(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
28 December 2017 (28.12.2017)

WIPO | PCT

(10) International Publication Number
WO 2017/220162 A1

(51) International Patent Classification:
H01M 4/131 (2010.01) *H01M 4/505* (2010.01)
H01M 4/1391 (2010.01) *H01M 10/0525* (2010.01)
H01M 4/38 (2006.01)

(21) International Application Number:
PCT/EP2016/064702

(22) International Filing Date:
24 June 2016 (24.06.2016)

(25) Filing Language: English

(26) Publication Language: English

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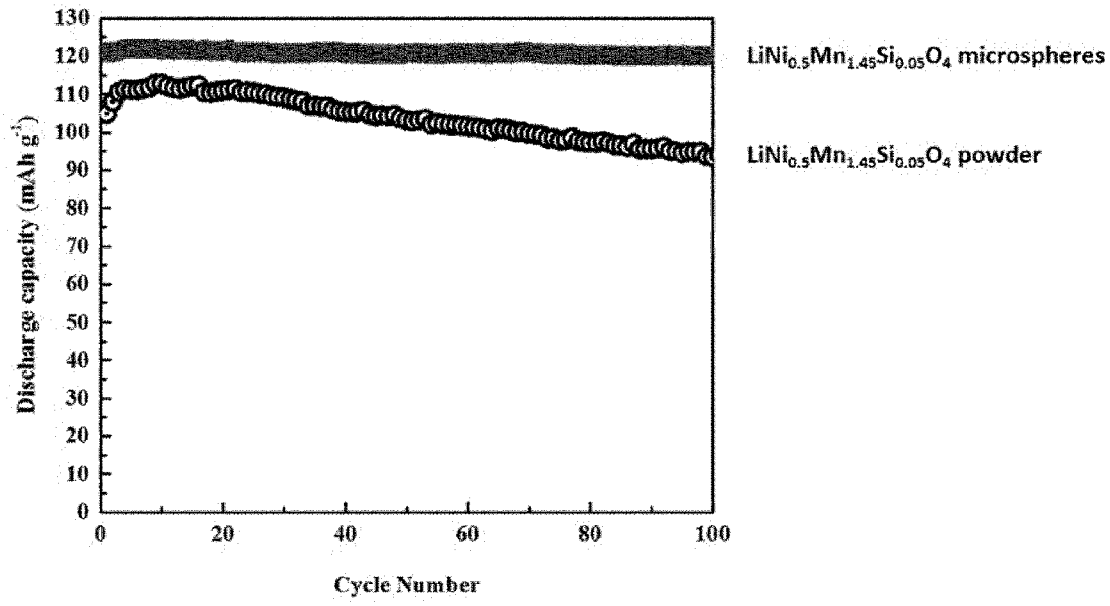
(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP,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

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH,

(54) Title: ELECTRODE MATERIAL, USE OF AN ELECTRODE MATERIAL FOR A LITHIUM-ION-BASED ELECTROCHEMICAL CELL, LITHIUM-ION-BASED ELECTROCHEMICAL CELL

Fig. 5



(57) Abstract: Electrode material, for a lithium-ion-based electrochemical cell, comprising primary particles of a Mn-containing spinel-type metal-oxide selected from the group consisting of spinel-type lithium-nickel-manganese-oxide, spinel-type lithium-manganese-oxide, or mixtures thereof, wherein Mn of the Mn-containing spinel-type metal oxide is partially substituted with a substitution-element selected from the group consisting of Si, Hf, Zr, Fe, Al, V and mixtures thereof and wherein the primary particles are aggregated in order to form secondary particles, the secondary particles having the shape of a microspheres.

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

Published:

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

Title

Electrode material, use of an electrode material for a lithium-ion-based electrochemical cell, lithium-ion-based electrochemical cell

Specification

The invention refers to an electrode material comprising primary particles of a Manganese-containing spinel-type metal-oxide, wherein Manganese of the Manganese-containing spinel-type metal oxide is partially substituted, and wherein the primary particles are aggregated to form secondary particles, with the secondary particles having the shape of microspheres. The invention moreover refers to a use of the electrode material for a lithium-ion-based electrochemical cell and to a lithium-ion-based electrochemical cell.

In order to improve state of the art electrochemical cells, such as lithium-ion-batteries, there is a demand for electrode materials with improved electrochemical performance.

This task is accomplished by an electrode material according to a first aspect of the present invention as provided in claim 1.

According to this the present invention refers to an electrode material, for a lithium-ion-based electrochemical cell, comprising primary particles of a Mn-containing spinel-type metal-oxide selected from the group consisting of

- spinel-type lithium-nickel-manganese-oxide,
- spinel-type lithium-manganese-oxide,
- or mixtures thereof,

wherein Mn of the Mn-containing spinel-type metal oxide is partially substituted with a substitution-element selected from the group consisting of Si, Hf, Zr, Fe, Al, V or

mixtures thereof, and wherein the primary particles are aggregated in order to form secondary particles, the secondary particles having the shape of microspheres.

The electrode material in particular refers to a high voltage electrode material and can be an active electrode material of the positive electrode in a lithium-ion-based electrochemical cell. The term lithium-ion-based electrochemical cell in particular refers to rechargeable lithium-ion-batteries.

The primary particles comprise or consist of the Mn-containing spinel-type metal-oxide. Examples of the Mn-containing spinel-type metal-oxides are $LiNi_{0.5}Mn_{1.5}O_4$ (LNMO) and $LiMn_2O_4$. The primary particles are by preference nanoparticles (i.e. particles with a diameter of at least 1 nm and less than 1000 nm). The primary particles are by preference not of an octahedral geometry, which is in contrast to $LiNi_{0.5}Mn_{1.5}O_4$-spinels and $LiMn_2O_4$-spinels, and can for instance be plate-shaped.

Mn of the Mn-containing spinel-type metal oxide is partially substituted with at least one or exactly one substitution-element selected from the group consisting of Silicon (Si), Hafnium (Hf), Zirconium (Zr), Iron (Fe), Aluminium (Al), Vanadium (V) or mixtures thereof.

The smaller primary particles are aggregated with one another and thus form larger secondary particles, the latter being shaped as microspheres. The secondary particles comprise or consist of the primary particles.

In this context the term “aggregated primary particles” means that the primary particles are permanently attached and connected with each other forming a mechanically and electrochemically stable microsphere as a secondary particle. The inventive electrode materials thus comprise particles (“primary particles”), wherein two or more primary particles

from an independent structure, i.e. a secondary structure, having the shape of microspheres ("secondary particles"). A secondary particle, i.e. a microsphere, can comprise or consist of more than 10, preferably more than 50, or even more than 100 primary particles.

The primary particles are for instance not spherical particles, i.e. they are not hollow.

Microspheres are spherical particles, with diameters in the micrometer range. The microspheres of the present invention are hollow, that is they comprise an internal void and a shell.

State of the art electrode materials based on unaltered (i.e. not substituted) Mn-containing spinel-type metal oxides, are prone to Manganese dissolution under operation conditions in an electrochemical cell.

In contrast to this the inventors of the present invention have found that Mn-containing spinel-type metal oxides, wherein Mn is partially substituted with a substitution-element selected from the group consisting of Si, Hf, Zr, Fe, Al, V or mixtures thereof, are characterized by an improved electrochemical stability.

Without being bound by theory, the enhanced electrochemical stability of the electrode material of the present invention is attributed to the high dissociation energies of the Si-O, Hf-O, Zr-O, Fe-O, Al-O and V-O bonds. Si, Hf, Zr, Fe, Al and V are all characterized by high oxophilicities and as such form very stable bonds with oxygen. The partial substitution of Mn with these elements does not only result in the reduction of the amount of Mn in the lattice of the Mn-containing spinel-type metal oxide, but also increases the oxygen lattice stability. In this way undesirable dissolution of Mn into the electrolyte can be reduced or prevented.

