DOPED SPINEL, METHOD FOR THE PRODUCTION THEREOF, THE USE THEREOF AND LITHIUM-ION BATTERY

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See application file for complete search history.

References Cited

U.S. PATENT DOCUMENTS

5,674,645 A 10/1997 Amatucci et al.
5,759,720 A 6/1998 Amatucci
252/518.1

501/137

FOREIGN PATENT DOCUMENTS

WO WO 201265029 A1 * 1/2012 ...................... H01M 4/505

OTHER PUBLICATIONS

STIC Search by J. Wang *
T. Yang et al.: “The influence of holding time on the performance of LiNi0.5Mn0.5O2 cathode for lithium ion battery”, Journal of Alloys and Compounds, vol. 502, pp. 215-219 (2010).
R. Santiannam et al.: “Research progress in high voltage spinel LiNi0.5Mn0.5O2 material”, Journal of Power Sources, vol. 195, pp. 5442-5451 (2010).
G. Q. Liu et al.: “Spinel LiNi0.5Mn0.5O2 and its derivatives as cathodes for high-voltage lithium-ion batteries”, J Solid State Electrochem., vol. 14, pp. 2191-2202 (2010).
T.-F. Yi et al.: “Recent developments in the doping of LiNi0.4Mn0.4O2 cathode material for 5 V lithium-ion batteries”, Ions, vol. 17, pp. 383-389 (2011).
(Continued)

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ABSTRACT

A doped spinel comprising the formula:

Li1-xMeyM2z-yMnz-o,4O4-F2

where, 0<x<1, 0.3<y<0.7, 0.3<z<0.7, x+y = 0.0001<y<0.35, and 0.0001<z<0.35.
Me1 is a metal selected from a group of elements consisting of Cr, Fe, Co, Ni, Cu, and Zn. Me2 is a metal selected from a group of elements consisting of Ni, Fe, Co, Mg, Cr, V, Ru, Mg, Al, Zn, Cu, Cd, Ag, Y, Sc, Ga, In, As, Sb, Pt, Au, and B.

1 Claim, 7 Drawing Sheets
References Cited

OTHER PUBLICATIONS


S. H. Park et al.: “Comparative study of different crystallographic structure of LiNi0.5Mn1.5O4 cathodes with wide operation voltage (2.0-5.0 V)”, Electrochimica Acta, vol. 52, pp. 7226-7230 (2007).

C. S. Johnson et al.: “Lithium-manganese oxide electrodes with layered-spinel composite structures xLi2MnO3•(1-x)Li1-yMn2-yO4 (0<x<1, 0<y<0.33) for lithium batteries”, Electrochemistry Communications, vol. 7, pp. 528-536 (2005).

S. Glatthaar et al.: “Improved electrochemical performance of iron and fluorine doped LiNi0.8Mn0.2O4 cathodes with wide operation voltage”, 219th ECS Meeting Abstracts, Montreal, p. 1 (2011).

S. Glatthaar et al.: “Improvement of the wide operation voltage capability of iron doped LiNi0.8Mn0.2O4 cathodes for lithium ion batteries by fluorination”, LiBa-5, Electrode materials, Arcachon, France, pp. 1-2 (Jun. 12-17, 2011).


* cited by examiner
3.5 - 5.0 V
23°C

C/2
4-5 mg/cm²
Electrolyte:
1M LiPF6, EC/DMC 1:1
Anode: Li metal
Swagelok cell

Spec. capacity/mAhg⁻¹

250
200
150
100
50
0

Number of cycles / -

Fig. 1

A  □  Li₁₀₀Ni₀.₅₂Ti₀.₀₂Mn₁.₃₆O₄
B  ○  Li₁₀₀Ni₀.₄₁Fe₀.₁₁Ti₀.₀₂Mn₁.₄₆O₄
C  △  Li₁₀₀₂Ni₀.₄₈Fe₀.₁₁Ti₀.₀₂Mn₁.₃₇O₄
D  ▽  Li₁₀₀₀Ni₀.₅₁Fe₀.₁₁Ti₀.₀₂Mn₁.₃₆O₃₈₄F₀.₁₆
E  ◇  Li₁₀₀₀₂Ni₀.₅₁Fe₀.₁₁Ti₀.₀₂Mn₁.₃₉O₃.₇₃F₀.₂₇
F  ▼  LiMn₂O₄
Cycle # 10
23°C
C/2
4-5 mg/cm²
Electrolyte:
1M LiPF₆, EC/DMC 1:1
Anode: Li metal
Swagelok cell

