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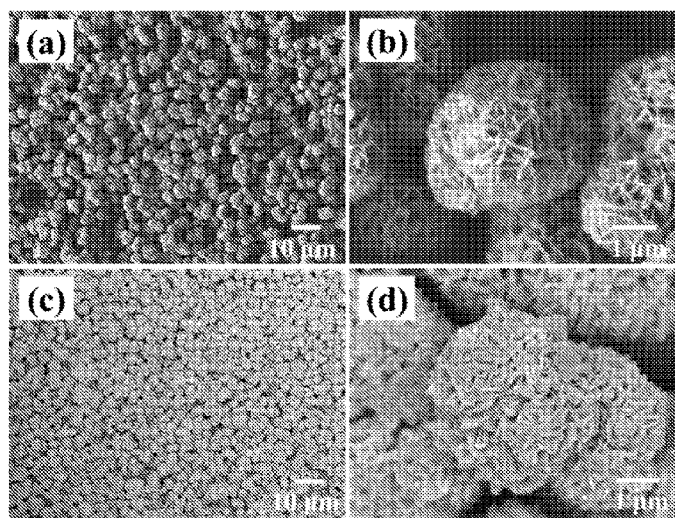


Fig. 3

(57) **Abstract:** A high-power cathode material for secondary batteries and its preparation methods are provided. The high-power cathode material can include porous structured secondary particles that are formed by flake-shaped primary particles. The high-power cathode material can have a composition represented by the formula: LiM_2O_2 , where M represents at least one metal element with an average oxidation state in a range between 2 and 3 in a fully uncharged state, or an average oxidation state in a range between 3 and 4 in a fully charged state. Precursors with flake-shaped primary particles can be prepared by mixing a precipitant, a complexing agent, and metal compounds; controlling at least one first condition of the precursor solution for the precursor solution to nucleate to generate nuclei; and incrementally adding the precursor solution to the base solution of a reactor with stirring to react while adjusting condition(s) of the reaction to a first condition(s), such that the precursor solution nucleates to generate nuclei; then adjusting condition(s) of the reaction



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to a second condition(s) while the precursor solution is incrementally added to a base solution, such that the nuclei grow to form the precursors with flake-shaped primary particles. Furthermore, the porous structured secondary particles can be prepared by mixing the precursors with lithium source and sintering the mixture at predetermined operation conditions.

DESCRIPTION

HIGH-POWER CATHODE MATERIAL FOR LITHIUM-ION BATTERIES

BACKGROUND

5 Lithium-ion batteries (LIBs) have become the dominant energy source for portable devices since the successful commercialization of LiCoO_2 /graphite cell in 1990s. Layered cathode materials ($\text{Li}[\text{Ni}_{1-x-y}\text{Mn}_x\text{Co}_y]\text{O}_2$, NMC) have drawn much attention of the battery manufacturers thanks to its low cost and high theoretical capacity.

10 However, energy output of the conventional cathode materials at high rates is very limited, mainly due to the large sizes of primary and secondary particles of NMC material. Retention lower than 75% at 5C relative to specific capacity at 0.1C makes it impractical for NMC to be utilized for the high-power applications such as electric vehicles, electric tools, and unmanned aerial vehicles.

15 Several NMC based cathode materials have been widely investigated to this effect. In U.S. Patent Application No. 13/626,212 and U.S. Patent Application No. 13/334,617, mixed pore-forming material and transition metal salts were calcined and crushed to form raw transition metal particles, followed by treatments of spherical machining and classification for product separation. Nevertheless, this design is associated with increased cost due to large amount of material waste in the manufacturing. In some other
20 investigations, facets (for example, 010) of crystals of cathode materials were chosen to be exposed for fast lithium deintercalation/intercalation. However, the sizes of these materials were smaller than one micron, leading to significant decrease of the energy density.

25 Further, in certain previously proposed investigations, porous LNMC were obtained by coprecipitation method in which polystyrene beads (PSBs) were dispersed in the reactor and cetyl trimethyl ammonium bromide was used as a surfactant. Then, the PSB-hydroxide precursors grew around the PSB seeds. After firing the precursors, the internal PSBs were decomposed to obtain porous (PSB-NCM) cathode materials. Although internal pores could be created through this method, improvement of rate performance of fuel cells was negligible.

BRIEF SUMMARY

There continues to be a need in the art for improved designs and techniques for a high-power cathode material for secondary batteries for outputting energy at high rates.

Embodiments of the subject invention pertain to a high-power cathode material including porous structured secondary particles formed by precursors with flake-shaped primary particles.

According to an embodiment of the invention, the cathode material for LIBs can comprise a plurality of secondary particles having porous structures, each secondary particle comprising a plurality of flake-shaped primary particles. The cathode material can have a composition represented by a formula: LiMO_2 , wherein M represents at least one metal element with an average oxidation state in a range between 2 and 3 in a fully uncharged state, or an average oxidation state in a range between 3 and 4 in a fully charged state. M of the formula can represent at least one element selected from Ni, Co, and Mn. The cathode material can further comprise at least one element selected from the group consisting of Mg, Al, Cu, Cr, W, Y, La, Nb, Zr, Ta, V, Sr, Ca, Ga, Nd, Ti, Sn, B, F, and Si. In addition, the plurality of secondary particles of the cathode material can have porosity in a range between about 20% and about 80% and particle sizes in a range between about 1 μm and about 30 μm . Furthermore, the plurality of primary particles of the cathode material can have particle sizes in a range between 100 nm and 5 μm .

In another embodiment, a method for preparing the flake-shaped primary particles of the cathode material for secondary batteries is provided. The method can comprise obtaining as starting materials a precipitant, a complexing agent, and a solution containing at least one metal compound and preparing solutions of the starting materials; incrementally adding the as-prepared solutions to a base solution with stirring to yield a precursor solution while adjusting condition(s) of the reaction to a first condition(s), such that the precursor solution nucleates to generate nuclei; maintaining the nucleating process for a time period; adjusting condition(s) of the reaction to a second condition(s) while the as-prepared solutions are incrementally added to the base solution, such that the nuclei grow to form agglomerations of the flake-shaped primary particles. In addition, the mixing a precipitant, a complexing agent, and at least one metal compound to form a precursor solution can be performed in a reactor under conditions of continuous stirring and continuously flowing an inert gas for oxygen removal. Moreover, the adjusting condition(s) of the reaction to a first

condition(s) such that the precursor solution nucleates to generate nuclei can comprise adjusting at least one of concentration of the complexing agent, pH value of the precursor solution, temperature of the precursor solution, and stirring speed of the stirring. Furthermore, the adjusting condition(s) of the reaction to a second condition(s) such that the nuclei grow to form secondary particles with flake-shaped primary particles can comprise
5 adjusting at least one of concentration of the complexing agent, pH value of the precursor solution, and temperature of the precursor solution. When the secondary particles formed have an average size equal to or greater than a predetermined size, the growing of the nuclei can be terminated and the precursors are then aged for better crystallinity by adjusting the
10 temperature of the precursor solution to a predetermined temperature for a predetermined period of time. Next, the resulting precursors can be washed, filtered, and dried.

In another embodiment, a method for preparing the porous structured secondary particles of the cathode material for LIBs is provided. The method can comprise mixing the precursors with lithium source; and sintering the mixture at predetermined conditions. The
15 solvent can stoichiometrically comprise an amount of lithium source. In addition, the sintering the mixture at predetermined conditions can comprise sintering the mixture at a certain temperature; sintering the mixture at a temperature that facilitates good crystallinity; and cooling down the mixture to room temperature, with compressed air being continuously purged over the mixture during the sintering steps and the cooling step.

BRIEF DESCRIPTION OF DRAWINGS

Figure 1 is a flow diagram illustrating a method of preparing precursors with flake-shaped primary particles of a high-power (HP) layered cathode material for LIBs, according to an embodiment of the subject invention.

Figure 2 is a flow diagram illustrating a method of preparing porous structured secondary particles of the high-power (HP) layered cathode material from the precursors with flake-shaped primary particles prepared as shown in Figure 1, according to an embodiment of the subject invention.

Figures 3(a) and **3(b)** show Scanning Electron Microscope (SEM) images of precursors with flake-shaped primary particles prepared as shown in Figure 1, according to an embodiment of the subject invention.

