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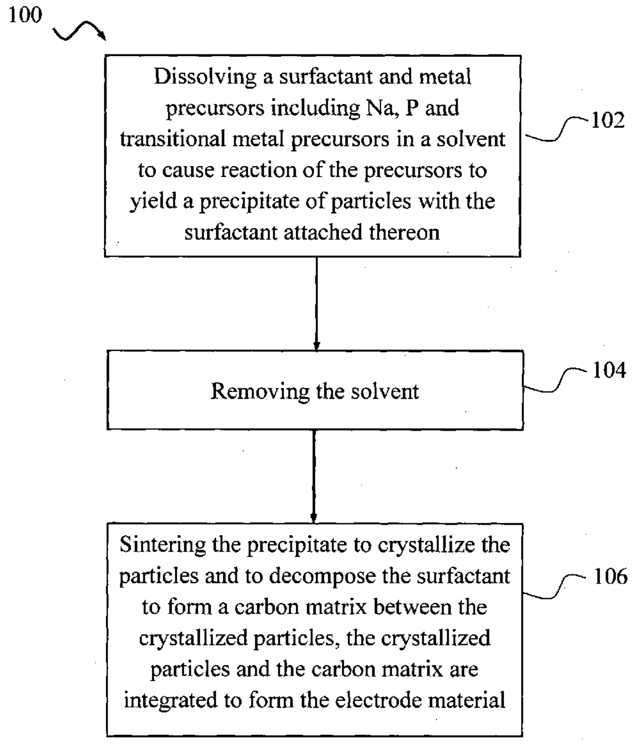
(54) Title: ELECTRODE MATERIAL AND METHOD OF SYNTHESIZING



(57) Abstract: The present disclosure provides a phosphate framework electrode material for sodium ion battery and a method for synthesizing such electrode material. A surfactant and precursors including a sodium precursor, a phosphate precursor, a transition metal precursor are dissolved in a solvent and stirred for sufficient mixing and reaction. The precursors are reacted to yield a precipitate of particles of $Na_xA_bM_y(PO_4)_zX_n$ compound and with the surfactant attached to the particles. The solvent is then removed and the remaining precipitate is sintered to crystallize the particles. During sintering, the surfactant is decomposed to form a carbon network between the crystallized particles and the crystallized particles and the carbon matrix are integrated to form the electrode material.

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Published:

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ELECTRODE MATERIAL AND METHOD OF SYNTHESIZING

TECHNICAL FIELD

The present disclosure relates to an electrode material for use in rechargeable batteries. In particular, the present disclosure relates to a phosphate framework electrode material for use in rechargeable sodium ion batteries and a method of synthesizing the phosphate framework electrode material.

BACKGROUND

Phosphate framework material possesses fairly well thermal stability and high voltage capabilities required for applications as electrodes e.g. anode or cathode in rechargeable sodium ion batteries. The major drawbacks which hinder the successful application of such type of material in commercial scale, however, lie in the poor electronic and ionic conductivity in its bulk form. Before such drawbacks are successfully overcome, this type of material may not be considered to be suitable for use in rechargeable sodium ion batteries. Attempts have been made to downsizing of the material to enhance the sodium intercalation / de-intercalation properties. However, downsizing will reduce the diffusion length for Na+ - ions but may not effectively enhance the electron transportation to the current collector since particle-to-particle boundaries also increased with the downsizing, which can cause electron transportation to be sluggish. As a consequence, electronic conductivity may remain poor and the overall sodium-ion storage is limited.

It is therefore desirable to provide an electrode material having the necessary thermal stabilities and high voltage capacity as well as the electronic / ionic conductivities at a level acceptable for rechargeable sodium ion battery applications. Such a solution is currently not available.

SUMMARY OF THE DISCLOSURE

According to one aspect, embodiments of the present disclosure provide a phosphate framework material for use as electrode, e.g. anode or a cathode material, for use in rechargeable sodium ion batteries. The material comprises a compound according to the following formula:

$Na_xA_bM_y(PO_4)_zX_n$ /C

where

$Na_xA_bM_y(PO_4)_zX_n$ denotes the structure of Na-transitional metal-Phosphate nanoparticles, in which,

M is a transition metal obtained from a compound selected from a group consisting of metal acetates, metal nitrate metal chloride and metal acetyl acetonate;

A is an additional doped or mixed cation(s) obtained from a compound selected from a group consisting of group 1 elements, transition metals, ammonium and hydrogen;

X is a substituted anion or polyanion(s) obtained from a compound selected from a group consisting of fluorine, hydroxide, vanadate, arsenate, chloride, pyrophosphate;

x, b, y, z and n denote the numbers of ions of a corresponding element, in which:

$1 \leq x \leq 3$;
$0 \leq b \leq 1$;
$1 \leq y \leq 2$;
$1 \leq z \leq 3$;
$0 \leq n \leq 3$;

and

C denotes a carbon content formed between the $Na_xA_bM_y(PO_4)_zX_n$ nanoparticles.

According to another aspect, embodiments of the present disclosure provide a method for synthesizing a phosphate framework electrode material. A surfactant and precursors including a sodium precursor, a phosphate precursor and a transition metal precursor are dissolved in a solvent, and maybe stirred for sufficient mixing and reaction. The precursors are reacted to yield a precipitate of particles of $Na_xC_bM_y(PO_4)_zX_n$ compound, and with the surfactant attached to the particles. The solvent is then removed and the remaining precipitate is dried and sintered to crystallize the particles. In the meantime, the surfactant remaining on the particles is decomposed to form a carbon network between the crystallized particles, and the crystallized particles and the carbon matrix are integrated to form the electrode material in bulk form.

Other aspects and advantages of the present disclosure will become apparent from the following detailed description, illustrating by way of example the inventive concept of the present disclosure.

BRIEF DESCRIPTION OF THE DRAWINGS

These and other aspects of the present disclosure will be described in detail with reference to the accompanying drawings, in which:

Fig. 1 is a block diagram showing a method of synthesizing an electrode material according to one embodiment of the present disclosure;

Fig.2 is a chart showing a Rietveld refinement pattern of X-ray diffraction data of a $Na_3V_2(PO_4)_3/C$ sample synthesized as an electrode material according to one embodiment of the present disclosure;

Fig. 3A is an FESEM image of a $Na_3V_2(PO_4)_3/C$ sample synthesized using C16 surfactant;

Fig. 3B is an enlarged view of Fig. 3A

Fig. 4A is a TEM image of a mesoporous $Na_3V_2(PO_4)_3/C$ particle;

Fig. 4B is an enlarged view of Fig. 4A;

Fig. 4C is an image of SAED pattern showing single crystalline nature of mesoporous $Na_3V_2(PO_4)_3/C$ particles;

Fig. 5 is a chart showing N_2 absorption / desorption isotherms of a $Na_3V_2(PO_4)_3/C$ sample;

Fig. 6A is a chart showing galvanostatic charge / discharge cycle curves of $Na_3V_2(PO_4)_3/C$ material used as cathode under different current rates;

Fig. 6B is a chart showing long term cyclability curve of $Na_3V_2(PO_4)_3/C$ material used as cathode at 1C;

Fig. 7A is a chart showing galvanostatic charge / discharge cycle curves of $Na_3V_2(PO_4)_3/C$ material used as anode under different current rates;

Fig. 7B is a chart showing long term cyclability curve of $Na_3V_2(PO_4)_3/C$ material used as anode at 1C.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

Fig. 1 illustrates a method 100 of synthesizing an electrode material according to one embodiment of the present disclosure. At block 102, a surfactant and metal precursors including a sodium precursor, a phosphate precursor and a transitional metal precursor are dissolved in a solvent to cause reaction of the precursors in the solvent. The solvent may be alcohol and/or a mixture of de-ionized water and alcohol. The mixture of the precursors may be stirred to help uniform mixing of the reactants at atomic level. The reaction yields a precipitate of amorphous sodium-transitional metal-phosphate compound particles with the surfactant attached thereto. At block 104, the solvent is removed and at block 106, the remaining precipitate is sintered, e.g. in a flowing, inert gas or a reducing atmosphere. During the sintering process, the surfactant remaining on the particles is decomposed to form an integrated conductive carbon matrix between the crystallized nanoparticles, and the crystallized nanoparticles and the carbon matrix are integrated to form the electrode material in bulk form.

The above method enables homogeneous mixing of the precursors and control of the particle size and morphology. The carbon matrix decomposed from the surfactant and formed between the nanoparticles prevents the particle agglomeration and growth during the sintering process. The carbon matrix also forms an in-situ coating of electrically conductive carbon layer on the crystallized nanoparticles. The carbon matrix therefore can greatly improve the electrical conductivity to make the electrode material suitable for rechargeable sodium ion battery applications.