Fig. 2

A \rightarrow Li_{1.00}Ni_{0.52}Ti_{0.02}Mn_{1.46}O_4
B \rightarrow Li_{1.00}Ni_{0.41}Fe_{0.11}Ti_{0.02}Mn_{1.46}O_4
C \rightarrow Li_{1.02}Ni_{0.48}Fe_{0.11}Ti_{0.02}Mn_{1.37}O_4
D \rightarrow Li_{1.00}Ni_{0.51}Fe_{0.11}Ti_{0.02}Mn_{1.36}O_3.84 F_{0.16}
E \rightarrow Li_{1.02}Ni_{0.51}Fe_{0.11}Ti_{0.02}Mn_{1.35}O_{3.73} F_{0.27}
Cycle # 100
23°C
C/2
4-5 mg/cm²
Electrolyte:
1M LiPF6, EC/DMC 1:1
Anode: Li metal
Swagelok cell

Fig. 3

A: Li_{1.00}Ni_{0.52}Ti_{0.02}Mn_{1.46}O_4
B: Li_{1.00}Ni_{0.41}Fe_{0.11}Ti_{0.02}Mn_{1.46}O_4
C: Li_{1.02}Ni_{0.48}Fe_{0.11}Ti_{0.02}Mn_{1.37}O_4
D: Li_{1.00}Ni_{0.51}Fe_{0.11}Ti_{0.02}Mn_{1.36}O_{3.84}F_{0.16}
E: Li_{1.02}Ni_{0.51}Fe_{0.11}Ti_{0.02}Mn_{1.35}O_{3.73}F_{0.27}
DOPED SPINEL METHOD FOR THE PRODUCTION THEREOF, THE USE THEREOF AND LITHIUM-ION BATTERY

CROSS REFERENCE TO PRIOR APPLICATIONS


FIELD

The present invention relates to a doped spinel, a process for preparation thereof and its use. The present invention also provides a lithium ion battery which comprises a spinel doped according to the present invention.

BACKGROUND

The present invention concerns the field of energy storage systems and relates to a subclass of cathode materials which are used as intercalation materials in lithium ion cells which are a main component of lithium ion batteries. A lithium ion cell is generally defined as an electrochemical element in which lithium ions occur as ionic charge carriers. The typical demands made of an energy store at the battery level, in particular, in respect of its energy density, power density, safety, longevity, environmental friendliness and costs, also apply at the cell level and ultimately for the individual components, i.e., also for cathode materials.

The present invention is based on the main class of the LiMn$_2$O$_4$ spinels, in particular, the LiMe$_1$Mn$_{1-x}$O$_2$ where Me= [Cr, Fe, Co, Ni, Cu, Zn], 0.3≤x≤0.7, as described in T. Ohsuzu et al., Journal of Power Sources 81-82, pp. 90-94 (1999) as high-voltage spinels. In contrast to other classes of cathode materials, especially LiCoO$_2$, LiNi$_{0.5}$Mn$_{1.5}$O$_2$, LiNi$_{0.5}$Co$_{0.5}$O$_2$, LiNi$_{0.5}$Al$_{0.5}$O$_2$, this main class is, according to Arnold, G., Journal of Power Sources 119-121, pp. 247-251 (2003), known for a high power density combined with improved intrinsic safety. Further advantages are its environmental friendliness and the somewhat lower materials costs due to the absence of cobalt. The high-voltage spinel LiNi$_{0.5}$Mn$_{1.5}$O$_2$ has been the subject of intensive research during the last decade. A distinction is made between the ordered spinels having the space group P4$_{2}$3m and the disordered spinels (Pd-3m), which, according to Yang, T., Journal of Alloys and Compounds 502, pp. 215-219 (2010) and Kunduracil, M., Chemistry of Materials 18, pp. 3585-3592 (2006), are more suitable as a cathode material because of improved electronic conductivity. Doping usually stabilizes the disordered spinel and partly or completely eliminates the Li$_{x}$Ni$_{1-x}$O foreign phase which frequently occurs in the synthesis.

