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(54) Title: PROCESS FOR PREPARING A CORE-SHELL STRUCTURED LITHIATED MANGANESE OXIDE

(57) Abstract: The invention relates to a process for preparing a core-shell structured lithiated manganese oxide, comprising the steps of providing spinel  $\text{LiM}_x\text{Mn}_{2-x}\text{O}_4$  particles, where M is one or more metal ions selected from the group consisting of Li, Mg, Cr, Al, Co, Ni, Zn, Cu, and La, and  $0 \leq x < 1$ , as core particles, and subjecting the spinel particles to a heat-treatment with a reactive chemical reagent in the form of liquid or gas to form a shell layer on the surface of the core particles, and to the prepared core-shell structured lithiated manganese oxide, and its use as a cathode material for a lithium ion battery



## PROCESS FOR PREPARING A CORE-SHELL STRUCTURED LITHIATED MANGANESE OXIDE

### FIELD OF THE INVENTION

The invention relates to a process for preparing a core-shell structured lithiated manganese oxide, the prepared core-shell structured lithiated manganese oxide and its use as a cathode material for a lithium ion battery.

### BACKGROUND OF THE INVENTION

In view of the economic and environmental advantages over commercially available  $\text{LiCoO}_2$ , spinel  $\text{LiMn}_2\text{O}_4$  is a potentially attractive alternative cathode material for lithium-ion batteries, especially for large-scale batteries. However, the spinel  $\text{LiMn}_2\text{O}_4$  suffers from severe capacity fading on cycling, especially at elevated temperatures. The cycling stability of the spinel has been improved by two main categories of approaches: ion doping to stabilize its crystal structure and surface coating to prevent Mn dissolution. It has been demonstrated that Mn dissolution increases with contact area of the spinel with electrolyte. Typically, sol-gel method and precipitation method are used for metal oxides surface coating.

Kenneth A. Walz et al., in "Elevated temperature cycling stability and electrochemical impedance of  $\text{LiMn}_2\text{O}_4$  cathodes with nanoporous  $\text{ZrO}_2$  and  $\text{TiO}_2$  coatings", *Journal of Power Sources*, 195 (2010) 4943-4951, describes coating  $\text{LiMn}_2\text{O}_4$  cathodes with  $\text{ZrO}_2$  and  $\text{TiO}_2$  by using sol-gel technique.

Xifei Li et al, in "Enhanced cycling performance of spinel  $\text{LiMn}_2\text{O}_4$  coated with  $\text{ZnMn}_2\text{O}_4$  shell", *Journal of Solid State Electrochem*, (2008) 12: 851-855, describes coating spinel  $\text{LiMn}_2\text{O}_4$  with  $\text{ZnMn}_2\text{O}_4$  shell by mixing  $\text{LiMn}_2\text{O}_4$  and  $\text{ZnO}$  in the ball mill, and calcining the mixed powders.

These methods can reduce the contact area of the spinel with electrolyte and improve cycling stability of the material to a certain extent. However, the resulting coating layers are not uniform and continuous. Instead, there are isolated nano-sized metal oxide particles attached on the surface of spinel particles. The improvement in the cycling performance of the obtained spinel is not satisfactory.

Therefore, there still remains a need for a more useful method for forming a uniform and continuous layer on the surface of spinel particles, to obtain a lithiated manganese oxide material, which exhibits significantly improved cycling stability at elevated temperatures.

## SUMMARY OF THE INVENTION

According to one aspect of the present invention, there is provided a process for preparing a core-shell structured lithiated manganese oxide, comprising the steps of providing spinel  $\text{LiM}_x\text{Mn}_{2-x}\text{O}_4$  particles, where M is one or more metal ions selected from the group consisting of Li, Mg, Cr, Al, Co, Ni, Zn, Cu, and La, and  $0 \leq x \leq 1$ , as core particles, and subjecting the spinel particles to a heat-treatment with a chemical reagent reactive towards the spinel  $\text{LiM}_x\text{Mn}_{2-x}\text{O}_4$  particles in the form of liquid or gas to form a continuous and uniform shell layer on the surface of the core particles.