The above method may be used to synthesize the entire phosphate polyanion family of electrode materials for the sodium ion battery applications. The base formula for these compounds takes the form of:

$Na_xA_bM_y(PO_4)_zX_n / C$

where

$Na_xA_bM_y(PO_4)_zX_n$ denotes the structure of Na-Transitional Metal-Phosphate nanoparticle, in which,

M is a transition metal obtained from a compound selected from a group consisting of metal acetates, metal nitrate metal chloride and metal acetyl acetonate;

A is an additional doped or mixed cation(s) obtained from a compound selected from a group consisting of group 1 elements, transition metals, ammonium and hydrogen;

X is a substituted anion or polyanion(s) obtained from a compound selected from a group consisting of fluorine, hydroxide, vanadate, arsenate, chloride, pyrophosphate;

x, b, y, z and n denote the numbers of ions of a corresponding element, in which:

$1 \leq x \leq 3$;

$0 \leq b \leq 1$;

$1 \leq y \leq 2$;

$1 \leq z \leq 3$;

$0 \leq n \leq 3$;

and

C denotes a carbon matrix formed between the $Na_xA_bM_y(PO_4)_zX_n$ nanoparticles.

The sodium precursor may be a sodium salt. The phosphate precursor may be an ammonium di-hydrogen phosphate or a phosphoric acid. The transitional metal precursor comprises a compound selected from the group consisting of metal acetates, metal nitrate, metal chloride, metal acetyl acetonate and metal hydroxide. The surfactant provides the necessary carbon content to form the carbon matrix during sintering to integrate with the crystallized nanoparticles. The surfactant comprises a compound selected from the group consisting of Sodium dodecyl sulfate (SDS), octyltrimethyl ammonium bromide (OTAB), dodecyltrimethyl ammonium bromide (DOTAB), cetyltrimethyl ammonium bromide (CTAB) and gluconic acid lactone.

Sample electrode material synthesized by the above method include, but not limited to, $Na_3V_2(PO_4)_3/C$, $Na_3V_2(PO_4)_2F_3/C$, Na_2FePO_4F/C, $NaVPO_4F/C$, $Na_2FePO_4(OH)/C$, $Na_2Fe_{0.5}Mn_{0.5}PO_4F/C$, $Na_2Ti_{0.5}Mn_{0.5}PO_4F/C$, $Na_2V_{0.5}Mn_{0.5}PO_4F/C$, $NaFePO_4/C$, $Na_3Ti_2(PO_4)_3/C$. These materials possess unique properties of small crystallite size, high purity, high crystallinity, large surface-to-volume ratio, and promising structural stability after prolonged charge-discharge cycles required to use in sodium ion rechargeable batteries.

Note that for materials containing additional cation, e.g. Fe in $Na_2Fe_{0.5}Mn_{0.5}PO_4F/C$, Ti in $Na_2Ti_{0.5}Mn_{0.5}PO_4F/C$ and V in $Na_2V_{0.5}Mn_{0.5}PO_4F/C$ and for those containing anion/polyanion e.g. F in $Na_3V_2(PO_4)_2F_3/C$, compounds or precursors containing the respective cation / anion are added and dissolved in the solvent for reaction together with the sodium precursor, phosphate precursor and transitional metal precursor.

The crystallized particles have a grain size between about 20 nm to 200 nm, and the carbon layer coated on the particles has a thickness of about 2 to 10 nm. The carbon matrix portion in the electrode material is not more than about 5% in weight, and forms a carbon coating layer covering the crystallized nanoparticles in a surface area of about 10 to 100 m^2 / gram. Therefore, electrode materials provided by embodiments of the present disclosure have electrically conductive carbon matrix sufficiently mixed and integrated with the crystallized Na-transitional metal-Phosphate nanoparticles. The crystallized Na-transitional metal-Phosphate nanoparticles provide enhanced sodium intercalation / de-intercalation. In the meantime, the interconnected carbon matrix between the nanoparticles provides electrical conductivity suitable for rechargeable sodium ion battery applications.

A $Na_3V_2(PO_4)_3/C$ (NVP/C) material formed according to the above method is now taken as a non-limiting example to illustrate the characteristics and performances for use as electrode in rechargeable sodium ion batteries. It should be appreciated that other types of phosphate framework material synthesized by the method according to embodiments of the present disclosure may be taken for performance study in a similar manner.

Figs. 2 to 5 show test results of structural characterization study and morphological analysis of NVP/C material synthesized according to an embodiment of the present disclosure.

Fig. 2 depicts a powder X-ray diffraction pattern (PXRD) of a porous NVP/C electrode material sample. Rietveld refinement of the PXRD pattern is performed to show the pure phase formation of NVP/C, without any impurity. This characteristic is evidenced by the close match of the calculated / fitted curve 22 and measured curve 24 and the difference 23 of curves 22 and 24.

Figs. 3A and 3B are field emission scanning electron microscope (FESEM) images of NVP/C sample, showing a network of NVP particles with an irregular morphology and various sized ranging from 500 to 900 nm. Transmission Electron Microscopy (TEM) analysis reveals that the NVP nano grains are well dispersed in the carbon matrix.

Figs. 4A and 4B show clear lattice fringes of NVP particle with a uniform carbon layer 42 of about 8nm formed on NVP particle 44. A selected area electron diffraction (SAED) pattern (Fig. 4C) shows single crystalline nature of the NVP nanoparticles which is consistent with the PXRD pattern shown in Fig. 2.

Nitrogen absorption / desorption isotherms 52, 54 shown in Fig. 5 indicate that the nanostructured NVP/C prepared according to embodiments of the present disclosure exhibits a distinct large hysteresis loop 56 and this type of behavior is a typical characteristic of mesoporous materials, namely a type-IV isotherm due to capillary condensation in the mesoporous channels and/or cages.

Figs. 6A, 6B, 7A and 7B show test results of electrochemical behaviour study of an NVP/C material synthesized according to embodiment of the present disclosure. The NVP/C material may be used as either a cathode or an anode for sodium ion battery.

Galvanostatic cycling curves obtained under current density of 117 mAg^{-1} from C/10 to 40C, for porous NVP/C material as a cathode in a Na-ion battery is shown in Fig. 6A. Here 1C refers to a capacity of 117 mAg^{-1} in one hour. As shown, the voltage profile has a flat charge plateau at about 3.39V before it rises steeply to the cutoff voltage of 3.9V, with a direct voltage drop to 3.36V followed by a very flat voltage plateau that spreads over a long range of sodium composition (up to 1.88 mole of Na^+) and then falls steeply to the cutoff voltage of 2.3V, leading to the storage capacity of 117 $mAhg^{-1}$. Accordingly, the flat voltage profile for a wide range of sodium ion molar concentrations observed for the NVP/C material synthesized according to embodiment of the present disclosure is much higher than conventional electrode material used for the same applications. During subsequent cycles, the observed voltage profiles remain unaltered, demonstrating excellent reversibility of the cycling process. As shown in Fig. 6B, at 1C rate the capacity can remain around 70 $mAhg^{-1}$ for at least 500 cycles.

When an NVP/C material synthesized according to embodiment of the present disclosure is used as an anode in a sodium-ion battery, as shown in Figs. 7A and 7B. A flat voltage profile was observed during the different charge/discharge current rates. Excellent long term cyclability was also observed when employed as anode.

As illustrated above, with respect to specific but non-limiting sample of NVP/C, an electrode material has Nasicon-type, phosphate framework nanoparticles integrated with carbon matrix between the particles.

Although embodiments of the present disclosure have been illustrated in conjunction with the accompanying drawings and described in the foregoing detailed description, it should be appreciated that the present disclosure is not limited to the embodiments disclosed. Therefore, the present disclosure should be understood to be capable of numerous rearrangements, modifications, alternatives and substitutions without departing from the spirit of the disclosure as set forth and recited by the following claims.

CLAIMS

1. A method for synthesizing an electrode material, the method comprising:
    dissolving a surfactant and precursors including a sodium precursor, a phosphate precursor and a transition metal precursor in a solvent to cause reaction of the precursors to yield a precipitate of particles, wherein the surfactant is attached to the particles;
    removing the solvent;
    sintering the precipitate to crystallize the particles, wherein during sintering the surfactant is decomposed to form a carbon matrix between the crystallized particles, and wherein the crystallized particles and the carbon matrix are integrated to form the electrode material.

2. The method of claim 1, wherein the surfactant comprises a compound selected from the group consisting of SDS, OTAB, DOTAB, CTAB and gluconic acid lactone.

3. The method of claim 1, wherein the sodium precursor is a sodium salt.

4. The method of claim 1, wherein the phosphate precursor is an ammonium phosphate salt or a phosphoric acid.

5. The method of claim 1, wherein the solvent is one of alcohol and a mixture of de-ionized water and alcohol.

6. The method of claim 1, wherein the transitional metal precursor comprises a compound selected from the group consisting of metal acetates, metal nitrate, metal chloride, metal acetyl acetonate and metal hydroxide.

7. The method of claim 6, wherein the metal is selected from a group consisting of vanadium, titanium, manganese and iron.

8. The method of claim 7, wherein the particles are formed of a compound selected from the group consisting of $Na_3V_2(PO_4)_3$, $NaFePO_4$, and $Na_3Ti_2(PO_4)_3$.

9. The method of claim 1, further comprising dissolving a substituted anion or polyanion in the solvent for reaction.

10. The method of claim 9, wherein the substituted anion or polyanion is obtained from a compound selected from a group consisting of fluorine, hydroxide, vanadate, arsenate, chloride and pyrophosphate.

