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[0004] Despite this background, there have been no adequate public disclosures of methods of sintering lithium-stuffed garnet in a thin film, or bilayer, format and using high-throughput continuous sintering methods such as roll-to-roll methods. Accordingly, there exists a need in the relevant field to which the instant disclosure pertains relating to high-throughput continuous sintering methods for making thin film lithium-stuffed garnet.

SUMMARY

[0004a] In one aspect, there is provided a continuous manufacturing line (CML) comprising: a front roller onto which is wound a bilayer, wherein the bilayer comprises a metal layer and a green body layer; wherein the metal layer contacts the front roller; an end roller; at least one furnace between the front roller and the end roller comprising a sintering section; the sintering section comprising: (a) a ramp that has a radius of curvature of at least 50 cm; and (b) three or more aligned rollers with an inner diameter between 2 cm to 100 cm that maintain contact between the metal layer and the ramp; and at least one atmospheric controller which controls at least one condition in the furnace selected from the group consisting of gas flow rate, flow direction, gas composition, pressure, and a combination thereof; wherein the gas composition comprises an atmosphere of Ar, N_2, H_2O, H_2, or a combination thereof.

[0005] In an example, set forth herein is a continuous manufacturing line (CML) including a front roller; an end roller; at least one sealed furnace, between the front roller and the end roller, wherein the at least one furnace comprises (a) a binder burn-out section; (b) a bisque section; and (c) a sintering section; and further wherein the CML includes at least one atmospheric controller which controls at least one condition in the furnace selected from the group consisting of gas flow rate, flow direction, gas composition, pressure, and a combination thereof.

[0006] In another example, set forth herein is a continuous manufacturing line (CML) including a front roller; an end roller; and at least one sealed furnace, between the front roller and the end roller, wherein the at least one sealed furnace comprises (a) a binder burn-out section; (b) a bisque section; and (c) a sintering section; and further wherein the CML includes at least one atmospheric controller which controls at least one condition in the furnace selected from the group consisting of gas flow rate, flow direction, gas composition, pressure, and a combination thereof.

[0007] In yet another example, set forth herein is a continuous manufacturing line (CML) including a front roller onto which is wound a bilayer, wherein the bilayer comprises a metal layer and a green body layer; an end roller; at least one furnace between the front roller and the end roller; and at least one atmospheric controller which controls at least one condition in the furnace selected from the group consisting of gas flow rate, flow direction, gas composition, pressure, and a combination thereof.

[0007a] In another aspect, there is provided a process for sintering, the process comprising: heating a bilayer comprising a green body layer disposed on a metal layer in a furnace at about 1100°C to about 1300°C for about 5 seconds to about 3 minutes; thereby providing a sintered bilayer comprising a lithium-stuffed garnet layer on the metal layer; wherein the bilayer has a thickness, after sintering, of between about 10 μm and about 50 μm.

[0008] In still another example, set forth herein is a process of using a continuous manufacturing line, comprising the following operations: (a) providing, or having provided, a CML as disclosed herein; (b) sintering a green body while moving the green body through the at least one furnace to produce a sintered body, and (c) winding the sintered body onto an end roller.

[0008a] In another aspect, there is provided a sintered bilayer prepared by the process as described herein.

[0009] In some other examples, set forth herein is a sintered article prepared by a process set forth herein.

[0010] In still some other examples, set forth herein is a rechargeable battery prepared by a process set forth herein.

BRIEF DESCRIPTIONS OF THE DRAWINGS

[0011] **FIG. 1** shows an example of a continuous manufacturing line.

[0012] **FIG. 2** shows another example of a continuous manufacturing line.

[0013] **FIG. 3** shows an example of part of a continuous manufacturing line.

[0014] **FIG. 4** shows cross-sectional scanning electron microscopy (SEM) of a sintered film of lithium-stuffed garnet on a metal foil. The scale bar is 40 μm.

[0015] **FIG. 5** shows a top-down SEM image of a sintered film of lithium-stuffed garnet. The scale bar is 10 μm.

[0016] **FIG. 6** shows a ramp and furnace/oven component of a continuous manufacturing line.

[0017] **FIG. 7A** shows a ramp component of a continuous manufacturing line. **FIG. 7B** shows a ramp component of a continuous manufacturing line.