Figures 3(c) and 3(d) show Scanning Electron Microscope (SEM) images of the porous structured secondary particles of the high-power (HP) layered cathode material prepared as shown in Figure 2, according to an embodiment of the subject invention.

Figure 4(a) illustrates rate performance of high-power (HP) layered cathode material tested at 0.2C charge rate and 0.1C, 0.2C, 0.5C, 1C, 2C, 3C, and 5C discharge rates according to an embodiment of the subject invention.

Figure 4(b) illustrates rate performance of commercial (CS) cathode material tested at 0.2C charge rate and 0.1C, 0.2C, 0.5C, 1C, 2C, 3C, and 5C discharge rates.

Figure 5(a) illustrates normalized capacity retentions of high-power (HP) layered cathode material according to an embodiment of the subject invention, in comparison with capacity retentions of commercial (CS) cathode material, at different rates.

Figure 5(b) illustrates specific energy densities versus specific power densities of high-power (HP) layered cathode material according to an embodiment of the subject invention, in comparison with specific energy densities versus specific power densities of commercial (CS) cathode material, at different rates.

Figure 5(c) illustrates average working voltages of high-power (HP) layered cathode material according to an embodiment of the subject invention, in comparison with average working voltages of commercial (CS) cathode material, at different rates.

Figure 5(d) illustrates ΔV of average charge and discharge voltages of high-power (HP) layered cathode material according to an embodiment of the subject invention, in comparison with ΔV of average charge and discharge voltages of commercial (CS) cathode material, at different rates.

Figure 6(a) illustrates cycling charge and discharge profiles of high-power (HP) layered cathode material at 0.5C charge rate and 1C discharge rate from 3rd to 200th cycle according to an embodiment of the subject invention.

Figure 6(b) illustrates cycling charge and discharge profiles of commercial (CS) cathode material at 0.5C charge rate and 1C discharge rate from 3rd to 200th cycle.

Figure 7(a) illustrates specific capacity responses as a function of cycle number of high-power (HP) layered cathode material according to an embodiment of the subject invention, in comparison with specific capacity responses as a function of cycle number of commercial (CS) cathode material.

Figure 7(b) illustrates normalized capacity retention responses as a function of cycle number of high-power (HP) layered cathode material according to an embodiment of the subject invention, in comparison with normalized capacity retention responses as a function of cycle number of commercial (CS) cathode material.

Figure 7(c) illustrates coulombic efficiency responses as a function of cycle number of high-power (HP) layered cathode material according to an embodiment of the subject invention, in comparison with coulombic efficiency responses as a function of cycle number of commercial (CS) cathode material.

DETAILED DESCRIPTION

Embodiments of the subject invention pertain to high-power layered cathode materials for secondary batteries for outputting energy at high rates. In particular, the high-power cathode materials according to embodiments of the subject invention have (i) small primary particles, enabling fast intercalation/deintercalation of metal ions (for example, lithium ions), which is essential to excellent rate capability; ii) porous structures with high specific surface area, enhancing the contact between active material and electrolyte; iii) unique structures, providing good suspension for the anisotropic volume change during charge and discharge and ensuring an excellent cyclability; and iv) precursors with flake-shaped primary particles prepared by changing the preparation conditions.

According to an embodiment of the subject invention, the high-power layered cathode material for LIBs is prepared by (i) preparing precursors with flake-shaped primary particles, and (ii) preparing porous structured cathode materials from the precursors with flake-shaped primary particles.

The following examples illustrate the subject innovation. Unless otherwise indicated in the following examples and elsewhere in the specification and claims, all parts and percentages are by weight, all temperatures are in degrees Centigrade, and pressure is at or near atmospheric pressure.

When the term “about” is used herein, in conjunction with a numerical value, it is understood that the value can be in a range of 90% of the value to 110% of the value, i.e. the value can be +/- 10% of the stated value. For example, “about 1 kg” means from 0.90 kg to 1.1 kg.

Preparation of Precursors with Flake-Shaped Primary Particles

According to one exemplary embodiment of the subject invention, the precursors with flake-shaped primary particles of the high-power layered cathode material for enabling fast intercalation/deintercalation of metal ions (for example, lithium ions) can be prepared by the following method:

1. preparing an aqueous mixed solution (solution A) of salts of nickel, manganese, and cobalt with a predetermined total metal ion concentration;
2. preparing an aqueous precipitant solution (solution B);
3. preparing an aqueous complexing agent solution (solution C);
4. adding a base solution up to a predetermined capacity of a reactor with stir, while an inert gas continuously flows through the reactor for oxygen removal;
5. adding the solutions A, B and C respectively obtained from the steps 1, 2, and 3 into the reactor at a predetermined adding rate to obtain a precursor solution, while adjusting the concentration of the solution C (complexing agent) to a first predetermined concentration, the pH value of the precursor solution in the reactor to a first predetermined pH value, the temperature of the precursor solution in the reactor to a first predetermined temperature, and the stirring speed of the reactor to a first predetermined speed for stimulating nucleation in the precursor solution;
6. keeping the nucleating for a predetermined period of time to generate nuclei of the precursors;
7. adjusting the concentration of the solution C to a second predetermined concentration value, the pH value of the precursor solution in the reactor to a second predetermined pH value, and the temperature of the precursor solution in the reactor to a second predetermined temperature, while adding solutions A, B and C to the reactor at a second predetermined adding rate, for stimulating the nuclei to grow to form the flake-shaped primary particles;
8. terminating the growing of the nuclei, when the precursors with flake-shaped primary particles formed have an average size equal to or greater than a predetermined size;
9. aging the precursors for improved crystallinity by raising the temperature of the reactor to a third predetermined temperature and keeping the aging for a second predetermined period of time;

10. washing the resulting precursors with flake-shaped primary particles;
11. filtering to separate out the precursors; and
12. drying the precursors at a fourth predetermined temperature for a third predetermined period of time.

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Figure 1 shows an example of the method of preparing precursors with flake-shaped primary particles of a high-power (HP) layered cathode material for secondary batteries, according to an embodiment of the subject invention. Referring to Figure 1, at step S100, an aqueous mixed solution (solution A) of nickel(II) sulfate (NiSO_4), cobalt(II) sulfate (CoSO_4), and manganese(II) sulfate (MnSO_4) in a molar ratio of 5:2:3 is prepared with a total metal ion concentration of 2.0 mol/L. Next, at step S105, a 4.0 mol/L aqueous solution of sodium hydroxide (NaOH) (solution B) is prepared as the precipitant. Then, at step S110, an appropriate amount of an aqueous ammonia solution (NH_4OH) (solution C) is prepared as the complexing agent.

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Further, at step S115, a base solution is added to a continuous stirring tank reactor (CSTR) up to two thirds of the capacity of the reactor (for example, if the reactor has a capacity of 1 liter, up to 2/3 liter base solution is added to the reactor), while nitrogen continuously purges into the reactor for oxygen removal and the base solution is continuously stirred. The base solution can comprise, for example, water or buffer solution containing complexing agents. Next, at step S120, the solutions A, B and C respectively obtained from the steps S100, S105, and S110 are added into the continuous stirring tank reactor (CSTR) by a pump (for example, a peristaltic pump) at a rate of about 1.0 mL/minute, while the concentration of the solution C (complexing agent) is adjusted to about 0.1 M, the pH value of the precursor solution in the reactor is adjusted to about 12.0, the temperature of the precursor solution in the reactor is adjusted to about 30°C, and the stirring speed is adjusted to about 800 rpm. As a result, the precursor solution nucleates to generate nuclei. Then, the nucleation process is kept for about one hour at step S135.

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Next, at step S140, the concentration of the solution C (complexing agent) is adjusted to 0.3 M, the pH value of the mixed solution in the reactor is adjusted to about 11.0, and the temperature of the precursor solution in the reactor is adjusted to about 50°C, while the solutions A, B and C are added into the reactor by the pump at a rate of about 1.0 mL/minute for stimulating the nuclei to grow to form precursors with flake-shaped primary

particles. The nuclei growth process is terminated, when the precursors with flake-shaped primary particles formed have an average size equal to or greater than a predetermined size at step S150.

