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(54) Title: SYNTHESIS OF LITHIUM TITANATE

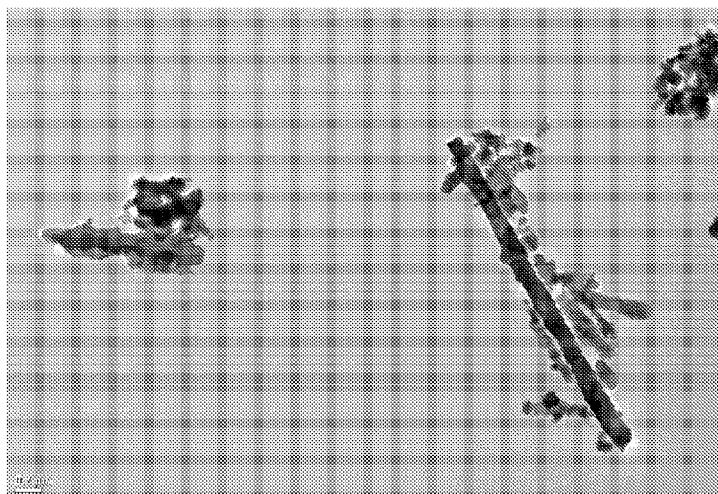


Figure 1

(57) Abstract: A method for the synthesis of lithium titanate, the method comprising the method steps of: (i) reacting a source of titanium ions with a source of lithium ions at increased temperature in one or more reaction vessels for a period of time; and (ii) calcining the product of step (i) to produce a lithium titanate product having a nano-tube type crystal structure. An electrode material produced by the method of the invention and a lithium ion battery utilising the electrode material are also disclosed.



“Synthesis of Lithium Titanate”

Field of the Invention

[0001] The present invention relates to a method for the synthesis of lithium titanate having a nano-tube type crystal structure.

[0002] More particularly, the lithium titanate produced is intended for use, in one form, in lithium ion batteries.

[0003] The present invention further relates to a lithium ion battery utilising lithium titanate produced in accordance with the present invention. More particularly, the lithium titanate is utilised as an anode material in such a lithium ion battery.

Background Art

[0004] Most current methods employed to produce lithium titanate ($\text{Li}_4\text{Ti}_5\text{O}_{12}$) produce lithium titanate ($\text{Li}_4\text{Ti}_5\text{O}_{12}$) having an amorphous micro-grained structure with poor electrochemical performance. This type of crystal structure has poor cyclic capacity for lithium ion batteries during high drain. Consequently, lithium titanate ($\text{Li}_4\text{Ti}_5\text{O}_{12}$) has not been considered a good anode material.

[0005] Nano-scale materials with nano-particles, such as nanocrystals, spinel nanocrystals, nanowires, nano-sheets, together with their composites with conductive additives, have consequently been considered as anode materials for lithium-ion batteries (LIBs). Nanostructured electrode materials may have an increased effective surface area and a shortened path for lithium-ion migration. Further, nanostructured electrode materials may show better rate capability than their micro-grained counterparts.

[0006] Despite the above, disadvantages of known lithium titanate materials as electrode materials, particularly anode materials, are considered to include a low intrinsic ionic conductivity and low electronic conductivity, poor rate performance, and a low theoretical capacity.

[0007] The method and product of the present invention have as one object thereof to overcome substantially one or more of the above mentioned problems associated with the methods and products of the prior art, or to at least provide useful alternatives thereto.

[0008] The preceding discussion of the background art is intended to facilitate an understanding of the present invention only. This discussion is not an acknowledgement or admission that any of the material referred to is or was part of the common general knowledge as at the priority date of the application.

[0009] Throughout the specification and claims, unless the context requires otherwise, the word "comprise" or variations such as "comprises" or "comprising", will be understood to imply the inclusion of a stated integer or group of integers but not the exclusion of any other integer or group of integers.

[0010] Throughout the specification and claims, unless the context requires otherwise, the term "lithium titanate" is to be understood to refer to $\text{Li}_4\text{Ti}_5\text{O}_{12}$. Similarly, the abbreviation LTO is to be understood to refer to "lithium titanate" or $\text{Li}_4\text{Ti}_5\text{O}_{12}$.

