

PRE-FILING SEARCH REPORT  
FOR  
"MESOPOROUS  $\text{FePO}_4$  AS HIGH-PERFORMANCE CATHODE MATERIAL FOR Li-ion  
BATTERIES"

<b>Client Matter:</b>	<b>IDF-1673</b>
<b>Maxval Reference No.:</b>	PS20180313
<b>Date:</b>	03/13/2018
<b>Client Contact:</b>	Prof. Parasuraman Selvam

A novelty search was conducted for docket titled "**Mesoporous  $\text{FePO}_4$  As High-Performance Cathode Material For Li-Ion Batteries**".

**Search Focus:**

1. A mesoporous iron phosphate (MIP) electrode material for use in lithium ion batteries (LIBs):
  - i) The MIP has a pore volume in the range of  $0.30\text{-}0.48\text{ cm}^3\text{g}^{-1}$ , a surface area in the range of  $110\text{-}130\text{ m}^2\text{g}^{-1}$ , or a pore size distribution (PSD) with a peak maximum in the range of  $2.9\text{-}3.6$ ;
  - ii) wherein the electrode is a cathode;
  - iii) wherein the electrode material shows good reversibility and long term cyclability
    - a) wherein first discharge capacity of MIP-41 (IL) electrode is about  $175\text{ mAh g}^{-1}$ , close to theoretical value and wherein first discharge capacity of MIP-41 (CS) electrode is about  $161\text{ mAh g}^{-1}$ ; and
    - b) wherein reversible capacity of MIP-41 (IL) electrode is about  $154\text{ mAh g}^{-1}$  at the end of at least 40 cycles, for a C/10 (0.1C) rate;
    - c) wherein reversible capacity of MIP-41 (IL) electrode is about  $102\text{ mAh g}^{-1}$  after at least 200 cycles, corresponding to  $\sim 100\%$  coulombic efficiency;
2. A method of fabricating an electrode from mesoporous iron phosphate, MIP-41 (IL) and MIP-41 (CS), comprising:
  - i) synthesizing MIP-41 (IL) from 1-hexadecyl-3-methylimidazolium chloride or ;
  - ii) synthesizing MIP-41 (CS) from cetyltrimethylammonium bromide (CTAB);
  - iii) the synthesis of MIP is done with assistance of HF;
  - iv) adding MIP to a slurry of  $\text{FePO}_4$ , acetylene black and poly(vinylidene difluoride) (PVDF) in the weight ratio 70:20:10;
  - v) loading active material on a conductive or stainless steel substrate at about  $2\text{ mg/cm}^2$  to obtain the electrode
  - vi. obtaining an electrode of area  $0.8\text{ cm}^2$ .

**Search Results:**

The search revealed at least five patent/application families and two non-patent literature documents disclosing at least one element of the given subject matter.

Representative patent/application references and/or any non-patent literature documents are listed below.

ASPECT	RATING				
NOVELTY	NO			YES✓	
Key	5 (low)	4	3	2	1 (high)
NON-OBVIOUSNESS			✓		

**Summary:**

The following table shows the summary search result of patent and non-patent references:

#	Patent & NPL References	1	1						2	2					
			i	ii	iii	iii (a)	iii (b)	iii (c)		i	ii	iii	iv	v	vi
1	<a href="#">CN103887499A</a>														
2	<a href="#">CN102403501A</a>														
3	<a href="#">US20060127750A1</a>														
4	<a href="#">US20130143123A1</a>														
5	<a href="#">CN101118978A</a>														
6	<a href="#">Mesoporous Iron Phosphonate Electrodes with Crystalline Frameworks for Lithium-Ion Batteries</a>														
7	<a href="#">Mechano-chemical synthesis of nanostructured FePO<sub>4</sub>/MWCNTs composites as cathode materials for lithium-ion</a>														

= Element is present, = Element is absent = Element is present with limitation/partial reference to the key element.

**Assignees:**

- Chemische Fabrik Budenheim KG
- Umicore NV
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- Du Pont
- Orthovita Inc
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- Nat Univ Tsing Hua
- Japan Government
- Dow Global Technologies Inc

**Summary:**

The present invention discloses mesoporous iron phosphate and a method of preparation thereof. The disclosed iron phosphate is employed as cathode in Lithium ion batteries. The electrode shows a capacitance nearing the theoretical capacitance. The highly efficient electrode material finds its application in electrochemical, chemical, electrical, energy, telecommunications, power industries, or the like.

**Results: Patents / Applications**

Publication No:	Title	Assignee/ Applicant	Publication Date	Equivalents
<a href="#">CN103887499A</a>	Iron phosphate, lithium iron phosphate as well as preparation methods of iron phosphate and lithium iron phosphate	UNIV TSINGHUA GRADUATE SCHOOL	June 25, 2014	CN103887499B

**Abstract**

The invention discloses iron phosphate, lithium iron phosphate as well as preparation methods of iron phosphate and lithium iron phosphate. The preparation method of iron phosphate comprises the following steps of (1) preparing a 0.1-1mol/L acrylic acid molten iron solution; (2) preparing a 0.1-2mol/L soluble phosphate water solution; (3) adding the acrylic acid molten iron solution in the step (1) into the soluble phosphate water solution in the step (2) under certain conditions according to the molar ratio (Fe: P) of 1:(1-1.05), then, adding ammonia water, and continuing to stir and react for 30-180min to obtain an ammonium acrylate and iron phosphate mixed suspension liquid; (4) adding a radical initiator into the mixed suspension liquid obtained in the step (3) to initiate ammonium acrylate to be subjected to monomer polymerization, heating to carry out polymerization reaction, then, cooling, filtering and drying to obtain iron phosphate. Iron phosphate prepared by using the preparation method disclosed by the invention is small and uniform in particle size, and furthermore, lithium iron phosphate with small and uniform particle sizes can be prepared; in addition, no wastewater discharge and environment pollution are caused in a preparation process.

