

## Dopant effects and conductivity studies on a new high voltage cathode material with inverse spinel structure

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**Abstract:** The dopant effects of introducing rare earth atoms into the  $\text{LiNiVO}_4$  inverse spinel structure were studied by measuring electrical conductivity of  $\text{LiNiVO}_4$  as a function of temperature, type of dopants, and dopant mole ratio. The dopant mole ratios of  $\text{LiNiVO}_4$  to Ln (where Ln = La, Gd or Yb) used in the reactions of  $\text{LiNiVO}_4$  and  $\text{Ln}_2\text{O}_3$  ranged from  $1 \times 10^6$  to  $1 \times 10^2$ . Using a d.c. polarization method, the best improvement in conductivity was achieved by the smallest Yb-doped samples at  $25^\circ\text{C}$ , an increase from  $10^{-10}$  to  $10^{-7}$  S/cm at a mole ratio of  $\text{LiNiVO}_4 : \text{Yb} = 10^4$ . They maintained high conductivity of  $10^{-7}$  S/cm up to a mole ratio of  $10^2$ . From  $10^\circ\text{C}$  to  $50^\circ\text{C}$ , the medium Gd-doped samples reached their highest conductivity, ranging from  $6.21 \times 10^{-7}$  to  $3.52 \times 10^{-7}$  S/cm when the mole ratio was  $10^4$ , but beyond that conductivity declined sharply to  $10^{-10}$  S/cm. At  $25^\circ\text{C}$ , the largest La-doped samples showed only a slight increase in conductivity from  $10^{-9}$  to  $10^{-8}$  S/cm at a mole ratio of  $10^4$ , much lower than  $2.21 \times 10^{-6}$  S/cm measured by a pseudo a.c. non-polarization method. During the doping process at lower dopant concentrations, activation energy decreased as concentration increased, but it remained virtually constant at higher dopant concentrations due to the reactions between  $\text{LiNiVO}_4$  and the dopants.

### INTRODUCTION

Since the discovery of both  $\text{LiNiVO}_4$  and  $\text{LiCoVO}_4$  as new systems of cathode materials for secondary lithium batteries (1), interest in inverse spinel materials has arisen due to their high voltage behavior. To our knowledge, limited literature has been reported on the electrical conductivity of inverse spinel type compounds. Ito investigated the electrical conductivity of  $\text{LiNiVO}_4$  over the temperature range from  $250$  to  $1050^\circ\text{C}$  (2) and later measured the electrical conductivity of  $\text{LiNiVO}_4$  and  $\text{LiCoVO}_4$  between  $450$  and  $1000^\circ\text{C}$  in air by the d.c. four-terminal method (3). The electrical conductivity of  $\text{LiNiVO}_4$  was in the order of  $10^{-5}$  S/cm at  $450^\circ\text{C}$  from Ito's data (3) and in the order of  $10^{-8}$  S/cm at ambient temperature according to our preliminary measurement. Since  $\text{LiNiVO}_4$  is a poor electrical conductor, during electrode preparation, it is necessary to mix it with significant amounts of binder and a good electrical conductor such as carbon black to ensure that the electrode has sufficient electrical conductivity. However, the addition of carbon black lowers the electrode material's energy density.

The use of a dopant or additive to a material of interest is a widely used method of increasing its electrical conductivity. Liang found that the incorporation of aluminum oxide substantially increased the conductivity of lithium iodide from  $10^{-7}$  S/cm to  $10^{-5}$  S/cm at  $25^\circ\text{C}$  (4). Itoh et al. measured a.c. conductivity for perovskite-type compound  $\text{LiTiO}_3$  and achieved high lithium ion conductivity of  $10^{-3}$  S/cm for  $\text{La}_{0.5}\text{Li}_{0.5}\text{TiO}_3$  at room temperature by substituting Li for La (5,6). Since the perovskite structure  $[\text{ABO}_3]$  can tolerate having different ions with different valence states on the A-site and B-site, the inverse spinel structure  $[\text{B}]_{\text{tetra}}[\text{AB}]_{\text{octa}}\text{O}_4$  may be similar. For example, the cation arrangement in  $\text{LiNiVO}_4$  can be represented as  $[\text{Ni}_x\text{V}_{1-x}]_{\text{tetra}}[\text{LiNi}_{1-x}\text{V}_x]_{\text{octa}}\text{O}_4$  [ $1 > x > 0.15$ ] (3). The incorporation of trace amounts of lanthanum element may increase the conductivity of  $\text{LiNiVO}_4$  significantly.

