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(54) CARBOPHOSPHATES AND RELATED COMPOUNDS

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(57)

ABSTRACT

The present invention generally relates to carbophosphates and other compounds. Such compounds may be used in batteries and other electrochemical devices, or in other applications such as those described herein. One aspect of the invention is generally directed to carbophosphate compounds, i.e., compounds containing carbonate and phosphate ions. For example, according to one set of embodiments, the compound has a formula $A_x(M)(PO_4)_a(CO_3)_b$, where M comprises one or more cations. A may include one or more alkali metals, for example, lithium and/or sodium. In some cases, x is greater than about 0.1, a is between about 0.1 and about 5.1, and b is between about 0.1 and about 5.1. In certain embodiments, the compound may have a unit cell atomic arrangement that is isostructural to unit cells of the minerals sidorenkite, bonshtedtite, bradleyite, crawfordite, or ferrotychite. In some embodiments, the compound may have a formula $A_x(M)(YO_4)_a(XO_3)_b$, where A comprises one or more alkali metals, M comprises one or more cations, X includes B, C, and/or N, and Y includes Si, P, As, S, V, Nb, Mo, and/or W. In some cases, x is greater than about 0.1, a is between about 0.1 and about 5.1, and b is between about 0.1 and about 5.1. Other aspects of the invention are generally directed to techniques for making or using such compounds, kits involving such compounds, and the like.

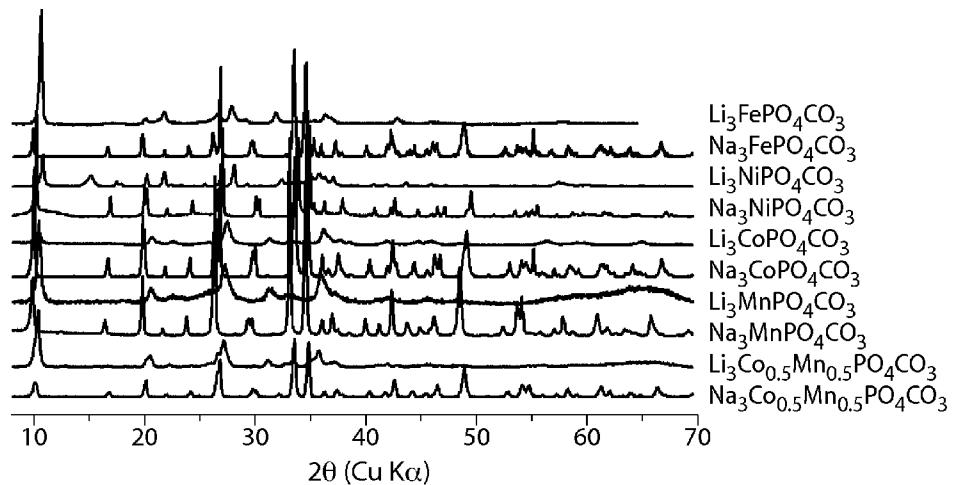


Fig. 1

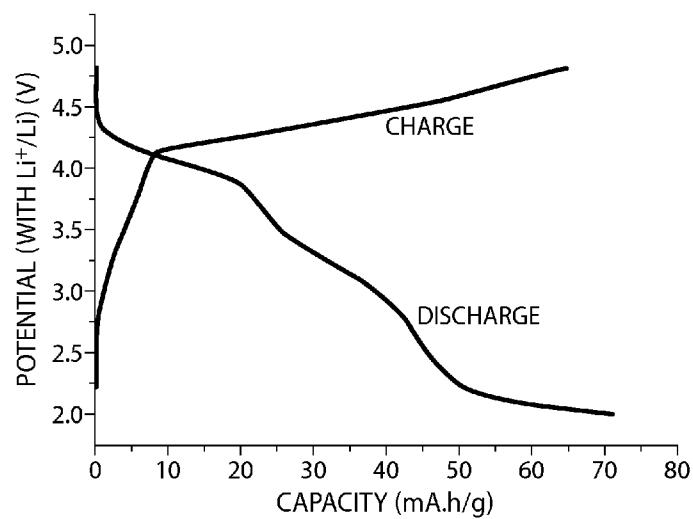


Fig. 2

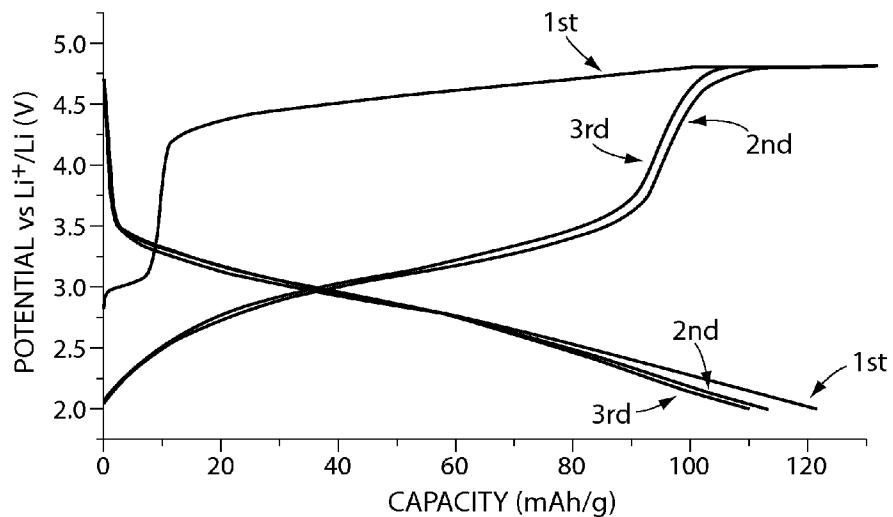


Fig. 3A

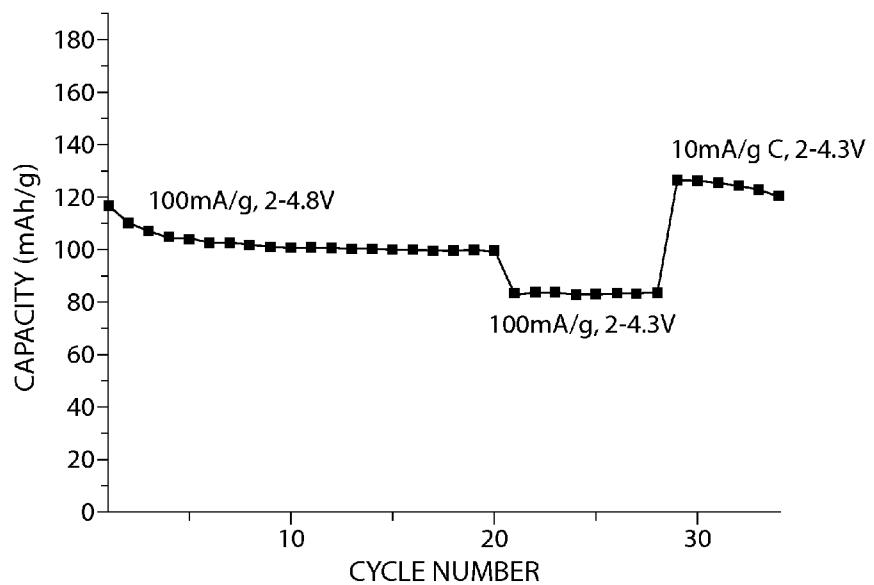


Fig. 3B

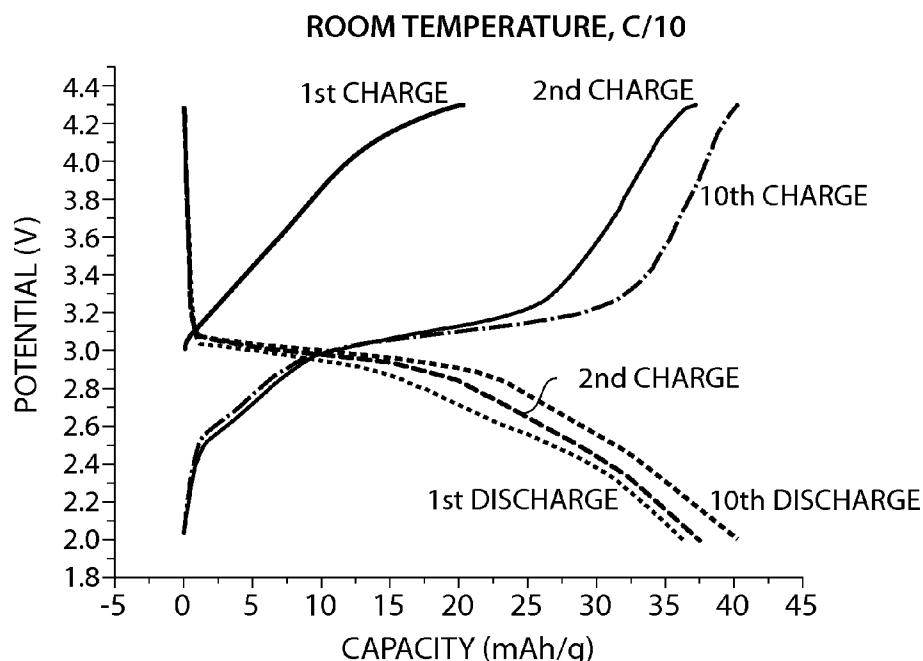


Fig. 3C

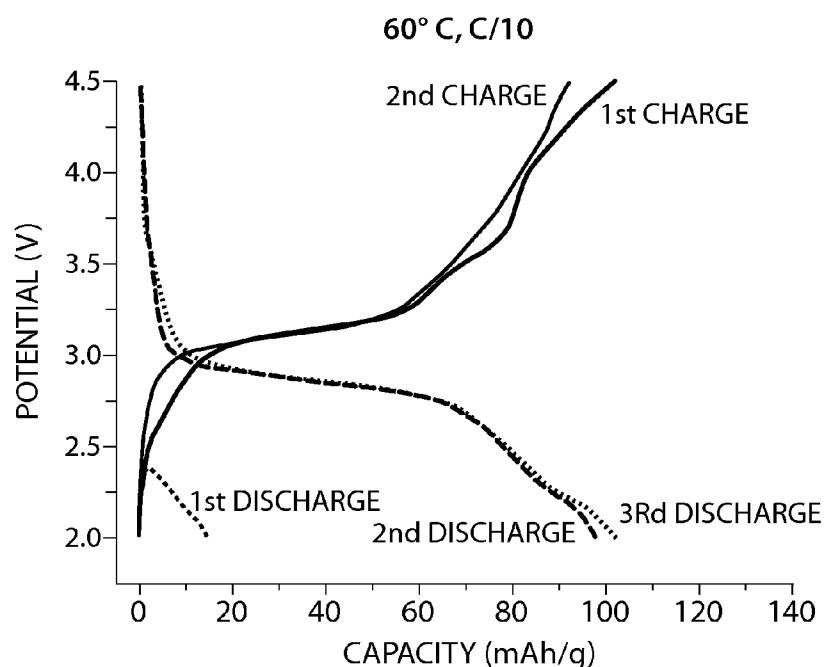


Fig. 3D

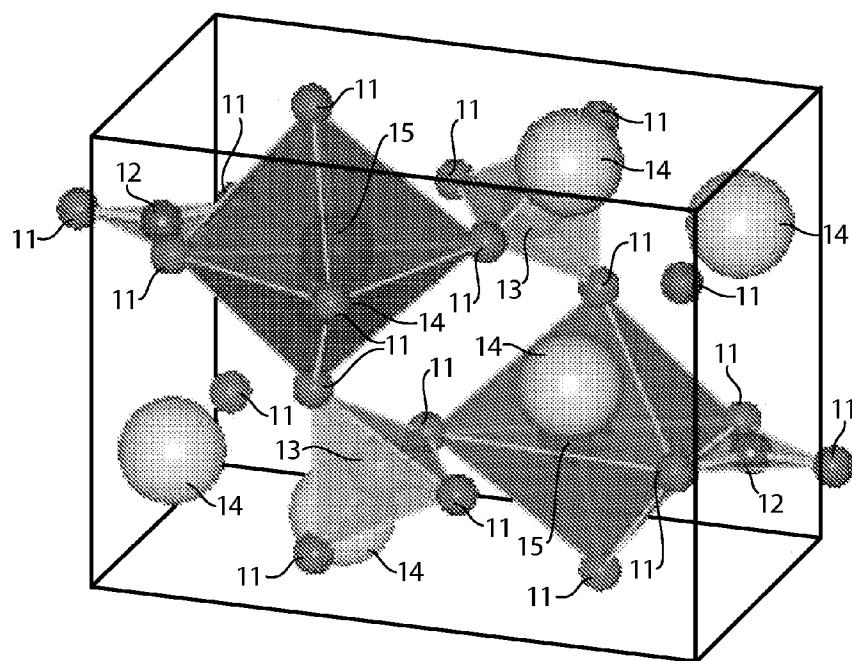


Fig. 4

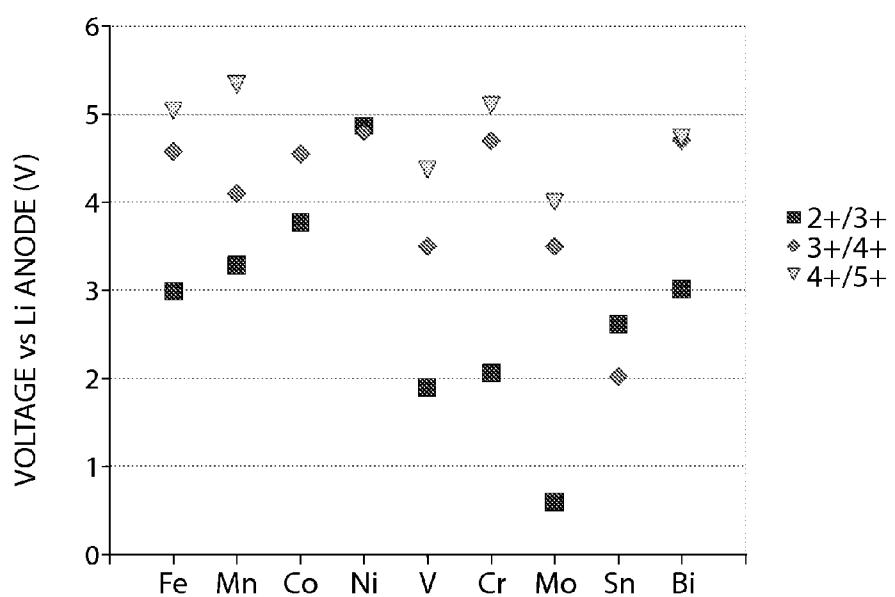


Fig. 5

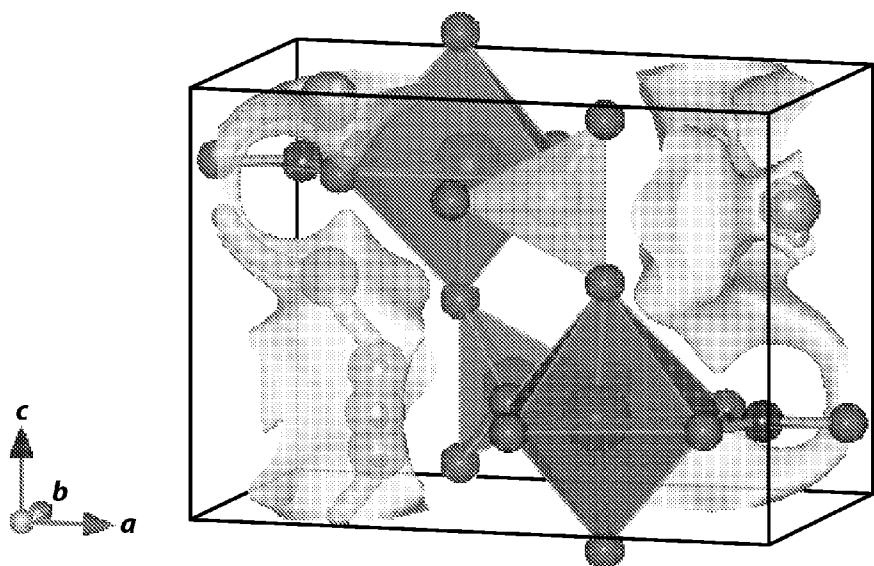


Fig. 6A

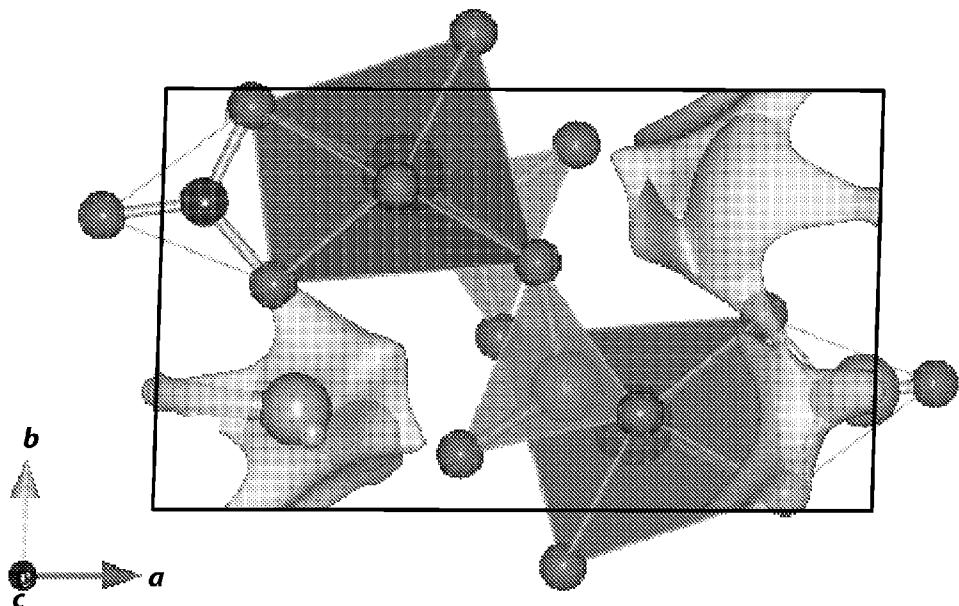


Fig. 6B

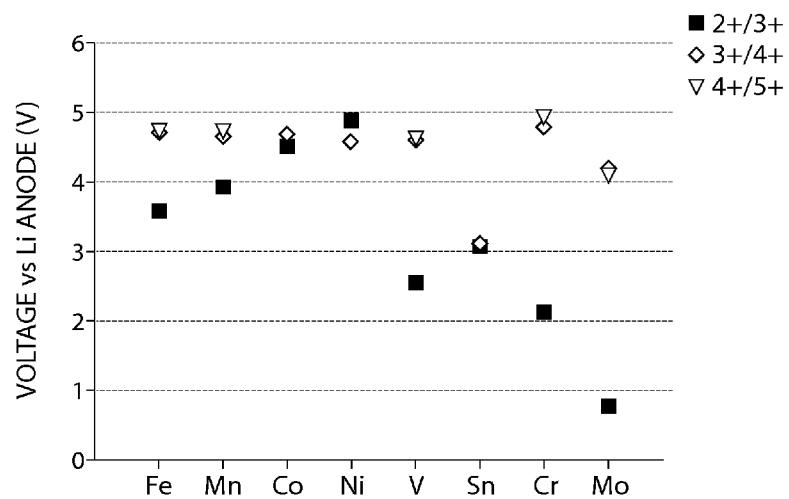


Fig. 7

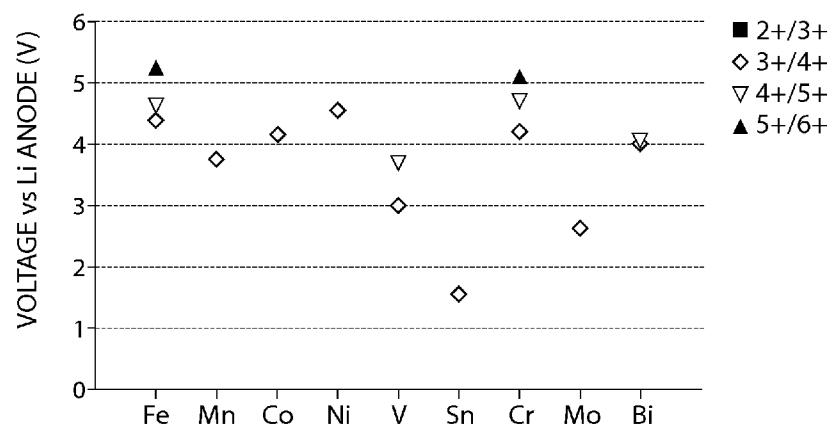


Fig. 8

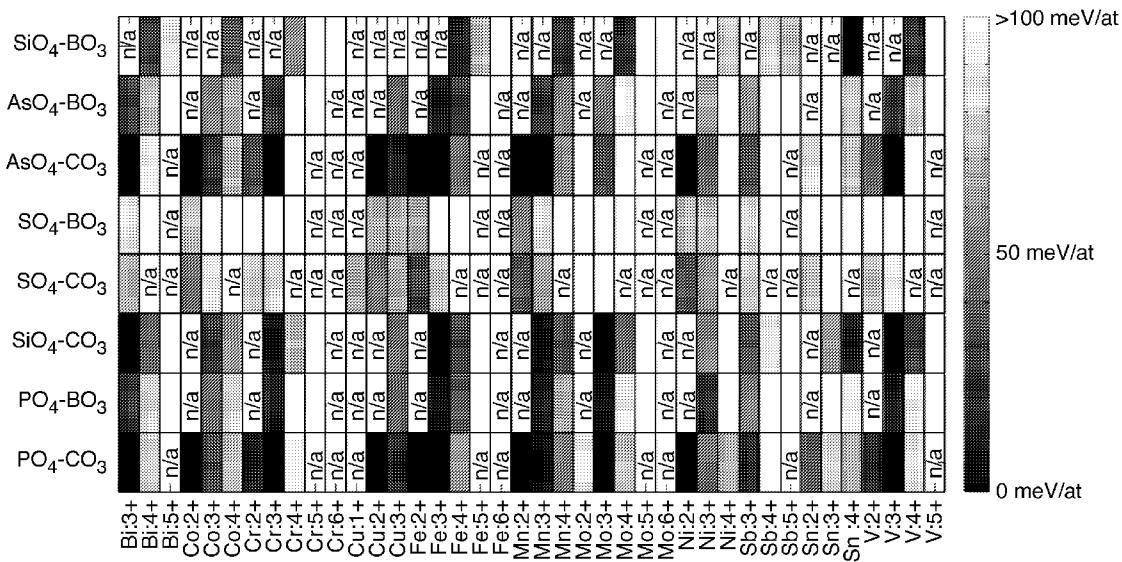


Fig. 9

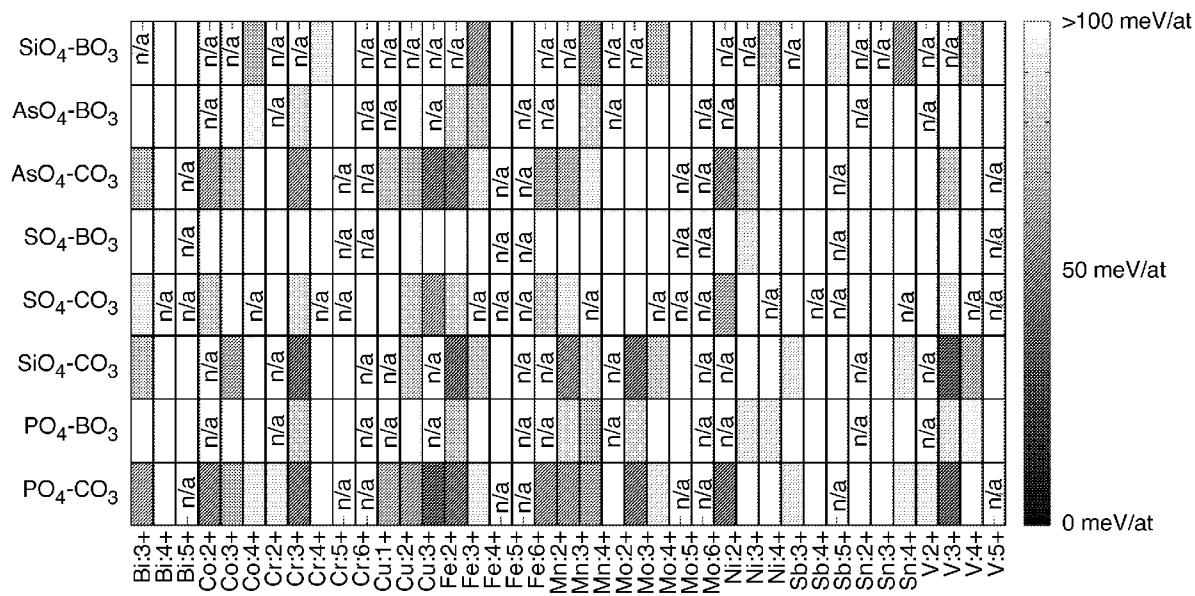


Fig. 10

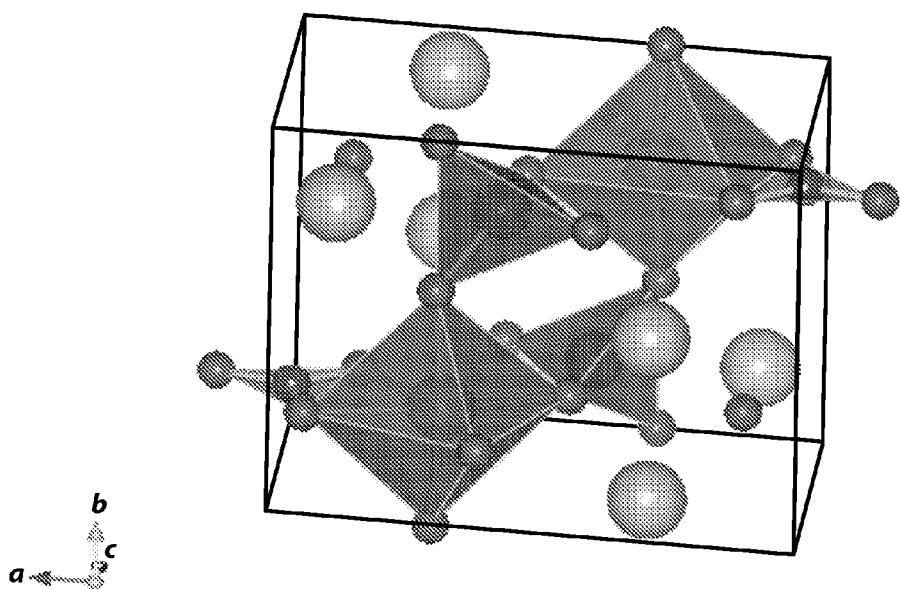


Fig. 11

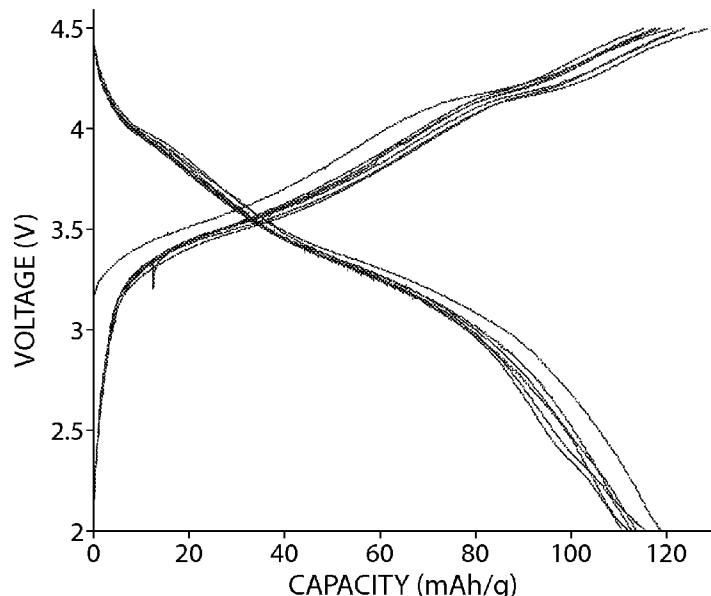


Fig. 12A

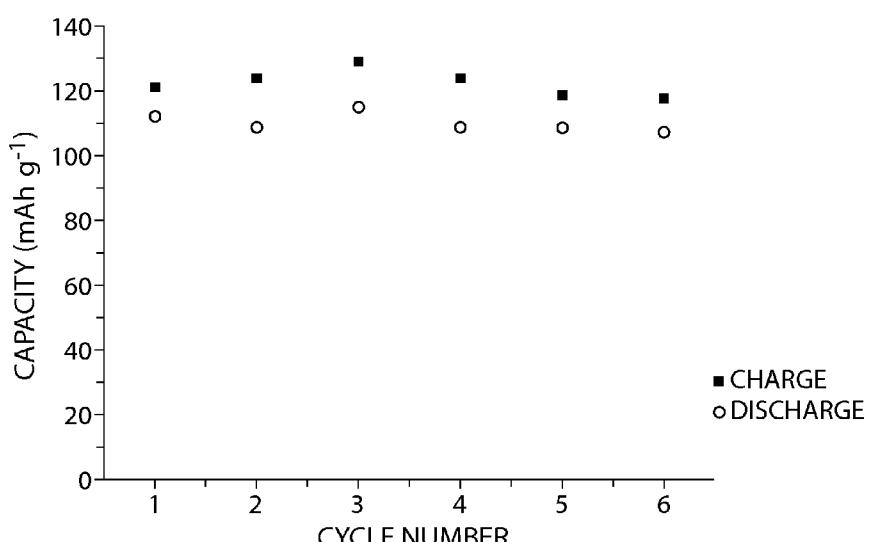


Fig. 12B

CARBOPHOSPHATES AND RELATED COMPOUNDS

RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Provisional Patent Application Ser. No. 61/306,670, filed Feb. 22, 2010, entitled "Carbophosphate and Related Compounds," by Ceder, et al., incorporated herein by reference.

FIELD OF INVENTION

[0002] The present invention generally relates to carbophosphates and other compounds, e.g., for use in batteries and other applications.

BACKGROUND

[0003] Demand for lightweight, high energy density batteries, for example, to power vehicles or portable electronic devices, continues to rise. However, although many compounds have been studied for use in batteries and other applications, it remains difficult to identify compounds having good characteristics of thermal stability and/or high energy densities. Accordingly, improvements in compounds for use in batteries and other applications are still needed.

SUMMARY OF THE INVENTION

[0004] The present invention generally relates to carbophosphates and other compounds, e.g., for use in batteries and other applications. The subject matter of the present invention involves, in some cases, interrelated products, alternative solutions to a particular problem, and/or a plurality of different uses of one or more systems and/or articles.

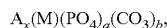
[0005] Compounds with polyanionic groups are generally more stable than oxides. In some cases, they may release less O₂ at elevated temperatures, which could be an important safety feature for certain applications such as lithium ion batteries. In addition, to lower the weight, lower-weight polyanionic groups such as carbonate and borate groups may be useful, e.g., for higher energy and power densities. Thus, some aspects of the invention are directed to carbonate groups and/or multi-polyanionic groups, for example, carbonate phosphates or silicate-carbonates.

[0006] In one aspect, the present invention is directed to a compound. In accordance with one set of embodiments, the compound has a formula:



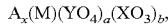
where M comprises one or more non-alkali metal cations, x is greater than about 0.1, a is between about 0.1 and about 5.1, and b is between about 0.1 and about 5.1. In some cases, at least about 25 mol % of M comprises one or more non-alkali/non-alkaline earth metals.

[0007] The compound, in another set of embodiments, has a formula:



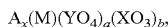
where A comprises one or more alkali metals, M comprises one or more non-alkali metal cations, x is greater than about 0.1, a is between about 0.1 and about 5.1, and b is between about 0.1 and about 5.1. In certain cases, at least about 25 mol % of M comprises one or more non-alkali/non-alkaline earth metals. In some embodiments, the compound is not one where, when A is Na, x is between 2 and 4, and M is Fe, Mg, Mn, or Sr.

[0008] In accordance with one set of embodiments, the compound has a formula:



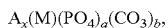
where A comprises one or more alkali metals; M comprises one or more non-alkali metal cations; X comprises one or more of B, C, or N; Y comprises one or more of Si, P, As, or S; x is greater than about 0.1; a is between about 0.1 and about 5.1; and b is between about 0.1 and about 5.1. In some instances, at least about 25 mol % of M comprises one or more non-alkali/non-alkaline earth metals. In some embodiments, the composition does not include any of the following combinations for A, M, Y, and X, respectively: Na, Al and Co, Si, N; Na, Fe, Si, B; Na, Al and Co, Si, C; Na, Mn, P, C; Na, Fe, P, C; Na, Co, P, B; Na, Mg and Fe, S, C; Na, Fe, S, C; Li, Cu, P, B; and Li, Zn, P, B.

[0009] The compound, in another set of embodiments, has a formula:



where A comprises one or more alkali metals; M comprises one or more non-alkali metal cations; X comprises one or more of B, C, or N; Y comprises one or more of V, Nb, Mo, and W; x is greater than about 0.1; a is between about 0.1 and about 5.1; and b is between about 0.1 and about 5.1. In one embodiment, at least about 25 mol % of M comprises one or more non-alkali/non-alkaline earth metals. In some cases, M does not comprise V, Nb, Mo, or W. In some instances, the composition does not include any of the following combinations for A, M, Y, and X, respectively: Na, Al and Co, Si, N; Na, Fe, Si, B; Na, Al and Co, Si, C; Na, Mn, P, C; Na, Fe, P, C; Na, Co, P, B; Na, Mg and Fe, S, C; Na, Fe, S, C; Li, Cu, P, B; and Li, Zn, P, B.

[0010] In yet another set of embodiments, the compound has a formula:



where A comprises one or more alkali metals; M comprises one or more non-alkali metal cations; x is greater than about 0.1; a is between about 0.1 and about 5.1; and b is between about 0.1 and about 5.1. In some cases, the compound is not Na₃Fe(PO₄)_a(CO₃)_b, Na₃Mg(PO₄)_a(CO₃)_b, Na₃Mn(PO₄)_a(CO₃)_b, or Na₃Sr(PO₄)_a(CO₃)_b. In some embodiments, at least about 25 mol % of M comprises one or more non-alkali/non-alkaline earth metals.

[0011] The compound, in another set of embodiments, has a formula:



where A comprises one or more alkali metals; M comprises one or more non-alkali metal cations; X is selected from the group consisting of B, C, or N; Y is selected from the group consisting of Si, P, As, S, V, Nb, Mo, or W; x is greater than about 0.1; a is between about 0.1 and about 5.1; and b is between about 0.1 and about 5.1. In some embodiments, at least about 10 mol % of M comprises one or more non-alkali/non-alkaline earth metals. In some cases, the compound is thermodynamically unstable at 25° C. and 1 atm. In some embodiments, at least about 25 mol % of M comprises one or more non-alkali/non-alkaline earth metals.

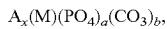
[0012] The compound, in yet another set of embodiments, has a formula:



where A comprises one or more alkali metals; M comprises one or more non-alkali metal cations; X is selected from the group consisting of B, C, or N; Y is selected from the group consisting of Si, P, As, S, V, Nb, Mo, or W; x is greater than about 0.1; a is between about 0.1 and about 5.1; and b is between about 0.1 and about 5.1. In some cases, the compound is not $\text{Na}_3\text{FePO}_4\text{CO}_3$, $\text{Na}_3\text{MnPO}_4\text{CO}_3$, $\text{Na}_6\text{Fe}_2\text{SO}_4(\text{CO}_3)_4$, $\text{NaH}_4\text{Co}(\text{PO}_4)_2\text{BO}_3$, $\text{Al}_{12}\text{CO}_4(\text{NO}_3)_2\text{Na}_4(\text{SiO}_4)_{12}$, or $\text{Fe}_9\text{H}_2\text{Na}(\text{SiO}_4)_6(\text{BO}_3)_3$. In some embodiments, at least about 25 mol % of M comprises one or more non-alkali/non-alkaline earth metals.

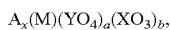
[0013] In yet another set of embodiments, the compound is a lithium-containing compound having a unit cell atomic arrangement that is isostructural to a sidorenkite unit cell, a bonshtedtite unit cell, a bradleyite unit cell, a crawfordite unit cell, or a ferrotychite unit cell. In still another set of embodiments, the compound is a lithium-containing compound comprising at least about 25 mol % lithium, the compound having a unit cell containing CO_3 triangular planar groups, PO_4 tetrahedral groups, and MO_6 octahedral groups, where M is a positive cation. The compound, in accordance with yet another set of embodiments, has an XRD diffraction pattern having maxima at 2 thetas of 10.7 ± 1 , 20.4 ± 1 , 21.4 ± 1 , 27.1 ± 1 , 28.8 ± 1 , 34.0 ± 1 , and 35.8 ± 1 degrees, where the XRD is acquired using an X-ray diffractometer having a copper K alpha source with a wavelength of 1.5418 angstrom.

[0014] In another aspect, the present invention is generally directed to a compound having a triclinic (P1) crystal structure. In accordance with one set of embodiments, the compound has a formula:



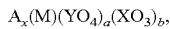
where A comprises one or more alkali metals, M comprises one or more non-alkali metal cations, x is greater than about 0.1, a is between about 0.1 and about 5.1, and b is between about 0.1 and about 5.1. In some cases, at least about 25 mol % of M comprises one or more non-alkali/non-alkaline earth metals.

[0015] The compound, in another set of embodiments, has a formula:



where A comprises one or more alkali metals; M comprises one or more non-alkali metal cations; X is selected from the group consisting of B, C, or N; Y is selected from the group consisting of Si, P, As, or S; x is greater than about 0.1; a is between about 0.1 and about 5.1; and b is between about 0.1 and about 5.1. In certain embodiments, at least about 25 mol % of M comprises one or more non-alkali/non-alkaline earth metals.

[0016] In accordance with yet another set of embodiments, the compound has a formula:



where A comprises one or more alkali metals; M comprises one or more non-alkali metal cations; X comprises one or more of B, C, or N; Y comprises one or more of V, Nb, Mo, and W; x is greater than about 0.1; a is between about 0.1 and about 5.1; and b is between about 0.1 and about 5.1. In some cases, at least about 25 mol % of M comprises one or more non-alkali/non-alkaline earth metals. In certain embodiments, M does not comprise V, Nb, Mo, or W.

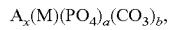
[0017] In still another aspect, the present invention is directed to an electrochemical device. In accordance with one set of embodiments, the electrochemical device comprises n

electrode comprising a lithium-containing compound. In certain embodiments, the compound may have a formula:



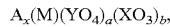
where M comprises one or more non-alkali metal cations, x is greater than about 0.1, a is between about 0.1 and about 5.1, and b is between about 0.1 and about 5.1. In certain instances, at least about 25 mol % of M comprises one or more non-alkali/non-alkaline earth metals. In some cases, the lithium-containing compound has a unit cell containing CO_3 triangular planar groups, PO_4 tetrahedral groups, and/or MO_6 octahedral groups.

[0018] In accordance with another set of embodiments, the electrochemical device comprises an electrode comprising a compound having a formula:



where A comprises one or more alkali metals, M comprises one or more metal cations having more than one oxidation state above the ground state, x is greater than about 0.1, a is between about 0.1 and about 5.1, and b is between about 0.1 and about 5.1. In some instances, at least about 25 mol % of M comprises one or more non-alkali/non-alkaline earth metals.

[0019] The electrochemical device, in another set of embodiments, comprises an electrode comprising a compound having a formula:



where A comprises one or more alkali metals; M comprises one or more non-alkali metal cations; X is selected from the group consisting of B, C, or N; Y is selected from the group consisting of Si, P, As, S, V, Nb, Mo, or W; x is greater than about 0.1; a is between about 0.1 and about 5.1; and b is between about 0.1 and about 5.1. In some cases, at least about 25 mol % of M comprises one or more non-alkali/non-alkaline earth metals.

[0020] In yet another set of embodiments, the electrochemical device comprises an electrode comprising a compound such as those described herein. For example, the compound may be a lithium-containing compound or a sodium-containing compound.

[0021] In some embodiments, the compound has an energy density of at least about 100 mA h/g. In certain embodiments, the compound comprises at least two different polyanionic groups. In some cases, the compound does not substantially decompose upon exposures to temperatures of at least about 250° C. The compound, in some instances, contains no more than about 5 mol % of anionic oxide. In still another set of embodiments, the compound does not exhibit a thermal transition below 300° C. when analyzed using differential scanning calorimetry (DSC). In some cases, the compound releases no more than 1 ml/g of oxygen when heated to a temperature of 250° C.

[0022] Yet another aspect of the present invention is directed to a method. In one set of embodiments, the method includes the acts of providing an aqueous liquid comprising a phosphate anion, a carbonate anion, an alkali metal cation, and a non-alkali metal cation; exposing the liquid to a controlled temperature of at least about 70° C.; and removing water from the liquid to recover a solid product.

[0023] In another set of embodiments, the present invention is directed to a method of making one or more of the embodiments described herein, and as one non-limiting example, compounds having the formula $\text{A}_x(\text{M})(\text{YO}_4)_a(\text{XO}_3)_b$, where

A comprises one or more alkali metals, M comprises one or more non-alkali metal cations, X is selected from the group consisting of B, C, or N, and Y is selected from the group consisting of Si, P, As, S, V, Nb, Mo, or W. In some cases, x is greater than about 0.1, a is between about 0.1 and about 5.1, and b is between about 0.1 and about 5.1.

[0024] Described herein, in accordance with certain aspects, is subject matter specified by the following clauses. These clauses are intended to exemplary and non-limiting.

[0025] 1. A compound, having a formula $\text{Li}_x(\text{M})(\text{PO}_4)_a(\text{CO}_3)_b$, wherein M comprises one or more non-alkali metal cations, wherein at least about 25 mol % of M comprises one or more non-alkali/non-alkaline earth metals, x is greater than about 0.1, a is between about 0.1 and about 5.1, and b is between about 0.1 and about 5.1.

[0026] 2. The compound of clause 1, wherein M comprises one or more bivalent or trivalent cations.

[0027] 3. The compound of any one of clauses 1 or 2, wherein M comprises one or more transition metals.

[0028] 4. The compound of any one of clauses 1-3, wherein M comprises one or more of Fe, Mn, Co, Ni, V, Cr, Cu, Ti, Bi, Sn, Sb, or Mo.

[0029] 5. The compound of any one of clauses 1-4, wherein M consists essentially of Fe and/or Mn.

[0030] 6. The compound of any one of clauses 1-5, wherein M comprises Fe.

[0031] 7. The compound of any one of clauses 1-4 and 6, wherein M comprises Ni.

[0032] 8. The compound of any one of clauses 1-4, 6, or 7, wherein M comprises Co.

[0033] 9. The compound of any one of clauses 1-5, wherein M comprises Mn.

[0034] 10. The compound of any one of clauses 1-4 or 6-8, wherein M comprises V.

[0035] 11. The compound of any one of clauses 1-4, 6-8, or 10, wherein M comprises Mo.

[0036] 12. The compound of any one of clauses 1-4, 6-8, 10, or 11, wherein M comprises an alkaline earth metal.

[0037] 13. The compound of any one of clauses 1-4, 6-8, or 10-12, wherein at least about 50 mol % of M comprises one or more non-alkali/non-alkaline earth metals.

[0038] 14. The compound of any one of clauses 1-13, wherein each cation in M has an oxidation state of between 1+ and 5+, inclusively.

[0039] 15. The compound of any one of clauses 1-14, wherein each cation in M has an oxidation state of between 1+ and 4+, inclusively.

[0040] 16. The compound of any one of clauses 1-15, wherein each cation in M has an oxidation state of between 2+ and 4+, inclusively.

[0041] 17. The compound of any one of clauses 1-16, wherein x is between about 1.5 and about 10.1.

[0042] 18. The compound of any one of clauses 1-17, wherein x is between about 1.9 and about 3.1.

[0043] 19. The compound of any one of clauses 1-18, wherein x is 3.

[0044] 20. The compound of any one of clauses 1-18, wherein x is 2.

[0045] 21. The compound of any one of clauses 1-20, wherein a is between about 0.1 and about 4.

[0046] 22. The compound of any one of clauses 1-21, wherein a is between about 0.9 and about 1.1.

[0047] 23. The compound of any one of clauses 1-22, wherein a is 1.

[0048] 24. The compound of any one of clauses 1-23, wherein b is between about 0.1 and about 4.

[0049] 25. The compound of any one of clauses 1-24, wherein b is between about 0.9 and about 1.1.

[0050] 26. The compound of any one of clauses 1-25, wherein b is 1.

[0051] 27. The compound of any one of clauses 1-26, wherein the compound has a unit cell atomic arrangement that is isostructural to a sidorenkite unit cell, a bonshtedtite unit cell, a bradleyite unit cell, a crawfordite unit cell, or a ferrotychite unit cell.

[0052] 28. The compound of any one of clauses 1-27, wherein the compound has a triclinic crystal structure.

[0053] 29. An electrochemical device, comprising an electrode comprising a compound as in any one of clauses 1-28.

[0054] 30. A compound, having a formula $\text{A}_x(\text{M})(\text{PO}_4)_a(\text{CO}_3)_b$, wherein A comprises one or more alkali metals, M comprises one or more non-alkali metal cations, wherein at least about 25 mol % of M comprises one or more non-alkali/non-alkaline earth metals, x is greater than about 0.1, a is between about 0.1 and about 5.1, and b is between about 0.1 and about 5.1; optionally with the proviso that the compound is not one wherein when A is Na, x is between 2 and 4, and M is Fe, Mg, Mn, or Sr.

[0055] 31. The compound of clause 30, wherein A consists essentially of one alkali metal.

[0056] 32. The compound of any one of clauses 30 or 31, wherein A comprises Li.

[0057] 33. The compound of any one of clauses 30-32, wherein A comprises Na.

[0058] 34. The compound of any one of clauses 30-32, wherein A consists essentially of Li.

[0059] 35. The compound of any one of clauses 30, 31, or 33, wherein A consists essentially of Na.

[0060] 36. The compound of any one of clauses 30, 32, or 34, wherein A consists essentially of Li and Na.

[0061] 37. The compound of any one of clauses 30-36, wherein M comprises one or more bivalent or trivalent cations.

[0062] 38. The compound of any one of clauses 30-37, wherein x is between about 1.5 and about 10.1.

[0063] 39. The compound of any one of clauses 30-38, wherein x is between about 1.9 and about 3.1.

[0064] 40. The compound of any one of clauses 30-39, wherein a is between about 0.1 and about 4.

[0065] 41. The compound of any one of clauses 30-40, wherein a is between about 0.9 and about 1.1.

[0066] 42. The compound of any one of clauses 30-41, wherein b is between about 0.1 and about 4.

[0067] 43. The compound of any one of clauses 30-42, wherein b is between about 0.9 and about 1.1.

[0068] 44. The compound of any one of clauses 30-43, wherein at least about 50 mol % of M comprises one or more non-alkali/non-alkaline earth metals.

[0069] 45. The compound of any one of clauses 30-44, wherein M comprises an alkaline earth metal.

[0070] 46. The compound of any one of clauses 30-45, wherein M comprises a transition metal.

[0071] 47. The compound of any one of clauses 30-46, wherein M comprises one or more of Fe, Mn, Co, Ni, V, Cr, Cu, Ti, Bi, Sn, Sb, or Mo.

[0072] 48. The compound of any one of clauses 30-47, wherein the compound has a unit cell atomic arrangement

that is isostructural to a sidorenkite unit cell, a bonshtedtite unit cell, or a bradleyite unit cell, a crawfordite unit cell, or a ferrotychite unit cell.