11. The method of claim 10, wherein the particles are formed of a compound selected from the group consisting of $Na_3V_2(PO_4)_2F_3$, $NaVPO_4F$, Na_2FePO_4F.

12. The method of claim 1, further comprising dissolving additional doped cation or mixed cations in the solvent for reaction.

13. The method of claim 12, wherein the additional doped cation or mixed cations is/are obtained from a compound selected from a group consisting of group 1 elements, transition metals ammonium and hydrogen.

14. The method of claim 13, wherein the additional doped cation or mixed cations is/are obtained from a compound selected from a group consisting of transition metals, and wherein the particles are formed of a compound selected from the group consisting of $Na_2Fe_{0.5}Mn_{0.5}PO_4F$, $Na_2Ti_{0.5}Mn_{0.5}PO_4F$ and $Na_2V_{0.5}Mn_{0.5}PO_4F$.

15. The method of claim 1, wherein the crystallized particles have a grain size between 20 nm to 200 nm.

16. The method of claim 1, wherein the carbon matrix forms a carbon layer coated on the crystallized particles, and wherein the carbon layer has a thickness of 2 to 10 nm.

17. The method of claim 1, wherein removing the solvent comprises separating the precipitate from the solvent and drying the precipitate.

18. The method of claim 1, wherein sintering is carried out in one of a flowing oxidizing atmosphere, an inert atmosphere and a reducing atmosphere.

19. An electrode material comprising a compound according to the following formula:

$Na_xA_bM_y(PO_4)_zX_n$ / C

wherein

M is a transition metal selected from a group consisting of metal acetates, metal nitrate metal chloride and metal acetyl acetonate

A is an additional doped or mixed cations selected from a group consisting of group 1 elements, transition metals, ammonium and hydrogen;

X is a substituted anion or polyanion selected from a group consisting of fluorine, hydroxide, vanadate, arsenate, chloride, pyrophosphate;

x, b, y, z and n denote the numbers of ions of a corresponding element, in which:.

$1 \leq x \leq 3$;

$0 \leq b \leq 1$;

$1 \leq y \leq 2$;

$1 \leq z \leq 3$;

$0 \leq n \leq 3$.

and

C denotes a carbon matrix formed between the $Na_xA_bM_y(PO_4)_zX_n$ nanoparticles.

20. The electrode material of claim 19, wherein the material is one selected from the group consisting of $Na_3V_2(PO_4)_3$, $Na_3V_2(PO_4)_2F_3$, $NaVPO_4F$, Na_2FePO_4F, $Na_2FePO_4(OH)$, $Na_2Fe_{0.5}Mn_{0.5}PO_4F$, $Na_2Ti_{0.5}Mn_{0.5}PO_4F$, $Na_2V_{0.5}Mn_{0.5}PO_4F$, $NaFePO_4$, $Na_3Ti_2(PO_4)_3$.

21. An electrode material comprising:

    crystallized mesoporous particles having a grain size between 20 nm to 200 nm;

    a carbon matrix disposed between the crystallized particles forming a carbon layer coated on the crystallized particles, and wherein the carbon layer has a thickness of 2 to 10 nm.

22. The electrode material of claim 21, wherein the crystallized particles are formed of a compound selected from the group consisting of $Na_3V_2(PO_4)_3$, $Na_3V_2(PO_4)_2F_3$, $NaVPO_4F$, Na_2FePO_4F, $Na_2FePO_4(OH)$, $Na_2Fe_{0.5}Mn_{0.5}PO_4F$, $Na_2Ti_{0.5}Mn_{0.5}PO_4F$, $Na_2V_{0.5}Mn_{0.5}PO_4F$, $NaFePO_4$, $Na_3Ti_2(PO_4)_3$.

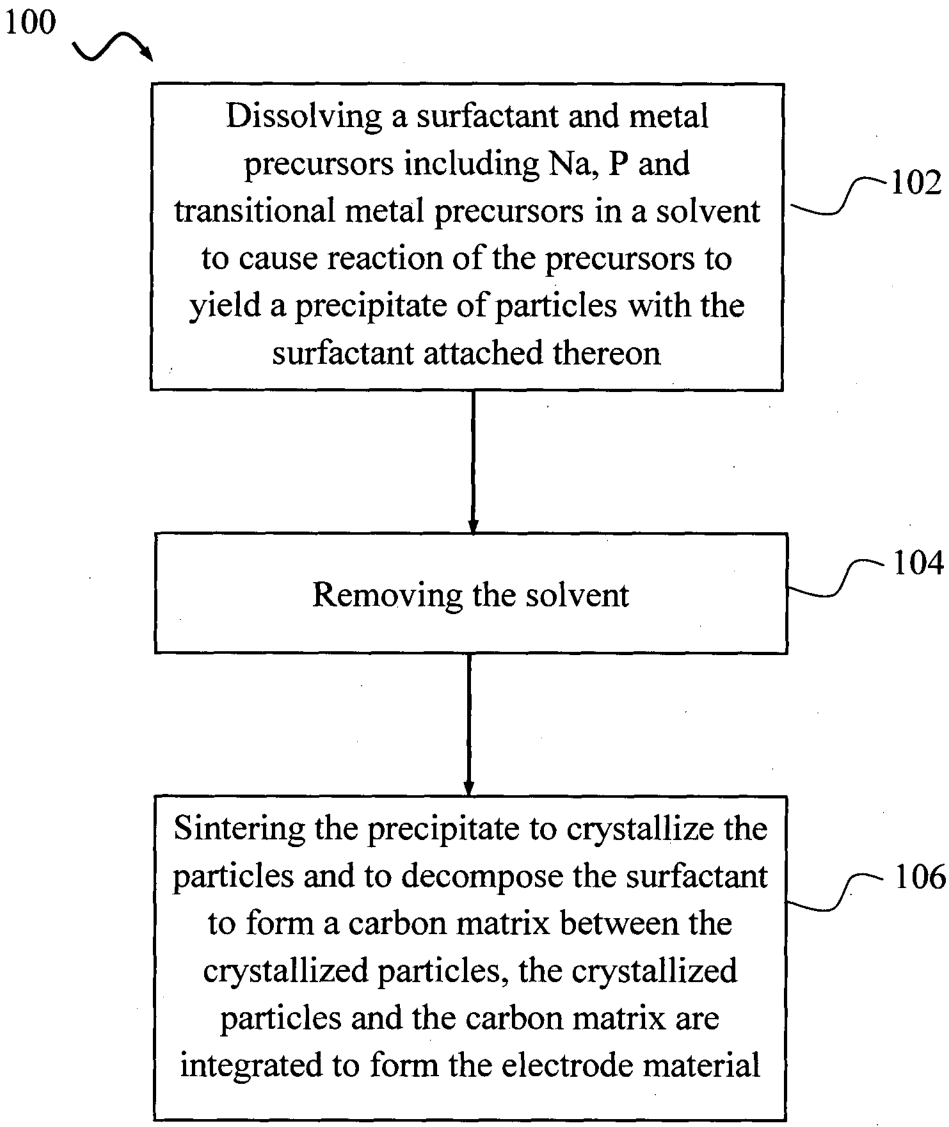

100
Dissolving a surfactant and metal precursors including Na, P and transitional metal precursors in a solvent to cause reaction of the precursors to yield a precipitate of particles with the surfactant attached thereon
102
Removing the solvent
104
Sintering the precipitate to crystallize the particles and to decompose the surfactant to form a carbon matrix between the crystallized particles, the crystallized particles and the carbon matrix are integrated to form the electrode material
106