In this work, we investigated the feasibility of improving electrical conductivity of  $\text{LiMVO}_4$  [ $M = \text{Ni}$  or  $\text{Co}$ ] by doping with various rare earth elements and studied the effects of temperature, the effects of varying amounts of these dopants, and their relationship to activation energy in the conduction process.

## EXPERIMENTAL

The doping process of  $\text{LiNiVO}_4$  with trace amounts of rare earth elements was conducted as follows. First,  $\text{LiOH} \cdot \text{H}_2\text{O}$ ,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{NH}_4\text{VO}_3$ , and  $\text{Ln}_2\text{O}_3$  [available from Aldrich, 99% purity, where  $\text{Ln} = \text{La}$ ,  $\text{Gd}$ , or  $\text{Yb}$ ] were weighed according to the mole ratio of  $\text{Li} : \text{Ni} : \text{V} : \text{Ln} = 1 : 1 : 1 : y$ , where  $y = 10^{-1}$ ,  $10^{-2}$ ,  $10^{-3}$ ,  $10^{-4}$ ,  $10^{-5}$ , or  $10^{-6}$ . Since  $\text{Ln}_2\text{O}_3$  is air-sensitive, it was weighed in a glovebox filled with argon. Then,  $\text{Ln}_2\text{O}_3$  was dissolved into dilute nitric acid, forming a colorless solution of trivalent cations of rare earth element. The acidic solution of  $\text{Ln}_2\text{O}_3$  was added to a green solution containing  $\text{LiOH}$ ,  $\text{Ni}(\text{NO}_3)_2$  and  $\text{NH}_4\text{VO}_3$ , and a yellowish brown precipitate was readily formed with sufficient stirring. After filtration, the precipitate was dried at  $100^\circ\text{C}$  and then heated at  $700^\circ\text{C}$  for 2 hours. A yellowish brown solid was obtained. Powder x-ray diffraction measurements were made with a Siemens D500 diffractometer equipped with a diffracted beam monochromator and  $\text{Cu K}\alpha$  radiation.

The cell was assembled and electrical conductivity was measured as follows. A weighed amount of powdery sample was pressed into a thin pellet under a pressure of 10 tons. The pellet was cut into a rectangular shape of  $1 \text{ cm} \times 0.2 \text{ cm} \times 0.06 \text{ cm}$  in dimension and mounted on a small Teflon block with double-sided Scotch tape. Teflon was employed due to its high bulk resistivity and easy cleaning. Two fine gold wires which acted as current and potential leads were glued to the sample of interest with silver paste. Parts of both wires were fixed to the double-sided Scotch tape. The Teflon block containing the basic unit for conductivity measurements was transferred into a glovebox. The Teflon unit was placed in and connected to a glass cell in the glovebox. The closed cell filled with argon was transferred to a Lauda thermostat bath. At various temperatures, the resistivity values were measured by means of a Keithley 617 programmable electrometer using a two probe technique. The conductivity of the pellet was calculated from the measured resistance and physical dimensions of the pellet.

## RESULTS AND DISCUSSION

Figure 1 shows that the powder x-ray diffraction (XRD) patterns of lanthanum-doped  $\text{LiNiVO}_4$  were similar to that of  $\text{LiNiVO}_4$  with the mole ratio of  $\text{LiNiVO}_4 : \text{La} = 10$  to  $10^5$ , indicating that  $\text{LiNiVO}_4$  samples were essentially single phase and had an inverse spinel structure after doping. However, with the mole ratio of  $\text{LiNiVO}_4 : \text{La} = 10$ , as shown in Figure 1-(a),  $\text{LiNiVO}_4$  along with  $\text{NiO}$  and  $\text{LaVO}_4$  were formed, revealing that a reaction between  $\text{LiNiVO}_4$  and  $\text{La}_2\text{O}_3$  had taken place and the doping process was no longer effective in improving conductivity.

