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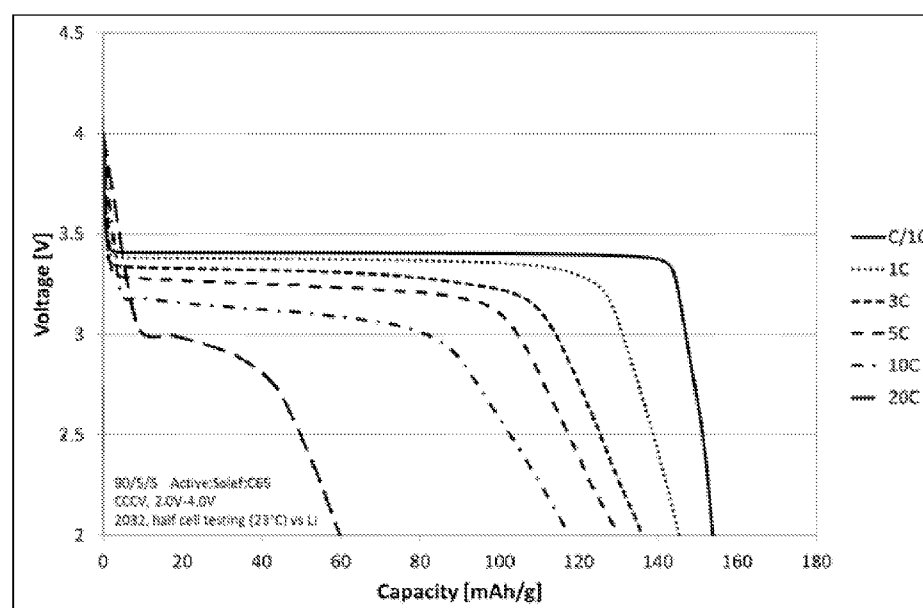
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(54) Title: LITHIUM METAL PHOSPHATE, ITS PREPARATION AND USE

Figure 2



(57) Abstract: A process for producing particulate carbon-coated aluminium-doped lithium iron phosphate material in which a sulfonic acid modified boehmite material is used as an aluminium- containing precursor. The use of such precursors can lead to lithium iron phosphate materials with improved electrochemical properties.

MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM,
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LITHIUM METAL PHOSPHATE, ITS PREPARATION AND USE

Field of the Invention

The present invention relates to lithium transition metal phosphate materials, their preparation and use as a cathode material in secondary lithium ion batteries.

Background of the Invention

Lithium metal phosphates with olivine structures have emerged as promising cathode materials in secondary lithium ion batteries. Advantages of lithium metal phosphates compared with other lithium compounds include the fact that they are relatively benign environmentally, and have excellent safety properties during battery handling and operation.

Melting processes, hydrothermal processes and solid-state processes are the most common synthesis routes for the preparation of lithium metal phosphates.

Relatively poor electrochemical performance of lithium metal phosphates has been attributed to their poor electronic conductivity, and their performance has been significantly improved by coating the particles with electronically conductive carbon.

It is known to add metal dopants to lithium metal phosphate materials with the aim of improving electrochemical performance. However, there remains a need for lithium metal phosphates which can be made by simple, cost effective and scalable processes, employ low cost precursors, and exhibit advantageous electrochemical properties such as increased discharge capacity.

Summary of the Invention

The present inventors have found that the electrochemical performance of carbon-coated aluminium-doped lithium iron phosphate can be improved by variation of the aluminium-containing precursor used in its preparation, and that the distribution of the dopant in the lithium iron phosphate structure can be enhanced. In particular, the present inventors have found that it is particularly advantageous to use sulfonic acid modified boehmite materials as aluminium-containing precursors in methods of producing aluminium-doped lithium iron phosphate materials.

Accordingly, in a first aspect the present invention provides a process for producing particulate carbon-coated aluminium-doped lithium iron phosphate, the process comprising:

- a milling step in which lithium-containing precursor, iron-containing precursor, aluminium-containing precursor, and carbon-containing precursor are combined and subjected to milling in a solvent; and
- a calcination step in which the product of the milling step is calcined to provide particulate carbon coated aluminium-doped lithium iron phosphate,

wherein the aluminium-containing precursor is a sulfonic acid modified boehmite material.

