

NEW HIGH VOLTAGE CATHODE MATERIALS FOR RECHARGEABLE LITHIUM BATTERIES

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1. INTRODUCTION

Since the $\text{LiCoO}_2/\text{Li}_x\text{C}_6$ "lithium-ion cell" was introduced into the consumer market by Sony Energytec, Inc. of Japan in 1990 [1], lithium secondary batteries have regained consumer confidence due to their improved long cycle life and safe cell operation. These improvements in cell performance are achieved at the expense of energy density by replacing the metallic lithium anode with an intercalation electrode material, usually a carbon. To compensate for the loss in energy density, the working voltage of the cathode in lithium-ion cells is required to be very high, preferably about 4 V during discharging.

To this date, three major systems of high voltage cathode materials have been developed and marketed for lithium-ion cells: (1) LiCoO_2 by Sony Energytec, Inc., (2) LiNiO_2 by Moli Energy (1990) Ltd., and (3) LiMn_2O_4 by Bellcore. Both LiCoO_2 and LiNiO_2 have a layered structure whereas LiMn_2O_4 has a spinel structure. The upper voltage limits of these cathode materials are in the 4.3–4.5 V range where most of the lithium ions can be electrochemically removed, resulting in a high specific energy.

In the context of this article, high voltage cathode will refer to those cathodes that require charging above 4 V vs. Li. Typical examples are the lithiated transition metal oxides mentioned above. In contrast, low voltage cathodes composed of materials such as TiS_2 [2–3], MoS_2 [4], MoO_3 [5, 6], NbSe_3 [7–8], MnO_2 [9], and vanadium oxides [5, 10–11], are fully charged well below 4 V.

In 1993, we discovered that LiNiVO_4 can be a high voltage cathode material for lithium secondary cells [12]. Our finding is significant because LiNiVO_4 not only exhibits a voltage of 4.8 volt, the highest observed for any known Li intercalation reaction, but is also the first material with an inverse spinel structure to be used as a cathode for rechargeable lithium cells. Further applications to thin-film cells and lithium-ion cells are feasible provided that a proper electrolyte stable to high oxidation potential can be developed.

In this paper, new preparation methods for LiNiVO_4 and its isostructural compound LiCoVO_4 [13] will be reported and the effects of starting materials, reactant stoichiometry, synthesis temperature, and reaction environment on the quaternary Li-Ni-V-O reaction will be discussed. In addition, the results from

TABLE 1

Preparation Methods and Reaction Conditions for LiMVO ₄ Compounds			
Compound	Reactants	Reaction Condition	Ref.
LiCoVO ₄	LiVO ₃ + CoC ₂ O ₄	500°C, 7 days	19
	LiCoO ₂ + V ₂ O ₃	700°C, 1 h	12
	LiCoO ₂ + V ₂ O ₅	700°C, 1 h	13
LiNiVO ₄	LiVO ₃ + NiCO ₃	500°C, 7 days	19
	Li ₂ O + NiO + V ₂ O ₅	800°C, 1 day to 500°C, 25 days	20
	LiNiO ₂ + V ₂ O ₃	500°C, 4 h and 800°C, 6 h	21
	LiNiO ₂ + V ₂ O ₅	700°C, 2 h	13
LiCuVO ₄	Li ₂ CO ₃ + CuO + V ₂ O ₅	530°C	22
LiMgVO ₄	Li ₂ CO ₃ + MgO + NH ₄ VO ₃	650°C, 4 days	17
	Li ₂ CO ₃ + MgCO ₃ + NH ₄ VO ₃	750°C, 1 day	18
	Li ₂ O + MgO + V ₂ O ₅	800°C, 1 day to 500°C, 25 days	20
LiCdVO ₄	Li ₂ CO ₃ + CdCO ₃ + NH ₄ VO ₃	600°C, 8 days	17
LiBeVO ₄	Li ₂ CO ₃ + BeO + NH ₄ VO ₃	750°C, 1 day	18
LiZnVO ₄	Li ₂ CO ₃ + ZnO + NH ₄ VO ₃	750°C, 1 day	18
	Li ₂ O + ZnO + V ₂ O ₅	800°C, 1 day to 500°C, 25 days	20
	Li ₂ CO ₃ + ZnO + V ₂ O ₅	500°–700°C	23

characterization, structural analysis, and cell performance of these new materials will also be presented.

