



(51) International Patent Classification:

H01M 4/136 (2010.01) *H01M 4/58* (2010.01)
B82Y 30/00 (2011.01) *H01M 4/62* (2006.01)
H01M 4/36 (2006.01)

(21) International Application Number:

PCT/GB2017/051426

(22) International Filing Date:

22 May 2017 (22.05.2017)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

1609016.9 23 May 2016 (23.05.2016) GB

(71) Applicant: **JOHNSON MATTHEY PUBLIC LIMITED COMPANY** [GB/GB]; 5th Floor, 25 Farringdon Street, London EC4A 4AB (GB).

(72) Inventors: **COPLEY, Mark**; Johnson Matthey Technology Centre, Blount's Court Road, Sonning Common, Reading Berkshire RG4 9NH (GB). **MARANSKI, Krzysztof Jerzy**; Flat 11 Bosworth House, Battle Square, Reading Berkshire RG30 1DU (GB).

(74) Agent: **GEE, Rachel Sarah**; Johnson Matthey Technology Centre, Blount's Court Road, Sonning Common, Reading Berkshire RG4 9NH (GB).

(81) Designated States (*unless otherwise indicated, for every kind of national protection available*): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

(54) Title: BATTERY CATHODE MATERIALS

(57) Abstract: The present invention relates to Li MPO₄ particles at least partially coated with carbon, and a process for the preparation thereof. Such particles are particularly effective for use as a cathode material for lithium batteries. The particles are typically in the form of single crystals, and may be prepared by flame spray pyrolysis.

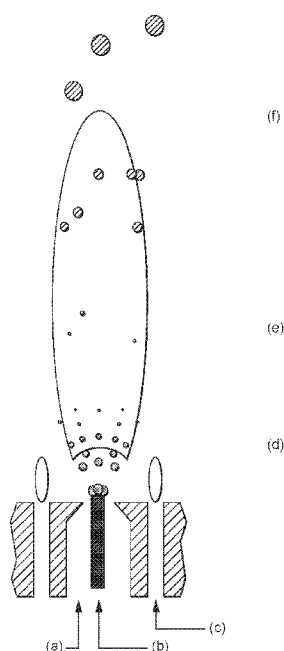


FIG. 1

Declarations under Rule 4.17:

- *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*
- *of inventorship (Rule 4.17(iv))*

Published:

- *with international search report (Art. 21(3))*

Battery Cathode Materials

Field of the Invention

- 5 The present invention relates to LiMPO_4 particles at least partially coated with carbon, and a process for the preparation thereof. Such particles are particularly effective for use as a cathode material for lithium batteries.

Background of the Invention

10

Lithium ion batteries are a type of rechargeable battery commonly used in consumer electronics. They are popular since they offer both high energy and high power densities. Accordingly, they are also a promising candidate for both hybrid and fully electric vehicles.

15

Lithium metal phosphate materials have been employed as electrode materials in batteries. For example, US6514640 describes the preparation of LiFePO_4 , LiMnPO_4 , LiCoPO_4 and LiNiPO_4 by solid state reaction. The document proposes use of these materials as cathode materials for lithium ion batteries. WO2007/100918 describes a method for producing LiMnPO_4 particles by a milling process, and suggests that these particles may be used to form electrodes of electrochemical cells.

20

When employed as electrode materials, the particles of lithium metal phosphate are typically coated with carbon to increase the conductivity thereof. Waser et al; *J. Aerosol Science*; Volume 42, Issue 10, October 2011, pages 657-667 describes synthesis of core-shell, nano-sized LiFePO_4 -carbon particles for lithium ion batteries. The particles were annealed in a reducing environment (5 vol% H_2 in Argon at 700°C for four hours.

25

- 30 Flame spray pyrolysis has been used to produce electrode materials. Flame spray pyrolysis involves the aerosolisation of a precursor solution within a chamber. The aerosol is ignited with a flame and undergoes rapid combustion within milliseconds, oxidising substantially all of the organic components and leaving predominantly inorganic species in the gas phase. These inorganic species thereafter nucleate to form clusters and finally nano-sized particles. The temperature of the gas cools rapidly, typically the equivalent to a 1000°C quench in less than 100 ms. Such rapid cooling typically leads to kinetic products and nanopowders that are non-aggregated.
- 35

While the kinetic product may be transformed to a desired thermodynamic product by heating, such heating typically results in an increase in the size of the particles, for example via sintering, which leads to a corresponding reduction in electrochemical performance. This is because in a larger particle the time required for lithium insertion and deinsertion is increased, resulting in decreased power capability.

EP-A-2292557 describes the synthesis of LiFePO_4 particles by flame spray pyrolysis. The particles are coated with acetylene carbon black by supplying acetylene to the flame, and then annealed in an inert environment to ensure complete crystallization to the olivine form.

It is desirable to provide an improved process for the production of LiMPO_4 particles at least partially coated with carbon and/or tackle at least some of the problems associated with the prior art or, at least, to provide a commercially useful alternative thereto.

Summary of the Invention

According to a first aspect there is provided a process for the preparation of LiMPO_4 particles at least partially coated with carbon, the process comprising:

providing a precursor solution comprising a lithium precursor, a phosphorus precursor and a M precursor, wherein M is selected from Fe, Mn, Ni and Co and mixtures thereof;

subjecting the precursor solution to flame spray pyrolysis to produce particles comprising lithium, phosphorus and M; and

heating the particles in the presence of a carbon precursor under an inert atmosphere to form LiMPO_4 particles at least partially coated with carbon.

As used herein the term LiMPO_4 is intended to include particles in which a slight stoichiometric deficit or excess of Li and/or M may be present, e.g. according to the following formula $\text{Li}_{1-x}\text{M}_{1-y}\text{PO}_4$, in which each of x and y is independently in the range from -0.5 to +0.5, e.g. from -0.1 to +0.1. Preferably, x is about 0. Preferably y is about 0.

The present invention will now be further described. In the following passages different aspects of the invention are defined in more detail. Each aspect so defined may be combined with any other aspect or aspects unless clearly indicated to the contrary. In particular, any feature indicated as being preferred or advantageous may
5 be combined with any other feature or features indicated as being preferred or advantageous.