R. Santhanam, B. Rambabu, Journal of Power Sources 195 pp. 5442-5451 (2010), G. Liu, L. Wen, Y. Liu, Journal of Solid State Electrochemistry 14, pp. 2191-2202 (2010), and L.-F. Yi, Y. Xie, M.-F. Ye, L.-J. Jiang, R.-S. Zhu, Y.-R. Zhu, J. Alloys Compounds 17, pp. 383-389 (2011) describe the high-voltage spinel LiNi$_{0.5}$Mn$_{1.5}$O$_2$, in particular, the influence of doping. On the cation side, nickel and manganese are partly replaced by magnesium, chromium, cobalt, iron, titanium, iron-titania, copper, aluminum, zirconium and ruthenium, while on the anode side, oxygen is replaced by fluorine and sulfur. Many positive influences are ascribed to dopings as long as only small amounts, usually x≤0.15, are added, although different synthesis processes, morphologies, characterization methods and cell preparations make direct comparison of the influences of doping more difficult. The effects of doping in the high-voltage range, as described therein, are a slightly increased redox potential (Mg$^{2+}$, Ti$^{4+}$), reduced polarization (Ru$^{3+}$, F$^{-}$), improved cycling stability (Mg$^{2+}$, Cr$^{3+}$, Fe$^{3+}$, F$^{-}$), improved electronic conductivity (Mg$^{2+}$, Cr$^{3+}$, Fe$^{3+}$, Co$^{3+}$, Ru$^{3+}$), improved Li$^{+}$ ion conductivity (Ti$^{4+}$, Co$^{3+}$, Ru$^{3+}$), improved performance as a cathode material (Cr$^{4+}$, Fe$^{3+}$, Ru$^{3+}$, F$^{-}$), a greater binding energy to oxygen (Cr$^{4+}$, Fe$^{3+}$, Co$^{3+}$), improved structural stability (Cr$^{4+}$), improved heat resistance (Cr$^{4+}$, F$^{-}$), and improved resistance to the standard electrolyte (Cr$^{4+}$, Fe$^{3+}$, F$^{-}$). Fluoride here increases the resistance to hydrofluoric acid, while Cr$^{4+}$ and Fe$^{3+}$ are stated in Goodenough, J. B., et al., Journal of Power Sources 196, pp. 6688-6694 (2011) to reduce electrolyte oxidation at voltages above 4.5 V by formation of a passivating covering layer on the interface of the cathode material to the electrolyte (solid electrolyte interphase, known as SEI layer for short). Apart from F$^{-}$ doping, a greater stability to hydrofluoric acid, which can form in the standard electrolyte system, can, according to G. Liu, L. Wen, Y. Liu, Journal of Solid State Electrochemistry 14, pp. 2191-2202 (2010), be achieved by means of coatings.

The electrochemical results in respect of the influence of doping consist virtually exclusively of cycling in the high-voltage range, i.e., from 3.5 V to 5.0 V. Aminie, K. et al., Journal of The Electrochemical Society 143, pp. 1607-1613 (1996), Strobel, P. et al., Journal of Material Chemistry, pp. 429-436 (2000), Morales, J. et al., Journal of Solid State Chemistry 2, pp. 420-426 (1998), and Wagenaar, M., Journal of The American Chemical Society 143, pp. 13526-13533 (2004) describe the spinel LiNi$_{0.5}$Mn$_{1.5}$O$_2$ as 3V material. Specific capacities of up to 170 mAh/g during discharging from 3.5 V to 2.0 V after the first cycle were, however, not found to be stable after a number of cycles. Sun, Y.-K. et al, Journal of Power Sources 161 19-26, (2006) describes stable cycling of an LiNi$_{0.5}$Mn$_{1.5}$O$_2$ spinel prepared by precipitation within a voltage range from 3.5 V to 2.4 V relative to Li/Li$^{+}$ over 50 cycles, improved by doping with sulfur.

Electrochemical characterizations over the entire voltage range from 5.0 V to 2.0 V have only infrequently been carried out. They require additional lithium in the cell. Park et al., Electrochimica Acta 52, pp. 7226-7230 (2007) described the structural changes in the ordered and disordered spinel over the entire voltage range. The degradation of the 4V spinel LiMn$_2$O$_4$ over the voltage range from 5.0 V to 2.0 V is described in Johnson et al., Electrochemistry Communications 7, pp. 528-536 (2005). Glaithauer, 219th ECS Meeting Abstracts, Montréal, B1, 194 (2011) and Glaithauer et al., LiBD—Electrode Materials, Arcachon, O17 (2011) described results in respect of the deep discharging of iron- and fluoride-doped LiNi$_{0.5}$Mn$_{1.5}$O$_2$, which display an increase in the cycling stability brought about by doping with iron and fluorine in the voltage range from 2.0 V to 5.0 V.