Disclosure of the Invention

[0011] In accordance with the present invention there is provided a method for the synthesis of lithium titanate, the method comprising the method steps of:

- (i) reacting a source of titanium ions with a source of lithium ions at increased temperature in one or more reaction vessels for a period of time; and
- (ii) calcining the product of step (i) to produce a lithium titanate product having a nano-tube type crystal structure.

[0012] The source of titanium ions used in step (i) is preferably one of the group of titanium dioxide (TiO_2), titanic acid ($\text{H}_4\text{Ti}_5\text{O}_{12}$), and sodium titanate ($\text{Na}_4\text{Ti}_5\text{O}_{12}$).

[0013] In one preferred form, the source of titanium ions used in step (i) is titanium dioxide (TiO_2). The TiO_2 used in step (i) is preferably in the anatase form.

[0014] The source of lithium ions used in step (i) is preferably one of the group of LiOH.H₂O or Li₂CO₃ or LiCl or Li₂SO₄.

[0015] In one preferred form, the source of lithium ions used in step (i) is LiOH.H₂O.

[0016] Preferably, the one or more reaction vessels of step (i) are provided in the form of one or more autoclaves, optionally one or more zirconium autoclaves.

[0017] Still preferably, the increased temperature of the reaction of step (i) is in the range of about 135°C to 180°C.

[0018] Still further preferably, the period of time of the reaction of step (i) is a period of at least several hours. Yet still further preferably, the period of time of the reaction of step (i) is a period of greater than 12 hours, preferably about 24 hours.

[0019] Preferably, the calcining of step (ii) takes place at a temperature of at least 650°C. Still preferably, the calcining of step (ii) takes place at a temperature of about 700°C.

[0020] The calcining of step (ii) preferably takes place over a period of greater than 1 hour. Still preferably, the calcining of step (ii) takes place for a period of about 2 hours.

[0021] In accordance with the present invention there is further provided an electrode material for use in lithium ion batteries, the electrode material comprising lithium titanate produced by the method described hereinabove.

[0022] Preferably, the electrode material is provided in the form of an anode.

[0023] Still preferably, the capacity of the lithium titanate electrode material is in the range of 150~170 mAh/g against lithium electrode potential. The charge capacity of greater than or equal to 150 mAh/g against lithium electrode potential is preferably able to be maintained over at least 40 cycles.

[0024] In accordance with the present invention there is still further provided a lithium ion battery comprising electrode material as described hereinabove.

[0025] In a preferred form of the invention the lithium ion battery comprises an anode comprising lithium titanate produced by the method described hereinabove.

[0026] In accordance with the present invention there is yet still further provided a lithium titanate in nano-tube type crystal form prepared by the method described hereinabove.

Brief Description of the Drawings

[0027] The present invention will now be described, by way of example only, with reference to the accompanying drawings, in which:-

Figure 1 is a first transmission electron microscopy (TEM) image of lithium titanate having a nano-tube type crystal structure having been synthesised in accordance with the method of the present invention;

Figure 2 is a second transmission electron microscopy (TEM) image of lithium titanate having a nano-tube type crystal structure having been synthesised in accordance with the method of the present invention; and

Figure 3 is a plot of discrete XRD peaks (each marked X) for the high purity lithium titanate ($\text{Li}_4\text{Ti}_5\text{O}_{12}$) produced by way of the experimental method of the present invention shown relative to the profile for a reference LTO (profile curve marked Y).

Best Mode(s) for Carrying Out the Invention

[0028] The present invention provides a method for the synthesis of lithium titanate, the method comprising the method steps of:

- (i) reacting a source of titanium ions with a source of lithium ions at increased temperature in one or more reaction vessels for a period of time; and

(ii) calcining the product of step (i) to produce a lithium titanate product.

[0029] The lithium titanate product of step (ii) advantageously is produced having a nano-tube type crystal structure.

[0030] The source of titanium ions used in step (i) is one of the group of titanium dioxide (TiO_2), titanic acid ($\text{H}_4\text{Ti}_5\text{O}_{12}$), and sodium titanate ($\text{Na}_4\text{Ti}_5\text{O}_{12}$), for example in a preferred form, titanium dioxide (TiO_2) in its anatase form.

[0031] The source of lithium ions used in step (i) is one of the group of $\text{LiOH}\cdot\text{H}_2\text{O}$ or Li_2CO_3 or LiCl or Li_2SO_4 , for example in a preferred form, $\text{LiOH}\cdot\text{H}_2\text{O}$.

