

(19) (12) (KR) (A)

(51) Int. Cl.<sup>7</sup>  
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10-2004-0094762  
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(87)

2003 09 18

(30) 10/092,317 2002 03 06 (US)

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89015 301

(72) , - - 10

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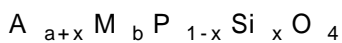
(74)

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(54) /

erial): (active mat

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[ ,

(a) A Li, Na, K ,  $0 < a < 1$ ,  $0 < x < 1$  ; ,

(b) M 가 , ,  $0 < b < 2$  ;

M, a, b x ]

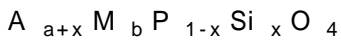


$M_2O_y$   
 $Li_3V_2(PO_4)_3$  NASICON LiFePO<sub>4</sub>  
 [S. Hossain, 'Rechargeable Lithium Batteries (Ambient Temperature),' *Handbook of Batteries*, 2d ed., Chapter 36, McGraw Hill (1995)]; 1980 3 18 4,194,062 (Carides, et al.); 1984 8 7 4,464,447 (Lazzari, et al.); 1991 7 2 5,028,500 (Fong et al.); 1992 7 14 5,130,211 (Wilkinson, et al.); 1995 5 23 5,418,090 (Koksbang et al.); 1996 5 7 5,514,490 (Chen et al.); 1996 7 23 5,538,814 (Kamauchi et al.); 1997 12 9 5,695,893 (Arai, et al.); 1998 9 8 5,804,335 (Kamauchi, et al.); 1999 2 16 5,871,866 (Barker et al.); 1999 6 8 5,910,382 (Goodenough, et al.); 2000 6 2 PCT WO/00/31812 (Barker, et al.); 2000 9 28 PCT WO/00/57505 (Barker); 2000 10 24 6,136,472 (Barker et al.); 2000 11 28 6,153,333 (Barker); 2001 2 22 PCT WO/01/13443 (Barker); 2001 7 26 PCT WO/01/54212 (Barker et al.); 2001 11 8 WO/01/84655 (Barker et al.)

가

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(a) A Li, Na, K ,  $0 < a < 1.0$  ;

(b) M 가 ,

$0 < b < 2, 0 < x < 1$  , M, a, b x

$M M'_c M'_d ( M' )$  4 11 ;  $M' 2, 3, 12$  ,  
 13 14 ;  $c + d = b$  ) 0.2  $a < 1.0$   
 0.1 a 0.8 1.0 b 1.5 가

$2$  ; 가 1 ;  
 (anode) (cathode) 가

가 , 가  
 가 , 가  
 가



1 .

$$\begin{aligned}
 & \text{, M} \quad \text{M}^1 \quad \text{e} \quad \text{M}^2 \quad \text{f} \quad \text{M}^3 \quad \text{g} \quad \text{( , M}^1 \quad \text{4} \quad \text{11} \\
 & \text{, M}^2 \quad \text{2} \quad \text{+2} \quad \text{, M}^3 \quad \text{13} \\
 & \text{+3} \quad \text{, e + f + g = b} \text{) .} \quad \text{, 0 < (e + f + g) 2} \\
 & \text{, 0.8 (e + f + g) 1.5 , 1 (e + f + g) 1.5 , 0 < (f} \\
 & \text{+ g) < 1 , 0.01 (f + g) 0.5 , 0.05 (f + g) 0.2 ,} \\
 & \text{0.05 (f + g) 0.1 .}
 \end{aligned}$$

Ti ( ), V ( ), Cr ( ), Mn ( ), Fe ( ), Co ( ), Ni ( ), Cu ( ),  
 Zr ( ), Nb ( ), Mo ( ), Ru ( ), Rh ( ), Pd ( ), Ag ( ), Cd ( ), Hf ( ),  
 Ta ( ), W ( ), Re ( ), Os ( ), Ir ( ), Pt ( ), Au ( ), Hg ( )

. Ti, V, Cr, Mn, Fe, Co, Ni, Cu  
 Fe, Co, Mn, V, Cr

1 ( 4 )  
 , Ti 가 가 , +2 가

M Be ( ), Mg ( ), Ca ( ), Sr ( ), Ba ( ); 3 Sc ( ), Y ( ), La ( ), Ce ( ),  
 Pr ( ), Nd ( ), Sm ( ); 12 Zn ( ), Cd ( ); 13 B ( ), Al ( ), Ga ( ), In ( ), Tl ( ); 14 Si ( ), Ge ( ), Sn ( ), Pb ( );  
 15 As ( ), Sb ( ), Bi ( ); 16 Te ( );  
 Mg, Ca, Zn, Sr, Pb, Cd, Sn, Ba, Be, Al  
 Mg, Ca, Zn, Ba, Al

O<sub>4</sub> 가 PO<sub>4</sub> P<sub>1-x</sub> Si<sub>x</sub> O<sub>4</sub> ( , 0 x 1 ) XO<sub>4</sub> , x = 0 X  
 , 0 x 0.8 , 0 x 0.5 .