**Excerpt****Translated text****Summary**

[0007] - kind of iron phosphate preparation method comprises the following steps: 1) an acrylic iron dissolved in deionized water or distilled water to prepare a concentration of 0.1 ~ 1mol / L acrylic acid aqueous solution of iron; 2) a soluble phosphate dissolved in de ion water or distilled water to prepare a concentration of 0.1 ~ 2mol / L aqueous solution of soluble phosphate; 3) at 25 ~ 50 ° C, a frequency of 30 ~ 100KHz and ultrasonic agitation, in a molar ratio Fe: P = 1: 1.05 ~ step 1) is added to the aqueous solution of ferric acrylate step 2) soluble in the aqueous phosphate solution, then adding ammonia to adjust the pH to 2 to 4, 30 ~ 60min ultrasonic reaction stopped after sonication, stirring was continued for 30 ~ 180min, iron phosphate and ammonium acrylate obtained mixed suspension; 4) mixing the suspension in step 3) obtained in 0.5 to 2.5% by mass corresponds to the ammonium acrylate radical initiator to said acrylic ammonium monomers, carried 1 ~ 8 hours the polymerization reaction heated to 50 ~ 80 ° C temperature conditions, and then cooled to room temperature, filtered, and dried to obtain iron phosphate.

**Detailed description**

[0023] 2) a soluble phosphate was dissolved in deionized or distilled water to prepare a concentration of 0.1~2mol / L aqueous solution of soluble phosphate. In this step, the soluble phosphate is diammonium hydrogen phosphate, ammonium dihydrogen phosphate, a phosphoric acid or a mixture of more thereof. Preferably, the soluble phosphate aqueous solution prepared by adding an aqueous solution of soluble phosphate in the theoretical mass to produce iron phosphate 2% ~ 8% of a surfactant. By the addition of a surfactant, it may be better disperse the reactants so as to better control the particle size of the iron phosphate product. Surfactant is a polyvinyl pyrrolidone, cetyl trimethyl ammonium bromide, cetyl trimethyl ammonium chloride one kind or more thereof.

[0030] The nanoscale iron phosphate prepared in specific embodiments of spherical nano-sized (average particle diameter 50~60nm), polypropylene coated ammonium regular shape, good dispersion, uniform particle size distribution. Lithium iron phosphate was further prepared porous spherical micro-nano structure, particle size distribution, the average particle diameter of primary particles 70~80nm, the average particle diameter of secondary particles 2~3 $\mu$ m, coated film, a good electrochemical performance.

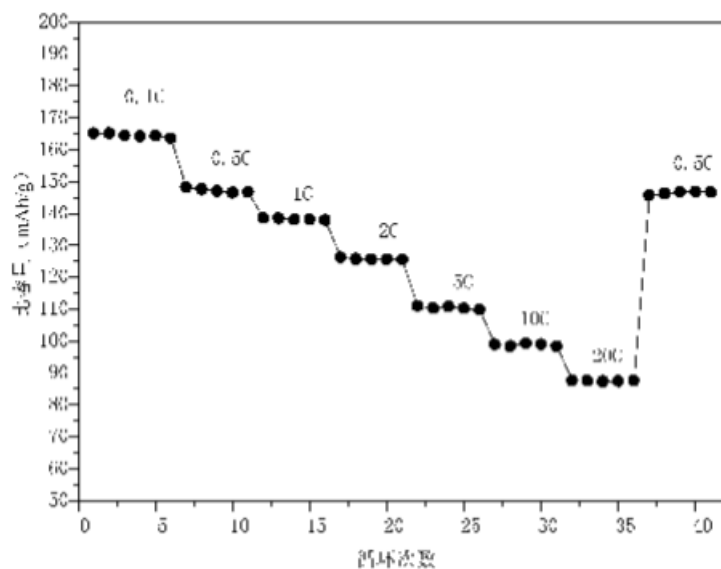


图 1

[CN102403501A](#)

Method for preparation of cathode material spherical FePO<sub>4</sub> of lithium-ion battery

UNIV SHANGHAI  
ELECTRIC  
POWER

April, 04,  
2012

None

#### Abstract

The invention discloses a method for preparation of an cathode material spherical FePO<sub>4</sub> of a lithium-ion battery. A spherical FePO<sub>4</sub> precursor is synthesized via coprecipitation in combination with spray drying with Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> and ammonia as raw materials and polyvinyl alcohol as a dispersant, and then the cathode material spherical FePO<sub>4</sub> of the lithium-ion battery can be prepared via sintering for 3-9h in a high-temperature tube type furnace with the temperature controlled to be 380-650 DEG C. The anode material spherical FePO<sub>4</sub> of the lithium-ion battery prepared in the method has a large specific surface area and high tap density. Moreover, the preparation method has the advantages of simple process, high operability, low equipment investment, low production cost and the like.