[0073] 49. The compound of any one of clauses 30-48, wherein the compound has a triclinic crystal structure.

[0074] 50. An electrochemical device, comprising an electrode comprising a compound as in any one of clauses 30-49.

[0075] 51. A lithium-containing compound having a unit cell atomic arrangement that is isostructural to a sidorenkite unit cell, a bonshtedtite unit cell, a bradleyite unit cell, a crawfordite unit cell, or a ferrotychite unit cell.

[0076] 52. A lithium-containing compound comprising at least about 25 mol % lithium, the compound having a unit cell containing CO_3 triangular planar groups, PO_4 tetrahedral groups, and MO_6 octahedral groups, wherein M is a positive cation.

[0077] 53. The compound of clause 52, wherein M is a positive bivalent or trivalent cation.

[0078] 54. The compound of any one of clauses 52 or 53, wherein the MO_6 octahedral group shares an edge with the CO_3 triangular planar group.

[0079] 55. The compound of any one of clauses 52-54, wherein the MO_6 octahedral group shares 4 vertices with PO_4 tetrahedral groups.

[0080] 56. The compound of any one of clauses 52-55, wherein M comprises Fe.

[0081] 57. The compound of any one of clauses 52-56, wherein M comprises Ni.

[0082] 58. The compound of any one of clauses 52-57, wherein M comprises Co.

[0083] 59. The compound of any one of clauses 52-58, wherein M comprises Mn.

[0084] 60. The compound of any one of clauses 52-59, wherein M comprises V.

[0085] 61. The compound of any one of clauses 52-60, wherein M comprises Cr.

[0086] 62. The compound of any one of clauses 52-61, wherein M comprises Cu.

[0087] 63. The compound of any one of clauses 52-62, wherein M comprises Ti.

[0088] 64. The compound of any one of clauses 52-63, wherein M comprises Bi.

[0089] 65. The compound of any one of clauses 52-64, wherein M comprises Sn.

[0090] 66. The compound of any one of clauses 52-65, wherein M comprises Sb.

[0091] 67. The compound of any one of clauses 52-66, wherein M comprises Mo.

[0092] 68. An electrochemical device, comprising an electrode comprising a compound as in any one of clauses 52-67.

[0093] 69. A lithium-containing compound having an XRD diffraction pattern having maxima at 2 theta of 10.7 ± 1 , 20.4 ± 1 , 21.4 ± 1 , 27.1 ± 1 , 28.8 ± 1 , 34.0 ± 1 , and 35.8 ± 1 degrees, wherein the XRD is acquired using an X-ray diffractometer having a copper K alpha source with a wavelength of 1.5418 angstrom.

[0094] 70. A compound having a formula $A_x(M)(\text{YO}_4)_a(\text{XO}_3)_b$, wherein A comprises one or more alkali metals; M comprises one or more non-alkali metal cations, wherein at least about 25 mol % of M comprises one or more non-alkali/non-alkaline earth metals; X comprises one or more of B, C, or N; Y comprises one or more of Si, P, As, or S; x is greater than about 0.1; a is between about 0.1 and about 5.1; and b is between about 0.1 and about 5.1; optionally with the proviso

that the composition does not include any of the following combinations for A, M, Y, and X, respectively: Na, Al and Co, Si, N; Na, Fe, Si, B; Na, Al and Co, Si, C; Na, Mn, P, C; Na, Fe, P, C; Na, Co, P, B; Na, Mg and Fe, S, C; Na, Fe, S, C; Li, Cu, P, B; and Li, Zn, P, B.

[0095] 71. A compound having a formula $A_x(M)(\text{YO}_4)_a(\text{XO}_3)_b$, wherein A comprises one or more alkali metals; M comprises one or more non-alkali metal cations, wherein at least about 25 mol % of M comprises one or more non-alkali/non-alkaline earth metals, and wherein M does not comprise V, Nb, Mo, or W; X comprises one or more of B, C, or N; Y comprises one or more of V, Nb, Mo, and W; x is greater than about 0.1; a is between about 0.1 and about 5.1; and b is between about 0.1 and about 5.1; optionally with the proviso that the composition does not include any of the following combinations for A, M, Y, and X, respectively: Na, Al and Co, Si, N; Na, Fe, Si, B; Na, Al and Co, Si, C; Na, Mn, P, C; Na, Fe, P, C; Na, Co, P, B; Na, Mg and Fe, S, C; Na, Fe, S, C; Li, Cu, P, B; and Li, Zn, P, B.

[0096] 72. The compound of any one of clauses 70 or 71, wherein M comprises one or more bivalent or trivalent cations.

[0097] 73. The compound of any one of clauses 70-72, wherein M comprises one or more alkaline earth metals.

[0098] 74. The compound of any one of clauses 70-73, wherein M comprises one or more transition metals.

[0099] 75. The compound of any one of clauses 70-74, wherein M comprises one or more of Fe, Mn, Co, Ni, V, Cr, Cu, Ti, Bi, Sn, Sb, or Mo.

[0100] 76. The compound of any one of clauses 70-75, wherein x is between about 1.5 and about 10.1.

[0101] 77. The compound of any one of clauses 70-76, wherein x is between about 1.9 and about 10.1.

[0102] 78. The compound of any one of clauses 70-77, wherein x is between about 1.9 and about 3.1.

[0103] 79. The compound of any one of clauses 70-78, wherein a is between about 0.1 and about 4.

[0104] 80. The compound of any one of clauses 70-79, wherein a is between about 0.9 and about 1.1.

[0105] 81. The compound of any one of clauses 70-80, wherein b is between about 0.1 and about 4.

[0106] 82. The compound of any one of clauses 70-81, wherein b is between about 0.9 and about 1.1.

[0107] 83. The compound of any one of clauses 70-82, wherein b is between about 2.9 and about 3.1.

[0108] 84. The compound of any one of clauses 70-83, wherein a is 1 and b is 3.

[0109] 85. The compound of any one of clauses 70 or 72-84, wherein X and Y are selected from one of the following combinations for X and Y: C, P; B, P; B, Si; C, Si; C, S; B, S; N, P; N, Si; and N, S.

[0110] 86. The compound of any one of clauses 71-85, wherein X and Y are selected from one of the following combinations for X and Y: C, V; B, V; and N, V.

[0111] 87. The compound of any one of clauses 70 or 72-86, wherein X is C and Y is P.

[0112] 88. The compound of any one of clauses 70-87, wherein the compound has a unit cell atomic arrangement that is isostructural to a sidorenkite unit cell, a bonshtedtite unit cell, or a bradleyite unit cell, a crawfordite unit cell, or a ferrotychite unit cell.

[0113] 89. The compound of any one of clauses 70-88, wherein the compound has a triclinic crystal structure.

[0114] 90. An electrochemical device, comprising an electrode comprising a compound as in any one of clauses 70-89.

[0115] 91. An electrochemical device, comprising an electrode comprising a compound having a formula $A_x(M)(PO_4)_a(CO_3)_b$, wherein A comprises one or more alkali metals, M comprises one or more metal cations having more than one oxidation state above the ground state, wherein at least about 25 mol % of M comprises one or more non-alkali/non-alkaline earth metals, x is greater than about 0.1, a is between about 0.1 and about 5.1, and b is between about 0.1 and about 5.1.

[0116] 92. The device of clause 91, wherein M comprises one or more non-alkali metal cations.

[0117] 93. The device of any one of clauses 91 or 92, wherein M comprises one or more bivalent or trivalent cations.

[0118] 94. The device of any one of clauses 91-93, wherein M comprises one or more alkaline earth metals.

[0119] 95. The device of any one of clauses 91-94, wherein M comprises one or more transition metals.

[0120] 96. The device of any one of clauses 91-95, wherein M comprises one or more of Fe, Mn, Co, Ni, V, Cr, Cu, Ti, Bi, Sn, Sb, or Mo.

[0121] 97. The device of any one of clauses 91-96, wherein x is between about 1.5 and about 10.1.

[0122] 98. The device of any one of clauses 91-97, wherein x is between about 1.9 and about 3.1.

[0123] 99. The device of any one of clauses 91-98, wherein a is between about 0.1 and about 4.

[0124] 100. The device of any one of clauses 91-99, wherein a is between about 0.9 and about 1.1.

[0125] 101. The device of any one of clauses 91-100, wherein b is between about 0.1 and about 4.

[0126] 102. The device of any one of clauses 91-101, wherein b is between about 0.9 and about 1.1.

[0127] 103. The device of any one of clauses 91-102, wherein the compound has a unit cell atomic arrangement that is isostructural to a sidorenkite unit cell, a bonshtedtite unit cell, or a bradleyite unit cell, a crawfordite unit cell, or a ferrotychite unit cell.

[0128] 104. An electrochemical device, comprising an electrode comprising a compound having a formula $A_x(M)(YO_4)_a(XO_3)_b$, wherein A comprises one or more alkali metals; M comprises one or more non-alkali metal cations, wherein at least about 25 mol % of M comprises one or more non-alkali/non-alkaline earth metals; X is selected from the group consisting of B, C, or N; Y is selected from the group consisting of Si, P, As, S, V, Nb, Mo, or W; x is greater than about 0.1; a is between about 0.1 and about 5.1; and b is between about 0.1 and about 5.1.

[0129] 105. The device of clause 104, wherein M comprises one or more bivalent or trivalent cations.

[0130] 106. The device of any one of clauses 104 or 105, wherein M comprises one or more alkaline earth metals.

[0131] 107. The device of any one of clauses 104-106, wherein M comprises one or more transition metals.

[0132] 108. The device of any one of clauses 104-107, wherein M comprises one or more of Fe, Mn, Co, Ni, V, Cr, Cu, Ti, Bi, Sn, Sb, or Mo.

[0133] 109. The device of any one of clauses 104-108, wherein x is between about 1.5 and about 10.1.

[0134] 110. The device of any one of clauses 104-109, wherein x is between about 1.9 and about 3.1.

[0135] 111. The device of any one of clauses 104-110, wherein a is between about 0.1 and about 4.

[0136] 112. The device of any one of clauses 104-111, wherein a is between about 0.9 and about 1.1.

[0137] 113. The device of any one of clauses 104-112, wherein b is between about 0.1 and about 4.

[0138] 114. The device of any one of clauses 104-113, wherein b is between about 0.9 and about 1.1.

[0139] 115. The device of any one of clauses 104-114, wherein the compound has a unit cell atomic arrangement that is isostructural to a sidorenkite unit cell, a bonshtedtite unit cell, or a bradleyite unit cell, a crawfordite unit cell, or a ferrotychite unit cell.

[0140] 116. A method, comprising providing an aqueous liquid comprising a phosphate anion, a carbonate anion, an alkali metal cation, and a non-alkali metal cation; exposing the liquid to a controlled temperature of at least about 70° C.; and removing water from the liquid to recover a solid product.

[0141] 117. The method of clause 116, wherein the product is crystalline.

[0142] 118. The method of any one of clauses 116 or 117, further comprising forming the solid product into an electrode.

[0143] 119. The method of any one of clauses 116-118, comprising adding a first compound comprising an alkali metal cation and a phosphate anion, and a second compound comprising a non-alkali metal cation and a carbonate anion, to water to form the aqueous liquid.

[0144] 120. The method of any one of clauses 116-118, comprising adding a first compound comprising an alkali metal cation and a carbonate anion, and a second compound comprising a non-alkali metal cation and a phosphate anion, to water to form the aqueous liquid.

[0145] 121. The method of any one of clauses 116-118, comprising adding a first compound comprising an alkali metal cation and a carbonate anion, a second compound comprising a non-alkali metal cation and a nitrate anion, and a third compound comprising a phosphate anion, to water to form the aqueous liquid.

[0146] 122. The method of any one of clauses 116-118, comprising adding a first compound comprising an alkali metal cation and a carbonate anion; a second compound comprising a chlorine anion, a sulfate anion, a bromine anion, and an iodine anion; and a third compound comprising a phosphate anion, to water to form the aqueous liquid.

[0147] 123. The method of any one of clauses 116-118, comprising adding a first compound comprising an alkali metal cation, a second compound comprising a non-alkali metal cation, a third compound comprising a carbonate anion, and a fourth compound comprising a phosphate anion, to water to form the aqueous liquid.

[0148] 124. The method of any one of clauses 116-123, wherein the ratio of alkali metal cation to phosphate anion in the aqueous liquid is between about 5:0.1 and about 1:50.

[0149] 125. The method of any one of clauses 116-124, wherein the ratio of alkali metal cation to phosphate anion in the aqueous liquid is between about 5:0.1 and about 1:10.

[0150] 126. The method of any one of clauses 116-125, wherein the ratio of alkali metal cation to phosphate anion in the aqueous liquid is between about 5:0.1 and about 1:5.

[0151] 127. The method of any one of clauses 116-126, wherein the ratio of alkali metal cation to phosphate anion in the aqueous liquid is about 1:1.

[0152] 128. The method of any one of clauses 116-127, wherein the ratio of alkali metal cation to carbonate anion in the aqueous liquid is between about 5:0.1 and about 1:50.

[0153] 129. The method of any one of clauses 116-128, wherein the ratio of alkali metal cation to carbonate anion in the aqueous liquid is between about 5:0.1 and about 1:10.

[0154] 130. The method of any one of clauses 116-129, wherein the ratio of alkali metal cation to carbonate anion in the aqueous liquid is between about 5:0.1 and about 1:5.

[0155] 131. The method of any one of clauses 116-130, wherein the ratio of alkali metal cation to carbonate anion in the aqueous liquid is about 1:1.

[0156] 132. The method of any one of clauses 116-131, wherein the ratio of phosphate anion to carbonate anion in the aqueous liquid is between about 1:0.1 and about 1:10.

[0157] 133. The method of any one of clauses 116-132, wherein the ratio of phosphate anion to carbonate anion in the aqueous liquid is between about 1:0.5 and about 1:2.

[0158] 134. The method of any one of clauses 116-133, wherein the ratio of phosphate anion to carbonate anion in the aqueous liquid is about 1:1.

[0159] 135. The method of any one of clauses 116-134, wherein the ratio of alkali metal cation to non-alkali metal cation is between about 1:0.1 and about 1:10.

[0160] 136. The method of any one of clauses 116-135, wherein the ratio of alkali metal cation to non-alkali metal cation is between about 1:0.2 and about 1:5.

[0161] 137. The method of any one of clauses 116-136, wherein the ratio of alkali metal cation to non-alkali metal cation is between about 1:0.5 and about 1:2.

[0162] 138. A compound having a triclinic (P1) crystal structure and a formula $A_x(M)(PO_4)_a(CO_3)_b$, wherein A comprises one or more alkali metals, M comprises one or more non-alkali metal cations, wherein at least about 25 mol % of M comprises one or more non-alkali/non-alkaline earth metals, x is greater than about 0.1, a is between about 0.1 and about 5.1, and b is between about 0.1 and about 5.1.

[0163] 139. A compound having a triclinic (P1) crystal structure and a formula $A_x(M)(YO_4)_a(XO_3)_b$, wherein A comprises one or more alkali metals; M comprises one or more non-alkali metal cations, wherein at least about 25 mol % of M comprises one or more non-alkali/non-alkaline earth metals; X comprises one or more of B, C, or N; Y comprises one or more of Si, P, As, or S; x is greater than about 0.1; a is between about 0.1 and about 5.1; and b is between about 0.1 and about 5.1.

[0164] 140. A compound having a triclinic (P1) crystal structure and a formula $A_x(M)(YO_4)_a(XO_3)_b$, wherein A comprises one or more alkali metals; M comprises one or more non-alkali metal cations, wherein at least about 25 mol % of M comprises one or more non-alkali/non-alkaline earth metals, and wherein M does not comprise V, Nb, Mo, or W; X comprises one or more of B, C, or N; Y comprises one or more of V, Nb, Mo, and W; x is greater than about 0.1; a is between about 0.1 and about 5.1; and b is between about 0.1 and about 5.1.

[0165] 141. An electrochemical device, comprising an electrode comprising a compound as in any one of clauses 138-140.

[0166] 142. An electrochemical device, comprising an electrode comprising a lithium-containing compound, the compound having a formula $Li_x(M)(PO_4)_a(CO_3)_b$, wherein M comprises one or more non-alkali metal cations, wherein at least about 25 mol % of M comprises one or more non-alkali/

non-alkaline earth metals, wherein the lithium-containing compound has a unit cell containing CO_3 triangular planar groups, PO_4 tetrahedral groups, and MO_6 octahedral groups, x is greater than about 0.1, a is between about 0.1 and about 5.1, and b is between about 0.1 and about 5.1.

[0167] In still another aspect, the present invention is directed to a method of using one or more of the embodiments described herein, for example, compounds such as the one described above, or other compounds as discussed below.

[0168] Other advantages and novel features of the present invention will become apparent from the following detailed description of various non-limiting embodiments of the invention when considered in conjunction with the accompanying figures. In cases where the present specification and a document incorporated by reference include conflicting and/or inconsistent disclosure, the present specification shall control. If two or more documents incorporated by reference include conflicting and/or inconsistent disclosure with respect to each other, then the document having the later effective date shall control.

BRIEF DESCRIPTION OF THE DRAWINGS

[0169] Non-limiting embodiments of the present invention will be described by way of example with reference to the accompanying figures, which are schematic and are not intended to be drawn to scale. In the figures, each identical or nearly identical component illustrated is typically represented by a single numeral. For purposes of clarity, not every component is labeled in every figure, nor is every component of each embodiment of the invention shown where illustration is not necessary to allow those of ordinary skill in the art to understand the invention. In the figures:

[0170] FIG. 1 illustrates XRD patterns for certain compounds of the invention;

[0171] FIG. 2 illustrates a typical cycling profile for a compound according to one embodiment of the present invention;

[0172] FIGS. 3A-3D illustrate various typical cycling profiles and discharge capacity retentions of certain compounds in accordance other embodiments of the invention;

[0173] FIG. 4 illustrates a crystal unit cell in accordance with one embodiment of the invention;

[0174] FIG. 5 illustrates voltages for certain redox active elements, for carbophosphate compounds, in one embodiment of the invention;

[0175] FIGS. 6A-6B illustrates Li diffusion paths in certain compounds in accordance with another embodiment of the invention;

[0176] FIG. 7 illustrates voltages for various carbosulfate compounds, in yet another embodiment of the invention;

[0177] FIG. 8 illustrates voltages for various carbosilicates, in still another embodiment of the invention;

[0178] FIG. 9 illustrates the stability of certain sodium metal compounds having different combinations of XO_4 and YO_3 groups, in accordance with one embodiment of the invention;

[0179] FIG. 10 illustrates the stability of certain lithium metal compounds having different combinations of XO_4 and YO_3 groups, in accordance with another embodiment of the invention;

[0180] FIG. 11 illustrates a crystal until cell of $Li_3V(CO_3)(SiO_4)$, in yet another embodiment of the invention; and

[0181] FIGS. 12A-12B illustrate cycling curves and capacities of $Na_3MnPO_4CO_3$, in accordance with some embodiments of the invention.

DETAILED DESCRIPTION

[0182] The present invention generally relates to carbophosphates and other compounds. Such compounds may be used in batteries and other electrochemical devices, or in other applications such as those described herein. One aspect of the invention is generally directed to carbophosphate compounds, i.e., compounds containing carbonate and phosphate ions. For example, according to one set of embodiments, the compound has a formula $A_x(M)(PO_4)_a(CO_3)_b$, where M comprises one or more cations. A may include one or more alkali metals, for example, lithium and/or sodium. In some cases, x is greater than about 0.1, a is between about 0.1 and about 5.1, and b is between about 0.1 and about 5.1. In certain embodiments, the compound may have a unit cell atomic arrangement that is isostructural to the unit cells of the minerals sidorenkite, bonshtedtite, bradleyite, crawfordite, or ferrotychite. In some embodiments, the compound may have a formula $A_x(M)(YO_4)_a(XO_3)_b$, where A comprises one or more alkali metals, M comprises one or more cations, X includes B, C, and/or N, and Y includes Si, P, As, S, V, Nb, Mo, and/or W. In some cases, x is greater than about 0.1, a is between about 0.1 and about 5.1, and b is between about 0.1 and about 5.1. Other aspects of the invention are generally directed to techniques for making or using such compounds, kits involving such compounds, and the like.

[0183] Certain aspects of the present invention are generally directed to compounds containing alkali metals such as lithium, sodium, or potassium, one or more other cations, and polyanionic groups such as carbonate and/or phosphate groups. In some cases, however, other groups besides or in addition to carbonate and/or phosphate groups may be present. Examples of suitable polyanionic groups are discussed below. The alkali metals are those associated with Group 1 of the Periodic Table, and include lithium (Li), sodium (Na), potassium (K), rubidium (Rb), cesium (Cs), or francium (Fr), and one or more than one may be present. Thus, for example, a "lithium-containing compound" contains lithium in addition to other ions, while a "sodium-containing compound" contains sodium in addition to other ions. While hydrogen (H) is not a metal, it is part of Group 1 and can in many cases be interchanged for alkali metals; thus, as used herein, an "alkali metal" includes hydrogen. In various formulae as described herein, one or more alkali metals may be present, including any of those described above. In some cases, the structural formulae described herein includes "A," which represents, in any such formula disclosed herein, one or more alkali metals.

[0184] It should be noted that the atoms forming the compounds are held together by chemical bonds, but the chemical bonds need not be covalent bonds (although some of the bonds may include covalent bonds), e.g., the compound may include ionic compounds, where at least some of the atoms are bonded to form compounds due to ionic or electrostatic bonds. Other bonding interactions are also possible, e.g., metallic bonds, van der Waals forces, or the like.

[0185] Phosphate anions (also referred to as phosphate) typically have the formula PO_4^{3-} , and carbonate anions (also referred to as carbonate) typically have the formula CO_3^{2-} . Both phosphate and carbonate are examples of polyatomic anions, or "polyanions," where a chemical anionic group composed of two or more atoms covalently bonded or complexed together can be considered as acting as a single unit (in contrast, an oxide ion, O^{2-} , consists of a single atom and is thus not a polyanion). In some cases, other polyanions may be

used in addition to or instead of phosphates and/or carbonates, as is further discussed below. Some non-limiting examples of polyanions include borate, nitrate, silicate, arsenate, sulfate, vanadate, niobate, molybdate, or tungstate.

[0186] Through electronic structure modifications, certain polyanionic groups such as phosphate groups (PO_4) have been shown to raise the operating voltage of a given transition metal ion. They may, in some cases, increase stability by binding oxygen more strongly in the compound. Certain polyanionic groups such as carbonate groups are relatively light compared to other polyanionic groups, e.g., phosphate groups. The use of such relatively light polyanionic groups, such as carbonate groups, with or without the presence of other polyanionic groups such as phosphate groups, can thus lead to relatively higher energy densities. To the inventors' knowledge, no lithium-containing compounds with combined carbonate and phosphate groups are known to be or have been tested as battery materials.

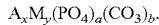
[0187] The compound may also include one or more cations. For example, in some cases, the compound may include monovalent cations (with a formal charge of 1+), bivalent cations (with a formal charge of 2+), and/or trivalent cations (with a formal charge of 3+). Examples of monovalent cations include alkali metals such as those previously described, as well as certain transition metal ions. Examples of bivalent or trivalent cations include, but are not limited to, various transition metal ions or alkaline earth metal ions. The alkaline earth metals are those associated with Group 2 of the Periodic Table and typically include beryllium (Be), magnesium (Mg), calcium (Ca), strontium (Sr), barium (Ba) and/or radium (Ra). One or more than one may be present, depending on the embodiment. The transition metals include Groups 3-12 of the Periodic Table, and include elements such as scandium (Sc), titanium (Ti), vanadium (V), chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), yttrium (Y), zirconium (Zr), niobium (Nb), molybdenum (Mo), tungsten (W), etc. Other examples of cations include non-transition metal cations such as bismuth (Bi), tin (Sn), antimony (Sb), etc.

[0188] As discussed herein, certain compounds of the invention are represented by structural formulae, which may include "M," which represents, in any such formula disclosed herein, one or more cations. For instance, M may comprise one or more bivalent and/or trivalent cations, according to certain embodiments. In some embodiments, M does not include alkali metals such as lithium or sodium, and/or monovalent cations. M also does not include alkaline earth metals such as magnesium or calcium, in certain embodiments of the invention. In some cases, at least about 10 mol % of the M cations may include one or more than one non-alkali, non-alkaline earth metal. In certain embodiments, at least about 25 mol %, at least about 50 mol %, at least about 75 mol %, or essentially all of the M cations may include one or more non-alkali, non-alkaline earth metal ions.

[0189] The compound, in some embodiments, may be solid, and in some cases, crystalline; for example, the cations and anions disclosed herein forming the compound may be arranged in a repeating array having a definite crystal structure, i.e., defining a unit cell atomic arrangement that is repeated to form the crystalline structure. For instance, the cations and anions may be arranged in certain compounds of the present invention such that the unit cell atomic arrangement is isostructural to a sidorenkite unit cell, a bonshtedtite

unit cell, a bradleyite unit cell, a crawfordite unit cell, or a ferrotychite unit cell, as discussed in more detail below.

[0190] In one aspect, the present invention is directed to a compound containing an alkali metal cation, a non-alkali metal cation or a metal cation having more than one oxidation state above the ground state (i.e., where the ground state is M^0), a phosphate anion, and a carbonate anion. The compound may be stoichiometric or off-stoichiometric. For example, the compound, in one set of embodiments, may have the formula:



In this formula, A is an alkali metal (e.g., Li, Na, K, etc.), and M comprises one or more cations. For example, M may comprise one or more non-alkali metal cations, one or more metal cations having more than one oxidation state above the ground state (i.e., M^0), one or more non-alkaline earth metal cations, one or more bivalent or trivalent cations, one or more transition metal ions, or the like, as well as combinations of these (e.g., M may comprise one or more cations that are not alkali metals and are not alkaline earth metals). Combinations of M are also possible, for example, M may include one or more bivalent cations and/or one or more trivalent cations, etc. In some cases, only some of the cations forming M may include transition metal ions. For example, as noted above, in some embodiments, at least about 10 mol %, at least about 25 mol % at least about 50 mol %, or at least about 75 mol % of the cations forming M may be transition metal ions. In certain embodiments, at least about 10 mol %, at least about 25 mol % at least about 50 mol %, or at least about 75 mol % of M comprises one or more non-alkali and non-alkaline earth metals. As specific non-limiting examples, in one set of embodiments, the formula may be $Li_x(M)(PO_4)_a(CO_3)_b$ or $Na_x(M)(PO_4)_a(CO_3)_b$.

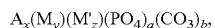
[0191] In any of the formulae herein, a may be between about 0.1 and about 5.1, between about 0.1 and about 4.1, between about 0.2 and about 4.1, between about 0.3 and about 3.1, between about 0.4 and 2.1, between about 0.5 and about 1.5, between about 0.7 and about 1.3, or between about 0.9 and about 1.1. b may also be between about 0.1 and about 5.1, between about 0.1 and about 4.1, between about 0.2 and about 4.1, between about 0.3 and about 3.1, between about 2.9 and about 3.1, between about 0.4 and 2.1, between about 0.5 and about 1.5, between about 0.7 and about 1.3, or between about 0.9 and about 1.1. In some embodiments, a is about 1, and/or b is about 1. In addition, y may be greater than about 0.1. For example, y may be between about 0.1 and about 5.1, between about 0.1 and about 4.1, between about 0.2 and about 4.1, between about 0.3 and about 3.1, between about 0.4 and 2.1, between about 0.5 and about 1.5, between about 0.7 and about 1.3, or between about 0.9 and about 1.1. y may also be 1 in some instances. x may also be greater than about 0.1. For example, x may be between about 0.1 and about 5.1, between about 0.1 and about 4.1, between about 1.5 and about 10.1, between about 1.9 and about 10.1, between about 0.2 and about 4.1, between about 1.5 and about 3.5, between about 1.7 and about 3.3, between about 1.9 and about 3.1, between about 1.8 and about 2.2, between about 1.9 and about 2.1, between about 2.8 and about 3.2 or between about 2.9 and about 3.1. For example, x may be 2 or 3 in some cases; other ranges for x are discussed below.

[0192] In one set of embodiments, x, y, a, and b are selected such that the quantity $(x+jy-3a-2b)$, where j is the total valency of M (mole-averaged if more than one M is present),

is between about -0.5 and about 0.5, between about -0.3 and about 0.3, or between -0.1 and about 0.1. In some (but not all) cases, the quantity $(x+jy-3a-2b)$ is about 0. As one non-limiting example, this relationship may be satisfied if a and b are each 1, x is 3, y is 1, and M is bivalent (so that j is 2). However, in other embodiments, these relations may not necessarily be required, for example, for certain off-stoichiometric compounds of the invention.

[0193] As discussed, M in any of the formulae herein may be a cation, such as a non-alkali metal cation. In some cases, some or all of the cations in M may have any oxidation state, for example, between 1+ and 5+ inclusively, between 1+ and 4+ inclusively, between 1+ and 3+ inclusively, between 1+ and 2+ inclusively, between 2+ and 5+ inclusively, between 2+ and 4+ inclusively, between 2+ and 3+ inclusively, between 3+ and 5+ inclusively, between 4+ and 5+ inclusively, or the like. In some cases, any M that is/are present may have a single oxidation state, e.g., 1+, 2+, 3+, 4+, 5+, 6+, etc. In some embodiments, M may comprise one or more metal cations having more than one oxidation state above the ground state (i.e., M^0). In some cases, M may include one or more monovalent, bivalent, or trivalent cations. For example, M may be a transition metal (e.g., Fe, Ni, Co, Mn, V, Mo, W, etc.), an alkaline metal (e.g., Mg or Sr), or the like, and/or M may comprise or consist essentially of two, three, four, or more such cations. In certain embodiments, at least about 10 mol %, at least about 25 mol % at least about 50 mol %, or at least about 75 mol % of the cations forming M may be transition metal ions. In some embodiments, at least about 10 mol %, at least about 25 mol % at least about 50 mol %, or at least about 75 mol % of M comprises one or more non-alkali and non-alkaline earth metals.

[0194] In some embodiments, M may include two or more bivalent cations, trivalent cations, or any combination of these. For example, in some embodiments, the compound may have the formula:



where M and M' are each independently bivalent or trivalent cations, M is not identical to M', and y and z may be chosen, at least in some cases, such that the quantity $(y+z)$ is between about 0.9 and about 1.1, or the quantity $(y+z)$ may be about 1. For example, y and z may each be about $\frac{1}{2}$, y may be about $\frac{1}{3}$ and z may be about $\frac{2}{3}$, y may be about $\frac{1}{4}$ and z may be about $\frac{3}{4}$, etc. In some (but not all) cases, x, y, z, a and b may be chosen such that the quantity $(x+jy+kz-3a-2b)$, where j is the valency of M and k is the valency of M', is between about -0.5 and about 0.5, between about -0.3 and about 0.3, or between -0.1 and about 0.1. In some cases, the quantity $(x+jy+kz-3a-2b)$ is about 0. As a specific non-limiting example, this relationship is satisfied if a and b are each 1, x is 3, y is $\frac{1}{2}$, and z is $\frac{1}{2}$ when M and M' are each bivalent (i.e., when j is 2 and k is 2). In still other embodiments, there may be 3, 4, or more bivalent and/or trivalent cations present within the compound.

[0195] Typically, compounds such as the ones described above (or any other compound and/or formulae discussed herein) will have subscripts selected such that the compound is essentially electrically neutral (uncharged) in the absence of an applied electric field. For example, the subscripts within the compound may be selected to be whole numbers, decimals, or fractions, so long as the positive and negative charges essentially balance, giving the compound an essentially neutral charge when no electric field is applied. Determining

whether a compound is electrically neutral can be performed by those of ordinary skill in the art, as the formal charges for each atom or polyanion are well-known (e.g., Li is 1+, K is 1+, PO₄ is 3-, CO₃ is 2-, etc.). However, in some cases, the compounds may have subscripts that do not necessarily require the compound to be essentially electrically neutral in the absence of an applied electric field, for example, for certain off-stoichiometric compounds as discussed herein.

[0196] In one set of embodiments, a compound of the present invention may have the formula:



where x is between about 2.9 and about 3.1, and A, M, a, and b, are the same as those discussed above. As non-limiting examples, x may be 3 in some cases; M may be a single bivalent cation; a may be between about 0.1 and about 5.1; and/or b may be between about 0.1 and about 5.1. For instance, the compound may have the formula A₃(M)(PO₄)(CO₃), for example, Li₃(M)(PO₄)(CO₃), Na₃(M)(PO₄)(CO₃), or K₃(M)(PO₄)(CO₃). Examples of bivalent cations include, but are not limited to, Fe, Ni, Co, Mn, V, Mo, Sr, Cr, Cu, Ti, Bi, Sn, Sb, or Mg. Thus, specific examples of compounds include, but are not limited to, Li₃FeCO₃PO₄, Li₃NiCO₃PO₄, Li₃CoCO₃PO₄, Li₃MnCO₃PO₄, Li₃VCO₃PO₄, Li₃MoCO₃PO₄, Na₃FeCO₃PO₄, Na₃NiCO₃PO₄, Na₃CoCO₃PO₄, Na₃MnCO₃PO₄, Na₃VCO₃PO₄, Na₃MoCO₃PO₄, K₃FeCO₃PO₄, K₃NiCO₃PO₄, K₃CoCO₃PO₄, K₃MnCO₃PO₄, K₃VCO₃PO₄, or K₃MoCO₃PO₄. Additional non-limiting examples include Li_xCrCO₃PO₄, Na_xCrCO₃PO₄, K_xCrCO₃PO₄, Li_xCuCO₃PO₄, Na_xCuCO₃PO₄, K_xCuCO₃PO₄, Li_xTiCO₃PO₄, Na_xTiCO₃PO₄, K_xTiCO₃PO₄, Li_xBiCO₃PO₄, Na_xBiCO₃PO₄, K_xBiCO₃PO₄, Li_xSnCO₃PO₄, Na_xSnCO₃PO₄, K_xSnCO₃PO₄, Li_xSbCO₃PO₄, Na_xSbCO₃PO₄, or K_xSbCO₃PO₄.

[0197] In some embodiments, however, more than one bivalent cation may be present, for example, as in the formula:



where x is between about 2.9 and about 3.1, M and M' are each independently single bivalent cations, and the quantity (y+z) is between about 0.9 and about 1.1, at least in some cases. These variables (e.g., A, M, a, b, y, and z) may otherwise be the same as those discussed above. For example, a may be between about 0.1 and about 5.1, and/or b may be between about 0.1 and about 5.1. For instance, the compound may have the formula A₃(M_{1/2}M'_{1/2})(PO₄)(CO₃), for example, Li₃(M_{1/2}M'_{1/2})(PO₄)(CO₃), Na₃(M_{1/2}M'_{1/2})(PO₄)(CO₃), or K₃(M_{1/2}M'_{1/2})(PO₄)(CO₃). Specific non-limiting examples include Li₃Fe_{1/2}Ni_{1/2}CO₃PO₄, Li₃Fe_{1/2}Co_{1/2}CO₃PO₄, Li₃Fe_{1/2}Mn_{1/2}CO₃PO₄, Li₃Fe_{1/2}V_{1/2}CO₃PO₄, Li₃Fe_{1/2}/Mo_{1/2}CO₃PO₄, Li₃Ni_{1/2}Co_{1/2}CO₃PO₄, Li₃Ni_{1/2}Mn_{1/2}CO₃PO₄, Li₃Ni_{1/2}V_{1/2}CO₃PO₄, Li₃Ni_{1/2}Mo_{1/2}CO₃PO₄, Li₃Co_{1/2}Mn_{1/2}CO₃PO₄, Li₃Co_{1/2}V_{1/2}CO₃PO₄, Li₃Co_{1/2}Mo_{1/2}CO₃PO₄, Li₃Mn_{1/2}V_{1/2}CO₃PO₄, Li₃Mn_{1/2}Mo_{1/2}CO₃PO₄, Li₃V_{1/2}Mo_{1/2}CO₃PO₄, Na₃Fe_{1/2}Ni_{1/2}CO₃PO₄, Na₃Fe_{1/2}Co_{1/2}CO₃PO₄, Na₃Fe_{1/2}Mn_{1/2}CO₃PO₄, Na₃Fe_{1/2}V_{1/2}CO₃PO₄, Na₃Fe_{1/2}Mo_{1/2}CO₃PO₄, Na₃Ni_{1/2}Co_{1/2}CO₃PO₄, Na₃Ni_{1/2}Mn_{1/2}CO₃PO₄, Na₃Ni_{1/2}V_{1/2}CO₃PO₄, Na₃Ni_{1/2}Mo_{1/2}CO₃PO₄, Na₃Co_{1/2}Mn_{1/2}CO₃PO₄, Na₃Co_{1/2}V_{1/2}CO₃PO₄, Na₃Co_{1/2}Mo_{1/2}CO₃PO₄, Na₃Co_{1/2}Fe_{1/2}CO₃PO₄, Na₃Co_{1/2}Fe_{1/2}Ni_{1/2}CO₃PO₄, Na₃Co_{1/2}Fe_{1/2}Mo_{1/2}CO₃PO₄, Na₃Co_{1/2}Fe_{1/2}V_{1/2}CO₃PO₄, Na₃Co_{1/2}Fe_{1/2}Fe_{1/2}CO₃PO₄, Na₃Co_{1/2}Fe_{1/2}Fe_{1/2}Ni_{1/2}CO₃PO₄, Na₃Co_{1/2}Fe_{1/2}Fe_{1/2}Mo_{1/2}CO₃PO₄, Na₃Co_{1/2}Fe_{1/2}Fe_{1/2}V_{1/2}CO₃PO₄, Na₃Co_{1/2}Fe_{1/2}Fe_{1/2}Fe_{1/2}CO₃PO₄, Na₃Co_{1/2}Fe_{1/2}Fe_{1/2}Fe_{1/2}Ni_{1/2}CO₃PO₄, Na₃Co_{1/2}Fe_{1/2}Fe_{1/2}Fe_{1/2}Mo_{1/2}CO₃PO₄, Na₃Co_{1/2}Fe_{1/2}Fe_{1/2}Fe_{1/2}V_{1/2}CO₃PO₄, Na₃Co_{1/2}Fe_{1/2}Fe_{1/2}Fe_{1/2}Fe_{1/2}CO₃PO₄, Na₃Co_{1/2}Fe_{1/2}Fe_{1/2}Fe_{1/2}Fe_{1/2}Ni_{1/2}CO₃PO₄, Na₃Co_{1/2}Fe_{1/2}Fe_{1/2}Fe_{1/2}Fe_{1/2}Mo_{1/2}CO₃PO₄, Na₃Co_{1/2}Fe_{1/2}Fe_{1/2}Fe_{1/2}Fe_{1/2}V_{1/2}CO₃PO₄, Na₃Co_{1/2}Fe_{1/2}Fe_{1/2}Fe_{1/2}Fe_{1/2}Fe_{1/2}CO₃PO₄, Na₃Co_{1/2}Fe_{1/2}Fe_{1/2}Fe_{1/2}Fe_{1/2}Fe_{1/2}Ni_{1/2}CO₃PO₄, Na₃Co_{1/2}Fe_{1/2}Fe_{1/2}Fe_{1/2}Fe_{1/2}Fe_{1/2}Mo_{1/2}CO₃PO₄, Na₃Co_{1/2}Fe_{1/2}Fe_{1/2}Fe_{1/2}Fe_{1/2}Fe_{1/2}V_{1/2}CO₃PO₄, Na₃Co_{1/2}Fe_{1/2}Fe_{1/2}Fe_{1/2}Fe_{1/2}Fe_{1/2}Fe_{1/2}CO₃PO₄, Na₃Co_{1/2}Fe_{1/2}Fe_{1/2}Fe_{1/2}Fe_{1/2}Fe_{1/2}Fe_{1/2}Ni_{1/2}CO₃PO₄, Na₃Co_{1/2}Fe_{1/2}Fe_{1/2}Fe_{1/2}Fe_{1/2}Fe_{1/2}Fe_{1/2}Mo_{1/2}CO₃PO₄, Na₃Co_{1/2}Fe_{1/2}Fe_{1/2}Fe_{1/2}Fe_{1/2}Fe_{1/2}Fe_{1/2}V_{1/2}CO₃PO₄, Na₃Co_{1/2}Fe_{1/2}Fe_{1/2}Fe_{1/2}Fe_{1/2}Fe_{1/2}Fe_{1/2}Fe_{1/2}CO₃PO₄, Na₃Co_{1/2}Fe_{1/2}Fe_{1/2}Fe_{1/2}Fe_{1/2}Fe_{1/2}Fe_{1/2}Fe_{1/2}Ni_{1/2}CO₃PO₄, Na₃Co_{1/2}Fe_{1/2}Fe_{1/2}Fe_{1/2}Fe_{1/2}Fe_{1/2}Fe_{1/2}Fe_{1/2}Mo_{1/2}CO₃PO₄, Na₃Co_{1/2}Fe_{1/2}Fe_{1/2}Fe_{1/2}Fe_{1/2}Fe_{1/2}Fe_{1/2}Fe_{1/2}V_{1/2}CO₃PO₄, Na₃Co_{1/2}Fe_{1/2}Fe_{1/2}Fe_{1/2}Fe_{1/2}Fe_{1/2}Fe_{1/2}Fe_{1/2}Fe_{1/2}CO₃PO₄, Na₃Co_{1/2}Fe_{1/2}Fe_{1/2}Fe_{1/2}Fe_{1/2}Fe_{1/2}Fe_{1/2}Fe_{1/2}Ni_{1/2}CO₃PO₄, Na₃Co_{1/2}Fe_{1/2}Fe_{1/2}Fe_{1/2}Fe_{1/2}Fe_{1/2}Fe_{1/2}Fe_{1/2}Mo_{1/2}CO₃PO₄, Na₃

having more than one oxidation state above the ground state (i.e., M^0), one or more non-alkaline earth metal cations, one or more bivalent or trivalent cations, one or more transition metal ions, or the like, e.g., as previously discussed, as well as combinations of these (e.g., M may comprise one or more cations that are not alkali metals and are not alkaline earth metals). In some embodiments, Y may be selected from the group consisting of P, Si, S, and V.

[0202] a may be between about 0.1 and about 5.1, between about 0.1 and about 4.1, between about 0.2 and about 4.1, between about 0.3 and about 3.1, between about 0.4 and 2.1, between about 0.5 and about 1.5, between about 0.7 and about 1.3, or between about 0.9 and about 1.1. b may also be between about 0.1 and about 5.1, between about 0.1 and about 4.1, between about 0.2 and about 4.1, between about 0.3 and about 3.1, between about 2.9 and about 3.1, between about 0.4 and 2.1, between about 0.5 and about 1.5, between about 0.7 and about 1.3, or between about 0.9 and about 1.1. In some embodiments, a is about 1, and/or b is about 1. In addition, y may be greater than about 0.1. For example, y may be between about 0.1 and about 5.1, between about 0.1 and about 4.1, between about 0.2 and about 4.1, between about 0.3 and about 3, between about 0.4 and 2.1, between about 0.5 and about 1.5, between about 0.7 and about 1.3, or between about 0.9 and about 1.1. y may also be 1 in some instances. x may also be greater than about 0.1. For example, x may be between about 0.1 and about 5.1, between about 0.1 and about 4.1, between about 1.5 and about 10.1, between about 1.9 and about 10.1, between about 0.2 and about 4.1, between about 1.5 and about 3.5, between about 1.7 and about 3.3, between about 1.9 and about 3.1, between about 1.8 and about 2.2, between about 1.9 and about 2.1, between about 2.8 and about 3.2 or between about 2.9 and about 3.1. For example, x may be 2 or 3 in some cases.

[0203] In one set of embodiments, X and Y are selected from one of the following combinations for X and Y, respectively: C, P; B, P; B, Si; C, Si; C, S; B, S; N, P; N, Si; N, S; C, V; B, V; or N, V. For example, in certain embodiments as previously discussed, X may be C and Y may be P.

[0204] Non-limiting examples of the compounds described above include $\text{Li}_x(\text{M})(\text{YO}_4)_a(\text{XO}_3)_b$, or $\text{Na}_x(\text{M})(\text{YO}_4)_a(\text{XO}_3)_b$. Specific examples of potentially suitable compounds include, but are not limited to, $\text{Li}_x(\text{M})(\text{PO}_4)_a(\text{CO}_3)_b$, $\text{Na}_x(\text{M})(\text{PO}_4)_a(\text{CO}_3)_b$, $\text{Li}_x(\text{M})(\text{PO}_4)_a(\text{BO}_3)_b$, $\text{Na}_x(\text{M})(\text{PO}_4)_a(\text{BO}_3)_b$, $\text{Li}_x(\text{M})(\text{SiO}_4)_a(\text{BO}_3)_b$, $\text{Na}_x(\text{M})(\text{SiO}_4)_a(\text{BO}_3)_b$, $\text{Li}_x(\text{M})(\text{SiO}_4)_a(\text{CO}_3)_b$, $\text{Na}_x(\text{M})(\text{SiO}_4)_a(\text{CO}_3)_b$, $\text{Li}_x(\text{M})(\text{SO}_4)_a(\text{CO}_3)_b$, $\text{Na}_x(\text{M})(\text{SO}_4)_a(\text{CO}_3)_b$, $\text{Li}_x(\text{M})(\text{SO}_4)_a(\text{BO}_3)_b$, $\text{Na}_x(\text{M})(\text{SO}_4)_a(\text{BO}_3)_b$, $\text{Li}_x(\text{M})(\text{PO}_4)_a(\text{NO}_3)_b$, $\text{Na}_x(\text{M})(\text{PO}_4)_a(\text{NO}_3)_b$, $\text{Li}_x(\text{M})(\text{SiO}_4)_a(\text{NO}_3)_b$, $\text{Na}_x(\text{M})(\text{SiO}_4)_a(\text{NO}_3)_b$, $\text{Li}_x(\text{M})(\text{SO}_4)_a(\text{NO}_3)_b$, $\text{Na}_x(\text{M})(\text{SO}_4)_a(\text{NO}_3)_b$, $\text{Li}_x(\text{M})(\text{VO}_4)_a(\text{CO}_3)_b$, $\text{Na}_x(\text{M})(\text{VO}_4)_a(\text{CO}_3)_b$, $\text{Li}_x(\text{M})(\text{VO}_4)_a(\text{BO}_3)_b$, $\text{Na}_x(\text{M})(\text{VO}_4)_a(\text{BO}_3)_b$, $\text{Li}_x(\text{M})(\text{VO}_4)_a(\text{NO}_3)_b$, or $\text{Na}_x(\text{M})(\text{VO}_4)_a(\text{NO}_3)_b$. Other combinations are also possible, in other embodiments of the invention.

[0205] In one set of embodiments, the compound does not include any of the following combinations for A, M, Y, and X, respectively: Na, Al and Co, Si, N; Na, Fe, Si, B; Na, Al and Co, Si, C; Na, Mn, P, C; Na, Fe, P, C; Na, Co, P, B; Na, Mg and Fe, S, C; Na, Fe, S, C; Li, Cu, P, B; and Li, Zn, P, B. However, in other embodiments, any of these compounds may also be included.

[0206] In some embodiments, more than one (YO_4) and/or (XO_3) may be present, including the above polyanions including Y and X and/or other polyanions. In some cases,

other compounds may be present, for example, as dopants and/or impurities, or there may be variances in the compound due to manufacturing techniques or impurities in the starting compositions, or due to gaps, defects, or vacancies in the crystalline structure. However, in one set of embodiments, the amount of anionic oxide (O^{2-}) present within the compound may be kept at relatively low levels. For example, the compound may have no more than about 20 mol %, about 15 mol %, about 10 mol %, or about 5 mol % of anionic oxide present (as previously mentioned, anionic oxide, O^{2-} , is not polyanionic).