According to another aspect of the present invention, there is provided a core-shell structured lithiated manganese oxide obtainable by the process according to the present invention.

According to a further aspect of the present invention, there is provided a cathode material for a lithium ion battery comprising the core-shell structured lithiated manganese oxide.

According to a further aspect of the present invention, there is provided a lithium ion battery comprising the core-shell structured lithiated manganese oxide as cathode material.

## BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is SEM image of the core-shell structured lithiated manganese oxide prepared according to Example 1.

Fig. 2 is TEM image of the core-shell structured lithiated manganese oxide prepared according to Example 1.

Fig. 3 is a graph showing comparison of the charge/discharge curves at  $60^\circ\text{C}$  of  $\text{LiMn}_2\text{O}_4$  with (according to Example 1) and without  $\text{P}_2\text{O}_5$  treatment.

Fig. 4 is graph showing comparison of the cycling stability at  $60^\circ\text{C}$  of  $\text{LiMn}_2\text{O}_4$  cathode materials with (according to Example 1) and without  $\text{P}_2\text{O}_5$  treatment.

## DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

In one aspect, the present invention provides a process for preparing a core-shell structured lithiated manganese oxide. The process comprises the steps of:

providing spinel  $\text{LiM}_x\text{Mn}_{2-x}\text{O}_4$  particles, where M is one or more metal ions selected from the group consisting of Li, Mg, Cr, Al, Co, Ni, Zn, Cu, and La, and  $0 \leq x \leq 1$ , as core particles, and

subjecting the spinel particles to a heat-treatment with a chemical reagent reactive towards the spinel particles in the form of liquid or gas, to form a continuous and uniform shell layer on the surface of the core particles.

The spinel  $\text{LiM}_x\text{Mn}_{2-x}\text{O}_4$  particles, where  $0 \leq x \leq 1$ , are commercially available products, or can be prepared by any suitable methods known to a person skilled in the art, such as solid-state reaction method, and co-precipitation method. In a preferred embodiment, the spinel  $\text{LiM}_x\text{Mn}_{2-x}\text{O}_4$  particles are prepared by a solid-state reaction of a stoichiometric mixture of a lithium compound, a manganese compound, and, if appropriate, a compound of M by heat treating. In the solid-state reaction process, the compounds, used as the precursors of the respective metals of lithium, manganese and M, are mixed under ball milling, and heat treated at a temperature of preferably  $650^\circ\text{C}$  for 5 h in air, and then cooled. The thus-obtained product is further calcinated at a temperature of  $900^\circ\text{C}$  for 10 h in air, and then cooled to room temperature.

As the respective precursors of Li, Mn and M, the lithium compound, the manganese compound and the compound of M are not particularly restricted, and examples thereof may include carbonates, nitrates, hydroxides, oxides of Li, Mn and M. Preferably, lithium carbonate, manganese oxide, and oxide of M are used.

The spinel  $\text{LiM}_x\text{Mn}_{2-x}\text{O}_4$  particles are then subjected to a heat-treatment with a chemical reagent reactive towards the spinel particles in the form of liquid or gas. The heat-treatment can be performed at a temperature of from  $100$  to  $800^\circ\text{C}$  for 0.5~5h.

By the heat-treatment, the spinel  $\text{LiM}_x\text{Mn}_{2-x}\text{O}_4$  particles react with the liquid or gaseous reactive chemical reagent, to form a continuous and uniform shell layer on the surface of the spinel particles.

As known to a person skilled in the art, spinel  $\text{LiM}_x\text{Mn}_{2-x}\text{O}_4$  suffers from Jahn-Teller distortion during charging-discharging process, which induces disproportion reaction of unstable  $\text{Mn}^{3+}$  with acid in electrolyte, and the reaction may be further enhanced at elevated temperature. The inventor has found that after treatment with the chemical reagent that can react with the spinel  $\text{LiM}_x\text{Mn}_{2-x}\text{O}_4$ , a uniform and continuous layer is formed on the particle surface, and this protective layer, which is not spinel structure, would not suffer from Jahn-Teller distortion. Moreover, it can significantly reduce the contact area of the core with the electrolyte, and thus effectively reduce Mn dissolution into the electrolyte solution.