#### Excerpt

Translated text

Description

[0018] The lithium-ion battery cathode material FePO<sub>4</sub> spherical electrochemistry:

The positive electrode prepared using the smear cells, the resulting lithium ion battery positive electrode material spherical FePO<sub>4</sub>, acetylene black (AB), polytetrafluoroethylene (PTFE) emulsion i.e. a mass ratio of spherical cathode material of lithium ion batteries FePO<sub>4</sub> = AB = PTFE was 62: 30: 1 ratio of 8 was thoroughly mixed in a planetary ball mill certificate, a positive electrode paste;

The resulting slurry was knife coated on the positive electrode pole piece, the control lithium ion

battery positive electrode material on a spherical  $\text{I}^{\wedge}$  mass  $\text{ePO}_4$  pole piece material is  $0.015\text{g} / \text{cm}^2$ , to obtain a positive electrode sheet after the completion of the smear, and then the positive electrode plate into the vacuum further drying oven drying, a drying temperature of  $120^{\circ}\text{C}$ , drying time of 12h, to obtain the positive electrode of the battery;

As used above pole pieces of stainless steel mesh, when used in welding the positive electrode coin cell cover.

<a href="#">US2006127750A1</a>	Method for preparing positive cathode material for lithium cell, and lithium cell	JAPAN GOVERNMENT [JP]; MITSUI SHIPBUILDING ENG [JP]	March 10, 2015	<a href="#">Family members</a>
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#### Abstract

A method for preparing a positive electrode material for a lithium cell, characterized in that it comprises admixing a compound liberating a phosphate ion in a solution and metallic iron, and dissolving the metallic iron, followed by firing, thereby synthesizing ferric phosphate. The above method further comprising reacting a raw material mixture while grinding it down or refluxing can produce ferric phosphate positive electrode material having a fine particle diameter and exhibiting high activity, through a precursor before firing having a fine particle diameter.

#### Excerpt

##### Description

##### Page No. 4, Paragraph No: [0051]

The cathode and anode are respectively prepared by adding a conductivity imparting agent, such as carbon black, in such an amount that the effects of the cathode and anode are not impaired and a binder such as a fluorine-type polymer, e.g., polytetrafluoroethylene or polyvinylidene fluoride; polyimide or polyolefin to the cathode or anode material, mixing and kneading the mixture with a polar organic liquid as needed, and forming the kneaded mixture into a sheet. Then, current collection is conducted using a metal foil or metal screen to construct a battery. When metal lithium is used for the anode, transitions between  $\text{Li}(0)$  and  $\text{Li}^+$  take place upon charging and discharging, and a battery is thereby formed.

##### Page No. 5, Paragraph No: [0058]

Diffraction peaks ascribable to impurities were not observed.

(2) Fabrication of secondary battery and its charge/discharge characteristics The cathode material, acetylene black as a conductivity imparting agent ["Denka Black" (registered trademark); product of Denki Kagaku Kogyo K.K., 50% pressed product], and PTFE (polytetrafluoroethylene) as a binder were prepared at a weight ratio of 70:25:5. The cathode material and acetylene black were mixed and ground in a ball mill (at a rotational speed of 200 rpm) for one day, and then mixed and kneaded with the PTFE. The resulting mixture was formed into a sheet with a thickness of 0.7 mm, and the sheet was punched out into disks with a diameter of 1.0 cm (area of  $0.7854\text{ cm}^2$ ) to form a pellet as a cathode.

##### Page No. 6, Paragraph No: [0077]

Example 5 Acetylene black (product of Denki Kagaku Kogyo K.K., 50% pressed product) was added to the cathode material  $\text{FePO}_4$  calcined at  $650^{\circ}\text{C}$  and having a crystal structure with point group P321 that was synthesized in Example 4 in an amount of 25% by weight based on the total weight of the mixture. The mixture was ground and mixed in a planetary ball mill at 200 rpm for one day to obtain a cathode material including cathode material particles coated with acetylene black (which will be hereinafter referred to as "carbon composite cathode material"). Then, the cathode material was formed into a cathode, and a coin-type lithium secondary battery was fabricated using a metal lithium anode in the same manner as in Example 1.

**Page Nos. 6 &7, Paragraph No: [0077]**

A charge and discharge test was conducted on the coin-type secondary lithium battery. The result is shown in FIG. 9. The batteries were alternately charged and discharged between 2.6 and 4V at a temperature of 25 C and a current density per apparent area of 0.2 mA/cm<sup>2</sup>. In FIG. 9, the result of the test conducted on a cathode material calcined at 650 C but not combined with carbon (which was alternately charged and discharged between 2.0 and 4V) is also shown.

FIG. 9 indicate that when combined with carbon, the FePO<sub>4</sub> cathode material had significantly improved discharge capacity as compared with a cathode material not combined with carbon and showed as high a value as about 130 inAh/g. This is considered to be because the combination with carbon improves the surface conductivity of the FePO<sub>4</sub> cathode material as a cathode active material and significantly enhances the utilization ratio of the positive active material.

This indicates that the combination with carbon is effective to improve the performance of a lithium battery using FePO<sub>4</sub> as a cathode active material.

[US20130143123A1](#)

Mesoporous metal phosphate materials for energy storage application

National University of Singapore

June 06, 2013

[Family members](#)
**Abstract**

Mesoporous particles each including LiFePO<sub>4</sub> or Li<sub>3</sub>V<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> crystallites and uniform coating of amorphous carbon on the surface of each of the crystallites. The crystallites have a size of 20-50 nm and the carbon coating has an average thickness of 2-7 nm. Also disclosed is a soft-template method of preparing the above-described mesoporous particles and the use of these mesoporous particles in lithium batteries.