[0207] As mentioned, the compounds discussed herein may be stoichiometric or non-stoichiometric. In an off-stoichiometric compound, the ratio between the various cations is not exact or stoichiometric, and/or the ratio between the various anions is not exact or stoichiometric. For example, the ratio between the cations and anions, or the ratio between the cations and the anions within an off-stoichiometric compound may be 1:0.99, 1:0.98, 1:0.97, 1:0.96, 1:0.95, 1:0.94, 1:0.93, 1:0.92, 1:0.91, 1:0.90, 1:0.88, 1:0.86, 1:0.84, 1:0.82, 1:0.80, 1:0.78, 1:0.76, 1:0.74, 1:0.72, 1:0.70, etc., with either the cations or the anions being in excess, depending on the embodiment. As another example, the ratio between first and second cations (e.g., A or M) in a compound may not necessarily be a simple whole number ratio (e.g., 1:1, 2:1, 3:1, etc.), but may be a fraction, for example 1-w:1, 1+w:1, 2-w:1, 2+w:1, 3-w:1, 3+w:1, etc., where w is a decimal number, e.g., w may be 0.01, 0.02, 0.03, 0.04, 0.05, 0.06, 0.07, 0.08, 0.09, 0.10, 0.12, 0.14, 0.16, 0.18, 0.20, 0.22, 0.24, 0.26, 0.28, 0.30, etc. Thus, in any subscript in any formula described herein (including the implicit 1's in formulae such as $\text{Li}_3\text{FeCO}_3\text{PO}_4$), any one or more of the subscripts may independently be modified by the addition of a +w or a -w, where w is defined as described above.

[0208] Thus, as various non-limiting examples, a compound of the present invention may have a formula $A_{x-w}M_y(PO_4)_a(CO_3)_b$, $A_{x-n}M_y(YO_4)_a(XO_3)_b$, $A_{x-n}(M_y)(M'_z)(PO_4)_a(CO_3)_b$, $A_{x-w}M_y(M_y)(M'_z)(YO_4)_a(XO_3)_b$, $A_{x-w}M_y(PO_4)_a(CO_3)_b$, $A_{x-w}M_y(YO_4)_a(XO_3)_b$, $A_{x-w}(M_y)(M'_z)(PO_4)_a(CO_3)_b$, $A_xM_{y-w}(PO_4)_a(CO_3)_b$, $A_xM_{y-w}(YO_4)_a(XO_3)_b$, $A_x(M_y)_{1-w}(M'_z)(PO_4)_a(CO_3)_b$, $A_x(M_y)_{1-w}(M'_z)(YO_4)_a(XO_3)_b$, $A_x(M_y)(M'_z)_{1-w}(PO_4)_a(CO_3)_b$, $A_x(M_y)_{1-w}(M'_z)(YO_4)_a(XO_3)_b$, $A_x(M_y)(M'_z)_{1-w}(PO_4)_a(CO_3)_b$, $A_x(M_y)_{1-w}(M'_z)(YO_4)_a(XO_3)_b$, $A_xM_{y-w}(PO_4)_a(CO_3)_b$, $A_xM_{y-w}(YO_4)_a(XO_3)_b$, $A_x(M_y)_{1-w}(M'_z)(PO_4)_a(CO_3)_b$, $A_x(M_y)_{1-w}(M'_z)(YO_4)_a(XO_3)_b$, $A_x(M_y)(M'_z)_{1-w}(PO_4)_a(CO_3)_b$, $A_x(M_y)(M'_z)_{1-w}(YO_4)_a(XO_3)_b$, $A_xM_y(PO_4)_{a-w}(CO_3)_b$, $A_xM_y(YO_4)_{a-w}(XO_3)_b$, $A_xM_y(PO_4)_{a-w}(CO_3)_b$, $A_xM_y(YO_4)_{a-w}(XO_3)_b$, $A_x(M_y)(M'_z)(PO_4)_{a-w}(CO_3)_b$, $A_x(M_y)(M'_z)(YO_4)_{a-w}(XO_3)_b$, $A_xM_y(PO_4)_{a-w}(CO_3)_b$, $A_xM_y(YO_4)_{a-w}(XO_3)_b$, $A_x(M_y)(M'_z)(PO_4)_{a-w}(CO_3)_b$, $A_x(M_y)(M'_z)(YO_4)_{a-w}(XO_3)_b$, $A_xM_y(PO_4)_{a-w}(CO_3)_b$, $A_xM_y(YO_4)_{a-w}(XO_3)_b$, $A_x(M_y)(M'_z)(PO_4)_{a-w}(CO_3)_b$, $A_x(M_y)(M'_z)(YO_4)_{a-w}(XO_3)_b$, or the like. The other variables in these formulae (e.g., A, x, M, M', Y, X, a, b, etc.) may otherwise be the same as those described anywhere herein. w may also be 0 in other embodiments (i.e., such that the compound is stoichiometric). In addition, as noted above, more than one cation and/or anion may be off-stoichiometric in some cases, for example, as in $A_{x-w}M_{y-v}(PO_4)_a(CO_3)_b$, $A_{x-w}M_y(PO_4)_{a-v}(CO_3)_b$, $A_{x-w}M_y(PO_4)_a(CO_3)_{b-v}$, $A_{x-w}M_{y-v}(PO_4)_{a-u}(CO_3)_b$, etc., where u and v are independently selected but defined similarly to w above.

[0209] In one aspect, the compound may have a structure such that the unit cell atomic arrangement is isostructural to a

sidorenkite unit cell, a bonshtedtite unit cell, a bradleyite unit cell, a crawfordite unit cell, or a ferrotychite unit cell. An example unit cell is shown in FIG. 4. As used herein, “isostuctural” means that the atoms in the structure are topologically arranged in 3-dimensional space in the same configuration (for example, the oxygen atoms, cations, anions, etc. are positioned in the same topological locations), although the exact dimensions or lattice parameters in the compound (e.g., the spacing between atoms) may be different than the corresponding unit cells. For example, a sidorenkite unit cell, a bonshtedtite unit cell, and a bradleyite unit cell are isostructural to each other. Those of ordinary skill in the art will be able to determine the unit cell and/or atomic positions of a compound of the present invention, using well-established techniques for determining unit cell lattice parameters, dimensions, atomic positions, etc., for example, using crystallographic techniques such as X-ray diffraction, neutron diffraction, or electron diffraction.

[0210] In some embodiments, the compound has a unit cell belonging to Space Group Number 11, as defined by the International Union of Crystallography. This structure is monoclinic, and has the International Short Symbol ($P12_1/m$). Thus, the compound may be one that adopts a monoclinic $P21/m$ (11) space group structure. A specific non-limiting example of a unit cell structure is shown in FIG. 4. In this figure, oxygen atoms are indicated by **11**, X atoms (e.g., carbon) are indicated by **12**, Y atoms (e.g., phosphorous) are indicated by **13**, A atoms (e.g., sodium) are indicated by **14**, and M atoms (e.g., manganese) are indicated by **15**. In one embodiment, the lattice vectors length are 8.997, 6.741, and 5.163, and the lattice vectors angle are 90°, 90.16°, and 90°. In some embodiments, however, some relaxation of the structure may occur, e.g., such that the structure relaxes from monoclinic to triclinic (P1), e.g., after some ion exchange has occurred.

[0211] In one set of embodiments, the compound may have a unit cell comprising CO_3 triangular planar groups (or other XO_3 triangular planar groups), PO_4 tetrahedral groups (or other YO_4 tetrahedral groups), and/or MO_6 octahedral groups. M may be a positive cation, for instance, a positive bivalent or trivalent cation, or other cations as described herein with respect to M. In some cases, the MO_6 octahedral group (e.g., the cluster around atom **15** in FIG. 4) may share an edge with a carbonate CO_3 or other XO_3 triangular planar group (e.g., the cluster around atom **12** in FIG. 4), and/or the MO_6 octahedral group may share 4 vertices with PO_4 or other YO_4 tetrahedral groups (e.g., the cluster around atom **13**).

[0212] As a specific example, in one embodiment, a compound of the invention may be determined using an X-ray diffractometer having a copper K alpha source with a wavelength of 1.5418 angstrom. The XRD diffraction pattern may have maxima at 2 theta (2θ) of 10.7±1, 20.4±1, 21.4±1, 27.1±1, 28.8±1, 34.0±1, and 35.8±1 degrees. Other example spectra can be seen in FIG. 1. In some embodiments, the compound may have a spectrum similar to those seen in FIG. 1, e.g., such that the person of ordinary skill in the art would agree that the compound has a spectrum that is essentially identical to one of those shown in FIG. 1.

[0213] In some cases, the compound is thermodynamically unstable at 25° C. and 1 atm. As used herein, the phrase “thermodynamically unstable” means that under such conditions, the compound may begin substantially degrading, without any external inputs (e.g., temperature changes, other reactants, energy, etc.), into other compounds or formulations

having lower thermodynamic energy over a nominal time scale, such as within 1 year or within 5 years. For instance, by way of example only, some carbonate-containing compounds will degrade by releasing carbonate as carbon dioxide (CO_2). However, for many compounds, kinetic limitations prevent a compound from degrading even in conditions in which it is thermodynamically unstable.

[0214] In some embodiments, the compound is thermally stable. For example, the compound may be sufficiently stable that it does not substantially decompose upon exposures to temperatures of 200° C., 250° C., 300° C., 350° C., 400° C., 450° C. or even 500° C. (e.g., at 1 atm), e.g., forming smaller decomposition compounds (for example, CO or CO_2) in an irreversible process. In some cases, the compound is sufficiently stable that it exhibits no more than about 3 ml/g of oxygen release when heated to a temperature of 250° C. or 300° C. In some cases, the compound may release no more than about 1 ml/g, about 0.3 ml/g, about 0.1 ml/g, or about 0.3 ml/g of oxygen upon exposure to such temperatures. Without wishing to be bound by any theory, it is believed that the thermal stability and/or the inability of the compound to release oxygen may be due to the presence of polyanionic groups within the compound, e.g., phosphate (PO_4) and/or carbonate (CO_3), unlike other compounds such as Li_xCoO_2 which do not contain such polyanionic groups. As previously mentioned, in some embodiments, the compound contains no more than about 20 mol %, about 15 mol %, about 10 mol %, or about 5 mol % of anionic (non-polyanionic) oxide.

[0215] The thermal stability of the compound may be determined using any suitable technique. One non-limiting example is differential scanning calorimetry (DSC). Thus, for example, the compound may exhibit no thermal transitions below 200° C., 250° C., 300° C., 350° C., or 400° C. when analyzed using differential scanning calorimetry (DSC). Examples of thermal transitions include glass transition (T_g) and/or melting (T_m) transitions.

[0216] In one set of embodiments, the compound has a specific capacity of at least about 50 mA h/g, and in some cases, at least about 60 mA h/g, at least about 80 mA h/g, at least about 100 mA h/g, at least about 120 mA h/g, at least about 140 mA h/g, at least about 160 mA h/g, at least about 180 mA h/g, at least about 200 mA h/g, at least about 210 mA h/g, at least about 220 mA h/g, or at least about 230 mA h/g, etc. as measured at a discharge rate of C/50 (C=116 mA/g). The compound may be, for example, a lithium-containing compound comprising at least two different polyanionic groups, a compound having the formula $Li_x(M)(PO_4)_a(CO_3)_b$, $A_x(M)(PO_4)_a(CO_3)_b$, $A_x(M)(YO_4)_a(XO_3)_b$, or any other compound disclosed herein. Such specific capacities may be measured, for example, by using the relevant compound as a positive electrode in an electrochemical cell against a Li anode, charging the compound to a maximum of 4.6 V, 4.9 V, or 5.2 V (relative to the potential of Li^+ /Li, i.e., relative to the potential of Li^+ in Li metal, e.g., in a Li metal anode), then discharging the compound to 2.0 V at a rate of at least about 116 mA/g. The current density of the compound, when used as an electrode, may be less than about 1 mA/cm² of electrode surface.

[0217] In some embodiments, various compositions as discussed herein can be selected and/or optimized, e.g., for use in batteries and/or other electrochemical devices, based on screening tests, for example, based on charging or cycling profiles. For instance, a composition may be formed into a cathode in an electrochemical cell and charged against a

lithium anode. By exposing the compound to various voltages (e.g., 4.6 V, 4.9 V, or 5.2 V, relative to the potential of Li⁺/Li), then discharging the compound to 2.0 V at a rate of at least about 116 mA/g, the performance of various compositions can be ascertained, and used to select or optimize compositions for use in a particular battery and/or other electrochemical device. A compound may be selected to have a specific capacity of at least about 50 mA h/g, and in some cases, at least about 60 mA h/g, at least about 80 mA h/g, at least about 100 mA h/g, at least about 120 mA h/g, at least about 140 mA h/g, at least about 160 mA h/g, at least about 180 mA h/g, at least about 200 mA h/g, at least about 210 mA h/g, at least about 220 mA h/g, or at least about 230 mA h/g, etc. As another example, the compound may be repeated charged and discharged as described above, with better or more optimized compounds yielding better charging characteristics after more charge/discharge cycles.

[0218] According to various aspects of the invention, compounds such as those described herein may be used for a wide variety of purposes. In some embodiments, the compound may be present within a composition which can optionally include other materials, such as binders, fillers, hardeners, or the like. For instance, in one set of embodiments, the compound may be present within an electrochemical device, for example, as a battery material, for use in applications such as power tools, hybrid electric vehicles, portable electronic devices, laptop computers, and the like. In some such embodiments, the compounds of the invention may be able to store charge, e.g., electronic charge. For example, the compounds may be present in an electrode within a suitable electrochemical device, e.g., as a positive electrode within a battery, fuel cell, etc.

[0219] As a specific example, in some embodiments, a compound as discussed herein may be used within a rechargeable alkali metal battery, for example, within or as an electrode. A rechargeable alkali metal battery, such as a lithium battery or a sodium battery, typically has electrodes that exchange lithium or sodium, respectively, during charge and discharge. The rate at which the alkali metal ions can be exchanged is important in many applications where high charge and/or discharge rates are required for the battery. For a cathode material, alkali metal ions and electrons are adsorbed during the discharge of the battery, and this process is reversed during the charge. Though the present invention is not limited to cathodes, as used herein, "charging" indicates removal of alkali metal ions from the material and "discharging" refers to insertion of alkali metal ions from the material.

[0220] Another aspect of the present invention is generally directed to systems and techniques for making compounds such as the one described herein. For example, in certain embodiments, a hydrothermal technique may be used to prepare the compounds. In some embodiments, an aqueous liquid containing various salts (e.g., a solution or a suspension, etc.) is heated, then the water is removed to recover the final compound. The liquid may contain various salts containing ions that will be used to form the final compound, which may be dissolved and/or suspended in the liquid. It should be understood that a "liquid," as used herein, also includes species that are contained within the liquid, e.g., dissolved or suspended therein, as in a solution or a suspension. As a specific example, a liquid may contain a phosphate anion, a carbonate anion, an alkali metal cation, and a non-alkali metal cation.

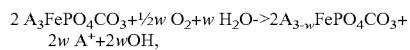
[0221] In the liquid, positive ions that should be present in the final compound may be balanced by suitable negative ions to produce the final desired product. As a specific non-limiting example, if Na₃MnCO₃PO₄ is to be produced, the starting salts may include Na₂CO₃, Na₃PO₄, MnCO₃, and/or Mn₃(PO₄)₂. To control the ratio of species in the final desired product, other entities may also be used that can be removed during the synthesis process. For instance, nitrates (NO₃⁻) or ammonium species (NH₄⁺) may be used. Thus, as a specific example, NaNO₃ or Mn(NO₃)₂ could be used to increase the amount of Na or Mn, respectively, while (NH₄)₂CO₃ or (NH₄)₃PO₄ could be used to increase the amount of CO₃ or PO₄, respectively, in the final product. Those of ordinary skill in the art will be able to prepare starting liquids (e.g., solutions and/or suspensions) containing the correct amounts of positive and negative species to produce a desired final product without an undue degree of experimentation, by calculating molar ratios or using other similar techniques.

[0222] For instance, in one set of embodiments, the initial liquid may be prepared by adding a first compound comprising an alkali metal cation and a carbonate anion, a second compound comprising a non-alkali metal cation and a nitrate anion, and a third compound comprising a phosphate anion, to water to form the aqueous liquid. In another set of embodiments, the initial liquid may be prepared by adding a first compound comprising an alkali metal cation and a carbonate anion; a second compound comprising a chlorine anion, a sulfate anion, a bromine anion, and an iodine anion; and a third compound comprising a phosphate anion, to water to form the aqueous liquid. According to yet another set of embodiments, the initial liquid may be prepared by adding a first compound comprising an alkali metal cation, a second compound comprising a non-alkali metal cation, a third compound comprising a carbonate anion, and a fourth compound comprising a phosphate anion, to water to form the aqueous liquid.

[0223] For example, if the final compound has a formula A_x(M)(PO₄)_a(CO₃)_b, where A comprises one or more alkali metals, M comprises one or more non-alkali metal cations, x is greater than about 0.1, a is between about 0.1 and about 5.1, and b is between about 0.1 and about 5.1, then the initial may be formed from a first compound comprising an alkali metal cation and a phosphate anion, and a second compound comprising a non-alkali metal cation and a carbonate anion; or a first compound comprising an alkali metal cation and a carbonate anion, and a second compound comprising a non-alkali metal cation and a phosphate anion; or the like. For example, the ratio of alkali metal cation to phosphate anion in an aqueous solution may be, for example, between about 5:0 and about 1:50, between about 5:0.1 and about 1:10, between about 5:0.1 and about 1:5, between about 1:0.1 and about 1:50, between about 1:0.1 and about 1:10, between about 1:0.1 and about 1:5, or about 1:1. Similarly, in some cases, the ratio of alkali metal cation to carbonate anion in the aqueous solution may be, for example, between about 5:0 and about 1:50, between about 5:0.1 and about 1:10, between about 5:0.1 and about 1:5, between about 1:0.1 and about 1:50, between about 1:0.1 and about 1:10, between about 1:0.1 and about 1:5, or about 1:1. In some embodiments, the ratio of phosphate anion to carbonate anion may be between about 1:0.1 and about 1:10, between about 1:0.5 and about 1:2, or about 1:1. In one set of embodiments, the ratio of alkali metal

cation to non-alkali metal cation is between about 1:0.1 and about 1:10, between about 1:0.2 and about 1:5, or between about 1:0.5 and about 1:2.

[0224] In some embodiments, the synthesis and/or ion exchange of certain compounds, such as those described herein (for instance, certain Li or Na iron carbonophosphates), may be carried out in a glove box, or other sealed reactor, such as a hydrothermal bomb. In some cases, the glove box or other reactor may contain an inert gas, such as pure nitrogen or a noble gas, e.g., to minimize exposure to oxygen. Without wishing to be bound by any particular theory, oxygen (e.g., in the air) in the environment or dissolved in the hydrothermal solution may, in some cases, oxidize Fe²⁺ to Fe³⁺. This oxidation reaction may result in an off-stoichiometric formulation of the iron carbonophosphates, e.g. the formula of the product becomes A_{3-w}Fe(II)_{1-w}Fe(III)_wPO₄CO₃. A may be Li or Na. The oxidation reaction may be written as:



where A represents Na or Li. In other embodiments, however, such compounds may be desirable.

[0225] In certain cases, however, the synthesis and/or ion exchange of certain compounds, such as those described herein (for example, certain Co or Ni carbonophosphates), may be performed with or without necessarily removing oxygen from the surrounding environment. Due to the stability of certain species such as Co(II) and Ni(II) against oxygen, there may be no need to remove oxygen from the surrounding environment. As another example, the synthesis and/or ion exchange of Mn carbonophosphates may be performed out with removing oxygen from the surrounding environment, since Mn(II) is generally more stable than Fe(II) against oxidation under operating conditions. While the oxidation of Mn(II) may occur, it typically oxidizes very slowly. Thus, there may be no need to remove oxygen from the surrounding environment.

[0226] The initial liquid may be prepared by dissolving and/or suspending the salts in water (or a solution, suspension, or other mixture in which water is present), and/or heating the liquid to a controlled temperature, sequentially and/or simultaneously, for example, at least about 50° C., at least about 60° C., at least about 70° C., at least about 80° C., at least about 90° C., at least about 100° C., at least about 110° C., at least about 120° C., at least about 130° C., at least about 140° C., at least about 150° C., at least about 160° C., at least about 170° C., at least about 180° C., at least about 190° C., at least about 200° C., or at least about 210° C. In certain embodiments, the temperature may be below about 220° C., about 210° C., or about 200° C. In some cases, the temperature and/or pressure of the liquid may be controlled during the heating process such that the aqueous solution is not boiled off.

[0227] After suitable exposure to such conditions (e.g., after 2, 3, 4, or more days), water may be removed using any suitable technique to produce the final product. For example, the liquid may be exposed to relatively high temperatures under dry (low-humidity) air, or by centrifugation separation to drive off excess water, thereby producing the final product. Techniques for drying solutions or suspensions will be familiar to those of ordinary skill in the art. In some cases, the final product may be recovered as a solid product, for instance, a crystalline product.

[0228] In some embodiments, the final product may be formed as particles. The particle size may be controlled, for example, by controlling the temperature and/or the time of formation. For instance, the particles may have an average diameter of between about 200 nm to about 10 micrometers, between about 200 nm and about 300 nm, between about 300 nm and about 1 micrometer, between about 1 micrometer and about 3 micrometers, or between about 3 micrometers and about 10 micrometers. The average diameter may be estimated, e.g., using SEM or TEM. In some cases, the particles may have a relatively narrow size distribution. For example, as observed using SEM or TEM, the particles may have a size such that at least about 50%, at least about 60%, at least about 70%, about 80%, at least about 85%, at least about 90%, or at least about 95% of the particles appears to have a diameter or volume that is no more than about 10% different, or no more than about 5% different from the average diameter or volume of the particles.

[0229] The invention also involves, in some aspects, the promotion of the use of a compound according to any of the techniques or compounds described herein. As used herein, “promoted” includes all methods of doing business including, but not limited to, methods of selling, advertising, assigning, licensing, contracting, instructing, educating, researching, importing, exporting, negotiating, financing, loaning, trading, vending, reselling, distributing, replacing, or the like that can be associated with the methods and compounds of the invention, e.g., as discussed herein. Promoting may also include, in some cases, seeking approval from a government agency. Methods of promotion can be performed by any party including, but not limited to, businesses (public or private), contractual or sub-contractual agencies, educational institutions such as colleges and universities, research institutions, governmental agencies, etc. Promotional activities may include instructions or communications of any form (e.g., written, oral, and/or electronic communications, such as, but not limited to, e-mail, telephonic, facsimile, Internet, Web-based, etc.) that are clearly associated with the invention. As used herein, “instructions” can define a component of instructional utility (e.g., directions, guides, warnings, labels, notes, FAQs (“frequently asked questions”), etc., and typically involve written instructions on or associated with the compound and/or with the packaging of the compound. Instructions can also include instructional communications in any form (e.g., oral, electronic, digital, optical, visual, etc.), provided in any manner such that a user will clearly recognize that the instructions are to be associated with the compound, e.g., as discussed herein.

[0230] U.S. Provisional Patent Application Ser. No. 61/306,670, filed Feb. 22, 2010, entitled “Carbophosphate and Related Compounds,” by Ceder, et al., is incorporated herein by reference in its entirety.

[0231] The following examples are intended to illustrate certain embodiments of the present invention, but do not exemplify the full scope of the invention.

Example 1

[0232] This example illustrates the synthesis of various sodium single-transition metal carbophosphate Na₃MCO₃PO₄ compounds, where M is Fe, Co, Mn, or Ni. These carbophosphate compounds were synthesized using hydrothermal methods. Additional sodium mixed-transition metal transition metal carbophosphates were also prepared using similar techniques, where M includes mixtures of Fe,

Co, Mn, and Ni (but were not limited to these elements). For example, Cr or V could be mixed in the M site with the four elements above.

[0233] The lithium forms of these compounds were prepared by Li—Na ion exchange in organic solvents. The details of the synthesis procedure are described below with $\text{Na}_3\text{MnCO}_3\text{PO}_4$ and $\text{Li}_3\text{MnCO}_3\text{PO}_4$ as specific representative examples.

[0234] The starting materials used for the synthesis of $\text{NaMnCO}_3\text{PO}_4$ included soluble sodium salt, such as Na_2CO_3 ; soluble Mn salt, such as $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ or $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$; soluble carbonates, such as Na_2CO_3 ; and soluble phosphates, such as $(\text{NH}_4)_2\text{HPO}_4$. As a representative procedure, 0.5 g of $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ was dissolved in 3 ml of distilled water to form a light pink solution (solution I); next, 2 g Na_2CO_3 and 0.264 g $(\text{NH}_4)_2\text{HPO}_4$ were dissolved in 12 ml distilled water to form a clear solution (solution II). Solution I was slowly added into solution II under strong magnetic stirring to form a light pink slurry. The slurry was transferred to a PTFE (polytetrafluoroethylene)-lined autoclaved and heated at 90° C. for three days, or at 160° C. for 16 hours. After the autoclave was cooled down to room temperature (about 25° C.), the final product was washed with distilled water 3 to 5 times and then dried at 90° C. overnight.

[0235] The starting materials could be other soluble salts which provide Na, Mn, CO_3^{2-} or PO_4^{3-} to the reaction, other than the salts listed above. The molar ratio of the starting materials could be varied accordingly.

[0236] The Li—Na ion exchange to synthesize $\text{Li}_3\text{MnCO}_3\text{PO}_4$ from as-prepared $\text{NaMnCO}_3\text{PO}_4$ was performed by stirring the powder of $\text{NaMnCO}_3\text{PO}_4$ in 2 M LiBr/1-hexanol solution for one week in a 90° C. oil bath. The temperature can also be between about 90° C. and about 135° C. The ion-exchanged product was washed by distilled water and methanol and dried at 70° C. overnight.

[0237] The same hydrothermal synthesis and ion-exchange procedures was used to synthesize other carbophosphates (M being Ni, Co, Fe or other metals), with the starting materials changed accordingly.

[0238] The XRD patterns of $\text{Na}_3\text{MCO}_3\text{PO}_4$ and their corresponding Li form $\text{Li}_3\text{MCO}_3\text{PO}_4$ (M=Mn, Fe, Co, Ni, and $\text{Co}_{0.5}\text{Mn}_{0.5}$) are shown in FIG. 1.

Example 2

[0239] This example shows testing involving certain compounds discussed in Example 1. The as-prepared $\text{Li}_3\text{MnCO}_3\text{PO}_4$ and $\text{Li}_3\text{FeCO}_3\text{PO}_4$ compound were tested as the cathode in an experimental half-cell lithium ion battery. $\text{Li}_3\text{MnCO}_3\text{PO}_4$ or $\text{Li}_3\text{FeCO}_3\text{PO}_4$ was mixed with carbon black and PVDF (polyvinylidene fluoride) binders with a weight ratio of 60%:30%:10% and casted on an aluminum foil as the cathode. Lithium metal foil was used as anode. 1 M LiPF_6 in 1:1 EC/DMC (ethylene carbonate/dimethyl carbonate) solution was used as electrolyte. The cell was cycled by using a Maccor 4000 electrochemical cycler or an Arbin 2000 electrochemical cycler with galvanostatic mode. The current density used was 2 mA/g for $\text{Li}_3\text{MnCO}_3\text{PO}_4$ and from 2 mA/g to 1000 mA/g for $\text{Li}_3\text{FeCO}_3\text{PO}_4$. The voltage window was 2.0 V to 4.8 V. FIG. 2 shows a typical cycling profile of $\text{Li}_3\text{MnCO}_3\text{PO}_4$, with the charge and discharge voltage plotted as a function of capacity. The current density was 2 mA/g, and the cycling window was 2.0 V to 4.8 V. FIG. 3A shows a typical cycling profile of off-stoichiometric $\text{Li}_3\text{FeCO}_3\text{PO}_4$ in the first three cycles, with the charge and discharge voltage

plotted as a function of capacity. The current density was 2 mA/g. FIG. 3B shows the capacity retention of $\text{Li}_3\text{FeCO}_3\text{PO}_4$ with different current densities at various rates. The off-stoichiometric samples also showed good rate capability and cycling retention.

[0240] In addition, FIGS. 3C and 3D illustrate cyclic curves of stoichiometric $\text{Li}_3\text{FeCO}_3\text{PO}_4$ at room temperature (about 25° C.) and at 60° C., at C/10 rates. In addition, when cycled at an elevated temperature, the $\text{Li}_3\text{FeCO}_3\text{PO}_4$ showed smaller polarization.

Example 3

[0241] Without wishing to be bound by any theory, this example illustrates that certain compounds having the YO_4 and XO_3 polyanions discussed herein have a sidorenkite structure and the properties recited herein based on a density functional theory framework using the Generalized Gradient Approximation (GGA) with a Hubbard correction term (GGA+U).

[0242] Voltages for different redox active elements M in the sidorenkite structure were computed, and are shown in FIG. 5. This figure also shows metal valence changes during the battery cycle (e.g., from 2+ to 3+, etc.). Mn, V, and Mo appear to be interesting, and the energy density for these elements are shown in Table 1.

TABLE 1

redox couple	Grav. Energy density (Wh/kg)	Vol. Energy density (Wh/l)
Mn2/4	859	2376
Mo3/5	744	2285
V3/5	968	2604

[0243] The thermodynamic stability for various $\text{Li}_x\text{M}(\text{PO}_4)(\text{CO}_3)$ compounds was estimated using ab initio computations. The results of the voltage computations are shown in FIG. 5. Many metals such as Fe, Mn, Co, V, Mo, and Bi display computational voltages which are suited to match the voltage limits of current electrolytes presently used in Li ion batteries. Other metals, including Ni and Cr are also interesting. The Li containing phases were found to be thermodynamically unstable; however, a few of them are only slightly higher in energy than the combination of phases with the lowest energy, so that they can be made in the lab by controlling the kinetics of the reactions, for example, as was shown in Example 1.

[0244] Analysis of certain $\text{Na}_x\text{M}(\text{PO}_4)(\text{CO}_3)$ isostructural compound showed that various sodium compounds are stable. For instance, for M elements in a 2+ oxidation state, $\text{Na}_3\text{M}(\text{PO}_4)(\text{CO}_3)$ appears stable for various elements, such as Fe, Mn, Mg, Ca, Co, Ni, Cu, Zn, etc. For M elements in a 3+ oxidation state, $\text{Na}_2\text{M}(\text{PO}_4)(\text{CO}_3)$ appears to be stable for V, Mo, Fe, Cr, Bi, Sc, Al, etc. Similarly, with potassium as an alkali, various compounds are also stable. For instance, for M elements in a 2+ oxidation state, $\text{K}_3\text{M}(\text{PO}_4)(\text{CO}_3)$ appears to be stable for Mg, Ca, Fe, Ni, Co, Sr, Mn, etc. For M elements in a 3+ oxidation state, $\text{K}_2\text{M}(\text{PO}_4)(\text{CO}_3)$ appears to be stable for Bi, Fe, Ti, Sb, Fe, Cr, Mn, etc. Accordingly, these computations illustrate that another approach for producing certain compounds of the invention involves first preparing a sodium compound or a potassium compound, then using ion-exchange to produce a lithium compound.

[0245] An empirical potential based on electrostatic interaction was also used to evaluate the Li diffusion path in certain compounds. FIGS. 6A and 6B show the diffusion paths of Li in the sidorenkite structure. The results from this analysis suggest that these compounds should exhibit good lithium ion diffusion. This diffusion was predicted to be 2-dimensional with the lowest barrier diffusion path along the b and c axis. See FIGS. 6A and 6B. The empirical potential barriers were estimated to be 521 meV, 394 meV, and 452 meV, respectively, for the Mn, Fe and V compounds.

[0246] A computational search for other possible stable polyanionic mixtures was also performed. For instance, every possible compound in the formula $A_3M(XO_4)(YO_3)$, where x is 1, 2, or 3; A is Na or Li; X is Si, P, As, or S; and Y is B or C was computed. It was found that certain Na compounds were stable. For instance, the stable compounds in the Na carbono-phosphate chemistries were also stable in the corresponding carbonoarsenate chemistries. Similarly, some Na borato-phosphates were also found to be close to stability in the formula $Na_3M(PO_4)(BO_3)$, where M is Fe, Mn, or Mo. Certain carbonosilicates such as $Na_3M(SiO_4)(CO_3)$, where M is Fe, Mo, or V were also found to be stable. The stability data for these compounds is shown in FIG. 9 for A=Na and FIG. 10 for A=Li, for the various ions as shown on the X and Y axes. "n/a" means no data is available. In these figures, the gray scale is shaded to illustrate the differential energy of these compounds to the combination of phases with the lowest energy. The voltages for the Li version for those carbonosilicates (i.e., $Li_3M(SiO_4)(CO_3)$) were evaluated and are shown in FIG. 8. For example, $Li_3V(CO_3)(SiO_4)$ has a gravimetric energy density of 799 Wh/kg and volumetric energy density of 2183 Wh/l. FIG. 11 shows the unit cell of this compound.

[0247] Other interesting crystal structures include those analogous to ferrotychite ($Na_6Fe_2(CO_3)_4(SO_4)$). Voltages for lithium analogues ($Li_6M_2(CO_3)_4(SO_4)$) are shown in FIG. 7. The voltages tended in general to be higher than the carbono-phosphates for the same redox couple.

Example 4

[0248] In this example, various sodium carbonophosphate compounds were tested as cathode materials for sodium-ion batteries. Testing conditions were similar to those used in Example 2, except for that Na metal was used as the anode instead of Li metal in Example 2 and 1 M $NaPF_6$ in 1:1 EC/DMC (ethylene carbonate/dimethyl carbonate) solution was used as electrolyte.

[0249] $Na_3MnPO_4CO_3$ showed relatively good capacity (~120 mAh/g), more the theoretical capacity of one-electron reaction (~95 mAh/g) and the discharge curve showed two plateaus, which indicates a possible two-electron reaction. The voltage of the plateaus, centered around 4 V and 3.2 V, generally agreed with computational predictions (4.0 V for Mn^{3+}/Mn^{4+} and 3.1 V for Mn^{2+}/Mn^{3+}). The cycling curves and capacities of $Na_3MnPO_4CO_3$ are shown in FIGS. 12A and 12B.

[0250] While several embodiments of the present invention have been described and illustrated herein, those of ordinary skill in the art will readily envision a variety of other means and/or structures for performing the functions and/or obtaining the results and/or one or more of the advantages described herein, and each of such variations and/or modifications is deemed to be within the scope of the present invention. More generally, those skilled in the art will readily appreciate that all parameters, dimensions, materials, and configurations

described herein are meant to be exemplary and that the actual parameters, dimensions, materials, and/or configurations will depend upon the specific application or applications for which the teachings of the present invention is/are used. Those skilled in the art will recognize, or be able to ascertain using no more than routine experimentation, many equivalents to the specific embodiments of the invention described herein. It is, therefore, to be understood that the foregoing embodiments are presented by way of example only and that, within the scope of the appended claims and equivalents thereto, the invention may be practiced otherwise than as specifically described and claimed. The present invention is directed to each individual feature, system, article, material, kit, and/or method described herein. In addition, any combination of two or more such features, systems, articles, materials, kits, and/or methods, if such features, systems, articles, materials, kits, and/or methods are not mutually inconsistent, is included within the scope of the present invention.

[0251] All definitions, as defined and used herein, should be understood to control over dictionary definitions, definitions in documents incorporated by reference, and/or ordinary meanings of the defined terms.

[0252] The indefinite articles "a" and "an," as used herein in the specification and in the claims, unless clearly indicated to the contrary, should be understood to mean "at least one."

[0253] The phrase "and/or," as used herein in the specification and in the claims, should be understood to mean "either or both" of the elements so conjoined, i.e., elements that are conjunctively present in some cases and disjunctively present in other cases. Multiple elements listed with "and/or" should be construed in the same fashion, i.e., "one or more" of the elements so conjoined. Other elements may optionally be present other than the elements specifically identified by the "and/or" clause, whether related or unrelated to those elements specifically identified. Thus, as a non-limiting example, a reference to "A and/or B", when used in conjunction with open-ended language such as "comprising" can refer, in one embodiment, to A only (optionally including elements other than B); in another embodiment, to B only (optionally including elements other than A); in yet another embodiment, to both A and B (optionally including other elements); etc.

[0254] As used herein in the specification and in the claims, "or" should be understood to have the same meaning as "and/or" as defined above. For example, when separating items in a list, "or" or "and/or" shall be interpreted as being inclusive, i.e., the inclusion of at least one, but also including more than one, of a number or list of elements, and, optionally, additional unlisted items. Only terms clearly indicated to the contrary, such as "only one of" or "exactly one of," or, when used in the claims, "consisting of," will refer to the inclusion of exactly one element of a number or list of elements. In general, the term "or" as used herein shall only be interpreted as indicating exclusive alternatives (i.e. "one or the other but not both") when preceded by terms of exclusivity, such as "either," "one of," "only one of," or "exactly one of." "Consisting essentially of," when used in the claims, shall have its ordinary meaning as used in the field of patent law.

[0255] As used herein in the specification and in the claims, the phrase "at least one," in reference to a list of one or more elements, should be understood to mean at least one element selected from any one or more of the elements in the list of elements, but not necessarily including at least one of each and every element specifically listed within the list of ele-

ments and not excluding any combinations of elements in the list of elements. This definition also allows that elements may optionally be present other than the elements specifically identified within the list of elements to which the phrase "at least one" refers, whether related or unrelated to those elements specifically identified. Thus, as a non-limiting example, "at least one of A and B" (or, equivalently, "at least one of A or B," or, equivalently "at least one of A and/or B") can refer, in one embodiment, to at least one, optionally including more than one, A, with no B present (and optionally including elements other than B); in another embodiment, to at least one, optionally including more than one, B, with no A present (and optionally including elements other than A); in yet another embodiment, to at least one, optionally including more than one, A, and at least one, optionally including more than one, B (and optionally including other elements); etc.

[0256] It should also be understood that, unless clearly indicated to the contrary, in any methods claimed herein that include more than one step or act, the order of the steps or acts of the method is not necessarily limited to the order in which the steps or acts of the method are recited.

[0257] In the claims, as well as in the specification above, all transitional phrases such as "comprising," "including," "carrying," "having," "containing," "involving," "holding," "composed of," and the like are to be understood to be open-ended, i.e., to mean including but not limited to. Only the transitional phrases "consisting of" and "consisting essentially of" shall be closed or semi-closed transitional phrases, respectively, as set forth in the United States Patent Office Manual of Patent Examining Procedures, Section 2111.03.

What is claimed is:

1-3. (canceled)

4. The compound of claim **6**, wherein M comprises an alkaline earth metal.

5. (canceled)

6. A compound, having a formula:



wherein:

A comprises one or more alkali metals,

M comprises one or more non-alkali metal cations, wherein at least about 25 mol % of M comprises one or more non-alkali/non-alkaline earth metals,

x is greater than about 0.1,

a is between about 0.1 and about 5.1, and

b is between about 0.1 and about 5.1,

with the proviso that the compound is not one wherein when A is Na, x is between 2 and 4, and M is Fe, Mg, Mn, or Sr.

7. The compound of claim **6**, wherein M comprises one or more bivalent or trivalent cations.

8. The compound of claim **6**, wherein M comprises a transition metal.

9. The compound of claim **6**, wherein M comprises one or more of Fe, Mn, Co, Ni, V, Cr, Cu, Ti, Bi, Sn, Sb, or Mo.

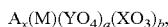
10. The compound of claim **6**, wherein the compound has a unit cell atomic arrangement that is isostructural to a sidorenkite unit cell, a bonshtedtite unit cell, or a bradleyite unit cell, a crawfordite unit cell, or a ferrotychite unit cell.

11-21. (canceled)

22. The device of claim **24**, wherein M comprises one or more of Fe, Mn, Co, Ni, V, Cr, Cu, Ti, Bi, Sn, Sb, or Mo.

23. The device of claim **24**, wherein the compound has a unit cell atomic arrangement that is isostructural to a sidorenkite unit cell, a bonshtedtite unit cell, or a bradleyite unit cell, a crawfordite unit cell, or a ferrotychite unit cell.

24. An electrochemical device, comprising an electrode comprising a compound having a formula:



wherein:

A comprises one or more alkali metals,

M comprises one or more non-alkali metal cations, wherein at least about 25 mol % of M comprises one or more non-alkali/non-alkaline earth metals,

X is selected from the group consisting of B, C, or N,

Y is selected from the group consisting of Si, P, As, S, V, Nb, Mo, or W,

x is greater than about 0.1,

a is between about 0.1 and about 5.1, and

b is between about 0.1 and about 5.1.

25. The device of claim **24**, wherein M comprises one or more bivalent or trivalent cations.

26. The device of claim **24**, wherein M comprises one or more alkaline earth metals.

27. The device of claim **24**, wherein M comprises one or more transition metals.

28-32. (canceled)

33. An electrochemical device, comprising an electrode comprising a lithium-containing compound, the compound having a formula:



wherein:

M comprises one or more non-alkali metal cations, wherein at least about 25 mol % of M comprises one or more non-alkali/non-alkaline earth metals, wherein the lithium-containing compound has a unit cell containing CO₃ triangular planar groups, PO₄ tetrahedral groups, and MO₆ octahedral groups,

x is greater than about 0.1,

a is between about 0.1 and about 5.1, and

b is between about 0.1 and about 5.1.

34. The compound of claim **6**, wherein A is Li.

35. The device of claim **24**, wherein Y is P and X is C.

* * * * *

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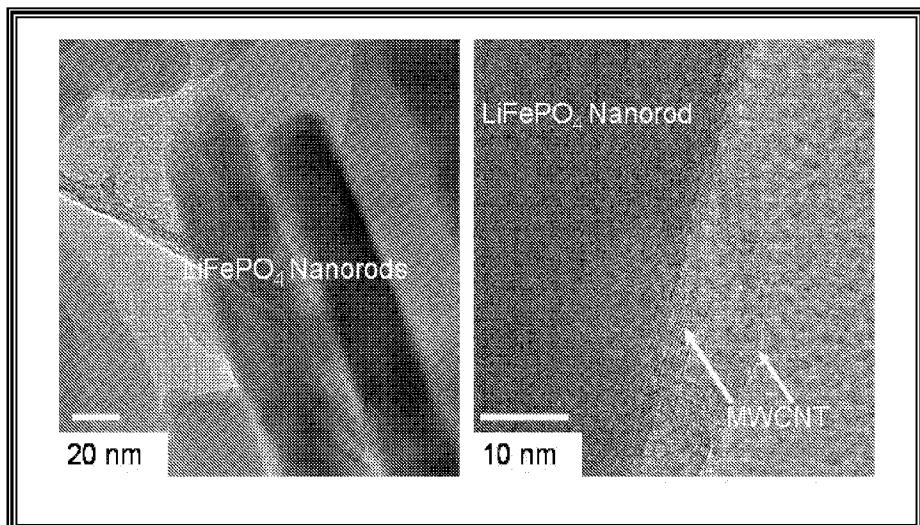
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FIG. 6



(57) Abstract: The present invention includes methods, coatings, and a nanostructured phospho-olivine composition Li_xMyPO_4 , capable of being formed hydrothermally or solvothermally in aqueous solutions and non-aqueous solutions M is one or more elements selected from the group consisting of Fe, Mn, Co, Ti, Ni, Cu, V, Mo, Zn, Mg, Cr, Al, Ga, B, Zr, Nb or combination thereof and x is between 0 and 1 and y is between 0.8 and 1.2. The phospho-olivine may also have the compositions like $\text{Li}_x\text{Fe}_{1-x}\text{PO}_4$, wherein x is between 0 and 1, and y is between 0 and 1.

RAPID MICROWAVE-SOLVOTHERMAL SYNTHESIS AND SURFACE MODIFICATION
OF NANOSTRUCTURED PHOSPHO-OLIVINE CATHODES FOR LITHIUM ION
BATTERIES

Technical Field of the Invention

5 The present invention relates in general to the field of cathode materials, and more specifically to rapid microwave-solvothermal synthesis employing aqueous and nonaqueous solvents and surface modification of nanostructured phospho-olivine cathodes for lithium ion batteries.

Background Art

Without limiting the scope of the invention, its background is described in connection with 10 phospho-olivine cathodes for lithium ion batteries. Generally, lithium ion batteries have become common place for portable electronic devices such as laptop computers and cell phones due to their higher energy density compared to other rechargeable systems. They are also being intensively pursued for transportation applications such as hybrid electric vehicles (HEV) and plug-in hybrid electric vehicles (PHEV). Conventional lithium ion batteries use the layered 15 LiCoO₂ as a cathode (i.e., positive electrode) material. The high cost and environmental concerns associated with cobalt as well as the safety concerns of lithium cobalt oxide have hampered the development of lithium ion battery technology for HEV and PHEV applications.

Alternative materials are being explored for HEV and PHEV, but they have their own 20 advantages and disadvantages. For example, LiFePO₄ crystallizing in the olivine structure is appealing due to the inexpensiveness of iron and its benign environmental impact; however, the olivine LiFePO₄ has a low electronic conductivity and low lithium diffusivity. These limitations translate to a poor rate capability for the LiFePO₄ cathodes and make it difficult to make full use of its capacity in lithium ion batteries.

The electrochemical performances have been found to increase by decreasing the particle size of 25 LiFePO₄ via various synthetic methods under different conditions including solid-state [Padhi, A.K., Nanjundasawamy, K.S., & Goodenough, J.B., Phospho-olivines as positive electrode materials for rechargeable lithium batteries. *J. Electrochem. Soc.*, **144**, 1188 - 1194 (1997)] and ball-milling [Hosoya et al US Patent No.7,101,521 B2, September 2006]. However, these methods require repeated regrinding and heat-treatment at high temperatures (500- 800°C) for 30 several hours (12 – 24 hours) in inert or reducing atmospheres, which lead to increase in particle size and a decrease in electrochemical performance.

As a result, soft-chemical routes to synthesize LiFePO₄ at low temperatures using aqueous and non-aqueous reaction medium have been explored (e.g., precipitation methods [Arnold, G., Garche, J., Hemmer, R., Ströbele, S., Vogler, C. & Wohlfahrt-Mehre, M. Fine-particle lithium iron phosphate LiFePO₄ synthesized by a new low-cost aqueous precipitation technique. *J. Power Sources*, **119-121**, 247-251 (2003)], sol-gel process [Yang, J. & Xu, J. J. Nonaqueous Sol-gel synthesis of high-performance LiFePO₄, *Electrochem. Solid-State Lett.*, **7**, A515-A518 (2004)], refluxing [Kim, D.-H. & Kim, J. Synthesis of LiFePO₄ nanoparticle in polyol medium and their electrochemical properties, *Electrochem. Solid- State Lett.*, **9**, A439 - A442 (2006)], and hydrothermal techniques [Ellis, B., Kan, W. H., Makahnouk, W. R. M., & Nazar, L. F. 10 Synthesis of nanocrystals and morphology control of hydrothermally prepared LiFePO₄. *J. Mater. Chem.* **17**, 3248 – 3254 (2007)]. However, these methods often involve lengthy procedures with several steps and need longer reaction times for the formation of well crystalline phase. In addition, post heat-treatment processing at high temperatures in reducing atmospheres is necessary to obtain well crystalline LiFePO₄, resulting in unwanted particle growth that is 15 detrimental to the characteristics of LiFePO₄ electrodes with low lithium ion conductivity.