M, X a, b, c, d x ( , A M ) ( , XO<sub>4</sub> )  
 , XO<sub>4</sub> , X -3 -4

가 가 :  
 A<sub>a</sub> M<sub>b</sub> XO<sub>4</sub> ,

$$(V^A)a + (V^M)b + (V^X)c = (V^O)4$$

( , V<sup>A</sup> A 가 , V<sup>M</sup> M 가 , V<sup>O</sup> -2 O( ) 가 ).

$$(V^A)a + (V^M)b + (V^X)c = 8$$

가 , ' 가' (a) 가  
 가 , (b) 가 가

$$(V^A)a = [(V^{A1})a^1 + (V^{A2})a^2 + \dots + (V^{An})a^n] / n; a^1 + a^2 + \dots + a^n = a$$

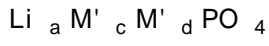
$$(V^M)b = [(V^{M1})b^1 + (V^{M2})b^2 + \dots + (V^{Mn})b^n] / n; b^1 + b^2 + \dots + b^n = b$$

가), 'c' , M , M , 'x' ( , XO<sub>4</sub> )  
 , M 가 , V<sup>A</sup> = 1 , :

$$(V^M)b = (V^A)4 + d - a - (V^X)$$

a, b x 가 , a, b x 가 , a, b x 가  
 , AaMbXO<sub>4</sub> , a, b x 가 , 가  
 Mg<sub>0.05</sub>PO<sub>4</sub> , AIMg(PO<sub>4</sub>)<sub>20</sub> , Li<sub>0.95</sub>Co<sub>0.9</sub>Al<sub>0.05</sub>Li<sub>19</sub>Co<sub>18</sub>

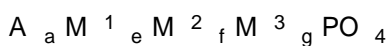
< >



- (a) 0 < a < 1.0 ;
- (b) M<sub>4</sub> 11 , c > 0 ;
- (c) M'<sub>2</sub> , 3 , 12 , 13 14 , d > 0 ;

M', M', a, c d  
 M'<sup>+2</sup> +3 Fe, Co, Ni  
 Mn, Cu, V, Zr, Ti, Cr , M' Ti, V, Cr, Mn, Fe, Co,  
 Ni, Cu , M' Ti, V, Cr, Mn +3  
 , M' Mg, Ca, Zn, Sr, Pb, Cd, Sn, Ba, Be, Al +2 +3  
 , M' Ti, V, Cr Mn M' Mg, Ca, Zn, Ba, Al +3

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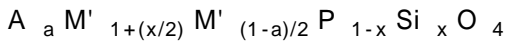


- (a) A Li, Na, K , 0 < a < 1 ;
- (b) M<sup>1</sup> , 0 < e ;
- (c) M<sup>2</sup> +2 ;
- (d) M<sup>3</sup> +3 ; ,

, M<sup>1</sup> , M<sup>2</sup> , M<sup>3</sup> , X, a, e, f g  
 , M<sup>1</sup> +2 , a + 2e + 2f + 3g = 3 , 0 < (e + f + g) 2  
 f + g) < 1 , 0.8 (e + f + g) 1.5 , 1 (e + f + g) 1.5 , 0 < (  
 0.05 (f + g) 0.1 , 0.05 (f + g) 0.2 ,  
 , M<sup>1</sup> 4 11 ; M<sup>2</sup> 2 , 12  
 14 ; M<sup>3</sup> 4 11 +3 , 3 13

$+3$   
 Fe, Co, Ni, Mn, Cu, V, Zr, Ti, Cr ; , M<sup>1</sup>  
 Fe, Co, Mn, Cu, V, Cr +2 ; M<sup>1</sup>  
 , M<sup>2</sup> +2 ;  
 , M<sup>2</sup> Be, Mg, Ca, Sr, Ba, Ra, Zn, Cd, Hg ,  
 , M<sup>3</sup> +3 , M<sup>3</sup> 4 11 ,  
 Ti, V, Cr, Mn, Fe , M<sup>3</sup> +3  
 , M<sup>3</sup> 3 13 Sc, Y, La, Ac, B, Al, Ga, In,  
 Tl

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(a) A Li, Na, K ,  $0 < a < 1$  ;

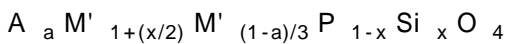
(b) M' +2 ; ,

(c) M' +2 ;

$x = 0$  , M', M', a x .