**Excerpt****Description****Page No. 2, Paragraph No: [0033]**

The nanocrystals thus obtained can then be sintered at a high temperature, e.g., between 600-800° C., so as to allow the nanocrystals to be closely packed to form particles having a size of micrometers or less, e.g., 50-1000 nm. In the particles, the nanostructures forming the particles are in close contact with their adjacent nanocrystals, forming mesopores having a nano size, e.g., 2-10 nm (the size of a pore is the longest possible distance between two points on the pore). The carbon-containing surfactant on the surface of the nanocrystals is decomposed at the high temperature to form uniform coating of amorphous carbon on the surfaces of the nanocrystals, the average thickness of the coating being about 2-7 nm. The term "uniform coating" refers to coating in which the thickness at the thickest spot is no more than 5 nm greater than that at the thinnest spot.

**Page No. 3, Paragraph No: [0039]**

Suitable binders include, but are not limited to, polyacrylic acid, carboxymethylcellulose, diacetylcellulose, hydroxypropylcellulose, polyethylene, polypropylene, ethylene-propylene-diene copolymer, polytetrafluoroethylene, polyvinylidene fluoride, styrene-butadiene rubber, tetrafluoroethylene-hexafluoropropylene copolymer, polyvinyl alcohol, polyvinyl chloride, polyvinyl pyrrolidone, tetrafluoroethylene-perfluoroalkylvinyl ether copolymer, vinylidene fluoride-hexafluoropropylene copolymer, vinylidene fluoride-chlorotrifluoroethylene copolymer, ethylenetetrafluoroethylene copolymer, polychlorotrifluoroethylene, vinylidene fluoride-pentafluoropropylene copolymer, propylene-tetrafluoroethylene copolymer, ethylene-chlorotrifluoroethylene copolymer, vinylidene fluoride-hexafluoropropylene-tetrafluoroethylene copolymer, vinylidene fluoride-perfluoromethylvinyl ether-tetrafluoroethylene copolymer, ethylene-acrylic acid copolymer, ethylene-methacrylic acid copolymer, ethylene-methyl acrylate copolymer, ethylene-methyl methacrylate copolymer, styrene-butadiene rubber, fluorinated rubber, polybutadiene, and mixtures thereof.

**Page No. 3, Paragraph No: [0040]**

Suitable electrically conductive agents include, but are not limited to, natural graphite (e.g. flaky graphite); manufactured graphite; carbon blacks such as acetylene black, Ketzen black, channel black, furnace black, lamp black, and thermal black; conductive fibers such as carbon fibers and metallic fibers; metal powders such as carbon fluoride, copper, and nickel; and organic conductive materials such as polyphenylene derivatives.

**Page No. 3, Paragraph No: [0046]**

Cetyl trimethylammonium bromide (CTAB), a surfactant, was dissolved in ethanol to give a solution at the concentration of 0.01 M. To prepare  $\text{LiFePO}_4/\text{C}$  particles,  $\text{LiH}_2\text{PO}_4$  (as lithium and phosphate sources) and  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  or  $\text{Fe}(\text{C}_2\text{H}_3\text{O}_2)_2$  were used as ion precursors. The weights of the components used to synthesize  $\text{LiFePO}_4/\text{C}$  are listed in Table 1 below. To prepare  $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$  particles, lithium acetate hydrate, vanadium (IV) oxide bis(2,4-pentanedionate), and ammonium dihydrogen phosphate were used as ion precursors. The weights of the components used to synthesize  $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$  are listed in Table 2 below. The ion precursors were added into the CTAB-ethanol solution. Then, de-ionized water was added to the solution with the ethanol-water volume ratio of 5:1 or 12:1. The solution was stirred for 24 hours and dried using a rotor evaporator at  $70^\circ\text{C}$ . After drying, the obtained powder was grounded using a mortar and a pestle. Finally, the ground powder was sintered in a tube furnace under  $\text{Ar}/\text{H}_2$  atmosphere (for preparing  $\text{LiFePO}_4$ ) or argon atmosphere (for preparing  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  at  $600\text{--}800^\circ\text{C}$ . for 4-6 hours.

**Page No. 4, Paragraph No: [0049]**

Composite electrodes were fabricated by mixing the  $\text{LiFePO}_4/\text{C}$  or  $\text{Li}_3\text{V}_2(\text{PO}_4)_3/\text{C}$  particles, super P carbon black, and binder (Kynar 2801) at the weight ratio of 70:15:15 in N-methylpyrrolidone. The electrodes with a thickness of  $10\text{ }\mu\text{m}$  and a geometrical area of  $2.0\text{ cm}^2$  were prepared using an etched aluminum foil as a current collector. A lithium metal foil, 1 M  $\text{LiPF}_6$  in ethylene carbonate and diethyl carbonate (1:1 VAT) (Merck), and Celgard 2502 membrane were used as a counter electrode, an electrolyte, and a separator, respectively, to assemble coin-type cells (size 2016) in an Ar-filled glove box (MBraun, Germany). The cells were aged for 12 h before measurement. Charge-discharge cycling at a constant current was carried out using a computer controlled Arbin battery tester (Model, BT2000, USA).