Moreover, state of the art Mn-containing spinel-type metal oxides such as unaltered $LiMn_2O_4$ and $LiNi_{0.5}Mn_{1.5}O_4$, are usually synthesized via simple reactions of stoichiometric amounts of oxides, acetates or nitrates of the respective elements forming the spinel-type metal oxide. These reactions typically result in powders of single crystals having an octahedral geometry. In contrast to this the primary particles of electrode materials of the present invention are by preference not octahedral in their geometry, which is a consequence of the partial substitution of the Mn in the Mn-containing spinel-type metal oxides. Single crystals having an octahedral geometry often degrade due to mechanical stress and high surface energy crystal planes, which are more reactive to the electrolyte. The higher reactivity of octahedral particles is for instance discussed by J. Akimoto et al. (Electrochemical and Solid-State Letters 2005, 8, 7, A361) or by R. Kanno et al. (Journal of The Electrochemical Society, 2007, 154, 11, A1065).

Moreover, the single crystals of state of the art Mn-containing spinel type metal oxides give powders of free particles or randomly aggregated particles. In this way no well-ordered secondary structure (i.e. secondary particles of a well-defined geometry) is achieved in the powder. Such materials undergo significant degradation as a consequence of mechanical stress during charge and discharge when employed as an electrode material in lithium-ion-based electrochemical cells.

In addition, said powders are characterized by comparatively large surface areas, which if exposed to the electrolyte during operation of a lithium-ion-based electrochemical cell, favor undesirable side reactions of the Li-ions at the interface between the electrode material and the electrolyte.

In contrast to this the inventive electrode materials depict a well-ordered secondary structure. Namely, the primary

particles of the inventive material are aggregated to secondary particles, the latter having the structure of microspheres.

The morphology of microspheres is - without being bound by theory – believed to support the electrochemical performance of the inventive electrode material due to the following reasons:

First, microspheres allow minimizing the surface area of the secondary particles. Therefore, the surface electrolyte interface (SEI), i.e. the interface between the electrode and the electrolyte, consumes the least amount of lithium ions and minimizes unwanted side reactions with the electrolyte.

Second, during the charging/discharging cycles, the deformation stress from stretching and shrinking of the spherical particles is axially isotropic. This leads to less micro-strains and therefore less cracks in the particle. The microspheres are thus characterized by a high mechanical and electrochemical stability under operation in an electro-chemical cell.

Third, the microspheres provide isotropic and short lithium ion diffusion pathways between particle bulk and surface. The specific geometry of microspheres compared to microparticles, which are not hollow, is crucial to ensure short diffusion pathways for the lithium-ions in the Mn-containing spinel-type metal-oxide.

The inventors of the present invention have accomplished to provide an electrode material, which combines the beneficial structural effects of microspheres formed from aggregated primary particles with effects related to material composition, i.e. partial substitution of Mn in the Mn-containing spinel-type metal-oxide. Experiments of the inventors demonstrate that respective electrode materials are

characterized by high electrochemical capacities and are furthermore capable of preserving these high capacities better than the case for most comparable electrode materials under cell operation. The electrode materials of the present invention are characterized by high cycle durability. Namely, they depict large capacities and rate capabilities even after extended amounts of charge and discharge cycles. These characteristics are beneficial for an increase in lifetime of electrochemical cells employing the inventive electrode material.

According to a preferred embodiment of the inventive electrode material, the Mn-containing spinel-type metal-oxide or the electrode material as a whole, does not comprise elements different from the elements selected from the group consisting of Li, Ni, Mn, O, Si, Hf, Zr, Fe, Al and V. The present invention is not dependent on further elements commonly used in electrode materials, which are often highly expensive or even toxic.

According to one embodiment of the inventive electrode material, the Mn-containing spinel-type metal-oxide or the electrode material as a whole is free of cobalt (Co). Currently, many positive active materials in automotive lithium ion cells utilize materials such as $LiNi_xMn_yCo_zO_2$ (NMC). These and similar materials comprise cobalt that is associated with environmental issues, noxious effects, and high costs. In contrast to this the electrode materials of the present invention are free of cobalt, which is beneficial with respect to their toxicity and environmental friendliness.

A further embodiment of the inventive electrode material of the present invention utilizes Si as a substitution-element. The inventors of the present invention have observed experimentally that electrode materials, wherein the substitution-element is Si have high electrochemical

capacities and rate capabilities. The cycle durability of these materials is excellent. The enhanced electrochemical performance might be attributed to the high Si-O bond dissociation energy of 798kJmol^{-1} at 298K, which is far beyond of the Mn-O and Ni-O bond (being 402 kJmol^{-1} and 392 kJmol^{-1}) and therefore assumed to enlarge the structural and chemical stability when silicon is incorporated into an oxygen rich crystal lattice and might suppress manganese dissolution.

According to one embodiment of the present invention the content of the substitution-element in the Mn-containing spinel-type metal-oxide is in the range of 0.01 to 0.5 moles per 1 mole of the Mn-containing spinel-type metal-oxide, preferably in the range from 0.01 to 0.2, more preferably in the range from 0.02 to 0.15, in particular in the range from 0.02 to 0.1 and most preferably in the range from 0.05 to 0.1 moles per 1 mole of the Mn-containing spinel-type metal-oxide. In these ranges unexpectedly high capacities and rate capabilities are achieved in combination with an excellent cycle durability.

In a further embodiment of the present invention the primary particles are not characterized by an octahedral shape. This is in contrast to unsubstituted LNMO powder, wherein the primary particles comprise an octahedral shape. Single crystals having an octahedral geometry often degrade due to mechanical stress and high energy surface planes. In contrast to this the primary particles of the present invention are for instance plate-shaped primary particles. Nonoctahedral primary particles, such as plate-shaped primary particles, show a reduced cation ordering compared to octahedra. In spinel-type lithium-nickel-manganese-oxides this results in minimizing isolated domains of active Ni redox centers separated by inactive Mn^{4-} ions and therefore the internal resistance is decreased. The non-octahedral structure of the primary particles is - without being bound by theory - at

least in part caused by the aggregation of the primary particles to form microspheres. Moreover, an increased degree of substitution of Mn appears to further facilitate the formation of flat, plate-shaped particles, which do not comprise an octahedral geometry.

According to one embodiment of the present invention the primary particles do not have a spherical shape. Namely, the primary particles preferably are not round and not hollow.

According to one embodiment of the present invention the primary particles comprise edges and flat surfaces.

According to one embodiment the primary particles are nanoparticles. It is preferred if the average diameter of the primary particles is in the range from 20 to 400 nm, preferably in the range from 50 to 250 nm, more preferably in the range from 75 to 125 nm. In the case of primary particles, which are of an irregular shape the average diameter is calculated as the arithmetic average of the longest and smallest distance from one to the other side of the particle.

In a preferred embodiment of the inventive electrode material the microspheres have an average outer-diameter (d50) in the range from 1 µm to 50 µm, preferably from 2 µm to 15 µm. Microspheres with an average outer-diameter in these ranges are adapted to the requirements at the electrode of an electrochemical cell. They have good mechanical properties for forming electrode materials for electrochemical cells.

Furthermore, according to an embodiment of the present invention, the microspheres have an average inner-diameter which corresponds to 0.6 to 0.99 times the outer-diameter of the microspheres.

Microspheres wherein the ratio of the inner- and outer-diameter is in the depicted range are characterized by good mechanical and electrochemical stabilities. Moreover, respective geometries result in very beneficial conditions for the diffusion of Li-ions. The larger the inner-diameter compared to the outer-diameter the shorter is the average length of the diffusion path, for the lithium-ions and the storage capability of the Mn-containing spinel type metal-oxide is thus used more efficiently. Furthermore this is beneficial for the rate capability as the incorporation and release of Li-ions can occur faster. However, if the inner-diameter becomes very large compared to the outer-diameter, i.e. the shell of the microsphere becomes very thin, the stability of the microspheres may decrease.