Then, at step S155, an aging process is performed for precursors with flake-shaped primary particles to obtain better crystallinity by raising temperature of the reactor to about 60°C and keeping the aging process for about 10 hours.

The resulting precursors with flake-shaped primary particles are washed at step S160, filtered to separate out the precursors with flake-shaped primary particles at step S165, and vacuum dried at about 120°C for about 12 hours at step 170.

In one embodiment, the resulting flake-shaped primary particles can have particle sizes in a range between 100 nm and 5 µm and the secondary particles can have particle sizes in a range between 1 µm and 30 µm.

Preparation of Porous Structured Secondary Particles from the Precursors with Flake-Shaped Primary Particles

According to an embodiment of the subject invention, the porous structured secondary particles of the high-power layered cathode material can be prepared from the precursors with flake-shaped primary particles following steps:

- 1) mixing the precursors prepared as described above with an amount of lithium source stoichiometrically by mechanical grinding until a homogenous consistency is achieved;
- 2) sintering the mixture with a sintering apparatus at a first predetermined temperature (with a first predetermined heating rate) for a first predetermined period of time, while compressed air continuously purges through the sintering apparatus;
- 3) sintering the mixture at a second predetermined temperature (with the first predetermined heating rate) for a second predetermined period of time, while compressed air continuously purges through the sintering apparatus, to form the porous structured secondary particles;
- 4) cooling the porous structured secondary particles at a predetermined cooling rate to room temperature, while compressed air continuously purges through the sintering apparatus;
- 5) mechanically grinding the porous structured secondary particles and passing the ground porous structured secondary particles through a sieve of a predetermined mesh size.

Figure 2 shows one example of the method of preparing the porous structured secondary particles from the precursors with flake-shaped primary particles. Referring to Figure 2, at step S200, the precursors with flake-shaped primary particles prepared as shown in Figure 1 are mixed with a stoichiometrical amount of lithium source by mechanical grinding until a homogenous consistency is achieved. Next, at step S210, the mixture obtained is sintered by a sintering apparatus such as a muffle furnace at a temperature of about 500°C (with a heating rate of about 1°C/minute) for about 5 hours. Then, at step S220, the mixture is sintered at a temperature of about 900°C for about 12 hours to form the porous structured secondary particles. Further, the porous structured secondary particles are cooled down (with a cooling rate of about 2°C/minute) to room temperature at step S230. It is noted that compressed air continuously purges through the sintering apparatus during the two sintering and one cooling processes. Next, at step S240, the resulting porous structured secondary particles are mechanically ground and sieved by a sieve of a mesh size of about 50 μm .

In one embodiment, the resulting cathode material formed by agglomerations of the porous structured secondary particles prepared as described above can have a composition represented by a formula: LiMO_2 , where M represents at least one metal element with an average oxidation state in a range between 2 and 3 in a fully uncharged state, or an average oxidation state in a range between 3 and 4 in a fully charged state.

In one embodiment, M of the formula can represent at least one element selected from Ni, Co, and Mn.

In one embodiment, the resulting cathode material can further comprise at least one element selected from the group consisting of Mg, Al, Cu, Cr, W, Y, La, Nb, Zr, Ta, V, Sr, Ca, Ga, Nd, Sr, Ti, Sn, B, F, and Si.

In one embodiment, the porous structured secondary particles prepared can have porosity in a range between about 20% and about 80%, and particle sizes in a range between about 1 μm and about 30 μm .

Characterization and Evaluation of the High-power Layered Cathode Material

Figures 3(a) and 3(b) illustrate scanning electron microscope (SEM) micrograms (at different magnifications) of the precursors with flake-shaped primary particles prepared according to embodiments of the subject invention.

Figures 3(c) and 3(d) illustrate scanning electron microscope (SEM) micrograms (at different magnifications) of the porous structured secondary particles of the high-power (HP) layered cathode material prepared according to an embodiment of the subject invention.

Referring to Figure 4(a), the rate performances of high-power (HP) layered cathode material according to an embodiment of the subject invention are tested at 0.2C charge rate and 0.1, 0.2, 0.5, 1, 2, 3, 5C discharge rates.

Figure 4(a) shows seven plots of voltage versus specific capacities of the high-power (HP) layered cathode material cycled in the voltage range between 2.7 V and 4.3 V at a charge rate of 0.2 C and also seven plots of voltage versus specific capacities of the high-power (HP) layered cathode material cycled in the voltage range between 2.7 V and 4.3 V at a discharge rate of 0.1C, 0.2C, 0.5C, 1C, 2C, 3C, and 5C, respectively.

As illustrated in Figure 4(a), the high-power (HP) layered cathode material delivers a specific capacity of 172.3, 168.9, 164.2, 159.7, 154.4, 150.6, and 145.1 mAh/g at 0.1, 0.2, 0.5, 1, 2, 3, and 5C, respectively.

In comparison, Figure 4(b) illustrates the rate performances of commercial (CS) cathode material tested at 0.2C charge rate and 0.1C, 0.2C, 0.5C, 1C, 2C, 3C, and 5C discharge rates. In Figure 4(b), seven plots are shown for voltage versus specific capacities of the commercial (CS) cathode material charged in the voltage range between 2.7V and 4.3V at a rate of 0.2C, and seven plots are shown for voltage versus specific capacities of the high-power (HP) layered cathode material charges in the voltage range between 2.7V and 4.3V at rates of 0.1C, 0.2C, 0.5C, 1C, 2C, 3C, and 5C, respectively.

For the example shown in Figure 4(b), a specific capacity of 168.4, 163.2, 154.6, 147.1, 137.8, 130.6, and 119.5 mAh/g could be delivered by the commercial (CS) cathode material at rates of 0.1, 0.2, 0.5, 1, 2, 3, and 5C, respectively.

Therefore, the high-power (HP) layered cathode material exhibits rate performance superior to that of the commercial (CS) cathode material.

Figure 5(a) shows a plot of normalized capacity retention at different rates of high-power (HP) layered cathode material according to an embodiment of the subject invention, in comparison with a plot of capacity retention at different rates of commercial (CS) cathode material.

In Figure 5(a), the normalized capacity retention of the high-power (HP) layered cathode material is decreased from about 100% to about 85%, when the discharge rate is increased from 0.1C to 5C. In comparison, the normalized capacity retention of the commercial (CS) cathode material is decreased from about 100% to about 70%, when the discharge rate is increased from 0.1C to 5C.

Thus, the high-power (HP) layered cathode material exhibits normalized capacity retention superior to that of the commercial (CS) cathode material at the same rate.

Figure 5(b) shows a plot of specific energy densities at different specific power densities of the high-power (HP) layered cathode material according to an embodiment of the subject invention, in comparison with a plot of specific energy densities at different specific power densities of the commercial (CS) cathode material.

In Figure 5(b), the specific energy densities of the high-power (HP) layered cathode material is decreased from about 655 Wh/kg to about 540 Wh/kg, when the specific power density is increased from about 0.06 kW/kg to about 3.0 kW/kg. In comparison, the specific energy density of the commercial (CS) cathode material is decreased from about 645 Wh/kg to about 410 Wh/kg, when the specific power density is increased from about 0.06 kW/kg to about 3.0 kW/kg.

Therefore, the high-power (HP) layered cathode material shows specific energy density superior to that of the commercial (CS) cathode material at the same specific power density.

Figure 5(c) shows a plot of average working voltages at different rates of the high-power (HP) layered cathode material according to an embodiment of the subject invention, in comparison with a plot of average working voltages at different rates of the commercial (CS) cathode material. The average working voltages of the high-power (HP) layered cathode material is increased from about 3.81 V to about 3.85 V, when charge rate is increased from 0.1C to 5C.

In Figure 5(c), the average working voltages of the high-power (HP) layered cathode material is decreased from about the 3.79V to about 3.60 V, when discharge rate is

increased from 0.1C to 5C. In comparison, the average working voltages of the commercial (CS) cathode material is increased from about 3.84 V to about 3.90 V, when charge rate is increased from 0.1C to 5C. In comparison, the average working voltages of the commercial (CS) cathode material is decreased from about 3.79 V to about 3.40 V, when discharge rate is increased from 0.1C to 5C.

