observed by SEM.

Electrode preparation

Sample electrodes for laboratory testing were prepared from slurries prepared by mixing the prepared lithium transition metal oxide particulate, carbon black (Super C65, Imerys Graphite and Carbon), and polyvinylidene fluoride binder (PVDF, Kynar HSV 900)) in an active particle/carbon black/PVDF mass ratio of 92/4/4 with an appropriate amount of N-methyl-2-pyrrolidone (NMP, Sigma Aldrich, anhydrous 99.5%). Slurries were mixed for 10 minutes using a high-shear mixer and then spread onto aluminum foil with a 0.006 inch gap coating bar. The coatings were then dried in air for 90 minutes at 120 °C, cut into 1.3 cm disks and then heated under vacuum for at least 12 hours at 120 °C with no further air exposure before assembling the cells.

Cell Preparation

To evaluate the various materials as electrode materials in Li-ion cells, laboratory test lithium half-cells were constructed and tested. Electrodes were assembled in 2325-type coin lithium half-cells with a lithium foil (99.9%, Sigma Aldrich) counter/reference electrode. (Note: as is well known to those skilled in the art, results from these test lithium half-cells allow for reliable prediction of electrode materials performance in lithium ion batteries.) Two layers of Celgard 2300 separator and one layer of blown microfiber (3M company) were used in each coin lithium half-cell. 1M $LiPF_6$ (BASF) in a solution of ethylene carbonate, diethyl carbonate and monofluoroethylene carbonate (volume ratio 3:6:1, all from BASF) was used as electrolyte. Cell assembly was carried out in an Ar-filled glove box. Cells were cycled galvanostatically at 30.0 ± 0.1°C.

Precursor Method 1 (inventive):

NMC622 Precursor Particulate Made by Jar Milling in a Steel Container and with Steel Grinding Media

In this method, "NMC" precursor particulate with a stoichiometric metal ratio of 60% Ni, 20% Mn, and 20% Co ("NMC622") was prepared by sealing in air 41.61 g NiO powder (Sigma-Aldrich, -325 mesh, 99%), 13.18 g MnO powder (Aldrich, -60 mesh, 99%), 14.90 g Co_3O_4 powder (Alfa Aesar, 99.7%), and 10 kg of 0.5 inch stainless steel balls in a 5 L stainless-steel milling jar (US Stoneware) and milled by rotating the jar for one week at 85 rpm. The resulting precursor particulate, hereafter referred to as PM1, was then collected by placing the stainless steel balls after milling on metal sifters stacked on a sieve shaker and running the sieve shaker. An XRD pattern of PM1 is shown in Figure 1. It has a disordered rock-salt structure with no impurity peaks, confirming that the transition metals are mixed at an atomic scale. The average grain size of the rock-salt phase was calculated to be ~11 nm from XRD pattern by the Scherrer method. No phases were present in the sample having grain size larger than 11 nm. The lattice constant of the precursor particulate rock-salt lattice was 4.187 Å.

Precursor Method 2 (inventive):

"NMC622" Precursor Particulate Made by High Energy Ball Milling in a Ceramic Container and with Ceramic Grinding Media

In this method, "NMC622" precursor particulate was prepared by sealing in air 2.50 g NiO powder (Sigma-Aldrich, -325 mesh, 99%), 0.79 g MnO powder (Aldrich, -60 mesh, 99%), 0.89 g Co_3O_4 powder (Alfa Aesar, 99.7%), and 98 g of 1/8 inch ZrO_2 balls in a 45 ml alumina milling vial (Spex CertiPrep, Metuchen, NJ) and milled using a high energy ball mill (SPEX Model 8000-D, Spex CertiPrep, Metuchen, NJ) for 1 hour. The resulting precursor particulate, hereafter referred to as PM2, was then collected by further milling the mixture with ~10 ml of ethanol for another 5 minutes, recovering the slurry and drying in air at 120°C. An XRD pattern of PM2 is shown in Figure 2. It has a semi-amorphous structure in which all the peaks can be assigned to NiO or a rock-salt phase, MnO, and Co_3O_4. The average grain size of the rock-salt phase was calculated to be ~19 nm. No phases were present in the sample having a grain size larger than 25 nm.

Precursor Method 3 (comparative):

"NMC622" Precursor Particulate Made by hand grinding

In this method, "NMC622" precursor particulate was prepared by mixing in air 2.50 g NiO powder (Sigma-Aldrich, -325 mesh, 99%), 0.79 g MnO powder (Aldrich, -60 mesh, 99%), and 0.89 g Co_3O_4

powder (Alfa Aesar, 99.7%), using a mortar and pestle for 10 minutes. The resulting precursor particulate, hereafter referred to as PM3, was then collected for further study. An XRD pattern of PM3 is shown in Figure PM3. It has a multiphase crystalline structure in which all the peaks can be assigned to NiO, MnO, and Co_3O_4. The average grain size of the rock-salt phase was too large to calculate from XRD (i.e. larger than 80 nm).

Precursor Method 4 (inventive):

NMC Precursor Particulate Optionally Containing Lithium Made by High Energy Ball Milling

NMC precursor particles with the formula $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ were prepared using an all-solid-state 15 method. Specifically, stoichiometric amounts of NiO (Sigma-Aldrich, 99%), MnO (Aldrich, 99%), Co_3O_4 (Alfa Aesar, 99.7%), and Li_2CO_3 (Alfa Aesar, 99%) with 10% excess Li_2CO_3 were mixed together by high energy ball milling using a SPEX8000 mixer. A sample size of ~2.4 g was milled with 180 g of 1.6 mm stainless steel balls (Thomson Linear Motion) for 4 hours. Resulting ball milled mixtures were then pelletized and heated at 900 °C in air for 3 hours. Finally, the pellets were then ground to fine powders to produce the NMC precursor particulate. In SEM images, irregular agglomerations of submicron NMC particles could be observed.

Inventive Example 1 (IE1)

A sample of SC-LiNMC lithium transition metal oxide particulate (hereafter referred to as SC-LiNMC-1) was prepared as follows. 3 g of the PM1 precursor was ground by mortar and pestle with 1.64 g of Li_2CO_3 (Alfa Aesar, 99%), corresponding to 10% excess lithium content, according to the Li:Ni:Mn:Co ratio given by the formula $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$, until a homogeneous mixture was obtained (~10 minutes). The resulting final mixture was placed in an alumina crucible and heated in a tube furnace in air for 12 hours at 940 °C. Finally, the product was ground to fine powder by hand in a mortar and pestle and passed through a 38 μm sieve to form SC-LiNMC-1 lithium transition metal oxide particulate, having a composition of $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$.

Figures 4a and 4b are SEM images of SC-LiNMC-1 at different magnifications. SC-LiNMC-1 is composed of particles, with an average particle size of 4 μm and having an average facet size of 3 μm, corresponding to an average facet size that is 75% of the average particle size. The single crystal particles have clear facets. Figure 4c shows an XRD pattern of SC-LiNMC-1. SC-LiNMC-1 is phase pure O3 phase, with no impurities, as can be seen in the expanded XRD pattern between 20° and 30° shown in Figure 4d. The Cu $K_{\alpha 1}/K_{\alpha 2}$ splitting of the (104) peak (at ~44.5°) is pronounced, as shown in Figure 4e, indicating an extremely high degree of crystallinity. The measured peak width of the (003) peak, shown in Figure 4f, is 0.11°, which is the instrumental broadening error. Therefore, the crystallite size is too large for the instrument to measure (i.e. larger than about 0.05 μm). The 003/104 intensity ratio is 1.308, and the c/a ratio is 4.957.

Figure 4g shows the first cycle potential profile of a laboratory test cell made with SC-LiNMC-1. When cycled between 2.5 V - 4.3 V at C/20 (10 mA/g), a reversible capacity of ~150 mAh/g can be obtained.

Inventive Example 2 (IE2)

Another sample of SC-LiNMC lithium transition metal oxide particulate (hereafter referred to as SC-LiNMC-2) was prepared as follows. 3 g of the PM1 precursor was ground by mortar and pestle with 1.71 g of Li_2CO_3 (Alfa Aesar, 99%), corresponding to 15% excess lithium content, according to the Li:Ni:Mn:Co ratio given by the formula $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$, until a homogeneous mixture was obtained (~10 minutes). The resulting final mixture was placed in an alumina crucible and heated in a tube furnace in air for 12 hours at 940 °C. Finally, the product was ground to fine powder by hand in a mortar and pestle and passed through a 38 μm sieve to form SC-LiNMC-2 lithium transition metal oxide particulate, having a composition of $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$.

Figures 5a and 5b are SEM images of SC-LiNMC-2 at different magnifications. SC-LiNMC-2 is composed of particles having an average particle size of 4 μm and an average facet size of 3 μm, corresponding to an average facet size that is 75% of the average particle size. The single crystal particles have clear facets. Figure 5c shows an XRD pattern of SC-LiNMC-2. SC-LiNMC-2 is phase pure O3 phase, with no impurities, as can be seen in the expanded XRD pattern between 20° and 30° shown in Figure 5d. The Cu $K_{\alpha1}/K_{\alpha2}$ splitting of the (104) peak (at ~44.5°) is pronounced, as shown in Figure 5e, indicating an extremely high degree of crystallinity. The measured peak width of the (003) peak, shown in Figure 5f, is 0.11°, which is the instrumental broadening error. Therefore, the crystallite size is too large for the instrument to measure (i.e. larger than about 0.05 μm). The 003/104 intensity ratio is 1.229, and the c/a ratio is 4.956.

Figure 5g shows the first cycle potential profile of a laboratory test cell made with SC-LiNMC-2. When cycled between 2.5 V - 4.3 V at C/20 (10 mA/g), a reversible capacity of ~160 mAh/g can be obtained.

Inventive Example 3 (IE3)

A sample of SC-LiNMC lithium transition metal oxide particulate (hereafter referred to as SC-LiNMC-3) was prepared as follows. 3 g of the PM1 precursor was ground by mortar and pestle with

1.79 g of Li_2CO_3 (Alfa Aesar, 99%), corresponding to 20% excess lithium content, according to the Li:Ni:Mn:Co ratio given by the formula $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$, until a homogeneous mixture was obtained (~10 minutes). The resulting final mixture was placed in an alumina crucible and heated in a tube furnace in air for 12 hours at 940 °C. Finally, the product was ground to fine powder by hand in a mortar and pestle and passed through a 38 μm sieve to form SC-LiNMC-3 lithium transition metal oxide particulate, having a composition of $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$.

Figures 6a and 6b are SEM images of SC-LiNMC-3 at different magnifications. SC-LiNMC-3 is composed of particles having an average particle size of 3 μm and an average facet size of 2 μm, corresponding to an average facet size that is 67% of the average particle size. The single crystal particles have clear facets. Figure 6c shows an XRD pattern of SC-LiNMC-3. SC-LiNMC-3 is phase pure O3 phase, with no impurities, as can be seen in the expanded XRD pattern between 20° and 30° shown in Figure 6d. The Cu $K_{\alpha1}/K_{\alpha2}$ splitting of the (104) peak (at ~44.5°) is pronounced, as shown in Figure 6e, indicating an extremely high degree of crystallinity. The measured peak width of the (003) peak, shown in Figure 6f, is 0.11°, which is the instrumental broadening error. Therefore, the crystallite size is too large for the instrument to measure (i.e., larger than about 0.05 μm). The 003/104 intensity ratio is 1.355, and the c/a ratio is 4.956. Figure 6g shows EDS mapping of SC-LiNMC-3. The elemental distributions of Ni, Mn, and Co are homogeneous across the sample.

Figure 6h shows the first cycle potential profile of a laboratory test cell made with SC-LiNMC-3. When cycled between 2.5 V - 4.3 V at C/20 (10 mA/g), a reversible capacity of ~160 mAh/g can be obtained.

Inventive Example 4 (IE4)

A sample of SC-LiNMC lithium transition metal oxide particulate (hereafter referred to as SC-LiNMC-4) was prepared as follows. 3 g of the PM1 precursor was ground by mortar and pestle with 1.79 g of Li_2CO_3 (Alfa Aesar, 99%), corresponding to 20% excess lithium content, according to the Li:Ni:Mn:Co ratio given by the formula $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$, until a homogeneous mixture was obtained (~10 minutes). The resulting final mixture was placed in an alumina crucible and heated in a tube furnace in flowing oxygen for 12 hours at 940 °C. Finally, the product was ground to fine powder by hand in a mortar and pestle and passed through a 38 μm sieve to form SC-LiNMC-4 lithium transition metal oxide particulate, having a composition of $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$.

Figures 7a and 7b are SEM images of SC-LiNMC-4 at different magnifications. SC-LiNMC-4 is composed of particles having an average particle size of 2 μm and an average facet size of 1 μm, corresponding to an average facet size that is 50% of the average particle size. The particle size is significantly smaller than SC-LiNMC-1, SC-LiNMC-2, and SC-LiNMC-3. This indicates that heating in oxygen does not promote crystal growth, compared to heating in air. Figure 7c shows an XRD pattern of SC-LiNMC-4. SC-LiNMC-4 is phase pure O3 phase, with no impurities, as can be seen in the expanded XRD pattern between 20° and 30° shown in Figure 7d. A shoulder on the right side of the (104) peak (at ~44.5°) can be observed, while no Cu $K_{\alpha1}/K_{\alpha2}$ peak splitting can be observed, as shown in Figure 7e, indicating the degree of crystallinity is not as high as SC-LiNMC-1, SC-LiNMC-2, and SC-LiNMC-3. The measured peak width of the (003) peak, shown in Figure 7f, is 0.11°, which is the instrumental broadening error. Therefore, the crystallite size is too large for the instrument to measure (i.e. larger than about 0.05 μm). The 003/104 intensity ratio is 1.162, and the c/a ratio is 4.964.

Figure 7g shows the first cycle potential profile of a laboratory test cell made with SC-LiNMC-4. When cycled between 2.5 V - 4.3 V at C/20 (10 mA/g), a reversible capacity of ~170 mAh/g can be obtained.