The inventors have surprisingly found that the process described herein may result in carbon-coated LiMPO_4 particles exhibiting good or excellent electrochemical
10 performance. Accordingly, the particles are particularly suitable for use as cathode materials in lithium ion batteries.

Typically, the particles have a low proportion of crystal defects. Without being bound by theory, it is considered that this is a result of the heating step. For example, the
15 heating step may remove defects including point defects and/or line defects in the crystal structure of the LiMPO_4 , in particular antisite defects. Reducing the number of crystal defects may increase the lithium ion conductivity of the particles, which in turn enhances electrochemical performance as it facilitates lithium ion insertion and
deinsertion.

Without being bound by theory, the presence of a low number of crystal defects is considered to have a particularly pronounced effect on the lithium ion conductivity of
20 particles of LiMPO_4 in view of the fact that LiMPO_4 compounds are typically one dimensional conductors, especially when they are in their olivine crystalline form.

The LiMPO_4 particles typically exhibit the olivine crystal structure (*Pmnb* space group). Such a polymorph is a particularly effective Li ion conductor. Without being bound by theory, it is considered that the olivine structure is present following the heating step. Phase pure olivine LiMPO_4 is typically obtained. The skilled person is
25 readily able to identify the olivine crystal form, for example using X-ray diffraction. XRD diffraction data for different olivine LiMPO_4 materials can be found at the following records in the PDF4+ 2014 database from the International Centre for
Diffraction Data:

35 LiMnPO_4 : 04-007-8711
 LiCoPO_4 : 04-007-4779

LiNiPO₄: 04-007-5495.

The present inventors have found that typically the majority of the particles are in the form of single crystals, more typically substantially all of the particles are in the form of single crystals. This is particularly advantageous for the performance of the particles as lithium ion conductors, since the presence of grain boundaries between separate crystallites in the particles can disrupt lithium ion conduction. The crystallite size can be determined for example using a powder X-ray diffraction processed by the Rietveld refinement method, which the skilled person is familiar with. Where the determined crystallite size is similar to the particle size (e.g. determined from the surface area as described below), this indicates that the particles are in the form of single crystals. For example, the crystallite size determined by Rietveld refinement of XRD data may differ from the particle size determined from the surface area by +/-25% or less, +/-20 % or less, +/-15% or less, or +/-10% or less. In such cases, the substantially all of the particles can be considered to be in the form of single crystals.

The particles may exhibit a small particle size. For example, the particles may have an average particle diameter (e.g. determined from the BET surface area) of less than 100 nm, e.g. less than 70nm, less than 60 nm, less than 50nm or less than 40nm. The average particle diameter may be at least 1nm, e.g, at least 5 nm, at least 10 nm, at least 15nm or at least 20nm.

As the skilled person will understand, the average particle diameter (D, in nm) may be determined from the BET surface area (SA, in m²/g), using the following formula, in which d is the density of LiMPO₄ in g/cm³:

$$D = \frac{6000}{d \times SA}$$

In this calculation, it is assumed that the particles are substantially spherical.

The particles may form agglomerates (or secondary particles) having a larger particle size. This may be advantageous for the processing of the cathode materials. The particle size calculation method above, which uses the BET surface area, provides the average diameter of the primary particles.

The particles may be in the shape of, for example, rods, plates and/or spheres. Typically, the majority of the particles are in the shape of spheres, more typically substantially all of the particles are in the shape of spheres. A spherical particle shape may be preferred as spherical particles can typically be processed more easily.

Surprisingly, the heating step in the present invention does not result in a substantial increase in particle size.

The term “precursor” used herein encompasses a species comprising the corresponding element. For example, a lithium precursor comprises lithium. The precursors may be the corresponding element (e.g. lithium, phosphorous, M or carbon), or may be a compound containing the corresponding element (e.g. lithium acetate, triphenylphosphine, M acetate or sucrose).

The particles are at least partially coated with carbon. Typically, the particles are substantially coated with carbon, more typically completely coated with carbon. For example, at least 50% of the surface area of the particles may be covered with carbon, typically at least 95 %. The presence of the carbon coating may increase the electronic conductivity of the particles, which may be advantageous when the particles are used as a cathode material.

Flame spray pyrolysis is known in the art, and is described in R. Strobel, S. E. Pratsinis, Journal of Materials Chemistry 2007, 17, 4743-4756. During flame spray pyrolysis, the precursor solution is aerosolised with an oxidising gas, typically oxygen or air, within a chamber and then ignited, typically using a hydrogen or methane pilot flame. The chamber is typically not pressurised. It may be at a pressure of from 0.5 to 2 bar, more typically about 1 bar. The solution is typically aerosolised by pumping the precursor solution and oxidising gas through a capillary and then dispersing within a nozzle. In many flame spray pyrolysis processes, the solvent of the precursor solution typically provides the “fuel” for the combustion. The initial combustion temperature is typically from 1500 to 2500 °C, more typically from 1700 to 2300 °C. Without being bound by theory, it is considered that the aerosol

undergoes rapid combustion within milliseconds, oxidising all of the organic components and leaving predominantly inorganic species (e.g. metal-oxyanions and phosphorous oxyanions) in the gas phase. These oxyanions thereafter nucleate to form clusters and finally nano-sized particles. The temperature of the gas cools rapidly. This is the equivalent to a 1000 °C quench in less than 100 ms, typically leading to kinetic products and nanopowders that are non-aggregated.

The resultant nanopowders may be collected by any suitable means, for example in a filter (e.g. by a filter sock system).

The collected nanopowders are typically at least partially crystalline, but may be substantially amorphous.

Flame spray pyrolysis rigs are known in the art. A schematic of a typical flame spray nozzle arrangement is shown in FIG. 1 and is discussed in more detail below.

The flame spray pyrolysis rig may include a secondary quenching ring. Such a quenching ring typically comprises a ring or tube of gas, typically nitrogen, which surrounds the downstream path of the particles exiting the flame. This may serve to increase the cooling rate of the particles, thereby resulting in a smaller particle size. A sheath gas may be employed during the flame spray pyrolysis. The use of a sheath gas is known in the art. An oxygen sheath gas may be employed, for example to maintain the required level of oxygen during the flame spray pyrolysis step so as to obtain the desired product.