In a second aspect, the present invention provides particulate carbon-coated aluminium-doped lithium iron phosphate obtained or obtainable by a process described herein.

In a further preferred aspect, the present invention provides use of carbon-coated aluminium-doped lithium iron phosphate of the present invention for the preparation of a cathode of a secondary lithium ion battery. In a further preferred aspect, the present invention provides a cathode which comprises carbon-coated aluminium-doped lithium iron phosphate of the present invention. In a further preferred aspect, the present invention provides a secondary lithium ion battery, comprising a cathode which comprises carbon-coated aluminium-doped lithium iron phosphate of the present invention. The battery typically further comprises an anode and an electrolyte.

Brief Description of the Drawings

Figure 1 shows the discharge capacity of the aluminium-doped lithium iron phosphate prepared in Comparative Example 1.

Figure 2 shows the discharge capacity of the aluminium-doped lithium iron phosphate prepared in Example 1

Detailed Description

Preferred and/or optional features of the invention will now be set out. Any aspect of the invention may be combined with any other aspect of the invention unless the context demands otherwise. Any of the preferred and/or optional features of any aspect may be combined, either singly or in combination, with any aspect of the invention unless the context demands otherwise.

The present invention provides a process for making particulate carbon-coated aluminium-doped lithium iron phosphate using sulfonic acid modified boehmite materials as aluminium precursors. Boehmites are aluminium oxide hydroxide (AlO(OH)) minerals. It is known that boehmite materials may be modified with sulfonic acid reagents. Typically, such modification

is carried out on the surface of particulate boehmite materials. For example, an aqueous slurry or other aqueous dispersion of a particulate boehmite material may be reacted at elevated temperature, such as between 90 and 300°C, with a sulfonic acid compound to form a sulfonic acid modified boehmite material.

5

Typically, the sulfonic acids used to prepare the sulfonic acid modified boehmite materials are sulfonic acids of the formula $R-SO_3H$, in which R is an optionally substituted C_1-C_{20} (e.g. C_1-C_{10} or C_1-C_5) hydrocarbon group. As used herein, the term hydrocarbon group is intended to include alkyl (including cycloalkyl), alkenyl, alkynyl, aryl and alkaryl. The hydrocarbon moiety may be linear or branched.

10

The hydrocarbon groups may be optionally substituted. As used herein, the term optionally substituted includes moieties in which a one, two, three, four or more hydrogen atoms of the hydrocarbon group have been replaced with other functional groups. Suitable functional groups include -F, -Cl, -OH, -SH, -OR₃, -SR₃, -NR₁R₁, C(O)COR₁, -OC(O)R₁, -NR₃C(O)R₁ and C(O)NR₁R₁, wherein each R₁ is independently H or C₁ to C₁₀ (e.g. C₁-C₅ or C₁-C₃) alkyl or alkenyl, preferably alkyl. For example, suitable substituent functional groups include -OH, -OR₁, -NR₁R₁, C(O)COR₁, -OC(O)R₁, -NR₁C(O)R₁ and C(O)NR₁R₁, wherein each R₁ is independently H or C₁ to C₁₀ (e.g. C₁-C₅ or C₁-C₃) alkyl or alkenyl, preferably alkyl.

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Preferably, the sulfonic acids used to prepare the sulfonic acid modified boehmite materials are aryl sulfonic acids, such as sulfonic acids in which the aryl group is a phenyl group, a tolyl group ($CH_3C_6H_4$), a xylyl group ($(CH_3)_2C_6H_3$), a naphthyl group, or other aromatic ring. In a preferred embodiment, the sulfonic acid is p-toluene sulfonic acid.

25

Sulfonic acid modified boehmite materials are commercially available, for example from Sasol Performance Chemicals. Examples include DISPERAL (RTM) OS-1, DISPAL (RTM) 25SR, DISPERAL (RTM) OS-2 and DISPAL (RTM) 25SRL.