Inventive Example 5 (IE5)

A sample of SC-LiNMC lithium transition metal oxide particulate (hereafter referred to as SC-LiNMC-5) was prepared as follows. 3 g of the PM1 precursor was ground by mortar and pestle with 1.79 g of Li_2CO_3 (Alfa Aesar, 99%), corresponding to 20% excess lithium content, according to the Li:Ni:Mn:Co ratio given by the formula $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$, until a homogeneous mixture was obtained (~10 minutes). The resulting final mixture was placed in an alumina crucible and heated in a tube furnace in air for 12 hours at 940 °C. The heated powder was ground using a mortar and pestle, and heated again in an alumina crucible in a tube furnace in flowing oxygen for 12 hours at 940 °C. Finally, the product was ground to fine powder by hand in a mortar and pestle and passed through a 38 μm sieve to form SC-LiNMC-5 lithium transition metal oxide particulate, having a composition of $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$.

Figures 8a and 8b are SEM images of SC-LiNMC-5 at different magnifications. SC-LiNMC-5 is composed of particles having an average particle size of 10 μm and an average facet size of 7 μm, corresponding to an average facet size that is 70% of the average particle size. The single crystal particles have clear facets. Figure 8c shows an XRD pattern of SC-LiNMC-5. SC-LiNMC-5 is phase pure O3 phase, with no impurities, as can be seen in the expanded XRD pattern between 20° and 30° shown in Figure 8d. The Cu $K_{\alpha1}/K_{\alpha2}$ splitting of the (104) peak (at ~44.5°) is pronounced, as shown in Figure 8e, indicating an extremely high degree of crystallinity. The measured peak width of the (003) peak, shown in Figure 8f, is 0.11°, which is the instrumental broadening error. Therefore, the crystallite size is too large for the instrument to measure (i.e., larger than about 0.05 µm). The 003/104 intensity ratio is 1.108, and the c/a ratio is 4.959.

Figure 8g shows the first cycle potential profile of a laboratory test cell made with SC-LiNMC-5. When cycled between 2.5 V - 4.3 V at C/20 (10 mA/g), a reversible capacity of ~160 mAh/g can be obtained.

Inventive Example 6 (IE6)

A sample of SC-LiNMC lithium transition metal oxide particulate (hereafter referred to as SC-LiNMC-6) was prepared as follows. 3 g of the PM2 precursor was ground by mortar and pestle with 1.79 g of Li_2CO_3 (Alfa Aesar, 99%), corresponding to 20% excess lithium content, according to the Li:Ni:Mn:Co ratio given by the formula $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$, until a homogeneous mixture was obtained (~10 minutes). The resulting final mixture was placed in an alumina crucible and heated in a tube furnace in air for 12 hours at 940 °C. The heated powder was ground using a mortar and pestle, and heated again in an alumina crucible in a tube furnace in flowing oxygen for 12 hours at 940 °C. Finally, the product was ground to fine powder by hand in a mortar and pestle and passed through a 38 µm sieve to form SC-LiNMC-6 lithium transition metal oxide particulate, having a composition of $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$.

Figures 9a and 9b are SEM images of SC-LiNMC-6 at different magnifications. SC-LiNMC-6 is composed of particles having an average particle size of 3 µm and an average facet size of 2 µm, corresponding to an average facet size that is 67% of the average particle size. The single crystal particles have clear facets. Figure 9c shows an XRD pattern of SC-LiNMC-6. SC-LiNMC-6 is phase pure O3 phase, with no impurities, as can be seen in the expanded XRD pattern between 20° and 30° shown in Figure 9d. The Cu $K_{\alpha1}/K_{\alpha2}$ splitting of the (104) peak (at ~44.5°) is pronounced, as shown in Figure 9e, indicating an extremely high degree of crystallinity. The measured peak width of the (003) peak, shown in Figure 9f, is 0.11°, which is the instrumental broadening error. Therefore, the crystallite size is too large for the instrument to measure (i.e. larger than about 0.05 µm). The 003/104 intensity ratio is 1.153, and the c/a ratio is 4.964. Figure 9g shows EDS mapping of SC-LiNMC-6. The elemental distribution of Ni, Mn, and Co are homogeneous across the sample.

Figure 9h shows the first cycle potential profile of a laboratory test cell made with SC-LiNMC-6. When cycled between 2.5 V - 4.3 V at C/20 (10 mA/g), a reversible capacity of ~160 mAh/g can be obtained.

Table 1 summarizes the preparation conditions, crystal parameters, average facet size, and average grain size of samples SC-LiNMC-1 through SC-LiNMC-6 prepared as described in the aforementioned Inventive Examples 1 through 6. In this Table, AFS = average facet size, APS = average particle size, and PFP = facet size as a percent of the average particle size of the final lithium transition metal oxide particulate samples SC-LiNMC-1 through SC-LiNMC-6.

Table 1.

Example	Sample Name	Precursor	Excess Li (%)	Heating Conditions	AFS (µm)	APS (µm)	PFP (%)	c/a
IE1	SC-LiNMC-1	PM1	*10*	air	*3*	*4*	*75*	*4.957*
IE2	SC-LiNMC-2	PM1	*15*	air	*3*	*4*	*75*	*4.956*
IE3	SC-LiNMC-3	PM1	*20*	air	*2*	*3*	*67*	*4.956*
IE4	SC-LiNMC-4	PM1	*20*	O_2	*1*	*2*	*50*	*4.964*
IE5	SC-LiNMC-5	PM1	*20*	air/O_2	*7*	*10*	*70*	*4.959*
IE6	SC-LiNMC-6	PM2	*20*	air/O_2	*2*	*3*	*67*	*4.964*

Table 2 summarizes the electrochemical performance parameters of samples SC-LiNMC-1 through SC-LiNMC-6 prepared as described in the aforementioned Inventive Examples 1 through 6. In this Table, RC = reversible capacity, IC = irreversible capacity, and AP = second cycle average polarization (measured as the difference between the average charge and discharge voltage during a cycle in a half-cell).

Table 2.

Example	Sample Name	RC (mAh/g)	IC (mAh/g)	AP (mV)
IE1	SC-LiNMC-1	*152*	*41*	*213*
IE2	SC-LiNMC-2	*157*	*39*	*118*
IE3	SC-LiNMC-3	*160*	*44*	*119*
IE4	SC-LiNMC-4	*165*	*31*	*96*
IE5	SC-LiNMC-5	*156*	*40*	*110*
IE6	SC-LiNMC-6	*162*	*24*	*90*

A high c/a ratio is known to be an indicator of ordered stacking in the O3 structure, which is desirable for NMC in order for the material to have fast lithium diffusion. This parameter is highest for the examples that include a step where the sample is heated in oxygen. Low average polarization (AP) and low irreversible capacity (IC) are desirable traits of "NMC" in Li-ion cells. Low values of AP and IC are also characteristic of good ion ordering in the O3 structure. The AP and IC are lowest for examples that include a step where the sample is heated in oxygen and in which a ceramic mill was used to make the precursor. The facet size and PFP becomes reduced, however, when only oxygen is used during heating. Therefore, in some embodiments, it seems preferred to heat firstly in air to promote grain growth and then secondly in oxygen to promote a more ordered crystal structure.

Without being bound by theory, it is believed that the reduced polarization in the IE6 sample is the result of the use of ball milling with a non-ferrous mill and milling balls. This avoids iron contamination in the sample. The presence of iron has been shown to induce cation mixing (Korean J. Chem. Eng., 24(5), 888-891 (2007)), which is known to increase polarization and cause cell fade. In addition, iron contamination changes the lithium : transition metal ratio from the intended value, which is not desired in a commercial production process.

Comparative Example 1

A sample of LiNMC lithium transition metal oxide particulate (hereafter referred to as CE-LiNMC-1) was prepared as follows: 3 g of the comparative PM3 precursor was ground by mortar and pestle with 1.79 g of Li_2CO_3 (Alfa Aesar, 99%), corresponding to 20% excess lithium content, according to the Li:Ni:Mn:Co ratio given by the formula $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$, until a homogeneous mixture was obtained (~10 minutes). The mixture was placed in an alumina crucible and heated in a tube furnace in air for 12 hours at 940 °C. Finally, the product was ground to fine powder by hand in a mortar and pestle and passed through a 38 µm sieve to form CE-LiNMC-1 lithium transition metal oxide particulate, having a composition of $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$.

Figure 10a shows an XRD pattern of CE-LiNMC-1. CE-LiNMC-1 is not phase pure, as multiple peaks can be seen in the expanded XRD patterns shown in Figure 10b and Figure 10c. Phase separation occurs for this sample. Figure 10d shows an EDS mapping of CE-LiNMC-1. It can be seen that while Ni and Co distribute homogeneously across the sample, Mn does not distribute evenly. These traits are not desirable for commercial "NMC".

The preceding examples demonstrate that high quality, high performance single crystal "NMC" lithium transition metal oxide particulate for electrode materials in lithium batteries can be prepared by a method of the invention. Such lithium transition metal oxide particulate was prepared simply by dry impact milling a precursor mixture comprising suitable transition metal powders and then heating a final mixture comprising this precursor particulate and a suitable Li compound. Hand grinding a similar precursor mixture however did not however result in an acceptable "NMC" lithium transition metal oxide particulate.

All of the above U.S. patents, U.S. patent applications, foreign patents, foreign patent applications and non-patent publications referred to in this specification, are incorporated herein by reference in their entirety.

While particular elements, embodiments and applications of the present invention have been shown and described, it will be understood, of course, that the invention is not limited thereto since modifications may be made by those skilled in the art without departing from the spirit and scope of the present disclosure, particularly in light of the foregoing teachings. Such modifications are to be considered within the purview and scope of the claims appended hereto.

Claims

1. A precursor particulate comprising:

a compound of Ni selected from the group consisting essentially of an oxide of Ni, a hydroxide of Ni, a carbonate of Ni, and mixtures thereof;

a compound of Mn selected from the group consisting essentially of an oxide of Mn, a hydroxide of Mn, a carbonate of Mn, and mixtures thereof;

optionally a compound of Co selected from the group consisting essentially of an oxide of Co, a hydroxide of Co, a carbonate of Co, and mixtures thereof; and

optionally a compound of A selected from the group consisting essentially of an oxide of A, a hydroxide of A, a carbonate of A, and mixtures thereof;

wherein:

A is a metal dopant;

the ratio of the total number of moles of Ni in the precursor particulate to the total number of moles of Mn in the precursor particulate to the total number of moles of optional Co in the precursor particulate to the total number of moles of optional A in the precursor particulate is equal to n:m:c:a wherein n, m, c and a are numbers wherein:

$n + m + c = 1$;
$n \geq 0.05$;
$m \geq 0.05$;
$c \geq 0$; and
$0 \leq a \leq 0.05$; and

the average grain size of each phase present in the precursor particulate is less than 50 nm.

2. The precursor particulate of claim 1 wherein the precursor particulate comprises grains of a rock-salt phase with an average grain size less than 50 nm.

3. The precursor particulate of claim 1 comprising an oxide compound of Ni, Mn, Co, A or mixtures thereof.

4. The precursor particulate of claim 1 wherein the precursor particulate consists essentially of oxide compounds.

5. The precursor particulate of claim 2 wherein the lattice constant of the rock-salt phase grains is greater than 4.18 Å.

6. The precursor particulate of claim 2 wherein the precursor particulate consists essentially of grains of a rock-salt phase.

7. A method of making the precursor particulate of claim 1 comprising:

obtaining an amount of the compound of Ni;

obtaining an amount of the compound of Mn;

preparing a precursor mixture comprising the amounts of the compound of Ni and the compound of Mn together; and

dry impact milling the precursor mixture sufficiently to produce a precursor particulate comprising grains of at least one phase wherein the average grain size of each phase present in the precursor particulate is less than 50 nm.

8. The method of claim 7 wherein the precursor mixture consists essentially of compounds selected from the group consisting of oxides, hydroxides, carbonates and mixtures thereof.

9. The method of claim 7 wherein the ratio of the total number of moles of Ni in the precursor mixture to the total number of moles of Mn in the precursor mixture to the total number of moles of optional Co in the precursor mixture to the total number of moles of optional A in the precursor mixture is equal to n:m:c:a.

10. A method of making a lithium transition metal oxide particulate with an O3 crystal structure and having the formula $Li_{1+x}[(Ni_nMn_mCo_c)_{1-a}A_a]_{1-x}O_2$ wherein:

A is a metal dopant; and

x, n, m, c and a are numbers wherein:

$-0.03 \leq x \leq 0.06$;

$n + m + c = 1$;

$n \geq 0.05$;

$m \geq 0.05$;

$c \geq 0$; and

$0 \leq a \leq 0.05$;

the method comprising:

obtaining an amount of the precursor particulate of claim 1;

preparing a final mixture comprising the amount of the precursor particulate and an amount of a Li compound selected from the group consisting essentially of Li oxide, Li hydroxide, Li carbonate and mixtures thereof; and heating the final mixture to react the Li compound with the precursor particulate and thereby produce the lithium transition metal oxide particulate with the O3 crystal structure.

11. A method of making a lithium transition metal oxide particulate with an O3 crystal structure and having the formula $Li_{1+x}[(Ni_nMn_mCo_c)_{1-a}A_a]_{1-x}O_2$ wherein:

A is a metal dopant; and

x, n, m, c and a are numbers wherein:

$-0.03 \leq x \leq 0.06$;

$n + m + c = 1$;

$n \geq 0.05$;

$m \geq 0.05$;

$c \geq 0$; and

$0 \leq a \leq 0.05$;

the method comprising:

preparing a precursor particulate according to the method of claim 7;

preparing a final mixture comprising an amount of the precursor particulate and an amount of a Li compound selected from the group consisting essentially of Li oxide, Li hydroxide, Li carbonate and mixtures thereof; and

heating the final mixture to react the Li compound with the precursor particulate and thereby produce the lithium transition metal oxide particulate with the O3 crystal structure.

12. The method of claim 11 wherein the precursor mixture consists essentially of compounds selected from the group consisting of oxides, hydroxides, carbonates and mixtures thereof.

