

Claims

1. A stabilised Na-ion oxide P3 phase of formula I:



where:

$$x > 0.66;$$

$$0.8 \leq y \leq 1.0;$$

$$z \leq 2; \text{ and}$$

M is selected from one or more of the group consisting of a 3d transition metal, a 4d transition metal, Al, Mg, B, Si, Sn, Sr and Ca, wherein the compound of formula I is suitable for use as a cathode active material in a Na-ion battery.

2. The compound of formula I according to Claim 1, wherein M is selected from one or more of the group consisting of Mn, Fe, Ni, Co, Cu, Ti, Cr, Zn, V, Sc, Y, Zr, Nb, Mo, Al, Mg, B, Si, Sn, Sr and Ca.

3. The compound of formula I according to Claim 1, wherein M is selected from one or more of the group consisting of Mn, Fe, Ni, Co, Cu, Ti, Cr, Zn, V, Sc, Y, Zr, Nb, Mo, Al, Mg, B, and Ca, optionally wherein M is Ti.

4. The compound of formula I according to any one of the preceding claims, wherein each M has an oxidation state of from +1 to +7.

5. The compound of formula I according to any one of the preceding claims, wherein one or more of the following apply:

$$0.8 < x \leq 1.2 \text{ (e.g. } 0.8 < x \leq 1.0\text{)};$$

$$1.9 < z \leq 2.$$

6. The compound of formula I according to Claim 1, where the compound has formula Ia:



where:

$$a > 0.66;$$

$$0.8 \leq (b+c+d) \leq 1.0;$$

$$e \leq 2; \text{ and}$$

M' M is selected from one or more of the group consisting of a 3d transition metal, a 4d transition metal, Al, Mg, B, Si, Sn, Sr and Ca.

7. The compound of formula Ia according to Claim 6, where M' is selected from one or more of the group consisting of Mn, Fe, Ni, Co, Cu, Ti, Cr, Zn, V, Sc, Y, Zr, Nb, Mo, Al, Mg, B, Si, Sn, Sr and Ca.

8. The compound of formula Ia according to Claim 6 or Claim 7, wherein M' is selected from one or more of the group consisting of Mn, Fe, Ni, Co, Cu, Ti, Cr, Zn, V, Sc, Y, Zr, Nb, Mo, Al, Mg, B, and Ca, optionally wherein M is Ti.

9. The compound of formula Ia according to Claim 8, where M' is Ti.

10. The compound of formula Ia according to any one of Claims 6 to 9, wherein each M' has an oxidation state of from +1 to +7.

11. The compound of formula Ia according to any one of Claims 6 to 10, wherein one or more of the following apply:

(a) $0.8 < a \leq 1.2;$

(b) $0.4 \leq b \leq 0.6;$

(c) $0.4 \leq c \leq 0.6;$

(d) $0 \leq d \leq 0.1;$ and

(e) $1.9 < e \leq 2.$

12. The compound of formula Ia according to Claim 11, wherein one or more of the following apply:

(a) $0.8 < a \leq 1.0;$

(a) b is 0.5;

(b) $0.4 \leq c \leq 0.5;$ and

(c) e is 2.

13. The compound of formula I according to any one of the preceding claims, wherein the compound is selected from:

- (a) $\text{P3-Na}_{0.8}\text{Fe}_{0.5}\text{Mn}_{0.5}\text{O}_2$;
- (b) $\text{P3-Na}_{0.8}\text{Fe}_{0.5}\text{Mn}_{0.45}\text{Ti}_{0.05}\text{O}_2$; and
- (c) $\text{P3-Na}_{0.8}\text{Fe}_{0.5}\text{Mn}_{0.4}\text{Ti}_{0.1}\text{O}_2$.

14. A cathode comprising a stabilised Na-ion oxide P3 phase of formula I as described in any one of Claims 1 to 13 as an active material therein.

15. A sodium-ion battery comprising a cathode as described in Claim 14 or a stabilised Na-ion oxide P3 phase of formula I as described in any one of Claims 1 to 13 as an active material therein.

16. A method of forming a stabilised Na-ion oxide P3 phase of formula I as described in any one of Claims 1 to 13, the process comprising the steps of:

- (a) providing a powder comprising $\text{Na}_x\text{M}_y\text{O}_z$; and
- (b) subjecting the powder to a temperature of from 750 to 1050 °C with a heating rate of from 2 to 15 °C/min and a cooling rate of from 1 to 10 °C/min for a total period of from 6 to 20 hours, wherein:

$$0.66 < x < 0.7;$$

$$0.8 \leq y \leq 1.0;$$

$$z \leq 2; \text{ and}$$

M is selected from one or more of the group consisting of a 3d transition metal, a 4d transition metal, Al, Mg, B, Si, Sn, Sr and Ca.

17. A method of forming a stabilised Na-ion oxide P3 phase of formula I as described in any one of Claims 1 to 13, the process comprising the steps of:

- (a) providing a powder comprising a mixture of $\text{P3-Na}_x\text{M}_y\text{O}_z$ and $\text{O3-Na}_x\text{M}_y\text{O}_z$; and
- (b) subjecting the powder to a temperature of from 350 to 700 °C with a heating rate of from 2 to 15 °C/min and a cooling rate of from 1 to 13 °C/min for a total period of from 2 to 24 hours, wherein:

$$x > 0.7;$$

$$0.8 \leq y \leq 1.0;$$

$$z \leq 2; \text{ and}$$

M is selected from one or more of the group consisting of a 3d transition metal, a 4d transition metal, Al, Mg, B, Si, Sn, Sr and Ca.

18. The method of Claim 17, wherein the powder comprising a mixture of $\text{P3-Na}_x\text{M}_y\text{O}_z$ and $\text{O3-Na}_x\text{M}_y\text{O}_z$ is obtained using the method of Claim 16, except that x is >0.7 .

19. A method of charging and discharging a Na-ion battery comprising a cathode as described in Claim 14 in a first charge/discharge cycle, wherein the method comprises the steps of charging and then discharging the Na-ion battery using a voltage window (cathode v/s Na/Na⁺) of from 4.45 ± 0.2 V to 2.0 ± 0.5 V.

20. A method of charging and discharging a Na-ion battery comprising a cathode as described in Claim 14 in a subsequent (i.e. after a first) charge/discharge cycle, wherein the method comprises the steps of charging and then discharging the Na-ion battery using a voltage window (cathode v/s Na/Na⁺) of from 4.2 ± 0.05 V to 2.0 ± 0.5 V.