FIG. 1

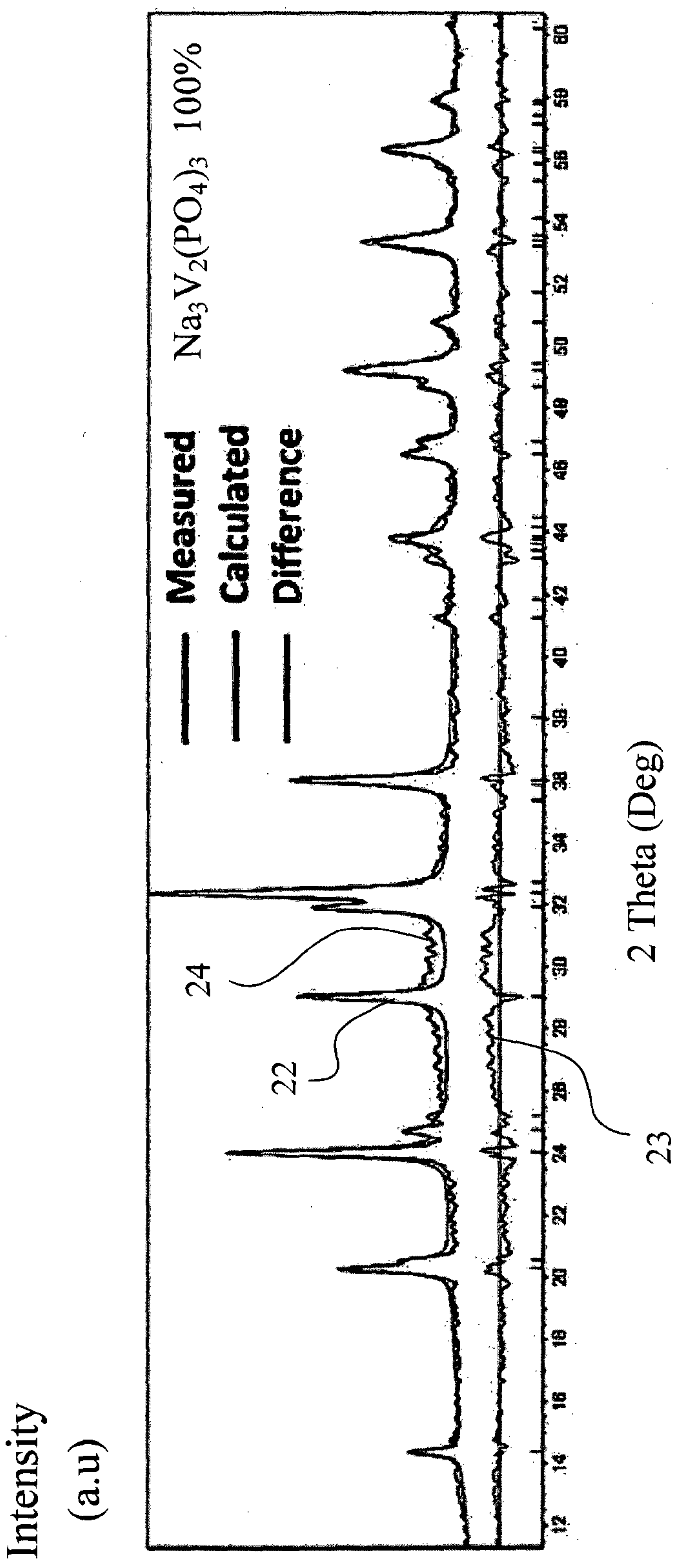

Intensity
(a.u)
Measured
Calculated
Difference
$Na_3V_2(PO_4)_3$ 100%
24
22
23
2 Theta (Deg)
12
14
16
18
20
22
24
26
28
30
32
34
36
38
40
42
44
46
48
50
52
54
56
58
60