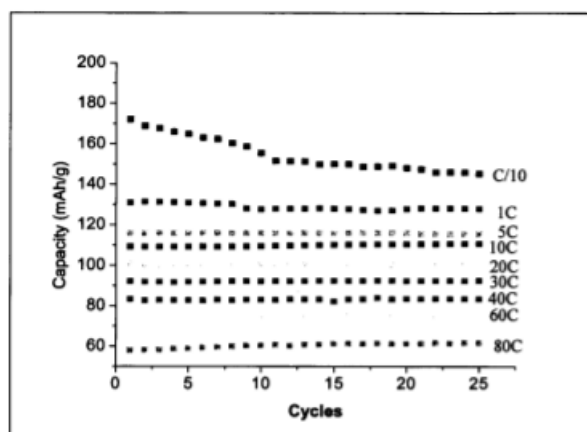


Figure 7

[CN101118978A](#)

Lithium ion battery with  $\text{FePO}_4/\text{Li}_x\text{C}_n$  as electrode couple and method for making same

LEI HAN [CN]

February  
06,2008

None



**Abstract**

The present invention discloses a lithium ion battery taking FePO<sub>4</sub>/LixCn as electrode couple as well as the preparing method therein, belonging to the field of energy technology. The present invention is characterized in that the lithium ion battery takes FePO<sub>4</sub> as the material of the anode for the battery, and LixCn as the cathode material for the battery. The present invention also takes Liquid paraffin, n-dodecane, tetrahydrofuran and polyethylene glycol oxide as the protecting agents. An environmental protecting type FePO<sub>4</sub> material is chosen as the material for the anode of the lithium ion battery. The phosphoric acid KTX includes a heterosite structure, the undefined structure, the monocline and the rhombic system structure; wherein, the heterosite structure and the undefined structure have high specific capacity. Through adopting the LixCn protecting agent, the cathode material of LixCn can be easily assembled into the battery, and thus a lithium free anode material FePO<sub>4</sub> can be successively applied into the lithium ion battery. The assembled battery can reach a first electric discharging capacity of 122mAh per gram(FePO<sub>4</sub>) under the current density of 0.1mA per cm<sup>2</sup>.

**Excerpt**

## Translated text

1) an iron powder and muscle paste material 04, the iron powder and NH grain P04 1: 1 (molar ratio) was added water the mixture was stirred at room temperature and dried at 95.C, the sample 60 (TC treated in a muffle furnace and then ground together with 15% of a conductive agent of acetylene black in a planetary ball mill, and then smear; ( 2) graphite, carbon black conductive agent, binder PVDF, by a certain percentage (90: 2: 8) were mixed in N- methylpyrrolidone performed on the copper foil Cloth, this is a cathode, lithium as the negative electrode plate, an electrolyte in a lithium ion cell, a small current discharge;

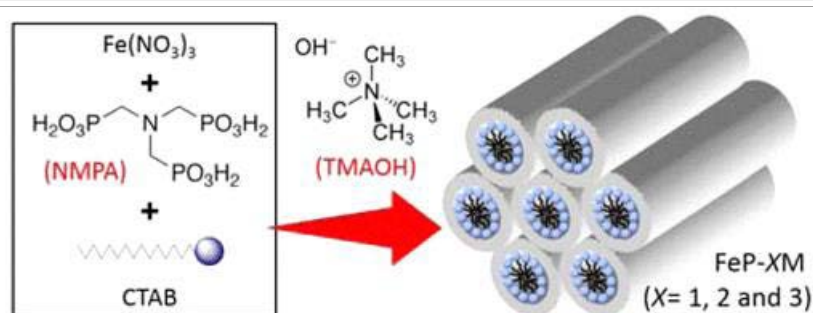
The resulting measured LixCn XRD pattern shown in Figure 2, the control card standard lithium - graphite intercalation compound. Example 1 obtained by two kinds of electrode materials in the following manner. 80:10:10 mass ratio obtained in Example 1 were weighed embodiment of the composite material: acetylene black: PTFE, electrodes made after polishing uniformity, to dissolve in the ethylene carbonate + dimethyl carbonate (volume ratio 1: 1) in a mixed solvent of 1mol / L LiPF<sub>6</sub> as electrolyte, a polypropylene microporous membrane as a separator, assembled into an analog respective battery cell 3 is at 4. 2-2 5V during first charge and discharge cutoff voltage curve. indicating that the measured battery has about 3. 2V discharge voltage plateau in Example 1 to calculate the reversible specific capacity of the positive electrode material embodiment is approximately 100mAh / g. FIG. 4 is a cycle performance at different current densities, reversible cycle after 100 weeks capacity is still more than 80% of the initial capacity. Like this embodiment the following embodiments. Example 2 and iron powder NH<sub>4</sub>H<sub>2</sub>P (X is a starting material. The 5.6 g of iron powder was added to water and 11.2g of NH<sub>4</sub>H<sub>2</sub>P04, stirred for 5 h at room temperature, and dried at 95T 10 h. The sample 60 (TC muffle 24 h treatment furnace (air) and then with 15% of a conductive agent of acetylene black triturated 24 h together in a planetary ball mill, and then smears of graphite, carbon black conductive agent, binder PVDF, according to a certain ratio in N-methylpyrrolidin-ketone embankment coating on a copper foil, this is a cathode, lithium as the negative electrode plate, an electrolyte in a lithium ion cell, a small current discharge, then we mentioned protecting agent (e.g., n dodecane, tetrahydrofuran, polyethylene oxide, etc.) to protect the electrode LixCn. n-dodecane, tetrahydrofuran evacuated prior to injection can be pumped, polyethylene oxide rapidly dissolves in the electrolyte, and the battery performance without any effect. the method of assembling the same simulation cell at 0. 1mA / cm<sup>2</sup> current density of the initial discharge capacity up to 122 mAh / g (FeP04).