13. The method of claim 11 wherein the ratio of the total number of moles of Ni in the precursor mixture to the total number of moles of Mn in the precursor mixture to the total number of moles of Co in the precursor mixture to the total number of moles of A in the precursor mixture is equal to n:m:c:a.

14. The method of claim 11 comprising:

obtaining an amount of a source of Co selected from the group consisting essentially of an oxide of Co, a hydroxide of Co, a carbonate of Co, and mixtures thereof; and

preparing the precursor mixture comprising the amounts of the compound of Ni, the compound of Mn, and the compound of Co together.

15. The method of claim 14 wherein the compound of Ni is NiO, the compound of Mn is MnO, and the compound of Co is Co_3O_4.

16. The method of claim 11 wherein the dry impact milling is conducted using non-ferrous milling apparatus.

17. The method of claim 11 wherein the dry impact milling comprises ball milling.

18. The method of claim 17 wherein the ball milling is conducted using a non-ferrous mill and non-ferrous milling media.

19. The method of claim 11 wherein the precursor particulate produced comprises grains of a rock-salt phase with an average grain size less than 50 nm.

20. The method of claim 19 wherein the lattice constant of the rock-salt phase grains is greater than 4.18 Å.

21. The method of claim 11 wherein the precursor particulate produced consists essentially of grains of a rock-salt phase.

22. The method of claim 11 wherein the Li compound is Li_2CO_3.

23. The method of claim 11 wherein the step of heating the final mixture comprises heating in oxygen.

24. The method of claim 1 wherein the step of heating the final mixture comprises heating in air.

25. The method of claim 24 wherein the step of heating the final mixture comprises heating in oxygen after heating in air.

26. The method of claim 11 wherein the step of heating the final mixture is conducted at greater than 600° C for greater than 6 hours.

27. The method of claim 11 wherein an excess of Li compound is employed in the final mixture and the method additionally comprises washing away excess unreacted Li compound from the produced lithium transition metal oxide particulate.

28. The method of claim 11 wherein the average particle size of the lithium transition metal oxide particulate produced is greater than 1 μm.

29. The method of claim 11 wherein the average facet size of the lithium transition metal oxide particulate produced is greater than 1 μm.

30. The method of claim 11 wherein the average facet size of the lithium transition metal oxide particulate produced is greater than 20% of the average particle size.

31. The method of claim 11 wherein the lithium transition metal oxide particulate with the O3 crystal structure has a c/a ratio of greater than 4.95.

32. A method of making a rechargeable battery comprising an electrode comprising lithium transition metal oxide particulate, the method comprising preparing the lithium transition metal oxide particulate according to the method of claim 11.

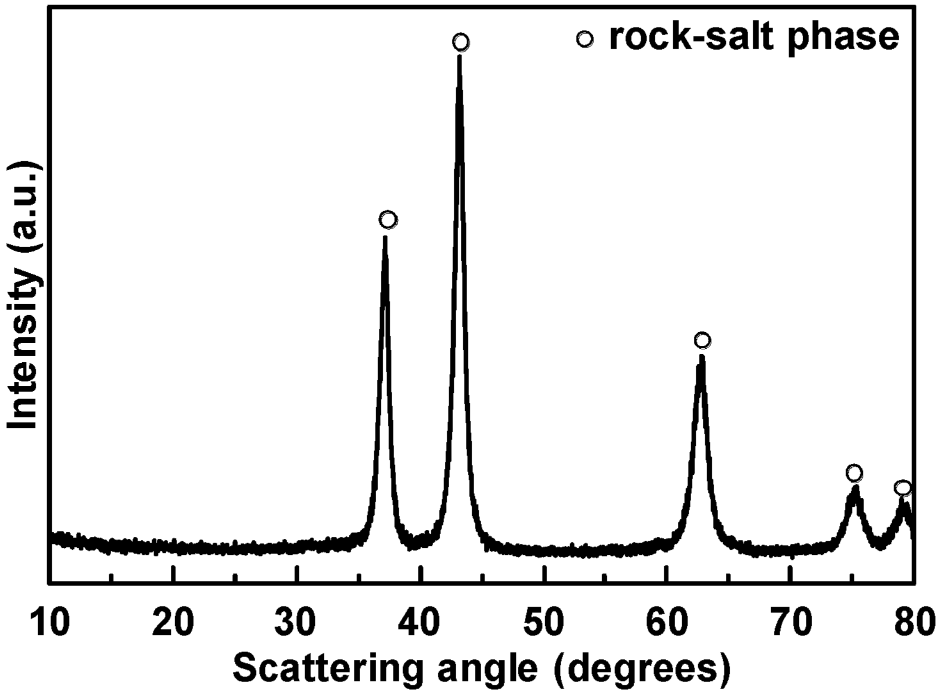
○ rock-salt phase
Intensity (a.u.)
10
20
30
40
50
60
70
80
Scattering angle (degrees)

FIG. 1

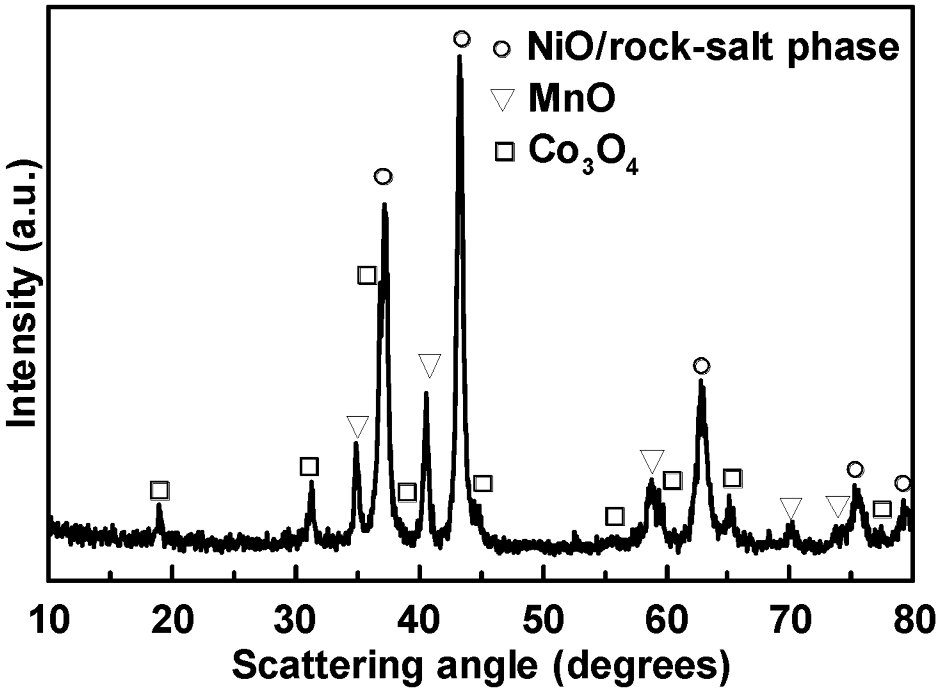
○ NiO/rock-salt phase
▽ MnO
□ Co_3O_4
Intensity (a.u.)
10
20
30
40
50
60
70
80
Scattering angle (degrees)

FIG. 2

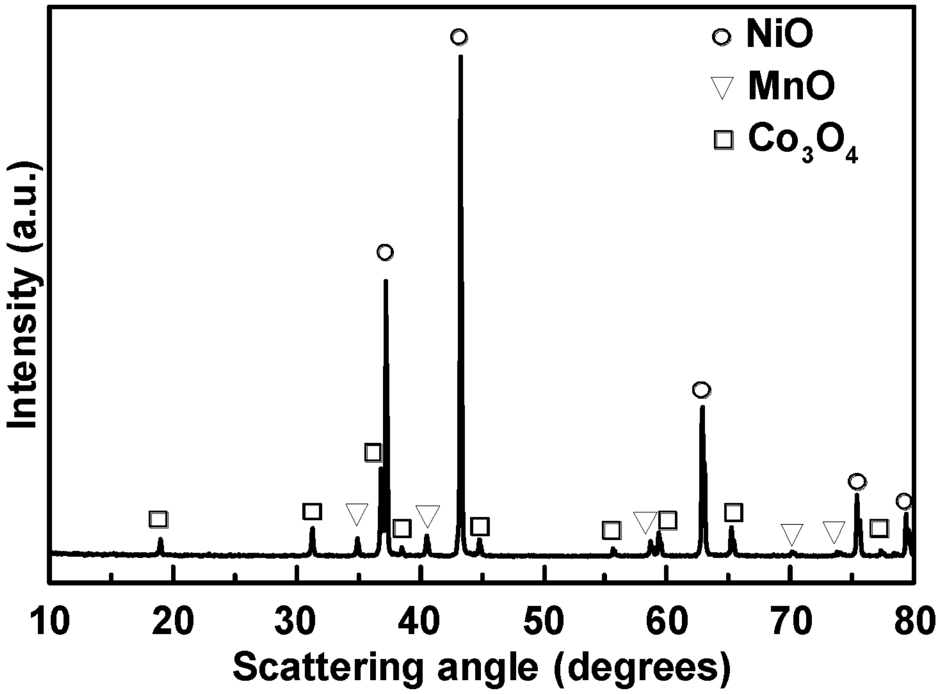
○ NiO
▽ MnO
□ Co_3O_4
Intensity (a.u.)
Scattering angle (degrees)
10
20
30
40
50
60
70
80

FIG. 3

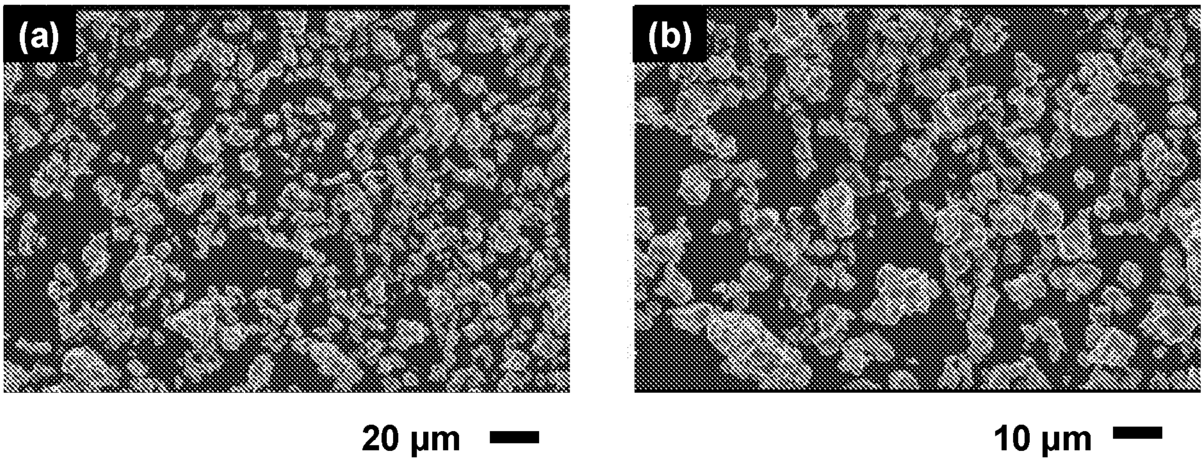
(a)
(b)
20 µm
10 µm

FIG. 4

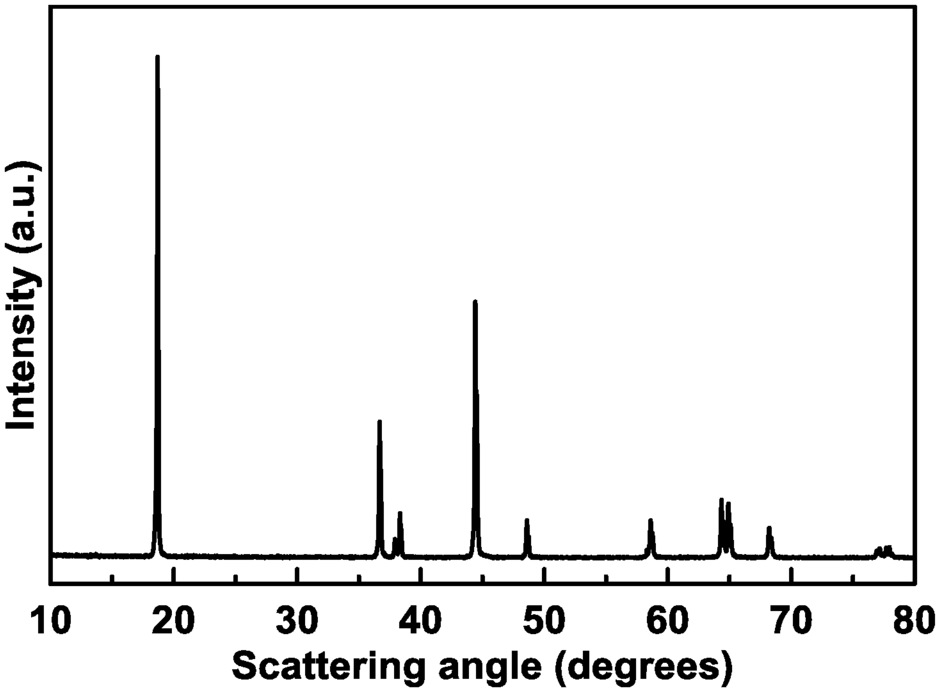
Intensity (a.u.)
10
20
30
40
50
60
70
80
Scattering angle (degrees)