The particles are heated in the presence of a carbon precursor under an inert atmosphere. Prior to heating, the particles are typically mixed with the carbon precursor, for example using a speedmixer with or without ZrO₂ balls, to ensure an even distribution. Such an even distribution may serve to ensure an even coating of the particles.

The heating may be carried out using any suitable heating means known in the art, for example a tube furnace or muffle furnace.

The inert atmosphere typically comprises nitrogen and/or argon. The inert atmosphere may be a vacuum.

M is selected from Fe, Mn, Ni and Co and mixtures thereof. Preferably, M includes at least one of Mn, Ni and Co, e.g. is selected from Mn, Ni and Co. Such materials provide a higher electrochemical potential than LiFePO_4 , meaning that for the same mass of material, more energy is produced. M preferably includes Co, e.g. is Co.

M may advantageously be a mixture of Fe and M' , where M' is selected from Co, Mn, and mixtures thereof, preferably Co. In that case, M may be $M'_{1-z}\text{Fe}_z$, in which z is greater than or equal to zero and less than 0.9, 0.5 or 0.2.

Any suitable solvent may be used for the precursor solution. The choice of solvent will depend on the solubility of the precursors therein and also the desired size of the carbon-coated particles. Solvents exhibiting lower heats of combustion, and therefore providing lower flame temperatures in the flame spray pyrolysis step, typically result in smaller particle sizes being produced. In contrast, solvents exhibiting higher heats of combustion, and therefore providing higher flame temperatures in the flame spray pyrolysis step, typically result in larger particle sizes being produced. A mixture of different solvents may be employed in order to fine tune the resulting particle sizes.

The solvent may be a polar solvent or a non-polar solvent. Depending on the particular precursors employed, a polar or non-polar solvent may be chosen so as to result in a stable precursor solution. The solvent may be an organic solvent or an inorganic solvent, but is typically an organic solvent. In contrast to inorganic solvents, organic solvents typically function more effectively as fuels during the flame spray pyrolysis step. To improve combustion, the solvent is typically substantially free of water, more typically it is anhydrous. However, water may be present in order to decrease the heat of combustion, and therefore decrease the size of the resulting particles.

The precursor solution preferably comprises a solvent selected from one or more of acetic acid, methanol, ethyl acetate, ethanol, acetonitrile, acetone, acetylacetone, 1-propanol, 1-butanol, 2-ethylhexanoic acid, hexane, heptane, 1-octanol, octane,

cyclohexane, toluene and xylene. Such solvents exhibit favourable heats of combustion, and/or are capable of dissolving a wide variety of precursors.

5 A variety of lithium precursors may be employed. The lithium precursors may be inorganic or organometallic. The lithium precursor preferably comprises one or more of lithium hydroxide, lithium acetate, lithium 2-ethylhexanoate, lithium acetylacetonate, lithium naphthenate and lithium nitrate. Such precursors are particularly suitable for use in flame spray pyrolysis. In particular, such precursors exhibit high solubility in a variety of organic solvents enabling a wide range of concentrations and provide stable precursor solutions. Such advantages are particularly pronounced for lithium 2-ethylhexanoate. However, lithium acetate and lithium hydroxide may be advantageously used for reasons of cost.

15 A variety of phosphorus precursors may be employed. The phosphorus precursor may be inorganic or organic. The phosphorus precursor preferably comprises one or more of a phosphine (for example, triphenylphosphine or triethylphosphine) and a phosphate (for example, an organic phosphate such as, for example, trimethyl phosphate or triethyl phosphate).

20 A variety of M precursors may be employed. The M precursors may be inorganic or organometallic. The M precursor preferably comprises one or more of M acetate, M 2-ethylhexanoate, M acetylacetonate, M naphthenate and M nitrate. Such precursors are particularly suitable for use in flame spray pyrolysis. In particular, such precursors exhibit high solubility in a variety of organic solvents enabling a wide range of concentrations and provide stable precursor solutions. Such advantages are particularly pronounced for M 2-ethylhexanoate. However, M acetate may be advantageously used for reasons of cost.

30 Where Li acetate (or LiOH) and/or M acetate is used as the Li/M precursor, the present inventors have found that it may be advantageous to include some ethylhexanoate (or ethylhexanoic acid) to the precursor solution and this can stabilise the precursor solution.

In a preferred embodiment:

35 the solvent comprises methanol;
the lithium precursor comprises lithium acetate or LiOH;
the phosphorous precursor comprises triethyl phosphate; and
the M precursor comprises M acetate.

Such a combination of solvents and precursors may provide a particularly stable precursor solution, and may be particularly effective at providing highly crystalline and small sized particles of LiMPO_4 .

In an alternative preferred embodiment:

the solvent comprises methanol and xylene;

the lithium precursor comprises Li 2-ethylhexanoate;

the phosphorous precursor comprises triphenylphosphine; and

the M precursor comprises M 2-ethylhexanoate.

Such a combination of solvents and precursors may provide a particularly stable precursor solution, and may be particularly effective at providing highly crystalline and small sized particles of LiMPO_4 .

In a typical process according to the present invention, the amounts of the different precursors in the precursor solution are selected according to the composition of the desired product. For example, if LiCoPO_4 is to be obtained, equimolar amounts of Co precursor, Li precursor, and phosphorus precursor are combined in the precursor solution.

The concentration of M (and all the other components) may be varied. The upper concentration limit is typically determined by the particular precursors employed and the solvent(s) used. The present inventors have found that including ethylhexanoate (e.g. 2-ethylhexanoate) or ethylhexanoic acid (e.g. 2-ethylhexanoic acid) can increase the solubility of the precursors in the organic solvent.

In the flame spray pyrolysis step, it is possible to vary the flow of precursor aerosol into the chamber by varying the flow rate of the dispersion gas and/or the precursor solution. The flow may be controlled to control the size of the resulting particles. Higher flow rates tend to produce particles having a smaller size, whereas lower flow rates tend to produce particles having a larger size.

The flow rates of precursor solution and dispersion gas will depend on the size of the flame spray pyrolysis rig used. Industrial rigs typically employ substantially higher flow rates than those reported in the examples herein. Increases the dispersion gas rate typically enhances dispersion of the precursors but may also cool the flame.