SUMMARY

An aspect of the present invention is to provide a doped spinel which overcomes the disadvantages and restrictions described in the prior art. A doped spinel or a doped
high-voltage spinel which can be cycled stably with signifi-
cantly more than one lithium per formula unit should, for
example, be provided.

An alternative aspect of the present invention is to provide
a process for preparing the doped spinels or doped high-
voltage spinels.

An alternative aspect of the present invention is to provide
a use of the doped spinels or doped high-voltage spinels.

An alternative aspect of the present invention is to provide
a lithium ion battery which comprises spinels or doped
high-voltage spinels of this type.

In an embodiment, the present invention provides a doped
spinel comprising the formula:

\[ \text{Li}_{1-x} \text{Me}_1 \text{Me}_2 \text{Mn}_{2-y} \text{Fe}_y \text{O}_4 \text{F}_z \]

where, 0.5 \text{aw} = 0.7, 0.3 \text{ax} = 0.7, \text{xy} = 0.0001 \text{zs} = 0.35,
and 0.0001 \text{az} = 0.3. \text{Me}1 is a metal selected from a group of
elements consisting of Cr, Fe, Co, Ni, Cu, and Zn. \text{Me}2 is a
metal selected from a group of elements consisting of Ni, Fe,
Co, Mg, Cr, V, Ru, Mg, Al, Zn, Cu, Cd, Ag, Y, Sc, Ga, In, As,
Sb, Pt, Au, and B.

**BRIEF DESCRIPTION OF THE DRAWINGS**

The present invention is described in greater detail below
on the basis of embodiments and of the Figures in which:

- FIG. 1 shows specific discharging capacities of the
samples A to E in 23°C and different voltage ranges;
- FIG. 2 shows charging and discharging curves of the
samples A to E in 23°C in the voltage range from 5.0 V to
2.0 V after 10 cycles;
- FIG. 3 shows charging and discharging curves of the
samples A to E in 23°C in the voltage range from 5.0 V to
2.0 V after 100 cycles;
- FIG. 4 shows the coulombic efficiency of the samples A
to E in 23°C and different voltage ranges;
- FIG. 5 shows specific energy densities of the samples A
to E in 23°C and different voltage ranges;
- FIG. 6 shows efficiency of the samples A to E in 23°C,
different voltage ranges; and
- FIG. 7 shows specific discharging capacities of the
samples A to E in 45°C and different voltage ranges.

**DETAILED DESCRIPTION**

The material according to the present invention is a
Ti-doped oxyfluoride-lithium-manganese spinel. In
an embodiment, the spinel can, for example, have the composition:

\[ \text{Li}_{1-x} \text{Me} \text{Me}_2 \text{Mn}_{2-y} \text{Ti}_y \text{O}_4 \text{F}_z \]

where, in the composition indicated,
0.5 \text{aw} = 0.7,
0.3 \text{ax} = 0.7,
\text{xy} = 0.3,
\text{zs} = 0.3,
and
\text{Me} is at least one element selected from the group of
elements consisting of Li, Ni, Fe, Co, Mg, Cr, V, Ru, Mg,
Al, Zn, Cu, Cd, Ag, Y, Sc, Ga, In, As, Sb, Pt, Au, B.
The value range selected for \text{w} corresponds to the maximum
possible stability range of a normal, i.e., non-inverse,
lithium transition metal spinel. At values of \text{z} = 0.3, the specific
capacity decreases to an increasing extent for industrially
relevant power densities.

In an embodiment of the present invention, a doped
high-voltage spinel which has the formula:

\[ \text{Li}_{1-x} \text{Me}_{1} \text{Me}_{2} \text{Mn}_{2-y} \text{Ti}_y \text{O}_4 \text{F}_z \]

where 0.3 \text{ax} = 0.7, in which Me, is replaced by \text{Me}1,
\text{Me}2, \text{Me}1 is selected from the group of elements con-
sisting of [Cr, Fe, Co, Ni, Cu, Zn] and \text{Me}2 is selected from the
group of elements consisting of [Li, Ni, Fe, Co, Mg, Cr,
V, Ru, Mg, Al, Zn, Cu, Cd, Ag, Y, Sc, Ga, In, As, Sb, Pt, Au,
B], can, for example, be provided.

