



Glycine-Assisted Sol-Gel Combustion Synthesis and Characterization of Aluminum-Doped LiNiVO_4 for Use in Lithium-Ion Batteries

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Phase-pure inverse spinel LiNiVO_4 and $\text{LiAl}_x\text{Ni}_{1-x}\text{VO}_4$ have been synthesized with good surface morphology by a sol-gel method using glycine as a chelating agent. The product was characterized by thermogravimetric and differential thermal analysis, X-ray diffraction, Fourier transform infrared spectroscopy, scanning electron microscopy, and galvanostatic cycling studies. Surface morphology examinations of the undoped LiNiVO_4 particles showed micrometer-sized, cube-shaped grains, while that of aluminum-doped particles showed uniform spherical particles. As compared to the solid-state synthesis route, the sol-gel combustion process greatly reduces the temperature (250°C) for preparing LiNiVO_4 and $\text{LiAl}_x\text{Ni}_{1-x}\text{VO}_4$. Subsequent calcination between 650 and 850°C significantly enhances the crystallinity of the synthesized LiNiVO_4 and $\text{LiAl}_x\text{Ni}_{1-x}\text{VO}_4$ powder. The discharge capacity and cycling performance of the $\text{LiAl}_{0.1}\text{Ni}_{0.99}\text{VO}_4$ was found to be superior at a calcination temperature of 250°C .

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Attempts to synthesize LiNiVO_4 were made as early in 1961 by Bernier et al.¹ However, cathodic properties of the LiNiVO_4 inverse spinel were first investigated by Fey et al. in 1994.² LiNiVO_4 rates better than layered cathode materials such as LiCoO_2 , LiNiO_2 , etc., in terms of toxicity, cost, and cell voltage (4.8 V).³⁻⁸ High-voltage cathodes (4.8 V) such as LiMnVO_4 , LiNiVO_4 , and LiCoVO_4 have been synthesized as an important class of materials for use in lithium batteries. Further, these oxides have also been doped with either Co, Mn, etc. in order to realize superior electrochemical properties.

Sol-gel chemistry offers the advantage of synthesizing materials of uniform particle size and morphology at low temperatures and often materials that have attractive electrochemical activity. This contrasts with the solid-state-fusion method, which is time-consuming and energy-intensive, and hence, economically unwise.⁹ Low-temperature synthesis of LiNiVO_4 has been reported by Prabaharan et al.¹⁰ from nitrate precursors using glycine as a fuel. The product formation was observed at 320°C with glycine at twice the molar fraction of the total stoichiometry of the starting materials. In contrast, we present in this paper our basic studies on the physical and electrochemical characterization of LiNiVO_4 and $\text{LiAl}_x\text{Ni}_{1-x}\text{VO}_4$, synthesized using a novel glycine-assisted sol-gel combustion method where the product formation is achieved at 250°C at a lower (1:1) stoichiometry of glycine to the total metal ions.

Experimental

A typical flow chart of the preparative process used in this work is presented in Fig. 1. Stoichiometric amounts of nitrate precursors (lithium, nickel, with or without aluminum) and ammonium metavanadate were stirred with glycine in deionized water for about 12 h. The amount of glycine was such that the molar ratio of the chelating agent to the total metal ions was maintained at 1:1. The pH of the mixture was maintained between 5 and 6. A foamy gel of the precursor of either LiNiVO_4 or $\text{LiAl}_x\text{Ni}_{1-x}\text{VO}_4$ obtained was dried in a vacuum oven at 110°C overnight. Thermogravimetric and differential thermal analyses of the precursor were carried out using a PL Thermal Sciences instrument model STA 1500. The experiments

were performed in air at a heating ramp of $20^\circ\text{C}/\text{min}$ with typically 50-mg samples. The dried precursor powder was finely ground and calcined at 250 , 450 , 650 , and 850°C for 4 h in alumina crucibles. The calcined materials were subjected to X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier transform infrared (FTIR) studies. Powder XRD studies were performed on a Jeol JDX-8030 X-ray diffractometer with nickel-filtered $\text{Cu K}\alpha$ radiation between scattering angles of 10 and 70° . FTIR spectra of the vanadate samples were recorded on a Perkin-Elmer Paragon-500 FTIR

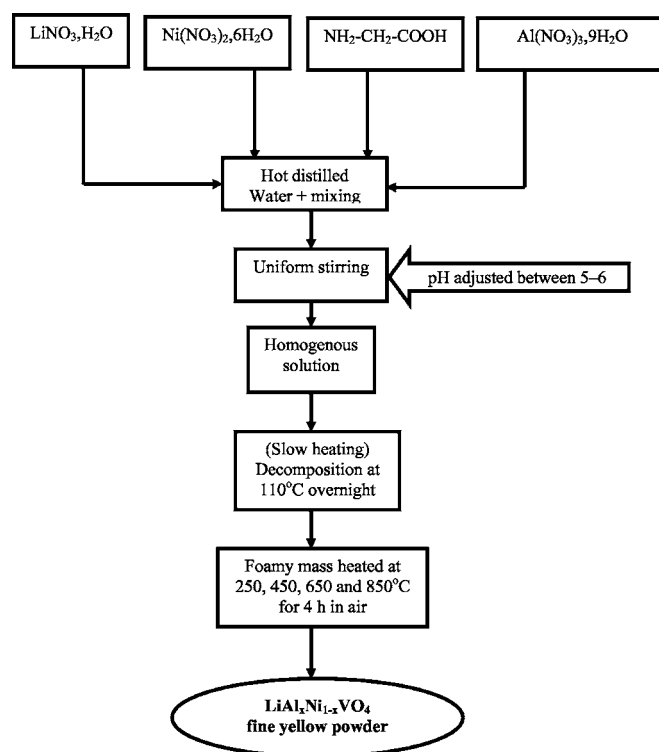


Figure 1. Flow chart for the synthesis of LiNiVO_4 by a sol-gel combustion method using glycine as a chelating agent.