[0032] The one or more reaction vessels of step (i) are provided in the form of one or more autoclaves, for example a single zirconium autoclave.

[0033] The increased temperature of the reaction of step (i) is in the range of between about 120°C to 220°C , and preferably about 135°C to 180°C . The period of time of the reaction of step (i) is a period of at least several hours, for example greater than about 12 hours, and preferably about 24 hours.

[0034] The calcining of step (ii) takes place at a temperature of at least 650°C , for example about 700°C . Further, the calcining of step (ii) takes place over a period of greater than 1 hour, for example between about 1 to 4 hours, and more particularly about 2 hours.

[0035] The present invention further provides an electrode material for use in lithium ion batteries, the electrode material comprising lithium titanate produced by the method described hereinabove. In one form of the invention, the electrode material is provided in the form of an anode.

[0036] The present invention still further provides a lithium ion battery comprising electrode material as described hereinabove.

EXAMPLE 1

[0037] The reagents used for preparation of LTO by this example of the method of the present invention were LiOH.H₂O and anatase TiO₂.

[0038] First, a LiOH solution was prepared by dissolving 44.1 g LiOH.H₂O in 350 mL water in a plastic beaker. An amount of anatase TiO₂ powder (~105 g, Sigma-Aldrich, USA), calculated on a stoichiometric basis, was added slowly to LiOH solution to prepare a homogeneous slurry under agitation. The prepared slurry was transferred (along with the washings of the beaker) to a Teflon lined autoclave container and the autoclave heated to the test temperatures. Once the set test temperatures (eg. 135°C and 180°C) were reached (after a period of less than 30 minutes), the reaction was continued for a further 24 hours. At the end of the test the autoclave was cooled and the slurry was transferred to a plastic container. As noted above, it is envisaged that a broad temperature range of about 120 °C to 220°C is applicable.

[0039] The final cooled autoclave slurry was split into two halves. The first half of the slurry was centrifuged and the resulting solid was repulped once with deionised (DI) water. The repulped slurry was centrifuged and the solid obtained after decanting the wash liquor was dried in an oven, for example at 80°C. The dried solid was named as 'Washed' solid to differentiate from the solid from other half of the slurry. The centrifuged liquor was analysed for Li and Ti content.

[0040] The second half of the slurry was transferred to four Teflon beakers and dried at ~110°C in the presence of nitrogen gas. The solid obtained from the second half of the slurry was named "Unwashed" solid.

[0041] The Washed and Unwashed solids were further processed separately but in an otherwise identical way. Both the dried solids were ground in a mortar/pestle to achieve the following particle size distribution:

d10 = 0.407 microns
d50 = 0.86 micron
d80 = 1.602 micron
d90 = 2.659 micron

[0042] The ground and dried solids were then calcined/sintered in a muffle furnace at 700°C for 2 h. The calcined/sintered solids were ground using mortar/pestle and submitted for characterisation study.

[0043] The final product was a high purity lithium titanate ($\text{Li}_4\text{Ti}_5\text{O}_{12}$). High purity is understood in the context of the lithium ion battery market as 99% lithium titanate by wt%. It is evident from the data presented in Table 2 that the Washed solids have provided a product with a smaller d50 and a greater surface area.

[0044] Figures 1 and 2 show transmission electron microscopy (TEM) images of the nano-tube type crystal structure of the lithium titanate formed in accordance with the method of the present invention and having a nano-tube type crystal structure, using JOEL 2100 TEM. The legends of Figures 1 and 2 denote 0.2 μm and 0.5 μm , respectively.

[0045] The product has properties set out in Table 1 below.