30

The aluminium-doped lithium iron phosphate of the present invention typically has the formula $Li_xFe_yPO_4$, in which x is 0.8-1.2 and y is 0.8-1.2, and in which up to 10 atom % (e.g. up to 6 atom %) of the Fe is replaced with a aluminium, up to 10 atom % (e.g. up to 5 atom %) of the phosphate may be replaced with SO_4 and/or SiO_4 , and up to 10 atom % of the Li may be replaced with Na and/or K.

35

The aluminium-doped lithium iron phosphate may have the formula $LiFePO_4$, in which up to 10 atom % (e.g. up to 5 atom %) of the Fe is replaced with aluminium and up to 10 atom %

(e.g. up to 5 atom %) of the phosphate may be replaced with SO_4 and/or SiO_4 , and up to 10 atom % of the Li may be replaced with Na and/or K.

The aluminium-doped lithium iron phosphate may preferably have the formula Li_yFe_1 .

- 5 $x\text{Al}_x\text{PO}_4$, in which $0.8 \leq y \leq 1.2$ and $0.01 \leq x \leq 0.09$, up to 10 atom % of the phosphate may be replaced with SO_4 and/or SiO_4 , and up to 10 atom % of the Li may be replaced with Na and/or K. Preferably, $0.01 \leq x \leq 0.06$.

- 10 The carbon-coated aluminium-doped lithium iron phosphate is prepared by a process comprising a milling step and a calcination step. The milling step is carried out in the presence of a solvent, such as water or an organic solvent. Suitable organic solvents include isopropyl alcohol, glycol ether, acetone and ethanol. The milling step may be a high energy milling step.

- 15 The term “high energy milling” is a term well understood by those skilled in the art, to distinguish from milling or grinding treatments where lower amounts of energy are delivered. For example, high energy milling may be understood to relate to milling treatments in which at least 100kWh of energy is delivered during the milling treatment, per kilogram of solids being milled. For example, at least 150kWh, or at least 200kWh may be delivered per
20 kilogram of solid being milled. There is no particular upper limit on the energy, but it may be less than 500kWh, less than 400kWh, or less than 350kWh per kilogram of solids being milled. Energy in the range from 250kWh/kg to 300kWh/kg may be typical. The milling energy is typically sufficient to cause mechanochemical reaction of the solids being milled.

- 25 In the milling step lithium-containing precursor, iron-containing precursor, aluminium-containing precursor and carbon-containing precursor are combined and subjected to milling. If phosphorus is not provided as part of one of the iron, lithium or aluminium precursors added in the milling step, a separate phosphorous-containing precursor (e.g. a phosphate-containing precursor) is typically added.

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Suitable lithium-containing precursors include lithium carbonate (Li_2CO_3), lithium hydrogen phosphate (Li_2HPO_4) and lithium hydroxide (LiOH). Li_2CO_3 may be preferred.

- 35 Suitable iron-containing precursors include iron phosphate (FePO_4) and iron oxalate. The iron phosphate may be hydrated (e.g. $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$) or may be dehydrated. The present inventors have found that it is particularly advantageous to use dehydrated iron phosphate as the iron-containing precursor in combination with the aluminium precursors described

herein, since this provides the observed excellent electrochemical properties while avoiding problems of caking and clogging during milling and/or calcining.

The skilled person will readily understand what is meant by dehydrated lithium iron phosphate. Iron phosphates are typically prepared in their dihydrate or tetrahydrate forms. Dehydrated iron phosphate is typically prepared by dehydration of hydrated iron phosphate, e.g. by heating (e.g. heating at 80°C in a vacuum oven for 12 hours). The dehydrated iron phosphate may include less than 5wt% water, less than 3 wt% water, less than 1 wt% water or less than 0.1 wt% water. It may be substantially free of water.