According to one embodiment the microspheres have a shell with an average thickness of not less than 50 nm and not more than 5 µm, preferably not less than 100 nm and not more than 2 µm, more preferably not less than 250 nm and not more than 1 µm. In these ranges good diffusion properties for the Li-ions and reasonable mechanical stabilities of the microspheres can be achieved.

According to an embodiment of the inventive electrode material the Mn-containing spinel-type metal-oxide has the general formula:

$$Li_aNi_bMn_{c-n}A_nO_{4-d}$$ with

- $0.9 < a < 1.1$
- $0 \leq b \leq 0.6$
- $1.4 \leq c \leq 2.0$
- $0 < n \leq 0.5$
- $0 \leq d$,

wherein A is the substitution element, being selected from the group consisting of Si, Hf, Zr, Fe, Al, V or mixtures thereof.

A certain oxygen non-stoichiometry, in particular an oxygen deficiency, can be present in the material (i.e. $0 < d$). This is likely compensated by the presence of a certain amount of Mn^{3+} ions (instead of Mn^{4+} ions) in the lattice. However it is preferred if d is 0.

According to a further development of the above explained embodiment a is 1.0, b is 0.0 and c is 2.0. In this case the general formula can be written as follows:

$$LiMn_{2-n}A_nO_{4-d}$$

It is however preferred that a is 1.0, b is 0.5 and c is 1.5. In this preferred embodiment of the present invention the Mn-containing spinel-type metal-oxide has the general formula:

$$LiNi_{0.5}Mn_{1.5-n}A_nO_{4-d}$$

$LiNi_{0.5}Mn_{1.5-n}A_nO_{4-d}$ are high voltage electrode spinel materials characterized by excellent electrochemical performances in particular with respect to capacity, rate capability and cycle durability.

In general n is in the range $0.001 \leq n \leq 0.5$. If n is smaller than 0.001 the beneficial effects from the substitution of Mn with the substitution element A become very weak. If n is larger than 0.5 the electrical capacity will be very low. High Si contents moreover, can reduce the electric conductivity of the particles and decrease the electrochemical performance, as Si is an electro-inactive compound.

Preferably n is in the range $0.01 \leq n \leq 0.2$. In this range both very good electrical capacities and cycle durabilities are achieved. The electrical performance further improves if n is in the range $0.02 \leq n \leq 0.15$. Even more preferably n is in the range $0.02 \leq n \leq 0.1$. Most preferably n is in the range $0.05 \leq n \leq 0.1$. In these ranges unexpectedly high capacities, rate capabilities are achieved and maintained on a very high level despite of extended charge and discharge

cycles under operation in a lithium-ion-based electrochemical cell.

A second aspect of the present invention refers to the use of the electrode material according to the inventive electrode material as an active material of a lithium-ion-based electrochemical cell. As depicted above the inventive electrode material is in particular suitable for applications in lithium-ion-based electrochemical cells.

A third aspect of the present invention refers to a lithium-ion-based electrochemical cell, comprising

- a first electrode,
- a second electrode, and
- an electrolyte,

wherein the electrolyte is conductively arranged between the first and second electrode, and
wherein the first electrode comprises the inventive electrode material according to the first aspect of the present invention.

The lithium-ion-based electrochemical cell be preference is a rechargeable lithium-ion-battery. The first electrode in particular refers to the positive electrode (i.e. cathode during discharge), while the second electrode in particular refers to the negative electrode (anode during discharge) of the electrochemical cell.

The inventive lithium-ion-based electrochemical cell preferably comprises a separator, which can be arranged between the first and second electrode. The separator can be a porous polymer-membrane such as polyethylene (PE), polypropylene (PP) or the like.
The electrolyte can be any electrolyte as commonly used in rechargeable lithium-ion-batteries. The electrolyte in particular can be selected from the group consisting of carbonates with a conducting salt. For instance dimethyl-

carbonate (DMC), diethyl-carbonate (DEC), ethylene-carbonate (EC), ethyl-methyl-carbonate (EMC) or mixtures thereof.
It is preferred that the electrolyte comprises a conducting salt. The conducting salt for instance can be selected from the group consisting of $LiPF_6$, $LiAsF_6$, $LiBF_4$, LiTFSI, LIBOB or mixtures thereof.

For the second electrode standard materials, as commonly employed in rechargeable lithium-ion-batteries, can be used. The active material of the second electrode for instance can be graphite.
In a preferred embodiment the first electrode comprises the inventive electrode material as the active material.

The first and/or second electrode can also comprise further components such as conductive additives and binders. Common conductive additives are conductive carbon materials such as soot, carbon blacks (e.g. Ketjen black, Acetylene black) or carbon-nanotubes (CNTs). Examples for binders are Polyvinylidene fluoride (PVDF) or CMC/SBR-binders (CMC = carboxymethyl cellulose, SBR = styrene-butadiene-rubber).
According to a fourth aspect the present invention also refers to a method for synthesizing an electrode material according to the first aspect of the present invention, comprising at least the steps of

a) providing:
   - Mn-containing microspheres,
   - a Ni-containing starting material,
   - a Li-containing starting material and
   - a starting material containing a the substitution-element
b) mixing the porous MnO_2 microspheres and the starting materials of step a) to obtain a mixture
c) calcinating the mixture to give the electrode material.

According to a preferred embodiment the Mn-containing microspheres are MnO_2 microspheres, for example porous MnO_2 microspheres.

According to a further preferred embodiment the MnO_2 microspheres are prepared by thermal treatment of $MnCO_3$ microspheres. The thermal treatment for instance can be performed at a temperature of above 300 °C, for instance at 400°C.

The Ni-containing starting material can be a nitrate, oxide, hydroxide or acetate of nickel, in particular a Ni(III)-nitrate.

The Li-containing starting material can be a nitrate, oxide, hydroxide or acetate of lithium, in particular Li(I)-hydroxide.

The substitution-element containing material for instance can be a Si-containing starting material such as $Si(OC_2H_5)_4$ (=TEOS, i.e. tetraethyl-orthosilicate), $Si(OCH_3)_4$ (=TMOS, i.e. tetramethyl-orthosilicate), $Si(OC_3H_7)_4$ (i.e. tetra-n-propyl-orthosilicate) or $Si(OC_3H_7)_4$ (i.e. tetra-iso-propyl-orthosilicate).

The substitution-element containing material also can be a Hf-containing starting material such as HfO_2, HfX_4, wherein X is a halogen such as F, Cl, Br, I, in particular Cl.

The substitution-element containing material also can be a Zr-containing starting material such as $Zr(C_5H_7O_2)_4$, (=i.e. zirconium(IV)-acetyl-acetonate), zirconium(IV)-ethoxide, zirconium-hydroxide, zirconium-acrylate, etc.

The substitution-element containing material also can be a Al-containing starting material such as Aluminum(III) Nitrate-9-Hydrate $Al(NO_3)_3*9H_2O$.

The substitution-element containing material also can be a Fe-containing starting material such as Iron(III) Nitrate nonahydrate $Fe(NO_3)_3*9H_2O$.

The substitution-element containing material also can be a V-containing starting material such as vanadium acetyl acetonate.

According to a preferred embodiment the mixing step b) is performed in the presence of an alcohol such as ethanol, wherein the starting materials and MnO_2 microspheres are dispersed and stirred at room temperature until the alcohol is evaporated.

According to a preferred embodiment a grinding step is performed after step b) but before step c).

Moreover, according to a further embodiment the calcination step c) is performed at a temperature between 500 and 1000°C, preferably at 700-900°C, for instance at 800°C.

The calcination step c) can take at least 1 hour, preferably at least 10 hours, for instance between 15 and 25 hours.

In the following the present invention is explained in more detail on the basis of Figures and Examples.

Figure 1 shows FESEM images (i.e. Field Emission Scanning Electron Microscopy images) of $LiNi_{0.5}Mn_{1.5}O_4$ (1A, 1B),

$LiNi_{0.5}Mn_{1.45}Si_{0.05}O_4$ (1C), $LiNi_{0.5}Mn_{1.4}Si_{0.10}O_4$ (1D), $LiNi_{0.5}Mn_{1.35}Si_{0.15}O_4$ (1E) and $LiNi_{0.5}Mn_{1.3}Si_{0.20}O_4$ (1F).