**Non-Patent references**

Journal/Source of Literature	Article Title	Authors	Date of Publication	Other details
Chemistry Of Materials	<a href="#">Mesoporous Iron Phosphonate Electrodes with Crystalline Frameworks for Lithium-Ion Batteries</a>	Malay Pramanik, Yoshihiro Tsujimoto, Victor Malgras, Shi Xue Dou, Jung Ho Kim, and Yusuke Yamauchi	2015	Chem. Mater., 2015, 27 (3), pp 1082– 1089 DOI: 10.1021/cm5044045

**Abstract**

A new family of mesoporous iron phosphonate (FeP) materials has been prepared through cooperative assembly of cetyltrimethylammonium bromide (CTAB), iron nitrate, and nitrilotris(methylene)triphosphonic acid (NMPA). CTAB is used as a structure directing agent, while the other two chemicals are used as precursors for the formation of pore walls. An extraction procedure is employed to remove the template without damaging the as-prepared ordered mesostructure. The obtained mesoporous FeP materials are well characterized by low angle X-ray diffraction (XRD), N<sub>2</sub> adsorption isotherms, and transmission electron microscopy. The mesostructural ordering of the obtained materials strongly depends on the synthetic conditions. The morphology and the crystallinity of the pore walls are investigated by scanning electron microscopy and wide-angle XRD measurements, respectively. It is revealed that the FeP framework is crystallized in the tetragonal crystal phase (I4<sub>1</sub>/amd), according to the Rietveld refinement of the XRD patterns through the MAUD program. The unit cell parameters of the obtained crystals are  $a = b = 5.1963$  (3) Å,  $c = 12.9808$  (1) Å ( $\alpha = \beta = \gamma = 90^\circ$ ). Also, the homogeneous distribution of both Fe species and organo-phosphonic acid groups in the mesoporous architectures is confirmed by Fourier transform infrared spectroscopy and elemental mapping. Mesoporous FeP materials with high surface area have great applicability as high performance electrode materials for lithium-ion (Li-ion) batteries, due to several advantages including a large contact area with the electrolyte, high structural stability, and short transport paths for Li<sup>+</sup> ions. Mesoporous FeP electrodes exhibit high reversible specific capacity with very good cycling stability and excellent retention of capacity.



**Synthesis of Mesoporous FeP Materials.** In a typical synthesis of mesoporous FeP materials, 1 mmol of CTAB was dissolved in 15 mL of distilled water at various temperatures (Step 1, Table 1). After 1 h, 1 mmol of NMPA was further added to the solution, and the pH of the synthetic medium was increased up to 5 by adding TMAOH solution. Then, the mixture was magnetically stirred for 2 h at the same temperature. In an another beaker, 4 mmol of Fe(NO<sub>3</sub>)<sub>3</sub> was dissolved in 5 mL of distilled water separately. The synthetic gel was prepared by the dropwise addition of the iron nitrate solution to the phosphonic acid solution, and then the pH of the gel was adjusted to 4 by further addition of TMAOH solution. The stirring of the synthetic mixture was continued for another 4 h, and was finally transferred to a Teflon-lined autoclave and kept at different temperatures (Step 2, Table 1) for 36 h. The autoclave was cooled down to room temperature by decreasing the temperature very slowly (5 °C·h<sup>-1</sup>). The product was collected by filtration, washed with water several times, and then dried under vacuum at room temperature. The surfactants were completely removed by an extraction process with ethanol solution containing HCl, which was repeated three times.<sup>28</sup> Finally, the mesoporous FeP materials were

obtained, as shown in Table 1. For comparison, FeP materials without mesopores were prepared without the addition of any surfactants (CTAB) in the reaction medium, as shown in Table 1.

The porosity of our FeP materials was investigated by N<sub>2</sub> adsorption-desorption isotherms at liquid nitrogen temperature. Among the mesoporous FeP samples (FeP-1ME, FeP-2ME, and FeP-3ME), the most well-ordered mesoporous FeP (FeP-1ME) sample exhibits a type IV isotherm with a hysteresis loop (Figure 4a).<sup>32,33</sup> The appearance of a well-defined step is due to the capillary condensation of N<sub>2</sub> gas inside the uniformly sized mesopores. The sharpness of the step indicates the uniformity of the mesopores in the material. Such well developed type IV isotherms have been hardly ever seen in phosphonate-based mesoporous materials.<sup>20</sup> Lin et al. and Zhu et al. have reported amorphous mesoporous zirconium and cerium phosphonate materials with broad pore size distributions, in which a well-defined capillary condensation step is not observed in the N<sub>2</sub> adsorption-desorption isotherms.<sup>34,35</sup> Although Kimura, Haskouri et al., and Ma et al. have reported a few mesoporous phosphonate materials with type IV isotherms and well resolved pore size distributions, they are restricted to very common Al- and Ti-based materials.<sup>20–24</sup> Interestingly, the pore size distribution curve of the FeP-1ME sample is sharp, and the mesopore size is found to be around 2.9 nm (Figure 4c). This pore diameter is quite similar to those of other mesoporous materials prepared by CTAB.<sup>20</sup> The isotherm for FeP-2ME has a small capillary condensation step, due to the distortion of mesopores, as mentioned above (Figures 1b and 2c). FeP-3ME has no capillary condensation step (Figure 4a). With increasing synthetic temperature, the surface area is greatly decreased, as shown in Figure 4e. The FeP-4, FeP-5, and FeP-6 samples prepared without CTAB were also studied by N<sub>2</sub> isotherms (Figure 4b). From the pore size distributions, these samples do not have any mesoporosity (Figure 4d).