The iron-containing precursor may have a D50 particle size of about 4 µm, e.g. in the range from 0.5 µm to 15 µm. The D50 particle size may be at least 1 µm or at least 2 µm. It may be less than 10 µm, less than 6 µm, less than 5 µm or less than 4.5 µm. The iron-containing precursor may have a D10 particle size of about 1.5 µm, e.g. 0.5 µm to 3 µm. The iron-containing precursor may have a D90 particle size of about 8 µm, e.g. 5 µm to 10 µm, e.g. 6 µm to 9 µm.

Typically, the aluminium, iron, lithium (and optionally phosphorus) containing precursors are combined in suitable proportions to give the desired stoichiometry to the lithium metal phosphate product.

The nature of the carbon-containing precursor is not particularly limited in the present invention. Carbon precursors are typically carbon-containing compounds which decompose to a carbonaceous residue when exposed to the calcination step. For example, the carbon-containing precursor may be one or more of starch, maltodextrin, gelatine, polyol, sugar (such as mannose, fructose, sucrose, lactose, glucose, galactose), and carbon-based polymers such as polyacrylate, polyvinyl acetate (PVA) and polyvinyl butyrate (PVB). Alternatively, the carbon-containing precursor may be elemental carbon, such as one or more of graphite, carbon black, acetylene black, carbon nanotubes and carbon fibres (such as vapour grown carbon fibres, VGCF). PVB may be preferred in some embodiments.

The amount of carbon precursor added is not particularly limited in the present invention. For example, the amount of carbon precursor may be selected to give a carbon content of 1 to 5 wt% in the carbon-coated lithium metal phosphate, e.g. 2 to 3 wt%. The amount of carbon precursor added in the milling step may be in the range from 3 to 15 wt%, e.g. 3 to 7 wt%, depending on the nature of the carbon precursor, and its carbonisation yield.

In the milling step, the lithium-containing precursor, iron-containing precursor, aluminium containing precursor, carbon-containing precursor (and optionally phosphorus containing precursor) are combined and subjected to milling. Prior to the milling step, the precursors may be mixed in order to intimately combine them, e.g. using a homogeniser.

5 Spray drying may be carried out between the milling and calcination steps.

In the calcination step, the product of the milling step is typically calcined under an inert atmosphere to provide the particulate carbon-coated lithium iron phosphate. The calcination step performs two functions. Firstly, it results in pyrolysis or carbonisation of the carbon precursor to form a conductive carbon coating on the lithium metal phosphate particles. Secondly, it results in crystallisation and the formation of the lithium metal phosphate into the desired olivine structure. Typically, the calcination is carried out in an inert atmosphere, for example in an inert gas such as argon or nitrogen. It may alternatively be carried out in a reducing atmosphere. It is typically carried out at a temperature in the range from 550°C to 800°C, e.g. from 600°C to 750°C, or from 600°C or 650°C to 700°C. 680°C is particularly suitable. Typically, the calcination is carried out for a period of 3 to 24h. The calcination time depends on the scale of manufacture (i.e. where larger quantities are prepared, longer calcination times may be preferred. At a commercial scale, 8 to 15 hours may be suitable, for example.

The process of the present invention may further comprise the step of forming an electrode (typically a cathode) comprising the carbon-coated aluminium-doped lithium iron phosphate. Typically, this is carried out by forming a slurry of the particulate carbon-coated aluminium-doped lithium iron phosphate, applying the slurry to the surface of a current collector (e.g. an aluminium current collector), and optionally processing (e.g. calendaring) to increase the density of the electrode. The slurry may comprise one or more of a solvent, a binder, additional carbon material and further additives.

Typically, the electrode of the present invention will have an electrode density of at least 2.3 g/cm³, at least 2.4 g/cm³, or at least 2.5 g/cm³. It may have an electrode density of 2.8 g/cm³ or less, or 2.65 g/cm³ or less. The electrode density is the electrode density (mass/volume) of the electrode, not including the current collector the electrode is formed on. It therefore includes contributions from the active material, any additives, and additional carbon material, and any binder used.