Figure 2 shows XRD patterns of $LiNi_{0.5}Mn_{1.5}O_4$, $LiNi_{0.5}Mn_{1.45}Si_{0.05}O_4$, $LiNi_{0.5}Mn_{1.4}Si_{0.10}O_4$, $LiNi_{0.5}Mn_{1.35}Si_{0.15}O_4$ and $LiNi_{0.5}Mn_{1.3}Si_{0.20}O_4$.

Figure 3 depicts the dependency of the lattice constant in Angstrom versus the amount n of the substitution-element Si.

Figure 4 shows the electrochemical performance of $LiNi_{0.5}Mn_{1.5}O_4$, $LiNi_{0.5}Mn_{1.45}Si_{0.05}O_4$, $LiNi_{0.5}Mn_{1.4}Si_{0.10}O_4$, $LiNi_{0.5}Mn_{1.35}Si_{0.15}O_4$ and $LiNi_{0.5}Mn_{1.3}Si_{0.20}O_4$, at room temperature, at 1C rate.

Figure 5 compares the electrochemical performance of $LiNi_{0.5}Mn_{1.45}Si_{0.05}O_4$-powder with $LiNi_{0.5}Mn_{1.45}Si_{0.05}O_4$-microspheres.

The morphology of the inventive materials was studied with high-resolution field-emission scanning electron microscopy (FE-SEM: JEOL JSM7600F) at an accelerating voltage of 5kV. The samples were mounted on metal stubs using conductive double-sided carbon tape, and a thin layer of platinum was sputtered on the sample using JEOL JFC-1200 prior to scanning. Specifically **Figure 1** shows FESEM-images of not substituted $LiNi_{0.5}Mn_{1.5}O_4$ materials (Figures 1A and 1B) and inventive materials (Figures 1C to 1F), wherein Mn is partially substituted with Si. The scale of the images (1A), (1C), (1E), (1F) is 1 µm and for images (B) and (D) is 100 nm. All samples are composed of uniform microspheres with diameters in the range from 1 to 5 µm. The microspheres of the present invention are formed from primary particles, which are aggregated into secondary particles having a

microsphere structure. The primary particles have a non-octahedral geometry. The geometry can rather be described as a plate-shaped geometry, i.e. the primary particles comprise edges and flat surfaces. The particles can be characterized as flat particles. The size of the primary particles is approximately 100 nm in diameter. The formation of nanoplates on the surface of the spherical particles is more pronounced for higher silicon contents, whereas in general no sufficient visible change in morphology is detected by substitution of Mn with Si, indicating that the applied templating approach based on MnO_2 is a useful strategy to preserve the spherical morphology when incorporating the substitution-element.

X-ray diffraction (XRD) was measured using a Bruker Advanced D8 XRD diffractometer operating at 40kV, $Cu_{K\alpha}$ radiation over the angular range 10 to 80° 2θ at 0.02° incremental step. The XRD data were characterized using the crystallographic software TOPAS 3. The XRD patterns of $LiNi_{0.5}Mn_{1.5}O_4$ microspheres and $LiNi_{0.5}Mn_{1.5}O_4$ microspheres, wherein Mn is partially substituted with Si according to the present invention, are shown in **Figure 2**. Sequence and sharpness of the peaks indicate a cubic spinel crystal structure (either Fd-3m or $P4_332$ space group) and well-crystalized materials. Minor residues peaks centered at 2θ = 37.51°, 43.62°, and 63.43° are observed that can be attributed to rock salt phase impurities such as Ni_xO, $Li_xNi_{1-x}O$ or $Li_xNi_yMn_zO$. Rock salt phase impurities are typically associated with Mn^{3+} ions and disordered cubic Fd-3m space group. It needs to be emphasized that the disordered Fd-3m phase is insufficiently stoichiometric, the correct formula of the here discussed materials should be $LiNi_{0.5}Mn_{1.5-n}Si_nO_{4-d}$ in which d indicates the oxygen deficiency, although the $LiNi_{0.5}Mn_{1.5-n}Si_nO_4$

designation is used for the examples depicted in the specification.

Figure 3 depicts the dependency of the lattice constant a in Angstrom versus the amount n of the substitution-element Si in more detail. The lattice parameters a in Angstrom (Å) are calculated from Rietvield analysis and found to be 8.168(1)Å for $LiNi_{0.5}Mn_{1.5}O_4$ (=LNMO), while for inventive samples - with Mn being partially substituted with small amounts of Si - slightly enlarged lattice constants of 8.175(6)Å ($LiNi_{0.5}Mn_{1.45}Si_{0.05}O_4$), 8.182(5)Å ($LiNi_{0.5}Mn_{1.4}Si_{0.10}O_4$) are observed. However, larger amounts of Si result in a decline in lattice constant. 8.172(7)Å is observed for $LiNi_{0.5}Mn_{1.35}Si_{0.15}O_4$, and 8.171(1)Å is observed for $LiNi_{0.5}Mn_{1.3}Si_{0.20}O_4$. The increase of the lattice constant/periodic repeating unit is thus largest in the range between n = 0.05 and n = 0.15. This might be due to an increased amount of Mn^{3+} ions, which exhibit a larger ionic radius than Mn^{4+} ions, 64.5pm and 53pm, respectively.

In general, $LiNi_{0.5}Mn_{1.5}O_4$ crystallizes in two different cubic space groups depending on the distribution of manganese and nickel in the crystal lattice. For $P4_332$ nickel and manganese occupy the 4a and 12d sites, respectively (ordered structure). For Fd-3m nickel and manganese ions are randomly distributed in the octahedral 16d sites (disordered structure). A slight oxygen non-stoichiometry is found for the Fd-3m structure, which is likely compensated by the presence of a sufficient amount of Mn^{3+}. An appropriate amount of Mn^{3+} may enhance the electrochemical performance. The electrochemical active manganese species participates in the redox reaction, which supports compensation of capacity loss caused by substitution of nickel by other elements.

Furthermore, Mn^{3+} ions support the electron hopping conduction mechanism by acting as internal carriers according to $Ni^{2+/3+} \rightarrow Mn^{4+} \rightarrow Ni^{3+/4+}$ as well as $Ni^{2+/3+} \rightarrow Mn^{4+} \leftrightarrow Mn^{3+} \rightarrow Ni^{3+/4+}$. These two additional pathways are not present at the $P4_332$ polymorph leading to comparatively faster charge transfer in the Fd-3m system. Also, it is assumed that the disordered Fd-3m phase supports the electrochemical performance by its comparatively higher conductivity for electrons and lithium ions. Moreover, the disordered occupancy of nickel and manganese is assumed to decrease the internal resistance since $Ni^{2+/3+/4+}$ electrochemically active centers isolated by inactive Mn^{4+} become accessible.

The properties of the samples was characterized by performing electrochemical experiments. For this purpose a composite cathode was prepared by mixing active material ($LiNi_{0.5}Mn_{1.5-n}Si_nO_4$), conducting additive (Timcal, Super C65) and PVDF binder (Kynar 2801) (70:20:10), using *N*-methyl pyrrolidone (NMP, Sigma Aldrich) as solvent. The resulting slurry was coated on Al foil (20µm in thickness, Targray) using doctor blade technique and subsequently dried in an oven at 80°C. The coated foils were pressed between stainless steel twin rollers to ensure good adhesion and punched into circular discs of 16 mm in diameter. Counter electrode lithium foil (~0.59 mm thick, Hohsen Corporation, Japan) of the same diameter was used for cell fabrication. The test cells were fabricated in CR2016 coin cell electrode in an argon-filled glovebox (H_2O, O_2 < 0.1ppm, Mbraun, Unilab, USA). LP50 electrolyte (Charlston Technologies PTE LTD, 1M $LiPF_6$ solution in ethylene carbonate (EC)-ethyl methyl carbonate (EMC) (1:1 Gew.%/Gew.%) and separator (Celgard 2400) were used for cell assembly. The electrochemical tests of the cells were conducted in an automatic galvanostatic charge-

discharge unit, battery cycler (BTS XWJ, Neware Tech. Co.), between 3.0V to 5.0V at room temperature at a current density of 1C based on cell configuration. Some results with respect to the electrochemical characterization are depicted in Figures 4 and 5.