Table 1

Test Details		Calcined/Sintered sample (700°C, 2 h)						
Hydrothermal Test no	Reagents used	Sample & ID	XRD phase	Particle size μm	Surface area (BET) m^2/g	Li %	Ti %	Na %
Hydrom-1 (180°C)	LiOH & Anatase	Unwashed (Sample ID – LTO-2DJ)	i) $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ii) TiO_2 (anatase)* iii) TiO_2 (rutile)*	d50 = 0.833 d80 = 1.337 d90 = 1.681	6.56 ± 0.014	5.81	55.4	-
		Washed (Sample ID – 1W)	i) $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ii) TiO_2 (anatase)* iii) TiO_2 (rutile)*	d50 = 0.451 d80 = 0.875 d90 = 1.402	10.22 ± 0.211	5.55	56.5	-
Hydrom-2 (135°C)	LiOH & Anatase	Unwashed	i) $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ii) TiO_2 (anatase)* iii) TiO_2 (rutile)*	d50 = 0.458 d80 = 0.841 d90 = 1.289	8.89 ± 0.043	5.99	56.4	-
		Washed (Sample ID – 2W)	i) $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ii) TiO_2 (anatase)* iii) TiO_2 (rutile)*	d50 = 0.415 d80 = 0.816 d90 = 1.294	10.92 ± 0.229	5.57	56.9	-
Hydrom-4 (150°C)	NaOH & Anatase – followed by LiOH treatment	Washed (Sample ID – 4W)	i) $\text{Li}_4\text{Ti}_5\text{O}_{12}$ ii) Un-identified minor peaks	d50 = 4.019 d80 = 12.335 d90 = 19.124	21.85	4.43	47.8	2.1

Note: * designates minor phase

[0046] For comparison purposes, Table 1 also provides results for an LTO prepared under the same conditions but by the combination of NaOH and anatase TiO_2 , followed by treatment with LiOH. Such a process is more complicated/difficult than the method of the present invention and would require significantly greater capital and operating expenditure.

EXAMPLE 2

[0047] A larger sample of high purity lithium titanate ($\text{Li}_4\text{Ti}_5\text{O}_{12}$) was first prepared by the method described above in Example 1, with weights adjusted to suit. The characterisation of the 750 g of high purity lithium titanate ($\text{Li}_4\text{Ti}_5\text{O}_{12}$) so produced is set out in Table 2 below.

Table 2

Sample	Autoclave conditions		Li analysis (autoclave final liquor)	Sintering conditions		Characterisation data				
	Temp. °C	Time h		Temp. °C	Time h	XRD phase	Particle size μm	Surface area (BET) m^2/g	Li %	Ti %
750 g LTO	135	24.0	911 mg/L – 953 mg/L	705	2.0	Only LTO peaks	d10 = 0.407 d50 = 0.86 d80 = 1.602 d90 = 2.659	13.17 \pm 0.253	5.90	49.80

[0048] Figure 3 provides the discrete XRD peaks (each marked X) for the high purity lithium titanate ($\text{Li}_4\text{Ti}_5\text{O}_{12}$) produced by way of the experimental method described immediately above relative to the profile for a reference LTO (profile curve marked Y). Only LTO peaks are evident.

Half-cell battery testing

[0049] Lithium titanate synthesised in accordance with the method of the present invention has been tested electrochemically by fabricating half cells. The synthesised lithium titanate, having the formula $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and being in nano-tube type crystal structure, was used as one electrode and lithium metal as the counter electrode in the fabrication of half-cells. The tests have been run at room temperature (22°C) as well as at high temperature (55°C) to determine initial capacity, as well as the ability of the material to handle high current densities. The tests have been compared with standard $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode material produced in accordance with the prior art and currently available in the market. The tests have shown that $\text{Li}_4\text{Ti}_5\text{O}_{12}$ formed using the process of the present invention shows far superior electrochemical performance than the standard $\text{Li}_4\text{Ti}_5\text{O}_{12}$ available commercially at present.

[0050] The results are summarised in Table 3 below, wherein 'Standard' refers to prior art lithium titanate and '2W' designates lithium titanate synthesised in accordance with the method of the present invention:

Table 3

Comparison of Cyclic Data			
Cell Identity:	2W	Synthesised by Applicant in accordance with invention	
	Standard	Standard from the market E.g. TRONOX TR-LTO-100™	
Tester	NEI CORPORATION, USA		
C Rate	0.001		
Ch. max. V	5.00 V		
DisCh. min. V	-5.00 V		
Ch. max. I	5.000 A		
DisCh. max. I	5.000 A		
	Cycle Number	Charge Cap mAh	Disch Cap mAh
Standard	1	175.665	178.59
2W	1	159.03	169.8
Standard	10	175.442	175.587
2W	10	159.056	158.927
Standard	20	175.283	175.492
2W	20	158.9	158.752
Standard	30	174.773	174.767
2W	30	154.383	154.202
Standard	40	156.013	155.736
2W	40	150.598	150.599
Standard	41	1.6395	156.012
2W	41	147.549	150.612
Standard	50	0.6004	0.6612
2W	50	148.105	147.892

[0051] The standard LTO failed after 40 cycles where Applicant's 2W continued to show strong electrochemical performance up to the 50 cycles tested.