FIG. 2

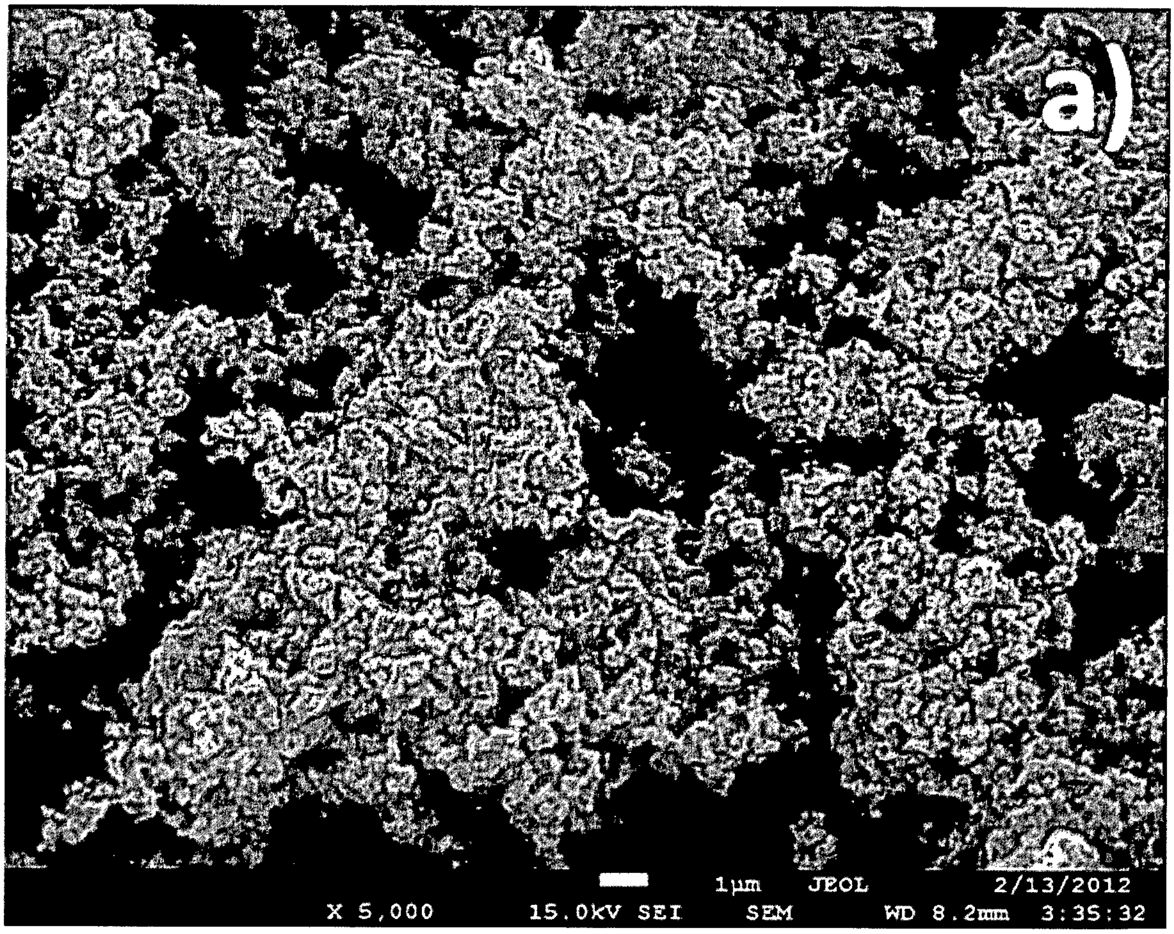


FIG.3A

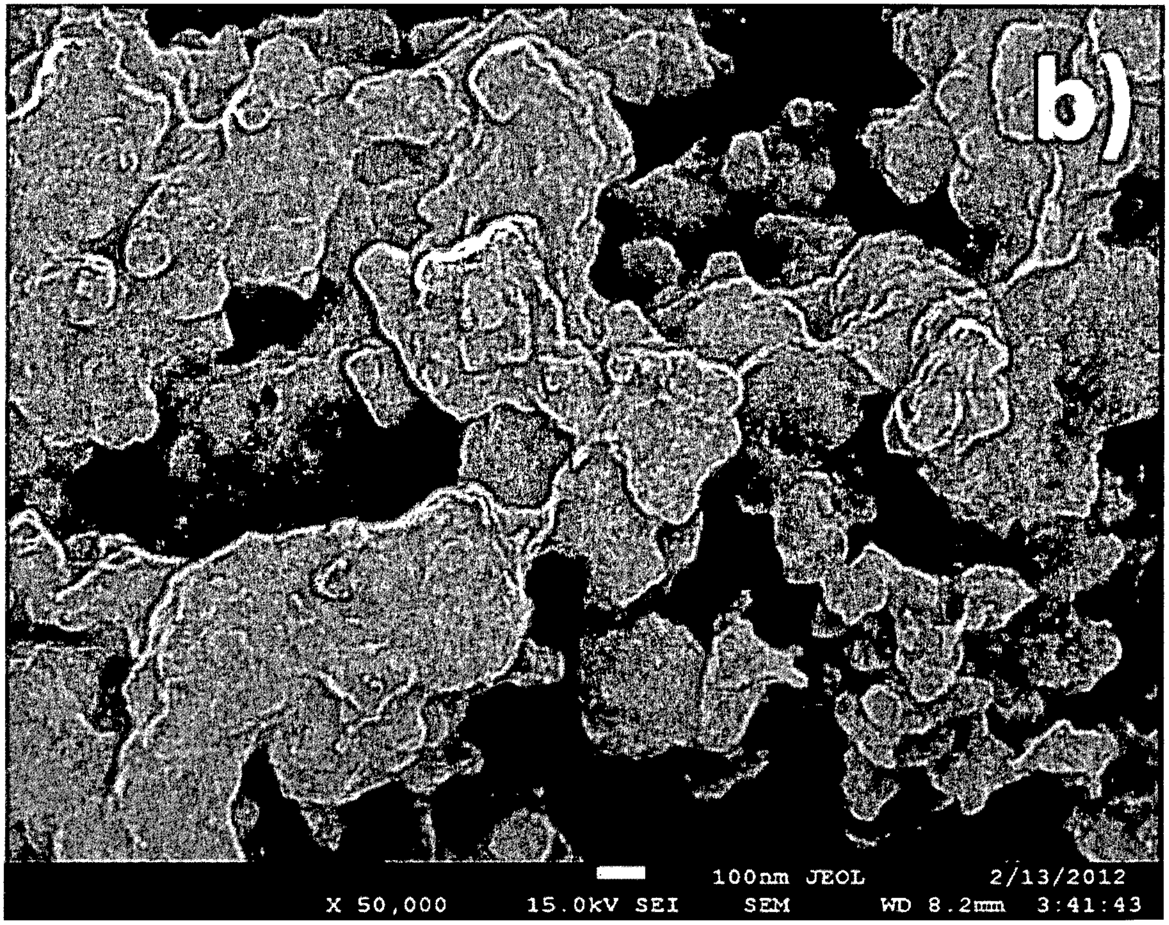


FIG. 3B

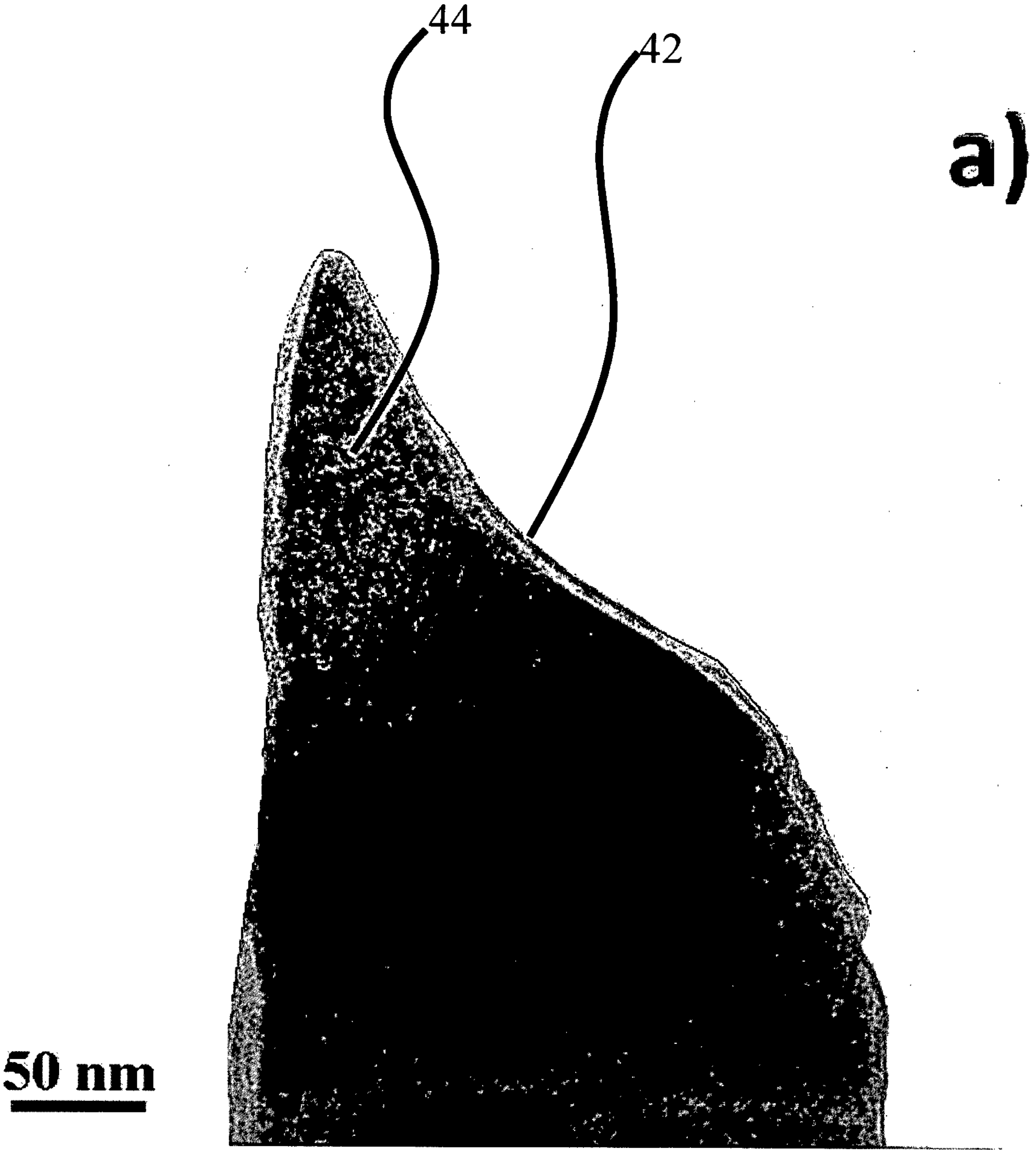


FIG. 4A

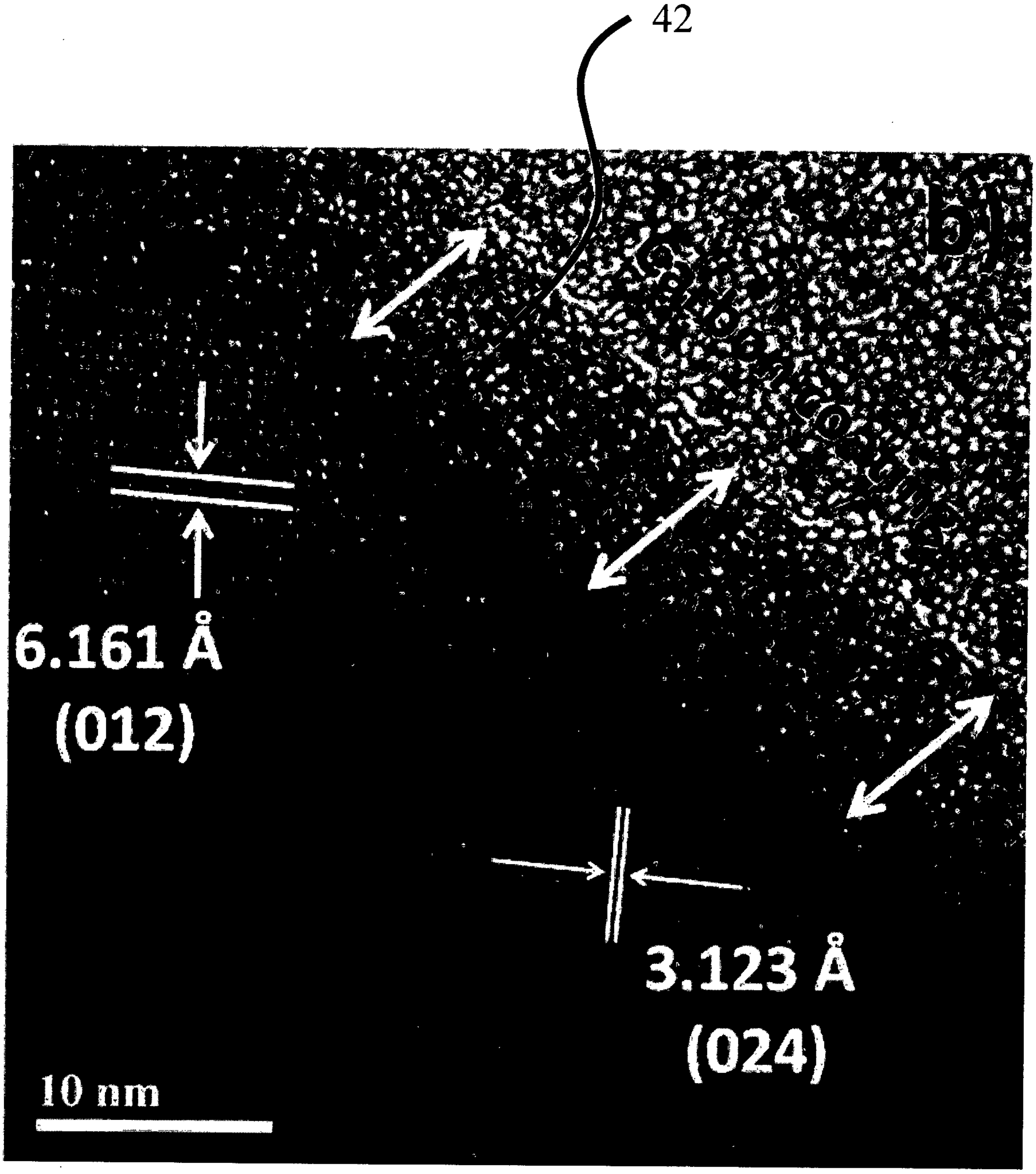


FIG. 4B

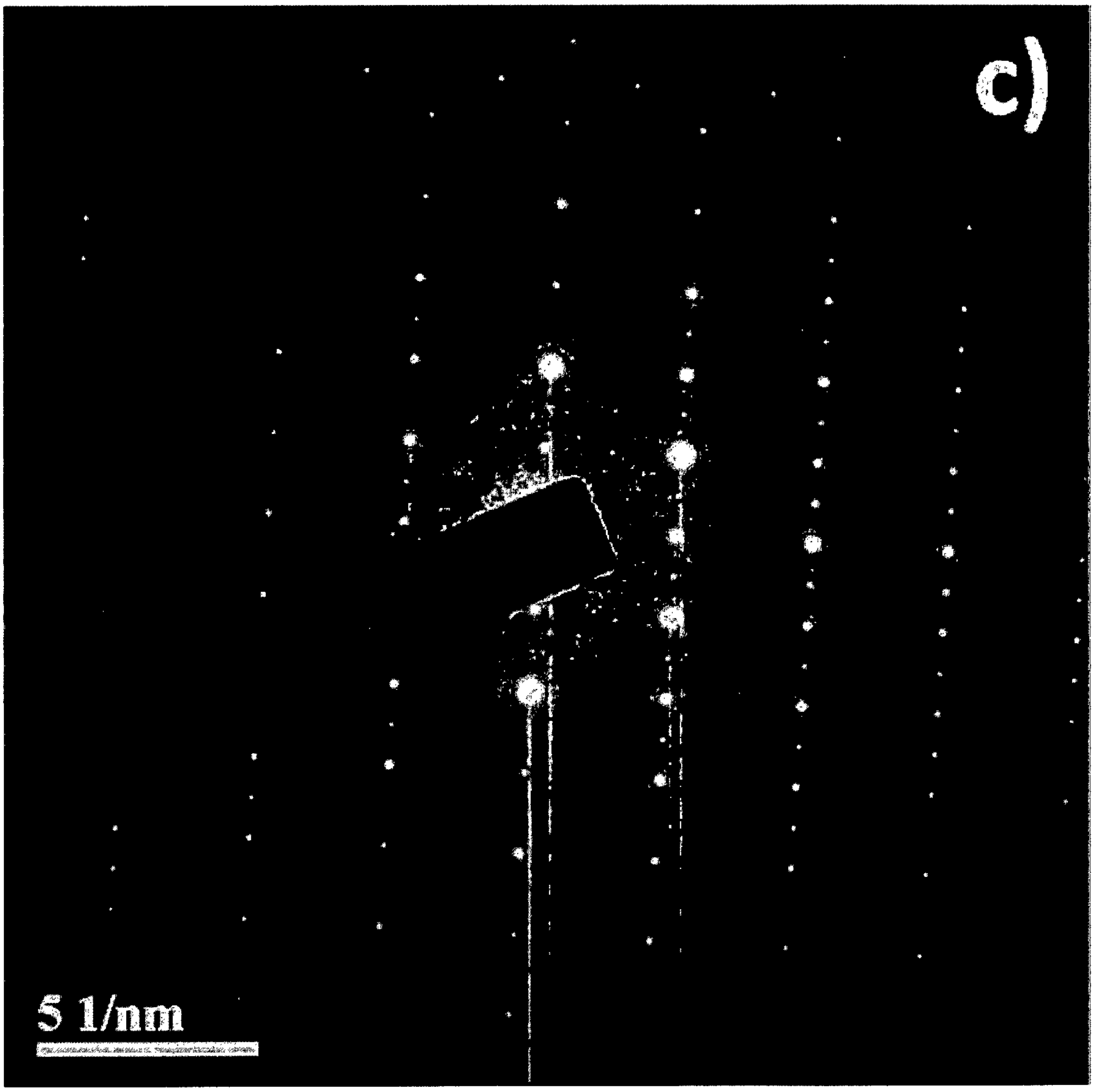