Figure 4 shows the cycling performance of $LiNi_{0.5}Mn_{1.5}O_4$, $LiNi_{0.5}Mn_{1.45}Si_{0.05}O_4$, $LiNi_{0.5}Mn_{1.4}Si_{0.10}O_4$, $LiNi_{0.5}Mn_{1.35}Si_{0.15}O_4$ and $LiNi_{0.5}Mn_{1.3}Si_{0.20}O_4$, at room temperature, at 1C rate. The sample with the silicon content of 0.05 moles and the pristine (i.e. not-substituted) $LiNi_{0.5}Mn_{1.5}O_4$ material show comparable behavior in terms of capacities in the range of $120mAhg^{-1}$ and high stabilities until cycle number 40, where for the pristine $LiNi_{0.5}Mn_{1.5}O_4$ sample the capacity begins to fade. In general, all silicon-substituted samples exhibit superior cycling stability over pristine $LiNi_{0.5}Mn_{1.5}O_4$, supporting the theory that silicon stabilizes an oxygen rich crystal lattice associated with enhanced electrochemical performance.

Figure 5 compares the electrochemical performance of $LiNi_{0.5}Mn_{1.45}Si_{0.05}O_4$-powder with $LiNi_{0.5}Mn_{1.45}Si_{0.05}O_4$-microspheres. It is evident from Figure 5 that the electrochemical performance against Li/Li^+, is superior for $LiNi_{0.5}Mn_{1.45}Si_{0.05}O_4$-microspheres compared to $LiNi_{0.5}Mn_{1.45}Si_{0.05}O_4$-powder. The microsphere structure thus evidently results in improved capacities and cycling durabilities over powders, wherein no microspheres are present.

Synthesis:

In the following the synthesis of inventive electrode materials is illustrated for the example of Si-substituted $LiNi_{0.5}Mn_{1.5}O_4$:

$LiNi_{0.5}Mn_{1.5}O_4$, $LiNi_{0.5}Mn_{1.45}Si_{0.05}O_4$, $LiNi_{0.5}Mn_{1.4}Si_{0.10}O_4$, $LiNi_{0.5}Mn_{1.35}Si_{0.15}O_4$ and $LiNi_{0.5}Mn_{1.3}Si_{0.20}O_4$ were obtained using the following starting materials:

Manganese (II) nitrate tetrahydrate ($(MnN_2O_6*4H_2O)$ Sigma Aldrich 97%), Ammonium bicarbonate ((NH_4HCO_3) Sigma Aldrich 99.5%), Nickel (II) Nitrate hexahydrate ($(Ni(NO_3)_2*6H_2O)$ Alfa Aeser 97%), Lithium hydroxide monohydrate ($(LiOH*H_2O)$ Sigma Aldrich >99.5%) and Tetraethyl orthosilicate (TEOS, $Si(OC_2H_5)_4$) Sigma Aldrich 99.99%).
The synthesis was performed as follows:

$LiNi_{0.5}Mn_{1.5}O_4$ wherein Mn is substituted with Si, with microsphere morphology, were synthesized via a templating approach based on MnO_2 microspheres. MnO_2 was obtained by a co-precipitation method followed by thermal decomposition as discussed elsewhere (Zhou *et al.* Angew. Chemie – Int. Ed., Vol. 51, no. 1, pp. 239-241, 2012). 7.5mmol of $MnN_2O_6*4H_2O$ and 75mmol of NH_4HCO_3 were separately dissolved in 525mL of distilled water. 52.5mL of ethanol and the NH_4HCO_3 solution were then added to the $MnN_2O_6*4H_2O$ solution in sequence under stirring. The mixture was stirred for 3h at room temperature and centrifuged. The sample was then washed with water and ethanol three times each. The as-obtained $MnCO_3$ microspheres were dried at 80°C. The porous MnO_2 microspheres were synthesized by thermal decomposition of the $MnCO_3$ microspheres at 400°C for 10 hours. To obtain

$LiNi_{0.5}Mn_{1.5-n}Si_nO_4$ microspheres, 15mmol of MnO_2 microspheres, 5mmol of $Ni(NO_3)_2*6H_2O$, 10.4mmol of $LiOH*H_2O$ were dispersed in 15mL of absolute ethanol, stoichiometric amounts of TEOS as a Si-source, were added into the mixture. The Si concentration was varied from 0.05 - 0.2moles. The ethanol was evaporated slowly at room temperature under stirring. The mixture obtained was ground manually for 10min and then calcined at 800°C for 20 hours in air.

The synthesis of respective Mn-containing spinel-type metal-oxides, such as $LiNi_{0.5}Mn_{1.5}O_4$, wherein Mn is partially substituted with further elements such as Hf, Zr, Fe, Al, V can be performed in the same way. Suitable sources for Hf, Zr, Fe, Al, V as depicted above when describing the fourth aspect of the present invention.

Example for a lithium-ion-based electrochemical cell:

An example for a lithium-ion-based electrochemical cell according to the third aspect of the present invention is given in the following (mass% refer to the mass of the complete electrode). The example refers to a rechargeable lithium-ion-battery comprising the following parts:

First electrode:

- 92 mass% $LiNi_{0,5}Mn_{1,45}Si_{0.05}O_4$ (active material);
- 8 mass% Carbon black (conductive additive);
- 8 mass% PVDF (binder).

Second electrode:

- 96 mass% graphite
- 1 mass% Carbon black (conductive additive);
- 3 mass% PVDF (binder).

Separator: - Celgard 2400

Electrolyte: - EC:EMC-mixture (1:1 wt.%);

Conducting salt: - 1M $LiPF_6$

The invention is not restricted by the examples given in the specification. The invention comprises any feature or combination of features described in the specification and claims, even if not explicitly depicted in this specific combination.

Claims

1. Electrode material, for a Lithium-ion-based electrochemical cell,
comprising primary particles of a Mn-containing spinel-type metal-oxide selected from the group consisting of
- spinel-type lithium-nickel-manganese-oxide,
- spinel-type lithium-manganese-oxide,
- or mixtures thereof,
wherein Mn of the Mn-containing spinel-type metal oxide is partially substituted with a substitution-element selected from the group consisting of Si, Hf, Zr, Fe, Al, V and mixtures thereof,
and wherein the primary particles are aggregated in order to form secondary particles, the secondary particles having the shape of microspheres.

2. Electrode material, according to the preceding claim, wherein the substitution-element is Si.

3. Electrode material, according to any of the preceding claims, wherein the content of the substitution-element per 1 mol of the Mn-containing spinel type metal-oxide is in the range from 0.01 to 0.5 moles, preferably in the range from 0.05 to 0.1 moles.

4. Electrode material, according to any of the preceding claims, wherein the primary particles are nanoparticles, which do not have an octahedral geometry.

5. Electrode material according to any of the preceding claims, wherein the microspheres have an average outer-diameter in the range from 1 µm to 50 µm, preferably from 2 µm to 15 µm.

6. Electrode material according to any of the preceding claims, wherein the microspheres have an average inner-

diameter which corresponds to 0.6 to 0.99 times the outer-diameter.

7. Electrode material, according to any of the preceding claims, wherein the Mn-containing spinel-type metal-oxide has the general formula:

$Li_aNi_bMn_{c-n}A_nO_{4-d}$ with

- $0.9 < a < 1.1$
- $0 \leq b \leq 0.6$
- $1.4 \leq c \leq 2.0$
- $0 < n \leq 0.5$
- $0 \leq d$,

wherein A is the substitution-element, being selected from the group consisting of Si, Hf, Zr, Fe, Al, V and mixtures thereof.