Thus, the high-power (HP) layered cathode material shows an average working voltage lower than that of the commercial (CS) cathode material at the same charge rate in charging; and an average working voltage higher than that of the commercial (CS) cathode material at the same discharge rate in discharging.

Figure 5(d) shows a plot of ΔV of average charge and discharge voltages at different rates of the high-power (HP) layered cathode material according to an embodiment of the subject invention, in comparison with a plot of ΔV of average charge and discharge voltages at different rates of the commercial (CS) cathode material.

In Figure 5(d), the ΔV of average charge and discharge voltages of the high-power (HP) layered cathode material is increased from about 0.02 V to about 0.25 V, when the rate is increased from 0.1C to 5C. In comparison, the ΔV of average charge and discharge voltages of the commercial (CS) cathode material is increased from about 0.05 V to about 0.5 V, when the rate is from 0.1C to 5C.

Thus, the high-power (HP) layered cathode material shows ΔV of average charge and discharge voltages lower than that of the commercial (CS) cathode material at the same rate.

Figure 6(a) illustrates five plots of voltages versus specific capacities of the high-power (HP) layered cathode material cycled in a voltage range between 2.7 V and 4.3 V at a charge rate of 0.5C for the 3rd, 50th, 100th, 150th, and 200th cycle, respectively; and five plots of voltages versus specific capacities of the high-power (HP) layered cathode material cycled in the voltage range between 2.7 V and 4.3 V at a discharge rate of 1C for 3rd, 50th, 100th, 150th, and 200th cycle, respectively. The specific capacity of the high-power (HP) layered cathode material is measured to be 159.0, 152.7, 148.2, 145.6, and 143.6 mAh/g at 3rd, 50th, 100th, 150th, and 200th cycle, respectively.

In comparison, Figure 6(b) illustrates five plots of voltages versus specific capacities of the commercial (CS) cathode material cycled in a voltage range between 2.7 V and 4.3 V at a charge rate of 0.5C for the 3rd, 50th, 100th, 150th, and 200th cycle, respectively; and five

plots of voltages versus specific capacities of the commercial (CS) cathode material cycled in the voltage range between 2.7 V and 4.3 V at a discharge rate of 1C at the 3rd, 50th, 100th, 150th, and 200th cycle, respectively. In Figure 6(b), for the commercial (CS) cathode material, the specific capacity delivered is measured to be 148.7, 142.4, 133.8, 125.9, and 120.2 mAh/g at the 3rd, 50th, 100th, 150th, and 200th cycle, respectively.

Figure 7(a) shows a plot of specific capacity responses as a function of cycle number of the high-power (HP) layered cathode material according to an embodiment of the subject invention, comparing with a plot of specific capacity responses as a function of cycle number of the commercial (CS) cathode material. The specific capacity of the high-power (HP) layered cathode material is decreased from about 160 mAh/g to about 150 mAh/g after 200 cycles.

In comparison, the specific capacity of the commercial (CS) cathode material is decreased from about 150 mAh/g to about 125 mAh/g after 200 cycles. Thus, the high-power (HP) layered cathode material exhibits a specific capacity higher than that of the commercial (CS) cathode material at the same cycle number.

Figure 7(b) shows a plot of normalized capacity retention responses as a function of cycle number of the high-power (HP) layered cathode material according to an embodiment of the subject invention, in comparison with a plot of normalized capacity retention responses as a function of cycle number of the commercial (CS) cathode material. The normalized capacity retention of the high-power (HP) layered cathode material is decreased from about 100% to about 93% after 200 cycles.

In comparison, the normalized capacity retention of the commercial (CS) cathode material is decreased from about 100% to about 81% after 200 cycles.

Thus, the high-power (HP) layered cathode material exhibits normalized capacity retention higher than that of the commercial (CS) cathode material at the same cycle number.

Figure 7(c) shows a plot of coulombic efficiency responses as a function of cycle number of the high-power (HP) layered cathode material according to an embodiment of the subject invention, in comparison with a plot of coulombic efficiency responses as a function of cycle number of the commercial (CS) cathode material. The coulombic efficiency of the high-power (HP) layered cathode material is increased from about 99.3% to about 99.8% after 200 cycles.

In comparison, the coulombic efficiency of the commercial (CS) cathode material is increased from about 99.1% to about 99.6% after 200 cycles.

The coulombic efficiency increase rate of the high-power (HP) layered cathode material is higher than that of commercial (CS) cathode material, indicating a faster cathode electrolyte interface formation for the high-power (HP) layered cathode material during cycling.

In one embodiment, the high-power layered cathode material can comprise primary particles of small particle sizes, resulting in fast intercalation/deintercalation of metal ions (for example, lithium ions) and thus excellent rate capability of LIBs.

In one embodiment, the high-power layered cathode material can comprise secondary particles with porous structure having high specific surface area, resulting in enhancement of the contact between active material and electrolyte of secondary batteries.

In one embodiment, the high-power layered cathode material can comprise unique porous structures providing good suspension for the anisotropic volume change during charge state and discharge state, ensuring an excellent cyclability of secondary batteries.

In one embodiment, the high-power layered cathode material can comprise flake-shaped primary particles prepared by adjusting its preparation conditions.

The subject invention includes, but is not limited to, the following exemplified embodiments.

Embodiment 1. A cathode material for secondary batteries, comprising:
a plurality of secondary particles having porous structures, each secondary particle comprising a plurality of flake-shaped primary particles.

Embodiment 2. The cathode material according to embodiment 1, the cathode material having a composition represented by a formula LiMO_2 , wherein M represents at least one metal element with an average oxidation state of 2 or 3 in a fully uncharged state, or an average oxidation state of 3 or 4 in a fully charged state.

Embodiment 3. The cathode material according to embodiment 2, wherein the M of the formula represents at least one element selected from Ni, Co, and Mn, and wherein the cathode material can further comprise at least one element selected from the

group consisting of Mg, Al, Cu, Cr, W, Y, La, Nb, Zr, Ta, V, Sr, Ca, Ga, Nd, Sr, Ti, Sn, B, F, and Si.

Embodiment 4. The catalyst according to any of embodiments 1-3, wherein the plurality of secondary particles has porosity in a range between about 20% and about 80%.

Embodiment 5. The cathode material according to any of embodiments 1-4, wherein the plurality of secondary particles has particle sizes in a range between about 1 μ m and about 30 μ m.

Embodiment 6. The cathode material according to any of embodiments 1-5, wherein the plurality of primary particles has particle sizes in a range between 100nm and 5 μ m.

Embodiment 7. A method for preparing flake-shaped primary particles of a cathode material for secondary batteries, comprising:

mixing a precipitant, a complexing agent, and at least one metal compound to

form a precursor solution;

incrementally adding the precursor solution to a base solution with stirring to react while adjusting condition(s) of the reaction to a first condition(s), such that

the precursor solution nucleates to generate nuclei;

keeping the nucleating process for a time period;

adjusting condition(s) of the reaction to a second condition(s) while the precursor solution is incrementally added to the base solution, such that the nuclei grow to form the flake-shaped primary particles.

Embodiment 8. The method according to embodiment 7, wherein the at least one metal compound comprises at least one of nickel, manganese, and cobalt ions.

Embodiment 9. The method according to any of embodiments 7-8, wherein the precipitant comprises a hydroxide, carbonate, or oxalate.

Embodiment 10. The method according to any of embodiments 7-9, wherein
5 the complexing agent comprises ammonia, phosphate, ethylenediaminetetraacetic acid (EDTA), or nitrilotriacetic acid (NTA).

Embodiment 11. The method according to any of embodiments 7-10, wherein
10 the mixing of a precipitant, a complexing agent, and at least one metal compound to form a precursor solution is performed in a reactor under conditions of continuous stirring and continuously flowing an inert gas for oxygen removal.

Embodiment 12. The method according to any of embodiments 7-11, wherein
15 the adjusting condition(s) of the reaction to a first condition(s) such that the precursor solution nucleates to generate nuclei comprises:
adjusting at least one of concentration of the complexing agent, pH value of
the
precursor solution, temperature of the precursor solution, and stirring speed
of
20 the stirring.