FIG. 4c

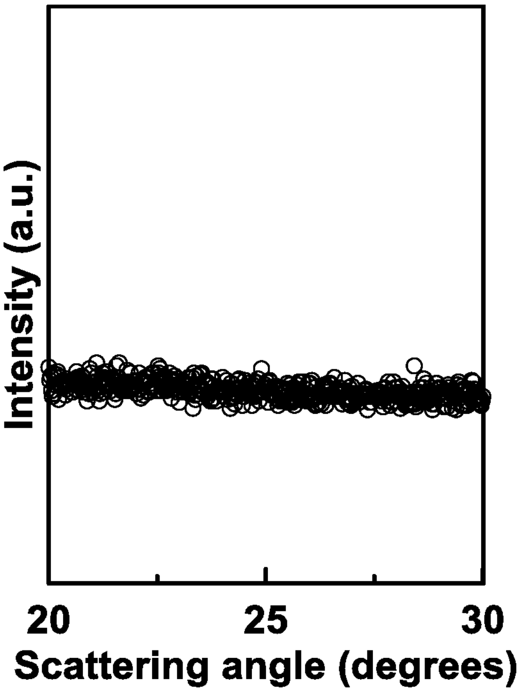
Intensity (a.u.)
20
25
30
Scattering angle (degrees)

FIG. 4d

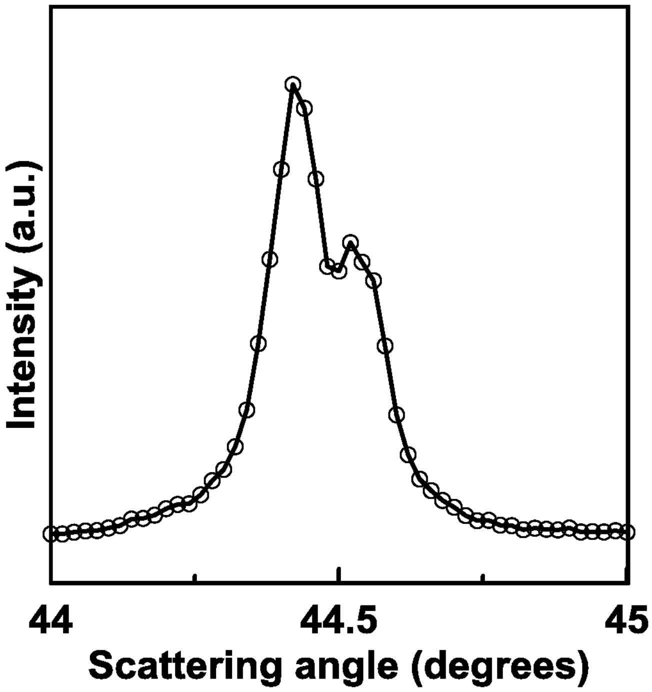
Intensity (a.u.)
44
44.5
45
Scattering angle (degrees)

FIG. 4e

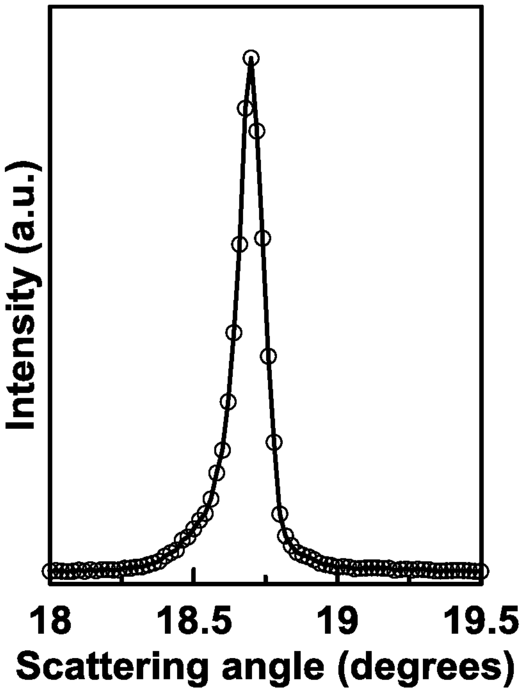
Intensity (a.u.)
18
18.5
19
19.5
Scattering angle (degrees)

FIG. 4f

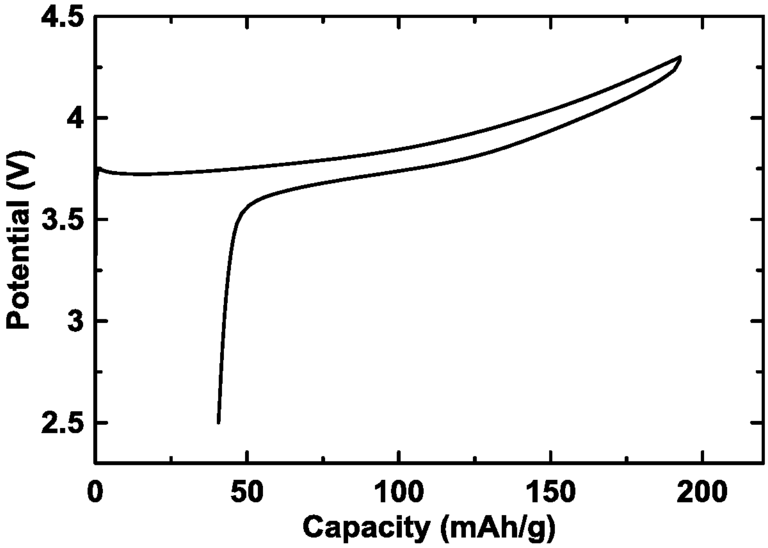
4.5
4
3.5
3
2.5
Potential (V)
0
50
100
150
200
Capacity (mAh/g)

FIG. 4g

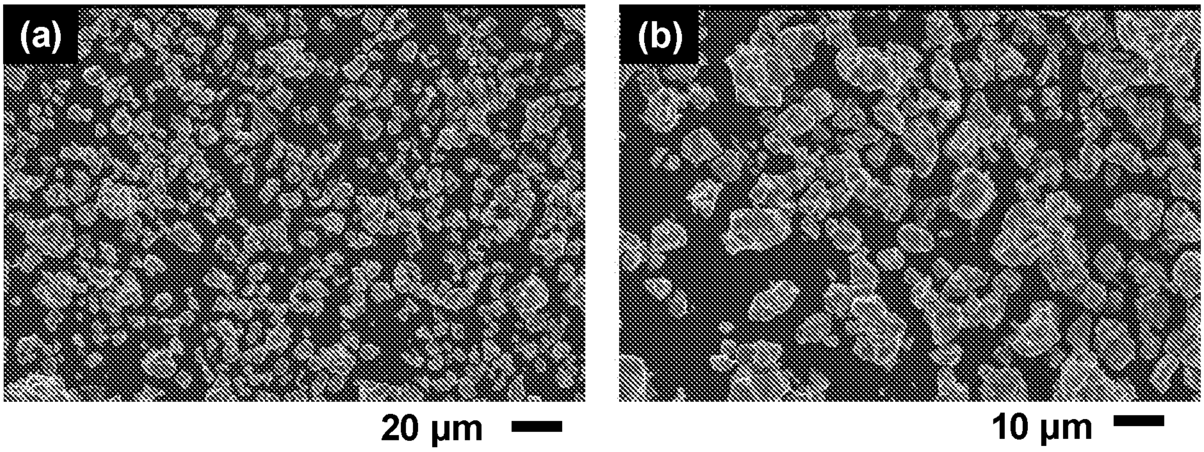
(a)
(b)
20 µm
10 µm

FIG. 5

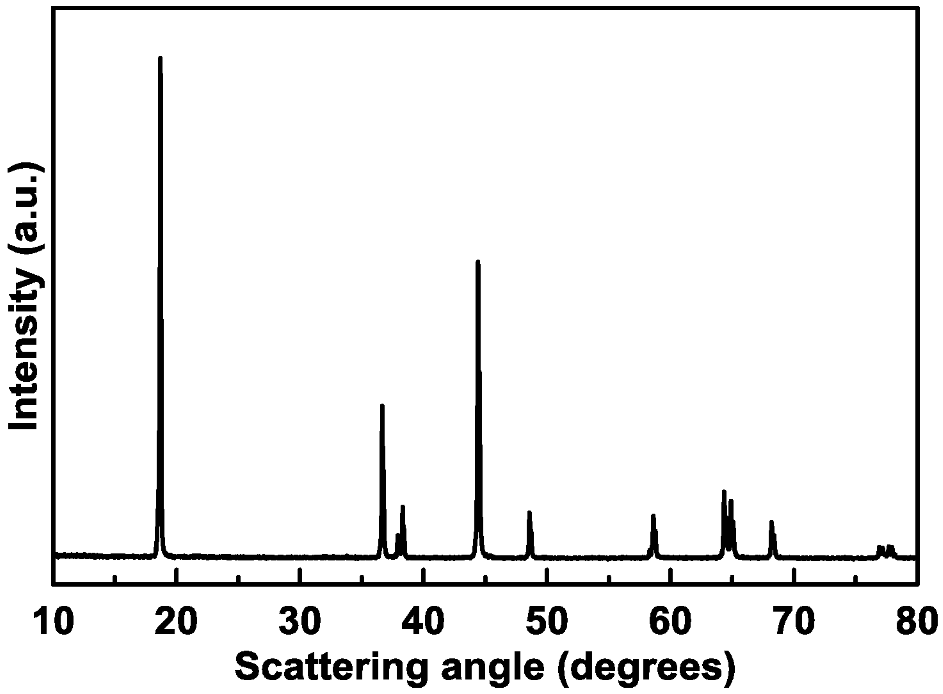
Intensity (a.u.)
10
20
30
40
50
60
70
80
Scattering angle (degrees)

FIG. 5c

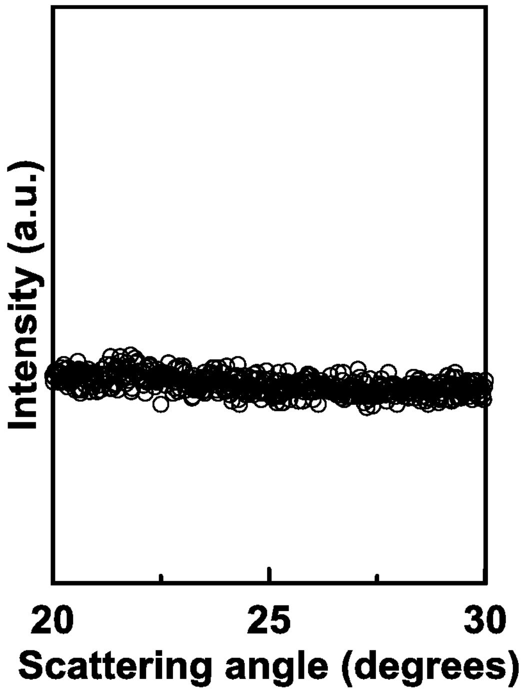
Intensity (a.u.)
20
25
30
Scattering angle (degrees)

FIG. 5d

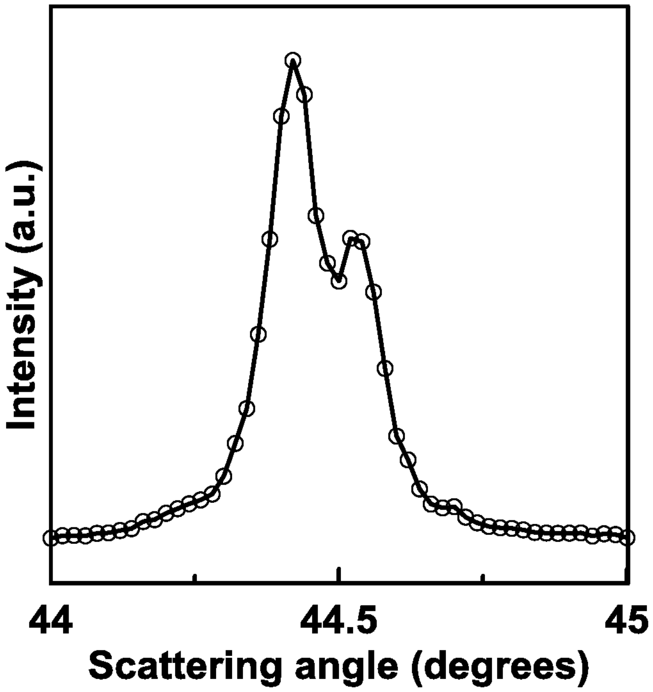
Intensity (a.u.)
44
44.5
45
Scattering angle (degrees)

FIG. 5e

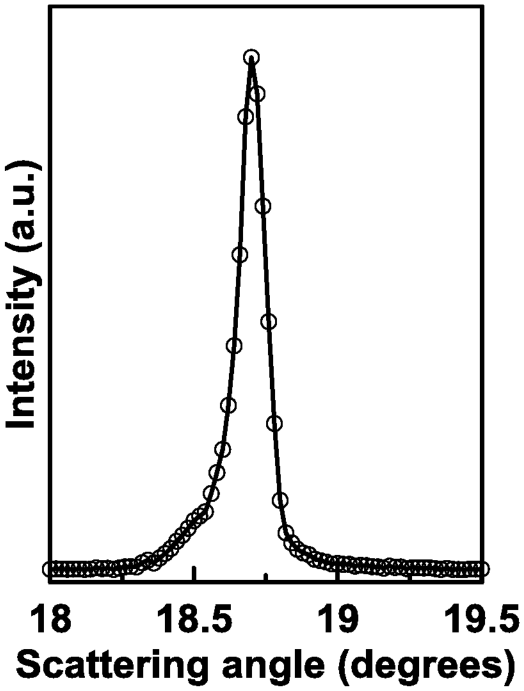
Intensity (a.u.)
18
18.5
19
19.5
Scattering angle (degrees)

FIG. 5f

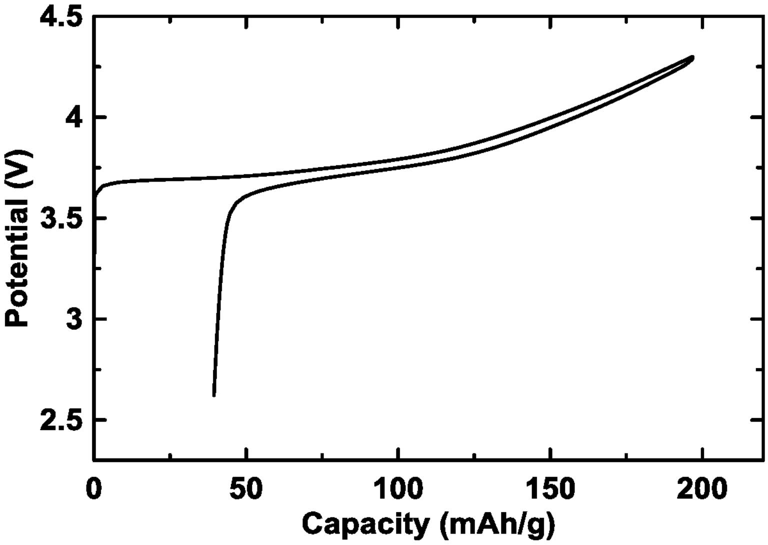
Potential (V)
4.5
4
3.5
3
2.5
0
50
100
150
200
Capacity (mAh/g)