The reactive chemical reagent is preferably selected from  $\text{NH}_3$ ,  $\text{P}_2\text{O}_5$ , and triphenyl phosphine.

In an embodiment of the invention,  $\text{NH}_3$  is used as the chemical reagent. Preferably,  $\text{NH}_3$  gas flow at a rate of 0.01~1 L/min, preferably 0.01~0.05L/min is introduced to the spinel particles. In this embodiment, the heat-treatment is performed at a temperature of from 650 to 750°C for 0.5~5h. It is contemplated that a shell layer of manganese nitride is coated on the surface of the spinel particles.

In a further embodiment of the invention,  $\text{P}_2\text{O}_5$  is used as the chemical reagent. Preferably, the spinel particles and  $\text{P}_2\text{O}_5$  powders are mixed in a weight ratio of from 10:1 to 50:1. In this embodiment, the heat-treatment is performed at a temperature of from 550 to 650°C for 0.5~2h. It is contemplated that a shell layer of lithium manganese phosphate is coated on the surface of the spinel particles.

In a still further embodiment of the invention, triphenyl phosphine is used as the chemical reagent. Preferably, the spinel particles and triphenyl phosphine powders are mixed in a weight ratio of from 10:1 to 50:1. In this embodiment, the heat-treatment is performed at a temperature of from 150 to 250°C for 0.5~5h. It is contemplated that a shell layer of manganese phosphate is coated on the surface of the spinel particles.

The thus-obtained lithated manganese oxide has a core-shell structure. The core consists of spinel  $\text{LiM}_x\text{Mn}_{2-x}\text{O}_4$  particles, where M is one or more metal ions selected from the group consisting of Li, Mg, Cr, Al, Co, Ni, Zn, Cu, and La, and  $0 \leq x \leq 1$ . The shell, which is not spinel structure, has a Mn-containing composition, and is produced through the reaction between the spinel  $\text{LiM}_x\text{Mn}_{2-x}\text{O}_4$  particles and the reactive chemical reagent. The shell has a thickness of 5-20nm.

The core-shell structured lithated manganese oxide has a uniform and continuous layer formed on the surface of the spinel lithiated manganese oxide. The protective layer can significantly reduce the contact area of the spinel with the electrolyte, thus effectively preventing Mn dissolution into the electrolyte solution, and thereby improving the cycling performance of the lithiated manganese oxide.

The core-shell structured lithiated manganese oxide according to the invention can be advantageously used as a cathode material for a lithium-ion battery. The oxide exhibits an improved cycling stability, especially at elevated temperatures.

The following examples further illustrate the process according to the invention, and the characteristics of the prepared compound used as cathode material for lithium ion battery. The examples are given by way of illustration only, and are not intended to limit the invention in any manner.

LiMn<sub>2</sub>O<sub>4</sub> powder was mixed with P<sub>2</sub>O<sub>5</sub> powder in a weight ratio of 10:1, and the mixture was heat treated at 600°C for 1 hour in a sealed reactor. The SEM and TEM images of the resulting compound indicated that a shell layer with a thickness of 10-20nm was continuously and uniformly coated on the lithiated manganese oxide particles (Fig. 1 and Fig. 2).

#### Example 2:

LiMn<sub>2</sub>O<sub>4</sub> powder was treated with NH<sub>3</sub> at a flow rate of 0.02L/min at 700°C for 1 hour in a sealed reactor. A shell layer with a thickness of 10-20nm was continuously and uniformly coated on the lithiated manganese oxide particles.

#### Example 3:

LiMn<sub>2</sub>O<sub>4</sub> powder was mixed with triphenyl phosphine powder in a weight ratio of 10:1, and the mixture was heat treated at 200°C for 1 hour in a sealed reactor. A shell layer with a thickness of 10-20nm was continuously and uniformly coated on the lithiated manganese oxide particles.