Embodiment 13. The method according to any of embodiments 7-12, wherein
the adjusting condition(s) of the reaction to a second condition(s) such that the nuclei grow
to form the flake-shaped primary particles comprises:
25 adjusting at least one of concentration of the complexing agent, pH value of
the precursor solution, and temperature of the precursor solution.

Embodiment 14. The method according to any of embodiments 7-13, further
comprising:
30 terminating the growing of the nuclei, when the precursors with flake-shaped
primary particles formed have an average size equal to or greater than a
predetermined

size.

Embodiment 15. The method according to any of embodiments 7-14, further comprising:

5 aging the flake-shaped primary particles formed for crystallinity, by adjusting the temperature of the precursor solution to a predetermined temperature, for a predetermined period of time.

Embodiment 16. The method according to any of embodiments 7-15, further comprising:

10 washing the precursors with flake-shaped primary particles.

Embodiment 17. The method according to any of embodiments 7-16, further comprising:

15 filtering to separate out the precursors with flake-shaped primary particles.

Embodiment 18. The method according to any of embodiments 7-17, further comprising:

20 drying the precursors with flake-shaped primary particles at a predetermined temperature for a predetermined time period.

Embodiment 19. A method for preparing porous structured secondary particles of a cathode material for secondary batteries, comprising:

25 mixing precursors with lithium source; and
sintering the mixture at predetermined conditions.

Embodiment 20. The method according to embodiment 19, wherein the lithium source comprises LiOH, LiNO₃, Li₂CO₃, or Li₂(acetate).

30 Embodiment 21. The method according to any of embodiments 19-20, wherein the primary particles have shapes of flakes and are prepared by:

preparing a precipitant, a complexing agent, and a solution comprising at least one metal compound;

incrementally adding the prepared solutions to a base solution with stirring to react while adjusting condition(s) of the reaction to a first condition(s), such that the precursor solution nucleates to generate nuclei;

keeping the nucleating process for a time period;

adjusting condition(s) of the reaction to a second condition(s) while the precursor solution is incrementally added to the base solution, such that the nuclei grow to form the flake-shaped primary particles.

Embodiment 22. The method according to embodiment 7, wherein the base solution comprises water or a buffer solution including complexing agents.

It should be understood that the examples and embodiments described herein are for illustrative purposes only and that various modifications or changes in light thereof will be suggested to persons skilled in the art and are to be included within the spirit and purview of this application and the scope of the appended claims. In addition, any elements or limitations of any invention or embodiment thereof disclosed herein can be combined with any and/or all other elements or limitations (individually or in any combination) or any other invention or embodiment thereof disclosed herein, and all such combinations are contemplated with the scope of the invention without limitation thereto.

All patents, patent applications, provisional applications, and publications referred to or cited herein are incorporated by reference in their entirety, including all figures and tables, to the extent they are not inconsistent with the explicit teachings of this specification.

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CLAIMS

What is claimed is:

1. A cathode material for secondary batteries, comprising:
a plurality of secondary particles having porous structures, each secondary particle comprising a plurality of flake-shaped primary particles.
2. The cathode material according to claim 1, the cathode material having a composition represented by a formula: LiMO_2 , wherein M represents at least one metal element with an average oxidation state in a range between 2 and 3 in a fully uncharged state, or an average oxidation state in a range between 3 and 4 in a fully charged state.
3. The cathode material according to claim 2, wherein the M of the formula represents at least one element selected from Ni, Co, and Mn.
4. The cathode material according to claim 2, the composition of the cathode material further comprising at least one element selected from the group consisting of Mg, Al, Cu, Cr, W, Y, La, Nb, Zr, Ta, V, Sr, Ca, Ga, Nd, Sr, Ti, Sn, B, F, and Si.
5. The cathode material according to claim 1, wherein the plurality of secondary particles has porosity in a range between about 20% and about 80%.
6. The cathode material according to claim 1, wherein the plurality of secondary particles has particle sizes in a range between about $1\mu\text{m}$ and about $30\mu\text{m}$.
7. The cathode material according to claim 1, wherein the plurality of primary particles has particle sizes in a range between 100nm and $5\mu\text{m}$.
8. A method for preparing precursors with flake-shaped primary particles of a cathode material for secondary batteries, comprising:
incrementally adding a precipitant, a complexing agent, and at least one metal compound solution to a base solution with stirring to react while adjusting condition(s) of

the reaction to a first condition(s), to obtain a precursor solution that nucleates to generate nuclei;

maintaining the nucleating process for a time period;

adjusting condition(s) of the reaction to a second condition(s) while the precipitant, complexing agent, and the at least one metal compound are incrementally added to the base solution, such that the nuclei grow to form the flake-shaped primary particles.

9. The method according to claim 8, wherein the at least one metal compound comprises at least one of nickel, manganese, and cobalt ions.

10. The method according to claim 8, wherein the precipitant comprises a hydroxide, carbonate, or oxalate.

11. The method according to claim 8, wherein the complexing agent comprises ammonia, phosphate, ethylenediaminetetraacetic acid (EDTA), or nitrilotriacetic acid (NTA).

12. The method according to claim 8, wherein the mixing of a precipitant, a complexing agent, and at least one metal compound to form a precursor solution is performed in a reactor under conditions of continuous stirring and continuously flowing an inert gas for oxygen removal.

13. The method according to claim 8, wherein the adjusting condition(s) of the reaction to a first condition(s) such that the precursor solution nucleates to generate nuclei comprises:

adjusting at least one of concentration of the complexing agent, pH value of the precursor solution, temperature of the precursor solution, and stirring speed of the stirring.

14. The method according to claim 8, wherein the adjusting condition(s) of the reaction to a second condition(s) such that the nuclei grow to form precursors with flake-shaped primary particles comprises:

adjusting at least one of concentration of the complexing agent, pH value of the precursor solution, and temperature of the precursor solution.

15. The method according to claim 8, further comprising:
terminating the growing of the nuclei, when the precursors with flake-shaped primary particles formed have an average size equal to or greater than a predetermined size.

16. The method according to claim 15, further comprising:
aging the precursors with flake-shaped primary particles formed for crystallinity, by adjusting the temperature of the precursor solution to a predetermined temperature, for a predetermined period of time.

17. The method according to claim 16, further comprising:
washing the precursors with flake-shaped primary particles;
filtering to separate out the precursors with flake-shaped primary particles; and
drying the precursors with flake-shaped primary particles at a predetermined temperature for a predetermined time period.

18. A method for preparing porous structured secondary particles of a cathode material for secondary batteries, comprising:
mixing precursors with a lithium source; and
sintering the mixture at predetermined conditions.

19. The method according to claim 18, wherein the precursors have flake-shaped primary particles and are prepared by:
incrementally adding a precipitant, a complexing agent, and at least one metal compound to a base solution with stirring to react while adjusting condition(s) of the reaction to a first condition(s), such that the mixture solution nucleates to generate nuclei;
maintaining the nucleating process for a time period; and
adjusting condition(s) of the reaction to a second condition(s) while the precipitant, the complexing agent, and the at least one metal compound are incrementally added to the

base solution, such that the nuclei grow to form the precursors having flake-shaped primary particles.