FIG. 5g

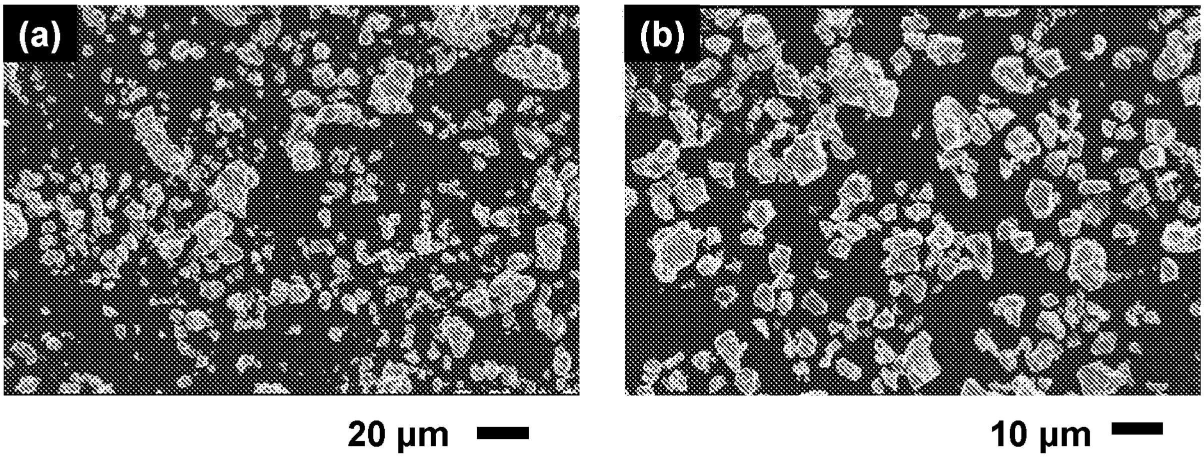
(a)
(b)
20 µm
10 µm

FIG. 6

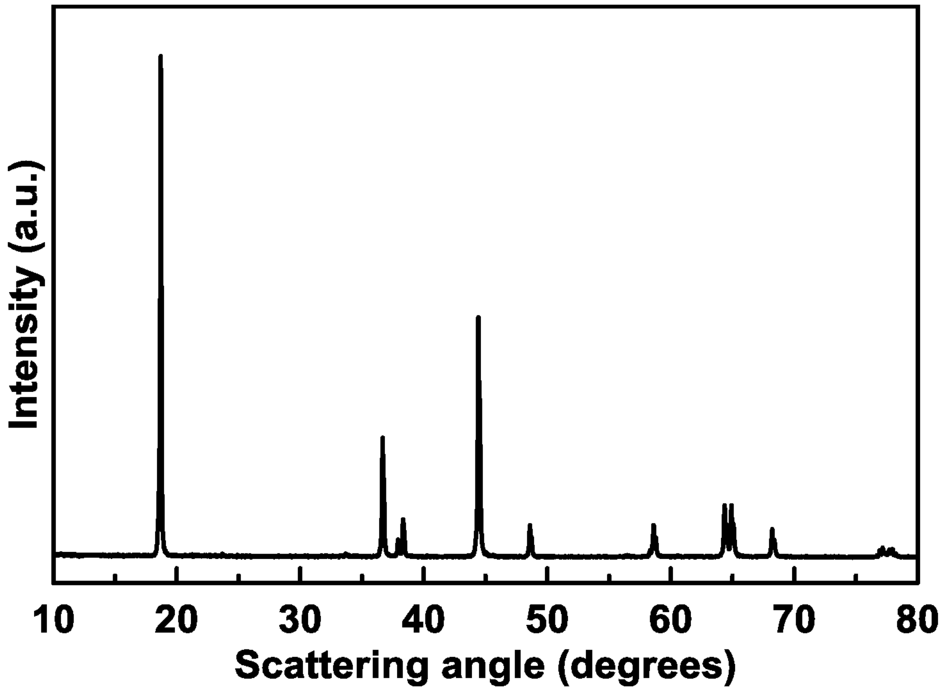
Intensity (a.u.)
10
20
30
40
50
60
70
80
Scattering angle (degrees)

FIG. 6c

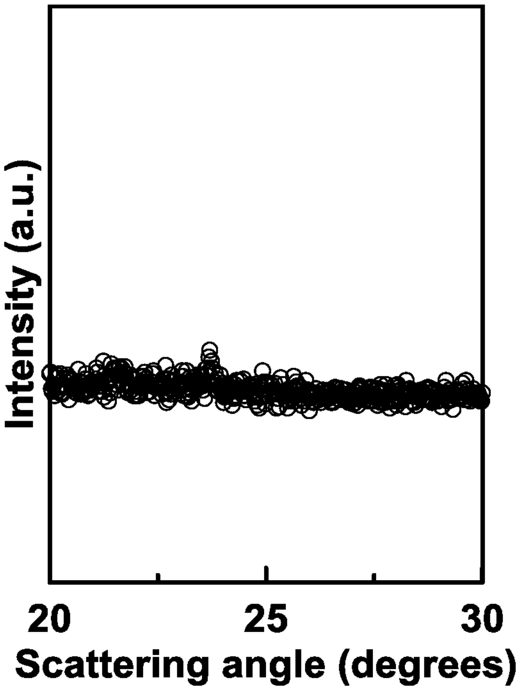
Intensity (a.u.)
20
25
30
Scattering angle (degrees)

FIG. 6d

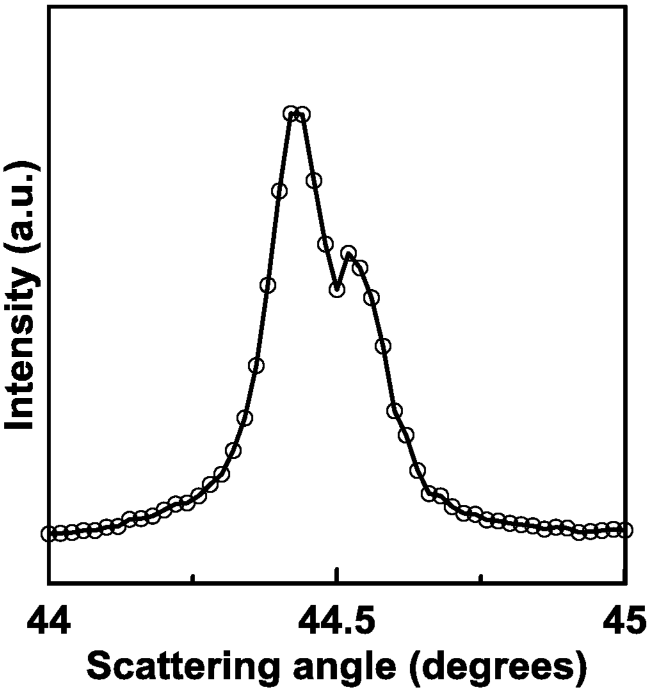
Intensity (a.u.)
44
44.5
45
Scattering angle (degrees)

FIG. 6e

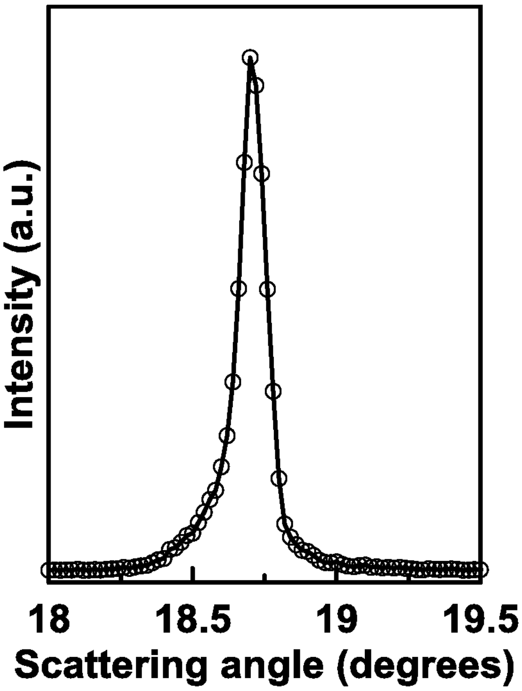
Intensity (a.u.)
18
18.5
19
19.5
Scattering angle (degrees)

FIG. 6f

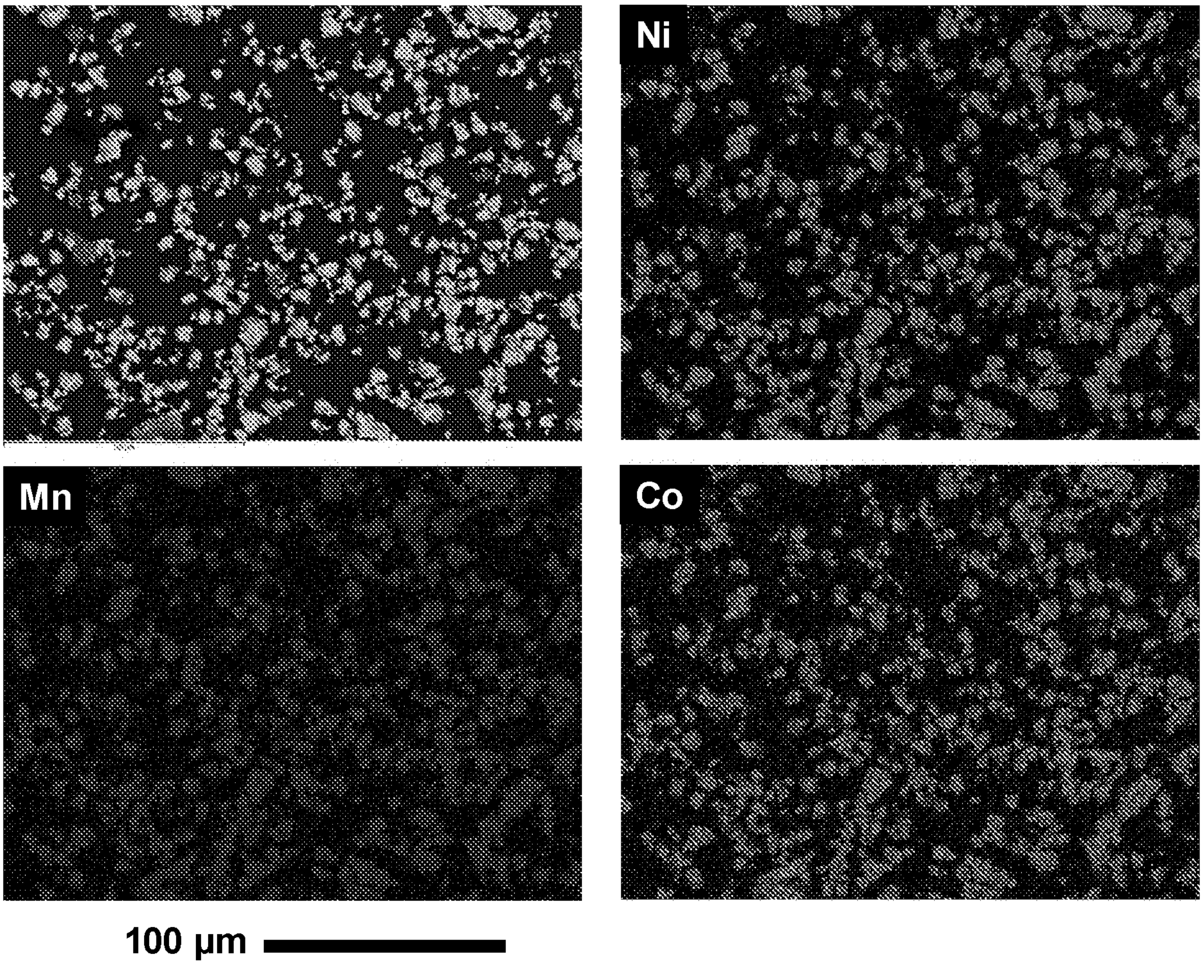
Ni
Mn
Co
100 µm

FIG. 6g

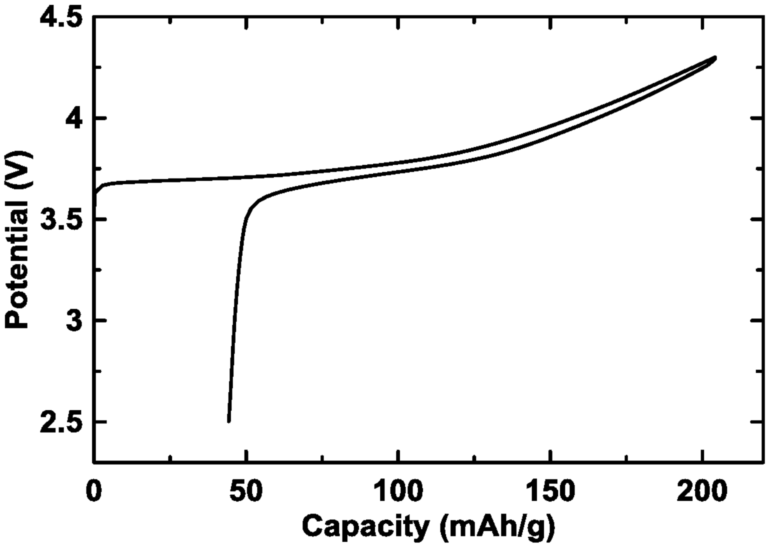
4.5
4
3.5
3
2.5
Potential (V)
0
50
100
150
200
Capacity (mAh/g)