8. Electrode material according to the preceding claim, with a = 1.0, b = 0.5 and c = 1.5.

9. Electrode material according to claim 7, with a = 1.0, b = 0.0 and c = 2.0.

10. Electrode material according to any of claims 7-9, with $0.001 \leq n \leq 0.5$, preferably $0.05 \leq n \leq 0.1$.

11. Use of the electrode material according to any of claims 1-10 as an active material of a lithium-ion-based electrochemical cell.

12. Lithium-ion-based electrochemical cell, comprising

- a first electrode,
- a second electrode, and
- an electrolyte,

wherein the electrolyte is conductively arranged between the first and second electrode, and

wherein the first electrode comprises the electrode material according to any of claims 1-10 as an active material.

13. Method for synthesizing an electrode material according to any of claims 1-10, comprising at least the steps of

a) providing:
   - Mn-containing microspheres,
   - a Ni-containing starting material,
   - a Li-containing starting material and
   - a starting material containing the substitution-element

b) mixing the porous MnO_2 microspheres and the starting materials of step a) to obtain a mixture

c) calcinating the mixture to give the electrode material.

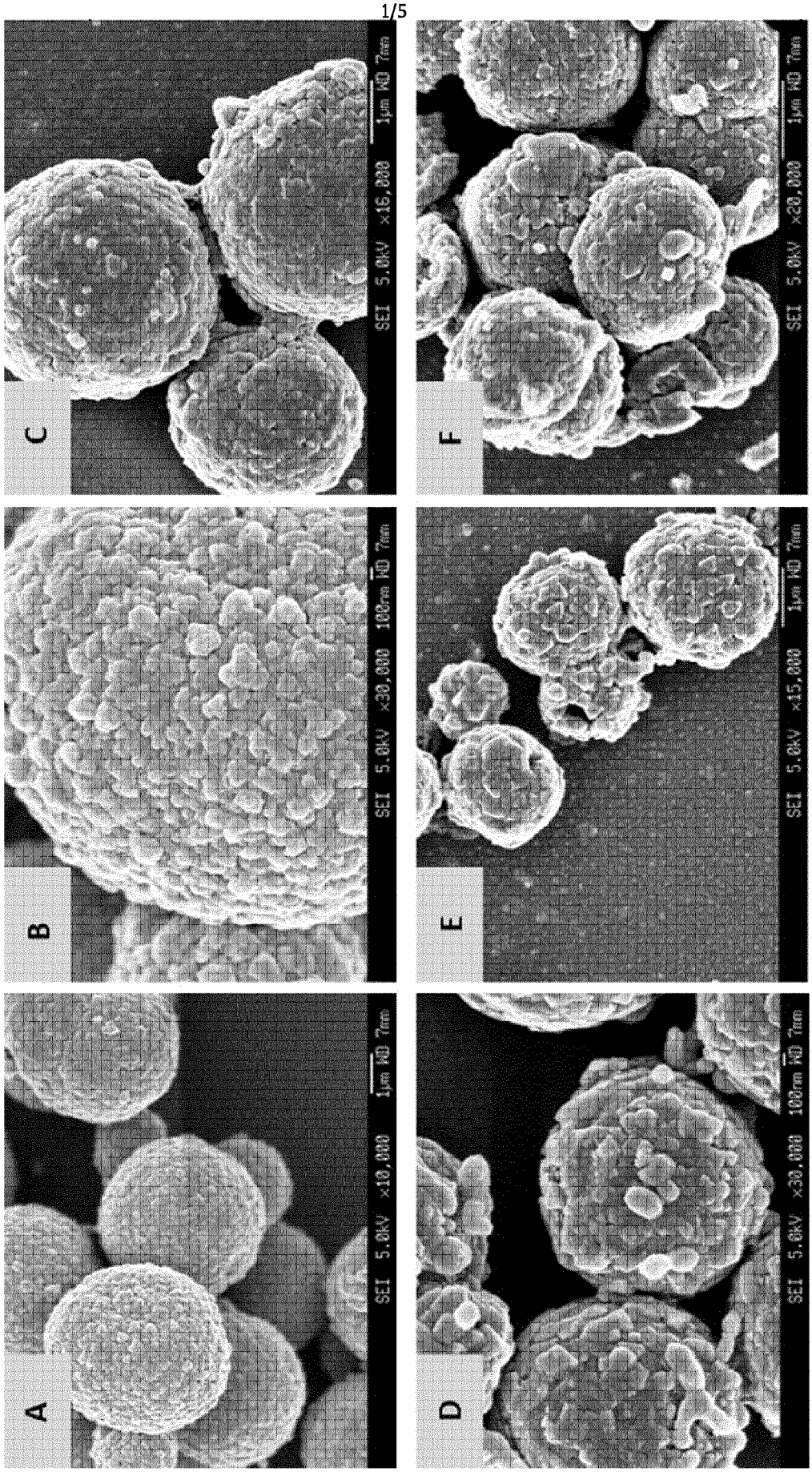
A
SEI 5.0kV ×10,000 1μm WD 7mm
B
SEI 5.0kV ×30,000 100nm WD 7mm
C
SEI 5.0kV ×16,000 1μm WD 7mm
D
SEI 5.0kV ×30,000 100nm WD 7mm
E
SEI 5.0kV ×15,000 1μm WD 7mm
F
SEI 5.0kV ×20,000 1μm WD 7mm

Fig. 1

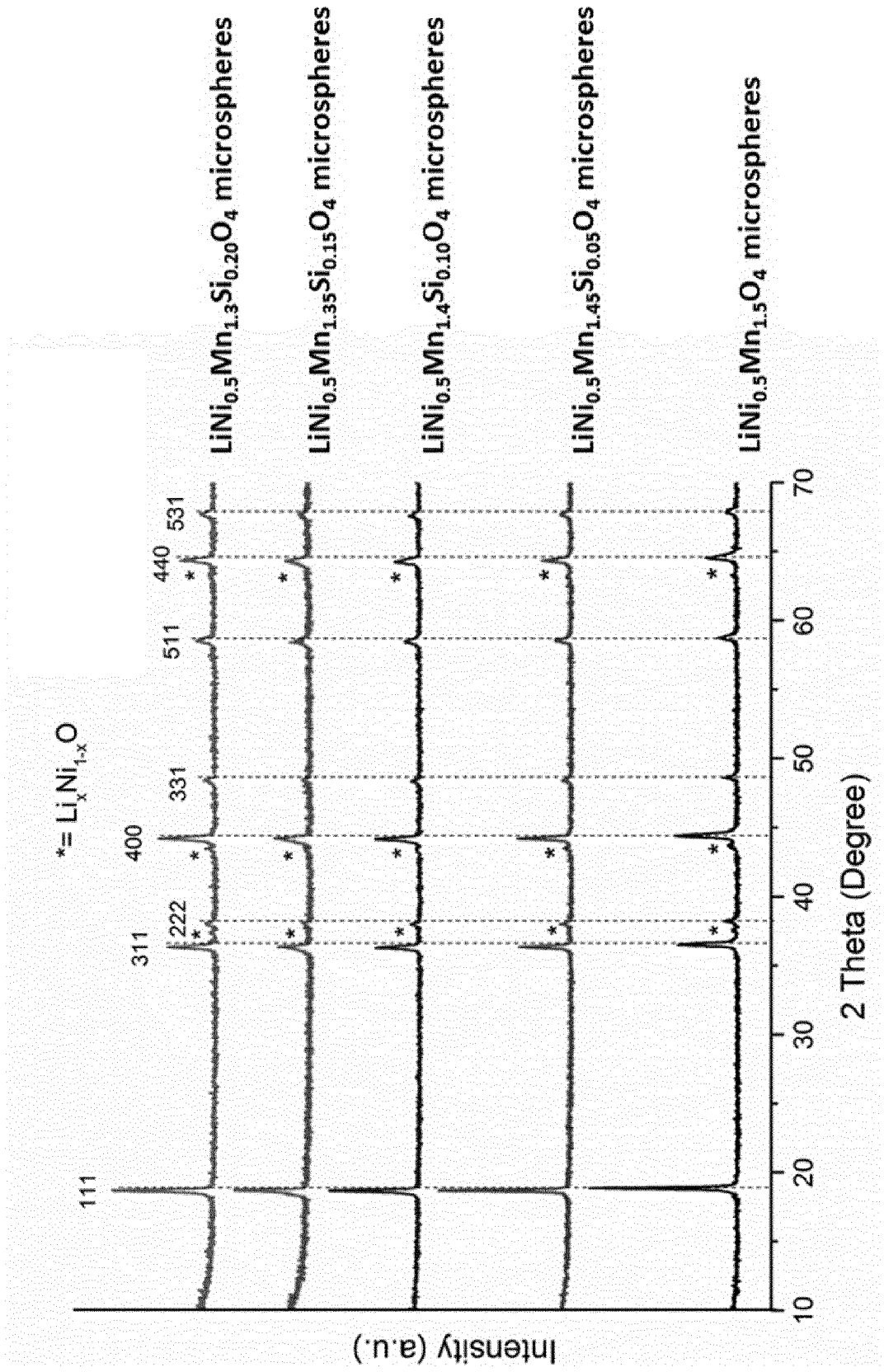
LiNi0.5Mn1.3Si0.20O4 microspheres
LiNi0.5Mn1.35Si0.15O4 microspheres
LiNi0.5Mn1.4Si0.10O4 microspheres
LiNi0.5Mn1.45Si0.05O4 microspheres
LiNi0.5Mn1.5O4 microspheres
*= LixNi1-xO
111
311
222
400
331
511
440
531
Intensity (a.u.)
2 Theta (Degree)
10
20
30
40
50
60
70