20. The method according to claim 8, wherein the base solution comprises water or a buffer solution.

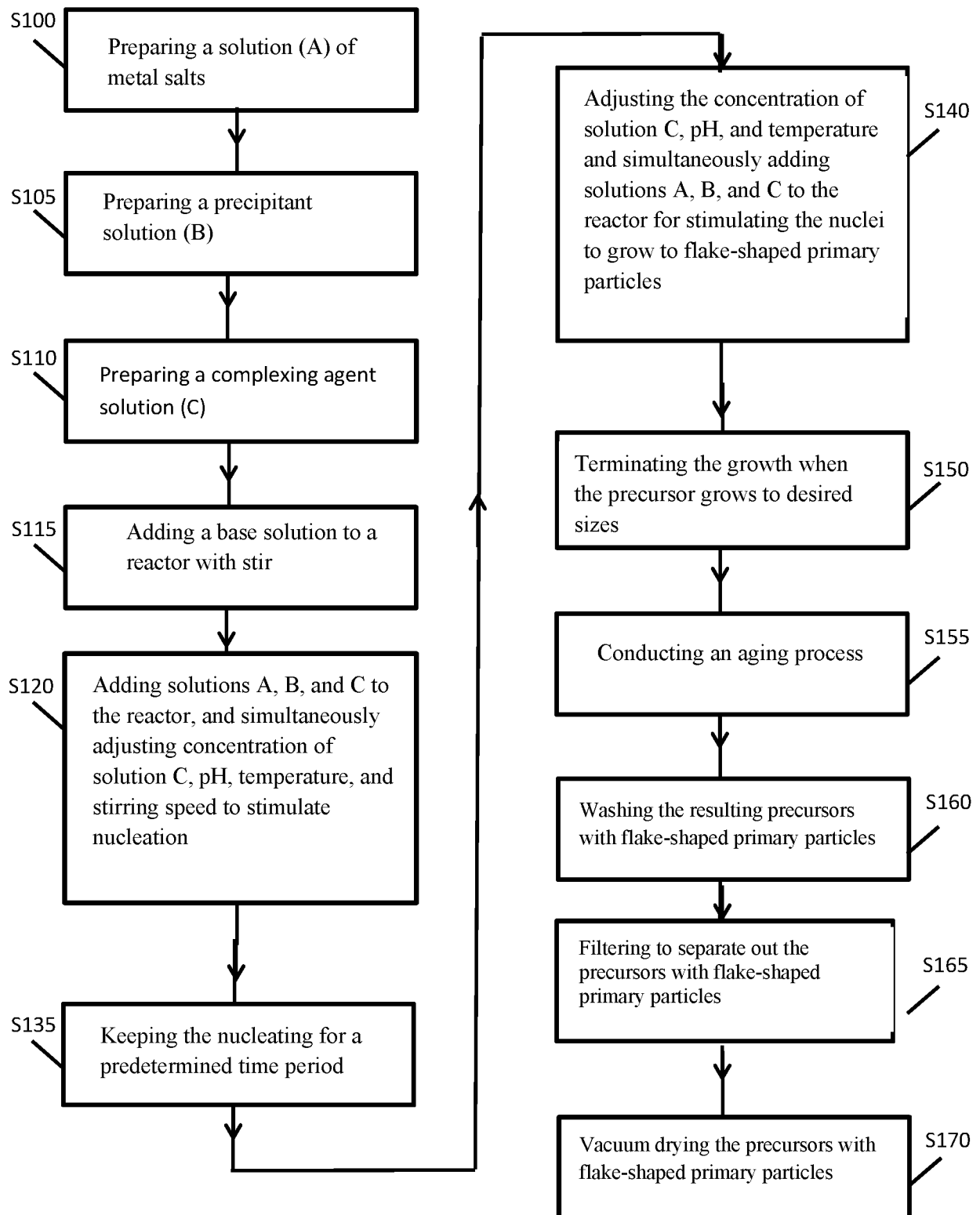


Fig. 1

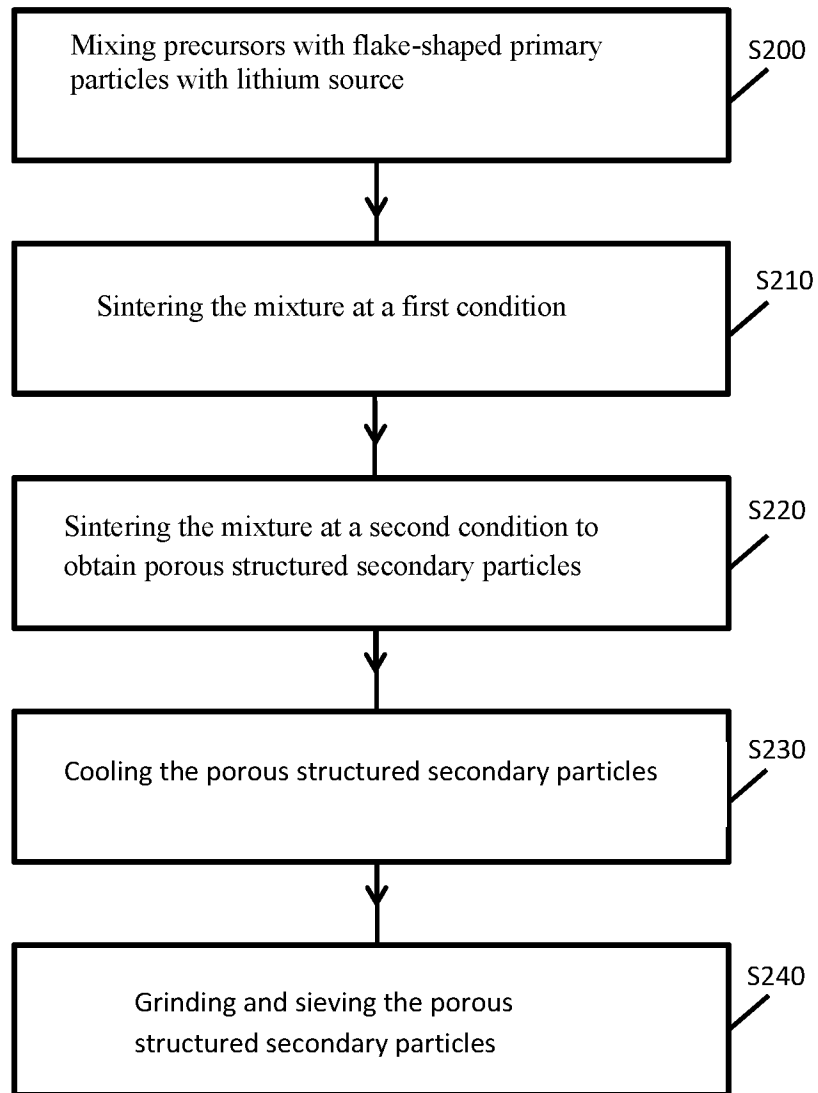


Fig. 2

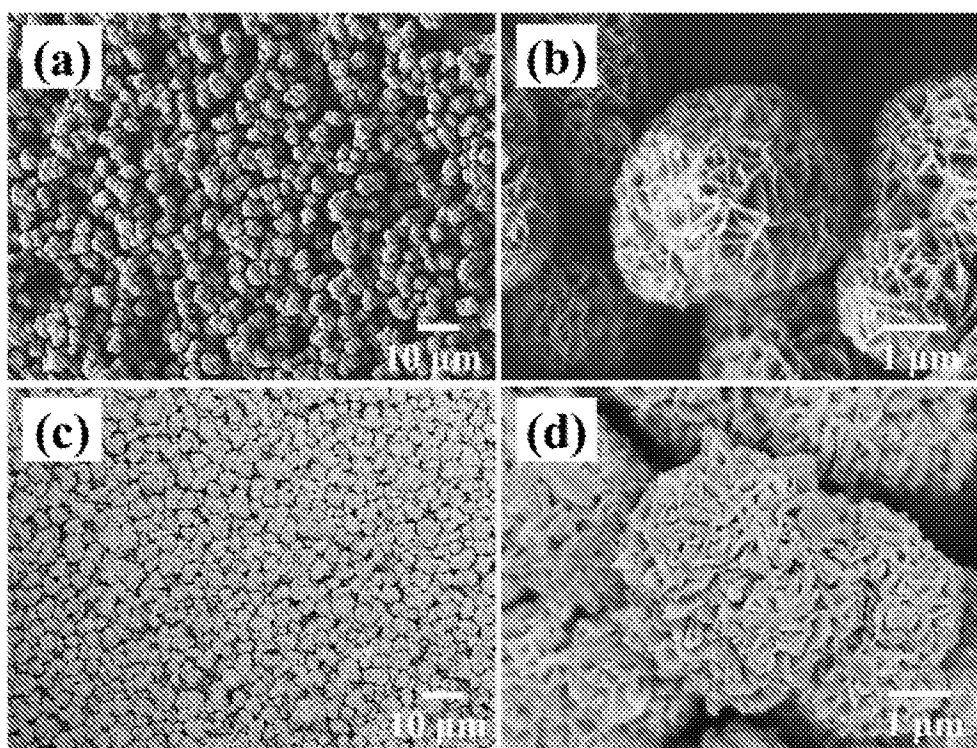


Fig. 3

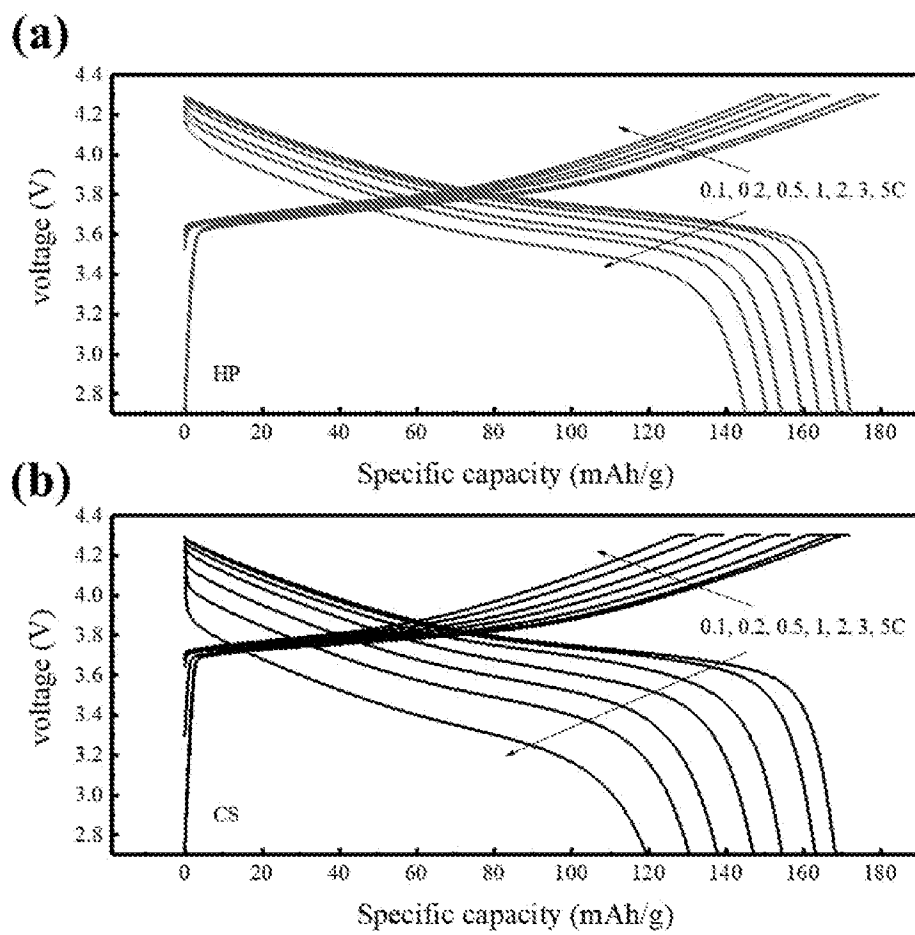


Fig. 4

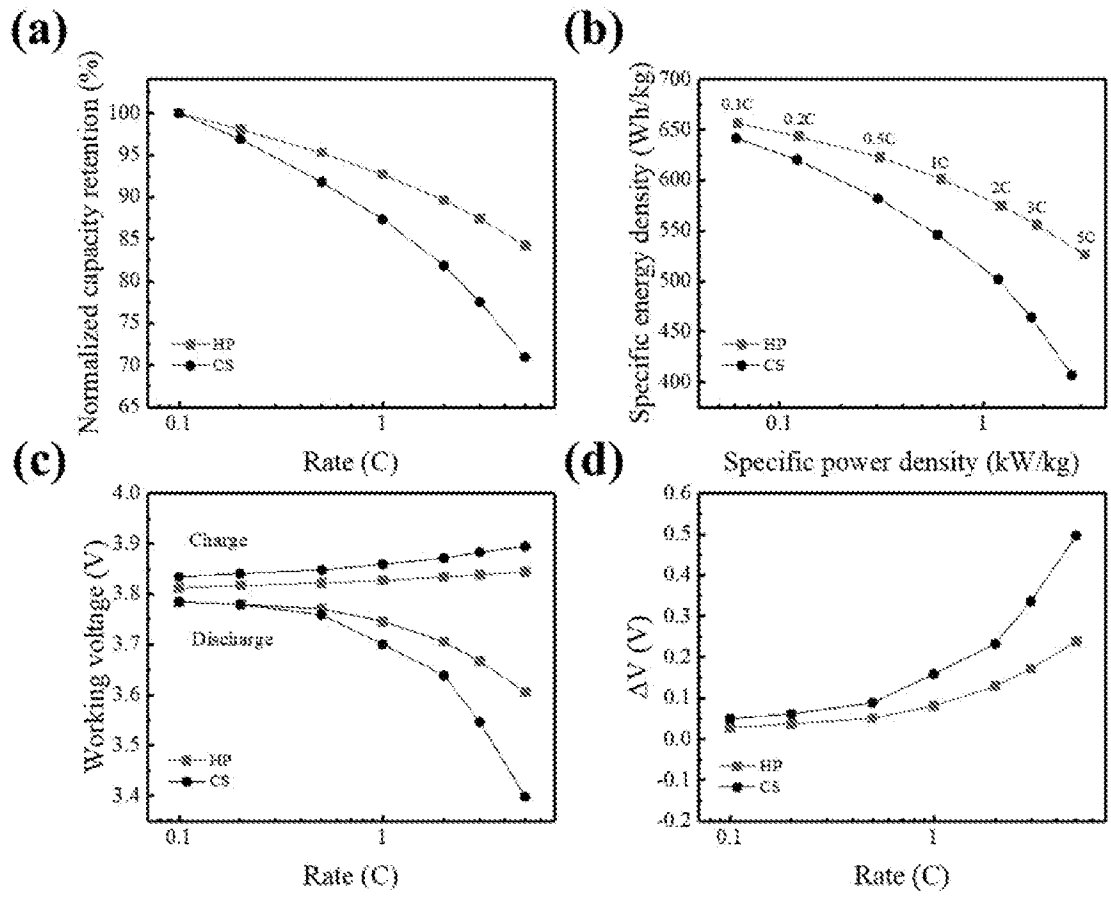


Fig. 5

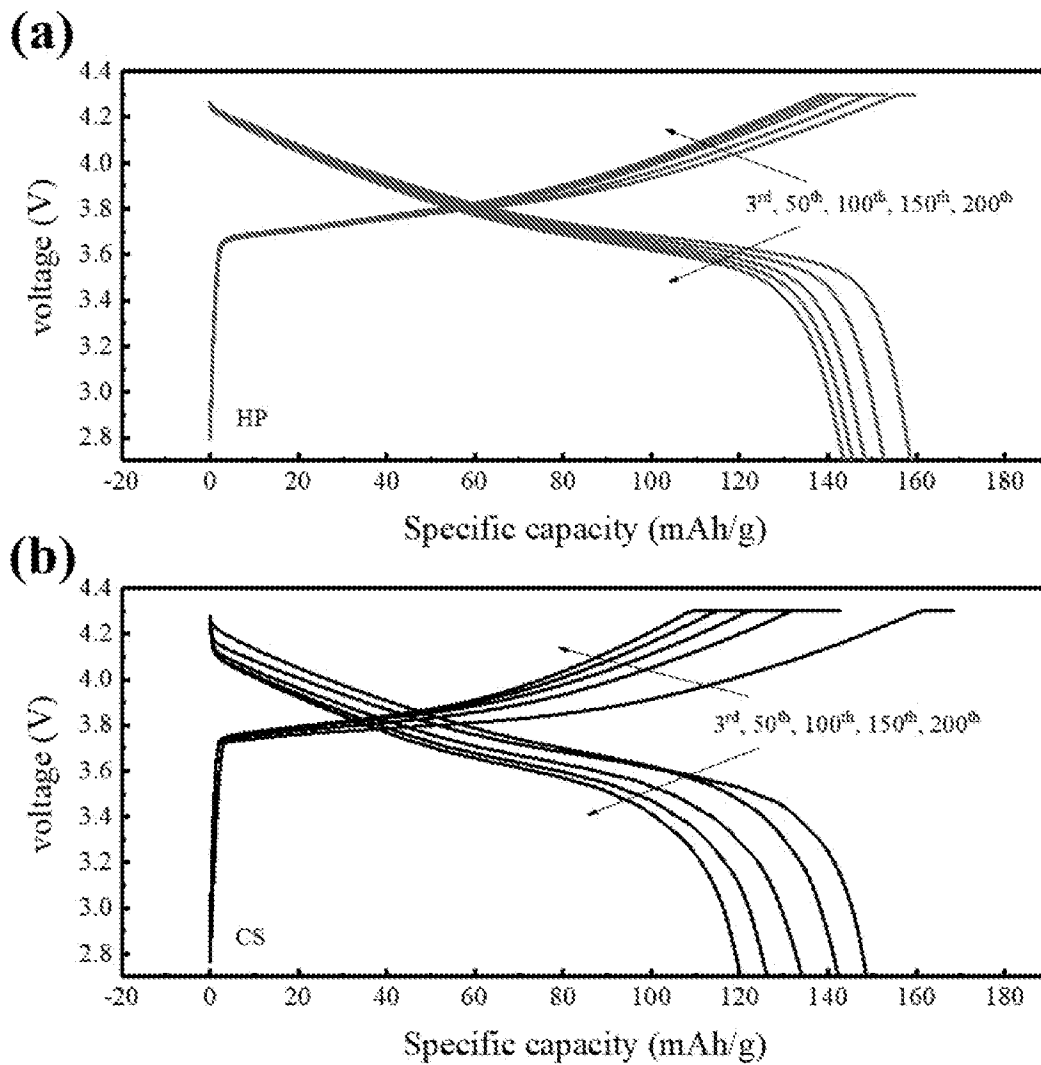


Fig. 6

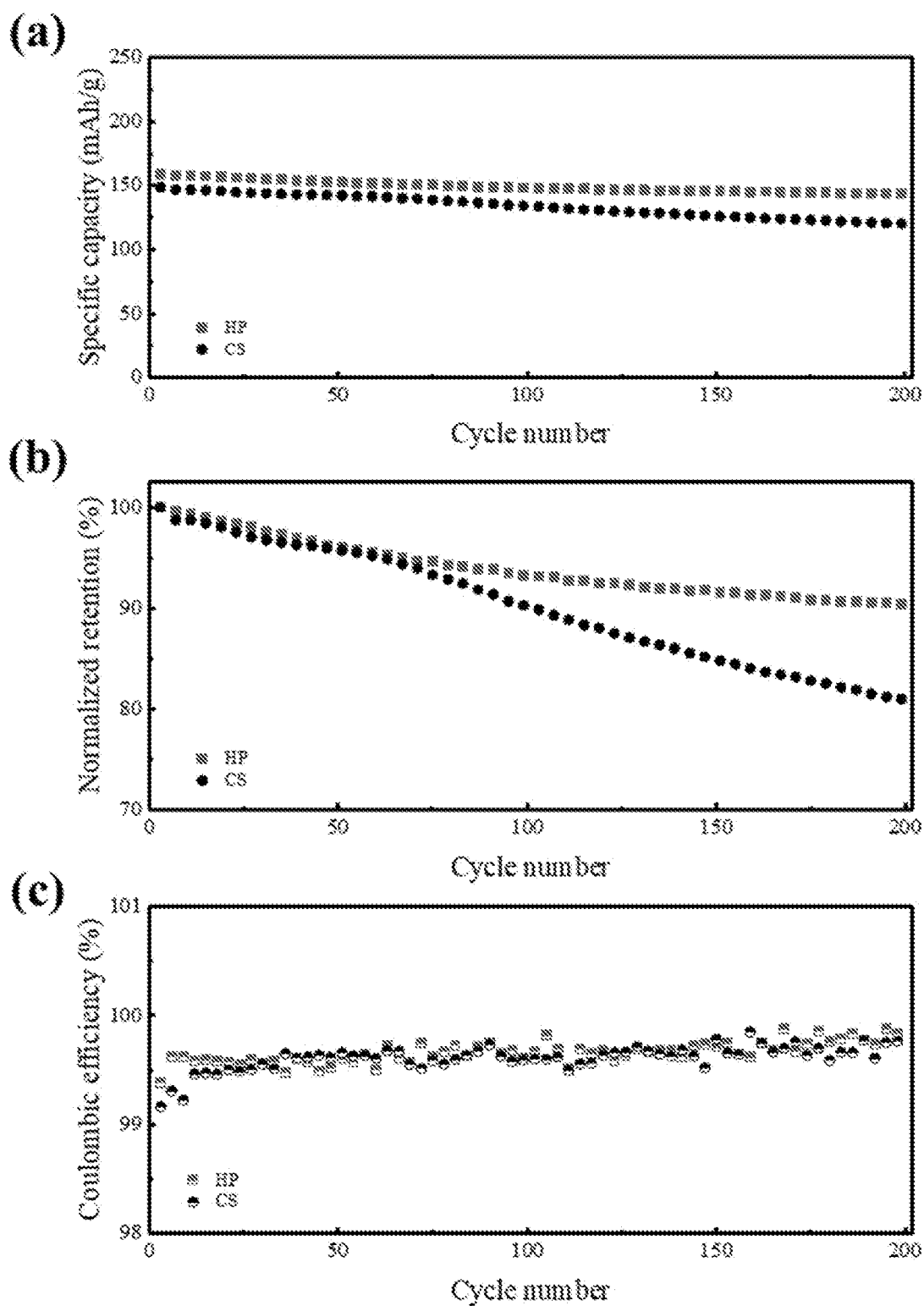


Fig. 7

INTERNATIONAL SEARCH REPORT

International application No.

PCT/IB2019/000310

A. CLASSIFICATION OF SUBJECT MATTER

H01M 4/36(2006.01)i; H01M 4/505(2010.01)i

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

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)

WPI,EPODOC,CNPAT,CNKI:primary, second, particle, flake, sheet, cathode, positive, Mn, Co, Ni, manganese, cobalt, nickel, lithium, Li, precipitant, complex, chelate, nuclei, seed

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CN 108899497 A (NINGDE AMPEREX TECHNOLOGY CO., LTD.) 27 November 2018 (2018-11-27) description, paragraphs 0049-0066, and figures 1-2,5	1-7, 18