, A Li Li Na K Na K , M' Ti, V, Cr,  
 Mn, Fe, Co, Ni , M' Mg, Ca, Zn, Sr, Pb, Cd, Sn  
 , Ba, Be +2 , M  
 ' Mg, Ca, Zn, Ba

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(a) A Li, Na, K ,  $0 < a < 1$  ;

(b) M' 가 +2 ;

(c) M' +3 ,

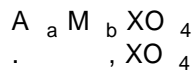
$x = 0$ , M', M', a x .

, A Li, Li Na K , A Na, K  
 , M' Ti, V, Cr, Mn, Fe, Co, Ni  
 , M' Mg, Ca, Zn, Sr, Pb, Cd, Sn, Ba, Be  
 +2 가 , M' Mg, Ca, Zn, Ba  
 Sc, Y, La, B, Al, Ga, In, Tl , M' 3 13 ,  
 , M' 4 11 , +3  
 +3 Cr, V, Ti, Mn



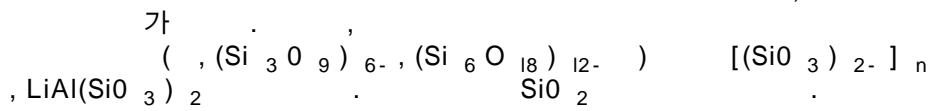


가



가

) M

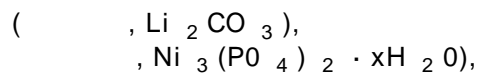


1 ( ) 가

가

가

AHP)



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800

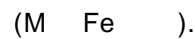
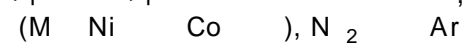
가

가

가

가

2 /



(a) 25% 95%, 50% 90% ;



); 5,712,059 (Barker et al., 1998. 1. 27 ); 5,700,287 (Shi et al., 1997. 12. 23  
 3 ); 6,103,419 (Saidi et al., 2000. 8. 15 ); 5,830,602 (Barker et al., 1998. 11.

(a) 25% 95%, 50% 90% ;

(b) 2% 95% ( , );

(c) 3% 20% ,

( , LiCoO<sub>2</sub> , LiNiO<sub>2</sub> ),  
 , LiCo<sub>1-m</sub>Ni<sub>m</sub>O<sub>2</sub> ( , 0 < m < 1) ,  
 , LiMn<sub>2</sub>O<sub>4</sub> 가 ,  
 6,183,718 (Barker et al., 2001. 2. 6 , ) 5,869,207 (1999. 2. 9  
 가 )

가

가

( )

가

가

(DMC),

(DEC),

(DPC),

(EMC),

EC/DMC, EC/DEC, EC/DPC EC/EMC

, LiAsF<sub>6</sub>, LiPF<sub>6</sub>, LiClO<sub>4</sub>, LiB(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>, LiAlCl<sub>4</sub>, LiBr  
 5% 65%,

8%

35%

60:30:10

EC:DMC:LiPF<sub>6</sub>

5,418,091 (Gozdz et al., 1995. 5. 23 );

5,508,130 (

Golovin, 1996. 4. 16 );

5,541,020 (Golovin et al., 1996. 7. 30 );

5,620,810

(Golovin et al., 1997. 4. 15 );

5,643,695 (Barker et al., 1997. 7. 1 );

5,712,0

59 (Barker et al., 1997. 1. 27 );

5,851,504 (Barker et al., 1998. 12. 22 );

6

,020,087 (Gao, 2001. 2. 1. );

6,103,419 (Saidi et al., 2000. 8. 15 )

(

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가

가 ( )

가

(fumed silica)

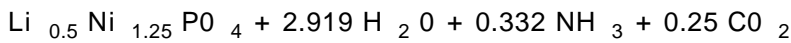
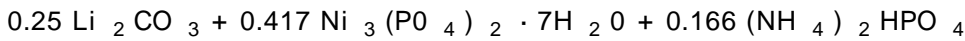


5,540,741 (Gozdz et al., 1996. 7. 30 ) ,

가 .