The selection of lanthanum (La), gadolinium (Gd), and ytterbium (Yb) as dopants in this work was based on the concept that all of the lanthanides form  $\text{M}^{3+}$  ions and the most stable tripositive ions are formed by elements which can attain the  $f^0$ ,  $f^7$ , and  $f^{14}$  configurations. Although  $\text{Yb}^{+3}$  attains the  $f^{13}$  configuration, it is less expensive than lutetium (Lu) whose tripositive ions have the  $f^{14}$  configuration. The radii of  $\text{La}^{3+}$ ,  $\text{Gd}^{3+}$ , and  $\text{Yb}^{3+}$  ions are 1.061, 0.938, and 0.858 angstrom, respectively (7). The gradual decrease in radius of these ions allows us to study the effect of dopant size on the electrical conductivity of  $\text{LiNiVO}_4$ .

The conductivity data of lanthanum-doped  $\text{LiMVO}_4$  [ $M = \text{Ni}$  or  $\text{Co}$ ] at room temperature are presented in Table 1. The data collected in this table were the initial conductivity values measured by a pseudo a. c. non-polarization method with minimum influence attributable to polarization. The initial value was an average of ten measurements from time = 0 by manually alternating electrode polarity back and forth continuously. The electrical conductivity values measured in this way represent sums of ionic and electronic conductivity, actually higher than those measured by a d.c. method which reduces ionic conductivity significantly due to extensive measuring time. Both pure  $\text{LiNiVO}_4$  and  $\text{LiCoVO}_4$  showed poor conductivity in the order of  $10^{-8}$  S/cm. Interestingly, the former exhibited remarkable conductivity improvement with an increase from  $10^{-8}$  to  $10^{-6}$  S/cm when the mole ratio of  $\text{LiNiVO}_4 : \text{La}$  was  $10^4$  while the latter showed no significant improvement after the doping process regardless of dopant concentrations. Therefore, no further study on the conductivity improvement of  $\text{LiCoVO}_4$  was attempted in this work.

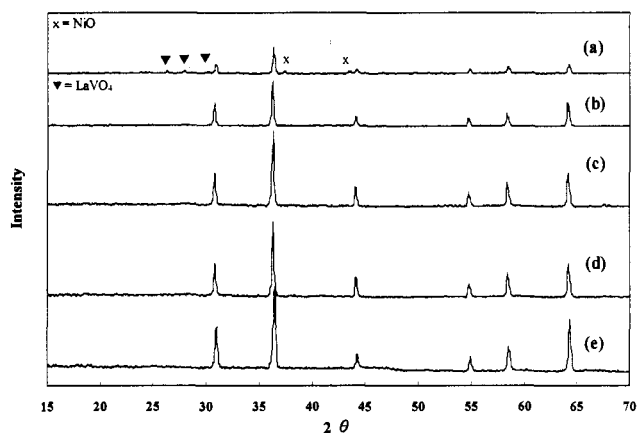


Fig. 1 Powder XRD patterns of lanthanum-doped  $\text{LiNiVO}_4$ . The mole ratio of  $\text{LiNiVO}_4$  : La = (a) 10, (b) 100, (c) 1000, (d) 10000, and (e) 100000.

TABLE 1. Initial Conductivity Values of Lanthanum-Doped  $\text{LiMVO}_4$  ( $M = \text{Co}, \text{Ni}$ ) Measured by a Pseudo A.C. Non-Polarization Method.

$\text{LiMVO}_4$ : La (mole ratio)		1:0	1:10E-6	1:10E-5	1:10E-4	1:10E-3	1:10E-2
Conductivity (S/cm)	M=Ni	8.12E-8	8.72E-9	3.67E-10	2.21E-6	3.26E-10	7.06E-8
	M=Co	8.44E-9	2.01E-8	1.16E-8	7.17E-8	5.02E-10	4.03E-10

To determine whether the conductivity of  $\text{LiNiVO}_4$  is ionic, electronic, or mixed, the variation of d.c. conductivity with time was investigated at a constant temperature using electrodes which block ionic conduction. The samples were supplied with a constant voltage of 1 V and conductivity readings were taken at the end of 4 hours. After being under the influence of a constant voltage for a prolonged period of time, the sample being polarized reached a stable conductivity value mainly due to electronic conductivity. This is consistent with the case of mixed conduction, where conductivity first decreases with time and then remains constant at some infinite value.