In an embodiment of the present invention, the element \text{Ni}
can, for example, be selected for \text{Me}1, with \text{Me}2, for
example, being selected from the group consisting of [Cr,
Fe, Co, Ni, Cu, Zn, Mg, V, Ru, Al], for example, \text{Fe} or
Ru, for example, Fe. In an embodiment, \text{Me}2=Fe, 0.5
(\text{xy} \leq 0.3, 0.0005 \text{zs} \leq 0.2, and 0.0005 \text{ax} \leq 0.3). For values of
(\text{xy} \leq 0.35, the specific capacity in the voltage range of 3.5
V of LiNi0.5Mn1.5TiO4 decreases again as described in
Alcantara et al., Journal of The Electrochemical Society 152,
pp. A13-A18 (2005). For values of \text{z} \geq 0.35, the specific
capacity in the voltage range of 3.5 V of LiNi0.5Mn1.5TiO4
decreases again as described in Alcantara et al., Chemistry of

A spinel doped according to the present invention is
obtained in good quality by a multistage preparative process.
Firstly, a solution of Li, Na, Me, \text{Me}1 and/or \text{Me}2 metal
compounds and trifluoroacetic acid is spray dried. Subse-
quent calcination in a first furnace operation forms the
spinel, for example, still without Ti doping. To introduce the
Ti doping, the pulverulent material can, for example, be
milled and spray-granulated as an ethanolic suspension in
which a lithium salt and a Ti alkoxide has been dissolved,
for example, as a sol. The product obtained in this way is
converted into a Ti-doped oxyfluoride spinel according to
the present invention in a second furnace operation.

The spinel doped according to the present invention makes it possible to cycle a spinel of the class LiMnO3 or a
high-voltage spinel of the class LiMe1 Me2 Mn1.5 Ti0.5 O4 where
\text{Me}1=[Cr, Fe, Co, Ni, Cu, Zn], 0.3 \text{ax} = 0.7, having signifi-
cantly more than one lithium per formula unit over many
cycles in a stable manner. For high cycling stability, specific
capacities above 150 mAh/g were measured, which corre-
sponds to the de/intercalation of one lithium per formula
unit. Although improved resistance to the electrolyte and
good cycling properties are known for doping with iron,
fluorine-doped LiNi0.5Mn1.5O4 has improved resistance to
hydrogen fluoride and improved heat resistance and, finally,
fluorine- and iron-doped LiNi0.5Mn1.5O4 improves the
reversibility of deep discharge down to 2.0 V, the class of
materials according to the present invention of Ti-doped
oxyfluoride spinels or high-voltage spinels combines, firstly,
the above-mentioned positive influences and, in addition,
achieves a higher energy density as a result of the de/inter-
calation of more than one lithium per formula unit. This also
applies at elevated temperature in combination with a liquid
electrolyte, which indicates improved aging stability.

In a range which is given by a doped spinel of the formula
Li1.5, Ni, Fe, Mn2-y, Ti1-y, O4, Fz wherein:
0.5 \text{aw} = 0.7,
0.3 \text{ax} = 0.7,
0.0005 \text{zy} = 0.3, and
0.0005 \text{zy} = 0.3,
it isfound that the doping element Fe increases electronic
conductivity. Iron-doped LiNi0.5Mn1.5O4 therefore gives
better performance than undoped material. The specific
capacity of iron-doped LiNi0.5Mn1.5O4 is higher than that of
undoped material at a medium discharge rate, i.e., over a
period of 2 hours, not only in the high-voltage range but also
in the 3V range. Fluorine doping improves the stability to
hydrogen fluoride formation in the electrolyte and increases
the thermal stability of the material since the spinel lattice is
stabilized by the introduction of fluoride ions. The combi-
nation of iron doping and fluorine doping thus results overall in increased thermal stability and a greater cycling stability in the case of deep discharge.