FIG. 4C

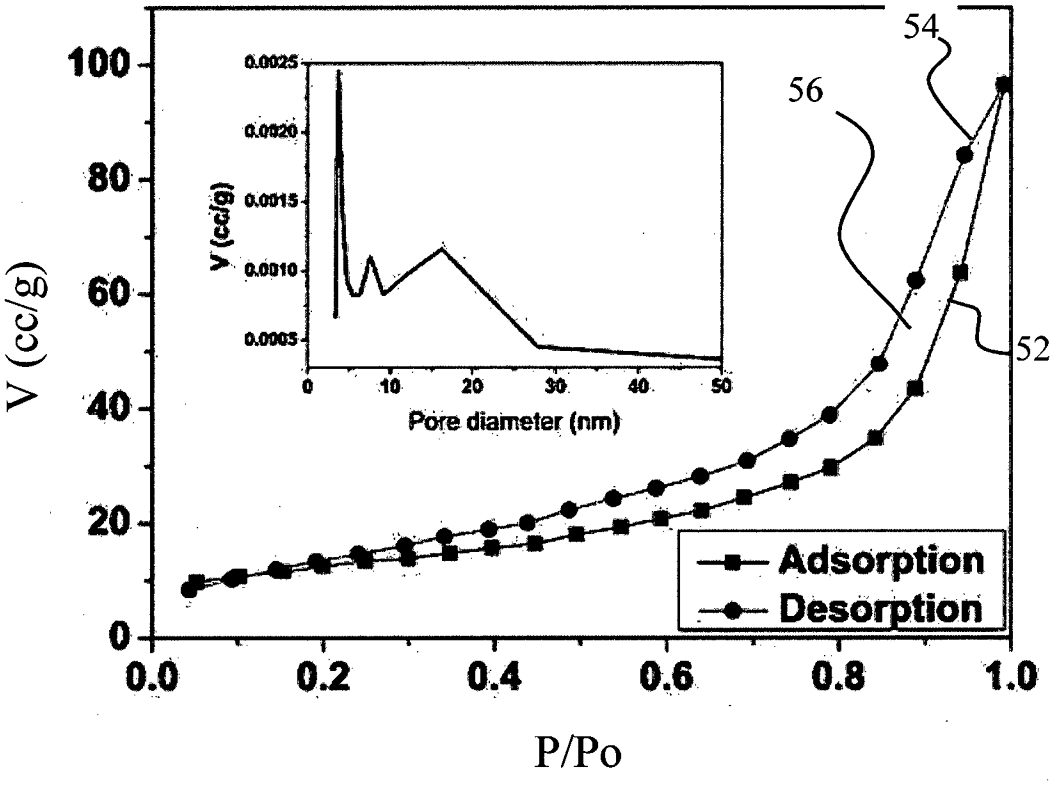
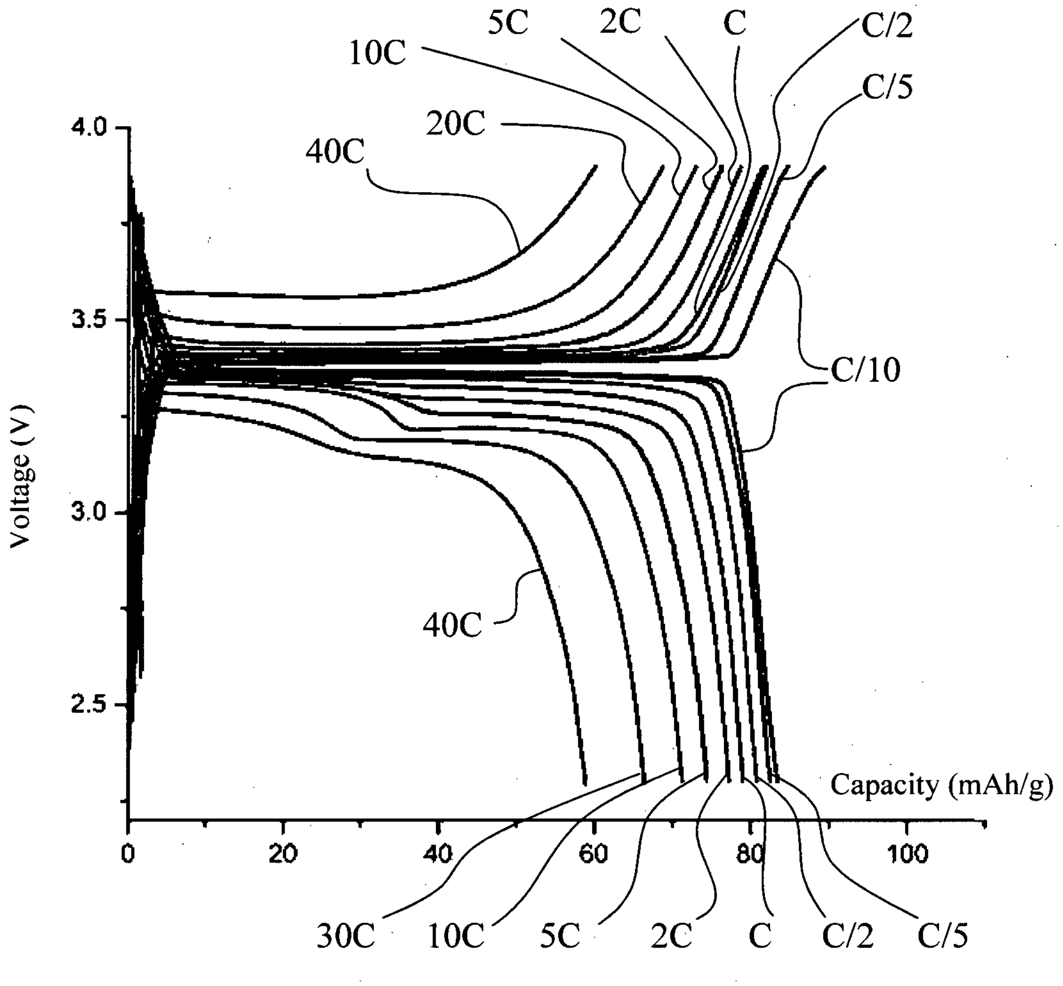

V (cc/g)
100
80
60
40
20
0
0.0
0.2
0.4
0.6
0.8
1.0
P/Po
Adsorption
Desorption
56
54
52
V (cc/g)
0.0025
0.0020
0.0015
0.0010
0.0005
0
10
20
30
40
50
Pore diameter (nm)