[0052] As can be seen with reference to the above description, the lithium titanate ($\text{Li}_4\text{Ti}_5\text{O}_{12}$) synthesised in accordance with the method of the present invention, having nano-tube type crystal structure, shows high battery cycle performance, stable discharge voltage, larger capacity relative to the prior art and is an inert material in terms of reaction with electrolyte. Though the theoretical capacity of lithium titanate ($\text{Li}_4\text{Ti}_5\text{O}_{12}$) is 180 mAh/g, the range of 150~170mAh/g can readily be achieved, against the lithium electrode potential. The voltage of lithium titanate ($\text{Li}_4\text{Ti}_5\text{O}_{12}$) anode batteries against lithium metal is 1.55V (that is Li / Li +). During the lithium ion insertion and de-embedding process, the material structure of the electrode remains almost unchanged, consequently demonstrating excellent cycle

performance relative to the prior art. It also demonstrates superior battery cycle performance, again relative to the prior art, across the temperature range of minus 30 to 60°C.

[0053] Modifications and variations such as would be apparent to the skilled addressee are considered to fall within the scope of the present invention.

CLAIMS

1. A method for the synthesis of lithium titanate, the method comprising the method steps of:
 - (i) reacting a source of titanium ions with a source of lithium ions at increased temperature in one or more reaction vessels for a period of time; and
 - (ii) calcining the product of step (i) to produce a lithium titanate product having a nano-tube type crystal structure.
2. The method of claim 1, wherein the source of titanium ions used in step (i) is one of the group of titanium dioxide (TiO_2), titanitic acid ($\text{H}_4\text{Ti}_5\text{O}_{12}$), and sodium titanate ($\text{Na}_4\text{Ti}_5\text{O}_{12}$).
3. The method of claim 2, wherein the source of titanium ions used in step (i) is titanium dioxide (TiO_2) in the anatase form.
4. The method of any one of claims 1 to 3, wherein the source of lithium ions used in step (i) is one of the group of $\text{LiOH}\cdot\text{H}_2\text{O}$ or Li_2CO_3 or LiCl or Li_2SO_4 .
5. The method of claim 4, wherein the source of lithium ions used in step (i) is $\text{LiOH}\cdot\text{H}_2\text{O}$.
6. The method of any one of the preceding claims, wherein the one or more reaction vessels of step (i) are provided in the form of one or more autoclaves, optionally one or more zirconium autoclaves.
7. The method of any one of the preceding claims, wherein the increased temperature of the reaction of step (i) is in the range of about 135°C to 180°C .
8. The method of any one of the preceding claims, wherein the period of time of the reaction of step (i) is a period of:
 - (i) at least several hours;

- (ii) greater than 12 hours; or
 - (iii) about 24 hours.
9. The method of any one of the preceding claims, wherein the calcining of step (ii) takes place at a temperature of:
- (i) at least 650°C; or
 - (ii) about 700°C.
10. The method of any one of the preceding claims, wherein the calcining of step (ii) takes place over a period of:
- (i) greater than 1 hour; or
 - (ii) about 2 hours.
11. An electrode material for use in lithium ion batteries, the electrode material comprising lithium titanate produced by the method of any one of the preceding claims.
12. The electrode material of claim 11, wherein the electrode material is provided in the form of an anode.
13. The electrode material of claim 11 or 12, wherein the capacity of the lithium titanate electrode material is in the range of 150~170 mAh/g against lithium electrode potential.
14. The electrode material of claim 13, wherein the charge capacity of greater than or equal to 150 mAh/g against lithium electrode potential is maintained over at least 40 cycles.
15. A lithium ion battery comprising electrode material according to any one of claims 11 to 14.