The result is typically smaller particles but if the flame is excessively cooled this can result in incomplete combustion and the formation of undesirable reaction products. The present inventors have found that it may be advantageous to control the ratio of precursor solution feed rate to dispersion gas flow rate. The ratio may be in the
5 range from 1:250 to 1:3000, e.g. from 1:500 to 1:2000.

During the flame spray pyrolysis, the particles comprising lithium, phosphorous and M are typically collected using techniques known in the art. The particles comprising lithium, phosphorous and M are preferably collected by electrostatic precipitator,
10 electrophoretic deposition or by a filter. Such collection techniques are particularly suitable.

The carbon precursor is preferably selected from one or more of a carbohydrate (e.g. cellulose, sucrose, glucose, lactose, starch), ascorbic acid, citric acid, polyacrylic
15 acid and a polymer (e.g. polyoxyethylen(20)-sorbitan-monooleate). Such carbon precursors are particularly effective at coating the particles and preventing sintering of the particles during the heating step. The carbon precursor preferably comprises a carbohydrate selected from one or more of cellulose, sucrose, glucose, lactose and starch. Such carbohydrates are particularly effective carbon precursors.

20 The carbon precursor is preferably present during the heating step in an amount of from 1 to 40 wt.% based on the total weight of the particles and the carbon precursor, preferably from 5 to 25 wt.%. Lower levels may result in inadequate coating of the particles. Higher levels may result in the presence of undesirable
25 carbonaceous impurities in the final particles. However, this is typically calculated based on the surface area of the materials and the desired thickness of the carbon coating.

30 The heating is preferably carried out for at least 30 minutes, more preferably from 1 to 10 hours, even more preferably from 1.5 to 3 hours, still even more preferably about 2 hours. Shorter heating times may result in inadequate conversion of the kinetic product to the desired thermodynamic product (for example, the olivine polymorph). Furthermore, the level of crystal defects may be too high, and/or carbon coating may be inadequate. Longer heating times may result in sintering of the
35 particles, and therefore an undesirably large particle size.

The heating process typically comprises gradually heating the material, then holding it at an elevated temperature in the range from 400 or 500 to 900 °C, more

preferably from 500 or 600 to 800 °C, even more preferably from 650 to 750 °C for a period of 5 minutes to 5 hours, e.g. from 10 minutes to 2 hours, e.g. about 30 minutes. Higher temperatures may result in an increase in the final product sizes, for example due to sintering, to the formation of an undesirable polymorph, or to the reduction of the LiMPO_4 to phosphides or other decomposition of the LiMPO_4 . Lower temperatures may not result in the correct polymorph (e.g. olivine) being formed, or may result in the particles exhibiting a higher level of crystal defects. Typically, the particles produced by flame spray pyrolysis are not heated prior to the step of heating in the presence of C precursor.

The process may also produce particles comprising metal phosphides such as M_2P . Such particles may be at least partially coated with carbon. Such phosphide materials are typically conductive. Accordingly, when the LiMPO_4 particles are used in a cathode, while the presence of M_2P may reduce the capacity of the material, the overall performance of the cathode may be increased due to the increase in electronic conductivity.

The M_2P is preferably Co_2P . Co_2P exhibits particularly high electronic conductivity. Co_2P may be produced when the LiMPO_4 particles comprise LiCoPO_4 , or when M includes Co

The M_2P is preferably present in an amount of from 1 to 5 wt.% based on the total weight of the particles, preferably from 2 to 4 wt.%. Such amounts are particularly favourable since they result in a balance of increased performance of a cathode (due to increased electronic conductivity) without unfavourable levels of reduced capacity. Without wishing to be bound by theory, it is believed that the phosphide material forms due to partial reduction of the LiMPO_4 material by the carbon in the carbon coating. Therefore, the phosphide typically forms at the surface of the particles rather than in the bulk of the particles. This is preferred.

The process may further comprise a step of forming the LiMPO_4 particles into an electrode (typically a cathode).

In a further aspect, the present invention provides LiMPO_4 particles produced according to the method described herein.

In a further aspect, the present invention provides LiMPO_4 particles at least partially coated with carbon, M being selected from Fe, Mn, Ni and Co and mixtures thereof, wherein:

- 5 the particles have an average particle diameter of less than 100 nm; and
 substantially all of the particles are in the form of single crystals.

The advantages and preferable features of the first aspect of the present invention apply equally to this aspect of the present invention.

- 10 In a further aspect, the present invention provides a cathode comprising the LiMPO_4 particles described herein.

The advantages and preferable features of the first aspect of the present invention apply equally to this aspect of the present invention.

- 15 In a further aspect, the present invention provides a lithium ion battery comprising the cathode described herein.

- 20 The advantages and preferable features of the first aspect of the present invention apply equally to this aspect of the present invention.

- 25 In a further aspect, the present invention provides a vehicle comprising the lithium ion battery described herein. The vehicle may be a boat (e.g. a ship or a submarine), an aircraft (e.g. a fixed wing aircraft or a rotary wing aircraft), a spacecraft or an automobile (e.g. a car, a van, a lorry, a bus or a train). The vehicle is preferably an automobile.

- 30 The advantages and preferable features of the first aspect of the present invention apply equally to this aspect of the present invention.

Brief Description of the Drawings

The invention will now be described in relation to the following non-limiting figures, in which:

- 35 FIG. 1 shows a schematic of a conventional flame spray pyrolysis rig.

FIG. 2 shows the results of electrochemical cycling testing.

FIG. 3 shows powder X-ray diffraction patterns of the LiMPO_4 particles of two examples of the present invention and a comparative example.

5

Detailed description

Referring to FIG. 1 there is shown a schematic of a conventional pyrolysis nozzle arrangement that may be used in the process of the present invention. A dispersion
 10 gas (a) is used to aerosolise a precursor solution (b) within a chamber (not shown for reasons of clarity). The aerosol is then ignited using a torch of methane and oxygen (c). On ignition, the aerosol experiences precursor dispersion, evaporation and combustion at (d) followed by nucleation at (e) and then coagulation and
 15 coalescence at (f). As discussed previously, the resulting nanoparticles may be captured using a filter or by electrophoretic deposition (neither shown for reasons of clarity).

The invention will now be further described with reference to the following non-limiting examples.