FIG. 6h

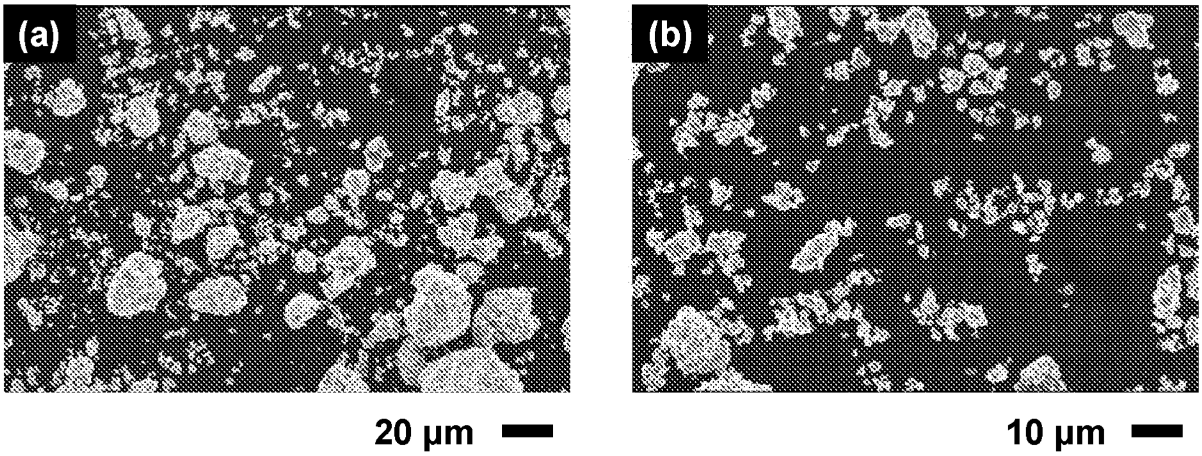
(a)
(b)
20 µm
10 µm

FIG. 7

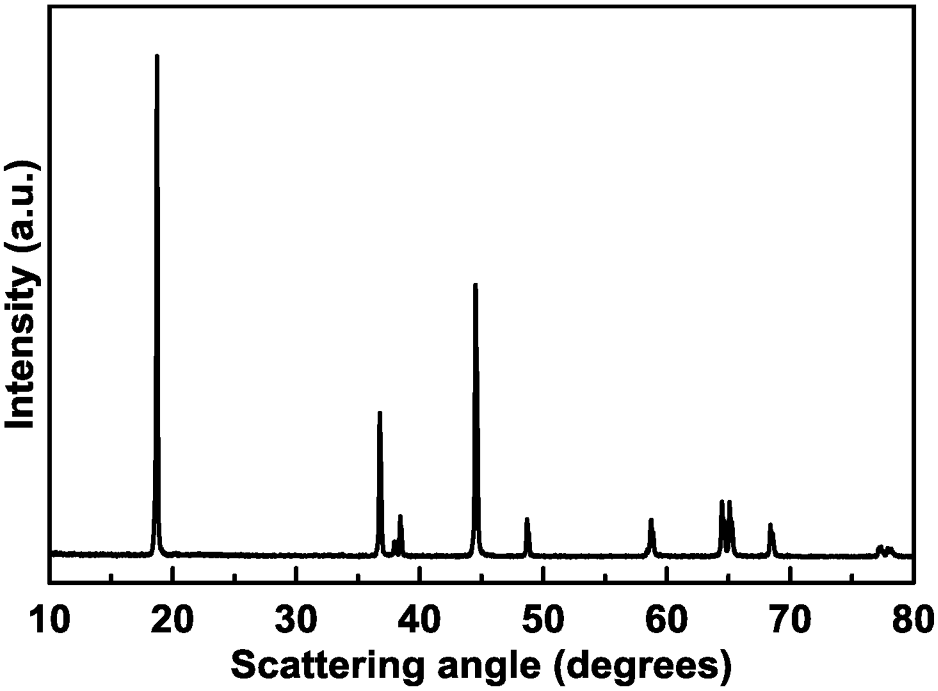
Intensity (a.u.)
10
20
30
40
50
60
70
80
Scattering angle (degrees)

FIG. 7c

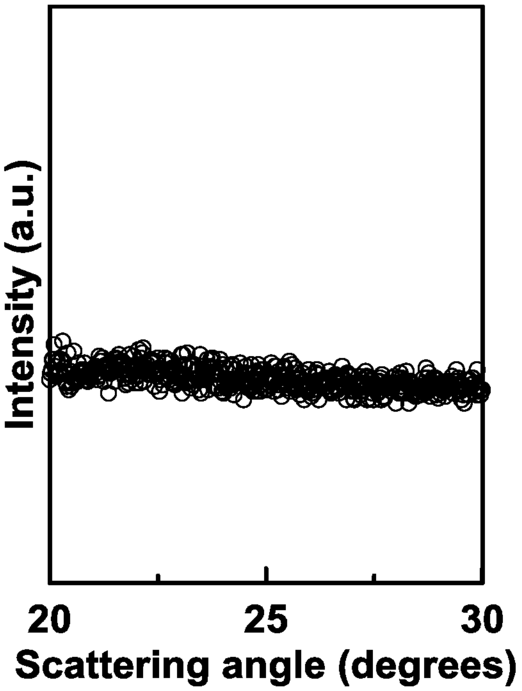
Intensity (a.u.)
20
25
30
Scattering angle (degrees)

FIG. 7d

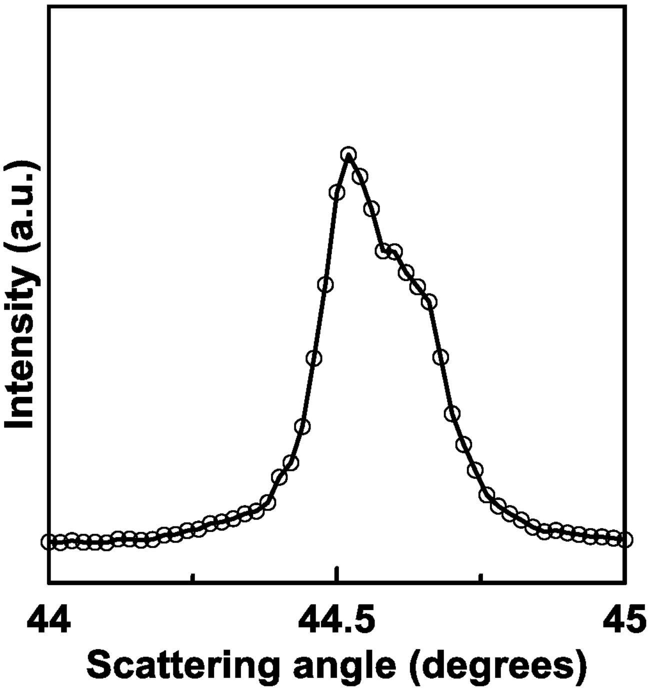
Intensity (a.u.)
44
44.5
45
Scattering angle (degrees)

FIG. 7e

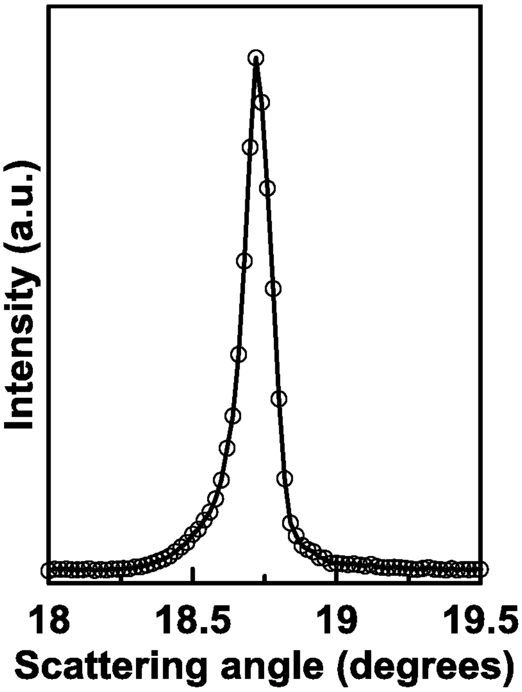
Intensity (a.u.)
18
18.5
19
19.5
Scattering angle (degrees)

FIG. 7f

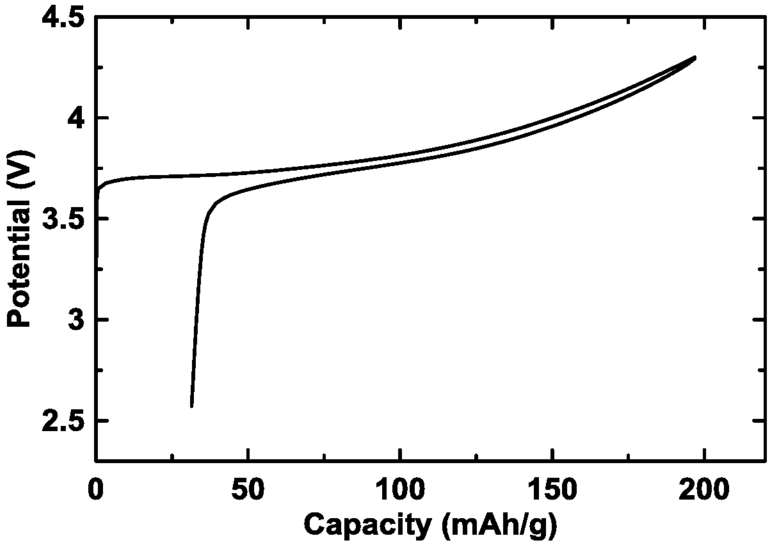
4.5
4
3.5
3
2.5
Potential (V)
0
50
100
150
200
Capacity (mAh/g)

FIG. 7g

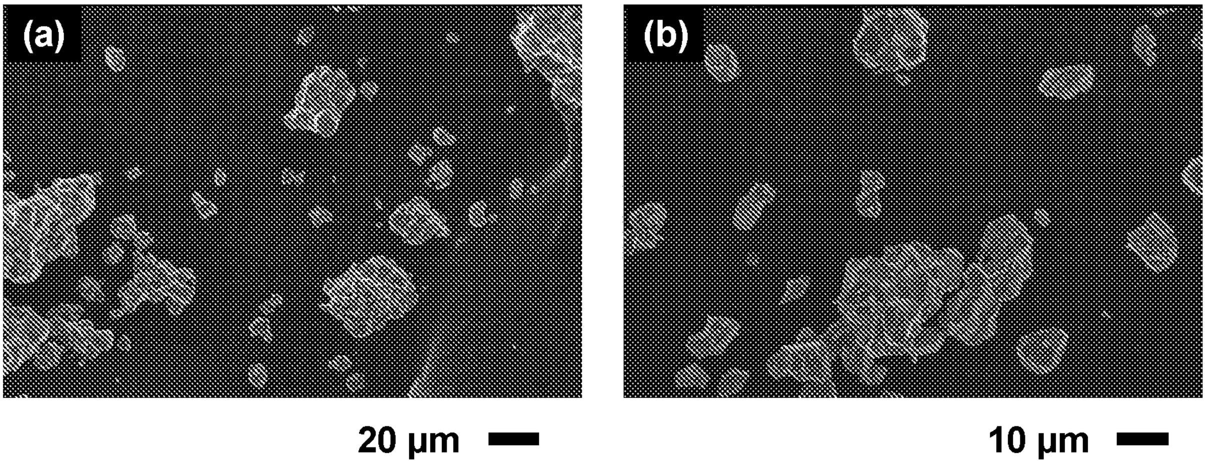
(a)
(b)
20 µm
10 µm

FIG. 8

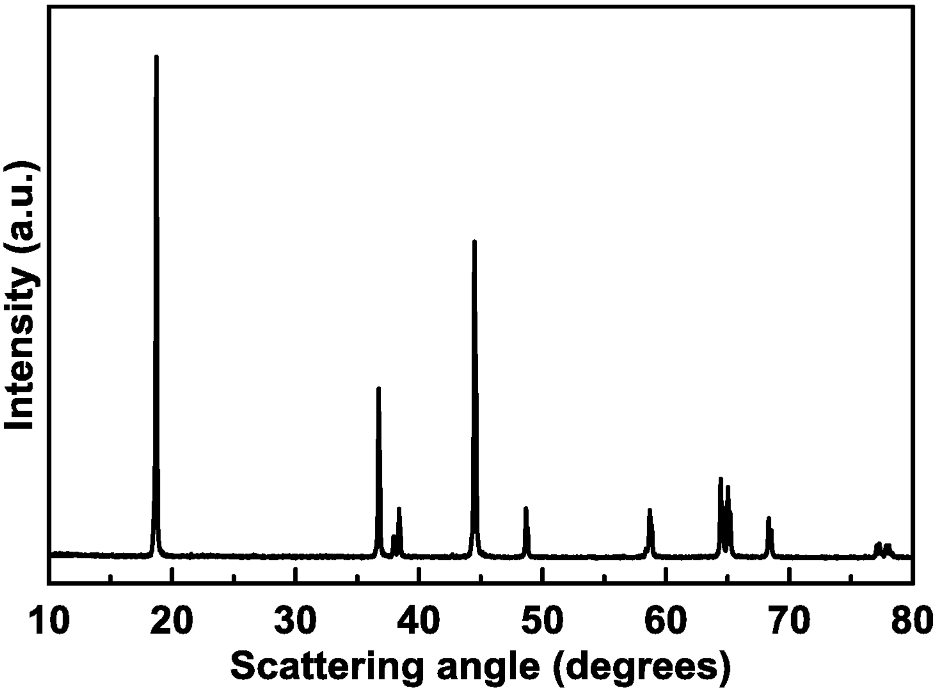
Intensity (a.u.)
10
20
30
40
50
60
70
80
Scattering angle (degrees)