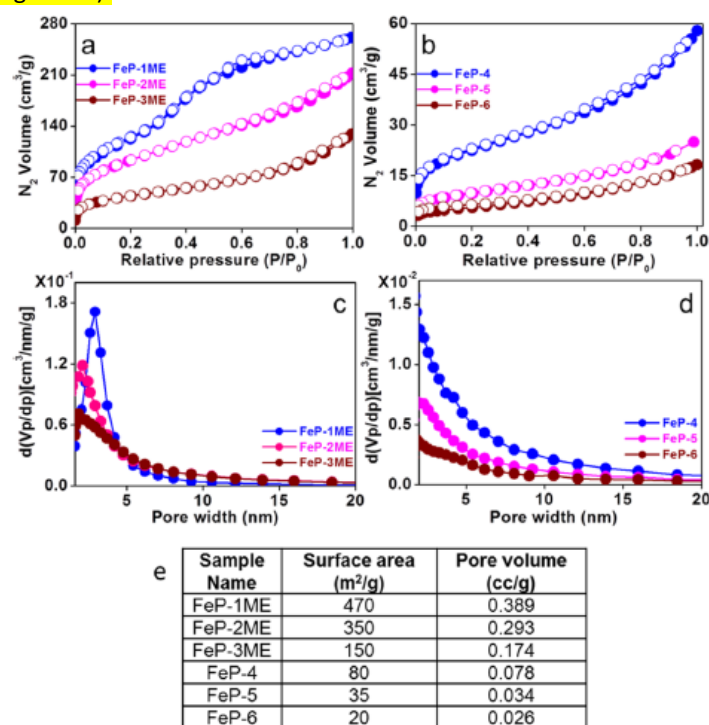


Figure 4. N<sub>2</sub> adsorption-desorption isotherms of (a) FeP-1ME, FeP-2ME, and FeP-3ME and (b) FeP-4, FeP-5, and FeP-6. Pore size distribution curves of (c) FeP-1ME, FeP-2ME, and FeP-3ME and (d) FeP-4, FeP-5, and FeP-6. (e) Summary of surface areas and pore volumes for all samples.

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for lithium-ion  
batteries](#)

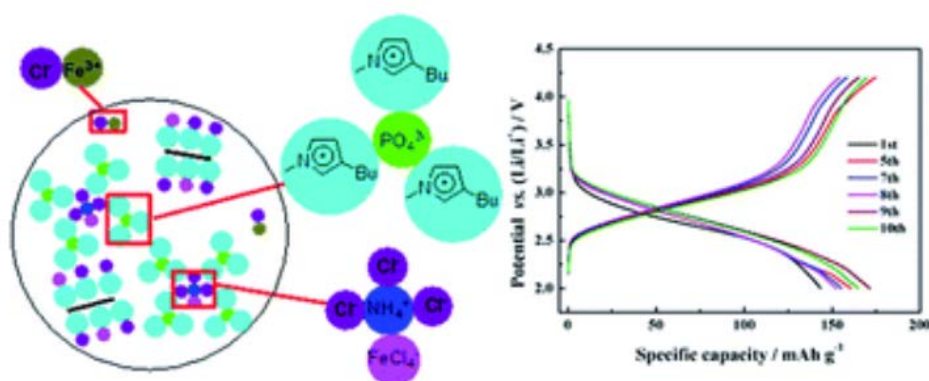
Hui Dou,  
Ping Niea and  
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2014

2,  
19536-19541

**Abstract**

Nanostructured iron phosphate/multi-walled carbon nanotubes (FePO<sub>4</sub>/MWCNTs) composites have been synthesized by a mechano-chemical process using 1-butyl-3-methylimidazolium tetrachloroferrate (bmimFeCl<sub>4</sub>) and (NH<sub>4</sub>)<sub>3</sub>PO<sub>4</sub>·3H<sub>2</sub>O as precursors in the presence of 1-butyl-3-methylimidazolium chloride (bmimCl). The bmimFeCl<sub>4</sub> serves not only to provide the necessary Fe-ion source, but also as a co-dispersant for the MWCNTs and as a soft co-template for structure control of the FePO<sub>4</sub> nanoparticles, together with the bmimCl. The obtained FePO<sub>4</sub>/MWCNTs composites were characterized by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), thermogravimetric and differential scanning calorimetry analysis (TG-DSC). As cathode materials for rechargeable lithium-ion batteries, the composites exhibited a capacity of 171 mA h g<sup>-1</sup> at a current density of 40 mA g<sup>-1</sup>, which is close to theoretical capacity for this material, and good cycle performance with a reversible capacity of 135 mA h g<sup>-1</sup> after 100 cycles at a rate of 50 mA g<sup>-1</sup>.