The aluminium-doped lithium iron phosphate may be capable of being formed into an electrode having an electrode density as defined above when formed into an electrode, e.g. by the electrode formation method of the Examples.

- 5 The process of the present invention may further comprise constructing a battery or electrochemical cell including the electrode comprising the carbon-coated aluminium-doped lithium iron phosphate. The battery or cell typically further comprises an anode and an electrolyte. The battery or cell may typically be a secondary (rechargeable) lithium ion battery.

10

The present invention will now be described with reference to the following examples, which are provided to assist with understanding the present invention, and are not intended to limit its scope.

15 Examples

Experiments were conducted to determine the effect of the aluminium precursor on the carbon-coated aluminium-doped LiFePO_4 obtained.

- 20 Li_2CO_3 , aluminium precursor, and dehydrated FePO_4 were mixed in the desired proportions, along with PVB as carbon source (at 4.5wt%). The precursors were mixed in an Ultra Turrax mixer for two minutes. The precursors were then subjected to high energy milling for 45 minutes, using 0.3 mm YSZ media. The milling was carried out in isopropyl alcohol (IPA), with a solids content of 33-34%, using a Netzsch lab star mill. Approximately 700g of slurry was prepared per batch. The milling slurry was then spray dried and calcined in argon at 25 680°C for 5 hours, to form olivine aluminium-doped lithium iron phosphate coated with conductive carbon.

- Different aluminium precursors were tested. In Comparative Example 1, aluminium hydroxide ($\text{Al}(\text{OH})_3$) was used. In Example 1, Disperal (RTM) OS-1 (boehmite modified with 30 p-toluene sulfonic acid, Sasol) was used. In each case, the aluminium precursor was added with a target doping level of 2wt%. Inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis showed that the Al content of the lithium iron phosphate produced in Comparative Example 1 was 0.68 wt% and in Comparative Example 2 was 1.43 wt%. This indicates an enhanced uptake of the dopant material using the p-toluene sulfonic 35 acid modified boehmite material.

XRD analysis

The samples were analysed by x-ray diffraction (XRD) and the diffractograms compared with a control sample which had aluminium dopant present on the iron sites of the lithium iron phosphate structure. The analysis of the sample from Comparative Example 1 indicated that there was no aluminium dopant on the iron sites of the structure. In contrast, a significant proportion of the sample from Example 1 had a structure in which aluminium was located in the iron sites of the lithium iron phosphate structure. The distribution of aluminium in Example 1 is proposed by the present inventors to provide improved lithium ion conductivity, and therefore enhanced electrochemical performance.

XPS analysis

The samples were analysed by x-ray photoelectron spectroscopy (XPS). This indicated an increased relative level of aluminium at the surface of the lithium iron phosphate prepared in Example 1 in comparison with that produced by Comparative Example 1. The presence of aluminium at the surface of the material is proposed by the present inventors to provide a resistance to transition metal oxidation and improves the electronic conductivity of the carbon coating.

Electrochemical Analysis

The obtained lithium iron phosphate materials were formed into electrodes, using an electrode coating formulation. The electrode coating formulation had a solids content of approximately 40% by weight. The solids portion consisted of 90wt% of active material (prepared as described above, using the PVBs shown in Table 2 below), 5wt% carbon black (C65 from Imerys™), 5 wt% binder (Solef 5130™ (polyvinylidene fluoride, 10wt% binder in n-methyl pyrrolidone). The coating formulations were used to cast electrodes on a 20µm aluminium foil using a vacuum coater, to provide an electrode loading of as shown in Table 2 below (the electrode loading refers to the mass of active material per area of electrode). The coated electrodes were calendared to provide an electrode density as shown in Table 2 below. The electrodes were then dried for 12 hours at 120°C.

Table 2

Example	Aluminium source	Electrode Density (g/cm³)
Comparative Example 1	Al(OH) ₃	2.05
Example 1	OS-1	2.14

Electrochemical coin cells (2032 button cell from Hohsen™) were formed. The electrolyte was LP30 from Solvonic™, which is 1M LiPF₆ in 1:1 by weight mixture of dimethyl carbonate and ethylene carbonate. The anode was 0.75mm thickness lithium, and the separator was a glass microfiber filter (Whatman™ GF/F). The pressure used to crimp the coin cell was 750 psi.