CLAIMS

What is claimed is:

1. A continuous manufacturing line (CML) comprising:

a front roller onto which is wound a bilayer, wherein the bilayer comprises a metal layer and a green body layer;

wherein the metal layer contacts the front roller;

an end roller;

at least one furnace between the front roller and the end roller comprising a sintering section;

the sintering section comprising:

(a) a ramp that has a radius of curvature of at least 50 cm; and

(b) three or more aligned rollers with an inner diameter between 2 cm to 100 cm that maintain contact between the metal layer and the ramp; and

at least one atmospheric controller which controls at least one condition in the furnace selected from the group consisting of gas flow rate, flow direction, gas composition, pressure, and a combination thereof; wherein the gas composition comprises an atmosphere of Ar, N_2, H_2O, H_2, or a combination thereof.

2. The CML of claim 1, wherein the at least one furnace further comprises (a) a binder burn-out section; and (b) a bisque section.

3. The CML of any one of claims 1-2, wherein the at least one furnace is sealed such that the at least one atmospheric controller controls the flow of gas into and out of the at least one furnace.

4. The CML of any one of claims 2-3, comprising a pressurized gas line between the bisque section and the sintering section which pumps gas into the bisque section and into the sintering section.

5. The CML of any one of claims 1-4, wherein the atmospheric controller maintains a reducing atmosphere in the sintering section.

6. The CML of any one of claims 1-5, wherein the CML is configured for more than one tape speed.

7. The CML of any one of claims 2-6, wherein the atmospheric controller maintains an atmosphere comprising less than 500 ppm O_2 in the bisque section, the sintering section, or both the bisque section and the sintering section.

8. The CML of any one of claims 1-7, wherein the H_2 gas is present at about 1, 2, 3, 4, or 5% v/v.

9. The CML of any one of claims 1-8, wherein the bilayer is suspended as it moves through the CML.

10. The CML of any one of claims 1-9, wherein the bilayer comprises lithium-stuffed garnet.

11. The CML of any one of claims 1-10, wherein the CML is configured to move the bilayer through the at least one furnace at a rate of at least 2 inches per minute.

12. The CML of any one of claims 1-11, further comprising a curved ramp before the sintering section.

13. A process for sintering, the process comprising:

heating a bilayer comprising a green body layer disposed on a metal layer in a furnace at about 1100°C to about 1300°C for about 5 seconds to about 3 minutes;

thereby providing a sintered bilayer comprising a lithium-stuffed garnet layer on the metal layer;

wherein the bilayer has a thickness, after sintering, of between about 10 μm and about 50 μm.

14. The process of claim 13, wherein the bilayer moves through the furnace at a rate of between about 2 inches/min to 25 inches/min.

15. The process of any one of claims 13-14, further comprising a binder burn-out step prior to heating a bilayer at about 1100°C to about 1300°C for about 5 seconds to about 3 minutes.

16. The process of claim 15, wherein the binder burn-out step occurs in a binder burn-out furnace.

17. The process of any one of claims 13-16, wherein the lithium-stuffed garnet layer comprises compounds having the formula $Li_ALa_BZr_CO_F$, $Li_ALa_BM'_CM''_DTa_EO_F$, or $Li_ALa_BM'_CM''_DNb_EO_F$, wherein $4<A<8.5$, $1.5<B<4$, $0<C\leq 2$, $0<D<2$; $0<E<2.5$, $10<F<13$, and M' and M'' are each, independently in each instance selected from Al, Mo, W, Nb, Ga, Sb, Ca, Ba, Sr, Ce, Hf, Rb, and Ta; or $Li_aLa_bZr_cAl_dMe''_eO_f$, wherein $5<a<7.7$; $2<b<4$; $0<c\leq 2.5$; $0<d<2$; $0<e<2$, $10<f<13$ and Me'' is a metal selected from Nb, V, W, Mo, Ta, Ga, and Sb.

18. The process of any one of claims 15-16, wherein the bilayer, prior to the binder burn-out step, comprises at least one member selected from a solvent, a binder, a dispersant, a plasticizer, a surfactant, or a combination thereof.

19. The process of any one of claims 13-18, wherein the metal layer comprises a metal selected from the group consisting of nickel, copper, iron, alloys thereof, and combinations thereof.

20. The process of any one of claims 13-19, wherein the furnace comprises an atmospheric controller that maintains an atmosphere in the furnace that comprises argon (Ar) gas; nitrogen (N_2) gas; hydrogen gas; or a mixture thereof.

21. The process of claim 20, wherein the atmospheric controller maintains an atmosphere in the furnace comprising less than 500 ppm O_2.

22. A sintered bilayer prepared by the process of any one of claims 13-21.