In the case of deep discharge, the transformation of the cubic spinel lattice into a tetragonal lattice at medium discharging rates is hindered. As a result, the Fe–Fe doped material is more stable to cycling but, due to the lower de/intercalation of Li in the 3V range, the specific capacity and energy density during cycling at 2.0-5.0 V increase only little compared to the capacity achieved during cycling at 3.5-5.0 V. Only doping with a third element allows the positive properties of the single doping, i.e., higher specific capacity as a result of iron doping, improved structural stability and improved resistance to the electrolyte as a result of fluorine doping, to be maintained in combination. The titanium-, fluorine- and iron-doped spinel thus displays a lower energy density combined with comparatively high cycling stability and thermal stability and is charged or discharged over the entire voltage range of 2.0-5.0 V in combination with a lithium anode.

The spinel or high-voltage spinel doped according to the present invention is suitable first and foremost for use as cathode material, for example, as an intercalation material, in lithium ion cells, for example, in lithium metal cells having lithium as an anode.

In an embodiment, the present invention provides a lithium ion battery which has at least one lithium ion cell whose cathode material contains a spinel or high-voltage spinel doped according to the present invention.

The present invention will be illustrated below with the aid of the working examples and the figures.

As a working example, titanium-, fluorine- and iron-doped spinels were prepared and used as the cathode material. Doping was carried out via a modified sol-gel process, starting from aqueous metal salt solutions with addition of tris trifluorocysalic acid, by which means the following samples A to E were prepared.

**EXAMPLES**

**Comparative Samples A to C**

Sample A: Li0.28Ni0.28Ti0.02Mn0.49O4
Sample B: Li0.28Ni0.28Ti0.02Mn0.49O4
Sample C: Li0.28Ni0.28Ti0.02Mn0.49O4

Samples D and E according to the present invention:

Sample D: Li0.28Ni0.28Fe0.01Ti0.02Mn0.58O3.87F0.13
Sample E: Li0.28Ni0.28Fe0.01Ti0.02Mn0.58O3.87F0.13

All samples were doped with titanium. Samples B to E additionally comprised Fe, while samples D and E additionally contained fluorine, so that only these two samples D and E fall within the class of materials according to the present invention. Samples A to C should therefore be regarded as comparative samples.

The composition of the samples was determined by means of chemical analysis and corresponds to the stoichiometric amounts weighed in. Except for sample A, which contained a small proportion of Li2Ni4,0 as a foreign phase, all samples were phase-pure according to X-ray diffraction. All samples were disordered spinels which, according to BET measurements, had specific surface areas of from 2.9 to 5.9 m2/g and, according to scanning electron micrographs, had comparable morphologies. Since the synthesis conditions were chosen to be the same for all samples, the differences in the electrochemical properties shown in FIGS. 1-7 actually show the respective influences of doping.

For the cell tests, 2-electrode Swagelok cells having lithium as the anode, 1M LiPF6 in EC/DMC 1:1 as the electrolyte and the samples A to E as the active material of the cathode were used. The cathode consisted of 80% of active material, 10% of polyvinylidene fluoride (PVDF), and 10% of carbon black. Specific values indicated are based on the mass of the active material.

FIG. 1 shows the specific discharging capacities of samples A to E at 23°C and different voltage ranges. In the high-voltage range, i.e., in the range from 3.5 V to 5 V, stable cycling was possible for all pure-phase samples. The advantages of the class of the materials according to the present invention in samples D and E become apparent, however, over the total voltage range. Over the first 50 cycles, there is, as shown in FIG. 1, no decrease in the specific capacity to be observed for these two samples. Sample D has a specific capacity of 176 mAh/g after 10 cycles.

If the theoretical specific capacity of 147 mAh/g corresponds to the lithium intercalation of one lithium into Li2Ni4O3, then the specific capacity of samples D and E, which are comprised of Li2Ni4O3 and Mn0.08O, is more than one lithium per formula unit is, as shown in FIG. 1, cycled in the voltage range from 5.0 V to 2.0 V in the case of samples B to E after 10 cycles, since these have a specific capacity higher than 147 mAh/g.

As shown in FIG. 3, in contrast, only the samples D and E according to the present invention display comparably high specific capacities as after 10 cycles after 100 cycles. Sample D is the only sample which still displays a specific capacity of 174 mAh/g, i.e., greater than 147 mAh/g, after 100 cycles. It is thus demonstrated that significantly more than one lithium per formula unit is intercalated in the case of sample D after 100 cycles at a C-rate of C/2.