2. MATERIAL BACKGROUND AND PREPARATION

As early as the 1950s and 1960s, LiMVO₄ materials, where M = Cu [14], Ni [15], Co [15], Zn [16], Cd [17], Mg [18], Be [18], etc., have been studied with an emphasis on their preparation and characterization. In general, the traditional method of solid state reaction at high temperature is employed for the preparation of LiMVO₄ compounds, by mixing and heating stoichiometric amounts of lithium carbonate, ammonium vanadate (or V₂O₅), and various divalent carbonates (or oxides). Typical examples of preparation methods, including reactants and reaction conditions, are listed in Table 1.

Based on early results shown in Table 2, LiMVO₄ compounds have three different structures: (1) spinel, (2) olivine, and (3) phenacite. However, both LiNiVO₄ and LiCoVO₄ are shown to be inverse spinel according to our recent results from powder XRD data calculation [12]. Interestingly, the structures of both LiMgVO₄ and LiZnVO₄ can be converted from olivine or phenacite to spinel

TABLE 2

Types of Structures of LiMVO₄ Compounds [17, 18, 24]

Structure	Compounds
Spinel	LiCuVO ₄ , LiNiVO ₄ [*] , LiCoVO ₄ [*]
Olivine	LiMnVO ₄ , LiCdVO ₄ , LiMgVO ₄
Phenacite	LiBeVO ₄ , LiZnVO ₄

^{*}Both LiNiVO₄ and LiCoVO₄ are shown to be inverse spinel from our recent results [12]

TABLE 3

Solid State Reactions for Preparing LiNiVO₄

Starting Reactants (mole ratio)	Reaction [†] Condition	Reaction Environment	Products
LiNiO ₂ + NH ₄ VO ₃	(1)	Argon	LiNiVO ₄ , Li ₃ VO ₄ , NiO, Ni, V ₂ O ₃
LiNiO ₂ + NH ₄ VO ₃	(1)	Ammonia	LiVO ₂ , Li ₃ VO ₄ , Ni, V ₂ O ₃ , *
LiNiO ₂ + NH ₄ VO ₃	(1)	Air	LiNiVO ₄ , Li ₃ VO ₄ , NiO
2LiNiO ₂ + V ₂ O ₃	(1)	Ammonia	LiVO ₂ , Li ₃ VO ₄ , Ni, V ₂ O ₄ , *
2LiNiO ₂ + V ₂ O ₃	(1)	Air	LiNiVO ₄
2LiNiO ₂ + V ₂ O ₅	(1)	Argon	LiNiVO ₄ , Li ₃ VO ₄ , NiO, V ₂ O ₃
2LiNiO ₂ + V ₂ O ₅	(1)	Air	LiNiVO ₄
Li ₂ CO ₃ + 2NiO + V ₂ O ₅	(2)	Air	LiNiVO ₄
Li ₂ CO ₃ + 2NiO + 2NH ₄ VO ₃	(3)	Air	LiNiVO ₄
LiNiO ₂ + V ₂ O ₃	(4)	Air	LiNiVO ₄
LiNiO ₂ + V ₂ O ₅	(4)	Air	LiNiVO ₄

[†]Reaction conditions: (1) 500°C, 4 h & 800°C, 8 h; (2) 600°C, 3 days, (3) 730°C, 12 h; (4) 700°C, 2 h.

*LiNiVO₄ produced after reducing at 500°C for 4 hours.

by high-pressure modification [16, 18]. Only compounds with spinel or spinel related structures will be discussed in this paper, because they are potential cathode materials for lithium secondary batteries.

Existing methods for preparing LiNiVO₄ are not economical because of the long reaction times and high temperatures required. Bernier et al. [15] reacted LiVO₃ and NiCO₃ at 500°C for 7 days and Ito [25] reacted LiVO₃ and NiO at 1000°C for 4 days.