By using the above d.c. polarization method, the electrical conductivity and activation energy of Ln-doped  $\text{LiNiVO}_4$  in the range from 10°C to 50°C were obtained in Table 2, 3, and 4 for the dopants containing La, Gd, and Yb elements, respectively. The dopant concentrations represented by the mole ratios of  $\text{LiNiVO}_4$  : Ln were from  $10^6$  to  $10^2$ . The higher the mole ratio, the lower the dopant concentration.

With almost all three dopants, the samples showed maximum electrical conductivity with the mole ratio of  $10^4$  and conductivity increased with temperature in the range from 10°C to 50°C. Gd-doped samples in Table 3 had the lowest activation energy of 0.31 eV at that mole ratio and highest conductivity, ranging from  $6.21 \times 10^{-7}$  to  $3.52 \times 10^{-7}$  S/cm, but contrary to expectations, conductivity decreased with increasing temperature in the temperature range of interest. The cause of this exceptional behavior in conductivity is not certain. La-doped samples in Table 2 had the lowest conductivity and the second highest activation energy. Although Yb-doped samples in Table 4 had the second highest conductivity, they showed the best improvement. However, they did not all achieve maximum conductivity at a mole ratio of  $10^4$  in the range from 10°C to 50°C, but maintained a high conductivity near  $10^{-7}$  S/cm around the mole ratio of  $10^4$  to  $10^2$ . In general, dopant size has an important effect on conductivity performance, demonstrated by the fact that the smallest Yb dopant provided the best results in improving conductivity.

TABLE 2. Electrical Conductivity and Activation Energy of Lanthanum-Doped  $\text{LiNiVO}_4$  in the Range from  $10^\circ\text{C}$  to  $50^\circ\text{C}$ .

$\text{LiNiVO}_4$ : La (Mole Ratio)	1:10E-6	1:10E-5	1:10E-4	1:10E-3	1:10E-2
Temperature ( $^\circ\text{C}$ )	Electrical Conductivity (S/cm)				
10	1.047E-10	1.048E-12	2.837E-9	2.175E-11	2.612E-11
20	4.305E-10	1.798E-12	1.922E-8	2.188E-11	2.894E-11
25	1.189E-9	4.063E-10	1.937E-8	1.173E-11	2.888E-11
30	1.898E-9	9.579E-10	2.054E-8	2.353E-11	1.428E-10
40	2.208E-9	1.101E-11	2.159E-8	2.925E-11	1.893E-10
50	2.196E-9	1.760E-11	2.220E-8	1.221E-10	2.339E-10
Activation Energy (eV)	0.59	0.58	0.37	0.34	0.33

TABLE 3. Electrical Conductivity and Activation Energy of Gadolinium-Doped  $\text{LiNiVO}_4$  in the Range from  $10^\circ\text{C}$  to  $50^\circ\text{C}$ .

$\text{LiNiVO}_4$ : Gd (Mole Ratio)	1:10E-6	1:10E-5	1:10E-4	1:10E-3	1:10E-2
Temperature ( $^\circ\text{C}$ )	Electrical Conductivity (S/cm)				
10	5.105E-10	3.655E-11	6.214E-7	1.121E-10	1.198E-11
20	9.931E-10	6.850E-10	4.134E-7	1.141E-10	2.121E-11
25	9.287E-10	9.686E-10	3.587E-7	1.064E-10	2.220E-11
30	2.034E-9	1.044E-10	3.629E-7	2.103E-9	4.018E-10
40	2.689E-9	1.097E-10	3.658E-7	2.514E-9	4.049E-10
50	3.301E-9	1.102E-10	3.520E-7	2.899E-9	5.533E-10
Activation Energy (eV)	0.87	0.76	0.31	0.33	0.31

TABLE 4. Electrical Conductivity and Activation Energy of Ytterbium-Doped  $\text{LiNiVO}_4$  in the Range from  $10^\circ\text{C}$  to  $50^\circ\text{C}$ .