The electrochemical performance of the samples was measured using a voltage window of 4.0V to 2.0V. The results are shown in Figures 1 and 2 and Table 3. Electrochemical testing indicated that the aluminium-doped lithium iron phosphate prepared using the sulfonic acid modified boehmite precursor showed a significantly increased capacity across a range of discharge rates in comparison with the material prepared using aluminium hydroxide.

Table 3

C-rate	Comparative Example 1 Discharge Capacity [mAh/g]	Example 1 Discharge Capacity [mAh/g]
0.1	148	154
1	138	145
3	128	136
5	121	130
10	110	118
20	62	60

A further boehmite material was tested that had not been modified by a sulfonic acid reagent (Disperal P2 (RTM), Sasol). This precursor provided a lithium iron phosphate material which, when analysed by XRD, did not show the presence of a structure in which aluminium was present in the iron sites of the lithium iron phosphate structure, and which showed no improvement in electrochemical performance when compared to lithium iron phosphate prepared using aluminium hydroxide.

Claims

1. Process for producing particulate carbon-coated aluminium-doped lithium iron phosphate, the process comprising:

- a milling step in which lithium-containing precursor, iron-containing precursor, aluminium-containing precursor, and carbon-containing precursor are combined and subjected to milling in a solvent; and
- a calcination step in which the product of the milling step is calcined to provide carbon-coated particulate aluminium-doped lithium iron phosphate,

wherein the aluminium-containing precursor is a sulfonic acid modified boehmite material.

2. Process according to claim 1 wherein the sulfonic acid is p-toluene sulfonic acid.

3. Process according to claim 1 wherein the carbon-containing precursor is polyvinyl butyral (PVB).

4. Process according to any one of the preceding claims wherein the lithium-containing precursor is lithium carbonate.

5. Process according to any one of the preceding claims in which the iron-containing precursor is iron phosphate, preferably dehydrated iron phosphate.

6. Process according to any one of the preceding claims wherein the milling step is a high energy milling step.

7. Process according to any one of the preceding claims wherein the solvent is an alcohol, preferably isopropyl alcohol.

8. Process according to any one of the preceding claims, in which the lithium iron phosphate has the formula $\text{Li}_y\text{Fe}_{1-x}\text{Al}_x\text{PO}_4$, in which $0.8 \leq y \leq 1.2$ and $0.01 \leq x \leq 0.09$, up to 10 atom % of the phosphate may be replaced with SO_4 and/or SiO_4 , and up to 10 atom % of the Li may be replaced with Na and/or K.

9. Process according to any one of the preceding claims, further comprising forming an electrode comprising the carbon-coated aluminium-doped lithium iron phosphate.

5 10. Process according to claim 9, further comprising constructing a battery including the electrode.

11. Particulate carbon-coated aluminium-doped lithium iron phosphate obtained or obtainable by a process according to any one of claims 1 to 8.

10 12. Use of particulate carbon-coated aluminium-doped lithium iron phosphate according to claim 11 in the preparation of an electrode for a secondary lithium ion battery.

13. An electrode for a secondary lithium ion battery comprising particulate carbon-coated aluminium-doped lithium iron phosphate according to claim 11.