FIG. 4 shows the coulombic efficiency of the samples in the first 30 cycles, this is defined as the ratio of discharging capacity to charging capacity. A coulombic efficiency of less than 1.0 indicates irreversible electrochemical secondary reactions. Possible causes are SEI formation, electrolyte decomposition, or dissolution of Mn2+ in the electrolyte. It is conspicuous in FIG. 4 that the coulombic efficiency is less than 1 for all samples. It is obvious that this reduction in the coulombic efficiency occurring even in the high-voltage range is attributable to the electrolyte used not being stable at above 4.5 V. It is interesting, however, that in the case of the two samples D and E which have been fluorine-doped according to the present invention there is, in contrast to samples A to C, no significant further reduction in the coulombic efficiency in the entire voltage range of 2.0-5.0 V, which represents an improvement over the samples which have not been fluorine-doped.

FIG. 5 shows the cycle-dependent specific discharging energy and FIG. 6 shows the efficiency of the samples. As in the case of the specific capacity, the samples D and E also cycle significantly more stably in terms of the energy density over the entire voltage range from 5.0 V to 2.0 V than the samples A to C which were not doped with fluorine. In the case of sample D, the energy density decreases slightly after 50 cycles in the right-hand graph. This is related to a voltage hysteresis in the 3V range which increases with increasing number of cycles, as the comparison of FIG. 2 and FIG. 3 for this sample shows.

The efficiency comprises energy losses due to the coulombic efficiency and losses due to the voltage difference between charging and discharging. Since cycling was carried out at a charging and discharging rate of C/2, i.e., 2 hours charging and 2 hours discharging, the efficiency
shown includes kinetic losses which lead to an overvoltage. The decrease in the efficiency is conspicuous in a cycle over the entire voltage range. The reason lies in the greater voltage hysteresis in the 3V range, which is caused by the energy losses in the phase transformation from cubic to tetragonal. It is conspicuous that improved efficiencies are once again achieved by the samples fluorine-doped according to the present invention.

FIG. 7 shows the specific capacities at 45° C. Samples D and E can be cycled stably over the first 50 cycles in the high-voltage range, which represents an improvement compared to the high-voltage spinels which have not been fluorine-doped in samples A to C. Relative improvements are likewise apparent over the entire voltage range. It is expected that the cycling stability can also be increased further at elevated temperature both by optimization of the material according to the present invention and by optimization in cell manufacture.

The present invention is not limited to embodiments described herein; reference should be had to the appended claims.

What is claimed is:

1. A doped spinel comprising the formula

\[ Li_{1-x}M_{1/3}M_{2}M_{1/3}F_{3} \]

where,
\[ 0 < x < 0.1 \]
\[ 0.3 < x < 0.7 \]
\[ 0.3 < y < 0.7 \]

2. A doped spinel comprising the formula

\[ Li_{1-x}M_{1/3}M_{2}M_{1/3}F_{3} \]

where,
\[ 0 < x < 0.1 \]
\[ 0.3 < x < 0.7 \]
\[ 0.3 < y < 0.7 \]

\[ y > 0.0001 \]

\[ 0.0001 < y < 0.35 \]

M1 is a metal selected from a group of elements consisting of Cr, Fe, Co, Ni, Cu, and Zn, and

M2 is a metal selected from a group of elements consisting of Ni, Fe, Co, Mg, Cr, V, Ru, Mg, Al, Zn, Cu, Cd, Ag, Y, Sc, Ga, In, As, Sb, Pt, Au, and B,

wherein, a specific capacity of the doped spinel from 1 to 50 cycles did not decrease in a voltage range of from 2.0 to 5.0 V, and

the doped spinel is prepared by a process consisting of:

- providing a solution of a metal-organic and/or inorganic Li, Mn, Me, M1 and/or M2 compound(s) as a precursor;
- spray drying the precursor with trifluoroacetic acid so as to obtain a sprayed precursor;
- calcining the sprayed precursor so as to provide the doped spinel in a form of a pulverulent material;
- milling the pulverulent material in ethanol so as to provide a suspension;
- adding a lithium compound and a titanium alkoxide in an ethanolic solution to the suspension so as to provide a resulting material;
- spray granulating the resulting material so as to obtain a spray-granulated material; and
- thermally converting the spray-granulated material so as to obtain a Ti-doped oxyfluoride spinel.

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