FIG. 5



5C
2C
C
C/2
10C
C/5
20C
40C
4.0
3.5
3.0
2.5
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C/10
40C
Capacity (mAh/g)
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40
60
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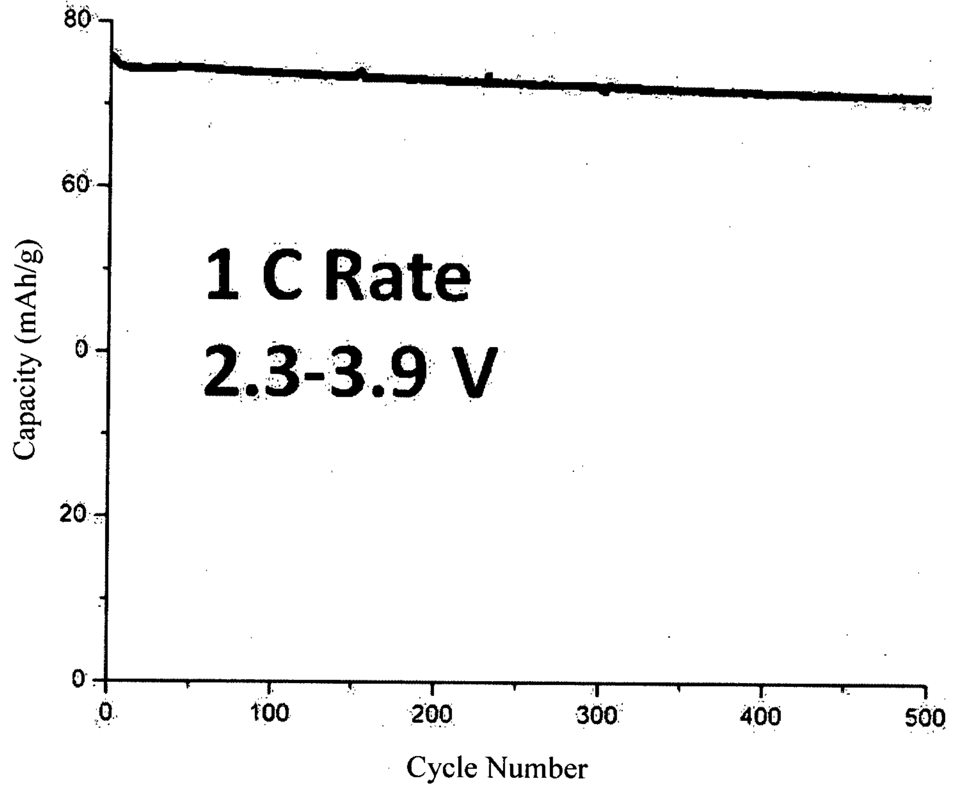
100
30C
10C
5C
2C
C
C/2
C/5

FIG. 6A


80
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Capacity (mAh/g)
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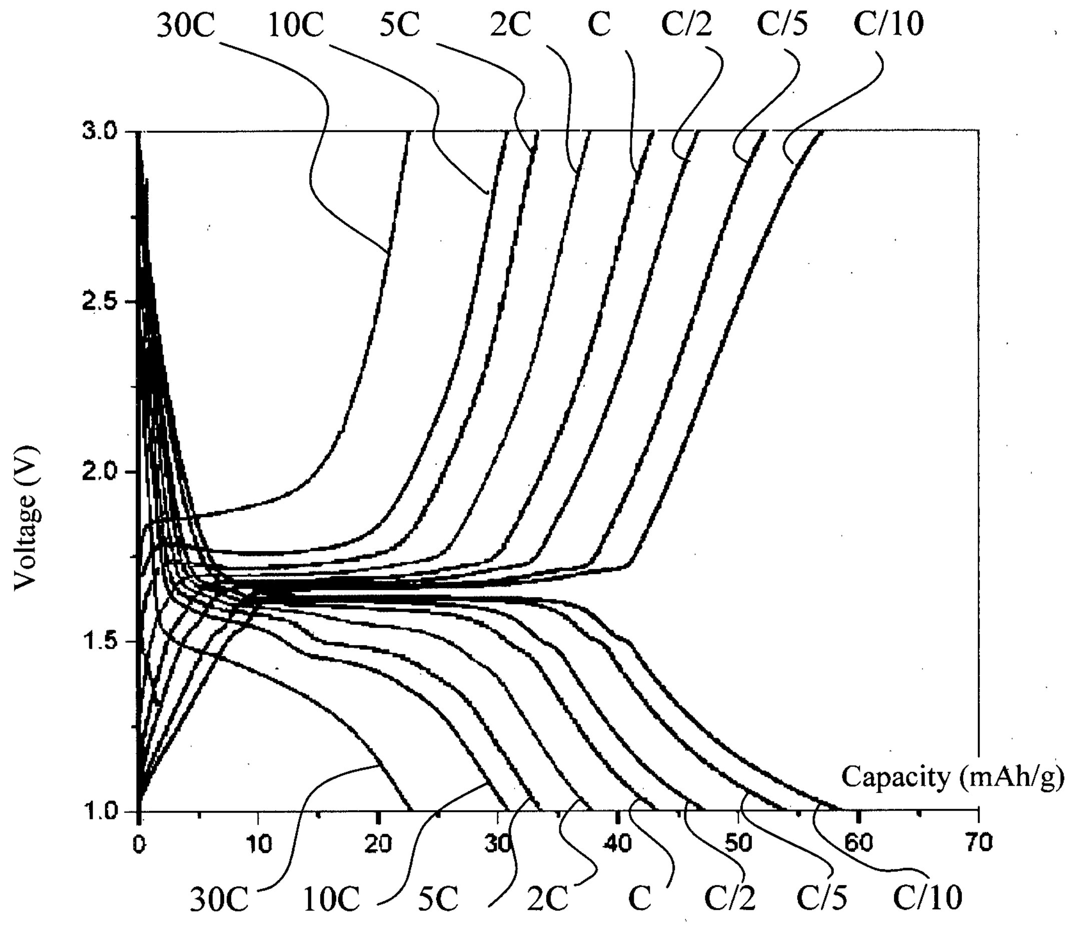
200
300
400
500
Cycle Number
1 C Rate
2.3-3.9 V

FIG. 6B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2.5
2.0
1.5
1.0
Voltage (V)
0
10
20
30
40
50
60
70
Capacity (mAh/g)
30C
10C
5C
2C
C
C/2
C/5
C/10

FIG. 7A

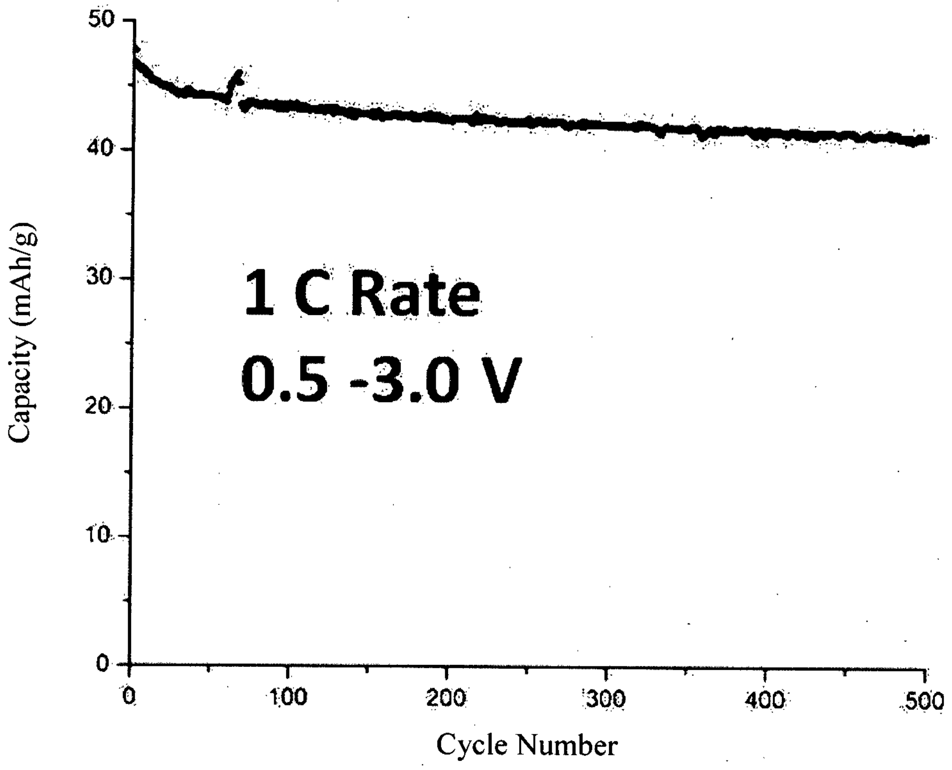
1 C Rate
0.5 -3.0 V
Capacity (mAh/g)
0
10
20
30
40
50
Cycle Number
0
100
200
300
400
500

FIG. 7B

INTERNATIONAL SEARCH REPORT

International application No.
PCT/SG2013/000164

A. CLASSIFICATION OF SUBJECT MATTER

H01M 4/00 (2006.01) H01M 2/00 (2006.01) H01M 4/48 (2010.01) H01M 4/36 (2006.01) H01M 4/1391 (2010.01) H01M 4/04 (2006.01)