FIG. 8c

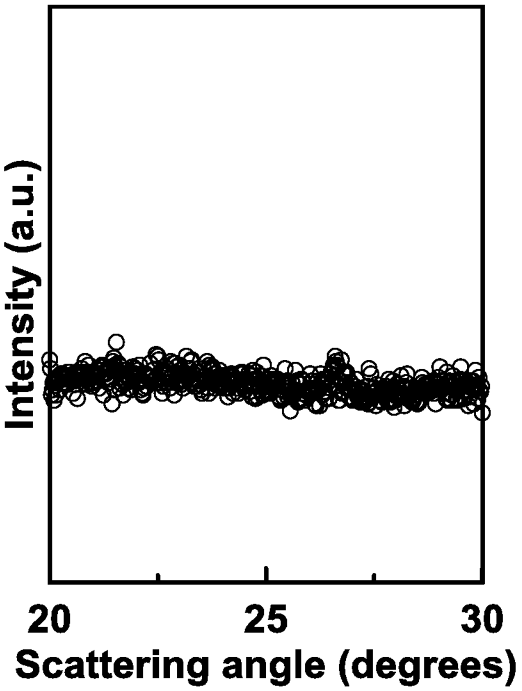
Intensity (a.u.)
20
25
30
Scattering angle (degrees)

FIG. 8d

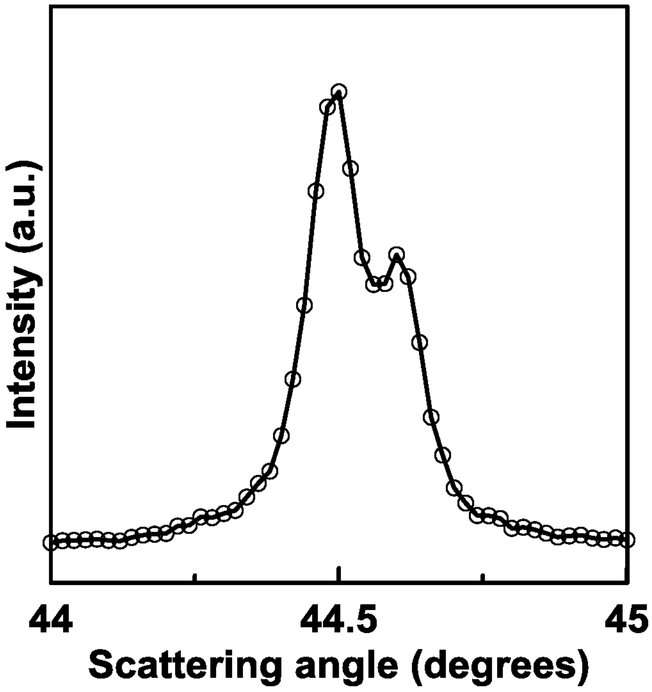
Intensity (a.u.)
44
44.5
45
Scattering angle (degrees)

FIG. 8e

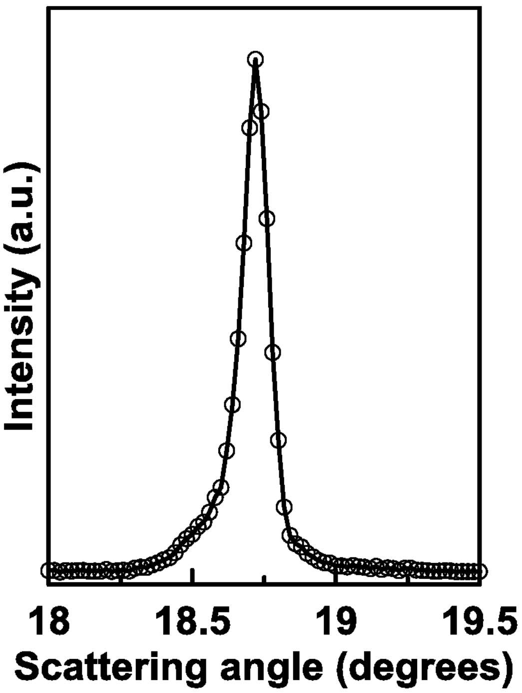
Intensity (a.u.)
18
18.5
19
19.5
Scattering angle (degrees)

FIG. 8f

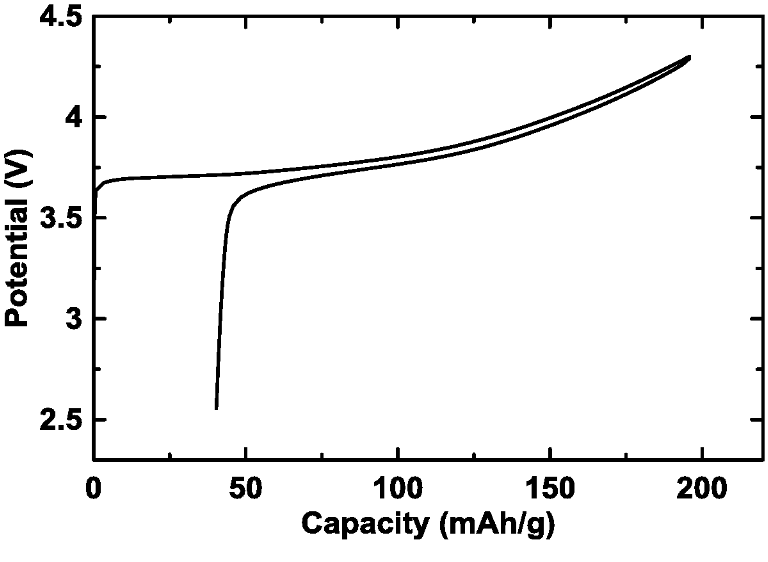
4.5
4
3.5
3
2.5
Potential (V)
0
50
100
150
200
Capacity (mAh/g)

FIG. 8g

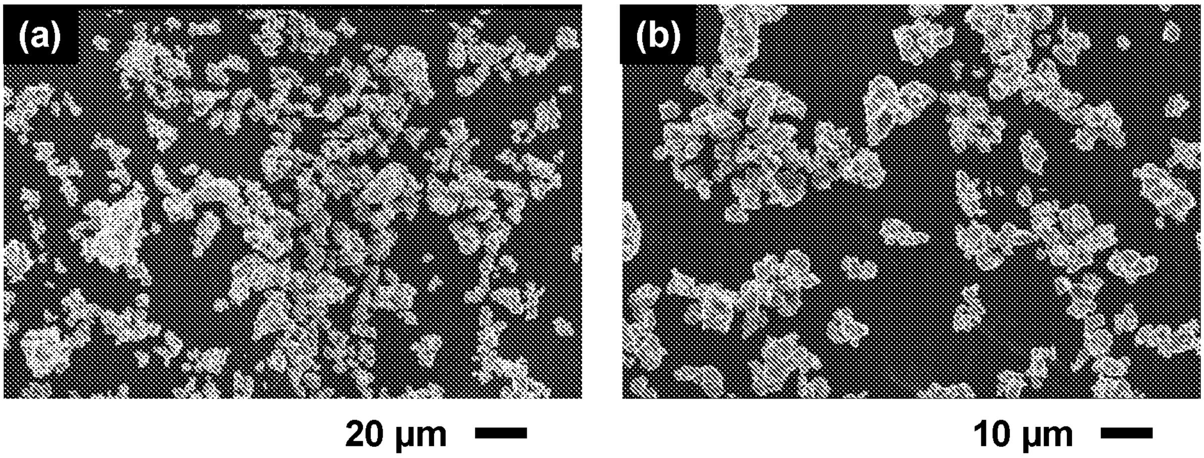
(a)
(b)
20 µm
10 µm

FIG. 9

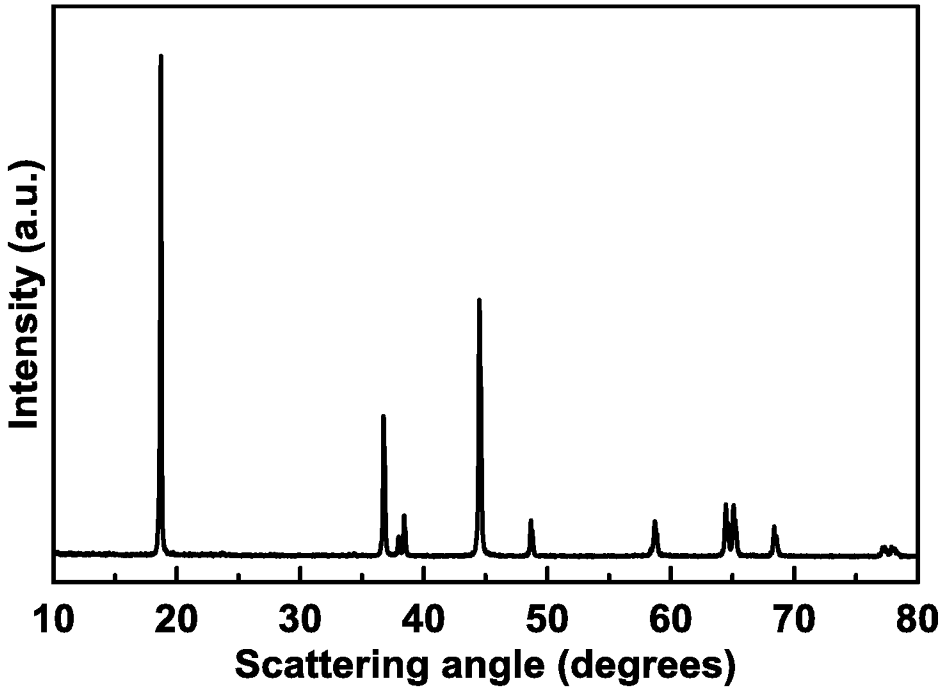
Intensity (a.u.)
10
20
30
40
50
60
70
80
Scattering angle (degrees)

FIG. 9c

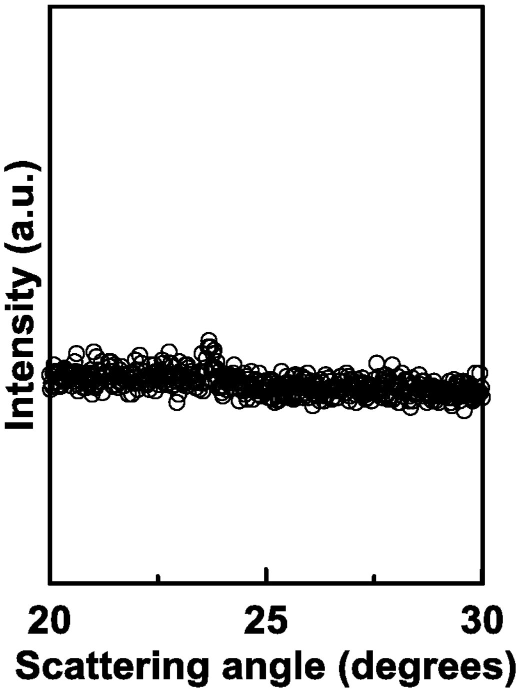
Intensity (a.u.)
20
25
30
Scattering angle (degrees)

FIG. 9d

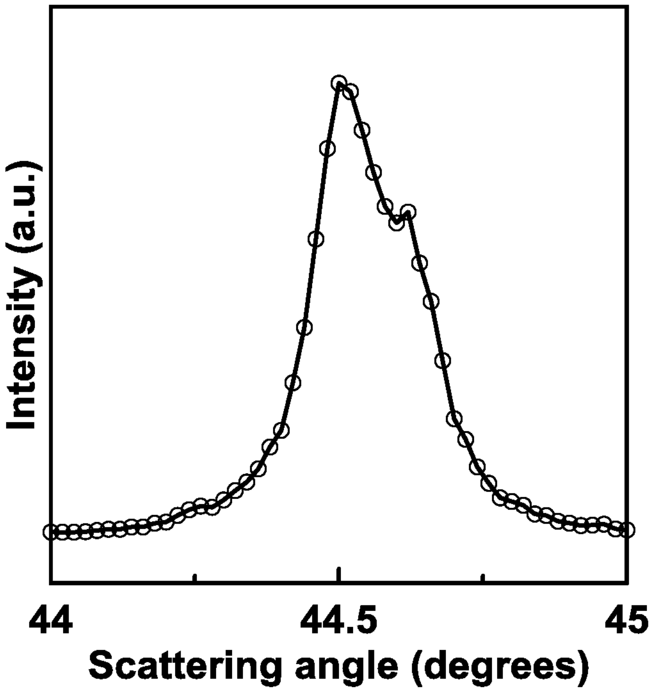
Intensity (a.u.)
44
44.5
45
Scattering angle (degrees)

FIG. 9e

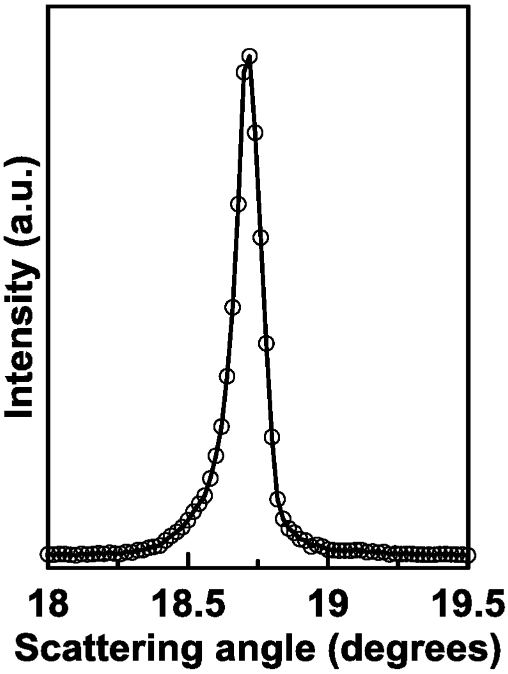
Intensity (a.u.)
18
18.5
19
19.5
Scattering angle (degrees)