#### Example 4:

Spinel LiLi<sub>0.1</sub>Mn<sub>1.9</sub>O<sub>4</sub> was prepared by a solid-state reaction process:

A stoichiometric amount of reagent grade Li<sub>2</sub>CO<sub>3</sub> (commercial battery class, micro-size), MnO<sub>2</sub> (commercial product) were mixed by ball-milling. The mixture were heat treated at 650°C for 5 h in air, cooled and mixed again, and then further calcinated at 900°C for 10 h in air, cooled slowly to 600°C and finally cooled to room temperature.

The resulting Li<sub>1.1</sub>Mn<sub>1.9</sub>O<sub>4</sub> powder was mixed with P<sub>2</sub>O<sub>5</sub> in a weight ratio of 30:1. A heat-treatment was conducted at 600°C in a hermetic reactor for 2 hours. A shell layer with a thickness of 10-20nm was continuously and uniformly coated on the spinel LiLi<sub>0.1</sub>Mn<sub>1.9</sub>O<sub>4</sub> particles.

#### Cell assembling and electrochemical tests:

The electrochemical performances of the spinel LiMn<sub>2</sub>O<sub>4</sub> with P<sub>2</sub>O<sub>5</sub> treatment according to Example 1 and a spinel LiMn<sub>2</sub>O<sub>4</sub> without P<sub>2</sub>O<sub>5</sub> treatment as a control were tested using R2016-type coin cells. The working electrode was prepared by pasting a slurry mixture of 90wt% of the active material, 4wt% of carbon black, 1wt% of KS-6 and 5wt% PVdF1 in NMP solvent on an aluminum foil . After coating the mixture on aluminum foil, the electrode was dried at 120°C in

vacuum for 12 h. The R2016-type coin cell was assembled in a glove box with H<sub>2</sub>O and O<sub>2</sub> less than 1 ppm using 1M LiPF<sub>6</sub> in EC-DMC-EMC3 (1:1:1 by volume) as the electrolyte, the spinel oxide electrode as the positive electrode, and Li metal as the negative electrode. The cycling performances were evaluated by using LAND cycler/Arbin battery testing system to charge/discharge cells in the potential range of 3-4.3 V, with the current density for charge/discharge test and cycling test being 1/3C. The test results are shown in Fig. 3 and Fig. 4.

Fig. 3 is a graph showing comparison of the charge/discharge curves at 60°C of LiMn<sub>2</sub>O<sub>4</sub> with (according to Example 1) and without P<sub>2</sub>O<sub>5</sub> treatment (control). Fig. 4 is graph showing comparison of the cycling stability at 60°C of LiMn<sub>2</sub>O<sub>4</sub> cathode materials with (according to Example 1) and without P<sub>2</sub>O<sub>5</sub> treatment (control).

As shown in Fig. 4, the capacity retention of the treated spinel after 200 cycles was about 82% at 60°C; while the capacity retention of the untreated spinel after 200 cycles was much smaller (about 50%). From Fig. 3 and Fig. 4, it can be seen that the treated spinel LiMn<sub>2</sub>O<sub>4</sub> particles according to the invention exhibit significantly improved cycling stability at elevated temperature of 60°C, while the capacity is reduced only by as little as 8mAh/h, compared to the untreated spinel LiMn<sub>2</sub>O<sub>4</sub>.

What is claimed is:

1. A process for preparing a core-shell structured lithiated manganese oxide, comprising the steps of providing spinel  $\text{LiM}_x\text{Mn}_{2-x}\text{O}_4$  particles, where M is one or more metal ions selected from the group consisting of Li, Mg, Cr, Al, Co, Ni, Zn, Cu, and La, and  $0 \leq x \leq 1$ , as core particles, and subjecting the spinel particles to a heat-treatment with a chemical reagent reactive towards the spinel  $\text{LiM}_x\text{Mn}_{2-x}\text{O}_4$  particles in the form of liquid or gas to form a continuous and uniform shell layer on the surface of the core particles, wherein the shell is not spinel structure.
2. The process according to claim 1, wherein, the spinel  $\text{LiM}_x\text{Mn}_{2-x}\text{O}_4$  particles are prepared by a solid-state reaction of a stoichiometric mixture of a lithium compound, a manganese compound, and, if appropriate, a compound of M by heat treating.
3. The process according to claim 2, wherein, the lithium compound is selected from the group consisting of lithium carbonates, lithium nitrates, lithium hydroxides, and lithium oxides.
4. The process according to claim 2, wherein, the manganese compound is selected from the group consisting of manganese carbonates, manganese nitrates, manganese hydroxides, and manganese oxides.
5. The process according to claim 2, wherein, the compound of M is selected from the group consisting of carbonates, nitrates, hydroxides, and oxides of M.
6. The process according to any one of claims 1 to 5, wherein, the heat-treatment is performed at a temperature of from 100 to 800°C for 0.5~5h.
7. The process according to any one of claims 1 to 6, wherein, the chemical reagent is selected from the group consisting of  $\text{NH}_3$ ,  $\text{P}_2\text{O}_5$ , and triphenyl phosphine.
8. The process according to claim 7, wherein,  $\text{NH}_3$  is used as the chemical reagent, and the heat-treatment is performed at a temperature of from 650 to 750°C for 0.5~5h.
9. The process according to claim 7, wherein,  $\text{P}_2\text{O}_5$  is used as the chemical reagent, and the heat-treatment is performed at a temperature of from 550 to 650°C for 0.5~2h.
10. The process according to claim 7, wherein, triphenyl phosphine is used as the chemical reagent, and the heat-treatment is performed at a temperature of from 150 to 250°C for 0.5~5h.
11. A core-shell structured lithiated manganese oxide prepared by the process according to any one of claims 1 to 10.

12. The core-shell structured lithiated manganese oxide according to claim 11, wherein, the shell has a thickness of 5-20 nm.

13. A cathode material for a lithium ion battery comprising the core-shell structured lithiated manganese oxide according to any one of claims 11 to 12 or prepared by the process according to any one of claims 1 to 10.

14. A lithium ion battery comprising the core-shell structured lithiated manganese oxide according to any one of claims 11 to 12 or prepared by the process according to any one of claims 1 to 10 as a cathode material.