20

Example 1

A precursor solution was prepared having the following composition:

Compound	n [mol]
$\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$	0.0187
Methanol	2.0300
$\text{CH}_3\text{COOLi} \cdot 2\text{H}_2\text{O}$	0.0187
$(\text{C}_2\text{H}_5\text{O})_3\text{PO}$	0.0187

25

Table 1 – Composition of precursor solution of Example 1.

To prepare the precursor solution, the lithium and cobalt acetates were dissolved in methanol, and then the triethyl phosphate was added.

30

The precursor solution was subjected to flame spray pyrolysis. The conditions of the flame spray pyrolysis are set out in Table 2.

Parameter	Value
O ₂ dispersion flow	5 L/min
Dispersion pressure p	1.5 bar
Precursor feed	5 mL/min
Sheath O ₂ flow	5 L/min
Flame O ₂ flow	3.2 L/min
Flame CH ₄ flow	1.5 L/min

Table 2 – Conditions of flame spray pyrolysis.

5 *Example 2*

A precursor solution was prepared having the following composition (Table 3):

Compound	n [mol]
Co(CH ₃ COO) ₂ ·4H ₂ O	0.0622
LiOH·H ₂ O	0.0622
(C ₂ H ₅ O) ₃ PO	0.0622
2-Ethylhexanoic acid	0.2052
Methanol	1.2146

10 Table 3 - Composition of precursor solution of Example 2.

To prepare the precursor solution, cobalt acetate tetrahydrate was mixed with excess of 2-ethylhexanoic acid (to also account for LiOH) and stirred for ~15 minutes. Then Li hydroxide was added, the stirring continued and methanol was
15 added. When clear solution has formed, triethyl phosphate was added.

The precursor solution was subjected to flame spray pyrolysis. The conditions of the flame spray pyrolysis are set out in Table 4.

Parameter	Value
O ₂ dispersion flow	20 L/min
Dispersion pressure p	1 bar
Precursor feed	10 mL/min
Sheath O ₂ flow	20 L/min

Flame O ₂ flow	3.2 L/min
Flame CH ₄ flow	1.5 L/min

Table 4 – Conditions of flame spray pyrolysis.

The material as synthesised by flame spray pyrolysis was mixed with cellulose at 10:1 weight ratio using a speedmixer. The sample was then carbonised in a furnace under an inert atmosphere. The heating programme was as follows:

1. Heating 5 °C/min to 500 °C,
2. Hold for 5 – 15 minutes,
3. Heating 2 °C/min to 700 °C,
4. Hold for 30 minutes.
5. Cool down 20 °C/min.

Example 3

Example 2 was repeated but using the precursor solution set out in Table 5 below and additional steps described below the table 5.

Compound	n [mol]
Co(CH ₃ COO) ₂ ·4H ₂ O	0.0933
LiOH·H ₂ O	0.0933
P(C ₆ H ₅) ₃	0.0933
2-Ethylhexanoic acid	0.3078
Xylene	1.1546
Methanol	2.4656

Table 5 - Composition of precursor solution of Example 3.

To prepare the precursor solution, cobalt acetate tetrahydrate was mixed with excess of 2-ethylhexanoic acid (to also account for LiOH). Then toluene was added and the mixture was azeotropically distilled (using Dean-Stark apparatus) in order to remove water and acetic acid. Once all the water had evaporated, the mixture was cooled down to below the boiling point of toluene/water azeotrope (<85 °C) and Li hydroxide was added. The mixture was reheated to evaporate water and once a clear solution was obtained, toluene was evaporated. The resulting viscous liquid

was then mixed with the solvent (i.e. xylene and methanol) and the source of phosphorus (i.e. Triphenylphosphine). The precursor solution was subjected to flame spray pyrolysis. The conditions of the flame spray pyrolysis are set out in Table 4.

- 5 The particles of Example 3 as synthesised by flame spray pyrolysis were carbon coated like in Example 2 and then subjected to electrochemical testing. The testing conditions were as follows:

Conductive carbon: C65 (10 wt.%)

10 Binder: PVdF HFP (5 wt %)

Electrolyte: LP30 (1M LiPF₆ 1:1 EC:DMC) or 1M LiPF₆ in 1:4 FEC:DMC

85: 10: 5 1.7 g: 0.2 g: 0.1 g 4 ml NMP, second aliquot of 2 ml NMP added with LCP (in some cases).

15

The particles were subjected to C/50 testing (LP30 electrolyte), C/10 testing (LP30 electrolyte) and C/10 testing (1M LiPF₆ 1:4 FEC:DMC electrolyte), and the results are shown in FIG. 2. The open symbols refer to the cycle efficiency values, with the squares corresponding to C/10 LP30, the diamonds corresponding to C/50 LP30 and the circles corresponding to C/10 FEC:DMC (1:4). Of the filled symbols, the squares correspond to charge capacities and the triangles correspond to discharge capacities, with increasing capacities in the order C/10 LP30, C/50 LP30 and C/10 FEC:DMC (1:4). The particles exhibited favourable cycling behaviour and high efficiency.

25

Example 4 – Comparative Example

Example 3 was repeated but during the heating step the particles were heated in air and without the presence of a carbon precursor.

30

Powder X-ray diffraction patterns of Examples 2, 3 and 4 are shown in FIG. 3. The respective widths of the peaks indicate that the crystallite sizes were smallest for Example 3 and largest for Example 4. The large particle size for Example 4 is presumably due to the absence of the carbon precursor during the heating step.

35

Particle sintering is observed.

The particle sizes were calculated using a number of different methods, and the results are shown in Table 4 below.

Example	Surface area [m ² /g]	Particle size [nm]		Crystallite size [nm]
		From surface area*	TEM/SEM	PXRD**
1***	36.2	50.3	-	-
2	38.0	41.9	40	36
3	48.2	33.0	29	29
4	-	-	450	121

Table 5 – Surface areas and particle sizes (*assuming spherical shape of particles);
 crystallite size, using a Rietveld refinement. *Example 1 data for as synthesised
 by FSP particles. Examples 2-4 for heat treated particles.

The similarity of the particle and crystallite sizes determined for Example 3 using the
 different techniques indicates that the majority of the particles are in the form of
 single crystals. This is also the case in Example 2.