FIG. 9f

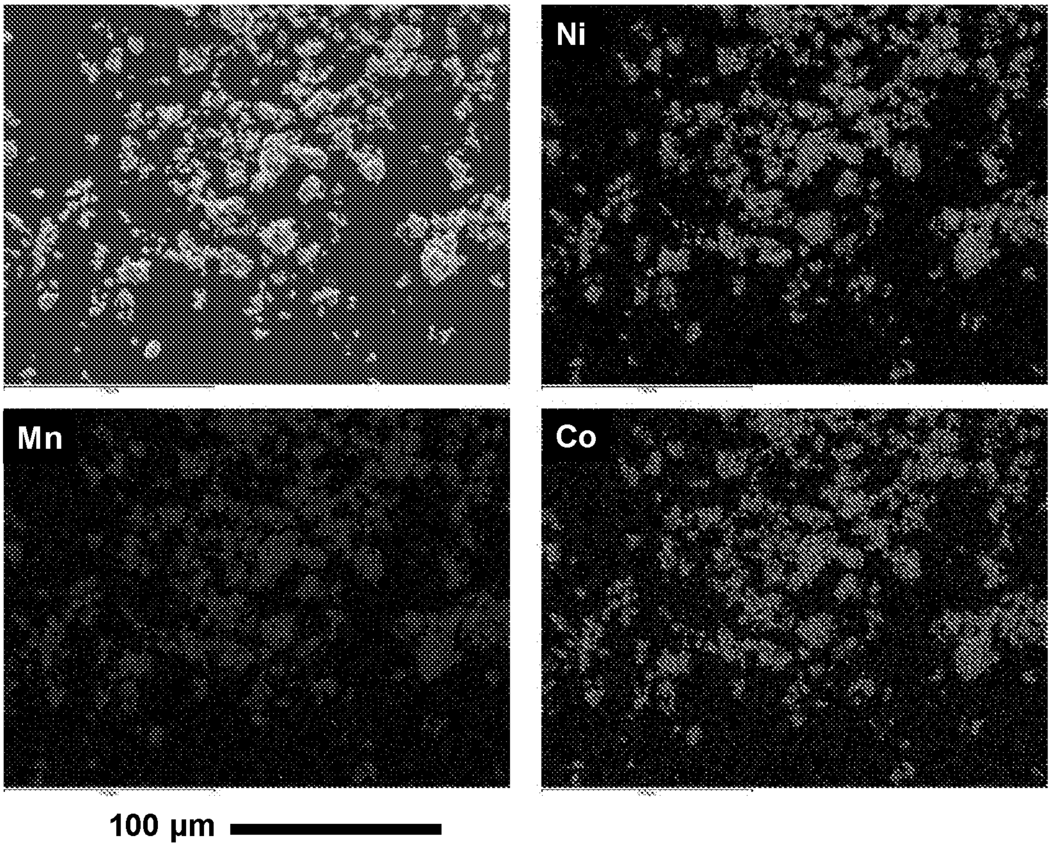
Ni
Mn
Co
100 µm

FIG. 9g

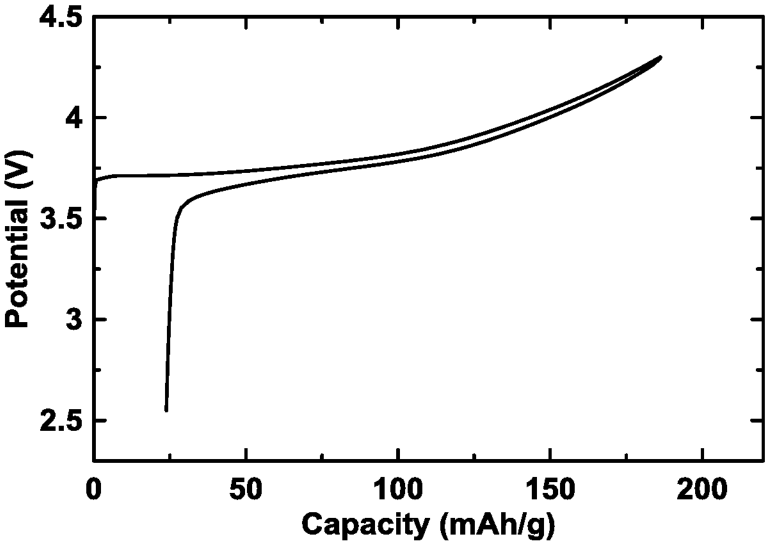

FIG. 9h

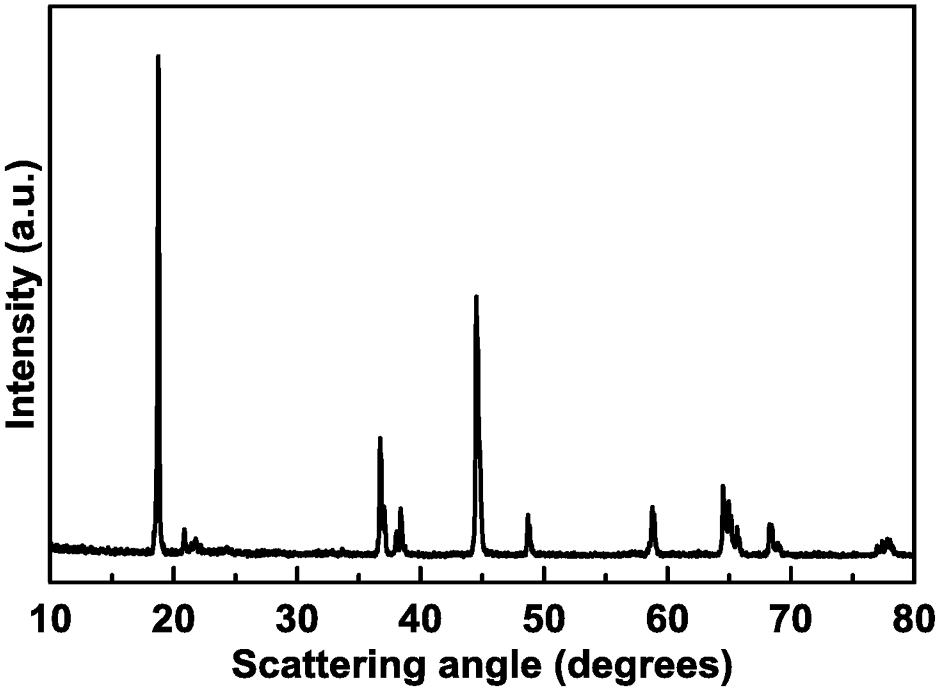

FIG. 10a

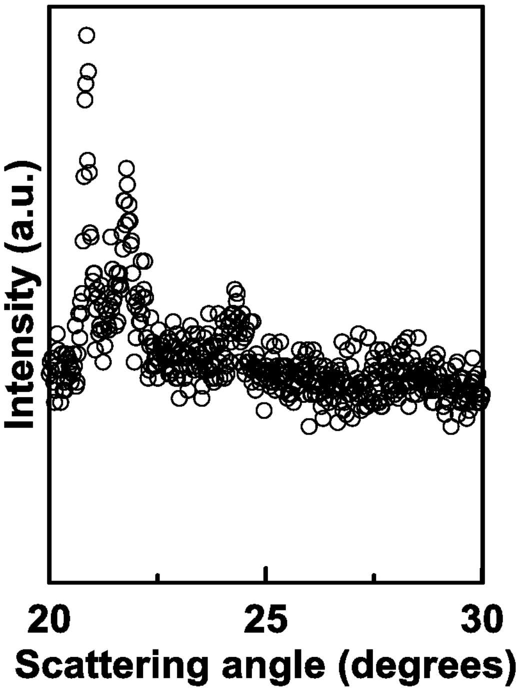

FIG. 10b

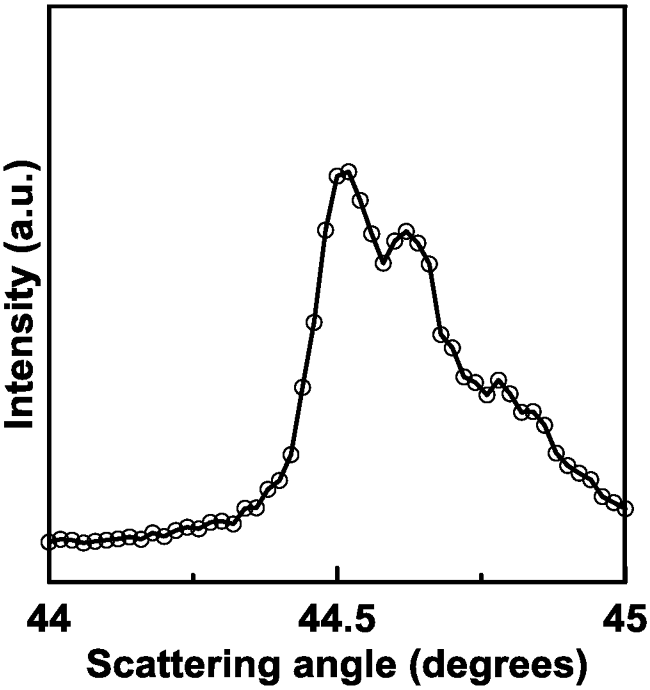

FIG. 10c

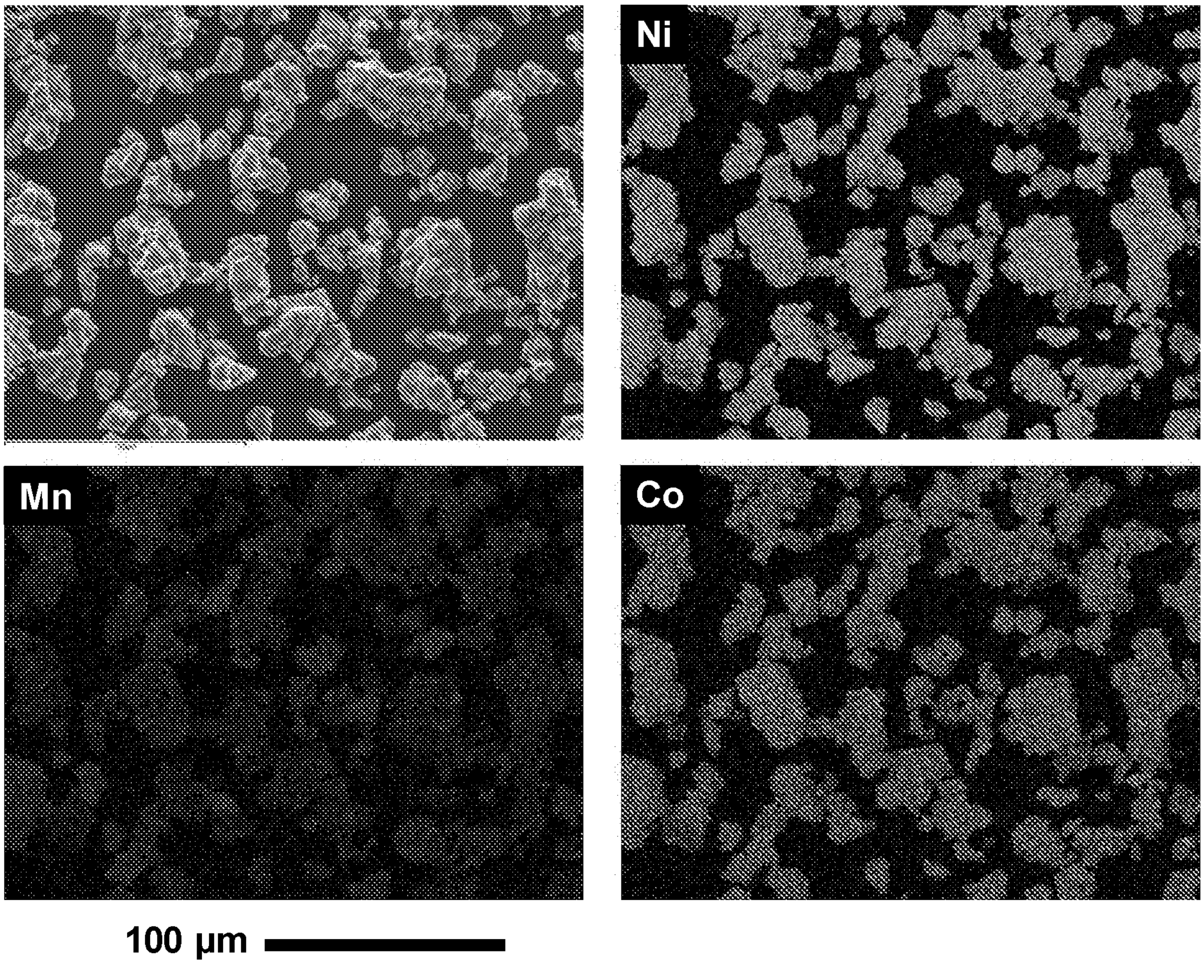

FIG. 10d

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2020/043599

A. CLASSIFICATION OF SUBJECT MATTER
INV. C01G53/00 H01M4/00
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C01G H01M

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

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

EPO-Internal, COMPENDEX, INSPEC, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2016/099469 A1 (PAULSEN JENS MARTIN [KR] ET AL) 7 April 2016 (2016-04-07) paragraph [0041] - paragraph [0044]; claims; figures; examples; tables	1-32
X	WO 2015/183568 A1 (DOW GLOBAL TECHNOLOGIES LLC [US]) 3 December 2015 (2015-12-03) page 3 - page 18; claims; examples; tables	1-32
X	WO 2012/163660 A1 (UMICORE NV [BE]; DE PALMA RANDY [KR] ET AL.) 6 December 2012 (2012-12-06) page 3 - page 8; claims; examples; tables	1,3,4, 7-9
X	US 2015/333328 A1 (JOHNSON CHRISTOPHER [US] ET AL) 19 November 2015 (2015-11-19) examples	1,4

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

☒ See patent family annex.

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Date of the actual completion of the international search 21 October 2020	Date of mailing of the international search report 02/11/2020
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Doslik, Natasa

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INTERNATIONAL SEARCH REPORT

International application No
PCT/US2020/043599

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2017/309894 A1 (HU JIN [BE] ET AL) 26 October 2017 (2017-10-26) the whole document -----	1-32

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2020/043599

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