$\text{LiNiVO}_4$ : Yb (Mole Ratio)	1:10E-6	1:10E-5	1:10E-4	1:10E-3	1:10E-2
Temperature ( $^\circ\text{C}$ )	Electrical Conductivity (S/cm)				
10	1.398E-10	1.307E-9	1.046E-8	1.656E-8	2.121E-8
20	3.966E-10	3.412E-9	2.476E-8	1.492E-8	1.147E-7
25	5.550E-10	3.873E-9	4.355E-7	2.736E-8	1.665E-7
30	5.759E-10	1.227E-8	1.829E-7	5.637E-8	1.748E-7
40	6.970E-10	1.958E-8	1.237E-7	1.473E-7	2.217E-7
50	8.364E-10	2.121E-8	1.768E-7	1.768E-7	2.464E-7
Activation Energy (eV)	0.61	0.56	0.52	0.48	0.52

Furthermore, dopant concentration also plays an important role in the study of improving conductivity. The doping process seemed most effective when the mole ratio was from  $10^6$  to  $10^4$  because in that range, conductivity was roughly proportional to dopant concentration and was highest when the mole ratio was  $10^4$ . Beyond the above range, the doping process for La- and Gd-doped samples became less effective and the reaction between  $\text{LiNiVO}_4$  and the dopant gradually dominated the process, resulting in a decrease in conductivity. However, for the smallest dopant, ytterbium, the doping process was effective for all mole ratios studied because conductivity increased with the mole ratio and remained around the level of  $10^{-7}$  S/cm. Samples doped with smaller  $\text{Yb}^{+3}$  than  $\text{La}^{+3}$  or  $\text{Gd}^{+3}$  showed high conductivity even at the mole

ratio of  $10^2$ , indicating that dopant size played a critical role in the conduction process. Beyond the optimum mole ratio of  $10^4$ ,  $\text{Li}^+$  ionic conductivity decreased with further increases in La or Gd content because they did not contribute to ionic conductivity, but decreased the available space and blocked the migration of  $\text{Li}^+$ . In contrast, when the smallest Yb dopant was used, high conductivity was maintained even at the mole ratio of  $10^2$ , as shown in Table 4, because the small Yb dopant did not block the migration of  $\text{Li}^+$ .

The activation energy calculations provided further evidence that the effectiveness of the dopants decreased and the reaction between  $\text{LiNiVO}_4$  and the dopant dominated once the mole ratio exceeded  $10^4$ . For all three dopants, activation energy was either at or around its lowest level when the mole ratio was  $10^4$ . For La-doped samples, activation energy fell from 0.59 eV at a mole ratio of  $10^6$  to 0.37 eV at a mole ratio of  $10^4$ . Over the same range, for Gd-doped samples, it fell from 0.87 to 0.31 eV and for Yb-doped samples, it fell from 0.61 to 0.52 eV. Beyond a mole ratio of  $10^4$ , the activation energy level plateaued and remained relatively constant. The activation energy of the La-doped sample decreased a small amount to 0.33 eV, the Gd-doped sample stayed between 0.31 and 0.33 eV, and the Yb-doped sample stayed between 0.48 to 0.52 eV. Obviously, there was no clear trend in the relationship between the conductivity of  $\text{LiNiVO}_4$  and activation energy of the related process. During the doping process, activation energy fluctuated when dopant concentrations were low. However, because of the reaction between  $\text{LiNiVO}_4$  and the dopant, activation energy underwent almost no change when dopant concentrations were high.

## CONCLUSIONS

The conductivity of  $\text{LiNiVO}_4$  increased significantly with the incorporation of trace amounts of the lanthanides  $\text{La}_2\text{O}_3$ ,  $\text{Gd}_2\text{O}_3$ , or  $\text{Yb}_2\text{O}_3$ . By using a d.c. polarization method, the smallest Yb-doped samples at 25°C showed the best improvement in conductivity by a factor of three, an increase from  $10^{-10}$  to  $10^{-7}$  S/cm at a mole ratio of  $\text{LiNiVO}_4 : \text{Yb} = 10^4$ , and even maintained high conductivity of  $10^{-7}$  S/cm up to a mole ratio of  $10^2$ . The medium Gd-doped samples reached their highest conductivity, ranging from  $6.21 \times 10^{-7}$  to  $3.52 \times 10^{-7}$  S/cm in the temperature range of interest at a mole ratio of  $10^4$ , but beyond that conductivity declined rapidly, back down to  $10^{-10}$  S/cm. The largest La-doped samples at 25°C only showed a slight increase in conductivity from  $10^{-9}$  to  $10^{-8}$  S/cm at a mole ratio of  $10^4$ , much lower than  $2.21 \times 10^{-6}$  S/cm measured by a pseudo a.c. non-polarization method. Activation energy varied with low dopant concentrations during the doping process but it remained virtually constant with high dopant concentrations due to the reaction between  $\text{LiNiVO}_4$  and the dopant.

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