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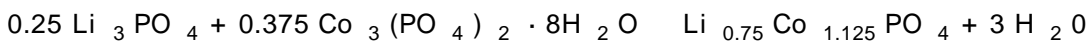
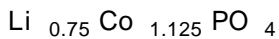
1



18.475 g(0.25 mol)  $\text{Li}_2 \text{CO}_3$  , 204.77(0.417 mol)  $\text{Ni}_3 (\text{PO}_4)_2 \cdot 7\text{H}_2\text{O}$  ,  
 21.92 g (0.166 mol)  $(\text{NH}_4)_2 \text{HPO}_4$  , 가  
 16 , ( 21 )

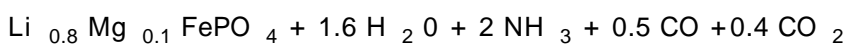
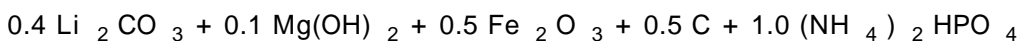
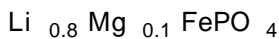
80% ; 8% Super P ; 12% KYNAR<sup>®</sup> (KYNAR<sup>®</sup>  
 PVdF:HFP )  $\text{Li}_{0.5} \text{Ni}_{1.25} \text{PO}_4$   
 2:1 EC DMC 1 LiPF<sub>6</sub>

2



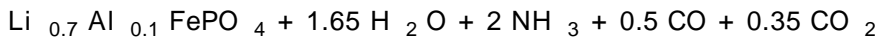
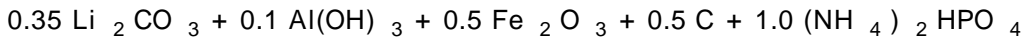
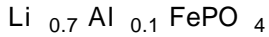
28.39 g(0.25 mol)  $\text{Li}_3 \text{PO}_4$  , 191.194 g(0.375 mol)  $\text{Co}_3 (\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$  , 가  
 800 , 가 , 8 , 2 /  
 25 .

3



29.56 g(0.4 mol)  $\text{Li}_2 \text{CO}_3$  , 5.83 g (0.1 mol)  $\text{Mg}(\text{OH})_2$  , 79.85 g(0.5 mol)  $\text{Fe}_2 \text{O}_3$  , 6.00 g(0.5 mol)  
 (100% ) 132.06 g(1.0 mol)  $(\text{NH}_4)_2 \text{HPO}_4$  , 가  
 48 2 / , 650-850 가 , ( 21 )

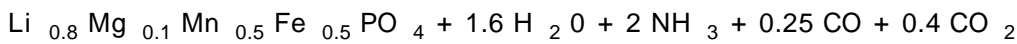
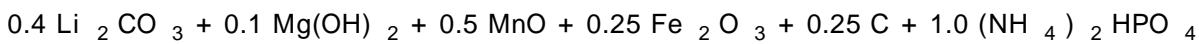
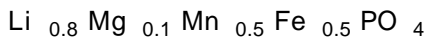
4



25.86 g(0.35 mol)  $\text{Li}_2 \text{CO}_3$ , 7.80 g (0.1 mol)  $\text{Al(OH)}_3$ , 79.85 g(0.5 mol)  $\text{Fe}_2 \text{O}_3$ , 6.00 g(0.5 mol)  $(\text{NH}_4)_2 \text{HPO}_4$   
 (100% ) 132.06 g(1.0 mol) 가

48 2 / 650-850 가 ( 21 )

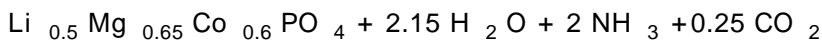
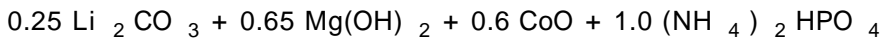
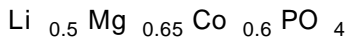
5



29.60 g(0.4 mol)  $\text{Li}_2 \text{CO}_3$ , 5.83 g (0.1 mol)  $\text{Mg(OH)}_2$ , 35.47 g(0.5 mol)  $\text{MnO}$ , 39.93 g(0.25 mol)  $\text{Fe}_2 \text{O}_3$ , 3.00 g(0.25 mol) (100% ) 132.06 g(1.0 mol)  $(\text{NH}_4)_2 \text{HPO}_4$   
 가

48 2 / 650-850 가 ( 21 )

6



18.47 g(0.25 mol)  $\text{Li}_2 \text{CO}_3$ , 37.91 g (0.65 mol)  $\text{Mg(OH)}_2$ , 44.96 g(0.6 mol)  $\text{CoO}$ , 132.06 g(1.0 mol)  $(\text{NH}_4)_2 \text{HPO}_4$   
 가

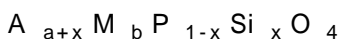
48 2 / 650-850 가 ( 21 )

(57)

1.