Fig. 2

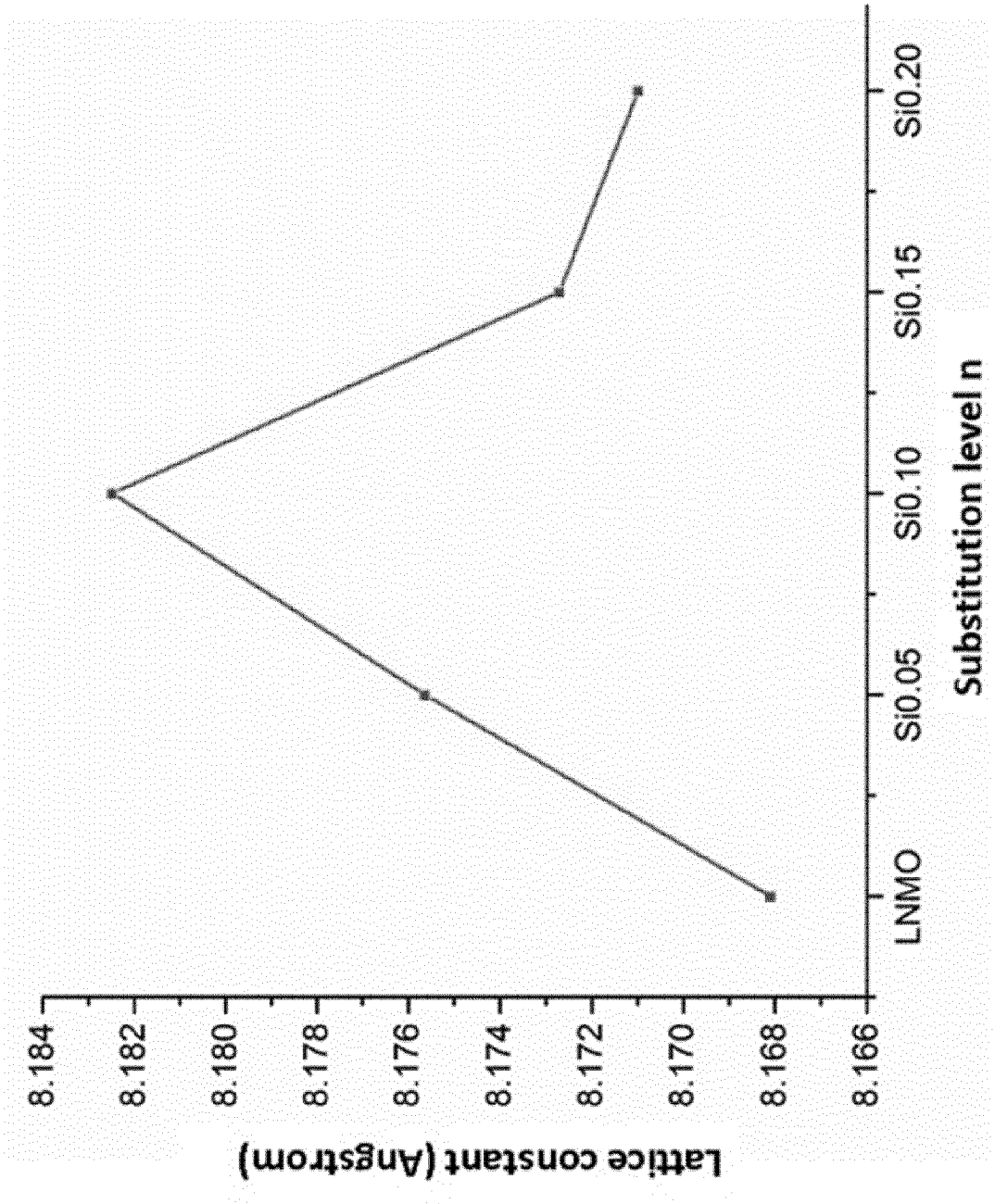
Lattice constant (Angstrom)
8.184
8.182
8.180
8.178
8.176
8.174
8.172
8.170
8.168
8.166
LNMO
Si0.05
Si0.10
Si0.15
Si0.20
Substitution level n