Disclosure of the Invention

The present inventors recognized the need for an efficient method of synthesis involving simplified preparation procedures and shorter reaction times. The present inventors recognized that the one-pot microwave-assisted, solution-based synthesis method offers several advantages 20 over conventional routes. For example, the microwave-assisted synthesis method of the present invention provides cleanliness, short reaction times, and energy economy while providing small particle size with a uniform size distribution in a shorter reaction time.

Although, microwave irradiated synthesis of LiFePO₄ using a mixture of its solid-state precursors under inert atmosphere has been pursued [Higuchi, M., Katayama, K., Azuma, Y., 25 Yukawa, M. & Suhara, M. Synthesis of LiFePO₄ cathode material by microwave processing, *J. Power Sources*, **119-121**, 258-261 (2003); Wang, L., Huang, Y., Jiang, R. & Jia, D. Preparation and characterization of nano-sized LiFePO₄ by low heating solid-state coordination method and microwave heating, *Electrochim Acta* ,**52**, 6778 - 6783 (2007)], there has been difficulty in obtaining pure-phase LiFePO₄ due to the oxidation of Fe²⁺ to Fe³⁺ or the hydrolysis of Fe²⁺ to 30 Fe³⁺ in aqueous solutions and the consequent formation of impurity phases containing Fe³⁺. In addition, processes to reduce this oxidation have been generally tedious, ineffective and have led to carbon residues. However, most importantly, the products prepared by these processes have

had a reduced discharge capacity of 125 mAh/g, which is much lower than the theoretical value of about 170 mAh/g.

As a result, the present inventors have developed a new microwave-solvothermal method (including microwave-hydrothermal method) of synthesizing LiFePO₄ that produces highly crystalline nanostructured LiFePO₄ within a short period of time (e.g., 5 - 15 minutes) at reasonable temperatures (e.g., 300°C) without any further heating in a furnace or in reducing atmospheres.

The present invention provides an enhanced capacity and rate capability for LiFePO₄ by doping with a number of cations and coating with electronically conducting additives such as carbon, multi-walled carbon nanotubes (MWCNT), and conjugated polymers. The capacity retention and rate capability increase with decreasing particle size, certain cation doping, and the incorporation of electronically conductive additives.

For example, United States Patent number 7,087,348, entitled, “coated electrode particles for composite electrodes and electrochemical cells,” disclosed electrodes for use in electrochemical devices. More particularly, coated electrode particles for use in solid electrochemical cells and materials and systems for improving electronic conductivity and repulsive force characteristics of an electrode network are disclosed. An article containing a plurality of distinct first particles that form an electrode network in which the distinct first particles are coated with a system of electrically conductive material is also disclosed. In some embodiments, the coating layer also includes a low refractive index material. In some embodiments, the coating layer of the electroactive material includes a plurality of second particles.

The present invention provides highly crystalline LiFePO₄ nanorod compositions and methods of making compositions within a short reaction time of 5 – 15 minutes at < 300 °C by a novel microwave-solvothermal (hereafter referred to as “MW-ST”) process and a microwave-hydrothermal (hereafter referred to as “MS-HT”) process. In order to improve the electrical conductivity, both an *ex situ* carbon coating by heating at 700 °C with sucrose the LiFePO₄ obtained by the MW-ST method and an *in situ* carbon coating by carrying out the MW-HT process in presence of glucose (MW-HT carbonization) followed by heating at 700 °C for 1 hour.

The MW-ST method offers smaller size nanorods (25 ± 6 nm width and up to 100 nm length) compared to the MW-HT method (225 ± 6 nm width and up to 300 nm length). Annealing at 700 °C improves the rate capability and cyclability without significant particle growth due to the

structural order of carbon and electronic conductivity. Moreover, the LiFePO₄/C nanocomposite obtained by the MW-ST method offers higher initial discharge capacity than that obtained by the MW-HT method due to a smaller particle size, illustrating that both lithium ion diffusion and electronic conductivity play a critical role in controlling the electrochemical properties.

- 5 The present invention provides a low cost manufacturing process that offers high performance nanostructured phospho-olivine cathodes in a consistent and reliable manner without requiring rigorous quality check during the manufacturing process. Specifically, the invention focuses on the preparation of nanostructured Li_xM_yPO₄, where 0 < x ≤ 1.2, 0.8 ≤ y ≤ 1.2, and M is at least one element selected from the group consisting of Fe, Mn, Co, Ti, Ni, Cu, V, Mo, Zn, Mg, Cr, Al, Ga, B, Zr and Nb [or] combinations thereof, by a simple microwave-solvothermal process and a coating of the product obtained by electronically conductive additives.
- 10

In addition, the present invention provides a simple, clean process involving low temperatures and short reaction times without requiring any post heat treatment process in inert or reducing gas atmospheres, while offering significant energy and cost savings. Moreover, the present 15 invention provides a low cost manufacturing process to produce high quality nanocrystalline cathode powder in a consistent and reliable manner with good control on particle size and distribution, while providing materials with high electronic and ionic conductivities needed for high power applications.

The present invention includes a nanostructured phospho-olivine composition having the olivine 20 Li_xM_yPO₄ structure. M is one or more elements selected from the group consisting of Fe, Mn, Co, Ti, Ni, Cu, V, Mo, Zn, Mg, Cr, Al, Ga, B, Zr, Nb or combination thereof and x is between 0 and 1.2 and y is between 0.8 and 1.2. The composition may also have the phospho-olivine Li_xFe_{1-y}M_yPO₄, wherein x is between 0 and 1, y is between 0 and 1.

In addition, the present invention also provides a method of making a nanostructured phospho-25 olivine cathode materials by dissolving lithium hydroxide and one or more metal salts, adding H₃PO₄ to the lithium hydroxide and the one or more metal salts to form a precursor solution with a 1:1:1 molar ratio of Li:M:P, heating solvothermally the precursor solution with a microwave irradiated synthesis system, and separating a LiMPO₄ material from the precursor solution. The one or more metal salts may be Fe, Mn, Co, Ti, Ni, Cu, V, Mo, Zn, Mg, Cr, Al, Ga, B, Zr, Nb or 30 combination thereof. The polymer may be an electronically conductive polymer, a doped polymer, an electronically and ionically conductive polymer, or a combination thereof, e.g., polypyrrole, polyaniline, polythiophene, poly-p-phenylene vinylene, poly(alkyl and

alkoxythiophenes) such as poly(3,4-ethylenedioxythiophene) (PEDOT) and their substituted derivatives.

The present invention also include a method of making a doped nanostructured phospho-olivine materials by dissolving lithium hydroxide, iron (II) salt and one or more metal salts, adding

- 5 H_3PO_4 to the lithium hydroxide and the one or more metal salts to form a precursor solution with a 1:1:1 molar ratio of Li : Fe(M) : P, heating solvothermally the precursor solution with a microwave irradiated synthesis system and separating a $\text{Li}_x\text{Fe}_{1-y}\text{M}_y\text{PO}_4$ material from the precursor solution. The polymer may be an electronically conductive polymer, a doped polymer or a combination thereof (e.g., polypyrrole, polyaniline, polythiophene, poly-p-phenylene
10 vinylene, poly(alkyl and alkoxythiophenes) such as poly(3,4-ethylenedioxythiophene) (PEDOT) and their substituted derivatives).

A method of making a nanostructured phospho-olivine hybrid composition by combining a polymer with a nanostructured phospho-olivine. The nanostructured phospho-olivine is formed by dissolving a lithium hydroxide complex and one or more metal salts, adding H_3PO_4 to the

- 15 lithium hydroxide complex and the one or more metal salts to form a precursor solution with a 1:1:1 molar ratio of Li : M : P, heating solvothermally the precursor solution with a microwave irradiated synthesis system, and separating the LiMPO_4 nanostructured phospho-olivine material from the precursor solution.

Description of the Drawings

- 20 For a more complete understanding of the features and advantages of the present invention, reference is now made to the detailed description of the invention along with the accompanying figures and in which:

FIGURE 1 is an image of the results of X-ray diffraction analysis of LiFePO_4 nanorods (or nanosheets) prepared by the microwave-solvothermal method of the present invention;

- 25 FIGURE 2 is an image of the XRD pattern after encapsulating the LiFePO_4 nanorods at room temperature within the mixed electronically and ionically conducting *p*- Toluene sulfonic acid (*p*-TSA) doped poly(3,4-ethylenedioxythiophene) (PEDOT) to form an organic-inorganic nanohybrid;

- 30 FIGURE 3 is an image of the XRD pattern of LiFePO_4 coated with carbon by firing at 700 °C for 1 hour;

FIGURE 4A is an SEM images of LiFePO₄ prepared by microwave-solvothermal process that has a nanoflower-like morphology and FIGURE 4B is an SEM image after encapsulating the LiFePO₄ nanorods at room temperature within the mixed electronically and ionically conducting *p*-TSA doped poly(3,4-ethylenedioxythiophene) (PEDOT) to form an organic-inorganic 5 nanohybrid;

FIGURES 5A, 5B and 5C are TEM images of LiFePO₄ nanorods prepared by the microwave-solvothermal method, and FIGURE 5D is a TEM image of LiFePO₄ nanorods encapsulated within the *p*-TSA doped PEDOT polymer;

FIGURE 6 shows TEM images of LiFePO₄ after encapsulating by electronically conducting 10 multi-walled carbon nanotubes (MWCNT) at room temperature;

FIGURE 7 is a plot comparing the first charge-discharge profiles of LiFePO₄ nanorods prepared by the microwave-solvothermal method and after encapsulating the LiFePO₄ nanorods within *p*-TSA doped-PEDOT at C/15 rate between 4.3 and 2.0 V. The inset shows the corresponding cycle life data;

15 FIGURE 8 is a plot comparing the first charge-discharge profiles of LiFePO₄ nanorods prepared by the microwave-solvothermal method and after encapsulating the LiFePO₄ nanorods within multi-walled carbon nanotubes (MWCNT) at C/15 rate between 4.3 and 2.0 V. The inset shows the corresponding cycle life data;

FIGURE 9 is a plot comparing the first charge-discharge profiles of LiFePO₄ nanorods prepared 20 by the microwave-solvothermal method and after encapsulating the LiFePO₄ nanorods within carbon at C/15 rate between 4.3 and 2.0 V. The inset shows the corresponding cycle life data;

FIGURE 10 is a plot comparing the first charge-discharge profiles of LiFePO₄ and LiFe_{0.95}Zn_{0.05}PO₄ nanorods prepared by the microwave-solvothermal method at C/15 rate between 4.3 and 2.0 V. The inset shows the corresponding cycle life data;

25 FIGURE 11A is a graph that compares the cyclability and FIGURE 11B is a graph that compares the rate capability of LiFePO₄ nanorods synthesized by the microwave-solvothermal method and after encapsulating the LiFePO₄ nanorods within *p*-TSA doped-PEDOT;

FIGURE 12 is a plot comparing the rate capability of LiFePO₄ nanorods prepared by the microwave-solvothermal method and after encapsulating the LiFePO₄ nanorods within multi-30 walled carbon nanotubes (MWCNT);

FIGURE 13 is a plot comparing the rate capability of LiFePO₄ nanorods prepared by the microwave-solvothermal method and after encapsulating the LiFePO₄ nanorods within carbon;

FIGURE 14 is a plot comparing the rate capability of pristine LiFePO₄ and LiFe_{0.95}Zn_{0.05}PO₄ electrodes;

5 FIGURE 15 is a schematic of the one pot synthesis of LiFePO₄/C nanocomposite by a microwave assisted hydrothermal (MW-HT) process involving hydrothermal carbonization of glucose;

FIGURES 16A and 16B are plots of the XRD patterns of synthesized LiFePO₄/C nanocomposite obtained by the facile one step microwave-hydrothermal process (about 15 minutes) and the

10 LiFePO₄/C nanocomposite after heating at 700 °C for 1 hour in 2 % H₂ – 98 % Ar, respectfully; FIGURE 16C is a Raman spectrum of the LiFePO₄/C nanocomposite;

FIGURES 17A and 17B are TEM images of LiFePO₄/C nanocomposite;

FIGURES 18A and 18B are discharge profiles of LiFePO₄/C nanocomposite obtained by the one step microwave-hydrothermal carbonization method, before and after heat treating, respectively;

15 FIGURE 19 is a graph of the cyclability data for the as-synthesized LiFePO₄/C sample, which exhibits some capacity fade, while the annealed sample exhibits excellent capacity retention;

FIGURE 20 is an illustration of the microwave-hydrothermal (MW-HT) and microwave-solvothermal (MW-ST) synthesis processes;

FIGURES 21A and 21B show the XRD patterns of the as-synthesized LiFePO₄ obtained by the
20 microwave irradiated solvothermal (MW-ST) method;

FIGURES 22A-22D shows the XRD patterns of the LiFePO₄ and LiFePO₄/C nanocomposite prepared by the MW-HT method shown in FIGURE 20B;

FIGURES 23A and 23B show the SEM images of the as-synthesized LiFePO₄ obtained by the
25 MW-ST method and the LiFePO₄/C composite obtained by a subsequent *ex situ* coating of carbon on LiFePO₄. FIGURES 23C and 23D show the SEM images of the as-synthesized LiFePO₄/C nanocomposite obtained by the MW-HT method with glucose and the product obtained after subsequent heating;

FIGURE 24 is a TEM image that demonstrates the well-defined crystalline nanorod morphologies with controlled size of the LiFePO₄/C nanocomposites;

30 FIGURES 25A-25C are graphs that show the Raman spectra of as-synthesized LiFePO₄.

FIGURES 26A and 26B are graphs of the electrochemical properties of the LiFePO₄ and LiFePO₄/C nanocomposite;

FIGURES 27A and 27B are graphs that compare the first charge-discharge profiles recorded at C/10 rate between 2.0 and 4.3 V and the cyclability of the as-synthesized LiFePO₄ obtained by
5 the MW-HT method;

FIGURES 28A and 28B are graphs that compare the rate capabilities of the as-synthesized LiFePO₄ nanorods obtained by the MW-ST method and LiFePO₄/C nanocomposite obtained by an *ex situ* carbon coating of the MW-ST LiFePO₄ nanorods by heating with sucrose;

FIGURES 29A, 29B and 29C are graphs that compare the rate capabilities of the LiFePO₄
10 nanorods obtained by the MW-HT method followed by heating, as-synthesized LiFePO₄/C nanocomposite obtained by an *in situ* carbon coating with glucose during the MW-HT process, and after heating the LiFePO₄/C nanocomposite in FIGURE 29B at 700 °C for 1 hour in a flowing 2 % H₂ – 98 % Ar atmosphere;

FIGURE 30 is a graph that compare the rate capabilities of LiFePO₄/C nanocomposite obtained
15 by an *ex situ* carbon coating of the MW-ST LiFePO₄ nanorods by heating with sucrose and LiFePO₄/C nanocomposite obtained by an *in situ* carbon coating with glucose during the MW-HT process, followed by heating;

FIGURE 31 are images of the product at various stages of the MW-ST process to produce nano LiMPO₄ (M= Mn, Fe, Co, Ni) and subsequent nanocomposite formation with MWCNT at
20 ambient temperatures;

FIGURE 32 is a graph of the XRD patterns of the nano LiMPO₄ (M= Mn, Fe, Co, Ni) prepared by the MW-ST method within 5 to 15 minutes at 300°C;

FIGURES 33A, 33B, 33C and 33D are TEM images of LiMPO₄ (M= Mn, Fe, Co, Ni) nanosheets prepared by the MW-ST method within 5 to 15 minutes at 300°C at higher
25 magnification; and

FIGURES 34A, 34B, 34C, 34D, 34E and 34F are graphs that compare the discharge capacity at various C-rates of the LiMPO₄ (M = Mn, Co, Ni) nanosheets before and after networking with MWCNT.

Description of the Invention

While the making and using of various embodiments of the present invention are discussed in detail below, it should be appreciated that the present invention provides many applicable inventive concepts that can be embodied in a wide variety of specific contexts. The specific embodiments discussed herein are merely illustrative of specific ways to make and use the

5 invention and do not delimit the scope of the invention.

To facilitate the understanding of this invention, a number of terms are defined below. Terms defined herein have meanings as commonly understood by a person of ordinary skill in the areas relevant to the present invention. Terms such as "a", "an" and "the" are not intended to refer to only a singular entity, but include the general class of which a specific example may be used for

10 illustration. The terminology herein is used to describe specific embodiments of the invention, but their usage does not delimit the invention, except as outlined in the claims.

The present invention provides a fast, low cost method to produce high performance nanostructured phospho-olivines by a novel microwave-solvothermal method. The process offers highly crystalline nanostructured LiFePO₄ within short time frames (e.g., 15 minutes or

15 less) and at temperatures as low as 300°C without any further heating in a furnace or in reducing atmospheres. The present invention also provides enhancements to the capacity and rate capability of pristine LiFePO₄ by doping with a number of cations and coating with electronically conducting additives such as carbon, multi-walled carbon nanotubes (MWCNT), and conjugated polymers. The capacity retention and power capability increase with decreasing

20 particle size, cation doping, and the incorporation of electronically conductive additives. The phospho-olivines and phospho-olivine based hybrid cathodes exhibit superior capacity retention, high rate (power) capability, and excellent storage characteristics compared to the conventional spinel LiMn₂O₄ and layered LiCoO₂cathodes.

Lithium-ion batteries have revolutionized the portable electronics market, but the high cost,

25 limited power capability, and safety concerns associated with the LiCoO₂ cathode remain to be an impediment to develop the lithium ion technology for transportation applications. In this regard, the phospho-olivine LiFePO₄ has attracted considerable attention in recent years as Fe is inexpensive and environmentally benign and the covalently bonded PO₄ groups offer excellent safety [Arico, A.S., Bruce, P., Scrosati, B., Tarascon, J.M., & van Shalk-wijk, W. Nanostructured

30 materials for advanced energy conversion and storage devices. *Nature Mater.* **4**, 366 - 377 (2005); Herle, P. S., Ellis, B., & Nazar, L. F. Nano-network conduction in olivine phosphates. *Nature Mater.* **3**, 147 - 152 (2004)].

The major drawback with LiFePO₄ is the poor lithium ion and electronic conductivity, resulting in inherently poor power capability [Chung, S.-Y., Bloking, J. T. & Chiang, Y.-M. Electronically conductive phospho-olivines as lithium storage electrodes. *Nature Mater.* 2, 123 – 128 (2002); Ellis, B., Perry, L. K., Ryan, D. H. & Nazar, L. F. Small polaron hopping in Li_xFePO₄ solid 5 solutions: Coupled lithium-ion and electron mobility. *J. Am. Chem. Soc.* 128, 11416 – 11422 (2006)]. This difficulty has been overcome in recent years by decreasing the lithium diffusion length via nanosize particles and increasing the electronic conductivity by a coating of the particles with conductive species like carbon. However, considering the multiple steps involved and post annealing treatments at > 600°C in reducing atmospheres, manufacturing of nanosize 10 LiFePO₄ with controlled particle size and uniform properties in a consistent and cost-effective manner for large volume applications will be a serious scientific challenge. The present inventors provide a method for the rapid microwave-solvothermal synthesis of nanostructured LiFePO₄ within 15 minutes at temperatures as low as 300°C without requiring any post heating in a furnace or reducing gaseous atmosphere. Subsequent ambient-temperature coating of the 15 nanosize LiFePO₄ with mixed electronically and ionically conducting doped poly(3,4-ethylenedioxythiophene) (PEDOT) offers 95% of the theoretical capacity with excellent cyclability and power capability.

While highly oxidized redox couples such as Co^{3+/4+} and Ni^{3+/4+} are generally desired in simple oxides like LiCoO₂ to maximize the cell voltage, they invariably lead to chemical instability and 20 safety concerns. Recognizing this, oxides with polyanions like (XO₄)²⁻ (X = S, Mo, and W) were first initiated by Manthiram and Goodenough [Manthiram, A. & Goodenough, J. B. Lithium Insertion into Fe₂(MO₄)₃ Frameworks: Comparison of M = W with M = Mo *J. Solid State Chem.* 71, 349-360 (1987); Manthiram, A. & Goodenough, J. B. Lithium Insertion into Fe₂(SO₄)₃-type Frameworks. *J. Power Sources* 26, 403-406 (1989)] as lithium 25 insertion/extraction hosts in the late 1980's since the covalently bonded groups like (SO₄)²⁻ can lower the redox energies of lower valent, chemically more stable couples like Fe^{3+/4+} through inductive effect and increase the cell voltage. Following this, the phospho-olivine LiFePO₄ consisting of a hexagonal close-packed oxygen framework with edge-shared LiO₆ octahedra, corner-shared FeO₆ octahedra, and PO₄ tetrahedra was identified as a cathode by Padhi *et al* 30 [Padhi, A.K., Nanjundasawamy, K.S., & Goodenough, J.B., Phospho-olivines as positive electrode materials for rechargeable lithium batteries. *J. Electrochem. Soc.*, 144, 1188 - 1194 (1997)] in 1997. The one-dimensional chains formed by the edge-shared LiO₆ octahedra along the *b*-axis of the orthorhombic structure lead to poor lithium ion conductivity. On the other hand,

the little or limited solubility between LiFePO₄ and FePO₄ and the localized Fe²⁺ or Fe³⁺ lead to poor electronic conductivity. The inferior lithium ion and electronic conductivities result in poor utilization of the available capacity and limited power capability, a performance parameter critical for vehicle applications.

5 Consequently, tremendous efforts have been made to overcome the electronic and ionic transport limitations by cationic doping, decreasing the particle size, and coating with electronically conducting agents [Wang, C., & Hong, J., Ionic / Electronic conducting characteristics of LiFePO₄ cathode materials, *Electrochem. Solid - State Lett.* **10**, A65–A69 (2007); Delacourt, C., Poizot, P., Levasseur, S. & Masquelier, C. Size effects on carbon-free LiFePO₄ powders: The
10 key to superior energy density. *Electrochem. Solid-State Lett.* **9**, A352 – A355 (2006)]. In particular, the aliovalent doping (e.g. Zr⁴⁺ and Nb⁵⁺) reported by Chung *et al.* [Chung, S.-Y., Bloking, J. T. & Chiang, Y.-M. Electronically conductive phospho-olivines as lithium storage electrodes. *Nature Mater.* **2**, 123 – 128 (2002)] to increase the conductivity by several orders of magnitude has stimulated considerable interest and controversy in the field. Nanosize LiFePO₄
15 coated with electronically conductive carbon has recently been shown to exhibit high power capability, and there is enormous worldwide interest to develop the phospho-olivines for hybrid electric vehicle applications. Nanosize LiFePO₄ has been synthesized by soft chemistry procedures such as precipitation, sol-gel, refluxing, and hydrothermal methods as they provide intimate mixing of the component elements in solution, allowing the formation finer particles by
20 rapid homogeneous nucleation of LiFePO₄.

However, these methods often involve longer reaction times to realize the formation of well crystalline phase. More importantly, they require post heat-treatment processing at temperatures as high as 700°C in reducing atmospheres (e.g. 5 % hydrogen) for longer periods of time (about 24 hours) to achieve high degree of crystallinity and coating with conductive carbon. Such
25 tedious processes not only increase the manufacturing cost and lead to unwanted particle growth, but may also necessitate strict quality check involving additional cost during large volume production needed for automotive applications.

In this regard, microwave synthesis is appealing as it involves short reaction times, providing cost savings [Rao, K. J., Vaidhyanathan, B., Ganguli, M., & Ramakrishnan, P. A. Synthesis of
30 Inorganic Solids Using Microwaves, *Chem. Mater.* **11**, 882 - 895 (1999); Vadivel Murugan, A., Kwon, C.W., Campet, G., Kale, B.B., Mandale, A. B., Sainker, S.R., Gopinath, C.S. & Vijayamohanan, K. A novel approach to prepare poly (3,4-ethylenedioxothiophene) nanoribbons

between V₂O₅ layers by microwave irradiation. *J. Phys. Chem. B*, 108, 10736 – 10742 (2004)]. Recently, Higuchi *et al.* [Higuchi, M., Katayama, K., Azuma, Y., Yukawa, M. & Suhara, M. Synthesis of LiFePO₄ cathode material by microwave processing, *J. Power Sources*, 119-121, 258-261 (2003)] and Wang *et al.* [Wang, L., Huang, Y., Jiang, R. & Jia, D. Preparation and 5 characterization of nano-sized LiFePO₄ by low heating solid-state coordination method and microwave heating, *Electrochim Acta*, 52, 6778 - 6783 (2007)] have pursued the microwave irradiation of mixtures consisting of the solid-state precursors to obtain LiFePO₄. One of the problems with such a process is the oxidation of Fe²⁺ to Fe³⁺, which could be controlled by conducting the microwave heating under an inert gas flow or by coating the raw materials with 10 activated carbon or carbonaceous substance [Park, K. S., Son, J. T., Chung, H. T., Kim, S. J., Lee, C. H. & Kim, H. G. Synthesis of LiFePO₄ by co-precipitation and microwave heating, *Electrochim Comm.* 5, 839 - 842 (2003)]. However, while the former is cumbersome, the latter leaves a lot of carbon residue. More importantly, the initial discharge capacity was much lower 15 (125 mAh/g) than the theoretical capacity (170 mAh/g) with some capacity fade. The present inventors invented a novel microwave-solvothermal approach in a non-aqueous solvent medium as well as an aqueous solvent medium to obtain well-defined nanoparticles of LiFePO₄ with high crystallinity in a short time (5 - 15 minutes) at temperatures as low as 300°C without requiring any inert atmosphere or post annealing at elevated temperatures in reducing gas atmospheres. The use of nonaqueous medium helps to prevent the hydrolysis of Fe²⁺ to Fe³⁺ and formation of 20 impurity phases containing Fe³⁺.

FIGURE 1 is an image of the XRD patterns of LiFePO₄ nanorods obtained by the microwave-solvothermal method and FIGURE 2 is an image of the XRD patterns after encapsulating the LiFePO₄ nanorods within the mixed electronically and ionically conducting *p*-TSA doped poly(3,4-ethylenedioxythiophene) (PEDOT) to form an organic-inorganic nanohybrid. The 25 crystal structure of LiFePO₄ and PEDOT coated LiFePO₄ are also indicated. FIGURE 3 is an image of the XRD pattern of LiFePO₄ coated with carbon by firing at 700 °C for 1 hour.

The use of a highly viscous, high boiling tetraethylenegycol (TEG) as a non-aqueous solvent provides a reducing environment to prevent the oxidation of Fe²⁺ and offers phase-pure nanocrystalline LiFePO₄ free from water contamination. In addition, TEG acts as a stabilizer, 30 limiting particle growth and prohibiting agglomeration. The XRD pattern shown in FIGURE 1 demonstrates the formation of highly crystalline LiFePO₄ without any detectable impurity phases such as Li₃PO₄ or Li₃Fe₂(PO₄)₃, which often appear in the traditional high temperature (800°C) synthesis and microwave irradiated solid-state reaction methods [Higuchi, M.,

Katayama, K., Azuma, Y., Yukawa, M. & Suhara, M. Synthesis of LiFePO₄ cathode material by microwave processing, *J. Power Sources*, 119-121, 258-261 (2003)]. All the reflections in FIGURE 1 could be indexed on the basis of an orthorhombic olivine-type structure, and Rietveld refinement of the XRD data with the *Pnma* space group gives $a = 10.320(1)$, $b = 6.000(1)$, and $c = 4.697(1)$ Å, which are in good agreement with the literature values [Andersson, A. S., Kalska, B., Häggström, L. & Thomas, J. O. Lithium extraction/ insertion in LiFePO₄: an X-ray diffraction and Mössbauer spectroscopy study, *Solid State Ionics*, 130, 41 – 52 (2000)]. The analysis of the XRD data with the Scherrer equation indicated an average crystallite size value of about 42 nm.

FIGURE 4A is an SEM images of LiFePO₄ prepared by microwave-solvothermal process that has a nanoflower-like morphology and FIGURE 4B is an SEM image after encapsulating the LiFePO₄ nanorods at room temperature within the electronically and ionically conducting doped poly(3,4-ethylenedioxythiophene) (PEDOT) to form an organic-inorganic nanohybrid.

FIGURES 5A, 5B and 5C are TEM images of LiFePO₄ nanorods prepared by the microwave-solvothermal method, and FIGURE 5D shows the LiFePO₄ nanorods encapsulated within the *p*-TASA doped PEDOT polymer. The nanocrystals show relatively uniform rod-like morphology with an average width of 40 nm and a length of few microns with a narrow size distribution.

The high resolution transmission electron microscopy (HRTEM) images shown in FIGURE 5B and 5C reveal well-defined crystalline nanorod morphology. The microstructure indicates a relatively uniform rod like morphology with an average width of 40 nm and a length of few microns and a narrow particle size distribution. These results are consistent with the XRD crystallite size data. The HRTEM lattice fringe shown in FIGURE 5C demonstrates the high crystalline nature of LiFePO₄ prepared by the microwave-solvothermal method. The highly crystalline nanorods obtained by the microwave-solvothermal method in a short time is appealing as most of the literature methods tend to produce poorly crystalline nanoparticles in the as-prepared stage or much larger size submicron particles following the post-heating process used to improve crystallinity and achieve carbon coating. Energy dispersive spectroscopic analysis of the LiFePO₄ nanocrystals indicated a Fe:P ratio of 1:1. FIGURE 6 shows TEM images of LiFePO₄ after encapsulating by electronically conduced multi-walled carbon nanotubes (MWCNT) at room temperature

FIGURE 7 is a plot comparing the first charge-discharge profiles of LiFePO₄ nanorods prepared by the microwave-solvothermal method and after encapsulating the LiFePO₄ nanorods within

doped-PEDOT at C/15 rate between 4.3 and 2.0 V. The inset shows the corresponding cycle life data. FIGURE 7 and FIGURE 11(a) show the first charge-discharge profile and cyclability of the LiFePO₄ sample prepared by the microwave-solvothermal method. The as-prepared sample exhibits a discharge capacity of 135 mAh/g at C/15 rate in the voltage range of 2.0 – 4.3 V with 5 a significant voltage difference between the charge and discharge curves and capacity fade.

Recognizing that the polarization loss could be due to the lack of adequate electronic and ionic conductivity and to avoid any high temperature post-annealing process normally involved with carbon coating, in one embodiment the present invention focuses on an ambient temperature coating of the LiFePO₄ nanorods with an electronically and ionically conducting polymer. Poly 10 (3,4-ethylenedioxythiophene) (PEDOT) is an attractive conducting polymer due to its high environmental stability, superior thermal stability, redox behavior over a wide range of potentials, and high electronic conductivity in its doped state compared to other commonly available conducting polymers [Han, M.G & Armes, S. P. Synthesis of poly (3, 4-ethylenedioxythiophene) / Silica Colloidal Nanocomposites. *Langmuir*, 19, 4523- 4526 (2003)]. 15 It has also been demonstrated that doped PEDOT (e.g. poly (styrene-4-sulphonate) doped PEDOT) has mixed electronic as well as ionic conductivity [Li, G & Pickup, P.G. Ion transport in poly (3,4-ethylenedioxythiophene)-poly(styrene-4-sulfonate) composite, *Phys. Chem. Chem. Phys.*, 2 , 1255-1260 (2000)].

The synergistic effects that could be provided by the electrochemically active PEDOT make it a 20 promising candidate to be used as an electronically and ionically conductive additive for energy storage applications such as lithium batteries and supercapacitors [Vadivel Murugan, A., Viswanath, A.K., Gopinath, C.S., & Vijayamohanan, K. Highly efficient organic-inorganic poly (3, 4- ethylenedioxythiophene) – molybdenum trioxide nanocomposite electrodes for electrochemical supercapacitor. *J. Appl. Phys*, 100, 0743191-0743193 (2006)]. Moreover, while 25 carbon coating by the high temperature post-annealing processes can result in non- continuous coating of the LiFePO₄ particles, the use of an electronically conducting polymer like PEDOT with better wetting properties can provide uniform coating.

Accordingly, the LiFePO₄ nanorods obtained by the microwave-solvothermal process were 30 coated with 8 wt. % *p*-toluene sulfonic acid (*p*-TSA) doped PEDOT at ambient temperature without any post annealing to obtain an organic-inorganic nanohybrid. The XRD pattern of the LiFePO₄–PEDOT nanohybrid shown in FIGURE 2 indicates that the nano-crystalline nature of LiFePO₄ is maintained without any diffraction peaks for PEDOT, possibly due to its low content.

The TEM image of the LiFePO₄-PEDOT nanohybrid shown in FIGURE 5D reveals the encapsulation of the LiFePO₄ nanorods (dark region) by PEDOT (grayish transparent region). The encapsulating doped PEDOT provides an electronically and ionically conducting nano-network without blocking the lithium ion diffusion between the adjacent LiFePO₄ nanorods.

- 5 FIGURE 8 is a plot comparing the first charge-discharge profiles of LiFePO₄ nanorods prepared by the microwave-solvothermal method and after encapsulating the LiFePO₄ nanorods within multi-walled carbon nanotubes (MWCNT) at C/15 rate between 4.3 and 2.0 V. The inset shows the corresponding cycle life data. FIGURE 9 is a plot comparing the first charge-discharge profiles of LiFePO₄ nanorods prepared by the microwave-solvothermal method and after
10 encapsulating the LiFePO₄ nanorods within carbon at C/15 rate between 4.3 and 2.0 V. The inset shows the corresponding cycle life data. FIGURE 10 is a plot comparing the first charge-discharge profiles of LiFePO₄ and LiFe_{0.95}Zn_{0.05}PO₄ nanorods prepared by the microwave-solvothermal method at C/15 rate between 4.3 and 2.0 V. The inset shows the corresponding cycle life data.
- 15 FIGURE 11A is a graph comparing the cyclability and FIGURE 11B is a graph comparing the rate capability of LiFePO₄ nanorods synthesized by the microwave-solvothermal method and after encapsulating the LiFePO₄ nanorods within *p*-TSA doped-PEDOT. The cyclability of doped PEDOT is also shown in FIGURE 11A.

The charge-discharge profile shown in FIGURE 7 reveals that the LiFePO₄-PEDOT nanohybrid
20 exhibits a high discharge capacity (166 mAh/g) close to that of the theoretical value (170 mAh/g) with little difference between the charge and discharge curves. The data in FIGURE 11A demonstrate excellent cyclability with about 3 % fade in 50 cycles for the LiFePO₄-PEDOT nanohybrid. The remarkable electrochemical performance of the LiFePO₄-PEDOT nanohybrid compared to as-synthesized LiFePO₄ can be attributed to the mixed electronic-ionic conductivity
25 of PEDOT. More importantly, the doped PEDOT exhibits a capacity of about 40 mAh/g with good cyclability in the voltage range of 2.5 – 4.0 V vs Li⁺/Li as seen in FIGURE 11A, illustrating the redox behavior and the synergistic effect that could be provided by PEDOT compared to the redox inactive carbon coating.

FIGURE 11B is a graph that compares the rate (power) capability of pristine LiFePO₄ and the
30 LiFePO₄-PEDOT nanohybrid at C/10 to 5C rates. The LiFePO₄-PEDOT nanohybrid exhibits superior power capability compared to the pristine LiFePO₄. The significantly improved electrochemical performances of the LiFePO₄-PEDOT nanohybrid compared to the pristine

LiFePO₄ is due to the synergistic effects provided by the electronically and ionically conducting doped PEDOT. The results demonstrate a cost effective, rapid method to manufacture high performance phospho-olivine cathodes for high volume applications such as hybrid electric vehicles and plug-in hybrid vehicles.

- 5 FIGURE 12 is a plot comparing the rate capability of LiFePO₄ nanorods prepared by the microwave-solvothermal method and after encapsulating the LiFePO₄ nanorods within multi-walled carbon nanotubes (MWCNT). FIGURE 13 is a plot comparing the rate capability of LiFePO₄ nanorods prepared by the microwave-solvothermal method and after encapsulating the LiFePO₄ nanorods within carbon. FIGURE 14 is a plot comparing the rate capability of pristine
10 LiFePO₄ and LiFe_{0.95}Zn_{0.05}PO₄ electrodes.

Method of microwave-solvothermal synthesis of nano-LiFePO₄: Lithium hydroxide (Fisher) and iron (II) acetate (Alfa Aesar) were first dissolved in tetraethyleneglycol (TEG) (ACROS-Organics), and H₃PO₄ (85%, Fisher) was then added dropwise to the TEG solution at room temperature to realize a Li: Fe: P molar ratio of 1:1:1. The homogeneous, yellow gel formed was
15 transferred into quartz vessel and placed on a turntable for uniform heating in an Anton Paar microwave irradiated synthesis system (Synthos-3000). The system was operated at a frequency of 2.45 GHz and a power of 1,000 W, and the temperature was raised to 300°C and maintained for 15 minutes. These vessels were transparent to microwave radiation, so the contents in these vessels could be heated solvothermally. When the reaction mixture was exposed to microwave
20 radiation, the microwave induced rotation of the dipoles within the liquid force the polar molecules to align and relax in the field of oscillating electromagnetic radiations and cause the liquid to become hot. Thus, the heat produced within the liquid is not transferred from the vessel unlike in other conventional systems. Precipitation of LiFePO₄ took place inside the reactor during this solvothermal process, and the reactor was cooled to room temperature after the
25 solvothermal process. The supernatant TEG solvent was carefully decanted, and the resulting cream-white LiFePO₄ nanocrystals were washed repeatedly by centrifugation with a mixture of acetone and methanol until the washings were colorless to ensure the complete removal of TEG. The obtained powder was then dried at 80°C for 1 hour in a vacuum oven.

Synthesis of *p*-toluenesulfonic acid (*p*-TSA) doped poly (3,4-ethylenedioxothiophene): The
30 electronically and ionically conductive *p*-TSA doped poly(3,4-ethylenedioxothiophene) (PEDOT) was prepared via oxidative chemical polymerization. Since the 3,4-ethylenedioxothiophene (EDOT) monomer (Aldrich) is only slightly soluble in water and

exhibits high oxidation potential for the polymerization to occur easily, the solubility of EDOT was controlled by mixing methanol with de-ionized water and *p*-toluenesulfonic acid (*p*-TSA), (Spectrum). The *p*-TSA organic acid is known as a good dopant for highly conducting PEDOT and it confers an increased solubility of EDOT in water, possibly due to the enhanced 5 protonation of EDOT. Appropriate quantities of *p*-TSA and EDOT monomer were added to a mixture of methanol and water (1:1 by volume), and the polymerization reaction was initiated by adding under constant stirring the oxidant, ammonium persulfate (Fisher) dissolved in minimum amount of water; the molar ratio of EDOT and ammonium persulfate was 1:1. After 24 hours of the polymerization reaction at 30°C, the supernatants were carefully decanted, and the resulting 10 dark blue conducting PEDOT was washed several times with a 1:1 mixture of methanol and water until the washings were colorless to ensure the complete removal of the unreacted monomer and oxidant. The *p*-TSA doped PEDOT thus obtained was then dispersed in ethanol to form a colloidal solution.

Synthesis of LiFePO₄ - doped PEDOT nanohybrid: An appropriate amount of the as-synthesized LiFePO₄ nanocrystals were mixed with ethanol and ultrasonicated for a few 15 minutes. The cream-white colored colloidal solution formed was then mixed with the dark blue colored colloidal solution containing *p*-PTSA doped PEDOT by magnetic stirring for a few minutes at room temperature to ensure complete encapsulation of the LiFePO₄ nanocrystals within the *p*-PTSA doped PEDOT to form an organic-inorganic nanohybrid, which was then 20 dried in a vacuum oven at 80°C. The weight ratio of LiFePO₄ and *p*-PTSA doped PEDOT was 92:8.

Materials characterization: The XRD data were collected with a Philips X-ray diffractometer and Cu K α radiation. The TEM data were collected with a JEOL JEM-2010F equipment by dispersing an ethanol suspension of the samples onto a holey carbon grid. Electrochemical 25 performances were evaluated with CR2032 coin cells at 4.3 - 2.0 V for LiFePO₄ and LiFePO₄-PEDOT hybrid and at 4.0 – 2.5 V for PEDOT with an Arbin battery cycler. The coin cells were fabricated with the LiFePO₄ or LiFePO₄ – PEDOT cathode, metallic lithium anode, 1 M LiPF₆ in 1:1 diethyl carbonate/ethylene carbonate electrolyte, and Celgard polypropylene separator. The cathodes were prepared by mixing 75 weight % active materials with 20 wt % conductive carbon 30 and 5 wt % polytetrafluoroethylene (PTFE) binder, rolling the mixture into thin sheets, and cutting into circular electrodes of 0.64 cm² area. The electrodes typically had an active material content of about 7 mg, and were dried under vacuum at 80°C for more than 3 hours before assembling the cells in an argon-filled glovebox.

Example 1: The present invention provides a simple, single step novel process based on microwave irradiated solvothermal reaction for the preparation of nanostructured phospho-olivine cathode materials for lithium secondary batteries. $\text{Li}_x\text{M}_y\text{PO}_4$ where $0 < x \leq 1.2$, $0.8 \leq y \leq 1.2$, and M is at least one element selected from the group consisting of Fe, Mn, Co, Ti, Ni, Cu,

- 5 V, Mo, Zn, Mg, Cr, Al, Ga, B, Zr, and Nb or combination thereof. The process involves first the dissolution of lithium hydroxide and metal salts like acetates, nitrates, or chlorides in tetraethyleneglycol, followed by an addition of H_3PO_4 drop-wise at room temperature so that the molar ratio of Li:M:P in the precursor solution is 1:1:1. The homogeneous, transparent yellow gel formed was transferred into quartz vessel and placed on a turntable for uniform heating in an
10 10 Anton Paar microwave irradiated synthesis system (Synthos-3000). The system was operated at a frequency of 2.45 GHz and a power of 1,000 W, and the temperature was raised to 300°C and maintained for 15 minutes. These vessels were transparent to microwave radiation, so the contents in these vessels could be heated solvothermally.

When the reaction mixture was exposed to microwave radiation, the microwave induced rotation
15 of the dipoles within the liquid forced the polar molecules to align and relax in the field of oscillating electromagnetic radiations and caused the liquid to become hot. Thus, the heat produced within the liquid is not transferred from the vessel unlike in other conventional systems. Precipitation of LiFePO_4 took place inside the reactor during this solvothermal process, and the reactor was cooled to room temperature after the solvothermal process. The supernatant

20 TEG solvent was carefully decanted, and the resulting cream-white LiFePO_4 nanocrystals were washed repeatedly by centrifugation with a mixture of acetone and methanol until the washings were colorless to ensure the complete removal of TEG. The obtained powder was then dried at 80°C for 1 hour in a vacuum oven and characterized by XRD, SEM, TEM, elemental analysis, and electrochemical measurements.

25 Example 2. The present invention provides a simple, single step novel process based on microwave irradiated solvothermal reaction for the preparation of nanostructured phospho-olivine cathode materials for lithium secondary batteries. Doped $\text{Li}_{x}\text{Fe}_{1-y}\text{M}_y\text{PO}_4$, where $0 < x \leq 1.2$, $0 < y \leq 1$, and M is at least one element selected from the group consisting of Mn, Co, Ti, Ni, Cu, V, Mo, Zn, Mg, Cr, Al, Ga, B, Zr, and Nb was prepared by first dissolving lithium
30 hydroxide and iron (II) and other metal salts like acetates, nitrates, and chlorides in tetraethyleneglycol, followed by adding H_3PO_4 drop-wise at room temperature so that the molar ratio of Li : Fe(M) : P in the precursor solution is 1:1:1. The homogeneous, transparent yellow gel formed was transferred into a quartz vessel and placed on a turntable for uniform heating in

an Anton Paar microwave irradiated synthesis system (Synthos-3000). The system was operated at a frequency of 2.45 GHz and a power of 1,000 W, and the temperature was raised to 300°C and maintained for 15 minutes.

These vessels were transparent to microwave radiation, so the contents in these vessels could be
5 heated solvothermally. When the reaction mixture was exposed to microwave radiation, the microwaves induced rotation of the dipoles within the liquid forced the polar molecules to align and relax in the field of oscillating electromagnetic radiations and caused the liquid to become hot. Thus, the heat produced within the liquid is not transferred from the vessel unlike in other conventional systems. Precipitation of LiFePO₄ took place inside the reactor during this
10 solvothermal process, and the reactor was cooled to room temperature after the solvothermal process. The supernatant TEG solvent was carefully decanted, and the resulting cream-white LiFePO₄ nanocrystals were washed repeatedly by centrifugation with a mixture of acetone and methanol until the washings were colorless to ensure the complete removal of TEG. The obtained powder was then dried at 80°C for 1 hour in a vacuum oven and characterized by XRD,
15 SEM, TEM, elemental analysis, and electrochemical measurements.

Example 3: An electronically and ionically conductive polymer such as polyaniline, polypyrrole, polythiophene, and substituted poly (3, 4-ethylenedioxothiophene) (PEDOT) was prepared via an oxidative chemical polymerization route. Since the 3, 4-ethylenedioxothiophene (EDOT) monomer (Aldrich) is only slightly soluble in water and exhibits high oxidation potential for the
20 polymerization to occur easily, the solubility of EDOT was controlled by mixing methanol with de-ionized water and by using *p*-toluenesulfonic acid (*p*-TSA), (Spectrum). The *p*-TSA organic acid is known as a good dopant for highly conducting PEDOT and it confers an increased solubility of EDOT in water, possibly due to the enhanced protonation of EDOT [Han, M.G & Armes, S. P. Synthesis of poly (3, 4- ethylenedioxothiophene) / Silica Colloidal
25 Nanocomposites. *Langmuir*, 19, 4523- 4526 (2003)].

Appropriate quantities of *p*-TSA and EDOT monomer were added to a mixture of methanol and water (1:1 by volume), and the polymerization reaction was initiated by adding under constant stirring the oxidant, ammonium persulfate dissolved in minimum amount of water; the molar ratio of EDOT and ammonium persulfate was 1:1. After 24 hours of the polymerization reaction
30 at 30°C, the supernatants were carefully decanted, and the resulting dark blue conducting PEDOT was washed several times with a 1:1 mixture of methanol and water until the washing

was colorless to ensure the complete removal of the unreacted monomer and oxidant. The *p*-TSA doped PEDOT thus obtained was then dispersed in ethanol to form a colloidal solution.

The nanostructured $\text{Li}_x\text{M}_y\text{PO}_4$ and $\text{Li}_{x-\gamma}\text{Fe}_{\gamma}\text{M}_y\text{PO}_4$ powders obtained by the microwave-

solvothermal method were then encapsulated within the electronically conductive polymer or

5 doped polymer (polypyrrole, polyaniline, polythiophene, poly-*p*-phenylene vinylene, PEDOT and their substituted derivatives) to obtain nanohybrids consisting of $\text{Li}_x\text{M}_y\text{PO}_4$ or $\text{Li}_{x-\gamma}\text{Fe}_{\gamma}\text{M}_y\text{PO}_4$ and the conductive polymer. The amount of the electronically conducting polymer varies from 0.1 wt % to 50 wt%. The obtained powder was characterized by XRD, SEM, TEM, elemental analysis, and electrochemical measurements.