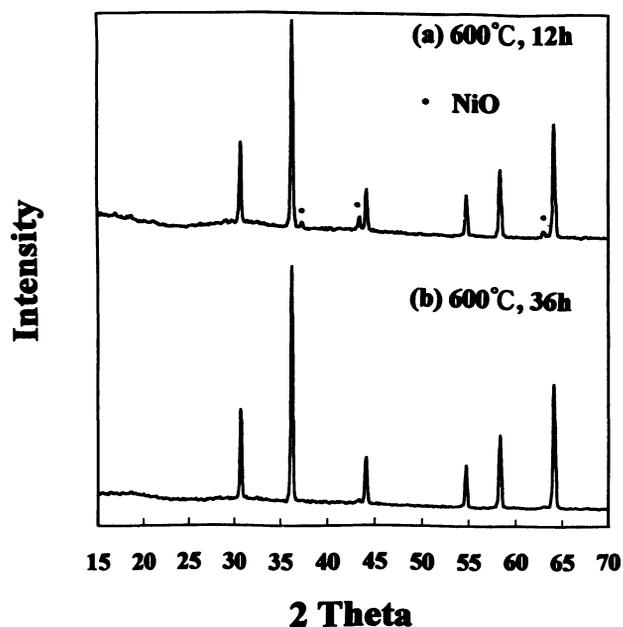


FIGURE 1 XRD Patterns of LiNiVO₄ Prepared from the Reaction of Li₂CO₃, NiO and V₂O₅.

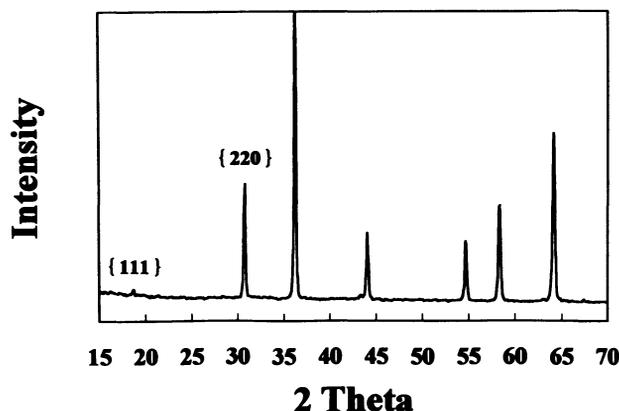


FIGURE 2 The XRD Pattern of LiNiVO_4 Prepared from the Reaction of Li_2CO_3 , NiO and NH_4VO_3 .

To develop a new and more practical method, we carried out a series of solid state reactions using different starting materials in various gaseous atmospheres. The results are presented in Table 3. The optimum preparation method of LiNiVO_4 used an air reaction atmosphere and LiNiO_2 and V_2O_3 or V_2O_5 as starting reactants. Pure LiNiVO_4 can be obtained by reacting LiNiO_2 and V_2O_3 or V_2O_5 at 700°C in 2 hours. In the majority of the reactions, small amounts of impurities such as Li_3VO_4 , NiO , Ni , and LiVO_2 were also produced. In an argon or ammonia atmosphere, such as when NH_4VO_3 is a starting reactant, LiNiO_2 can further be reduced to nickel metal. The strongest NiO Bragg peaks confirmed by JCPDS data were near 16.2 , 21.5 , and 24.3 degrees. Figure 1 illustrates that these NiO peaks can be removed by extending reaction time from 12 hours to 36 hours at 600°C during the reaction of Li_2CO_3 , NiO and V_2O_5 . The XRD pattern of pure LiNiVO_4 in Figure 2, obtained by reacting Li_2CO_3 , NiO and NH_4VO_3 at 730°C for 12 hours, is identical to that of the product from the 2 LiNiO_2 and V_2O_5 reaction at 700°C for 2 hours.

Figures 3a, 3b and 3c display the thermogravimetric behavior of the 2 LiNiO_2 and V_2O_3 reaction, the 2 LiNiO_2 and V_2O_5 reaction, and the Li_2CO_3 , 2 NiCO_3 and V_2O_5 reaction in air, respectively. From 700°C to 950°C , the weight of the specimen remained almost constant. Using XRD to characterize the TGA residue, we were able to confirm that LiNiVO_4 was produced and conclude that LiNiVO_4 can be prepared by reacting 2 LiNiO_2 and V_2O_3 or V_2O_5 in air around 700°C . The isostructural compound LiCoVO_4 was produced by reacting 2 LiCoO_2 with V_2O_3 or V_2O_5 at 700°C for only 1 hour in air. Both reactions required less than 2 hours. Because incomplete reactions occur at lower temperatures, the synthesis of these vanadates should be at above 650°C . LiCoVO_4 can also be prepared by reacting Li_2CO_3 , Co_3O_4 , and V_2O_5 at 800°C for 12 hours, the XRD pattern shown in Figure 4. Because of the relatively low reaction temperature and the much shorter reaction time, we can conclude that the reaction of LiMO_2 (where $M = \text{Ni}$ or Co) with V_2O_3 or V_2O_5 is a practical method for producing a large quantity of good quality LiMVO_4 ($M = \text{Ni}$ or Co).