This reference is shortlisted based on abstract

**Field of Search**

Source	Period	Databases	Query	Search scope
Derwent Innovation	Till 2018-03-13	US EP WO JP DE GB FRA CA CN RU	ALL=(((("iron ADJ phosphate") OR FePO4 OR (transition ADJ metal ADJ oxide)) NEAR5 ((electrode OR cathode OR positive ADJ electrode) NEAR5 (prepar* OR fabricat* OR mak*3 OR manufactur* OR produc*)) AND ((lithium ADJ ion ADJ batter*) OR (Li? ADJ ion ADJ batter*) OR (secondary ADJ battery))));	Full text No. of hits 230
Derwent Innovation	Till 2018-03-13	US EP WO JP DE GB FRA CA CN RU	CTB=(((electrode OR cathode OR positive ADJ electrode) NEAR5 (prepar* OR fabricat* OR mak*3 OR manufactur* OR produc*)) AND ((lithium ADJ ion ADJ batter*) OR (Li? ADJ ion ADJ batter*)) AND ((iron ADJ phosphate) OR FePO4));	Title, Claims and abstract No. of hits 392
Derwent Innovation	Till 2018-03-13	US EP WO JP DE GB FRA CA CN RU	ALL=("iron phosphate" OR "ferric phosphate" OR FePO4 OR FePO4.9H2O) AND AIC=(C01B0025375) AND AIC=(H01M);	Full text No. of hits 294
Derwent Innovation	Till 2018-03-13	US EP WO JP DE GB FRA CA CN RU	ALL=(((("iron ADJ phosphate") OR FePO4) NEAR5 ((electrode OR cathode OR positive ADJ electrode) NEAR5 (prepar* OR fabricat* OR mak*3 OR manufactur* OR produc*)) AND ((lithium ADJ ion ADJ batter*) OR (Li? ADJ ion ADJ batter*))));	Full text No. of hits 245
Derwent Innovation	Till 2018-03-13	US EP WO JP DE GB FRA CA CN RU	ALL=(((("iron ADJ phosphate") OR FePO4 OR (TRANSITION ADJ METAL ADJ OXIDE)) NEAR10 ((electrode OR cathode OR positive ADJ electrode) NEAR5 (prepar* OR fabricat* OR mak*3 OR manufactur* OR produc*)) AND ((lithium ADJ ion ADJ batter*) OR (Li? ADJ ion ADJ batter*)) OR (secondary ADJ battery))) AND acetylene ADJ black and (poly ADJ (vinylidene ADJ difluoride) OR (PVDF)));	Full text No. of hits 220
Derwent Innovation	Till 2018-03-13	US EP WO JP DE GB FRA CA CN RU	ALL=(((("iron ADJ phosphate") OR (ferric ADJ phosphate) OR FePO4 OR Fe-P-O) AND (ionic ADJ liquid) AND (mesoporous OR meso-porous));	Full text No. of hits 183

Source	Period	Databases	Query	Search scope
<i>Derwent Innovation</i>	Till 2018-03-13	US EP WO JP DE GB FRA CA CN RU	CTB=("Cetyl trimethylammonium" OR CTAB OR "cetyl trimethyl ammonium" OR *imidazolium OR "ionic liquid") AND ALL=("iron phosphate" OR "ferric phosphate" OR FePO4 OR FePO4.9H2O OR Fe-P-O) AND (mesoporous OR mesoporous));	Title, Claims and abstract <b>No. of hits</b> <b>94</b>
<i>Derwent Innovation</i>	Till 2018-03-13	US EP WO JP DE GB FRA CA CN RU	ALL=("iron phosphate" OR "ferric phosphate" OR FePO4 OR FePO4.9H2O OR Fe-P-O) AND (mesoporous OR mesoporous) AND ((lithium?ion ADJ batter* OR Li?ion ADJ batter* OR LIB OR LIBs));	Full text <b>No. of hits</b> <b>62</b>
<i>Derwent Innovation</i>	Till 2018-03-13	US EP WO JP DE GB FRA CA CN RU	ALL=(((("iron ADJ phosphate") OR FePO4) NEAR10 ((electrode OR cathode OR positive ADJ electrode) NEAR5 (prepar* OR fabricat* OR mak*)) AND ((lithium ADJ ion ADJ batter*) OR (Li? ADJ ion ADJ batter*))));	Full text <b>No. of hits</b> <b>33</b>
<i>Derwent Innovation</i>	Till 2018-03-13	US EP WO JP DE GB FRA CA CN RU	ALL=(((("iron ADJ phosphate") OR FePO4) NEAR3 ((electrode OR cathode OR positive ADJ electrode) NEAR5 (prepar* OR fabricat* OR mak*)) AND ((lithium ADJ ion ADJ batter*) OR (Li? ADJ ion ADJ batter*))));	Full text <b>No of hits:</b> <b>7</b>
<i>Google patents</i>	Till 2018-03-13	USA USG	mesoporous iron phosphate cathode for LIB	Full Text <b>No. of hits</b> <b>73</b>
<i>Google patents</i>	Till 2018-03-13	USA USG	mesoporous "iron phosphate" cathode for LIB and ionic liquid	Full Text <b>No. of hits</b> <b>30</b>
<i>Google scholar</i>	Till 2018-03-13	-	mesoporous iron phosphate cathode for LIB	Full Text <b>No. of hits</b> <b>&gt;100</b>
<i>Google scholar</i>	Till 2018-03-13	-	"iron phosphate" and "FePO4" and acetylene black and poly(vinylidene difluoride) to make cathode for LIB	Full Text <b>No. of hits</b> <b>89</b>

\*Databases Searched: Thomson Innovation - Collections searched: US, EP, WO/PCT, JP, AR, AT, AU, BE, BR, CA, CH, CN, DD, DE, DK, EA, ES, FI, FR, GB, IE, IN, IT, KR, LU, MC, MX, NL, PT, RU, SE, SU as of March 13, 2018.



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