10 Example 4: The nanostructured $\text{Li}_x\text{M}_y\text{PO}_4$ and $\text{Li}_{x-\gamma}\text{Fe}_{\gamma}\text{M}_y\text{PO}_4$ powders obtained by the microwave-solvothermal method were then encapsulated within electronically conducting multi-walled carbon nanotubes (MWCNT). MWCNT was refluxed with nitric acid at 80 °C for 10 hours and washed with distilled water until the pH value of the filtrate reached 7. MWCNT was ultrasonically dispersed in toluene for a few minutes, the pristine $\text{Li}_x\text{M}_y\text{PO}_4$ or $\text{Li}_{x-\gamma}\text{Fe}_{\gamma}\text{M}_y\text{PO}_4$

15 was added under constant magnetic stirring, and dried in an oven at 80 °C to form a LiFePO_4 -MWCNT or $\text{Li}_{x-\gamma}\text{Fe}_{\gamma}\text{M}_y\text{PO}_4$ -MWCNT nanohybrid. The amount of MWCNT varies from 0.1 wt% to 50 wt%.

Example 5: The nanostructured $\text{Li}_x\text{M}_y\text{PO}_4$ and $\text{Li}_{x-\gamma}\text{Fe}_{\gamma}\text{M}_y\text{PO}_4$ powders obtained by the microwave-solvothermal method were then encapsulated within electronically conducting 20 carbon. The nanostructured $\text{Li}_x\text{M}_y\text{PO}_4$ or $\text{Li}_{x-\gamma}\text{Fe}_{\gamma}\text{M}_y\text{PO}_4$ powders were mixed with an appropriate amount of sucrose solution in ethanol and the dried solid product was heated at 700 °C for 1 hour in 5 % hydrogen and about 95 % argon atmosphere to form a LiFePO_4 -carbon or $\text{Li}_{x-\gamma}\text{Fe}_{\gamma}\text{M}_y\text{PO}_4$ -carbon nanohybrid. The amount of carbon varies from 0.1 weight % to 50 weight %.

Example 6: The electrochemical performances were evaluated with CR2032 coin cells between 25 4.3 and 2.0 V. The coin cells were fabricated with the phospho-olivine based cathode, metallic lithium anode, 1 M LiPF₆ in 1:1 diethyl carbonate/ethylene carbonate electrolyte, and a Celgard polypropylene separator. The active material in the cathode was nanostructured $\text{Li}_x\text{M}_y\text{PO}_4$ or $\text{Li}_{x-\gamma}\text{Fe}_{\gamma}\text{M}_y\text{PO}_4$ or after encapsulating $\text{Li}_x\text{M}_y\text{PO}_4$ or $\text{Li}_{x-\gamma}\text{Fe}_{\gamma}\text{M}_y\text{PO}_4$ within an electronically 30 conducting polymer, MWCNT, or carbon. The cathodes were prepared by mixing 75 weight % active materials with 20 weight % conductive carbon and 5 weight % polytetrafluoroethylene (PTFE) binder, rolling the mixture into thin sheets, and cutting into circular electrodes of 0.64 cm² area. The electrodes typically had an active material content of about 7 mg, and were dried

under vacuum at 80 °C for more than 3 hours before assembling the cells in an argon-filled glovebox.

The present inventors discovered a microwave assisted synthesis approach to shorten the reaction time to a few minutes with significant energy savings while controlling the chemical composition, crystallite size, and particle shape.

The conventional hydrothermal process involves an extremely long reaction time (e.g., between 5 and 12 hours) to synthesize LiFePO₄ and *in-situ* coating of carbon on LiFePO₄ using carbon precursors during the hydrothermal process have been unsuccessful producing compositions with low rate capabilities. [K. Shiraishi, K. Dokko, K. Kanamura J. Power Sources 2005, 146, 555;

- 10 S. Franger, F. Le Cras, C. Bourbon and H. Rouanlt, J. Power Sources, 2003, 119–121, 252; S. Tajimi, Y. Ikeda, K. Uematsu, K. Toda and M. Sato, Solid State Ionics, 2004, 175, 287; J. Lee and A.S. Teja, Mater. Lett., 2006, 60, 2105; K. Dokko, S. Koizumi, K. Sharaishi and K. Kananura, J. Power Sources, 2007, 165, 656; G. Meligrana, C. Gerbaldi, A. Tuel, S. Bodoardo, N. Penazzi, J. Power Sources 2006, 160, 516; B. Jin, H. –B. Gu, Solid State Ionics 2008, 178, 15 1907; E. M. Jin, B. Jin, D. –K. Jun, K.-H. Park, H. –B. Gu, K.-W. Kim, J. Power Sources 2008, 178, 801; K. Dokko, K. Shiraishi, K. Kanamura, J. Electrochem. Soc., 2005, 152, 11 A2199.]

Recently, Beninati [S. Beninati, L. Damen and M. Mastragostino, J. Power Sources, 2008, 180, 875] and Wang [L. Wang, Y. Huang, R. Jiang and D. Jia, Electrochim Acta, 2007, 52, 6778] reported the microwave synthesis of LiFePO₄ by irradiating a mixture of the solid-state raw materials and microwave absorbants such as carbon or carbonaceous substance in a microwave oven. However, the compositions produced were questionable as the initial discharge capacity of the sample obtained was much lower (125 mAh/g) than the theoretical value (170 mAh/g), and they were unable to control the particle size with the microwave irradiated solid state reaction.

The present inventors developed a novel facile, one pot synthesis of carbon coated LiFePO₄ nanorods within a short time (e.g., 15 minutes) by a microwave assisted hydrothermal (MW-HT) method. The instant method uses microwave irradiation and the hydrothermal effect to prepare nanocrystalline materials. [I. Bilecka, I. Djerdj and M. Niederberger, Chem. Commun., 2008, 886; X. Hu and J. C. Yu, Adv. Funct. Mater., 2008, 18, 880; A Vadivel Murugan, A. Kasi Viswanath, B. A. Kakade, V. Ravi and V Saaminathan, Appl. Phys. Lett., 2006, 89, 123120.]

- 20 30 The instant method offers a drastic reduction in synthesis time (e.g., about 15 minutes) compared to the time consuming (e.g., between 5 and 24 hours), traditional refluxing [D. -H. Kim and J. Kim, Electrochem. Solid State Lett., 2006, 9, A439] or heating in a furnace or autoclave.[S.

Franger, F. Le Cras, C. Bourbon and H. Rouanlt, J. Power Sources, 2003, 119–121, 252; J. Lee and A.S. Teja, Mater. Lett., 2006, 60, 2105] The instant compositions provide an enhancement in electronic conductivity by a simultaneous *in situ* coating of a thin nanolayer of carbon on the LiFePO₄ nanorods *via* a hydrothermal carbonization of glucose during the synthesis process.

- 5 The hydrothermal carbonization of glucose not only acts as a reducing agent and offers an *in-situ* coating of carbon on LiFePO₄, but also helps to prevent the growth or agglomeration of the LiFePO₄ nanoparticles during the hydrothermal process. The LiFePO₄/C nanocomposite thus obtained by the microwave-hydrothermal process shows uniform carbon coating with high rate capability and excellent cyclability.
- 10 FIGURE 15 is a schematic representation of the microwave-hydrothermal process employed to prepare the LiFePO₄/C nanocomposite. A mixed aqueous solution 10 containing LiOH (Fisher), H₃PO₄ (85%, Fisher), and glucose was first stirred for a few minutes; glucose (0.5 mol L⁻¹) was added as an *in situ* reducing agent to minimize the oxidation of Fe²⁺ to Fe³⁺ and to provide the carbon coating on LiFePO₄. An aqueous solution of FeSO₄.7H₂O (Spectrum-Chemicals) was
- 15 then added into the above mixture so that the Li : Fe : P molar ratio was 3:1:1. The reaction mixture with a cream colored white precipitate was transferred into a quartz vessel 12, sealed, and heated at about 235 °C for about 15 minutes under the microwave-hydrothermal condition. These quartz vessel was transparent to microwave radiation 14, so the reaction mixture with a polar solvent in the vessel could be heated hydrothermally. The vessel 12 was then cooled to
- 20 room temperature, the black colored product 16 was isolated by filtration, washed with deionized water and absolute ethanol, and dried in a vacuum oven at about 80 °C. The resultant *in situ* carbon coated LiFePO₄ powder 18 was subsequently carbonized under a flowing 2 % H₂ - 98 % Ar atmosphere at about 700 °C for a short duration of about 1 hour to produce product 20. The formation of a black product 20 confirms the coating of carbon on LiFePO₄ during the
- 25 microwave-hydrothermal process.

FIGURES 16A and 16B are plots of the XRD patterns of synthesized LiFePO₄/C nanocomposite obtained by the facile one step microwave-hydrothermal process (about 15 minutes) and the LiFePO₄/C nanocomposite after heating at 700 °C for about 1 hour in 2 % H₂ – 98 % Ar, respectfully. FIGURE 16C is a Raman spectrum of the LiFePO₄/C nanocomposite. FIGURE 30 16A is a plot of the XRD pattern of the LiFePO₄/C nanocomposite obtained by the microwave irradiated hydrothermal method. The sharp diffraction peaks without any impurity phases indicate the formation of a highly crystalline, phase pure LiFePO₄ at a low temperature of 235 °C in a short reaction time of 15 minutes by the novel microwave-hydrothermal process employed

here. In order to improve the structural order of the carbon coating, the as-synthesized LiFePO₄/C nanocomposite was further heated in an inert atmosphere at about 700 °C for about 1 hour, and the corresponding XRD pattern is shown in FIGURE 16B. All the reflections in FIGURES 16A and 16B could be indexed on the basis of an orthorhombic olivine-type structure with the *Pnma* space group and lattice parameter values of $a = 10.321(1)$, $b = 6.001(1)$, and $c = 4.696(1)$ Å, which are in good agreement with the literature values.² No reflections corresponding to carbon is seen due to its low content and/or its poor crystallinity. Thermogravimetric (TGA) analysis (not shown) further confirmed the carbon content in the LiFePO₄/C nanocomposit to be about 5 weight %.

- The Raman spectrum in FIGURE 16C shows the characteristic bands for both carbon and LiFePO₄, indicating the coating of carbon on LiFePO₄. The sharp band at 948 cm⁻¹ together with those at 995 and 1068 cm⁻¹ are attributed to the symmetric PO₄³⁻ stretching vibration of LiFePO₄ as shown in the inset of FIGURE 16C. The band observed at 1607 cm⁻¹ corresponds to the graphite band (G-band), which is characteristic of a high degree of ordered structure in carbon materials.^{8b,c} On the other hand, the band observed around 1337 cm⁻¹ corresponds to a disorder-induced phonon mode (D-band) for disordered carbon materials. It is generally believed that the I_D/I_G value (the peak intensity ratio between the 1337 and 1607 cm⁻¹ peaks) provides a useful index for comparing the degree of crystallinity of various carbon materials,⁸ *i.e.*, smaller the ratio of I_D/I_G , higher the degree of ordering in the carbon material. [M.S. Bhuvaneswari, N.N. Bramnik, D. Ensling, H. Ehrenberg and W. Jaegermann, *J. Power Sources*, 2008, 180, 553; Q. Wang,; H.Li,; L.Chen,; X.Huang, *Carbon* 2001, 39, 2211; M. S . Dresselhaus, G. Dresselhaus, A. Jorio, A. G. Souza Filho and R. Saito, *Carbon*, 2002, 40, 2043; X. Sun and Y. Li, *Angew. Chem. Int. Ed.* 2004, 43, 597]. A smaller I_D/I_G ratio in FIGURE 16C indicates a high degree of ordering in the carbon coated on LiFePO₄.
- FIGURES 17A and 17B are TEM images of LiFePO₄/C nanocomposite. FIGURE 17A is a TEM image of the LiFePO₄/C nanocomposite obtained by the microwave-hydrothermal method after heat treatment, illustrating the nanorod-like morphology. FIGURE 17B is a high resolution TEM image of LiFePO₄/C, illustrating the thin carbon coating on LiFePO₄. The transmission electron microscopy (TEM) images of the carbon coated LiFePO₄ prepared by the microwave-hydrothermal process is shown in FIGURES 17A and 17B. The images demonstrate a well-defined, crystalline nanorod morphology with controlled size. The high resolution TEM image of the LiFePO₄/C nanocomposite shown in FIGURE 17B contrasts the LiFePO₄ nanorods (dark region) from the carbon coating (white region). Typically, the carbon coating was found to be

between about 5 and 12 nm while the core LiFePO₄ nanorod was found to have a diameter of around $225 \pm$ about 6 nm. The crystallite dimensions was deduced from the TEM data for the LiFePO₄ nanorods before and after heat treatment at 700 °C for 1 hour, and the data suggest that the high temperature treatment does not change the crystallite size of LiFePO₄ as the carbon coating inhibits the crystallite growth normally encountered during high temperature heat treatment.

FIGURE 18 shows the discharge profile collected at different C- rates (rate capability) and the cyclability of the as-synthesized LiFePO₄/C obtained by the microwave irradiated hydrothermal method and after annealing the LiFePO₄/C nanocomposite at 700 °C for 1 hour. FIGURES 18A and 18B are discharge profiles that relate the voltage and capacity of as-synthesized LiFePO₄/C nanocomposite obtained by the one step microwave-hydrothermal carbonization method and heat treating the LiFePO₄/C nanocomposite at 700 °C for 1 hour in 2 % H₂- 98 % Ar atmosphere respectively. FIGURES 18A and 18B compare the rate capabilities of the as-synthesized LiFePO₄/C and the annealed LiFePO₄/C at 0.1C to 10C rates. The annealed LiFePO₄/C nanocomposites exhibit an initial discharge capacity 150 mAh/g at C/10 rate, which is 88% of the theoretical capacity. Although the first initial discharge capacity values of the as-synthesized (144 mAh/g) and annealed samples (150 mAh/g) do not differ much, the annealed LiFePO₄/C nanocomposite exhibits better rate capability compared to the as-synthesized LiFePO₄/C.

FIGURE 19 is a graph of the discharge profiles that shows the cyclability of the as-synthesized LiFePO₄/C nanocomposite obtained by the microwave-hydrothermal method and after heat treating the LiFePO₄/C nanocomposite at 700 °C for 1 hour in 2 % H₂- 98 % Ar atmosphere. The cyclability data in FIGURE 19 reveal that while the as-synthesized LiFePO₄/C sample exhibits some capacity fade, the annealed sample exhibits excellent capacity retention. This could be related to the differences in the degree of ordering in the carbon. While the carbon obtained by the hydrothermal carbonization of glucose may have a significant sp³ component, that obtained after annealing may have a high fraction of the more conductive sp² carbon as reported elsewhere. [Q. Wang,; H.Li,; L.Chen,; X.Huang, Carbon 2001, 39, 2211; X. Sun and Y. Li, Angew. Chem. Int. Ed. 2004, 43, 597]. The highly ordered, conductive sp² carbon in the annealed sample appears to provide improved kinetics during the charge-discharge process.

The present invention provides a LiFePO₄/C nanocomposite obtained by a novel microwave-hydrothermal synthesis approach involving an *in situ* carbonization exhibits high capacity with excellent cyclability and rate capability in lithium ion cells. The microwave-hydrothermal

approach presented is much more rapid (e.g., about 15 minutes) compared to the known methods in the literature (e.g., a few to several hours) to synthesize LiFePO₄, and it has the potential to tune the crystallite size with a high degree of control. The method of the present invention offers a cost effective, energy efficient approach involving inexpensive water as solvent to scale up the 5 production of LiFePO₄/C cathodes for high-power hybrid electric vehicle (HEV) and plug-in hybrid electric vehicle (PHEV) applications as well as other phospho-olivines LiMPO₄ (M = Mn, Fe, Co, and Ni) and their nanocomposites LiMPO₄/C.

All chemicals were used as received without further purification. De-ionized water and tetraethyleneglycol (TEG) (ACROS-Organics) were used as solvents, respectively, in the 10 microwave-hydrothermal and microwave-solvothermal synthesis processes illustrated in FIGURE 20, employing an Anton Paar, Synthos-3000 microwave synthesis system.

Microwave-solvothermal (MW-ST) synthesis. Lithium hydroxide (Fisher) and iron (II) acetate (GFS-Chemicals) were first dissolved in tetraethyleneglycol (TEG) (ACROS-Organics). H₃PO₄ (85%, Fisher) was then added dropwise to the TEG solution at room temperature to realize a Li: 15 Fe: P molar ratio of 1:1:1 in a quartz vessel. The homogeneous, brown gel reaction mixture was sealed in a closed high-pressure quartz vessel, which was fitted with a pressure and temperature probe housed in a sturdy thermowell and protected from chemical attack. The rotor containing the closed quartz vessels was then placed on a turntable for uniform heating in an Anton Paar microwave synthesis system (Synthos-3000). The desired exposure time and temperature were 20 programmed with the Anton Paar, Synthos-3000 software. The automatic temperature and pressure control system allowed continuous monitoring and control of the internal temperature (± 1 °C). The preset profile (desired time, temperature, and pressure) was followed automatically by continuously adjusting the applied power (0- 600 W) and pressure (up to 80 bar). The system was operated at a frequency of 2.45 GHz and the temperature was raised to 25 300 °C and maintained for 5 minutes under the solvothermal condition. The resulting LiFePO₄ nanocrystals were washed repeatedly with acetone until the washings were colorless to ensure the complete removal of TEG and the powder was dried in an air-oven.

Ex situ coating of carbon on LiFePO₄ nanocrystals: the LiFePO₄ nanocrystals obtained by the microwave assisted solvothermal process were mixed with 10 weight % sucrose powder and 30 carbonized in a flowing 2 % H₂ and 98 % Ar at 700 °C for 1 hour to achieve the carbon coating.

Microwave-hydrothermal (MW-HT) synthesis: A mixed aqueous solution of LiOH (Fisher) and H₃PO₄ (85%, Fisher) was first stirred for few minutes. An aqueous solution of FeSO₄ (Spectrum-

Chemicals) was then added to this mixture so that the Li:Fe:P molar ratio was 3:1:1. The reaction solution with a cream colored white precipitate of $\text{Fe}_3(\text{PO}_4)_2$ was transferred into a quartz vessel, sealed, and heated at 235 °C for 15 minutes under the microwave-hydrothermal condition. The vessel was then cooled to room temperature and the product was collected, 5 washed with de-ionized water and absolute ethanol, and dried in a vacuum oven at 80 °C. The sample was subsequently heated in a flowing 2 % H₂ and 98 % Ar at 700 °C for 1 hour.

An *in situ* coating of carbon on LiFePO₄ was attempted during the MW-HT process, employing glucose as the carbon source. A mixed aqueous solution of LiOH (Fisher), H₃PO₄ (85%, Fisher), and glucose was first stirred for few minutes. An aqueous solution of FeSO₄ (Spectrum-10 Chemicals) was then added to this mixture so that the Li:Fe:P molar ratio was 3:1:1 and the LiFePO₄ to carbon ratio in the final product was anticipated to be 95:5 wt. %. The reaction solution with the cream colored white precipitate of $\text{Fe}_3(\text{PO}_4)_2$ was then transferred into a quartz vessel, sealed, and heated at 235 °C for 15 minutes under the microwave-hydrothermal condition. A simplified reaction mechanism for carbon coating under the MW-HT condition 15 involves the dehydration of the carbohydrate followed by a polymerization and carbonization of glucose. The vessel was then cooled to room temperature and the black colored product of LiFePO₄/C nanocomposite was collected, washed with de-ionized water and absolute ethanol, and dried in a vacuum oven at 80 °C. Further, in order to improve the structural order of the carbon coating, the carbon coated LiFePO₄ powder was subsequently carbonized in 2 %H₂ and 20 98 % Ar at 700 °C for 1 hour.

X-ray diffraction (XRD) characterization of the samples was carried out with a Philips PW1830 X-ray diffractometer and filtered Cu K α radiation. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) characterizations were carried out, respectively, with a JEOL-JSM5610 SEM and a JEOL JEM-2010F equipments. Raman spectroscopic analysis was 25 performed with a Renishaw InVia system utilizing a 514.5 nm incident radiation and a 50 x aperture (N.A = 0.75), resulting in approximately a 2 μm diameter sampling cross section. Electrochemical performances were evaluated with CR2032 coin cells at 4.3 - 2.0 V with an Arbin battery cycler. The coin cells were fabricated with the LiFePO₄ or LiFePO₄/C cathode, metallic lithium anode, 1 M LiPF₆ in 1:1 diethyl carbonate/ethylene carbonate electrolyte, and 30 Celgard polypropylene separator. The cathodes were prepared by mixing 75 weight % active materials with 12.5 weight % conductive carbon and 12.5 weight % teflonated acetylene black binder, rolling the mixture into thin sheets, and cutting into circular electrodes of 0.64 cm² area. The electrodes typically had an active material content of about 7 mg, and were dried under

vacuum at 80 °C for more than 3 hours before assembling the coin cells in an argon-filled glovebox.

The present invention provides a microwave-hydrothermal and microwave-solvothermal synthesis processes. FIGURE 21A shows the XRD pattern of the as-synthesized LiFePO₄

5 obtained by the microwave irradiated solvothermal (MW-ST) method using TEG at 300 °C within 5 minutes. FIGURE 21B shows the XRD pattern recorded after an *ex situ* coating at 700 °C with carbon of the LiFePO₄ obtained by the MW-ST method (FIGURE 20A). All the reflections in both the samples could be indexed on the basis of an orthorhombic olivine-type LiFePO₄ structure without any detectable impurity phases.

10 FIGURES 22A-22D show the XRD patterns of the LiFePO₄ and LiFePO₄ /C nanocomposite prepared by the MW-HT method (FIGURE 20B). Although the as-synthesized sample shows a weak reflection at $2\theta = 27^\circ$ corresponding to the impurity phase²⁸ Fe₃(PO₄)₂(OH)₂ in addition to the reflections of LiFePO₄ (FIGURE 22A), subsequent annealing at 700 °C in 2 % H₂ and 98 % Ar for 1 hour offers single phase LiFePO₄ without any impurity phase (FIGURE 22B).

15 Interestingly, the as-synthesized LiFePO₄/C nanocomposite prepared at 235 °C for 15 minutes by the one-pot MW-HT process with glucose does not show any impurity phase as seen in FIGURE 22C in contrast to the product obtained in FIGURE 22A in the absence of glucose. It reveals that hydrothermal carbonization of glucose not only offers the carbon coating but also provides a reducing atmosphere to favor the formation of phase pure LiFePO₄. Subsequent heating of the

20 product at 700 °C for 1 hour in 2 % H₂ and 98 % Ar maintains the sharp reflections of LiFePO₄ as seen in FIGURE 22D while improving the ordered structure of carbon. Nevertheless, no detectable reflections corresponding to carbon could be seen in FIGURES 22C and 22D due to its low content or its amorphous structure. TGA analysis of the product confirmed the carbon content to be 5 weight % in the LiFePO₄/C nanocomposite.

25 The particle size and shape of the products formed were examined by both SEM and TEM. FIGURES 23A and 23B show the SEM images of the as-synthesized LiFePO₄ obtained by the MW-ST method and the LiFePO₄/C composite obtained by a subsequent *ex situ* coating of carbon on LiFePO₄ at 700 °C. FIGURES 23C and 23D show the SEM images of as-synthesized LiFePO₄/C nanocomposite obtained by the MW-HT method with glucose and the product 30 obtained after subsequent heating at 700 °C. All the SEM images reveal a nanorod-like morphology. FIGURES 23B, 23C and 23D also reveal the absence of any bulk deposition or

agglomeration of carbon on the surface of LiFePO₄. The images also indicate that no significant change in morphology occurs after heating at 700 °C for 1 hour.

The TEM images in FIGURE 24 demonstrate the well-defined crystalline nanorod morphologies with controlled size of the LiFePO₄/C nanocomposites. It is interesting that highly crystalline

5 nanorods are formed in short time of about 5 to 15 minutes under the microwave conditions in contrast to the 5 to 24 hours involved with other conventional methods like the hydrothermal and solvothermal methods. The dimensions of the nanorods depend on the solvents used to prepare LiFePO₄ (e.g. viscosity and boiling point of the solvents), which could help to tune the rate capability and volumetric energy density. For example, while the sample obtained by the MW-
10 ST method with TEG as a solvent shows small nanorods with a width of 25 ± 6 nm and a length of up to 100 nm (FIGURE 24A), the sample obtained by the MW-HT method with water as a solvent shows large nanorods with a width of 225 ± 6 nm and a length of up to 300 nm (FIGURE 24C). The high resolution TEM images of the LiFePO₄/C nanocomposites in FIGURES 24B and 24D show a uniform carbon nanocoating (amorphous region) on the
15 LiFePO₄ nanorods (crystalline fringe region). The images indicate a “core-shell” structure with a 5 to 12 nm carbon shell on the 25 ± 6 or 225 ± 6 nm LiFePO₄ core. Moreover, the high temperature (700 °C) treatment does not alter the particle size significantly, suggesting that the carbon coating inhibits the crystallite growth normally encountered during high temperature heat treatment. Elemental mapping by scanning TEM (STEM) in FIGURE 24 indicates a uniform
20 distribution of Fe, P, and C in the LiFePO₄/C nanocomposite, while energy dispersive spectroscopic analysis of the LiFePO₄ nanocrystals in SEM indicated a Fe:P ratio of 1:1.

FIGURES 25A-25C are graphs that show the Raman spectra of as-synthesized LiFePO₄.

FIGURE 25A is a graphs that shows the Raman spectra of as-synthesized LiFePO₄ obtained by the MW-ST method and the LiFePO₄/C nanocomposites obtained by an *ex situ* coating of carbon
25 at 700 °C on the MW-ST LiFePO₄ and by an *in situ* coating of carbon on LiFePO₄ by the MW-

HT method followed by heating at 700 °C. The sharp band at 948 cm⁻¹ along with the bands at 995 and 1068 cm⁻¹ in FIGURE 5A can be attributed to the symmetric PO₄³⁻ stretching vibration²⁰

of LiFePO₄. On the other hand, the broad bands in FIGURES 25B and 25C that are characteristic of carbon along with the weak bands of PO₄³⁻ suggest the coating of structurally
30 ordered carbon on LiFePO₄. The strong band at 1607 cm⁻¹ in FIGURES 25B and 25C, which is called the graphite band (G-band), is characteristic of carbon materials with a high degree of ordered structure. This band corresponds to one of the E_{2g} modes arising from the movement in

opposite directions of the two neighboring carbon atoms in a graphene sheet. On the other hand,

the band observed at 1337 cm⁻¹ in FIGURES 25B and 25C, which is called the disorder-induced phonon mode (D-band), is characteristic of carbon materials with disordered structure.³⁴ The I_D/I_G value (the peak intensity ratio between the 1337 and 1607 cm⁻¹ peaks) generally provides a useful index for comparing the degree of crystallinity of various carbon materials, *i.e.*, smaller the ratio of I_D/I_G , higher the degree of ordering in the carbon material. A smaller I_D/I_G ratio in FIGURES 25B and 25C indicates a high degree of ordering in the carbon coated on LiFePO₄.

FIGURES 26A and 26B are graphs of the electrochemical properties of the LiFePO₄ and LiFePO₄/C nanocomposite. FIGURE 26 compares the first charge-discharge profiles and cyclability of LiFePO₄ and LiFePO₄/C nanocomposite obtained by the MW-ST method. The as-synthesized LiFePO₄ obtained by the MW-ST method exhibits a discharge capacity of 140 mAh/g with a significant voltage difference between the charge and discharge curves as seen in FIGURE 26A. It also exhibits a significant capacity fade during the initial cycles as seen in FIGURE 26B. Recognizing that the polarization loss could be due to the lack of adequate electronic conductivity, in one embodiment the present invention focuses on an *ex situ* coating of the LiFePO₄ nanorods with carbon by heating with sucrose at 700 °C for 1 hour the LiFePO₄ obtained by the MW-ST method. The LiFePO₄/C nanocomposite thus obtained exhibits a high discharge capacity of 162 mAh/g, which is close to the theoretical value of 170 mAh/g, with little difference between the charge and discharge curves as seen in FIGURE 26A. It also exhibits excellent cyclability with no noticeable fade in 30 cycles as seen in FIGURE 26B.

FIGURES 27A and 27B show the first charge-discharge profiles and cyclability of the LiFePO₄ and LiFePO₄/C nanocomposites obtained by the MW-HT method before and after heating at 700 °C. FIGURES 27A and 27B show a comparison of the first charge-discharge profiles recorded at C/10 rate between 2.0 and 4.3 V and the cyclability of the as-synthesized LiFePO₄ obtained by the MW-HT method, after heating the MW-HT LiFePO₄ at 700 °C for 1 hour in a flowing 2 % H₂ – 98 % Ar atmosphere, as-synthesized LiFePO₄/C nanocomposite obtained by an *in situ* carbon coating with glucose during the MW-HT process, and after heating the MW-HT LiFePO₄/C nanocomposite at 700 °C for 1 hour in a flowing 2 % H₂ and 98 % Ar atmosphere, respectively. The as-synthesized LiFePO₄ obtained by the MW-HT method exhibits a discharge capacity of 123 mAh/g with a significant voltage difference between the charge and discharge curves as seen in FIGURE 27A. The lower discharge capacity could be partly due to the presence of the impurity phase Fe₃(PO₄)₂(OH)₂ and larger particle size compared to that obtained by the MW-ST method. It also exhibits capacity fade as seen in FIGURE 27B. Although the capacity retention increases slightly on annealing the LiFePO₄ sample obtained by

the MW-HT method at 700 °C for 1 hour due to an improvement in crystallinity, the capacity decreases slightly to 120mAh/g. On the other hand, the as-synthesized LiFePO₄/C nanocomposite obtained by an *in situ* coating of carbon with glucose during the MW-HT process exhibits a higher discharge capacity of 144 mAh/g (FIGURE 27A). Although the capacity increases only slightly to 146 mAh/g on annealing the as-synthesized LiFePO₄/C (MW-HT) nanocomposite at 700 °C, the capacity retention improves remarkably as seen in FIGURE 27B. The excellent cyclability could be related to a significant improvement in the ordered structure of carbon and the electronic conductivity as has been reported elsewhere.

FIGURES 28A and 28B are graphs that compare the rate capabilities (at C/10 to 10C rates) of LiFePO₄ and LiFePO₄/C nanocomposite obtained by the MW-ST method. FIGURE 28A is a graph comparing the rate capabilities of the as-synthesized LiFePO₄ nanorods obtained by the MW-ST method and FIGURE 28B is a graph comparing the rate capabilities of a LiFePO₄/C nanocomposite obtained by an *ex situ* carbon coating of the MW-ST LiFePO₄ nanorods by heating with sucrose at 700 °C for 1 hour in a flowing 2 % H₂ and 98 % Ar atmosphere. The LiFePO₄/C nanocomposite obtained by heating at 700 °C exhibits better rate capability compared to the as-synthesized LiFePO₄.

FIGURES 29A, 29B and 29C are graphs that compare the rate capabilities (at C/10 to 10C rates) of LiFePO₄ and LiFePO₄/C nanocomposite obtained by the MW-HT method. FIGURE 29A is a graph of the comparison of the rate capabilities of the LiFePO₄ nanorods obtained by the MW-HT method followed by heating at 700 °C for 1 hour in a flowing 2 % H₂ and 98 % Ar atmosphere, FIGURE 29B is a graph comparing the rate capabilities of the as-synthesized LiFePO₄/C nanocomposite obtained by an *in situ* carbon coating with glucose during the MW-HT process, and FIGURE 29C is after heating the LiFePO₄/C nanocomposite in FIGURE 29B at 700 °C for 1 hour in a flowing 2 % H₂ and 98 % Ar atmosphere. The LiFePO₄/C nanocomposite obtained after heating at 700 °C exhibits better rate capability as seen in FIGURE 29C than the pristine LiFePO₄ heated at 700 °C (FIGURE 29A) and the as-synthesized LiFePO₄/C nanocomposite (FIGURE 29B) due to the improved kinetics provided by the structurally ordered, electronically conducting carbon coating on LiFePO₄.

FIGURE 30 is a graph that compares the rate capabilities of the LiFePO₄/C nanocomposite obtained by heating the MW-ST LiFePO₄ with sucrose at 700 °C and by heating at 700 °C the LiFePO₄/C nanocomposite obtained by the MW-HT method. FIGURE 30A is a graph that compares the rate capabilities of LiFePO₄/C nanocomposite obtained by an *ex situ* carbon

coating of the MW-ST LiFePO₄ nanorods by heating with sucrose at 700 °C for 1 hour in a flowing 2 % H₂ and 98 % Ar atmosphere and LiFePO₄/C nanocomposite obtained by an *in situ* carbon coating with glucose during the MW-HT process, followed by heating at 700 °C for 1 hour in a flowing 2 % H₂ and 98 % Ar atmosphere. Although both samples were subjected to a 5 constant annealing of 1 hour at 700 °C, the former exhibits higher initial discharge capacity due to a smaller particle size (25 ± 6 nm and a length of up to 100 nm) compared to the latter (width of 150 ± 6 nm and a length of up to 225 nm). The observation demonstrates that both the lithium ion conduction and electronic conduction play a critical role in controlling the electrochemical properties of LiFePO₄. A smaller lithium diffusion length in the MW-ST sample leads to better 10 electrochemical properties.

The present invention provides a rapid synthesis process taking advantage of microwave irradiation and solvothermal or hydrothermal effect to obtain highly crystalline LiFePO₄ nanorods within a short reaction time (e.g., 5 to 15 minutes) at < 300 °C. However the skilled artisan will recognize this process may be extended to shorter or longer periods of time in some 15 embodiments, e.g., 0.1-5 minutes, 15-30 minutes, 30-60 minutes, 1-2 hours, 2-6 hours, 6-12 hours or longer than 12 hours, including incremental variations thereof. In addition, the temperature may be varied in some embodiments from 200-225, 225-250, 250-275, 275-300, 300-325, and 325-350 °C. The microwave-solvothermal process employing a polyol (TEG) as a solvent offers much smaller particle size than the microwave-hydrothermal process employing 20 water as a solvent, resulting in a higher initial discharge capacity for the former. The LiFePO₄/C nanocomposites annealed at 700 °C for a short time exhibit better cyclability and higher rate capability compared to the as-prepared LiFePO₄ or LiFePO₄/C nanocomposites due to a high degree of ordering in the carbon and enhanced electrical conductivity. Both a short lithium diffusion length and a high electronic conductivity are critical to achieve high performance 25 LiFePO₄ cathodes. The short reaction time involved with these microwave assisted solvothermal and hydrothermal processes has the potential to lower the manufacturing cost with significant energy savings to obtain various phospho-olivines LiMPO₄ (M = Mn, Fe, Co, and Ni) with different nanomorphologies.

The present invention provides the direct synthesis of LiMPO₄ (M= Mn, Fe, Co, Ni) nanosheets 30 within a short reaction time (e.g., 5 to 15 minutes) using the highly viscous, high boiling tetraethyleneglycol (TEG) solvent *via* the MW-ST method disclosed herein. In one embodiment a non-aqueous solvent not only provides a reducing environment to prevent the oxidation of M²⁺ to M³⁺, but also helps to prohibit the growth and agglomeration of the nanoparticles formed.

The MW-ST method takes advantage of both the microwave irradiation and the solvothermal effect to produce nanocrystalline LiMPO₄. The present invention provides a nano-networking of the LiFePO₄, LiMnPO₄, and LiCoPO₄ formed with MWCNT at ambient temperatures to enhance the mobility of electrons during the lithiation/delithiation process. A schematic representation of 5 the MW-ST process employed and the subsequent networking with MWCNT to obtain the LiMPO₄-MWCNT nanocomposite are shown in FIGURE 31.

FIGURE 31 is a schematic representation of the MW-ST process to produce nano LiMPO₄ (M= Mn, Fe, Co, Ni) and subsequent nanocomposite formation with MWCNT at ambient temperatures. Column 30 is an image of each sample before treatment under reaction conditions 10 seen in column 32 to form the corresponding products shown in the image shown in column 34. A corresponding SEM image is taken of the products and displayed in column 36. TEM images of the treatment of the product with MWCNT are shown in column 38.

FIGURE 32 is an image of the XRD patterns of the nano LiMPO₄ (M= Mn, Fe, Co, Ni) prepared by the MW-ST method within 5 to 15 minutes at 300°C. FIGURE 32 shows the XRD patterns 15 of the pristine LiMnPO₄, LiFePO₄, LiCoPO₄, and LiNiPO₄. All the reflections could be indexed on the basis of the orthorhombic olivine structure (space group: *Pnma*), indicating the formation of phase pure samples without any impurity phases. [Padhi, A. K.; Nanjundasawamy, K. S.; Goodenough, J. B. *J. Electrochem. Soc.* 1997, 144, 1188; Kim, D. -H.; Kim, J. *Electrochem. Solid State Lett.* 2006, 9, A439]. The sharp diffraction peaks illustrate the highly crystalline 20 nature of LiMPO₄ achievable by the MW-ST process within a short time without post annealing at elevated temperatures. The reflections in FIGURE 32 shift gradually to higher angles on going from M = Mn to Fe to Co to Ni due to the decrease in the ionic radii values. Energy dispersive spectroscopic (EDS) analysis in SEM and atomic absorption spectroscopic analysis of the as-synthesized LiMPO₄ confirmed a Li:M:P ratio of 1:1:1.

25 FIGURES 33A, 33B, 33C and 33D are TEM images of LiMPO₄ (M= Mn, Fe, Co, Ni) nanosheets prepared by the MW-ST method within 5 to 15 minutes at 300°C at increasing magnification. The TEM images shown in FIGURES 33A, 33B, 33C and 33D illustrate the highly crystalline nature of the LiMPO₄ samples with a nanosheet morphology. The high resolution TEM image reveals that the nanosheets grow along the direction with the lithium 30 diffusion direction (the *b* axis) perpendicular to the nanosheets, which is particularly attractive to achieve fast lithium diffusion and high rate capability. Thus the MW-ST approach presented here offers a unique nanostructure, facilitating fast lithium ion diffusion.

FIGURES 34A, 34B, 34C, 34D, 34E and 34F are graphs that compares the discharge capacity at various C-rates of the LiMPO₄ (M = Mn, Co, Ni) nanosheets before and after networking with MWCNT. Although LiMPO₄ nanosheets have low electronic conductivity, the networking with MWCNT leads to a significant improvement in electronic conductivity and rate capability.

- 5 Moreover, the lithium diffusion direction (*b* axis) perpendicular to the nanosheets particularly shortens the diffusion length and enhances the rate capability of the LMPO₄ nanosheets. The superior rate performance of the LiMPO₄-MWCNT nanocomposite is due to the combined effect of the small lithium diffusion path length in the short nanosheets and the electronically conductive matrix provided by the carbon nanotubes. With a theoretical voltage of 5.1 V vs
10 Li/Li⁺, LiNiPO₄ poses an even tougher challenge on the electrolyte issue, and we were not able to carry out the electrochemical tests of the synthesized LiNiPO₄ with the available conventional electrolytes (1 M LiPF₆ in 1:1 diethyl carbonate/ethylene carbonate).

The present invention provides compositions and methods for the synthesis of LiMPO₄ (M= Mn, Fe, Co, Ni) nanosheets within a short reaction time (e.g., 5 to 15 min) by a novel, low cost
15 microwave-solvothermal approach without requiring any elevated temperature post processing in reducing gas atmospheres. Subsequent networking of the LiMPO₄ nanosheets with multi-walled carbon nanotubes at ambient temperatures to obtain LiMPO₄-MWCNT nanocomposite offers high capacity with excellent rate capability. Furthermore, the lithium diffusion direction (*b* axis) perpendicular to the nanosheets offers particular advantage to achieve fast lithium
20 diffusion and high power capability necessary for automotive applications.

- The present invention also includes a method of making a nanostructured phospho-olivine hybrid composition by dissolving lithium hydroxide and one or more metal salts in an aqueous solvent, adding one or more monosaccharides to the solvent, adding H₃PO₄ to the aqueous solvent to form a precursor solution with a 1:1:1 molar ratio of Li:M:P, heating solvothermally
25 the precursor solution with a microwave device, separating the LiMPO₄ nanostructured phospho-olivine material from the precursor solution and encapsulating the LiMPO₄ nanostructured phospho-olivine material with one or more polymers selected from an electronically conductive polymer, a doped polymer, an electronically and ionically conductive polymer, or a combination thereof, wherein the polymer varies from 0.1 weight % to 50 weight %.
30 The present invention may include the addition of one or more monosaccharides, e.g., Trioses (e.g., Ketotriose (Dihydroxyacetone), Aldotriose (Glyceraldehyde)), Tetroses (e.g., Erythrulose, Erythrose, Threose) Pentoses (e.g., Arabinose, Deoxyribose, Lyxose, Ribose, Ribulose, Xylose,

Xylulose), Hexoses (e.g., Glucose, Galactose, Mannose, Gulose, Idose, Talose, Allose, Altrose, Fructose, Sorbose, Tagatose, Psicose, Fucose, Fuculose, Rhamnose), Heptose, Octose, Nonose, Decose, in addition to modifications thereof. In addition, the monosaccharides may include one or more modifications to the ring. Furthermore, some embodiments can use disaccharides such 5 as sucrose, lactose, trehalose or maltose. In addition to monosaccharides the present invention may also include disaccharides, polysaccharides, surfactants, biosurfactants, organic acids, polyalcohols or combinations thereof.

The microwave irradiated synthesis system operates at a frequency of about 2.0 to 3.0 GHz and a power of 1 to 2,000 W. The skilled artisan will recognize that the operating frequency may be 10 less than 2.0 and greater than 3.0, e.g., 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 1.1, 1.2, 1.3, 1.4, 1.5, 1.6, 1.7, 1.8, 1.9, 2.0, 2.1, 2.2, 2.3, 2.4, 2.5, 2.6, 2.7, 2.8, 2.9, 3.0, 3.1, 3.2, 3.3, 3.4, 3.5, 3.6, 3.7, 3.8, 3.9, 4.0 and greater. Similarly, the power may be from 1 to 2,000 W, in some instances the power may be less than 1 and greater than 2,000 W. It is also equally understood that the power may be incremental variations thereof.

15 Generally, the heating raises the temperature from about 100 to about 400 °C for between about 1 minute to about 24 hours. The skilled artisan will recognize that different embodiments of the present invention may be heated at any temperature within that range and includes all incremental variations between those ranges. Similarly, the time can be any time within that range and includes all incremental variations between those ranges. The skilled artisan will 20 readily recognize that this applies to all ranges and temperatures disclosed herein.

The conductive polymers of the present invention include, without limitation, polyanilines (e.g., poly(2-methoxyaniline)), polythiophenes (e.g., poly(3-octylthiophene), and poly(3,4-ethylene dioxythiophene)), and polypyrroles, and their derivatives.

25 The present invention may also include layers and/or blends of polymers, copolymers and/or conductive polymers, e.g., a polymer blend is poly(3-hexylthiophene) (P3HT), poly(2-methoxyaniline) ("POMA") or poly(3-octylthiophene) ("POTh") with PVDF or PEO.

In addition, the electrically conductive material can also be pure elements, metal oxides, metal sulfides, carbon, and conductive polymers, e.g., conducting elements include, carbon black, silver, copper, lithium, nickel, and zinc; conductive polymers include polythiophenes, 30 polyanilines, polypyrroles, poly(alkyl and alkoxythiophenes), and polyethylenes and their derivatives. Nonlimiting examples of such conducting polymers include, without limitation, poly(3-octylthiophene), poly(3-hexylthiophene), poly(3,4-ethylenedioxythiophene). Exemplary

conductive oxides include, without limitation, vanadium oxide, indium tin oxide, titanium oxide, manganese oxide, nickel oxide, ruthenium oxide, molybdenum oxide, tungsten oxide, or their alloys.

In addition, the present invention includes coating materials that may be a conducting polymer,

- 5 such as a single polymer, or a polymer blend that includes a conductive polymer and a secondary material (e.g., a fluorinated polymer, blends include poly(3,4-ethylene dioxythiophene) ("PEDOT") or poly(3,4 ethylene dioxythiophene)-polystyrene sulfonate ("PEDT-PSS"), poly(3,4-ethylenedioxypyrrole) ("PEDOP"), poly(3-hexylthiophene) ("P3HT"), where the secondary material includes polytetrafluoroethylene ("PTFE") or derivatives thereof or
10 poly(vinylidene fluoride) ("PVDF"). In other embodiments, the coating layer includes at least one polytetrafluoroethylene, poly(vinylidene fluoride) and poly(ethylene oxide).

The coating material can include a dopant that improves the conductivity of the conducting

material. The dopant can be, but is not limited to, a counter-ion source including, without limitation, polystyrene sulfonate, hydrochloric acid, tosylate ion, camphorsulfonic acid,

- 15 dodecylbenzene sulfonic acid, perfluorodecane sulfonic acid, trifluoroacetic acid, or perchloric acid.

The phospho-olivine structures of the present invention may have a particle size that ranges from

1 to 1000nm, e.g., the particles may be 1, 2 , 3, 4, 5, 6, 7, 8, 9, 10, 20 , 30, 40, 50, 60, 70, 80, 90,

20 100, 200 , 300, 400, 500, 600, 700, 800, 900, 1000nm and incremental variations of the sizes listed herein, e.g., 101, 7.5, 604.7 and so forth.

As used herein the term "solvothermally" may be used in its broadest sense to denote heating of

a solvent where the solvent is an aqueous solvent or a non-aqueous solvent or a mixture thereof.

More specifically, the term may be used to specify heating of a non-aqueous solvent or a solvent that is predominantly a non-aqueous solvent. As used herein the term "hydrothermally" is used

- 25 to refer to the heating of an aqueous solvent or a solvent that is predominantly an aqueous solvent.

It is contemplated that any embodiment discussed in this specification can be implemented with respect to any method, kit, reagent, or composition of the invention, and vice versa. Furthermore, compositions of the invention can be used to achieve methods of the invention.

- 30 It will be understood that particular embodiments described herein are shown by way of illustration and not as limitations of the invention. The principal features of this invention can be employed in various embodiments without departing from the scope of the invention. Those

skilled in the art will recognize, or be able to ascertain using no more than routine experimentation, numerous equivalents to the specific procedures described herein. Such equivalents are considered to be within the scope of this invention and are covered by the claims.

All publications and patent applications mentioned in the specification are indicative of the level
5 of skill of those skilled in the art to which this invention pertains. All publications and patent applications are herein incorporated by reference to the same extent as if each individual publication or patent application was specifically and individually indicated to be incorporated by reference.

The use of the word “a” or “an” when used in conjunction with the term “comprising” in the
10 claims and/or the specification may mean “one,” but it is also consistent with the meaning of “one or more,” “at least one,” and “one or more than one.” The use of the term “or” in the claims is used to mean “and/or” unless explicitly indicated to refer to alternatives only or the alternatives are mutually exclusive, although the disclosure supports a definition that refers to only alternatives and “and/or.” Throughout this application, the term “about” is used to indicate
15 that a value includes the inherent variation of error for the device, the method being employed to determine the value, or the variation that exists among the study subjects.

As used in this specification and claim(s), the words “comprising” (and any form of comprising, such as “comprise” and “comprises”), “having” (and any form of having, such as “have” and “has”), “including” (and any form of including, such as “includes” and “include”) or
20 “containing” (and any form of containing, such as “contains” and “contain”) are inclusive or open-ended and do not exclude additional, unrecited elements or method steps.

The term “or combinations thereof” as used herein refers to all permutations and combinations of the listed items preceding the term. For example, “A, B, C, or combinations thereof” is intended to include at least one of: A, B, C, AB, AC, BC, or ABC, and if order is important in a
25 particular context, also BA, CA, CB, CBA, BCA, ACB, BAC, or CAB. Continuing with this example, expressly included are combinations that contain repeats of one or more item or term, such as BB, AAA, MB, BBC, AAABCCCC, CBBAAA, CABABB, and so forth. The skilled artisan will understand that typically there is no limit on the number of items or terms in any combination, unless otherwise apparent from the context.