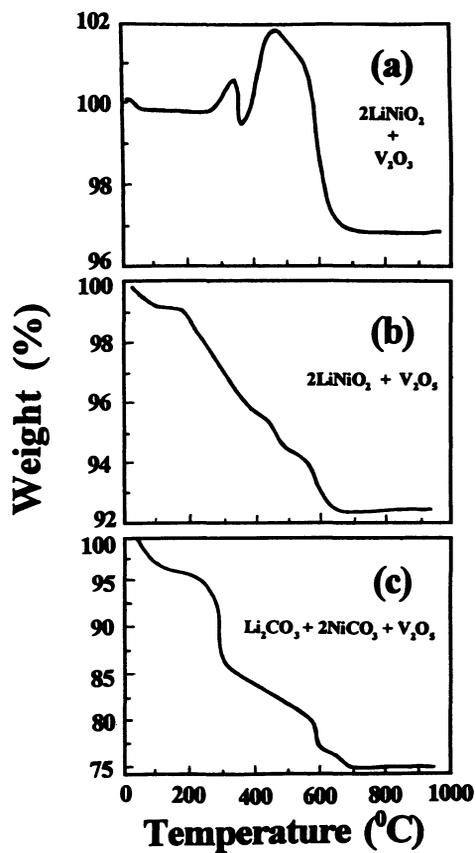
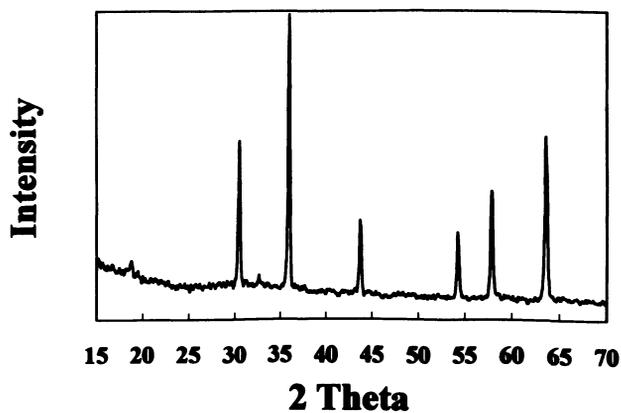


FIGURE 3 TGA Diagrams of Solid State Reactions in Air.

FIGURE 4 The XRD Pattern of LiCoVO_4 Prepared from the Reaction of Li_2CO_3 , Co_3O_4 and NH_4VO_3 .

3. EFFECTS OF REACTANTS STOICHIOMETRY ON THE FORMATION OF LiNiVO_4

The products of solid state reactions between LiNiO_2 and NH_4VO_3 with various stoichiometry in ammonia were characterized [13]. The reactions took place under reductive conditions, first at 500°C for 4 hours and then at 650°C for 24 hours. In all cases, only nickel metal was produced and no LiNiVO_4 was formed. When the reactant ratio of LiNiO_2 to NH_4VO_3 was less than one, V_2O_3 and LiVO_2 were the main products. When it was greater than one, Li_3VO_4 was the main product. When the mole ratios were one, nickel, V_2O_3 , LiVO_2 , and Li_3VO_4 were produced. Because NH_4VO_3 did not seem to be an effective starting reactant, V_2O_3 and V_2O_5 were later used.

The products of solid state reactions between LiNiO_2 and V_2O_3 in air, which took place first at 500°C for 4 hours and then at 800°C for 6 hours were also characterized [13]. When the ratio of LiNiO_2 to V_2O_3 was less than two, a complicated mixture of Li_3VO_4 , NiV_2O_7 , and $\text{Ni}_3(\text{VO}_4)_2$ was formed. When the ratio was greater than two, LiNiVO_4 was the main product with some impurities such as Li_3VO_4 and NiO . When the ratio was equal to two, pure LiNiVO_2 was produced. This finding was a major breakthrough in developing a preparation method for LiNiVO_4 .