Fig. 1

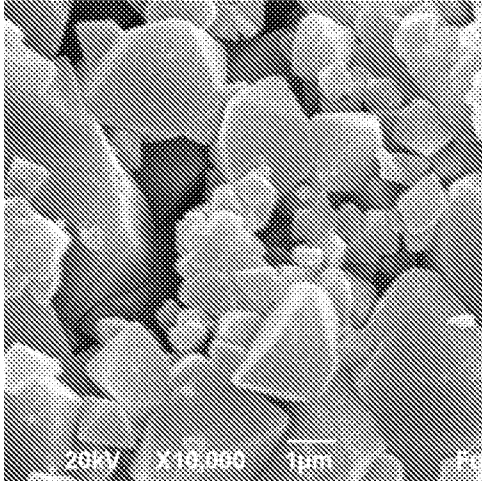


Fig. 2

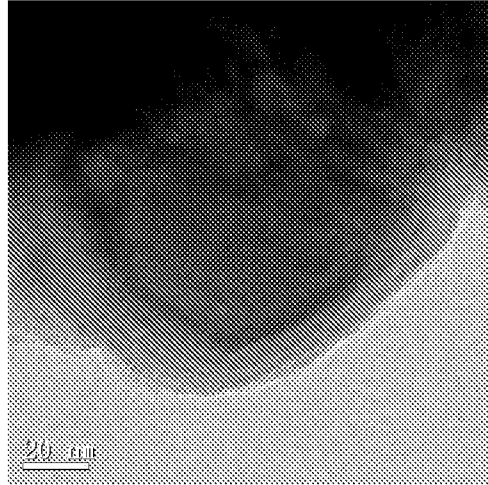


Fig. 3

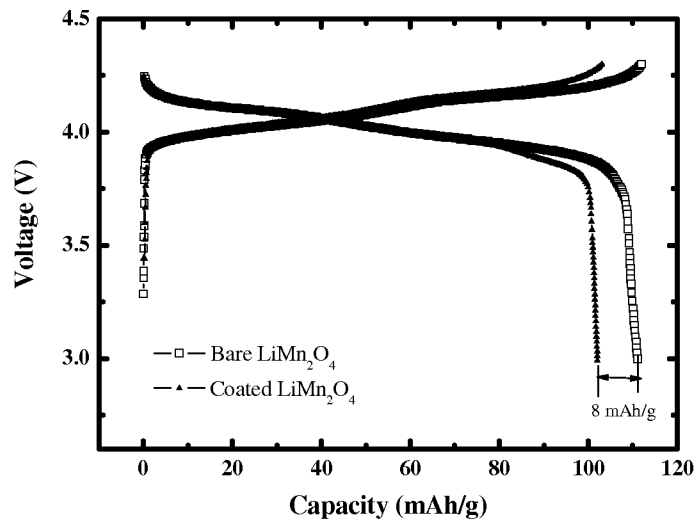
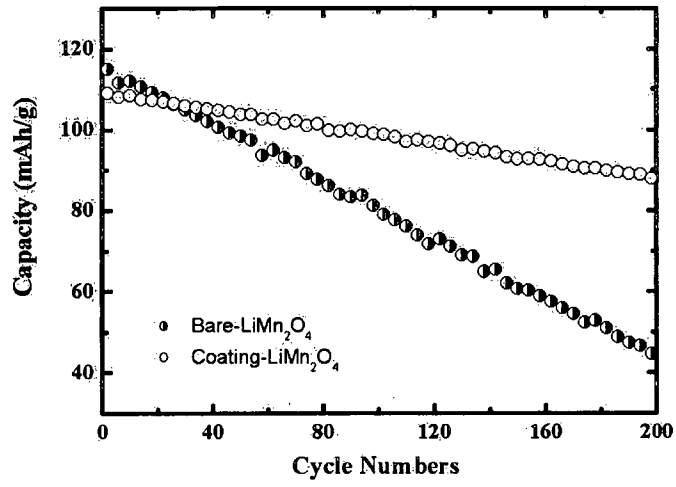


Fig. 4



# INTERNATIONAL SEARCH REPORT

International application No.  
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## A. CLASSIFICATION OF SUBJECT MATTER

See extra sheet

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)

IPC: C01G45/-, C01G1/-, H01M4/-, H01M10/-

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)

WPI, EPODOC, CNPAT, CNKI: lithium, Li, lithiated, manganese, Mn, manganate, core, shell, coat???, gas, liquid, heat???

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US2011/0294006A1(AMINE, Khalil et al.), 01 Dec. 2011 (01.12.2011), description paragraphs [0014]-[0027]	1-6, 8,10-14
Y		7, 9, 11-14
Y	CN101859887A(UNIV. HUAZHONG SCI.&TECHNOLOGY), 13 Oct. 2010 (13.10.2010), description paragraphs [0005]-[0008]	7, 9, 11-14
A	CN101038965A(SHENZHEN BAK BATTERY CO. LTD.), 19 Sep. 2007 (19.09.2007), claims 1-10	1-14
A	CN101740752A(SHENZHEN DYNANONIC CO. LTD.), 16 Jun. 2010 (16.06.2010), claims 1-10	1-14

Further documents are listed in the continuation of Box C.       See patent family annex.

<p>* Special categories of cited documents:</p> <p>“A” document defining the general state of the art which is not considered to be of particular relevance</p> <p>“E” earlier application or patent but published on or after the international filing date</p> <p>“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)</p> <p>“O” document referring to an oral disclosure, use, exhibition or other means</p> <p>“P” document published prior to the international filing date but later than the priority date claimed</p>	<p>“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</p> <p>“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</p> <p>“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</p> <p>“&amp;”document member of the same patent family</p>
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**INTERNATIONAL SEARCH REPORT**  
Information on patent family members

International application No.  
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Patent Documents referred in the Report	Publication Date	Patent Family	Publication Date
US2011/0294006A1	01.12.2011	None	
CN101859887A	13.10.2010	None	
CN101038965A	19.09.2007	CN100547831C	07.10.2009
CN101740752A	16.06.2010	WO2011072547A1	23.06.2011
		CN101740752B	18.01.2012

# INTERNATIONAL SEARCH REPORT

International application No.

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Continuation: A. CLASSIFICATION OF SUBJECT MATTER

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C01G 1/02 (2006.01) i

H01M 4/50 (2006.01) i

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