30 All of the compositions and/or methods disclosed and claimed herein can be made and executed without undue experimentation in light of the present disclosure. While the compositions and methods of this invention have been described in terms of preferred embodiments, it will be

apparent to those of skill in the art that variations may be applied to the compositions and/or methods and in the steps or in the sequence of steps of the method described herein without departing from the concept, spirit and scope of the invention. All such similar substitutes and modifications apparent to those skilled in the art are deemed to be within the spirit, scope and
5 concept of the invention as defined by the appended claims.

CLAIMS:

- 1 1. A nanostructured phospho-olivine composition comprising:
 - 2 $\text{Li}_x\text{M}_y\text{PO}_4$, wherein x is between 0 and 1.2 and y is between 0.8 and 1.2 and M is one or more elements selected from the group consisting of Fe, Mn, Co, Ti, Ni, Cu, V, Mo, Zn, Mg, Cr, Al, Ga, B, Nb, Zr or combinations thereof.
 - 1 2. The composition of claim 1, wherein the nanostructured phospho-olivine composition comprises LiMnPO_4 , LiFePO_4 , LiCoPO_4 , LiNiPO_4 , LiCuPO_4 , or combinations thereof.
 - 1 3. The composition of claim 1, further comprising one or more dopants to form a composition selected from a $\text{Li}_{x'}\text{Fe}_{1-y}\text{M}_y\text{PO}_4$ composition, a $\text{Li}_{x'}\text{Mn}_{1-y}\text{M}_y\text{PO}_4$ composition, a $\text{Li}_{x'}\text{Ni}_{1-y}\text{M}_y\text{PO}_4$ composition, a $\text{Li}_{x'}\text{Co}_{1-y}\text{M}_y\text{PO}_4$ composition, and a $\text{Li}_{x'}\text{Cu}_{1-y}\text{M}_y\text{PO}_4$ composition, wherein x is between 0 and 1, y is between 0 and 1, and M is selected from the group consisting of Mn, Fe, Co, Ti, Ni, Cu, V, Mo, Zn, Mg, Cr, Al, Ga, B, Zr, and Nb.
 - 1 4. The composition of claim 1, wherein the phospho-olivine comprises a nanomorphology selected from a nanorod nanomorphology, a nanowire nanomorphology, a nanosphere nanomorphology, a nanowhisker nanomorphology, a nanoflower nanomorphology, a nanosheet nanomorphology and combinations thereof wherein the nanomorphology provides fast lithium ion diffusion and facilitates high power capability with an easy lithium diffusion direction (*b*-axis) perpendicular to the nanomorphology.
 - 1 5. The composition of claim 1, wherein the phospho-olivine has a particle size of 2 nm to 900 nm.
 - 1 6. The composition of claim 1, wherein the nanostructured phospho-olivine composition comprises a coating, an electrode or a combination thereof.
 - 1 7. A method of making a nanostructured phospho-olivine material comprising the steps of:
 - 2 dissolving a lithium-containing compound such as lithium hydroxide and one or more metal salts in a solvent;
 - 4 adding H_3PO_4 or a phosphate-containing compound to the solvent to form a precursor solution with a 1:1:1 molar ratio of Li:M:P;
 - 6 heating solvothermally or hydrothermally the precursor solution with a microwave irradiated synthesis system in the presence or absence of a carbon precursor to form a nanostructured

8 phospho-olivine LiMPO₄ material, wherein the microwave irradiated synthesis system operates
9 at a frequency of between 1.5 and 3.5 GHz and a power of between 1 and 3,000 W; and
10 separating the nanostructured phospho-olivine LiMPO₄ material from the precursor solution.

1 8. The method of claim 7, wherein the one or more metal salts comprise Fe, Mn, Co, Ti, Ni,
2 Cu, V, Mo, Zn, Mg, Cr, Al, Ga, B, Zr, Nb or combination thereof and are in the form of metal
3 acetates, metal nitrates, metal chlorides, metal carbonates, metal oxalates, metal sulfates, metal
4 alkoxides or a combination thereof.

1 9. The method of claim 8, wherein the solvent comprises an aqueous solvent or a nonaqueous
2 solvent, wherein the aqueous solvent comprises water and acidic and basic solutions.

1 10. The method of claim 7, wherein the solvent comprises high boiling polyol,
2 tetraethyleneglycol, triethyleneglycol, ethyleneglycol, (tri-*n*-octylphosphine oxide), (tri-*n*-
3 octylphosphine), (tri-*n*-butylphosphine), tri-*n*-octylamine, squalene, octacosane, 1-ethyl-3-
4 methylimidazolium bis(fluorosulfonyl)imide (EMI-FSI), 1-ethyl-3-methylimidazolium
5 bis(trifluoromethanesulfonyl)imide (EMI-TFSI), 1-butyl-2,3-dimethylimidazolium
6 bis(trifluoromethanesulfonyl)imide (BMMI-TFSI), 1-propyl-1-methylpyrrolidinium,
7 bis(fluorosulfonyl)imide (Py13-FSI), 1-butyl-1-methylpiperidinium
8 bis(trifluoromethanesulfonyl)imide (Pp14-TFSI), and *N*-trimethyl-*N*-butylammonium
9 bis(trifluoromethanesulfonyl)imide (TMBA-TFSI), or combinations thereof.

1 11. The method of claim 7, wherein the heating raises the temperature from about 100 to
2 about 400 °C for between about 1 minute to about 24 hours.

1 12. The method of claim 7, further comprising the step of encapsulating the nanostructured
2 phospho-olivine LiMPO₄ material with a polymer of between 0.1 wt % and 50 wt %, wherein
3 the polymer is selected from an electronically conductive polymer, a doped polymer, an
4 electronically and ionically conductive polymer, or a combination thereof.

1 13. The method of claim 12, wherein the polymer comprises polypyrrole, polyaniline,
2 polythiophene, poly-p-phenylenevinylene, poly(alkyl and alkoxythiophenes), poly(3,4-
3 ethylenedioxothiophene) (PEDOT), poly(3,4-ethylenedioxypyrrrole), (PEDOP), poly(3-
4 hexylthiophene),(P3HT), and their substituted derivatives or doped derivatives.

1 14. The method of claim 12, further comprising the step of adding one or more dopants to
2 the polymer.

1 15. The method of claim 14, wherein the one or more dopants comprises polystyrene sulfonate,
2 hydrochloric acid, tosylate ion, camphorsulfonic acid, dodecylbenzene sulfonic acid,
3 perfluorodecane sulfonic acid, trifluoroacetic acid, perchloric acid, or combinations thereof.

1 16. The method of claim 7, further comprising the step of forming the nanostructured
2 phospho-olivine LiMPO₄ material into an electrode.

1 17. The method of claim 16, further comprising the step of adding *p*-toluene sulfonic acid
2 doped poly(3,4-ethylenedioxythiophene) to modify the nanostructured phospho-olivine hybrid
3 composition to improve the electronic and ionic conductivity.

1 18. The method of claim 12, further comprising the step of modifying the nanostructured
2 phospho-olivine LiMPO₄ material by multi-wall carbon nanotubes (MWCNT), carbon
3 nanofibers, or a combination thereof.

1 19. The method of claim 7 further comprising the step of modifying the nanostructured
2 phospho-olivine LiMPO₄ material by both *ex-situ* and *in-situ* carbon coating, conductive oxide
3 coating, conductive ceramic coating, conductive metal or alloy coating, conductive polymer
4 coating, or combinations thereof.

1 20. The method of claim 7 wherein the carbon precursors include monosaccharides,
2 disaccharides, polysaccharides, surfactants, biosurfactants, organic acids, polyalcohols or
3 combinations thereof followed by heating at 100 – 800 °C.

1 21. A method of making a nanostructured phospho-olivine material comprising the steps of:
2 dissolving a lithium-containing compound such as lithium hydroxide, iron (II) and one or
3 more metal salts in a solvent, wherein the solvent is an aqueous solvent or a non-aqueous
4 solvent;

5 adding H₃PO₄ or a phosphate-containing compound to the solvent to form a precursor solution
6 with a 1:1:1 molar ratio of Li:Fe(M):P;

7 heating solvothermally or hydrothermally the precursor solution with a microwave device in the
8 presence or absence of a carbon precursor; and

9 separating a nanostructured Li_xFe_{1-y}M_yPO₄ phospho-olivine material from the precursor solution.

1 22. The method of claim 21, further comprising the step of adding one or more
2 monosaccharides to the solvent.

1 23. The method of claim 21, further comprising the step of encapsulating the nanostructured
2 $\text{Li}_x\text{Fe}_{1-y}\text{M}_y\text{PO}_4$ phospho-olivine material with a polymer, wherein the polymer varies from 0.1 wt
3 % to 50 wt% and the polymer is selected from an electronically conductive polymer, a doped
4 polymer, an electronically and ionically conductive polymer, or a combination thereof.

1 24. The method of claim 21, wherein the polymer comprises polypyrrole, polyaniline,
2 polythiophene, poly-p-phenylene vinylene, poly(alkyl and alkoxythiophenes), poly(3,4-
3 ethylenedioxythiophene) (PEDOT) and their substituted derivatives or doped derivatives.

1 25. The method of claim 21, further comprising the step of adding one or more dopants to
2 the polymer, wherein the one or more dopants are selected from polystyrene sulfonate,
3 hydrochloric acid, tosylate ion, camphorsulfonic acid, dodecylbenzene sulfonic acid,
4 perfluorodecane sulfonic acid, trifluoroacetic acid, perchloric acid, or combinations thereof.

1 26. A method of making a nanostructured phospho-olivine hybrid composition comprising
2 the steps of:

3 dissolving a lithium-containing compound such as lithium hydroxide and one or more
4 metal salts in an aqueous solvent;

5 adding one or more monosaccharides to the solvent;

6 adding H_3PO_4 or a phosphate-containing compound to the aqueous solvent to form a precursor
7 solution with a 1:1:1 molar ratio of Li:M:P;

8 heating hydrothermally the precursor solution with a microwave device that operates at a
9 frequency of between 1.5 and 3.5 GHz and a power of between 1 and 3,000 W;

10 separating the LiMPO_4 nanostructured phospho-olivine material from the precursor solution; and
11 encapsulating the LiMPO_4 nanostructured phospho-olivine material with one or more polymers
12 selected from an electronically conductive polymer, a doped polymer, an electronically and
13 ionically conductive polymer, or a combination thereof, wherein the polymer varies from 0.1 wt
14 % to 50 wt%.

1 27. The method of claim 26, further comprising the step of adding an iron (II) composition to
2 the aqueous solvent to form a nanostructured phospho-olivine material having the formula
3 $\text{Li}_x\text{Fe}_{1-y}\text{M}_y\text{PO}_4$.

1 28. The method of claim 26, wherein the polymer comprises polypyrrole, polyaniline,
2 polythiophene, poly-p-phenylene vinylene, poly(alkyl and alkoxythiophenes), poly(3,4-
3 ethylenedioxythiophene) (PEDOT and their substituted derivatives or doped derivatives.

1 29. The method of claim 26, further comprising the step of adding one or more dopants to
2 the one or more polymers, wherein the one or more dopants comprises polystyrene sulfonate,
3 hydrochloric acid, tosylate ion, camphorsulfonic acid, dodecylbenzene sulfonic acid,
4 perfluorodecane sulfonic acid, trifluoroacetic acid, perchloric acid, or combinations thereof.

1 30. The method of claim 26, further comprising the step of adding *p*-toluene sulfonic acid
2 doped poly(3,4-ethylenedioxythiophene) to modify the nanostructured phospho-olivine hybrid
3 composition to improve the electronic and ionic conductivity.

1 31. A method of making a nanostructured phospho-olivine hybrid composition comprising
2 the steps of:

3 dissolving a lithium-containing compound such as lithium hydroxide and one or more
4 metal salts in a non-aqueous solvent;
5 adding H₃PO₄ or a phosphate-containing compound to the non-aqueous solvent to form a
6 precursor solution with a 1:1:1 molar ratio of Li:M:P;
7 heating solvothermally the precursor solution with a microwave device that operates at a
8 frequency of between 1.5 and 3.5 GHz and a power of between 1 and 3,000 W;
9 separating the LiMPO₄ nanostructured phospho-olivine material from the precursor solution; and
10 encapsulating the LiMPO₄ nanostructured phospho-olivine material with one or more polymers
11 selected from an electronically conductive polymer, a doped polymer, an electronically and
12 ionically conductive polymer, or a combination thereof, wherein the polymer varies from 0.1 wt
13 % to 50 wt%.

1 32. The method of claim 31, further comprising the step of adding a iron (II) composition to
2 the non-aqueous solvent to form a nanostructured phospho-olivine material having the formula
3 Li_xFe_{1-y}M_yPO₄.

1 33. The method of claim 31, wherein the polymer comprises polypyrrole, polyaniline,
2 polythiophene, poly-p-phenylene vinylene, poly(alkyl and alkoxythiophenes), poly(3,4-
3 ethylenedioxythiophene) (PEDOT and their substituted derivatives or doped derivatives.

1 34. The method of claim 31, further comprising the step of adding one or more dopants to
2 the one or more polymers, wherein the one or more dopants comprises polystyrene sulfonate,
3 hydrochloric acid, tosylate ion, camphorsulfonic acid, dodecylbenzene sulfonic acid,
4 perfluorodecane sulfonic acid, trifluoroacetic acid, perchloric acid, or combinations thereof.

1 35. The method of claim 31, further comprising the step of adding *p*-toluene sulfonic acid
2 doped poly(3,4-ethylenedioxythiophene) to modify the nanostructured phospho-olivine hybrid
3 composition to improve the electronic and ionic conductivity.

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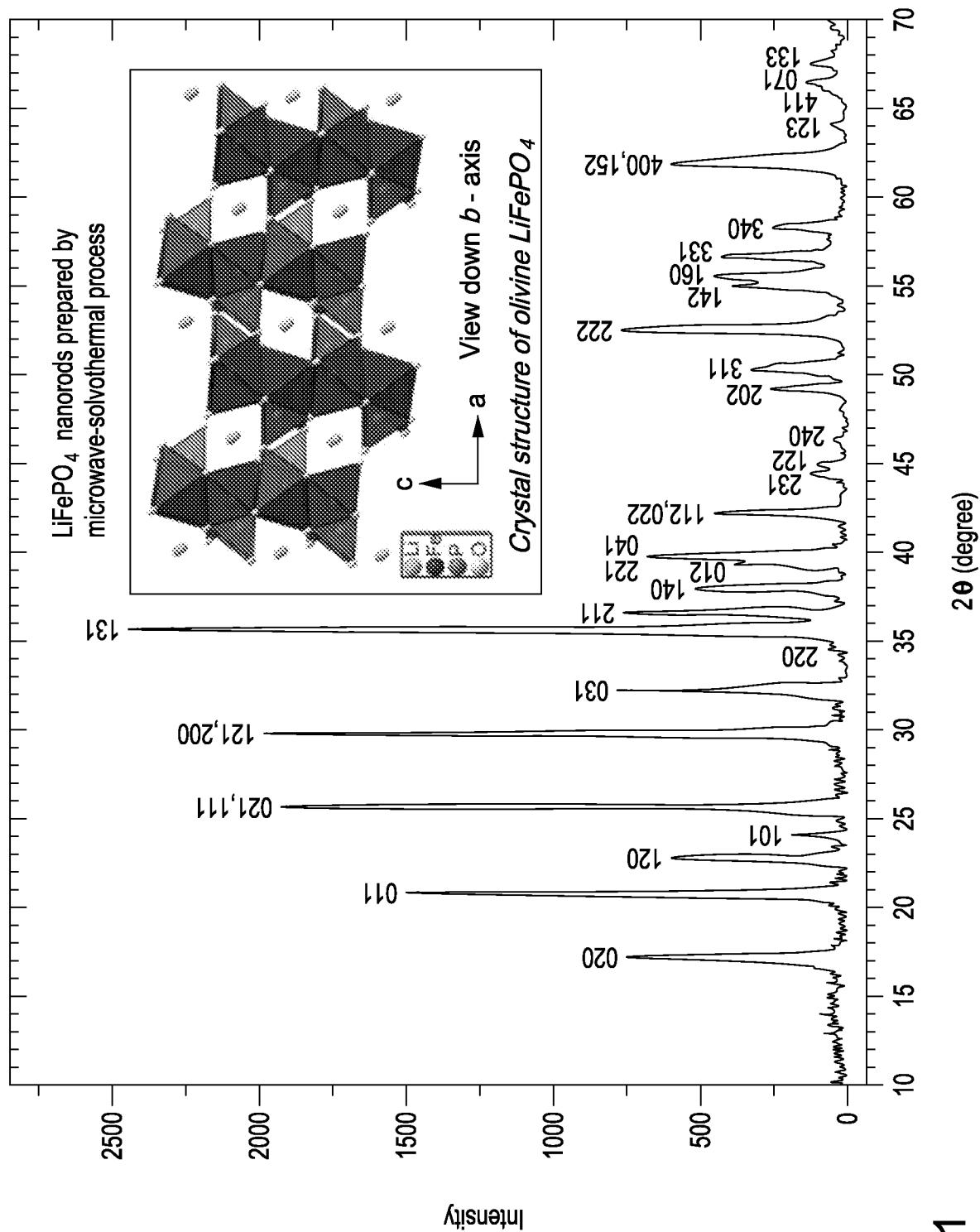


FIG. 1

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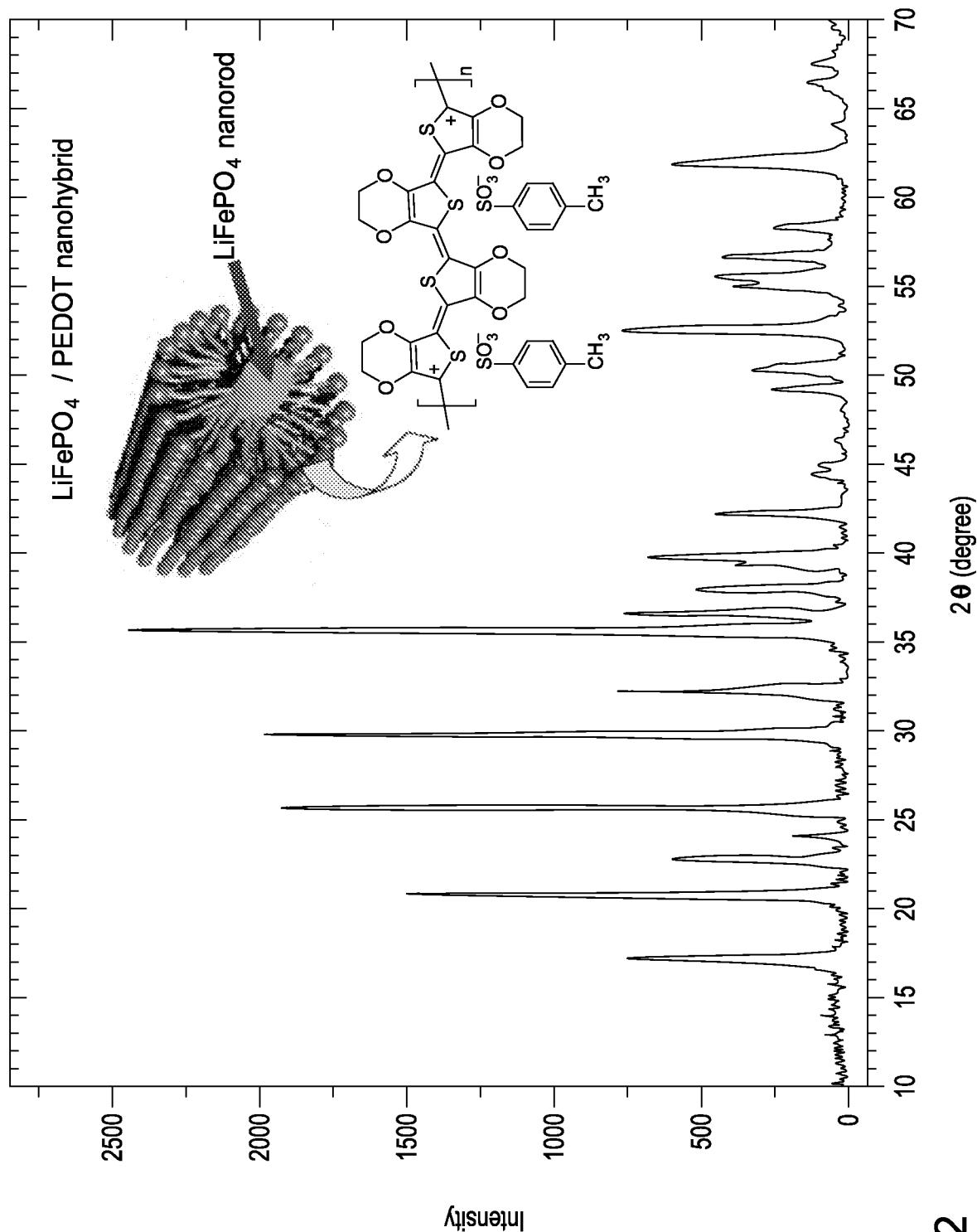


FIG. 2

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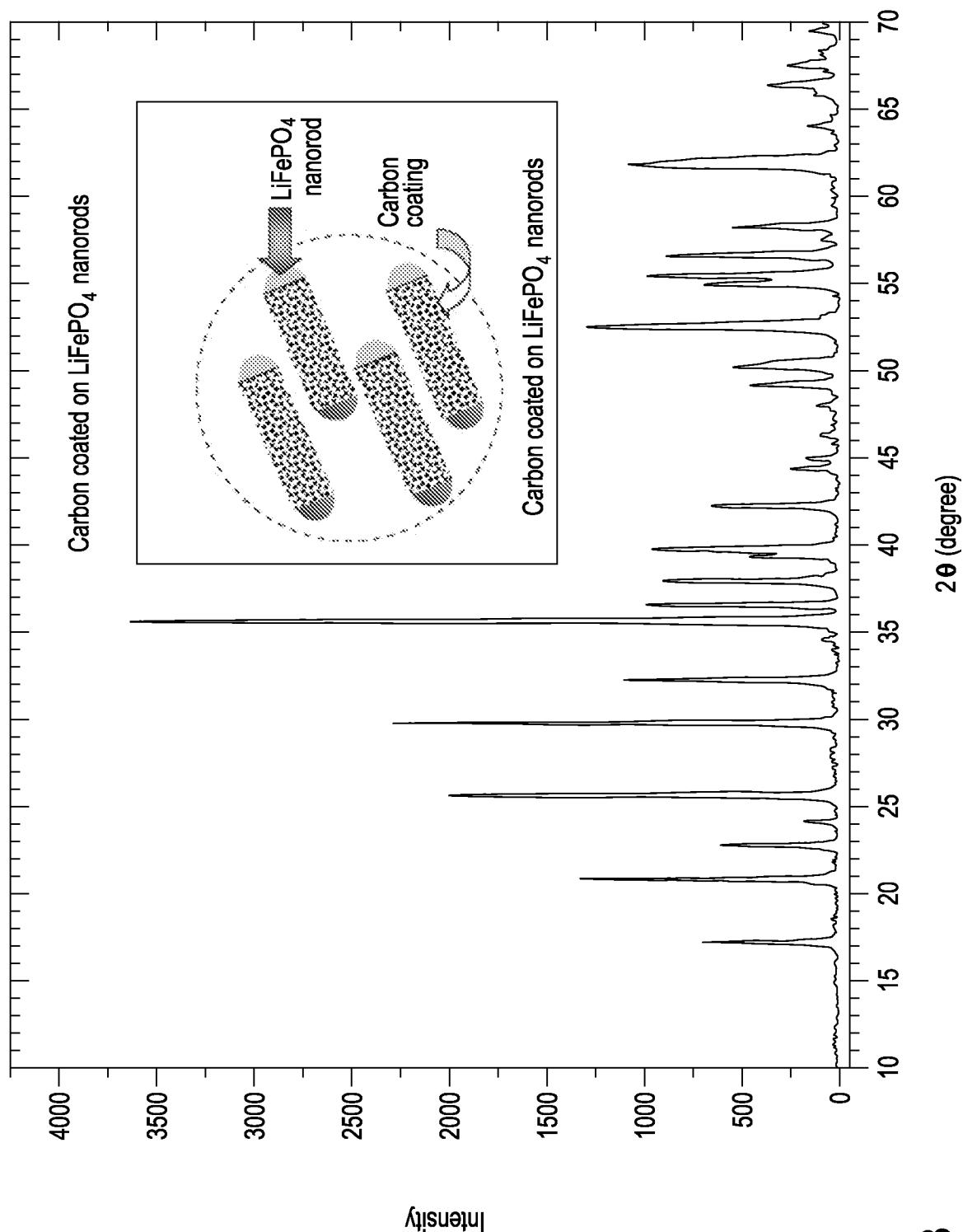
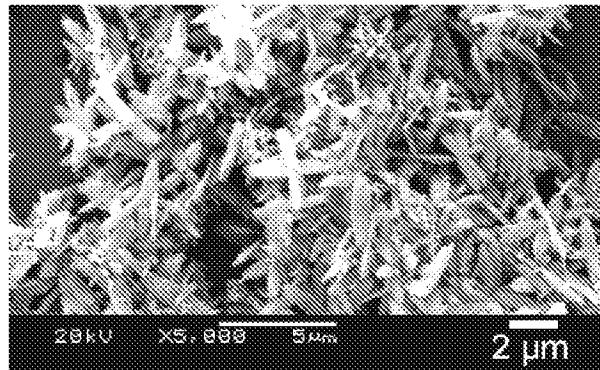
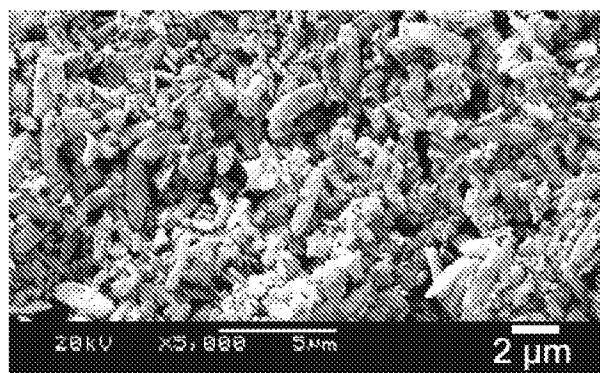
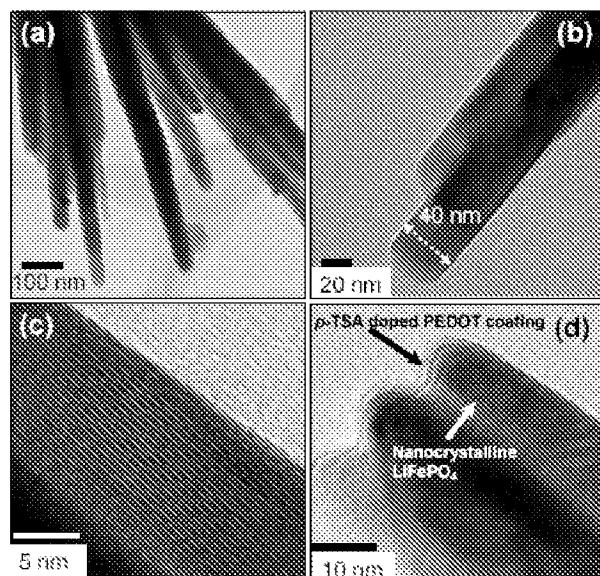
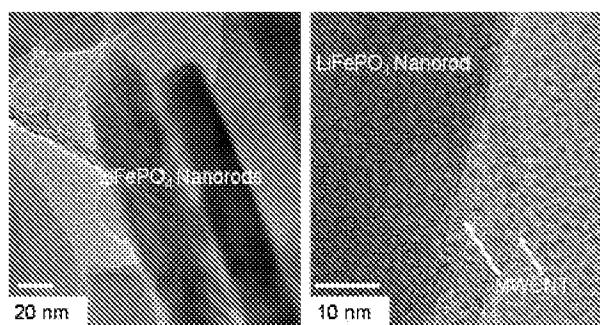


FIG. 3

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FIG. 4a**FIG. 4b****FIG. 5****FIG. 6**

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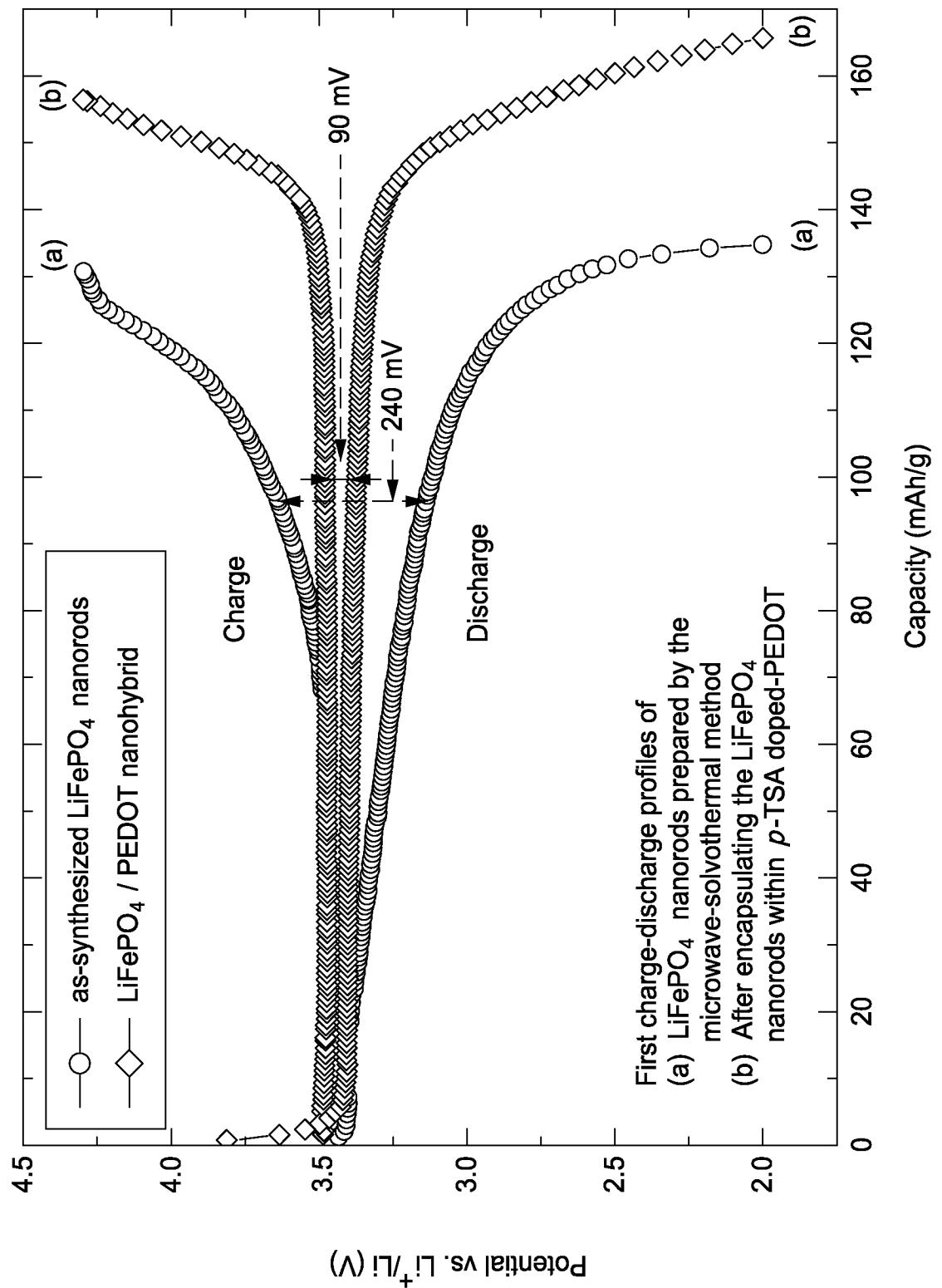
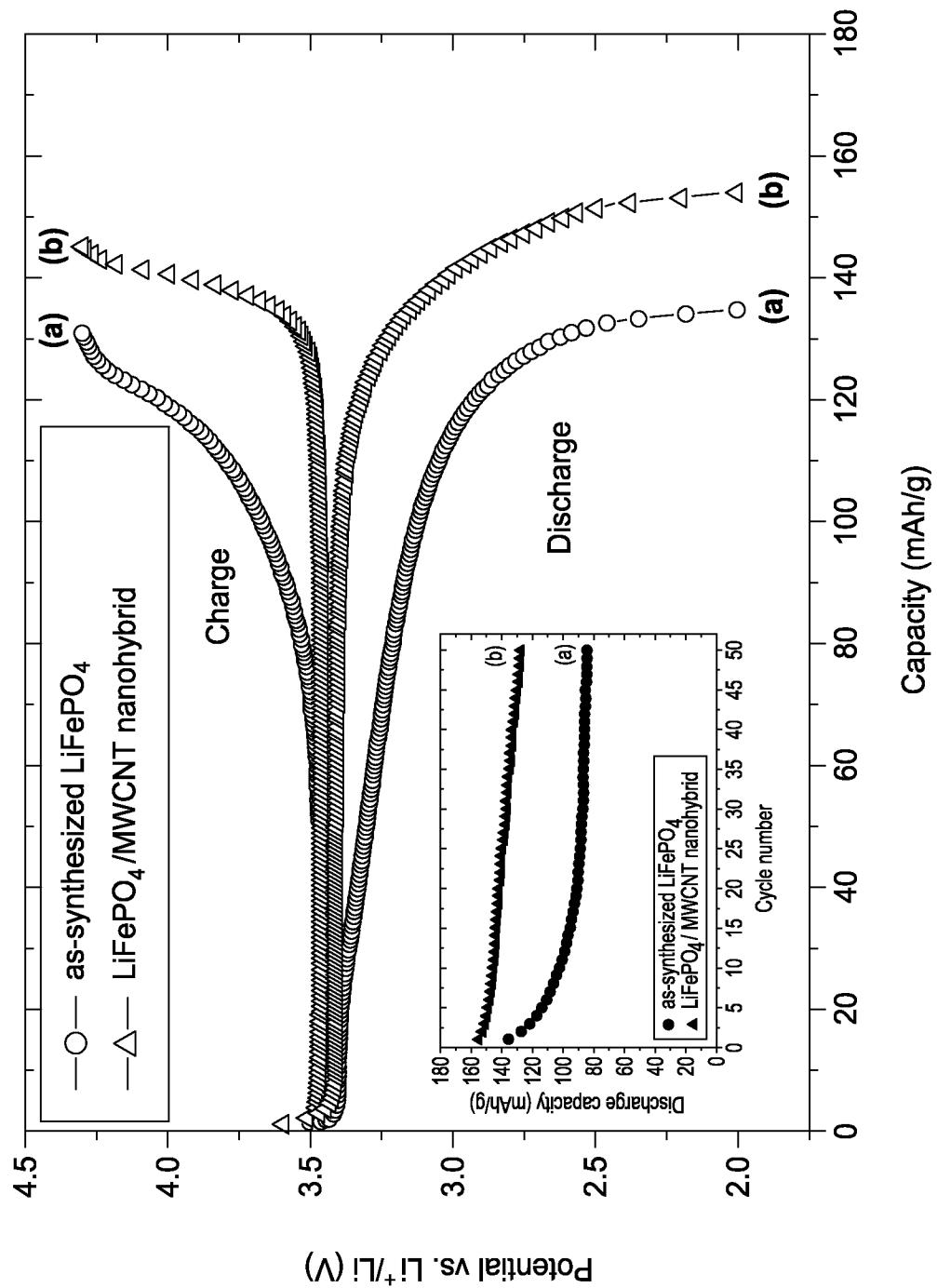
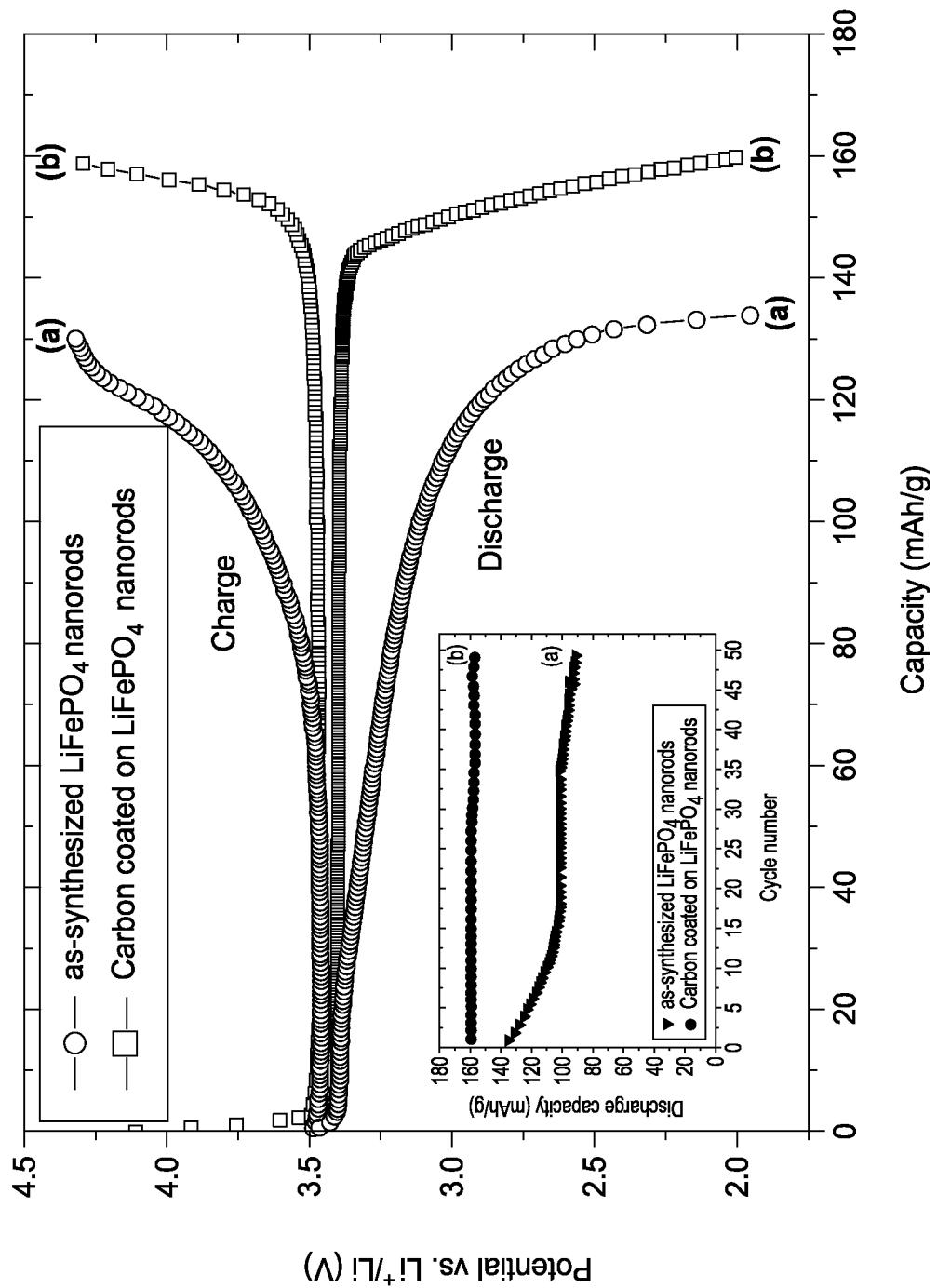


FIG. 7

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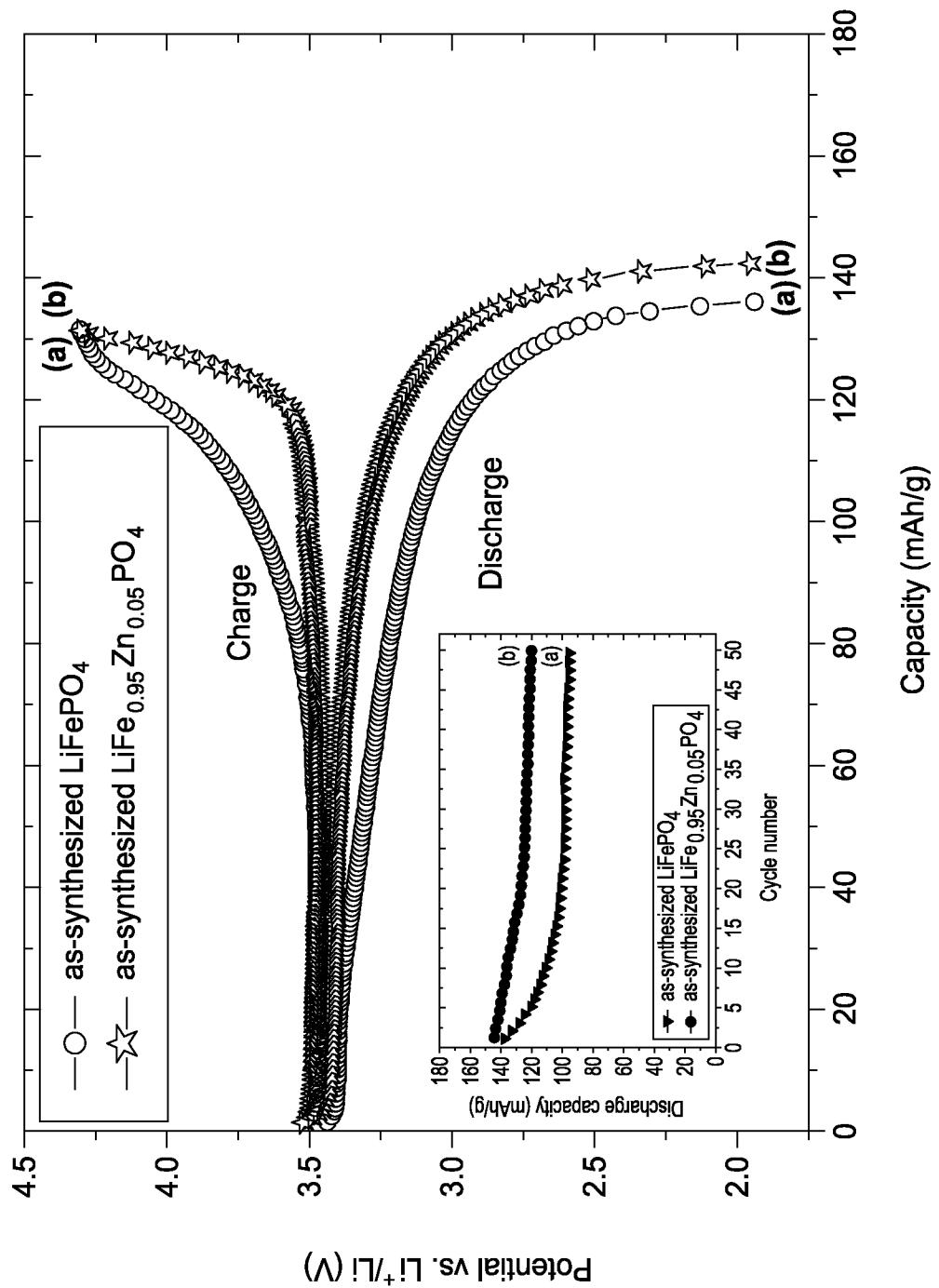
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First charge-discharge profiles of
(a) LiFePO_4 nanorods prepared by the microwave-solvothermal method
(b) After encapsulating the LiFePO_4 nanorods coated with carbon

FIG. 9

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First charge-discharge profiles of
(a) LiFePO_4 nanorods prepared by the microwave-solvothermal method
(b) $\text{LiFe}_{0.95}\text{Zn}_{0.05}\text{PO}_4$ nanorods

FIG. 10

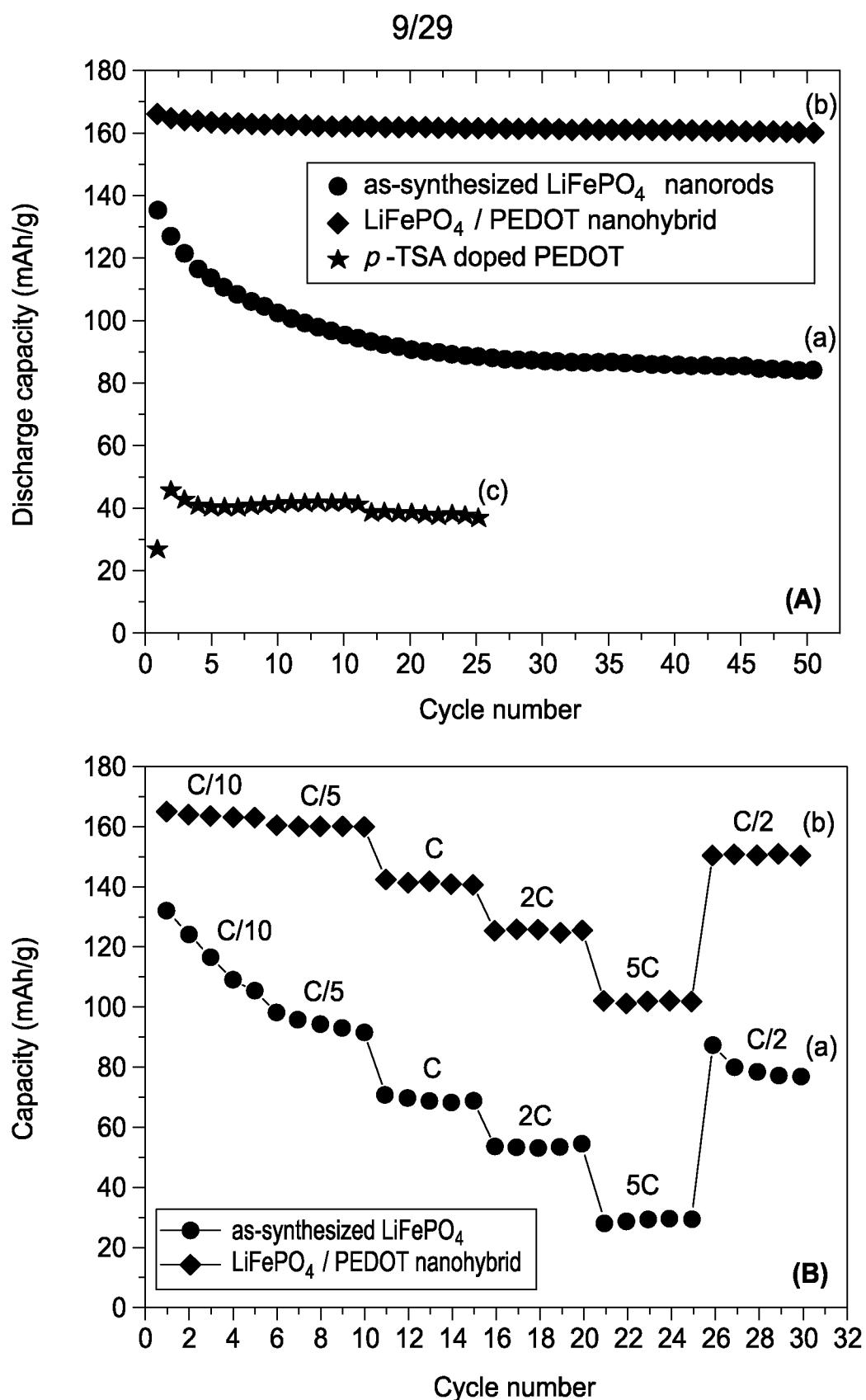
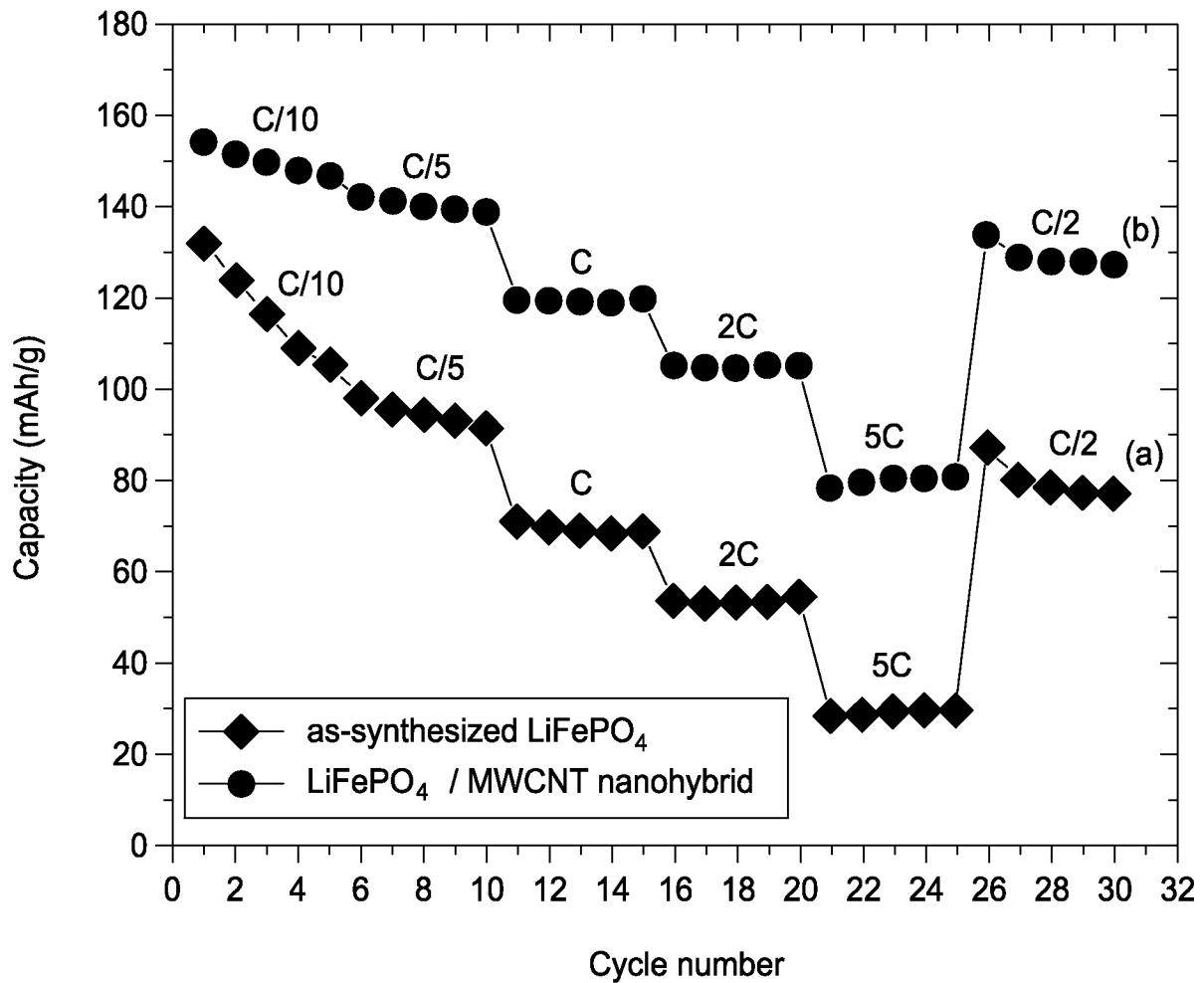