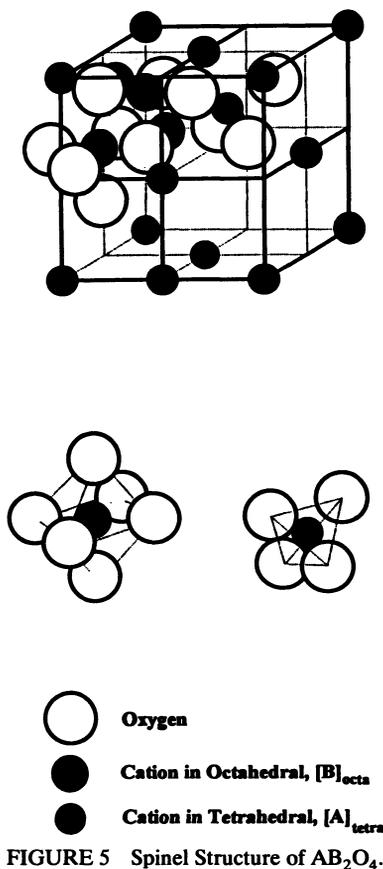
4. STRUCTURES OF LiMVO_4 COMPOUNDS ($\text{M} = \text{Ni, Co, Cu}$)

There are two kinds of spinel for AB_2O_4 oxides: one is normal spinel and the other is inverse spinel. In normal spinel structure compounds, such as LiMn_2O_4 and LiTi_2O_4 , oxygen atoms are in a closely packed cubic array with transition metal atoms residing in the interstices to form an octahedron with the six closest oxygen atoms. The lithium atoms also reside in interstices forming a tetrahedron with four neighboring oxygen atoms. The structural arrangement can be represented as $[\text{A}]_{\text{tetra}}[\text{B}_2]_{\text{octa}}\text{O}_4$ and is depicted in Figure 5.

The above distribution of atoms creates a three dimensional network of tunnels. Because Li atoms are located throughout and can diffuse through these tunnels, their presence is thought to be essential to the intercalation and deintercalation of lithium from these materials. These compounds can also react further with lithium to produce $\text{Li}_2\text{Ti}_2\text{O}_4$ and $\text{Li}_2\text{Mn}_2\text{O}_4$. If lithium is removed from LiTi_2O_4 and LiMn_2O_4 , $\lambda\text{-MnO}_2$ and $\text{Li}_{1-x}\text{Ti}_2\text{O}_4$ are formed, respectively.

In inverse spinel compounds, the cations are arranged differently. In LiNiVO_4 , the Li and Ni atoms are thought to be equally and randomly distributed among octahedrally coordinated interstices and the V atoms distributed among tetrahedrally coordinated interstices. The above structural arrangement can be represented as $[\text{B}]_{\text{tetra}}[\text{AB}]_{\text{octa}}\text{O}_4$. In relation to LiMn_2O_4 , the Li and Ni atoms correspond to the 2 Mn atoms and the V atom to the Li atom.

Unlike LiMn_2O_4 , there are no obvious tunnels for mobile Li atoms to move through, so it is surprising that intercalation takes place. However, using in situ

FIGURE 5 Spinel Structure of AB_2O_4 .

diffraction (XRD), we have shown that lithium can be removed from $LiNiVO_4$ and reversibly inserted again [12]. The intercalation/deintercalation takes place at a plateau near 4.8 V in $Li/LiNiVO_4$ cells [12]. To our knowledge, this is the Li intercalation reaction with the highest voltage. Although $LiCoVO_4$ is an isostructural compound that also demonstrates reversible lithium intercalation, its voltage is only around 4.2 V versus Li. We do not yet understand why the voltage of $Li/LiNiVO_4$ cells is so high. It may be partly attributed to the fact that lithium atoms are octahedrally surrounded by six oxygen atoms in an inverse spinel structure. It is more difficult to remove a Li atom from an octahedron of six oxygen atoms than from a tetrahedron of four oxygen atoms such as in a spinel structure.