(active material).

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[ ,

(a) A Li, Na, K ,  $0 < a < 1$ ,  $0 < x < 1$  ; ,

(b) M 가 , ,  $0 < b < 2$  ;

M, a, b x ]

2. 1, 0.1 a 0.9 .

3. 1, 1.0 b 1.5 .

4. 1, M +3 .

5. 1, M +2 .

6. 1, M M' c M' d , M'가 4 11 ; M'가  
2, 12, 13 14 ; c + d = b .

7. 6, 0 < (c + d) 2 .

8. 7, 1.0 (c + d) 1.5 .

9. 4, M'가 Ti, V, Cr, Mn, Fe, Co, Ni, Cu .

10. 4, M'가 Mg, Ca, Zn, Sr, Pb, Cd, Sn, Ba, Be, Al .

11. 1, A가 Li .

12. .

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[ ,

(a)  $0 < a < 1$  ;

(b) M' 가 ,  $c > 0$  ;

(c) M' ,  $d > 0$  ;

0.8 (c + d) 1.5 , M', M', a, c d ]

13. 12, M'가 +2 .

13 14. , M'가 Ti, V, Cr, Mn, Fe, Co, Ni Cu .

12 15. , M'가 +2 +3 .

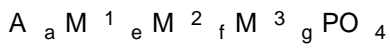
15 16. , M'가 Mg, Ca, Al, B .

12 17. , M'가 +3 .

17 18. , M'가 V, Cr, Ti, Mn .

19.

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[ ,

(a) A Li, Na, K ,  $0 < a < 1$  ;

(b)  $M^1 +2$  ,  $e > 0$  ;

(c)  $M^2 +2$  ;

(d)  $M^3 +3$  ; ,

$$, a + 2e + 2f + 3g = 3 ]$$

19 20. ,  $M^1$  Fe, Co, Ni, Ti, V, Cr, Mn .

19 21. ,  $M^2$  가 Be, Mg, Ca, Sr, Ba .

19 22. ,  $M^3$  가 B, Al, Ga, In .

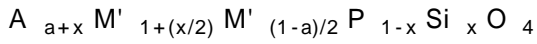
19 23. ,  $0 < (e + f + g) < 2$  .

23 24. ,  $0.8 < (e + f + g) < 1.5$  .

24 25. ,  $1.0 < (e + f + g) < 1.5$  .

26.

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[ ,

(a) A Li, Na, K ,  $0 < a < 1$  ,  $x = 0$  ;

(b) M' +2 ; ,

(c) M' +2 ;

M', M', a x ]

**27.**

26 , A Li .

**28.**

26 , M' Ti, V, Cr, Mn, Co, Fe, Ni, Cu .

**29.**

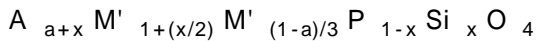
26 , M'가 Be, Mg, Ca, Sr, Ba .

**30.**

29 , M'가 Be, Mg, Ca, Sr, Ba .

**31.**

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[ ,

(a) A Li, Na, K ,  $0 < a < 1$  ,  $x = 0$  ;

(b) M' 가 +2 ; ,

(c) M' +3 ;

M', M', a x ]

**32.**

31 , A가 Li .

**33.**

32 , M'가 +3 .

**34.**

33 , M'가 Ti, V, Cr, Mn .

**35.**

31 , M'가 +3 .

36.  
35 , M'가 B, Al, Ga, In .
37.  
31 , M'가 Ti, V, Cr, Mn, Fe, Co, Ni, Cu .
38.  
37 , M'가 가 +2 .
39.  
38 , Be, Mg, Ca, Sr, Ba, Ra .
40.  
1 , .
41.  
12 , .
42.  
19 , .
43.  
26 , .
44.  
31 , .
45.  
(a) 1 1 ;  
(b) 1 2 ;  
(c) .
46.  
45 , 1 , 2 .
47.  
46 , 2 , , , .
48.  
(a) 12 1 ;  
(b) 1 2 ;  
(c) .
49.  
(a) 19 1 ;  
(b) 1 2 ;  
(c) .