15

14. A secondary lithium ion battery comprising an electrode according to claim 13.

Figure 1

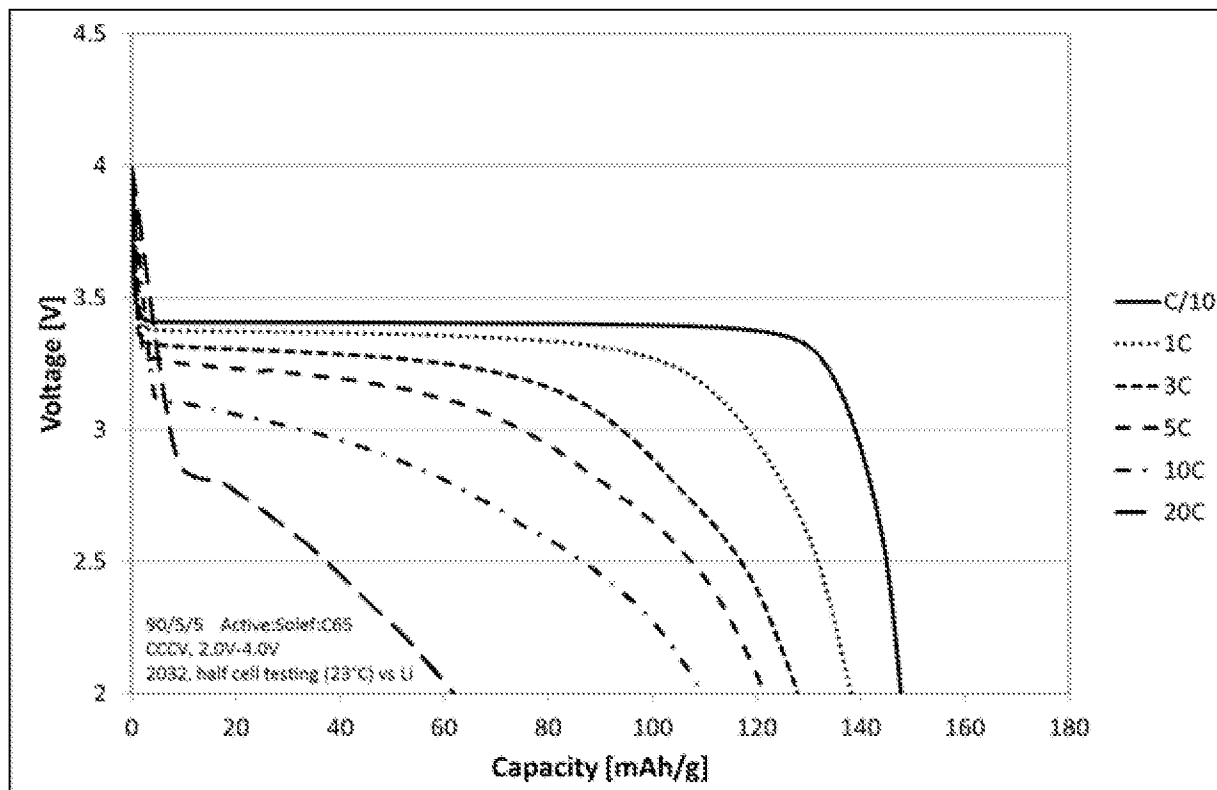
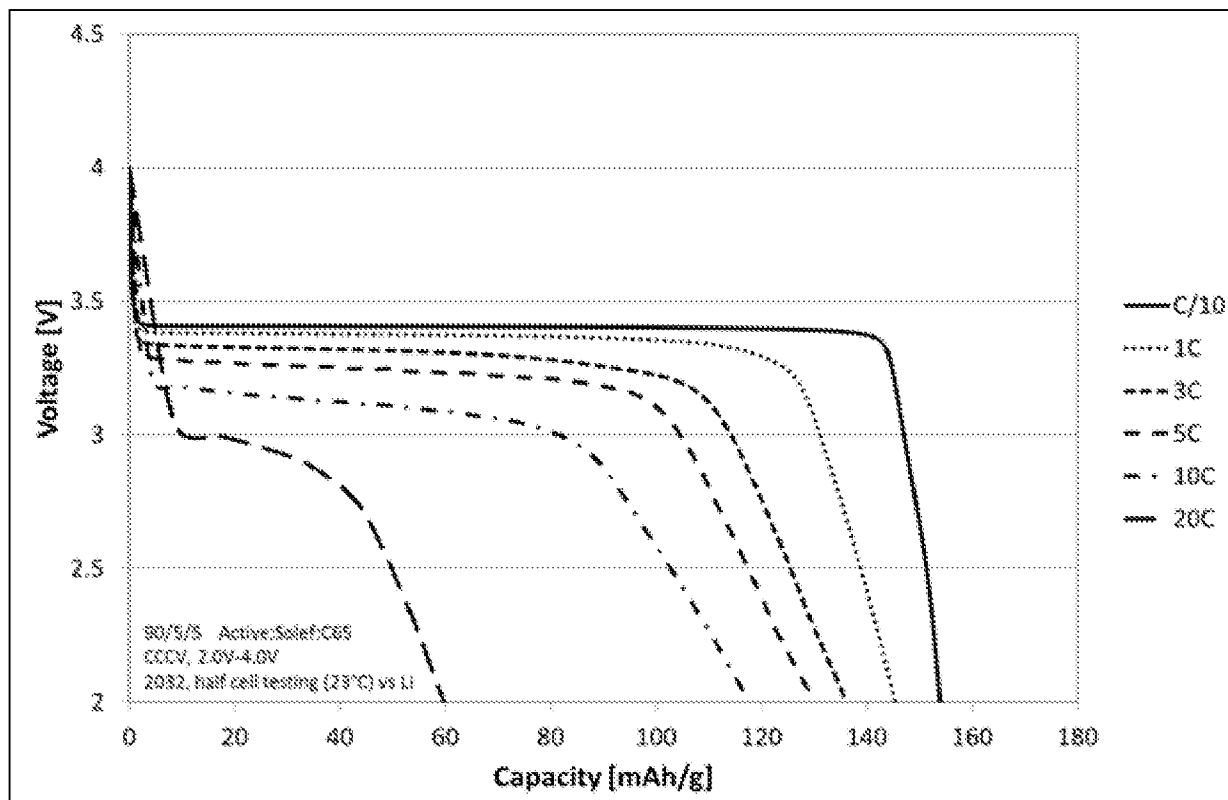