Example 5

Batches of particles of LiCoPO₄ and batches of particles of LiNiPO₄ were prepared
 using the process of the present invention. Variation of the flow rate of the dispersion
 gas resulted in a variation of the surface area of the samples, indicating a variation in
 the particles sizes. The O₂ dispersion flow rate of 20 L/min resulted in the production
 of smaller particles than a flow rate of 5 L/min. Higher yield was achieved by using
 more advanced collection system. The results are shown in Table 5.

LiMPO ₄	Flow rate = 5 L/min		Flow rate = 20 L/min	
	SA [m ² /g]	Yield [%]	SA [m ² /g]	Yield [%]
LiCoPO ₄	42.6	24	63.6	84
LiNiPO ₄	40.4	22	77.1	57

Table 5 – Surface areas and yields for various flow rates.

The foregoing detailed description has been provided by way of explanation and
 illustration, and is not intended to limit the scope of the appended claims. Many
 variations in the presently preferred embodiments illustrated herein will be apparent

to one of ordinary skill in the art and remain within the scope of the appended claims and their equivalents.

The work leading to the invention has received funding from the European Union
5 *Seventh Framework Programme under Grant Agreement No: 609201.*

Claims:

1. LiMPO_4 particles at least partially coated with carbon, M being selected from Fe, Mn, Ni and Co and mixtures thereof, wherein:
 - 5 the particles have an average particle diameter of less than 100 nm; and
the majority of the particles are in the form of single crystals.
2. A process for the preparation of LiMPO_4 particles at least partially coated with carbon, the process comprising:
 - 10 providing a precursor solution comprising a lithium precursor, a phosphorus precursor and a M precursor, wherein M is selected from Fe, Mn, Ni and Co and mixtures thereof;
subjecting the precursor solution to flame spray pyrolysis to produce particles comprising lithium, phosphorus and M; and
15 heating the particles in the presence of a carbon precursor under an inert atmosphere to form LiMPO_4 particles at least partially coated with carbon.
3. The process of claim 2, wherein M includes Co, e.g. where M is Co.
- 20 4. The process of claim 2 or claim 3, wherein the precursor solution comprises a solvent selected from one or more of acetic acid, methanol, ethyl acetate, ethanol, acetonitrile, acetone, acetylacetone, 1-propanol, 1-butanol, 2-ethylhexanoic acid, hexane, heptane, 1-octanol, octane, cyclohexane, toluene and xylene.
- 25 5. The process of any one of claims 2 to 4, wherein the lithium precursor comprises one or more of lithium hydroxide, lithium acetate, lithium 2-ethylhexanoate, lithium acetylacetonate, lithium naphthenate and lithium nitrate.
6. The process of claim 5, wherein the lithium precursor comprises lithium 2-ethylhexanoate.
30
7. The process of any one of claims 2 to 6, wherein the phosphorous precursor comprises one or more of a phosphine and a phosphate.
- 35 8. The process of any one of claims 2 to 7, wherein the M precursor comprises one or more of M acetate, M 2-ethylhexanoate, M acetylacetonate, M naphthenate and M nitrate.

9. The process of claim 8, wherein the M precursor comprises M 2-ethylhexanoate.

10. The process of any one of claims 2 to 9, wherein:
5 the solvent comprises methanol;
the lithium precursor comprises lithium acetate;
the phosphorous precursor comprises triethyl phosphate; and
the M precursor comprises M acetate.

10 11. The process of any one of claims 2 to 9, wherein:
the solvent comprises methanol and xylene;
the lithium precursor comprises lithium hydroxide;
the phosphorous precursor comprises triphenylphosphine; and
the M precursor comprises M 2-ethylhexanoate.

15 12. The process of any one of claims 2 to 11, wherein the flame spray pyrolysis uses a precursor flow rate of from 1 to 50 L/min, preferably from 3 to 40 L/min, more preferably from 5 to 30 L/min, even more preferably from 15 to 25 L/min, still even more preferably about 20 L/min.

20 13. The process of any one of claims 2 to 12, wherein the carbon precursor is selected from one or more of a carbohydrate, ascorbic acid, citric acid, polyacrylic acid and a polymer.

25 14. The process of claim 13, wherein the carbon precursor comprises a carbohydrate selected from one or more of cellulose, sucrose, glucose, lactose and starch.

30 15. The process of any one of claims 2 to 14, wherein the carbon precursor is present during the heating step in an amount of from 1 to 40 wt.% based on the total weight of the particles and the carbon precursor, preferably from 5 to 25 wt.%.

35 16. LiMPO₄ particles at least partially coated with carbon produced according to the method of any one of claims 2 to 15.