Y	CN 108899497 A (NINGDE AMPEREX TECHNOLOGY CO., LTD.) 27 November 2018 (2018-11-27) description, paragraphs 0049-0066, and figures 1-2,5	19
X	CN 106784786 A (SUNWODA ELECTRONICS CO., LTD.) 31 May 2017 (2017-05-31) description, paragraphs 0030-0057	8-17, 20
Y	CN 106784786 A (SUNWODA ELECTRONICS CO., LTD.) 31 May 2017 (2017-05-31) description, paragraphs 0030-0057	19
X	CN 107644982 A (SAMSUNG SDI CO., LTD.) 30 January 2018 (2018-01-30) description, paragraphs 0047-0117,0145-0150,0159-0161, figures 1C,1D	1-7, 18
Y	CN 107644982 A (SAMSUNG SDI CO., LTD.) 30 January 2018 (2018-01-30) description, paragraphs 0047-0117,0145-0150,0159-0161, figures 1C,1D	19



Further documents are listed in the continuation of Box C.



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“Y” document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

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Date of the actual completion of the international search

07 December 2019

Date of mailing of the international search report

20 December 2019

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Telephone No. 86-(10)-53961281

INTERNATIONAL SEARCH REPORT

International application No.

PCT/IB2019/000310**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CN 107644981 A (SAMSUNG SDI CO., LTD.) 30 January 2018 (2018-01-30) description, paragraphs 0062-0151,0180-0184,0194, figures 1C,1D	1-7, 18
Y	CN 107644981 A (SAMSUNG SDI CO., LTD.) 30 January 2018 (2018-01-30) description, paragraphs 0062-0151,0180-0184,0194, figures 1C,1D	19
A	CN 108502937 A (HARBIN INST. TECHNOLOGY) 07 September 2018 (2018-09-07) the whole document	1-20

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/IB2019/000310

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				EP	272711	A1	24 January 2018
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				JP	2018014326	A	25 January 2018
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				US	2018026268	A1	25 January 2018
CN	108502937	A	07 September 2018	None			