Fig. 3

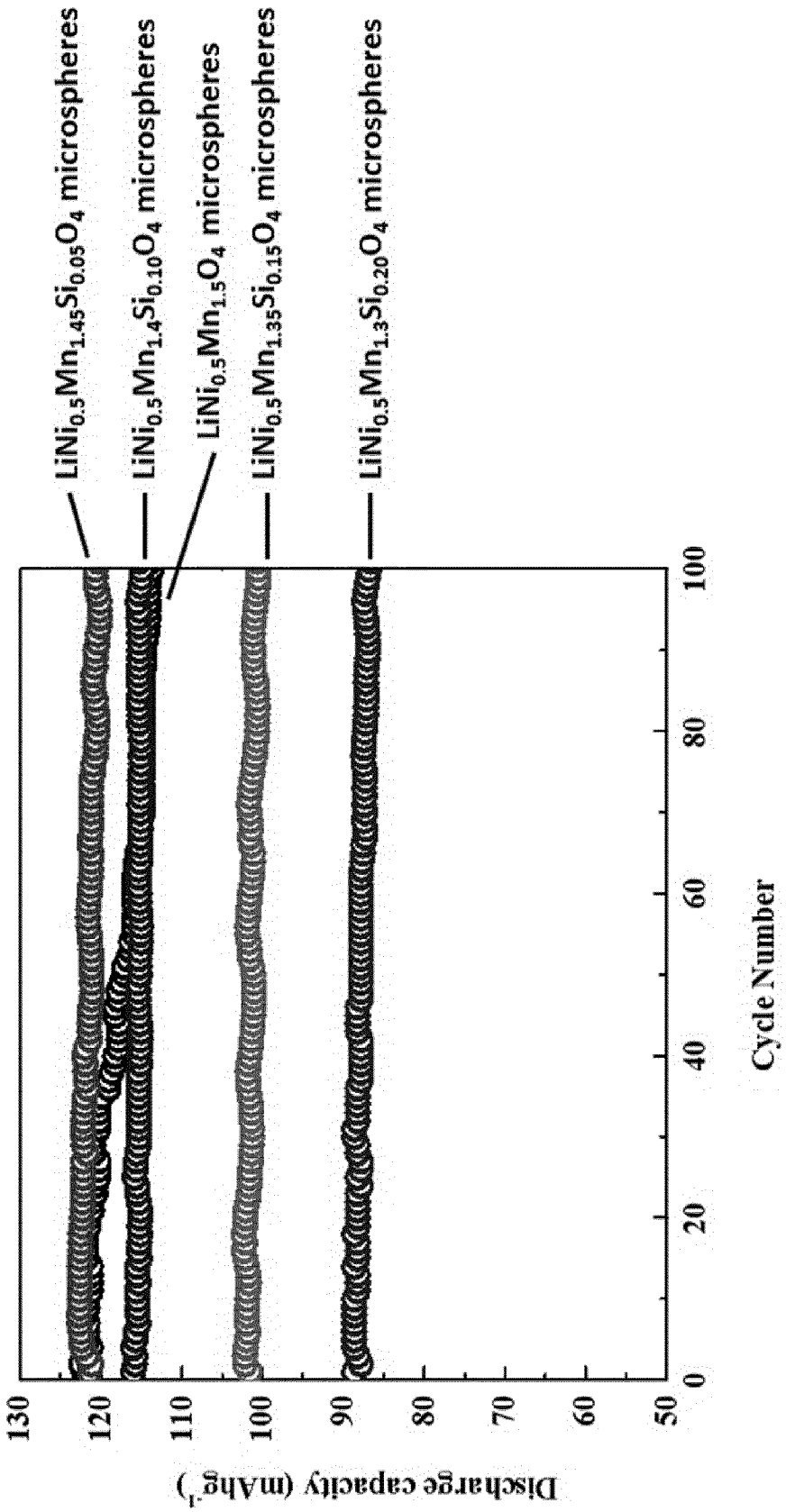
LiNi0.5Mn1.45Si0.05O4 microspheres
LiNi0.5Mn1.4Si0.10O4 microspheres
LiNi0.5Mn1.5O4 microspheres
LiNi0.5Mn1.35Si0.15O4 microspheres
LiNi0.5Mn1.3Si0.20O4 microspheres
Discharge capacity (mAhg-1)
Cycle Number
130
120
110
100
90
80
70
60
50
0
20
40
60
80
100

Fig. 4

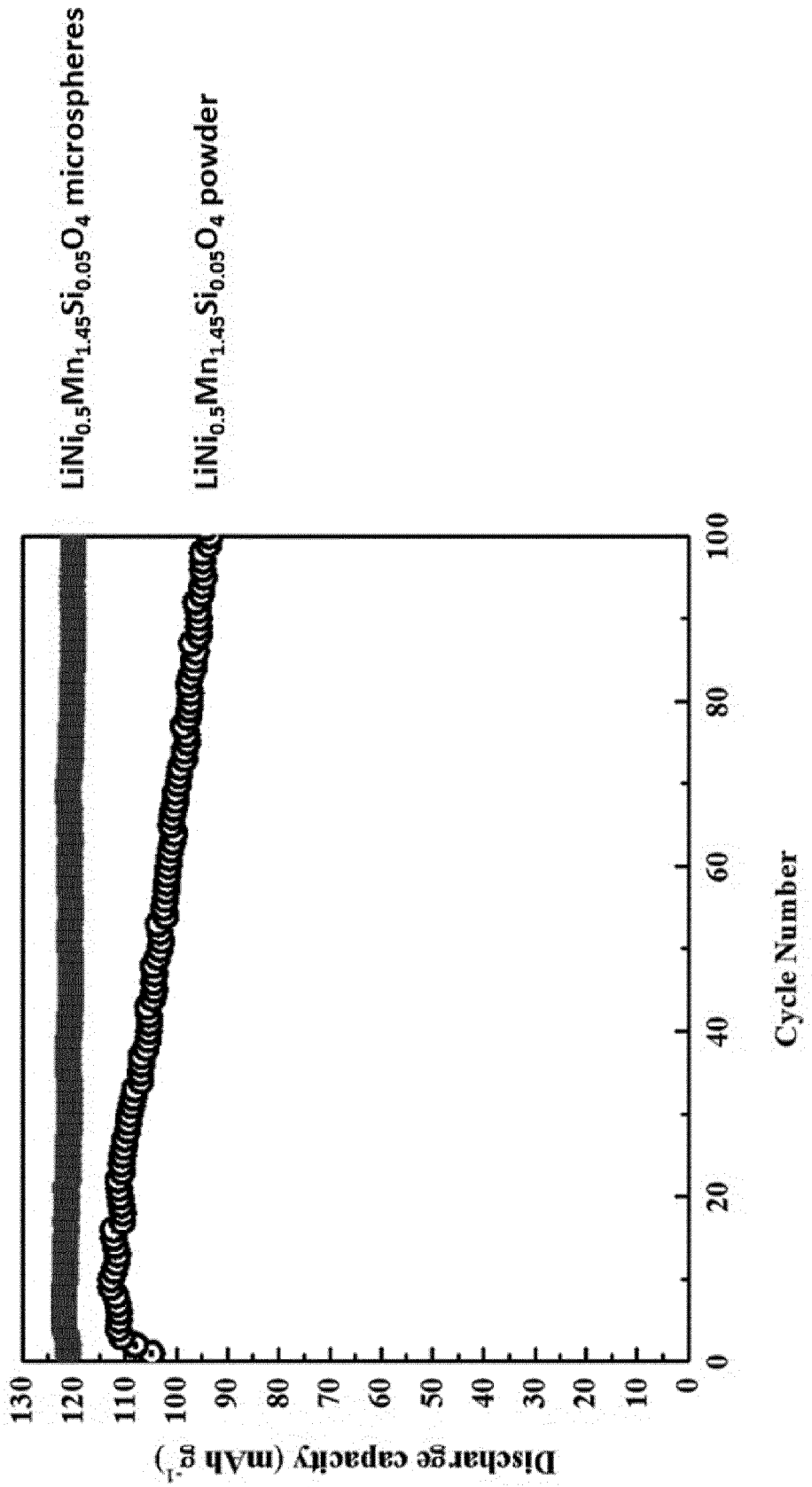
LiNi0.5Mn1.45Si0.05O4 microspheres
LiNi0.5Mn1.45Si0.05O4 powder
Discharge capacity (mAh g-1)
Cycle Number
0
10
20
30
40
50
60
70
80
90
100
110
120
130
0
20
40
60
80
100

Fig. 5

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/064702

A. CLASSIFICATION OF SUBJECT MATTER
INV. H01M4/131 H01M4/1391 H01M4/38 H01M4/505 H01M10/0525
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

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CN 101 898 799 A (UNIV FUDAN) 1 December 2010 (2010-12-01) Summary of the invention; figure 2	1,5,6,13
X	EP 2 717 360 A1 (NINGBO INST MAT TECH & ENG CAS [CN]; HUBEI WANRUN NEW ENERGY TECHNOLOG) 9 April 2014 (2014-04-09) paragraphs [0006], [0007], [0029]; figures 2,3a	1-4,7-12
A	US 2003/082453 A1 (NUMATA TATSUJI [JP] ET AL) 1 May 2003 (2003-05-01) paragraphs [0062] - [0063]	1-3

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

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"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
26 July 2016	03/08/2016

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Letilly, Marika

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Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/064702

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	XIANG MING HE ET AL: "Preparation of spherical spinel LiMn2O4 cathode material for lithium ion batteries", JOURNAL OF SOLID STATE ELECTROCHEMISTRY ; CURRENT RESEARCH AND DEVELOPMENT IN SCIENCE AND TECHNOLOGY, SPRINGER, BERLIN, DE, vol. 9, no. 6, 15 December 2004 (2004-12-15), pages 438-444, XP019352602, ISSN: 1433-0768, DOI: 10.1007/S10008-004-0593-Y page 441, left-hand column, line 19 - line 26 -----	13

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2016/064702

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		JP 2014515541 A	30-06-2014
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