16. A lithium titanate in nano-tube type crystal form prepared by the method of any one of claims 1 to 10.

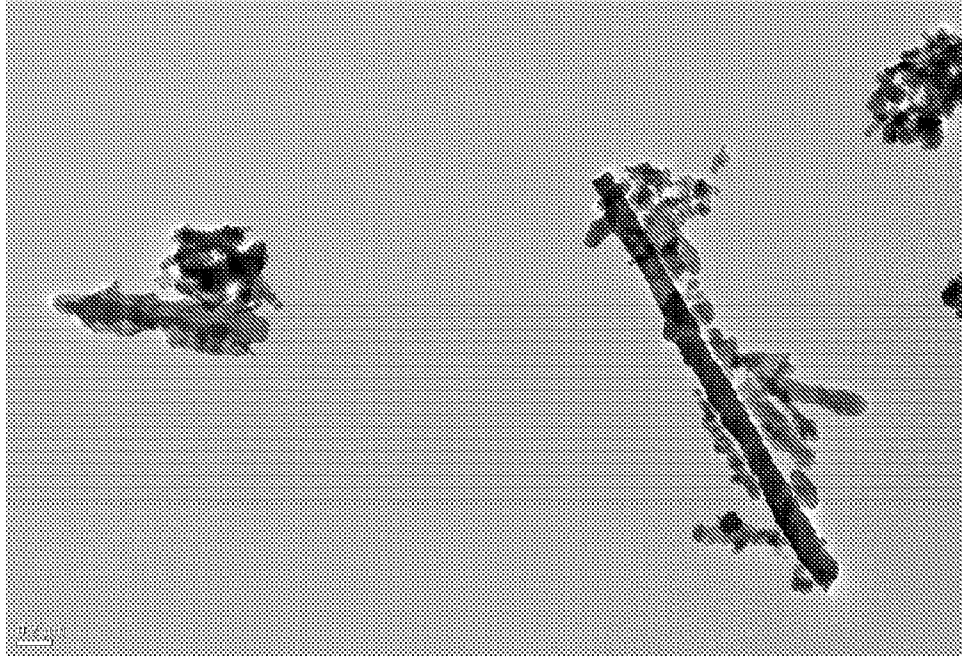


Figure 1

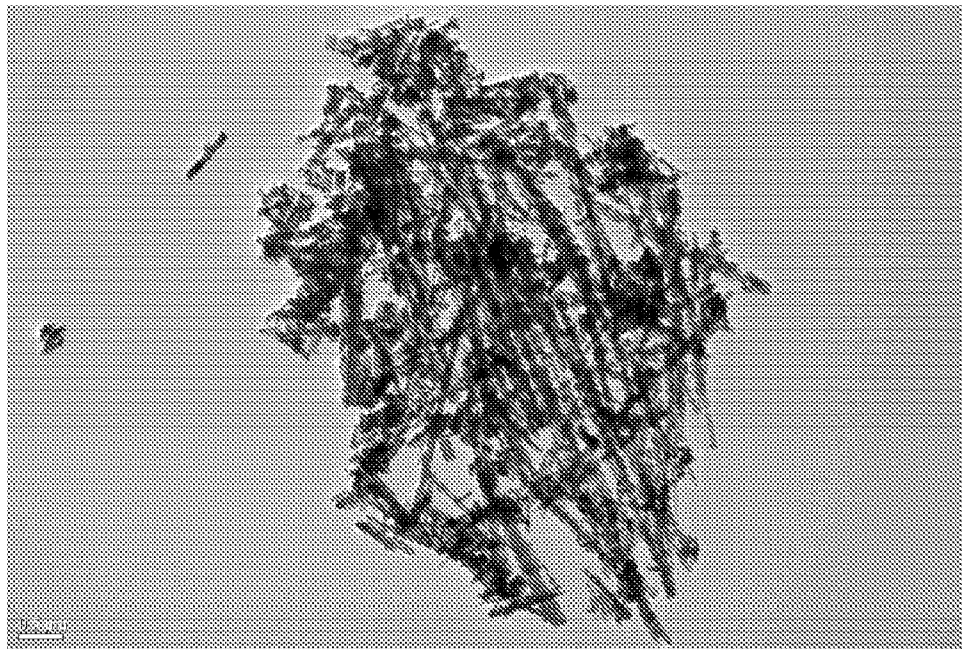


Figure 2

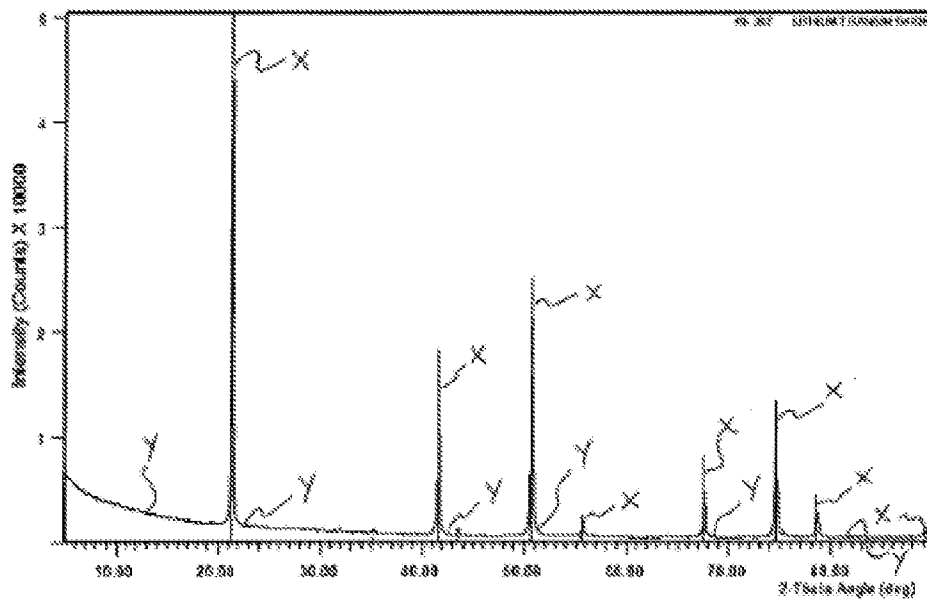


Figure 3

INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU2018/050899

A. CLASSIFICATION OF SUBJECT MATTER

H01M 10/052 (2010.01) C01D 15/00 (2006.01) C01G 23/00 (2006.01) B82Y 40/00 (2011.01)

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)

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)

DATABASE PATENW USING IPC/CPC MARKS (C01D15, C01G23/005/LOW, C01G23/002/LOW, C01G23/003/LOW, H01M10/052/LOW, H01M4/382/LOW, B82Y, B82B) AND KEYWORDS (LI4TI5O12, CALCINE, NANOTUBE, NM, TUBE AND OTHER SIMILAR TERMS); STN SEARCH ON CAPLUS USING KEYWORDS (LITHIUM, TITANATE, LI4TI5O12, SPINEL, NANOTUBE, CALCINE AND OTHER SIMILAR TERMS); GOOGLE PATENTS (LI4TI5O12, LITHIUM TITANATE, SPINEL, NANOTUBE, CALCINE AND OTHER SIMILAR TERMS); APPLICANT(S)/INVENTOR(S) SEARCH USING AUSPAT, ESP@CENET AND INTERNAL DATABASES PROVIDED BY IP AUSTRALIA

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	Documents are listed in the continuation of Box C	



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17 September 2018

Date of mailing of the international search report

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Name and mailing address of the ISA/AU

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INTERNATIONAL SEARCH REPORT

International application No.

C (Continuation).

DOCUMENTS CONSIDERED TO BE RELEVANT

PCT/AU2018/050899

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CN 1725530 A (清华大学) 25 January 2006, English translation obtained from ESP@CENET Examples, figures	1-16
X	CN 101486488 A (河南大学) 22 July 2009, English translation obtained from ESP@CENET Page 3 of English translation; examples; figures	1-12, 15-16
X	CN 101580273 A (清华大学) 18 November 2009, English translation obtained from ESP@CENET Examples; figures	1-16

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/AU2018/050899

This Annex lists known patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document/s Cited in Search Report		Patent Family Member/s	
Publication Number	Publication Date	Publication Number	Publication Date
CN 1725530 A	25 January 2006	CN 1725530 A	25 Jan 2006
CN 101486488 A	22 July 2009	CN 101486488 A	22 Jul 2009
		CN 101486488 B	26 Jan 2011
CN 101580273 A	18 November 2009	CN 101580273 A	18 Nov 2009

End of Annex

Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.

Form PCT/ISA/210 (Family Annex)(January 2015)