Figure 2



INTERNATIONAL SEARCH REPORT

International application No
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A. CLASSIFICATION OF SUBJECT MATTER INV. H01M4/04 H01M4/1397 H01M4/36 H01M4/58 H01M4/62 H01M10/0525 C01B25/30 C01B25/45 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 C01B 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 <table border="1" style="width: 100%; border-collapse: collapse;"> <thead> <tr> <th style="width: 10%;">Category*</th> <th style="width: 70%;">Citation of document, with indication, where appropriate, of the relevant passages</th> <th style="width: 20%;">Relevant to claim No.</th> </tr> </thead> <tbody> <tr> <td style="text-align: center; vertical-align: top;">X</td> <td style="vertical-align: top;">CN 102 299 327 B (UNIV SHAANXI SCIENCE & TECH) 12 March 2014 (2014-03-12) embodiments 1 and 2; claims 1-5</td> <td style="text-align: center; vertical-align: top;">1-14</td> </tr> <tr> <td style="text-align: center; vertical-align: top;">X</td> <td style="vertical-align: top;">US 2013/029226 A1 (NOH HYUN KUK [KR] ET AL) 31 January 2013 (2013-01-31) claims 1-17</td> <td style="text-align: center; vertical-align: top;">1-9, 11-14</td> </tr> </tbody> </table>			Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.	X	CN 102 299 327 B (UNIV SHAANXI SCIENCE & TECH) 12 March 2014 (2014-03-12) embodiments 1 and 2; claims 1-5	1-14	X	US 2013/029226 A1 (NOH HYUN KUK [KR] ET AL) 31 January 2013 (2013-01-31) claims 1-17	1-9, 11-14
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X	CN 102 299 327 B (UNIV SHAANXI SCIENCE & TECH) 12 March 2014 (2014-03-12) embodiments 1 and 2; claims 1-5	1-14									
X	US 2013/029226 A1 (NOH HYUN KUK [KR] ET AL) 31 January 2013 (2013-01-31) claims 1-17	1-9, 11-14									
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Date of the actual completion of the international search 25 November 2019		Date of mailing of the international search report 06/12/2019									
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