The XRD patterns and JCPDS data were identical for both $LiNiVO_4$ and $LiCoVO_4$, which had been prepared using the above method. The inverse spinel structure is evident because the $\{220\}$ peak is more intense than the $\{111\}$ peak, the opposite of what happens with normal spinel compounds. Transition metal atoms on the tetrahedrally coordinated interstices cause an increase in the $\{220\}$ peak at the expense of the $\{111\}$ peak. Our SEM results indicate that individual particles of

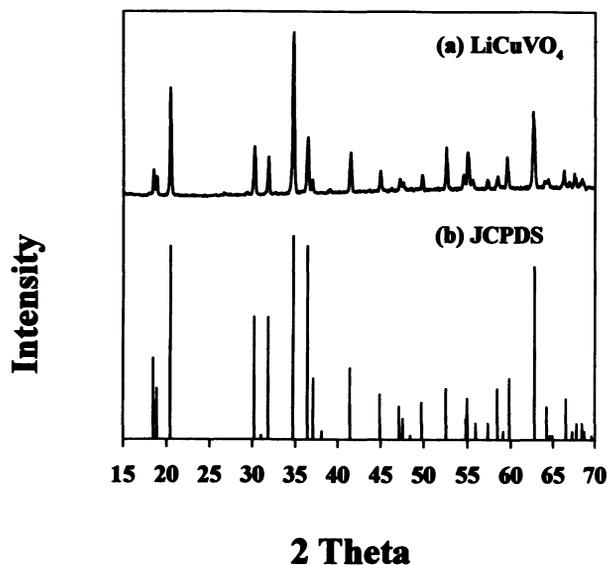


FIGURE 6 The XRD Pattern of LiCuVO₄ Prepared from the Reaction of LiVO₃ and CuO.

LiNiVO₄ powders are in the shape of an octahedron and well-formed crystallites of approximately 20 μm [13].

Although the measured powder diffraction profile for LiNiVO₄ is very close to a calculated pattern [12], assuming the inverse spinel structure suggested in reference [26], it is not close enough to completely understand the structure of this compound. Further structural analysis using neutron diffraction and ESCA is currently under way.

In the past, LiNiVO₄, LiCoVO₄ and LiCuVO₄ were all considered to have a spinel structure [14, 15]. From the above discussion, LiNiVO₄ and LiCoVO₄ are shown to possess an inverse spinel structure. Figure 6 displays the X-ray diffraction pattern of LiCuVO₄ prepared from the reaction of LiVO₃ and CuO at 600°C for 36 hours. The pattern is identical to that of a JCPDS sample of spinel LiCuVO₄ but very different from that of LiNiVO₄ or LiCoVO₄ shown in Figure 2 or Figure 5. Notably, the {220} peak is not more intense than the {111} peak, implying that LiCuVO₄ does not possess an inverse spinel structure. However, a new refinement of the room-temperature structure of LiCuVO₄ [27] indicates that LiCuVO₄ is an orthorhombic distortion of the cubic spinel structure, with V⁵⁺ ions on tetrahedral sites and Li⁺ and Cu²⁺ ions ordered among octahedral sites. The orthorhombic distortion is caused by the one dimensional ordering of the lithium and copper ions [28]. Interestingly, the nature of the disorder in LiCuVO₄ is similar to Li⁺ and Ni²⁺ or Co²⁺ ions in the octahedral cation sublattice of LiNiVO₄ or LiCoVO₄, respectively. Lithiated Li_{1+x}CuVO₄, a cathode candidate for secondary lithium batteries, is electrochemically reversible in the range of 0 < x < 1.5 [22].

5. LiNiVO_4 AS A HIGH VOLTAGE CATHODE MATERIAL FOR LITHIUM CELLS

Since both LiNiVO_4 and LiCoVO_4 are not moisture sensitive, they can be handled under ambient atmosphere. To evaluate LiNiVO_4 as a cathode material, we tested the performance of 2325 coin-type lithium cells with 125 μm thick Li metal foil anodes, Celgard 2502 microporous polypropylene separators, and electrolytes of 1 M solution of LiBF_4 dissolved in a 66/17/17 volume percent mixture of DMC, PC, and EC, respectively. The electrolyte solution was proposed to be oxidation resistant in the patent literature [29].

The Li/ LiNiVO_4 test cells displayed a very high voltage of 4.8 V, reasonable capacity, and reasonable rate capability. Figure 7 shows a diagram of voltage versus time for a Li/ LiNiVO_4 coin cell which was cycled between 3.0 and 4.9 V. Cell capacity diminished after the first charge and was much smaller than the theoretical capacity (148 mAh/g) expected from the complete removal of Li from LiNiVO_4 . However, the discharge capacity being on the low end of achievable capacity was probably caused by the problem of electrolyte oxidation occurring under these conditions.