17. A cathode comprising the LiMPO₄ particles of claim 1 or claim 16.

18. A lithium ion battery comprising the cathode of claim 17.

19. A vehicle comprising the lithium ion battery of claim 18.

1 / 3

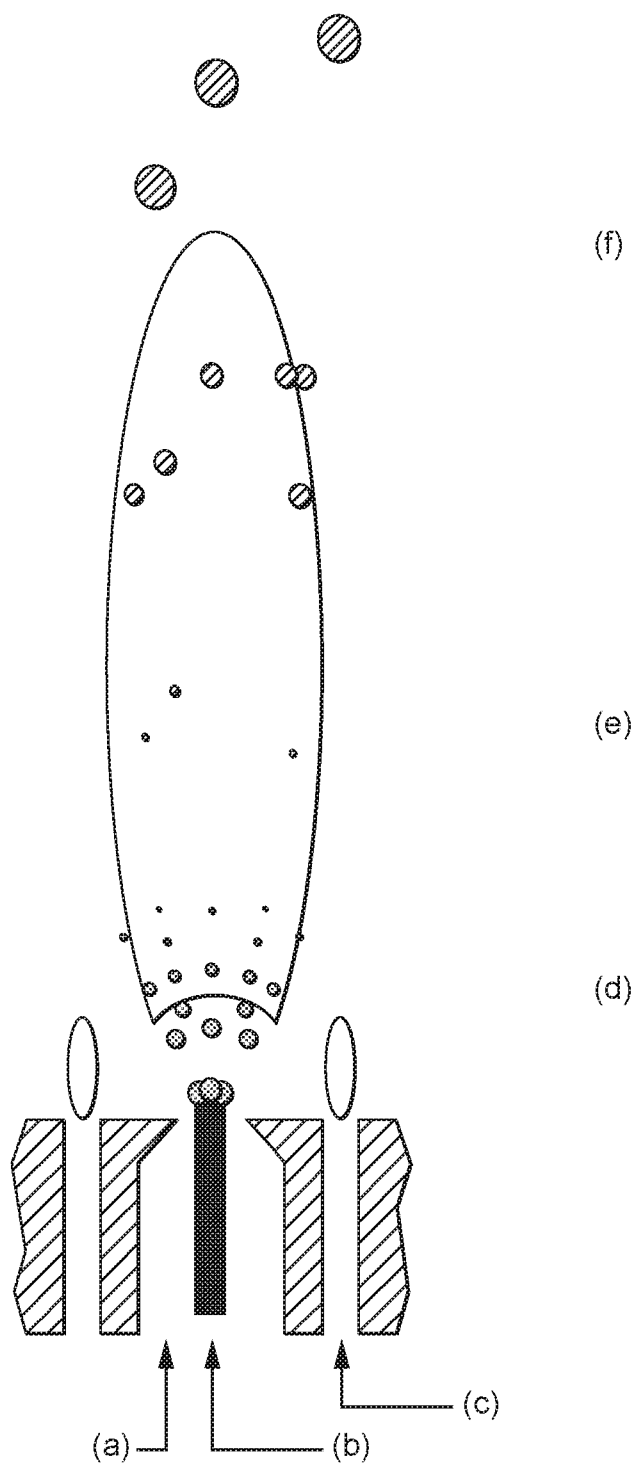


FIG. 1

2 / 3

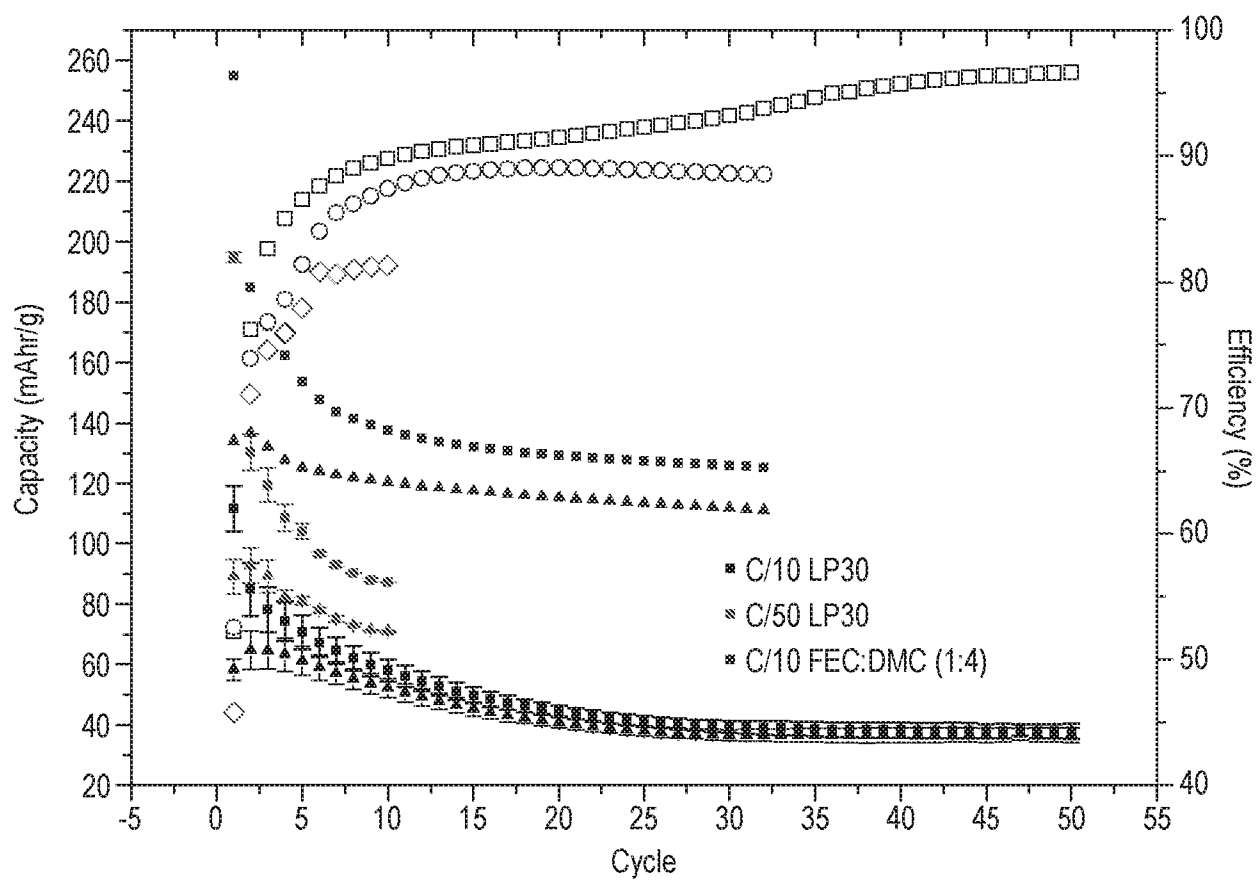


FIG. 2

3 / 3

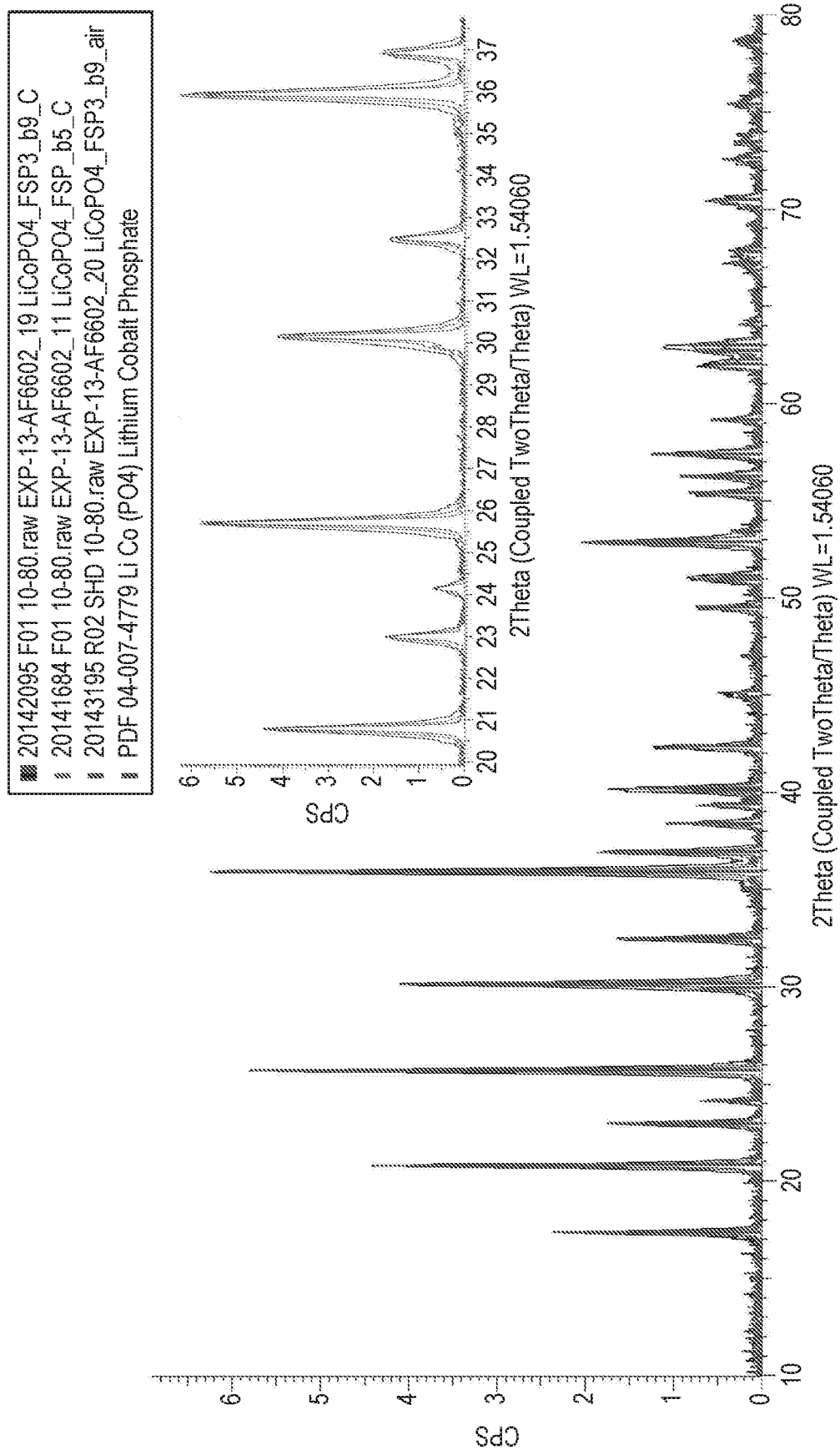


FIG. 3

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2017/051426

A. CLASSIFICATION OF SUBJECT MATTER INV. H01M4/136 B82Y30/00 H01M4/36 H01M4/58 H01M4/62 ADD.		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) H01M B82Y		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 2013 193927 A (FURUKAWA ELECTRIC CO LTD) 30 September 2013 (2013-09-30)	2,5,8, 13,14, 16-19 6,10-12
A	claims 1,7; figure 1 paragraphs [0024], [0036], [0042] - [0048], [0050], [0053], [0055], [0064] - [0066], [0094] -----	
X	EP 2 292 557 A1 (CLARIANT INT LTD [CH]) 9 March 2011 (2011-03-09)	1,2,4,5, 7,8, 16-19 6,10-12
A	claims 1,10; example 1 paragraphs [0010] - [0016], [0019], [0025], [0027] -----	
X	WO 2013/176067 A1 (HITACHI LTD [JP]) 28 November 2013 (2013-11-28) examples 1-3 -----	1,17-19
	-/-	
☒ 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 another 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 "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search	Date of mailing of the international search report	
23 June 2017	07/07/2017	
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Fitzpatrick, John	

INTERNATIONAL SEARCH REPORT