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)

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	

☒ 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	"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
"E"	earlier application or patent but published on or after the international filing date	"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
"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)	"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
"O"	document referring to an oral disclosure, use, exhibition or other means	"&"	document member of the same patent family
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search 15 July 2013	Date of mailing of the international search report 15 July 2013
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA Email address: pct@ipaustralia.gov.au Facsimile No.: +61 2 6283 7999	**Authorised officer** Gregory Diven AUSTRALIAN PATENT OFFICE (ISO 9001 Quality Certified Service) Telephone No. 0262832992

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a)

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

See Supplemental Box for Details

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☒ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	US 2008/0138710 A1 (LIAW ET AL.) 12 June 2008	
X	abstract; paragraphs [0005]-[0011], [0033], [0035], [0037]-[0039], [0042], [0045]-[0046], [0066], [0080]; examples 1-3, 8; claims	1-4, 6-15, 17-20
Y	abstract, paragraphs [0034], [0080]	22
	US 2008/0308773 A1 (LIAW ET AL.) 18 December 2008	
X	abstract; paragraphs [0007]-[0008], [0020], [0021], [0026]-[0031]; examples; claims	1-7, 17-19
	US 2012/0064397 A1 (KALLFASS ET AL.) 15 March 2012	
X	abstract; paragraphs [0001], [0007]-[0029], [0037], [0104]-[0106]; examples	1, 3-5, 7, 9, 10, 12-15, 17-20
	WO 2008/141422 A1 (TRANSFERT PLUS S.E.C) 27 November 2008	
X	abstract; paragraphs[0004]-[0020], [0031], [0038]-[0039]	1, 6-8, 13-15, 17-20
	US 2011/0269022 A1 (KAWAKAMI ET AL.) 03 November 2011	
X	abstract; paragraphs [0009], [0018], [0025]-[0032], [0075], [0084]-[0085], [0096]	21
Y	abstract; paragraphs [0009], [0018], [0025]-[0032], [0075], [0084]-[0085], [0096]	22
	US 5872074 A (SCHULZ ET AL.) 16 February 1999	
X	abstrcat; col 2 lines 11-27, col 5 lines 3-8; example 7	21-22
	CN 1681145 A (PHYSICAL INST CHINESE ACADEMY) 12 October 2005	
X	Espace abstract	21-22

Supplemental Box

Continuation of: **Box III**

This International Application does not comply with the requirements of unity of invention because it does not relate to one invention or to a group of inventions so linked as to form a single general inventive concept.

This Authority has found that there are different inventions based on the following features that separate the claims into distinct groups:

- Claims 1-18 are directed to a method for synthesizing an electrode material, the method comprising: dissolving a surfactant and precursors including a sodium precursor, a phosphate precursor and a transition metal precursor in a solvent to cause reaction of the precursors to yield a precipitate of particles, wherein the surfactant is attached to the particles; removing the solvent; sintering the precipitate to crystallize the particles, wherein during sintering the surfactant is decomposed to form a carbon matrix between the crystallized particles, and wherein the crystallized particles and the carbon matrix are integrated to form the electrode material. The feature of a method for synthesizing an electrode material, the method comprising: dissolving a surfactant and precursors including a sodium precursor, a phosphate precursor and a transition metal precursor in a solvent to cause reaction of the precursors to yield a precipitate of particles, wherein the surfactant is attached to the particles; removing the solvent; sintering the precipitate to crystallize the particles, wherein during sintering the surfactant is decomposed to form a carbon matrix between the crystallized particles, and wherein the crystallized particles and the carbon matrix are integrated to form the electrode material is specific to this group of claims.

- Claims 19-20 are directed to an electrode material comprising a compound according to the following formula: NaxAbMy(P04)zXn/C wherein M is a transition metal selected from a group consisting of metal acetates, metal nitrate metal chloride and metal acetyl acetonate A is an additional doped or mixed cations selected from a group consisting of group 1 elements, transition metals, ammonium and hydrogen; X is a substituted anion or polyanion selected from a group consisting of fluorine, hydroxide, vanadate, arsenate, chloride, pyrophosphate; x, b, y, z and n denote the numbers of ions of a corresponding element, in which:. $1 \leq x \leq 3$; $0 \leq b \leq 1$; $1 \leq y \leq 2$; $1 \leq z \leq 3$; $0 \leq n \leq 3$ and C denotes a carbon matrix formed between the NaxAbMy(P04)zXn nanoparticles. The feature of an electrode material comprising a compound according to the following formula: NaxAbMy(P04)zXn/C wherein M is a transition metal selected from a group consisting of metal acetates, metal nitrate metal chloride and metal acetyl acetonate A is an additional doped or mixed cations selected from a group consisting of group 1 elements, transition metals, ammonium and hydrogen; X is a substituted anion or polyanion selected from a group consisting of fluorine, hydroxide, vanadate, arsenate, chloride, pyrophosphate; x, b, y, z and n denote the numbers of ions of a corresponding element, in which:. $1 \leq x \leq 3$; $0 \leq b \leq 1$; $1 \leq y \leq 2$; $1 \leq z \leq 3$; $0 \leq n \leq 3$ and C denotes a carbon matrix formed between the NaxAbMy(P04)zXn nanoparticles is specific to this group of claims.

- Claims 21-22 are directed to an electrode material comprising: crystallized mesoporous particles having a grain size between 20 nm to 200 nm; a carbon matrix disposed between the crystallized particles forming a carbon layer coated on the crystallized particles, and wherein the carbon layer has a thickness of 2 to 10 nm. The feature of an electrode material comprising: crystallized mesoporous particles having a grain size between 20 nm to 200 nm; a carbon matrix disposed between the crystallized particles forming a carbon layer coated on the crystallized particles, and wherein the carbon layer has a thickness of 2 to 10 nm is specific to this group of claims.

Supplemental Box

PCT Rule 13.2, first sentence, states that unity of invention is only fulfilled when there is a technical relationship among the claimed inventions involving one or more of the same or corresponding special technical features. PCT Rule 13.2, second sentence, defines a special technical feature as a feature which makes a contribution over the prior art.

When there is no special technical feature common to all the claimed inventions there is no unity of invention.

There are considered to be two distinct groups of claims
Group 1: Claims 1-18 and 19-20
Group 2: Claims 21-22
In the above groups of claims, the identified features may have the potential to make a contribution over the prior art but are not common to all the claimed inventions and therefore cannot provide the required technical relationship. Therefore there is no special technical feature common to all the claimed inventions and the requirements for unity of invention are consequently not satisfied *a priori*.

INTERNATIONAL SEARCH REPORT Information on patent family members	International application No. **PCT/SG2013/000164**

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**
US 2008/0138710 A1	12 Jun 2008	CA 2588494 A1	11 Nov 2007
		CA 2633284 A1	18 Dec 2008
		CA 2635245 A1	18 Dec 2008
		CA 2643861 A1	14 May 2009
		CN 101304083 A	12 Nov 2008
		CN 101304083 B	06 Jul 2011
		CN 101345099 A	14 Jan 2009
		CN 101345099 B	13 Jun 2012
		CN 101345307 A	14 Jan 2009
		CN 101345307 B	08 Jun 2011
		CN 101436664 A	20 May 2009
		CN 101436664 B	26 Oct 2011
		EP 1855334 A2	14 Nov 2007
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		JP 2008311224 A	25 Dec 2008
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		KR 20080111387 A	23 Dec 2008
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		KR 101169495 B1	27 Jul 2012
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		KR 20070109903 A	15 Nov 2007
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		TW 200921966 A	16 May 2009
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Publication Number	**Publication Date**	**Publication Number**	**Publication Date**
		TW 200908423 A	16 Feb 2009
		TW I377727 B	21 Nov 2012
		TW 200901535 A	01 Jan 2009
		US 2007207080 A1	06 Sep 2007
		US 7524529 B2	28 Apr 2009
		US 2007059598 A1	15 Mar 2007
		US 7700236 B2	20 Apr 2010
		US 2007207385 A1	06 Sep 2007
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		US 7799457 B2	21 Sep 2010
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		US 7892676 B2	22 Feb 2011
		US 2009152512 A1	18 Jun 2009
		US 7964117 B2	21 Jun 2011
		US 2009081549 A1	26 Mar 2009
		US 8168329 B2	01 May 2012
		US 2006257307 A1	16 Nov 2006
		US 2008138710 A1	12 Jun 2008

INTERNATIONAL SEARCH REPORT Information on patent family members	International application No. **PCT/SG2013/000164**

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INTERNATIONAL SEARCH REPORT Information on patent family members	International application No. **PCT/SG2013/000164**

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		EP 2376376 A2	19 Oct 2011
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		US 2012064397 A1	15 Mar 2012
		WO 2010066439 A2	17 Jun 2010
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		JP 4490510 B2	30 Jun 2010
		US 5872074 A	16 Feb 1999
		WO 9832885 A1	30 Jul 1998
CN 1681145 A	12 Oct 2005	None	

End of Annex

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