Similar Li/ LiCoVO_4 coin cells cycled between 3.0 and 4.5 V demonstrated better cycle life (Figure 8). For reasons not yet known, the voltage was much lower than the Li/ LiNiVO_4 cell. The reversible capacity was only 40 mAh/g and the discharge capacity failed to increase when the cell was charged to 4.9 V.

Some important lithiated transition metal oxides and sulfides and their approximate working voltages with respect to the lithium metal electrode are shown in Figure 9. Other potential anode materials such as lithiated graphite, lithium aluminum alloy, and lithium silicon alloy are also included for comparison and application. For instance, the combination of a 4-volt cathode material and natural graphite gives a lithium-ion secondary battery. Notably, both LiNiVO_4 and LiCoVO_4 are possible for 4-volt cathode candidates for lithium ion batteries.

The voltage range of the individual cathode materials in Figure 9 depends upon lithiation depth, x , or the number of reacting lithium atoms. LiCuVO_4 shows a lower voltage but a larger extent of lithium insertion than the nickel and cobalt

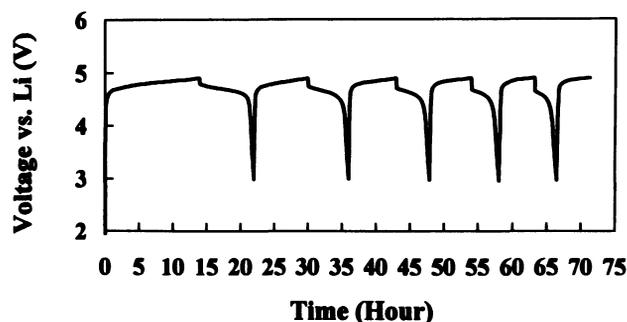


FIGURE 7 Voltage versus Time for a Li/ LiNiVO_4 Cell

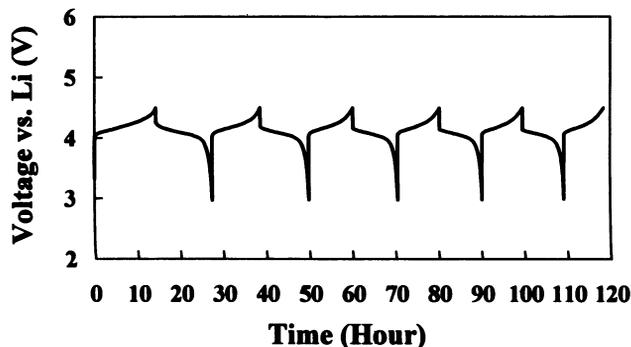


FIGURE 8 Voltage versus Time for a Li/LiCoVO₄ Cell

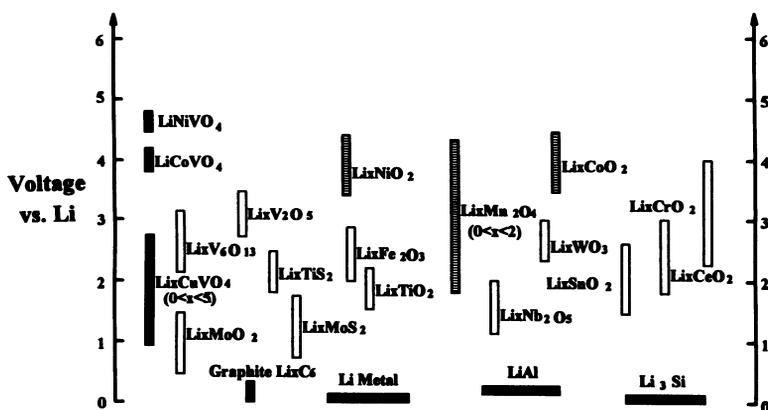


FIGURE 9 Approximate Working Voltage of Lithiated Transition Metal Oxides and Sulfides.

vanadates. The lithiation depth for LiCuVO₄ can go as high as $x = 5$ [22]. The voltage range for both LiNiVO₄ and LiCoVO₄ is small and the exact x range for both vanadates has not yet been determined. Nevertheless, LiNiVO₄ can discharge at 4.8 V vs. Li, the highest voltage among all known cathode materials. Based on in situ x-ray cell results [12], the LiNiVO₄ structure, is not destroyed during charging to 5.3 V and lithium atoms in LiNiVO₄ can be reversibly extracted and reinserted near 4.8 V versus Li metal.