FIG. 11

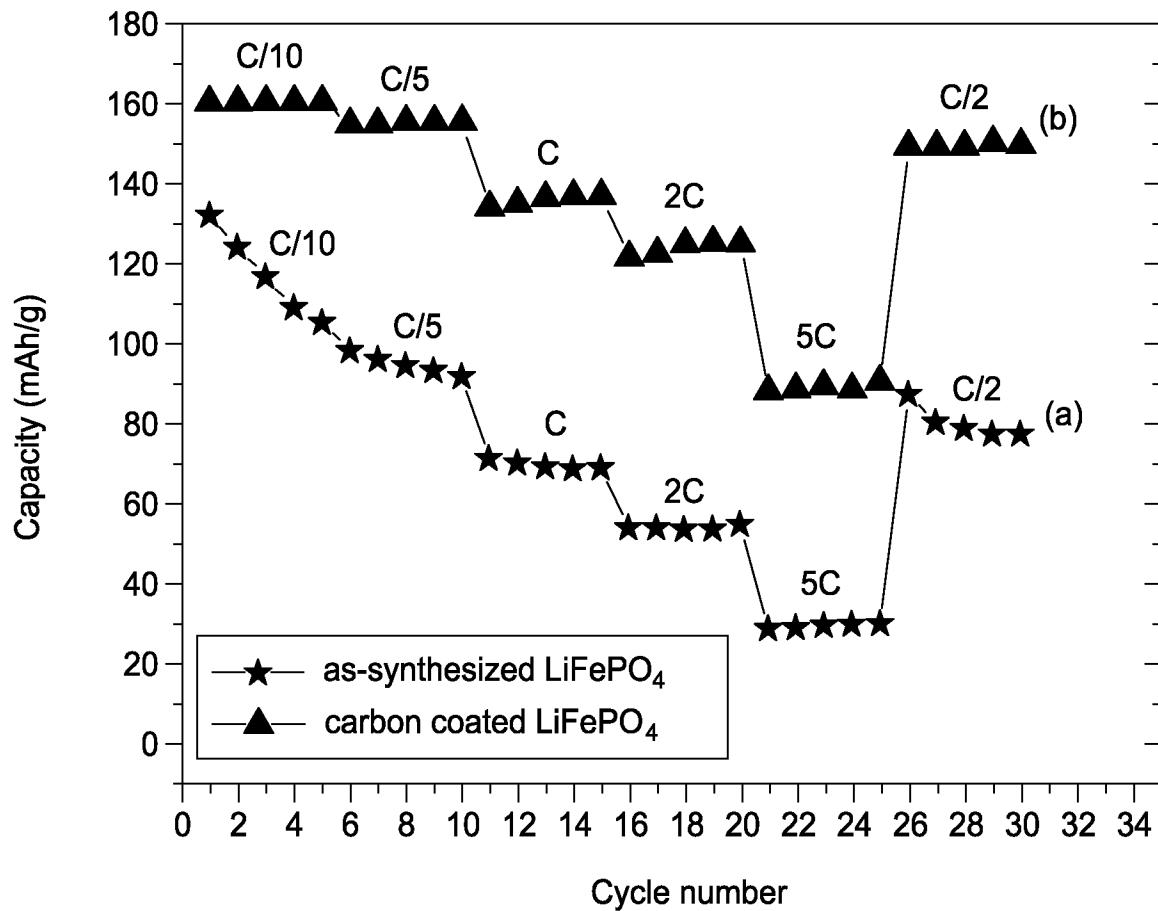
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- (a) LiFePO_4 nanorods prepared by the microwave-solvothermal method
(b) After encapsulating the LiFePO_4 nanorods coated with MWCNT

FIG. 12

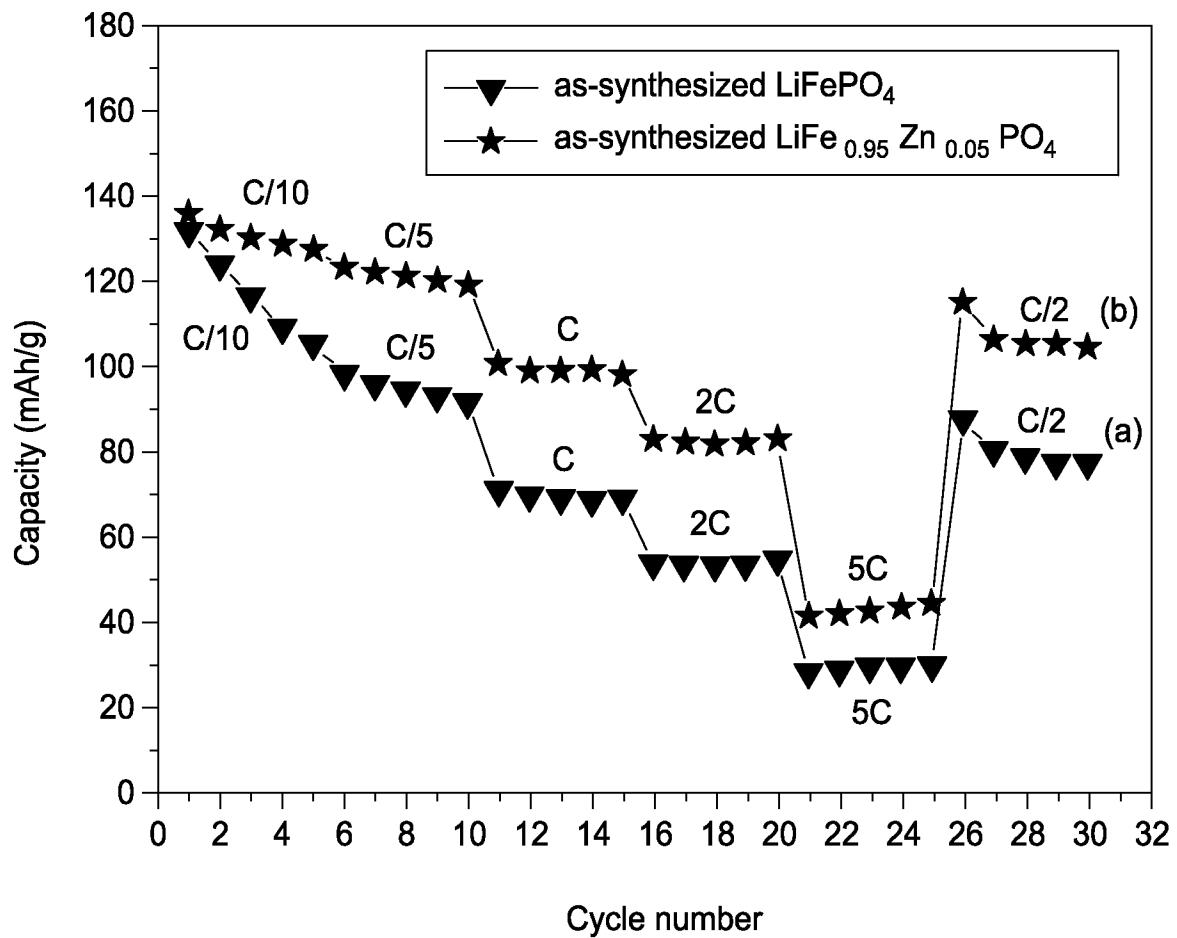
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- (a) *LiFePO₄ nanorods prepared by the microwave-solvothermal method*
(b) *After encapsulating the LiFePO₄ nanorods coated with carbon*

FIG. 13

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- (a) LiFePO_4 nanorods prepared by the microwave-solvothermal method
(b) $\text{LiFe}_{0.95}\text{Zn}_{0.05}\text{PO}_4$ nanorods

FIG. 14

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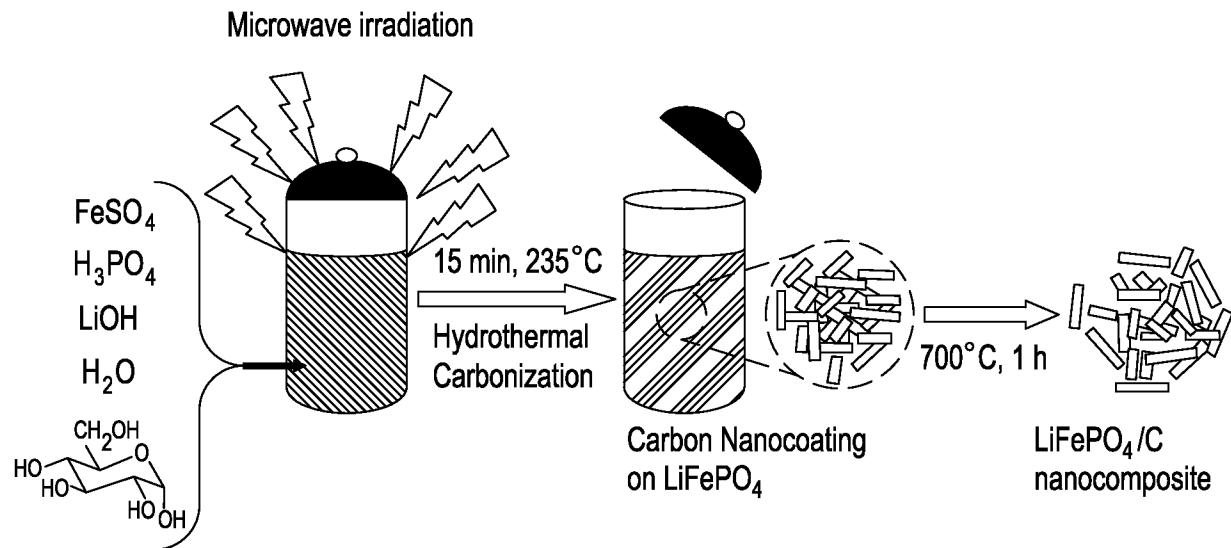


FIG. 15

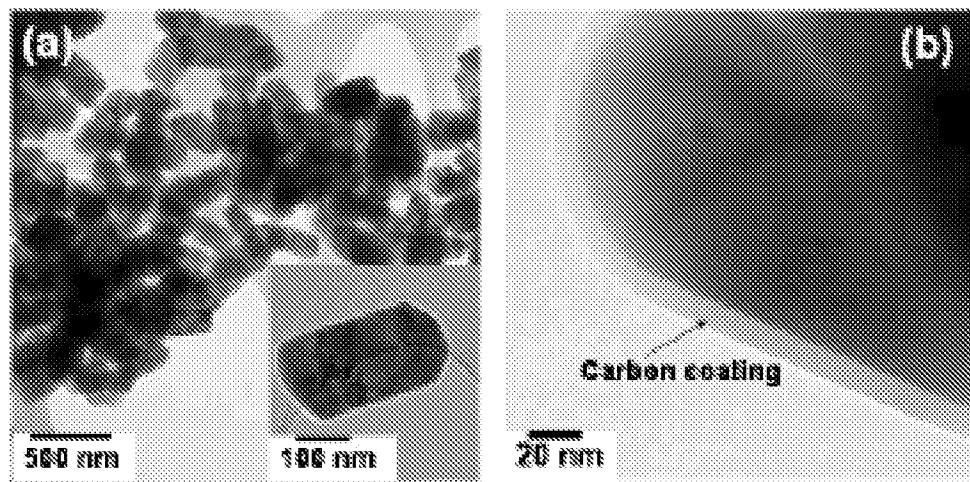


FIG. 17

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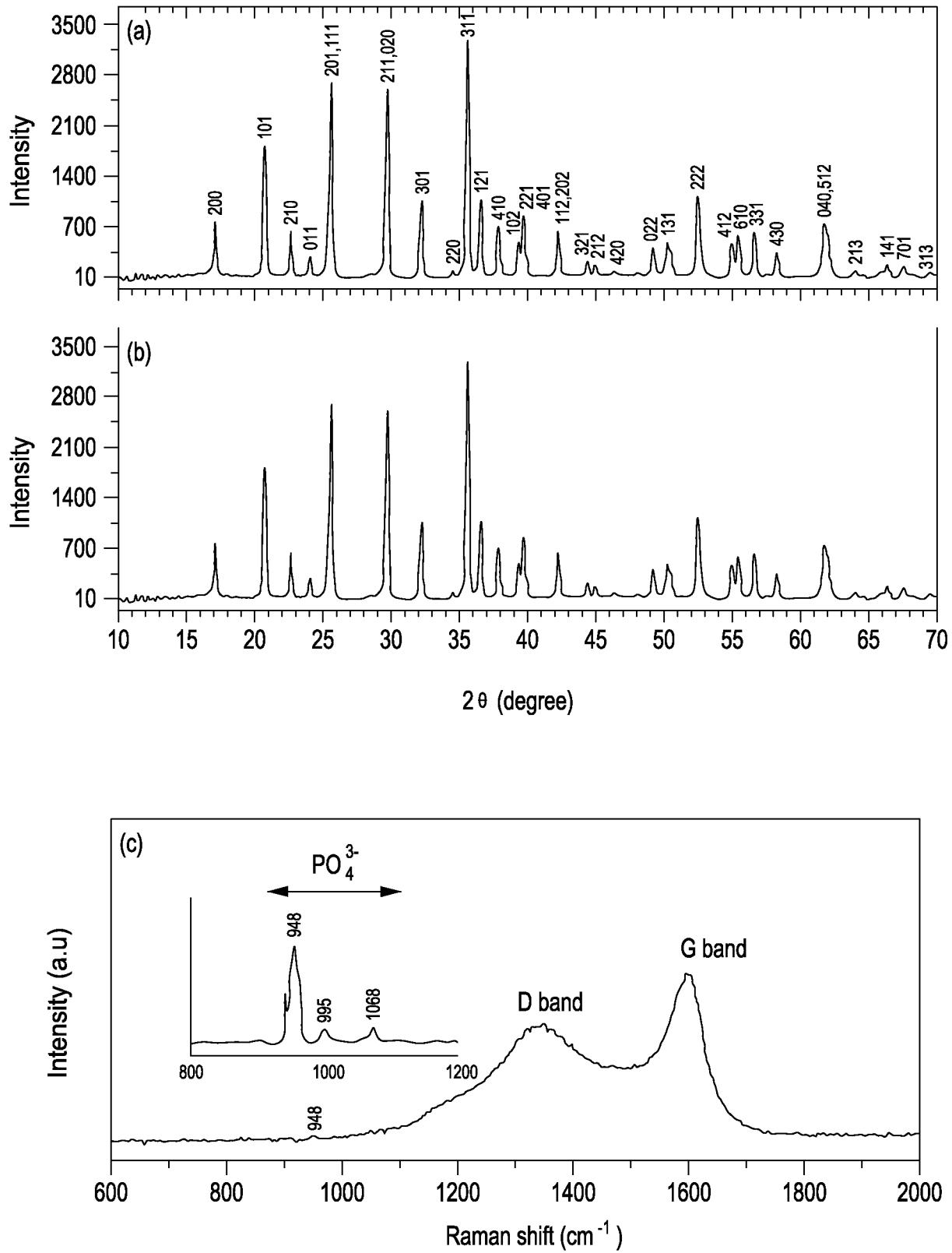


FIG. 16

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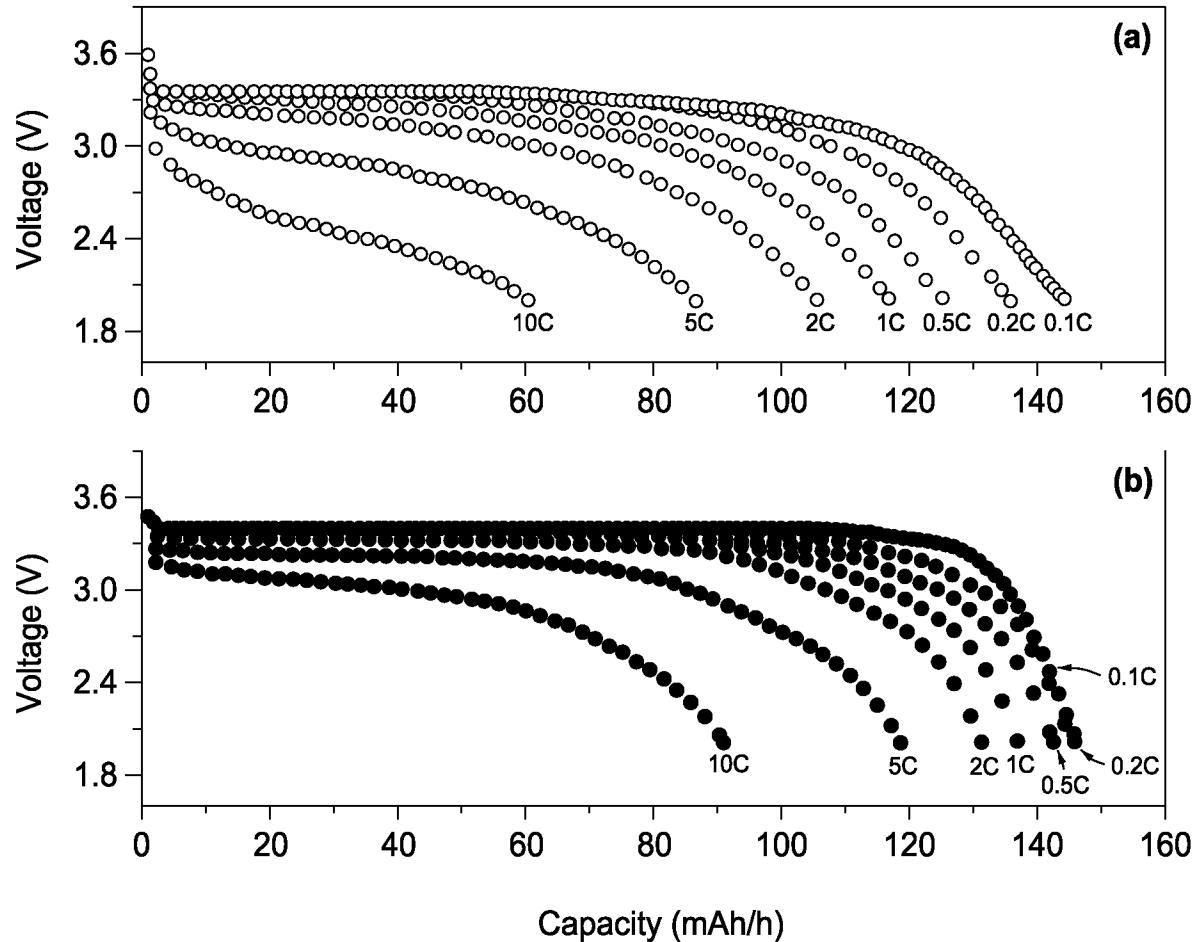


FIG. 18

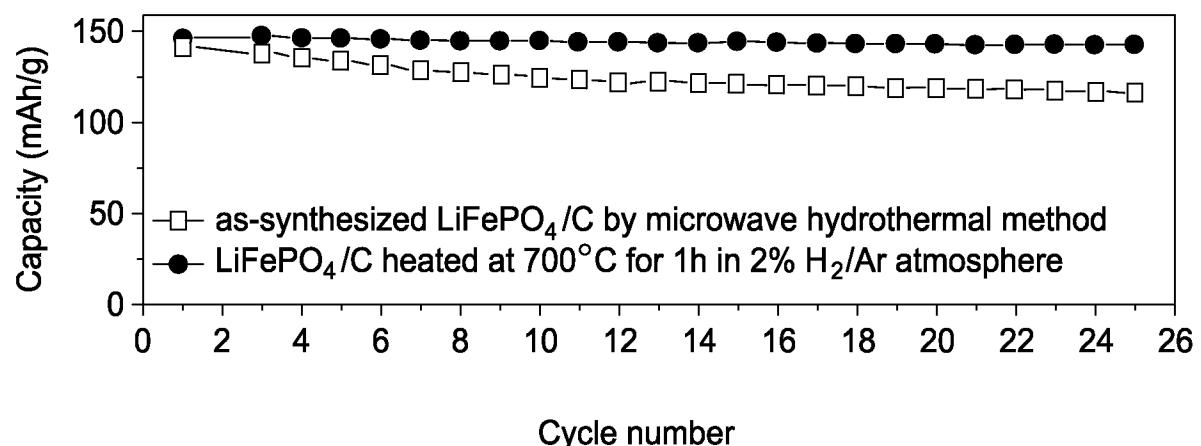


FIG. 19

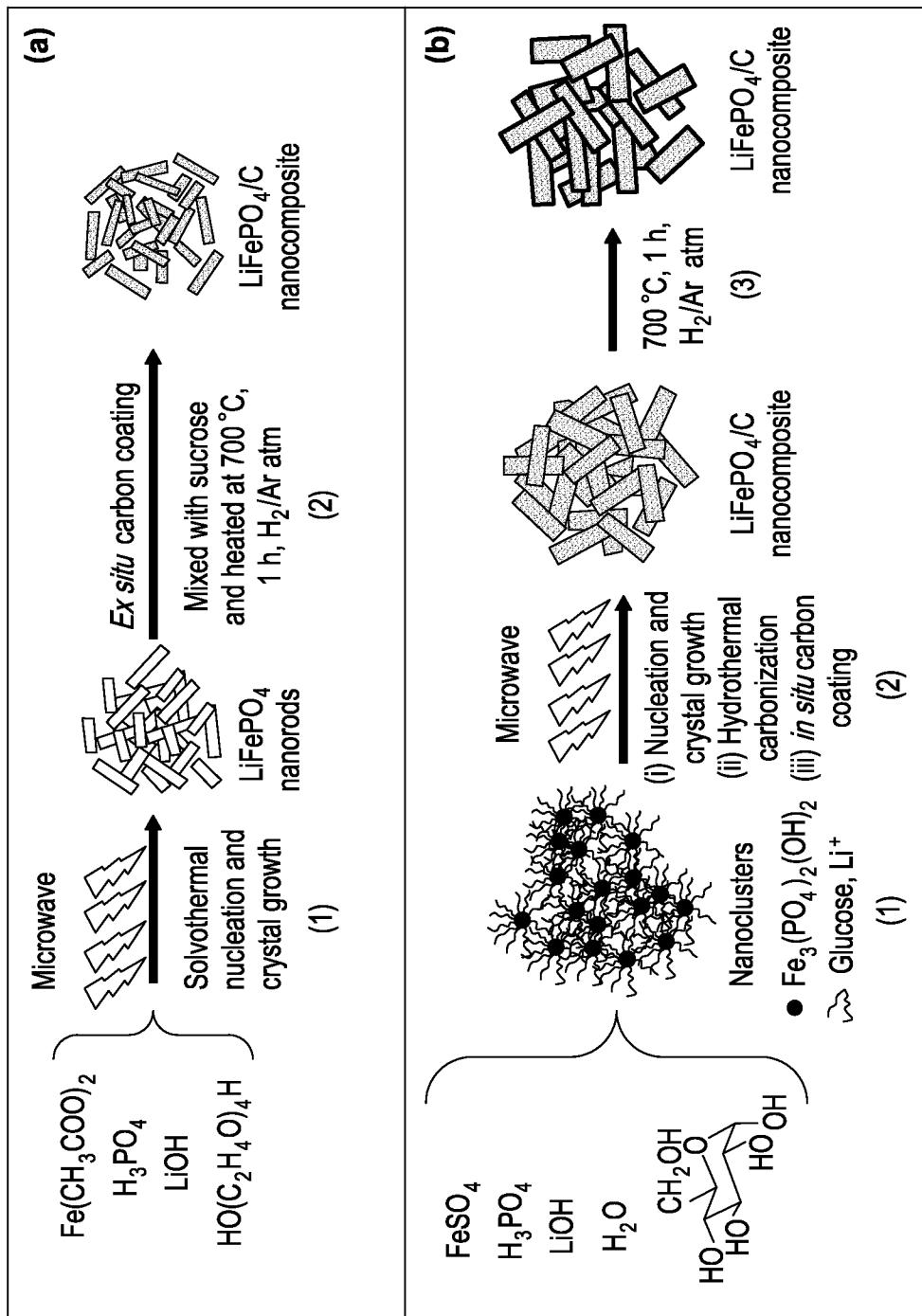


FIG. 20

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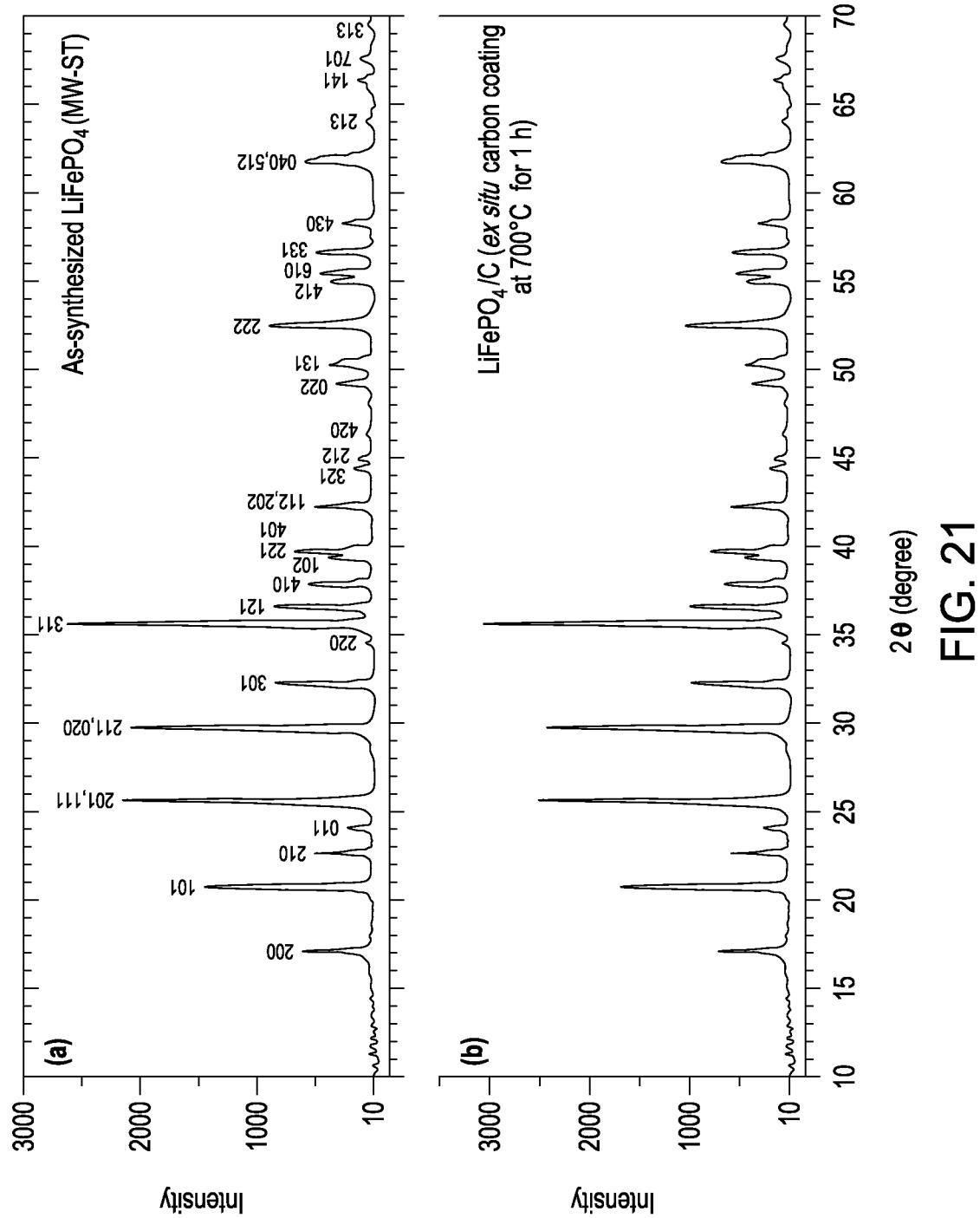


FIG. 21

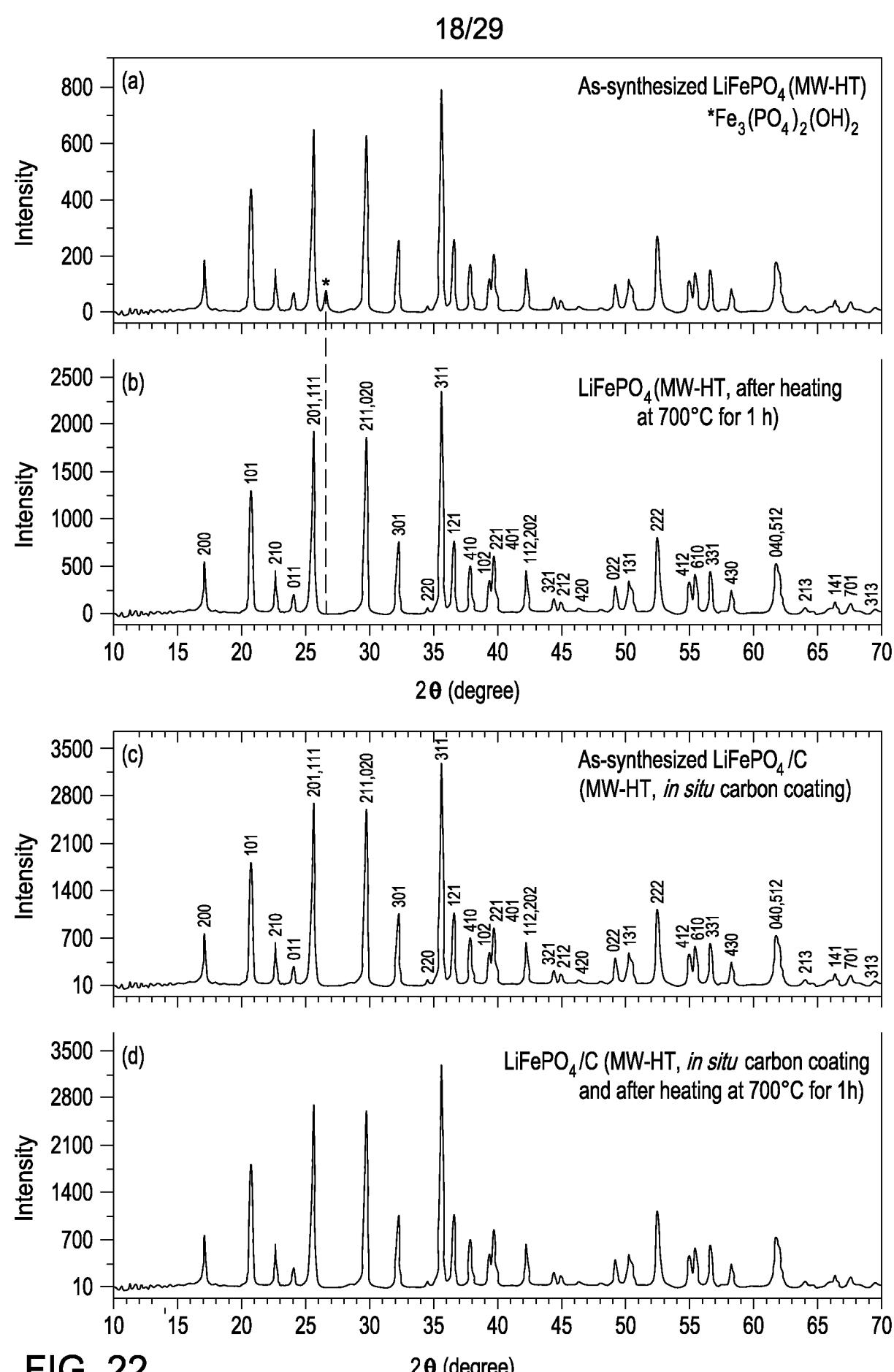


FIG. 22

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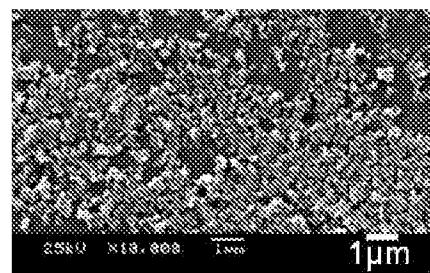


FIG. 23A

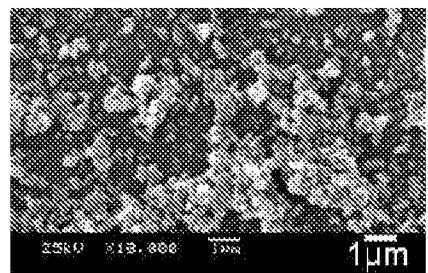


FIG. 23B

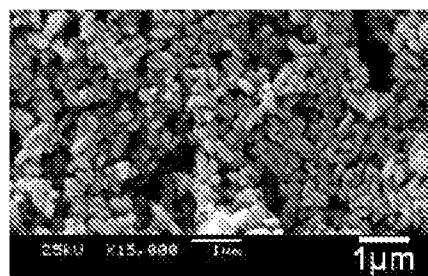


FIG. 23C

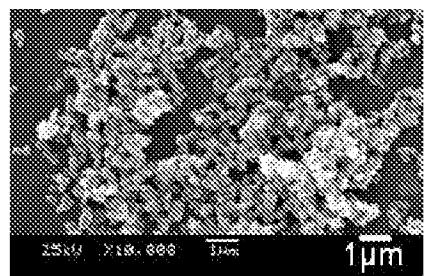


FIG. 23D

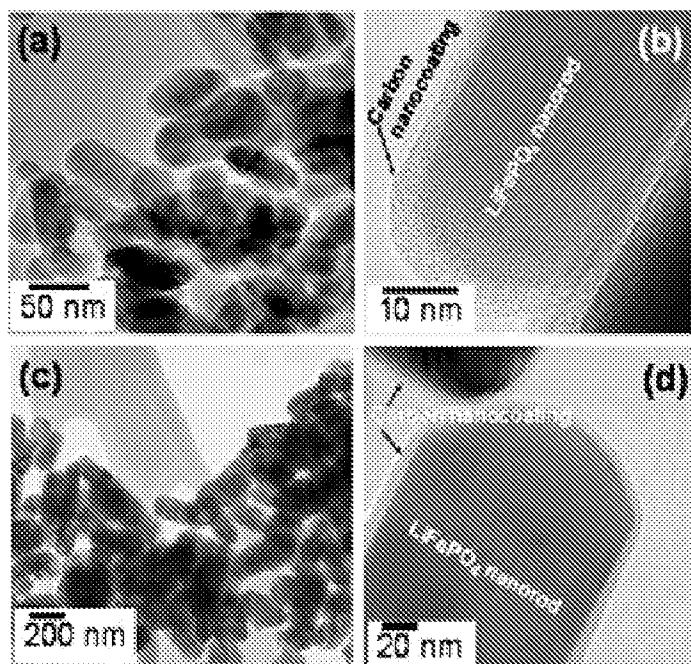
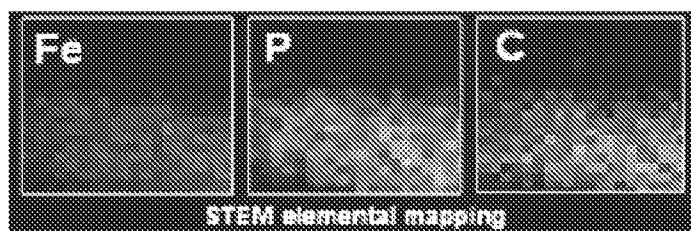


FIG. 24



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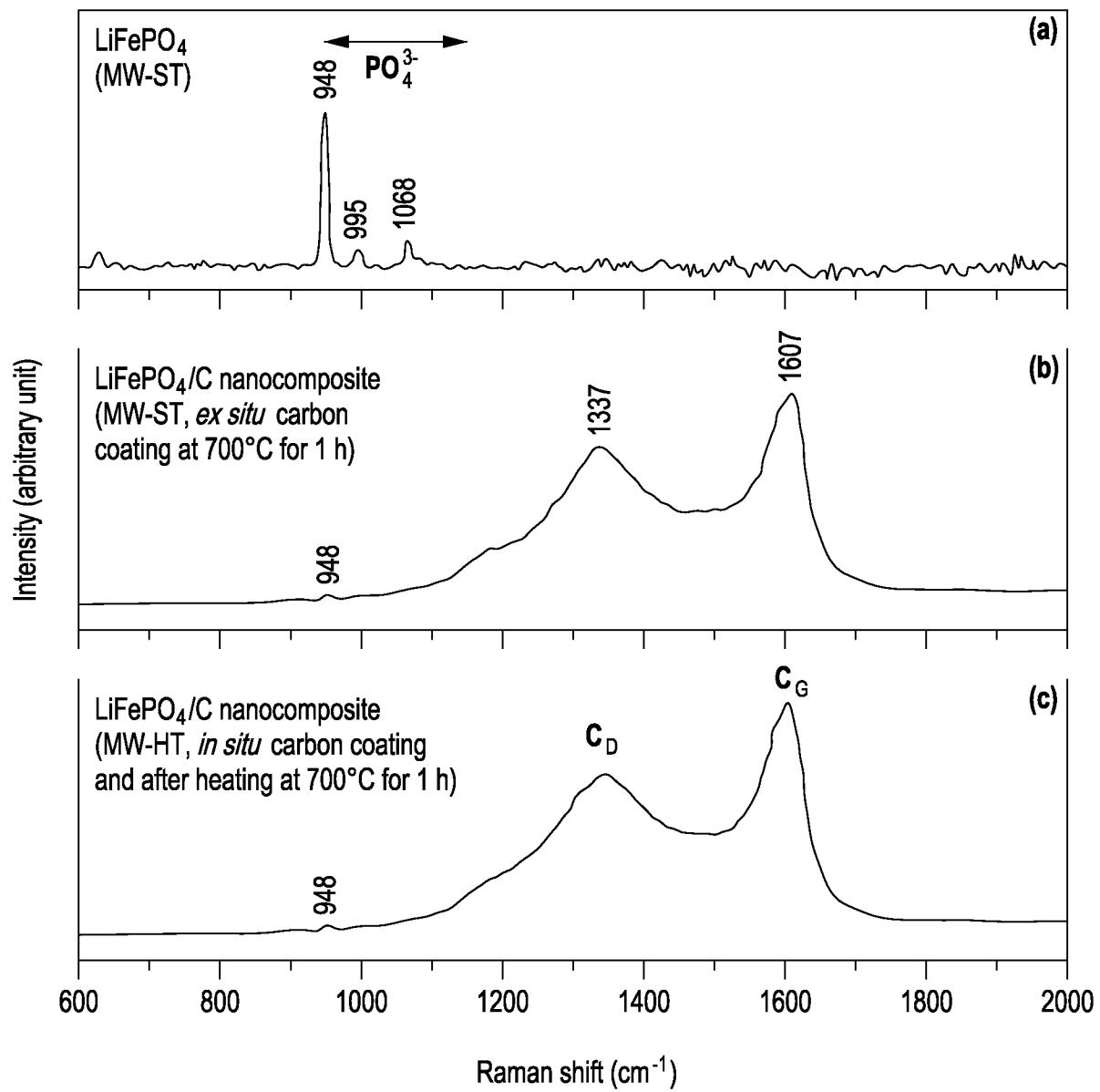
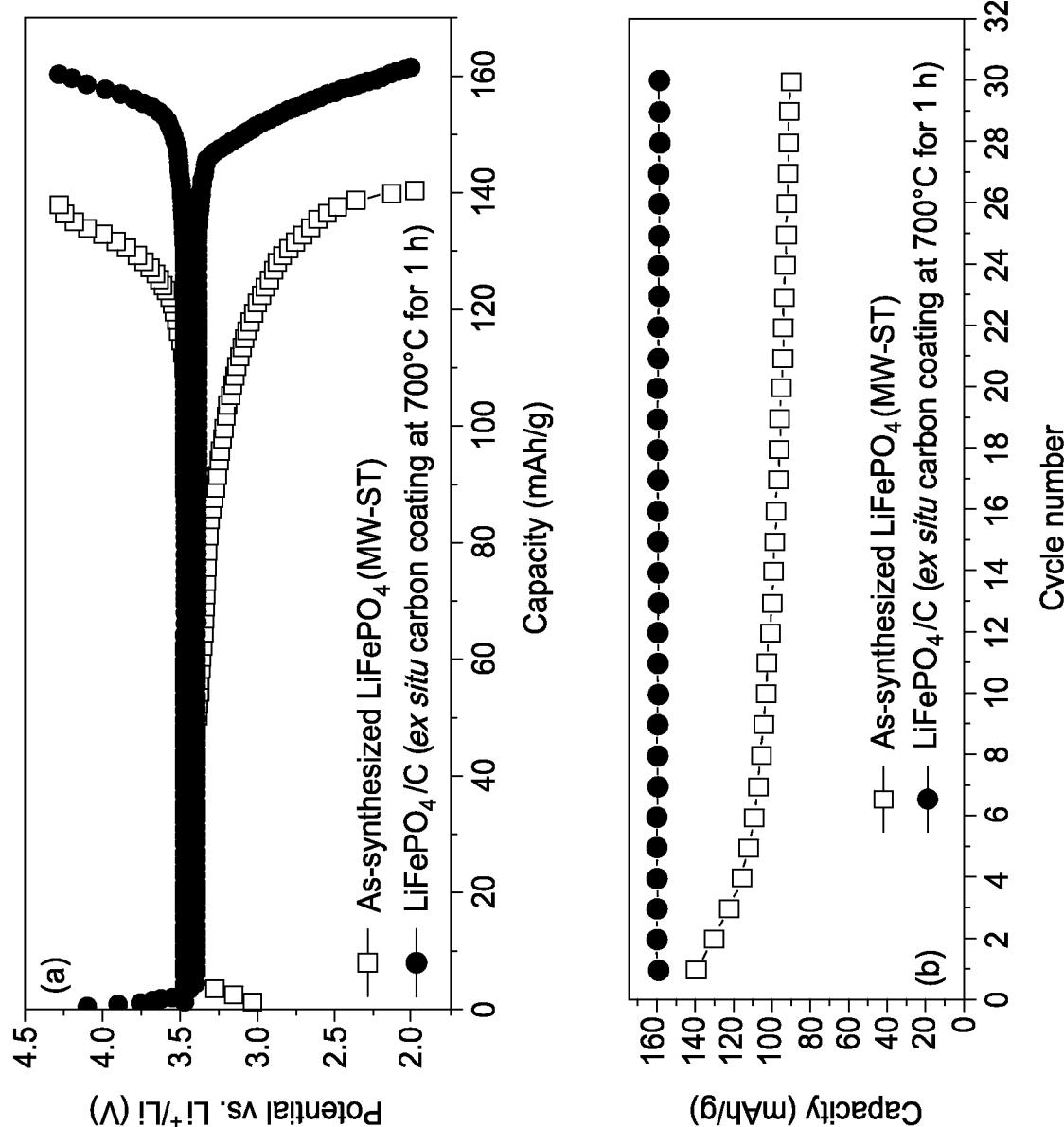