International application No
PCT/GB2017/051426

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2012/301780 A1 (KITAGAWA KAN [JP] ET AL) 29 November 2012 (2012-11-29) paragraph [0101]; example 1 -----	1,17-19
X	WO 2008/077447 A1 (UMICORE NV [BE]; CENTRE NAT RECH SCIENT [FR]; LEVASSEUR STEPHANE [BE];) 3 July 2008 (2008-07-03) claims 13,17 -----	1,17-19
X	US 2013/316233 A1 (HIRAYAMA YOSUKE [JP] ET AL) 28 November 2013 (2013-11-28) claims 1-5,7,15,16; figure 1; example 1 paragraphs [0030], [0032] - [0038], [0044], [0046], [0050] -----	1-4,7-9, 13-19

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/GB2017/051426

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 2013193927 A	30-09-2013	JP 5863525 B2 JP 2013193927 A	16-02-2016 30-09-2013
EP 2292557 A1	09-03-2011	CN 102482091 A EP 2292557 A1 EP 2475615 A1 US 2012168686 A1 WO 2011026581 A1	30-05-2012 09-03-2011 18-07-2012 05-07-2012 10-03-2011
WO 2013176067 A1	28-11-2013	JP 2013246936 A WO 2013176067 A1	09-12-2013 28-11-2013
US 2012301780 A1	29-11-2012	CN 102800861 A JP 5736965 B2 JP 2012248378 A US 2012301780 A1	28-11-2012 17-06-2015 13-12-2012 29-11-2012
WO 2008077447 A1	03-07-2008	CA 2672952 A1 EP 2032504 A1 EP 2103570 A2 JP 4465412 B2 JP 2009544563 A WO 2008077447 A1	03-07-2008 11-03-2009 23-09-2009 19-05-2010 17-12-2009 03-07-2008
US 2013316233 A1	28-11-2013	CN 103347812 A JP 5995726 B2 JP WO2012105637 A1 KR 20130057471 A US 2013316233 A1 WO 2012105637 A1	09-10-2013 21-09-2016 03-07-2014 31-05-2013 28-11-2013 09-08-2012