6. CONCLUSION

In the area of battery research, many studies have been done on spinel compounds such as LiMn₂O₄, which has already been successfully used as a cathode material in the C/Li_{1+x}Mn₂O₄ lithium ion battery. In contrast, there have been relatively few detailed studies on inverse spinel compounds, but our results show that further research may be very promising. The development of a commercially viable cell poses a challenge for the near future. For example, a great deal more must be learned about the structure of this material and better electrolytes with oxidation

resistance of at least 5 volts must be developed. Indeed, LiNiVO_4 may be a prime cathode material for future higher voltage cells, especially since LiNiVO_4 can now be prepared in a much faster and more economical way than in the past.

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REFERENCES

1. T. Nagaura and T. Tozawa, *Progress in Batteries & Solar Cells*, 9, 20 (1990).
2. M.S. Whittingham, *J. Electrochem. Soc.*, 123, 315 (1976).
3. M.S. Whittingham, *Progress in Solid State Chem.*, 12, 41 (1978).
4. A.J. Jacobson, R.R. Chianelli and M.S. Whittingham, *J. Electrochem. Soc.*, 126, 2277 (1979).
5. M.S. Whittingham and M.B. Dines, *J. Electrochem. Soc.*, 124, 1388 (1977).
6. L. Campanella and G. Pistoia, *J. Electrochem. Soc.*, 118, 1905 (1971).
7. J. Broadhead and F.A. Trumbore, *Electrochem. Soc. Ext. Abstr.*, 73-1, 445 (1973).
8. D.W. Murphy and F.A. Trumbore, *J. Electrochem. Soc.*, 123, 960 (1976).
9. F.W. Dampier, *J. Electrochem. Soc.*, 121, 656 (1974).
10. D.W. Murphy, P.A. Christian, F.J. Di Salvo and J. N. Carides, *J. Electrochem. Soc.*, 126, 497 (1979).
11. C.R. Walk and J.S. Gore, *Electrochem. Soc. Ext. Abstr.*, 75-1, 60 (1975).
12. G.T.K. Fey, W. Li and J.R. Dahn, *J. Electrochem. Soc.*, 141, 2279 (1994).
13. G.T.K. Fey and W.B. Perng, *J. Power Sources*, To be published.
14. A. Durif, J.C. Joubert and J.C. Grenier, *Compt. Rend. Acad. Sci. (Paris)*, 260, 2472 (1965).
15. J.C. Bernier, P. Poix and A. Michel, *Compt. Rend. Acad. Sci. (Paris)*, 253, 1578 (1961).
16. G. Blasse, *J. Inorg. Nucl. Chem.*, 25, 136 (1963).
17. M. Th. Paques-Ledent and P. Tarte, *Spectrochimica Acta*, 30A, 673 (1974).
18. G. Blasse, *Philips Res. Rept. Suppl. No. 3* (1964).
19. J. Preudhomme and P. Tarte, *Spectrochimica Acta*, 28A, 69 (1972).
20. L.L.Y. Chang and F.Y. Wang, *J. Amer. Cera. Soc.*, 71, 689 (1988).
21. W.B. Perng, Master Thesis, National Central University, Taiwan, R.O.C. (1993).
22. R. Kanno, Y. Takeda, M. Hasegawa, Y. Kawamoto and O. Yamamoto, *J. Solid State Chem.*, 94, 319 (1991).
23. M.M. Aslanukova, A.M. Khubiev, and E.G. Semin, *J. Appl. Chem. U.S.S.R.*, 53, 1880 (1980).
24. R. Kanno, Y. Kawamoto, Y. Takeda, M. Hasegawa and O. Yamamoto, *Solid State Ionics*, 40/41, 576 (1980).
25. Y. Ito, *Nippon Kagaku Kaishi*, 111, 1483 (1979).
26. J.C. Bernier, P. Poix, and A. Michel, *Bull. Soc. Chim. France*, 1661 (1963).
27. M.A. Lafontaine, M. Leblanc and G. Ferey, *Acta Cryst.*, C45, 1205 (1989).
28. R. Kanno, Y. Kawamoto, Y. Takeda, M. Hasegawa, O. Yamamoto, and N. Kinomura, *J. Solid State Chem.*, 96, 397 (1992).
29. D. Guyomard and J.M. Tarascon, *U.S. Pat.* 5.192,629 (1993).



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