FIG. 25

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FIG. 26



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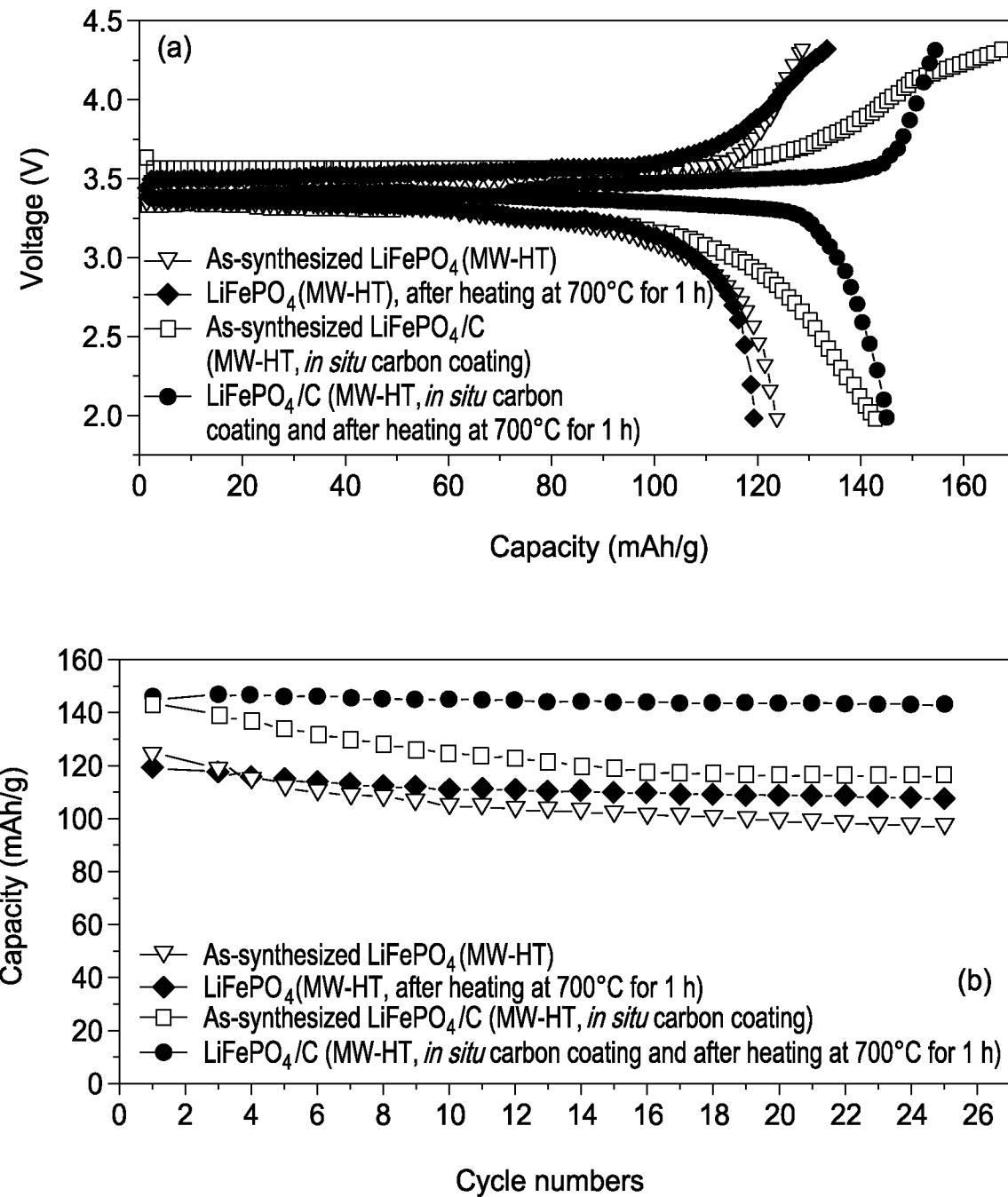


FIG. 27

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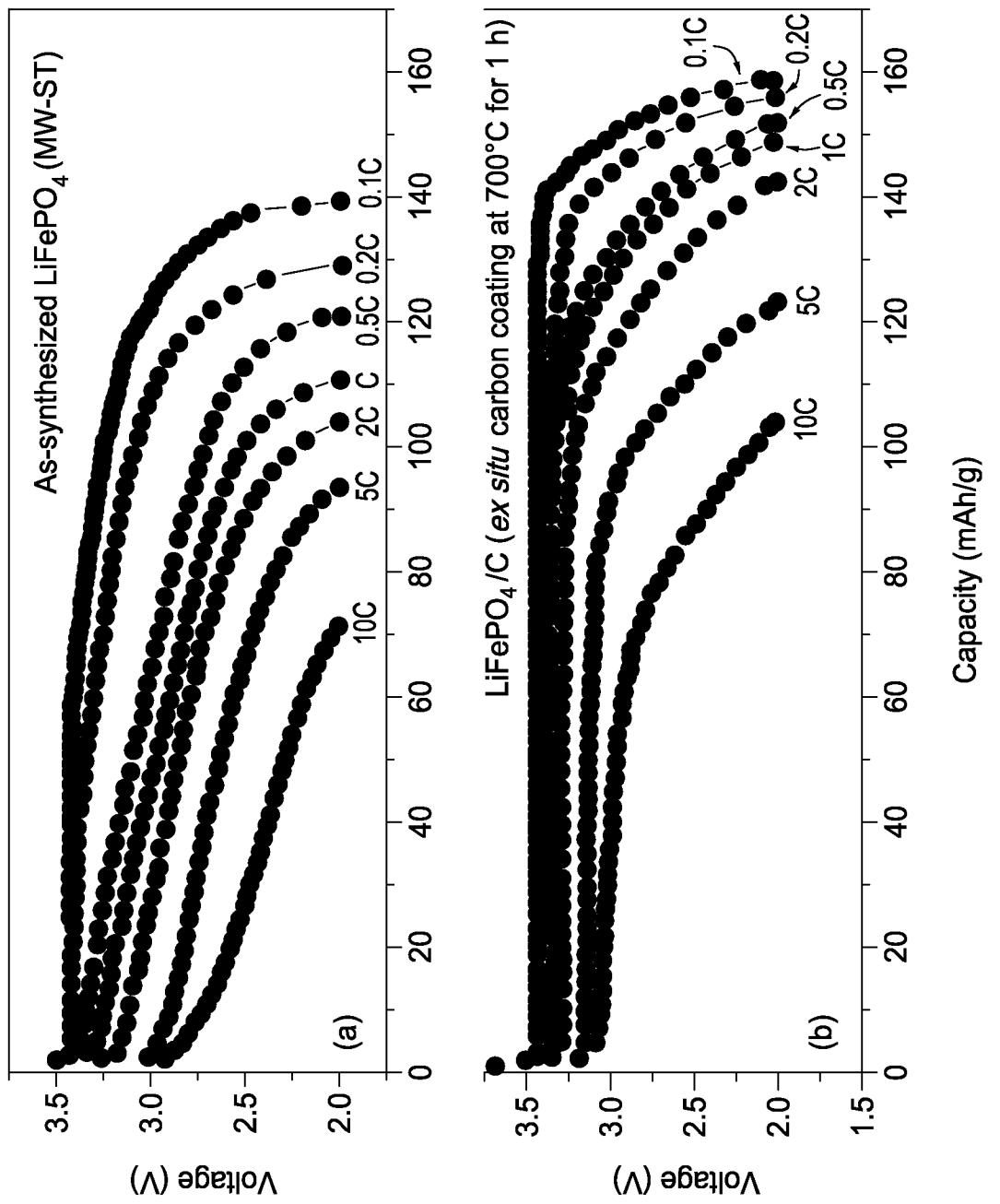
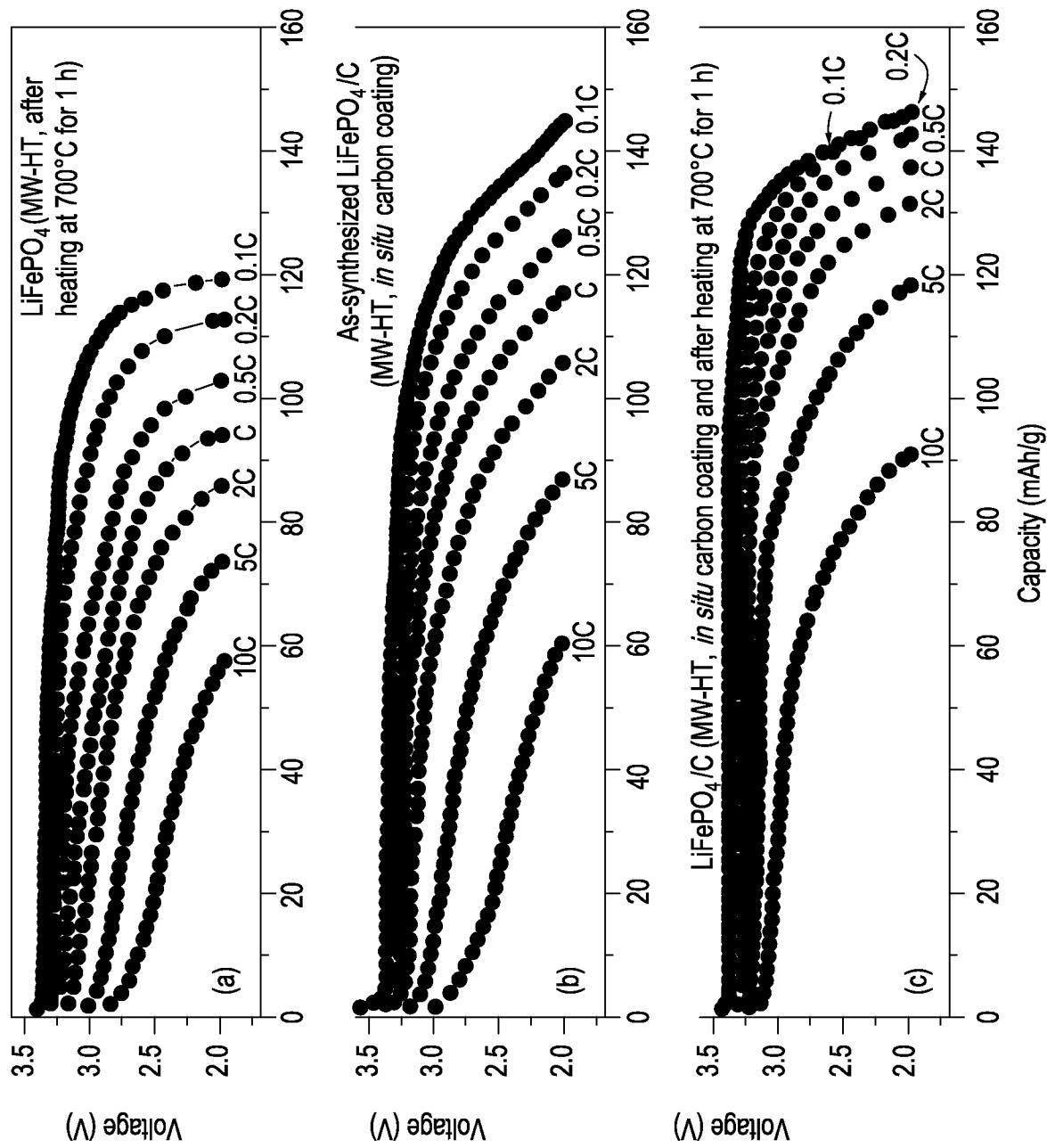


FIG. 28

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FIG. 29



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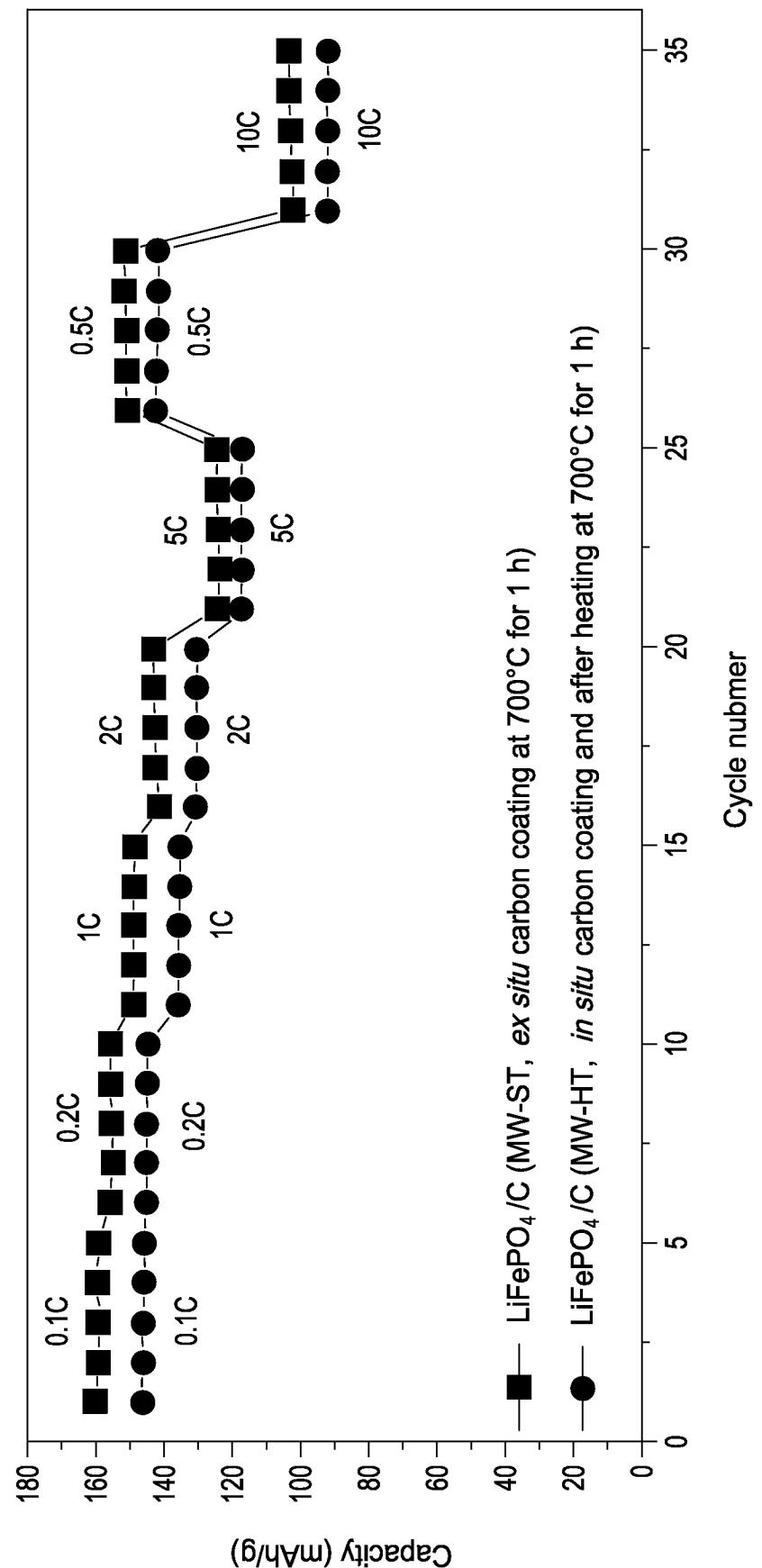
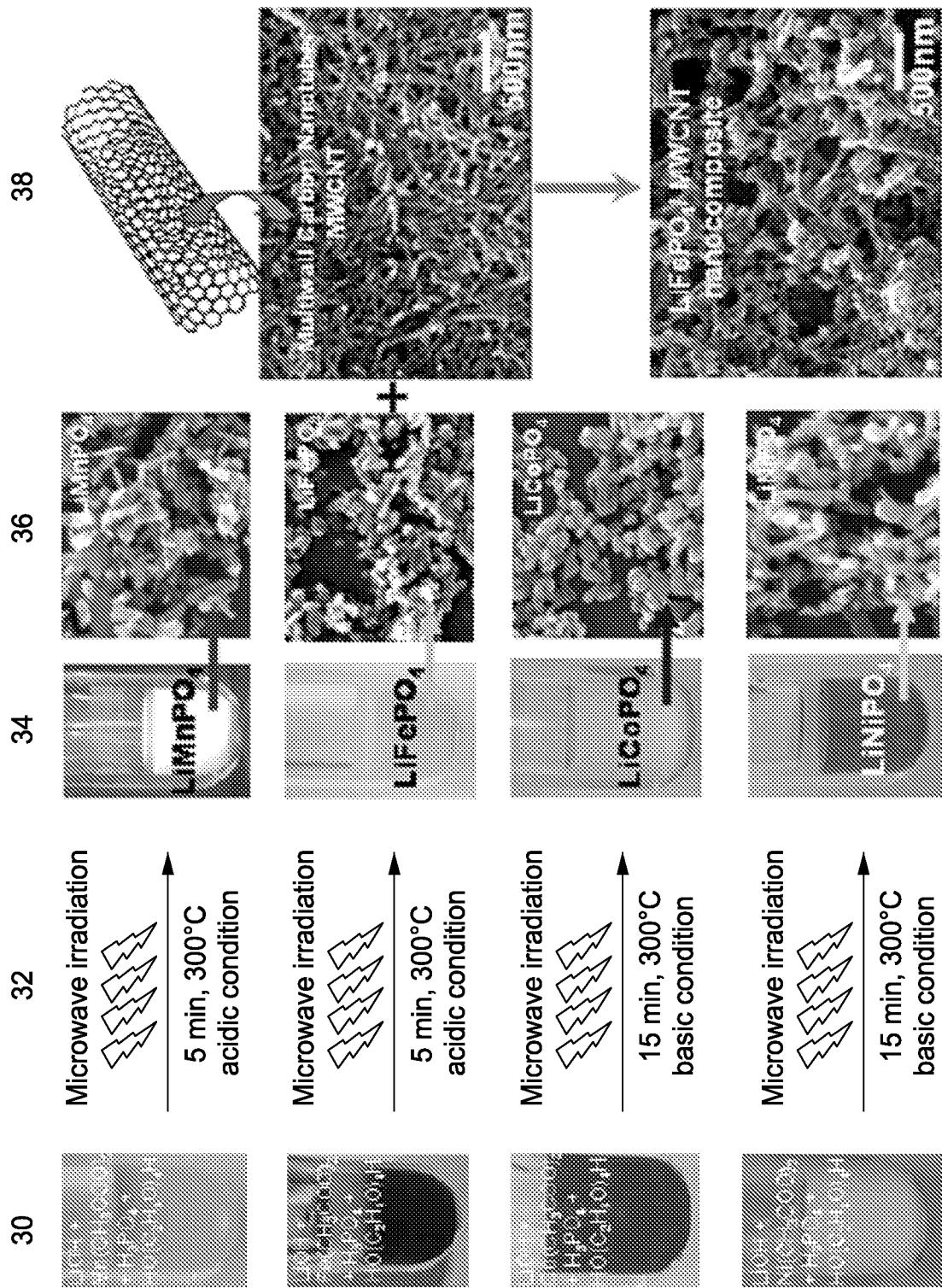


FIG. 30

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FIG. 31



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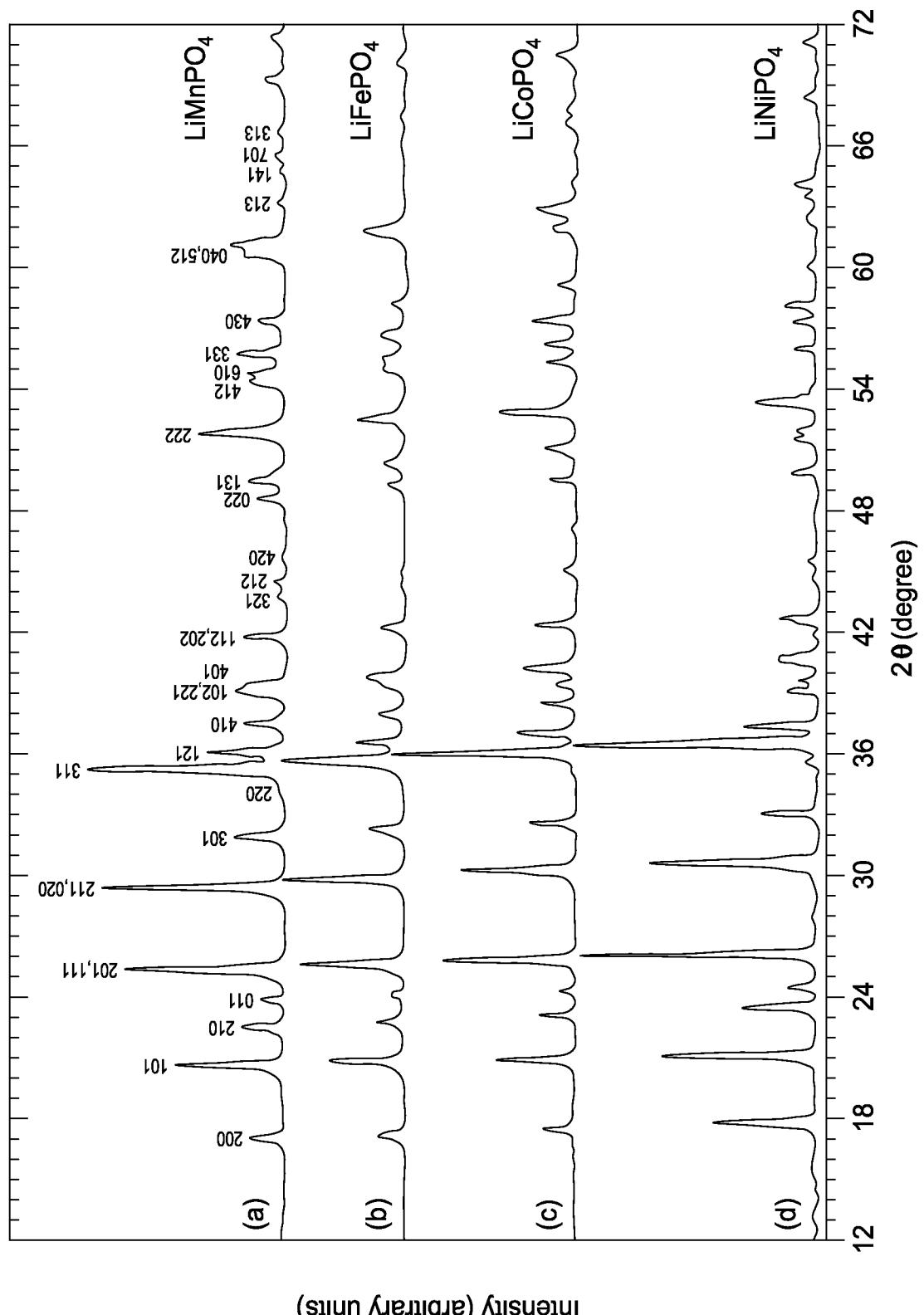


FIG. 32

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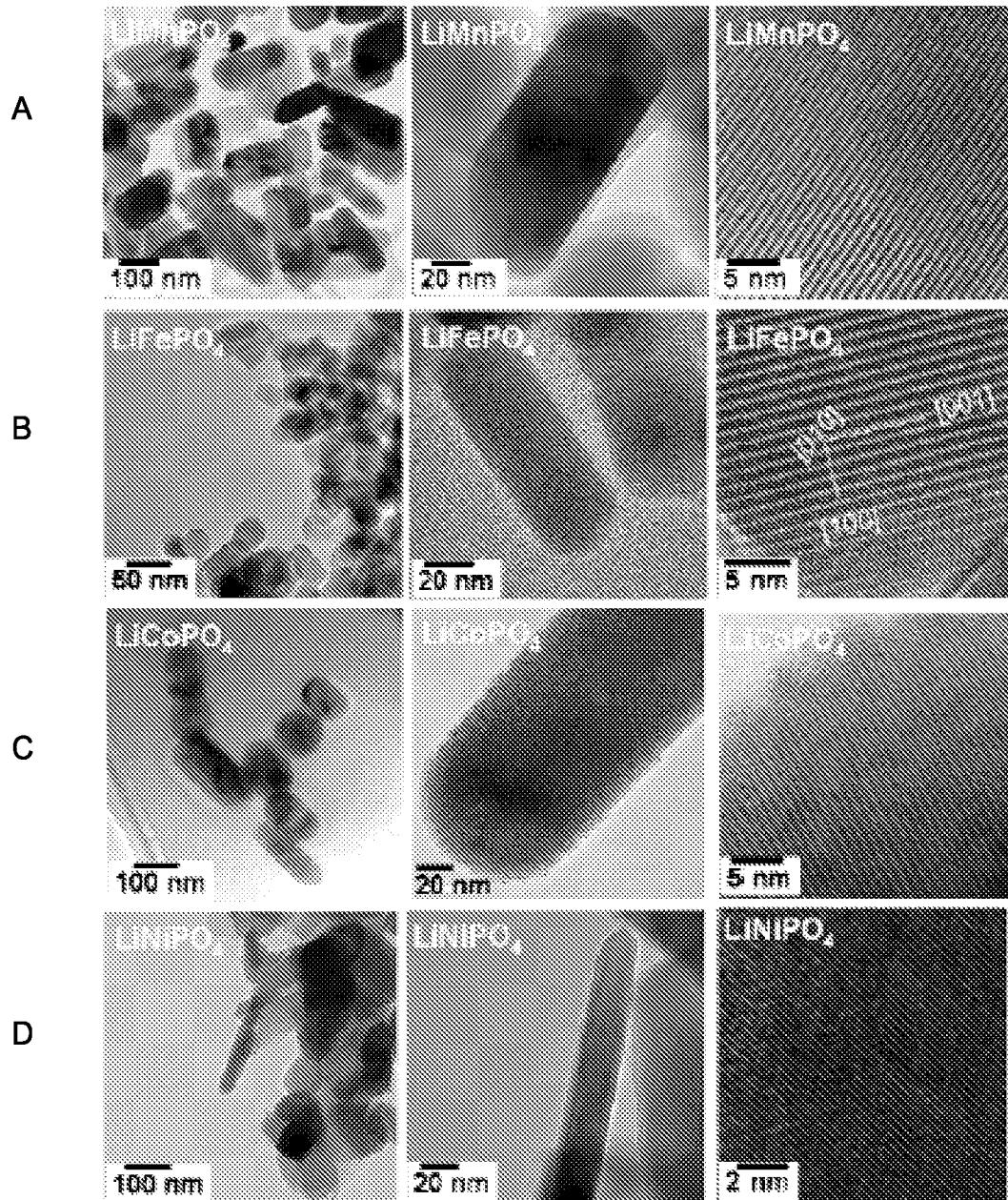


FIG. 33

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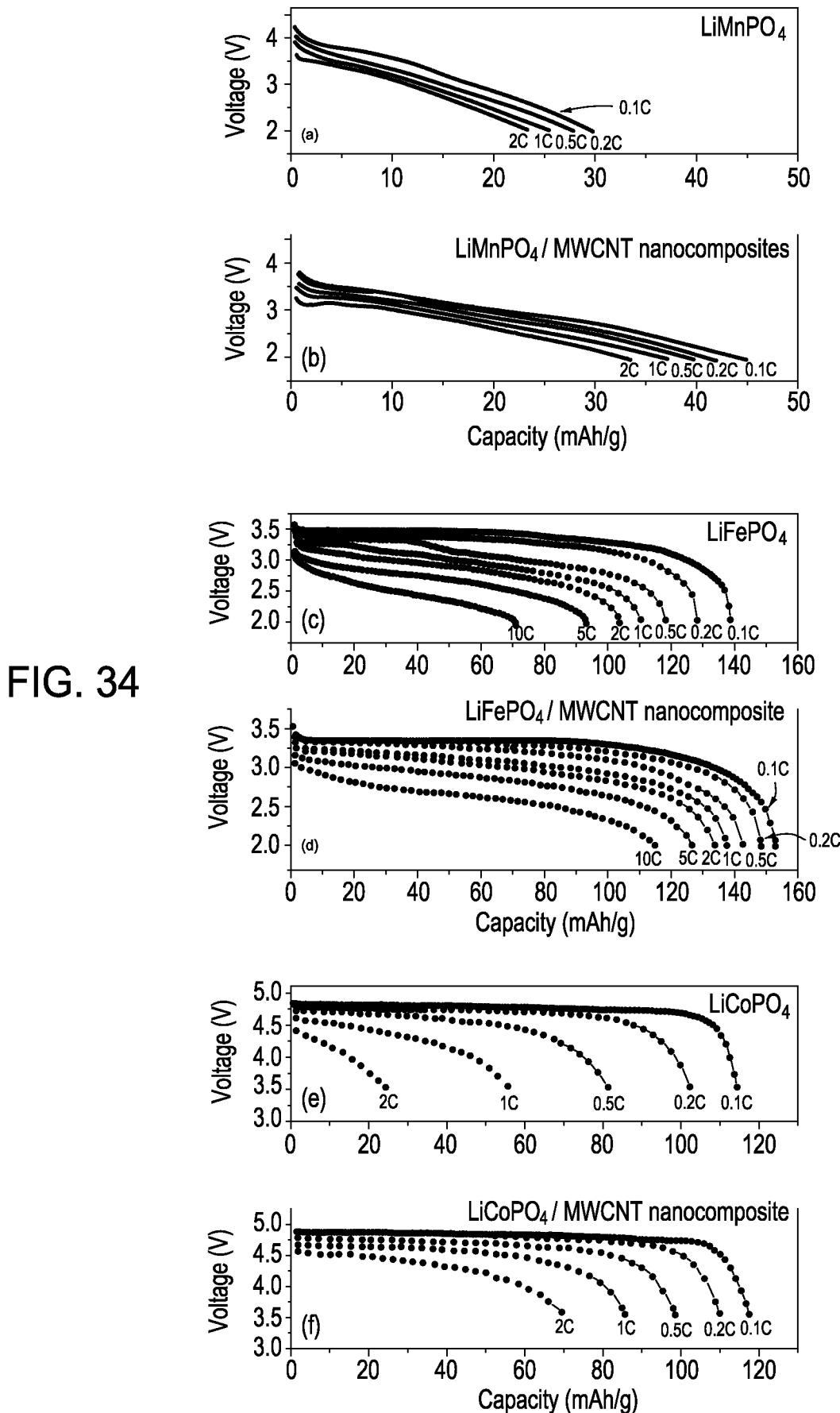


FIG. 34

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2008/082515

A. CLASSIFICATION OF SUBJECT MATTER

H01M 4/58(2006.01)i, H01M 4/04(2006.01)i, H01M 10/36(2006.01)i, C01B 25/26(2006.01)i, B82B 3/00(2006.01)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)

IPC H01M 4/04, C10B 25/45, H01M 4/58

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)
e-KIPASS (KIPO internal) and keywords: lithium metal phosphate, olivine, microwave, solvothermal, hydrothermal, and similar terms

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	KR 10-2007-0096063 A (KIM, J. K.) 2 OCTOBER 2007 See abstract, claims 1-22, paragraphs 34-36, example 1, figures 2a, 2b	1, 2, 4-6
Y		3
A		7-35
Y	KR 10-2004-0011498 A (ZENTRUM FUR SONNENENERGIE-UND WASSERSTOFF-FORSCHUNG BADEN-WURTTEMBERG, GEMEINNUTZIGE STIFTUNG) 5 FEBRUARY 2004 See abstract, claims 1-8, and examples 1-6	3
A		1, 2, 4-35
A	KR 10-2004-0069156 A (KOREA ADVANCED INSTITUTE OF SCIENCE AND TECHNOLOGY) 4 AUGUST 2004 See abstract, claims 1-5, and example	1-35
A	KR 10-2001-0025116 A (SONY CORPORATION) 26 MARCH 2001 See abstract, claims 1-26, and examples 1-12	1-35

Further documents are listed in the continuation of Box C.

See patent family annex.

- * Special categories of cited documents:
- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier application or patent but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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Microwave hydrothermal synthesis of calcium phosphates using inorganic condensed phosphate salts as precursors



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ABSTRACT

As a potential phosphate source, inorganic soluble condensed phosphate salts represent a viable alternative to both orthophosphate and organic condensed phosphate salts. The present work demonstrates a simple but versatile microwave hydrothermal method to prepare calcium phosphates using pyrophosphate and tripolyphosphate salts. After 5-min microwave heating, white fine powders are precipitated from calcium and condensed phosphate containing solution. The as-synthesized precipitates are crystallized calcium pyrophosphate hydrate whiskers and calcium tripolyphosphate hydrate porous microspheres. After calcination, both ceramics are converted into calcium pyrophosphate. *In vitro* study reveals both precipitates and calcined powders are cytocompatible compared to microwave hydrothermally synthesized hydroxyapatite. With all of these attributes, it is expected different inorganic soluble condensed phosphate salts together with microwave can be used to generate a series of calcium phosphates with unique features.

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1. Introduction

Microwave-assisted synthesis of calcium phosphates (CaPs) in liquid phase has attracted many research interests [1]. A variety of CaPs with different morphologies, including rods, whiskers, spheres and mesoporous particles, have been prepared [2,3]. It is noticed in the synthesis process, the crystal phase and morphology of as-prepared ceramics are strongly influenced by the reactants. For example, Wang et al. prepared hydroxyapatite (HA, $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) powders of rod-like or prism-like nature using microwave-assisted hydrothermal system with orthophosphate salt as precursor [4]. Meanwhile, Zhu et al. reported the microwave-assisted hydrothermal production of mesoporous amorphous calcium phosphate (ACP) microspheres with adenosine 5'-triphosphate (ATP) or adenosine 5'-diphosphate (ADP) as the

phosphorus source [5,6]. Therefore it is reasonable to speculate that the replacement of regular orthophosphate salts using soluble condensed phosphate salts can induce significant changes to the as-synthesized CaPs.

In nature, condensed phosphate salts can be divided into two groups, organic and inorganic. To the best of our knowledge, only organic condensed phosphate salts have been used together with microwave energy to synthesize CaPs. Reports on the application of soluble inorganic condensed phosphate salts in microwave-assisted hydrothermally synthesizing CaPs are limited. However, it is noted that inorganic condensed phosphate salts have been applied to generate CaPs in other systems. For example, free calcium ions can react with inorganic condensed phosphate salts to form amorphous porous complex once contacted [7,8]. After that, with thermal or chemical treatment, the complex can be converted into a series of CaPs, such as calcium pyrophosphate, HA, monetite etc. [7,9]. Hence, the purpose of present work is to evaluate whether the usage of inorganic condensed phosphate salts as phosphate source can result in CaPs with unique crystal phase or morphology to regular orthophosphate one.

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2. Material and methods

Two inorganic condensed phosphate salts, $\text{Na}_4\text{P}_2\text{O}_7$ and $\text{Na}_5\text{P}_3\text{O}_{10}$, were used. Typically, $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ was first dissolved in H_2O , followed by adding $\text{Na}_4\text{P}_2\text{O}_7$ or $\text{Na}_5\text{P}_3\text{O}_{10}$ separately to make a Ca/P molar ratio of 1.5. In order to have settled solution, the pH was adjusted to 4.5 by 1 M hydrochloric acid. Solution of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and NaH_2PO_4 with Ca/P at 1.5 was used as control. Beaker with solution was placed into a 720 W household microwave oven for 5 min heating at maximum power. After that, the solution was successively filtered. The collected precipitates were washed with deionized water and dried at 80 °C overnight.

Precipitates were firstly characterized by X-ray diffraction (XRD, Rigaku) to determine the material phases. The chemical bands were analyzed using Fourier-transformed infrared spectroscopy (FTIR, Digilab). The thermal transition of precipitates was measured using a thermogravimetry differential scanning calorimetry analyzer (TGA, TAcompany). The powders, calcined at 1000 °C, were also characterized using XRD and SEM. The surface morphologies were studied using a scanning electron microscope (SEM, Zeiss). Osteoblast cells (MC3T3-E1) were used to study the cytocompatibility of precipitates before and after calcination. Wells containing 1000 mg/mL powders in 500 μl culture medium were incubated 48 h prior to the cell seeding. After that, MC3T3-E1 cells were seeded on to wells at a density of 10,000 cells/well. Immediately after seeding, powder extracts were added to the wells. The medium was changed every other day. Cell density was measured using MTT after 1 and 7 days.

3. Results and discussion

All precipitates are white fine powders. As shown in Fig. 1(a), the precipitates from Ca-P are HA as expected (PDF #09-0432). In

Table 1.

Compositions of aqueous mixture used in microwave hydrothermal experiment.

Sample	$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (g)	Phosphate source (g)	H_2O (mL)	Ca/P	
Ca-P	0.294	NaH_2PO_4	0.16	200	1.5
Ca-P2	0.294	$\text{Na}_4\text{P}_2\text{O}_7$	0.177	200	1.5
Ca-P3	0.294	$\text{Na}_5\text{P}_3\text{O}_{10}$	0.1635	200	1.5

previous work we have shown that a calcium orthophosphate solution under microwave irradiation can only generate HA due to the thermal driving force unless stabilizer added [10]. It is known condensed phosphates can easily react with Ca^{2+} to produce amorphous complex in aqueous solution. However, due to HCl addition and microwave-assisted HCl evaporation, these complexes follow a precipitation-dissolution-precipitation process in response to pH change, and the end product is found to be crystallized. The precipitates from Ca-P2 are mainly crystallized calcium pyrophosphate hydrate (CPPH, $\text{Ca}_2\text{P}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$, PDF #41-0488). However, the material phase of precipitates from Ca-P3 is unidentified. In FTIR (Fig. 1(b)), all precipitates showed peaks at 1010 cm^{-1} , referred to phosphate. Absorption peaks from water were shown in 1656 and 3448 cm^{-1} for all precipitates. In addition, both Ca-P2 and Ca-P3 precipitates show various P-O bands at wavelengths of 766, 918, 1093, 1162, and 1238 cm^{-1} , attributed to the presence of condensed phosphate bands (Fig. 1(b)). Therefore, it is suggested Ca-P3 precipitates should be calcium condensed phosphate. After calcination, both Ca-P2 and Ca-P3 become dehydrated crystallized CPP (PDF #09-0346) (Fig. 1(c)). In the TGA experiment (Fig. 1(d)), Ca-P3 presents a sudden weight change between 100 and 200 °C, possibly caused by the loss of absorbed water in Ca-P3. After that, both Ca-P2 and Ca-P3 show similar weight change behavior with loss of crystal water. In our previous work we have shown amorphous complex of Ca^{2+} and

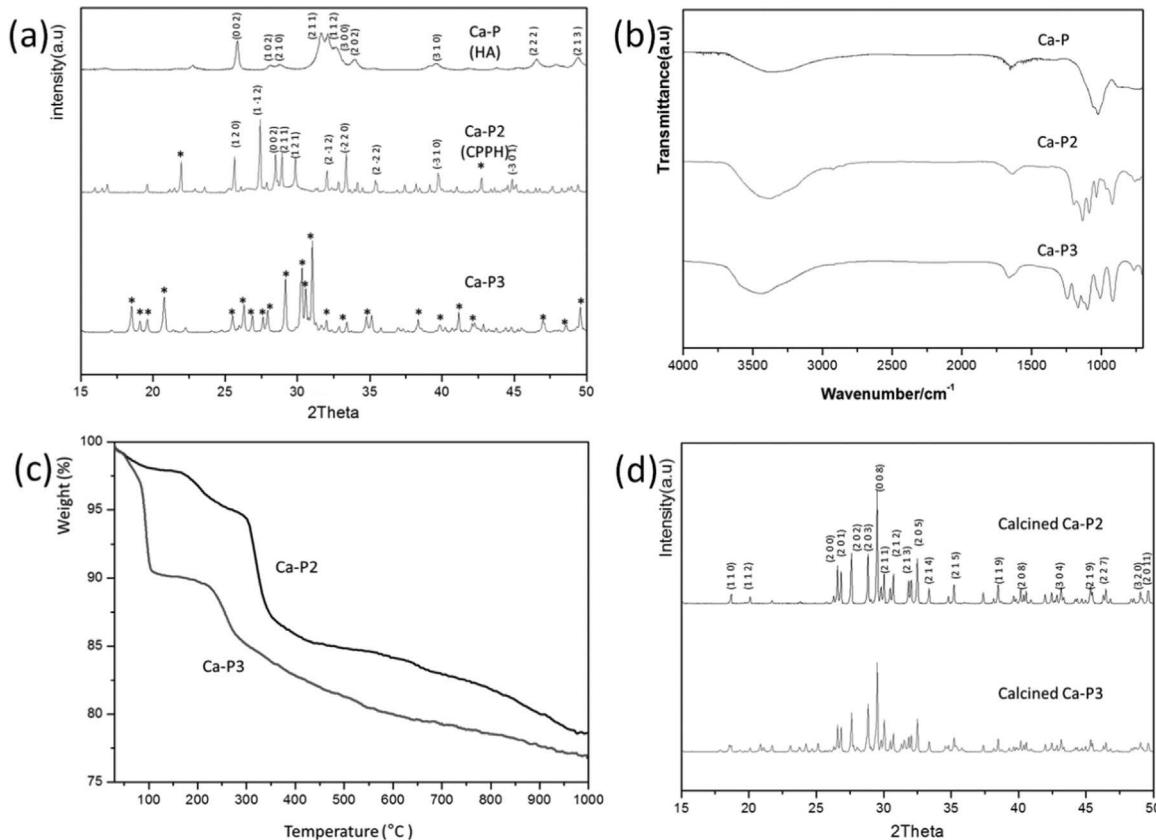


Fig. 1. (a) XRD of precipitates, “**” refers to unidentified pattern; (b) FTIR of precipitates; (c) TGA of Ca-P2 and Ca-P3; (d) XRD of calcined powders.

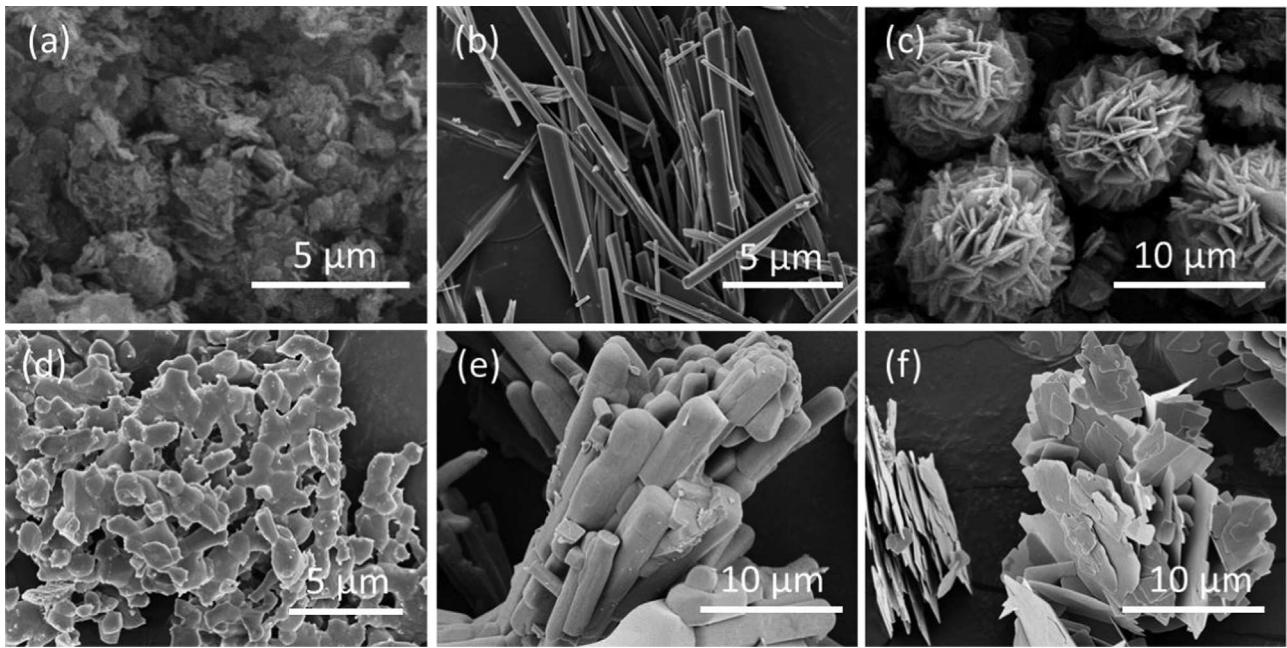


Fig. 2. Representative SEM images of precipitates: (a) Ca-P; (b) Ca-P2; (c) Ca-P3; and calcined powders: (d) Ca-P; (e) Ca-P2; (f) Ca-P3.

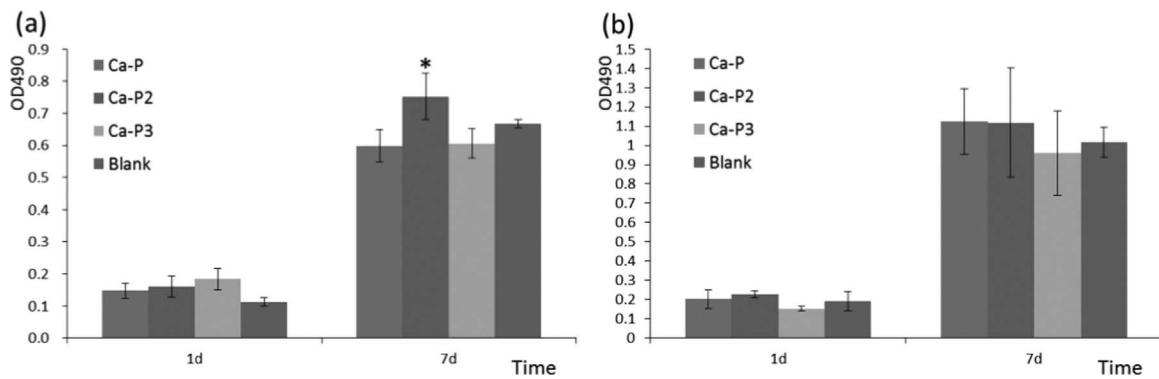


Fig. 3. *In vitro* study of 7 days osteoblast cell culture using (a) precipitates and (b) calcined powders.

$\text{P}_3\text{O}_{10}^{5-}$ can be thermally transformed into CPP [7]. Therefore, based on XRD, FTIR and TGA, it is speculated the precipitates from Ca-P3 are thermally unstable calcium tripolyphosphate hydrate ($\text{Ca}_5(\text{P}_3\text{O}_{10})_2 \cdot n\text{H}_2\text{O}$, CTPH). Meanwhile, based on the water loss observed in TGA, n is calculated to be 3.87. (Table 1).

The representative SEM images of as-prepared Ca-P, Ca-P2 and Ca-P3 precipitates are presented in Fig. 2(a)–(c). For Ca-P, it shows plate-like HA crystals together with some microspheres. We have reported amorphous calcium phosphate (ACP) microspheres can be formed when microwave irradiation is applied [10]. Due to the water-boiling, these ACP microspheres are immediately transformed into HA, though sphere-like structure can be partially preserved. For Ca-P2 the precipitates are whiskers with a length of a few microns, and a width of sub-microns. CPPH particles with different morphology have been reported. Vasant et al. have generated CPPH nanoparticles in the range from 4 nm to 40 nm [11]. Groves et al. synthesized elongated CPPH crystals, 45–190 μm long, with considerable variation in length/width ratio [12]. However, it is the first time reporting such crystal structure of CPPH. These CPPH whiskers can be potentially used in constructing matrix as reinforcement additives. Meanwhile, the precipitates from Ca-P3 are plate-like particles assembled microspheres. The EDS study indicates the P/Ca molar ratio is in the range of 1.2–1.25, matching the speculated CTPH chemical formula. The morphology

of precipitates after calcination is shown in Fig. 2(d)–(f). In Ca-P solid-state diffusion in crystalline solids is seen, similar to reported calcined CaP [13]. Ca-P2 shows bonded long rods and Ca-P3 becomes irregular agglomerates of plate-like particles.

Fig. 3(a) shows both Ca-P2 and Ca-P3 are cytocompatible. In addition, the extracts from Ca-P2 have the best cell proliferation after 7 days ($p < 0.05$). CPP based ceramics have been reported to be potential bone repairing materials with higher biodegradation than HA *in vivo* and possibility to intensify osteoblast differentiation via releasing Ca^{2+} and PO_4^{3-} [14,15]. Therefore our finding is in agreement with these reports. On the other hand, precipitates from Ca-P3 are also comparable to Ca-P1, possibly attributed to the presences of Ca, P, O in its composition. While for calcined powders, no significant difference was observed (Fig. 3(b)). Possibly due to the calcination, the degradation rate of materials was limited.

4. Conclusions

Soluble inorganic condensed phosphate salts together with microwave can be used to prepare biocompatible calcium condensed phosphates with unique morphologies. Depending on the condensed phosphate source used, CPPH whiskers as well as CTPH

microspheres can be generated after 5 min microwave heating. The potential applications of these materials as well as microwave hydrothermal synthesis of CaPs using other soluble inorganic condensed phosphate salts will be investigated in future.

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