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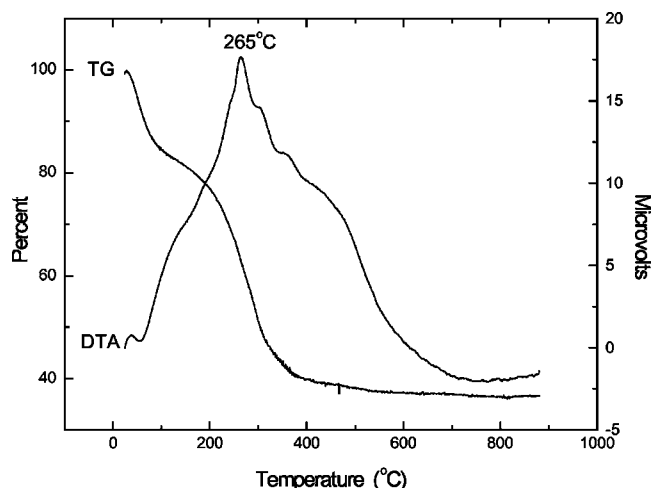


Figure 2. TG and DTA curves of LiNiVO_4 precursor.

spectrophotometer. Morphological features of the products were examined in a Hitachi S-3000 H scanning electron microscope. Standard 2016 coin cells were assembled using lithium metal as anode, a Celgard 2400 separator, and 1 M solution of LiPF_6 in a 50:50 (v/v) mixture of ethylene carbonate and diethyl carbonate. Cathodes were 1.8-cm-diam disks spread-coated with an 80:10:10 slurry of the cathode active powder, graphite, and polyvinylidene fluoride in *N*-methyl-2-pyrrolidone. Cathode active material loadings in the samples varied from 0.087 to 0.098 g. Charge-discharge studies were performed using an in-house charging facility between 3 and 5 V at 0.1 C rate.

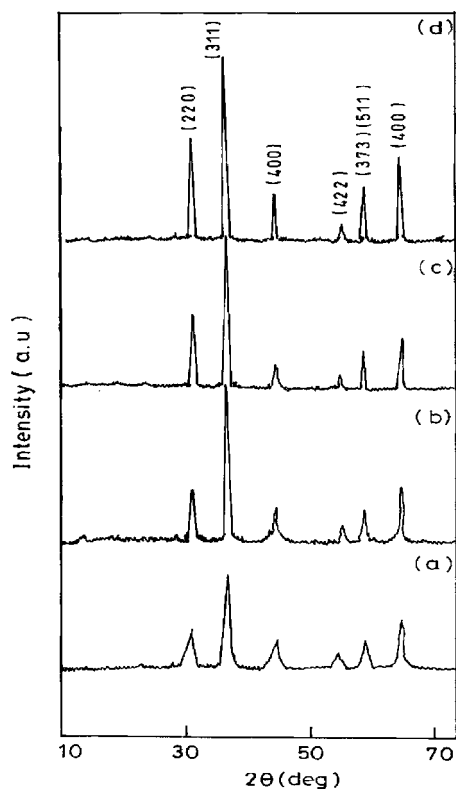


Figure 3. XRD patterns of the sol-gel-derived LiNiVO_4 powders calcined at different temperatures: (a) 250, (b) 450, (c) 650, and (d) 850°C.

Results and Discussion

Thermal studies.—Figure 2 shows the thermogravimetric (TG)/differential thermal analysis (DTA) characteristics of the LiNiVO_4 precursor. The TG curve shows two rapid weight loss regions, sandwiching a slow weight loss region. The first rapid weight loss between room temperature and 100°C, accounting for a weight loss of 15%, can be attributed to the loss of superficial water. The second weight loss of 10% extending up to 200°C is relatively slow. Subsequently, a third weight loss region, which accounts for as much as 35%, is observed between 200 and 400°C. Major decomposition reactions of the reactants to yield the product occur in the second and third regions. No significant changes occur beyond 400°C, which indicates the completion of thermal events. The products form at temperatures represented by the second and third regions, supported by large exothermic peaks centered at around 265°C in the DTA curve. This inference is vindicated by the well-defined fingerprint XRD pattern of LiNiVO_4 (Fig. 3), obtained by the calcination of the precursor at 250°C. Combustion synthesis with chelated precursors can be initiated at low temperatures; however, the local temperatures in the system can rise to more than 1000°C. The short duration and the high local temperatures facilitate bond formation and crystallization processes. Thus, thermal analysis data indicate the formation of LiNiVO_4 at temperatures around 250°C.

Figure 4 shows the TG/DTA curves for $\text{LiAl}_x\text{Ni}_{1-x}\text{VO}_4$ powders with different Al doping. Two exothermic peaks are seen in all the samples between 225 and 400°C, augmented with two weight-loss (45%) zones at around 100 and 250°C, attributed to the removal of water and the formation of the vanadate. A majority of the formation reactions ceases around 300°C, and beyond that no significant reactions take place with low Al doping levels. In the case of samples with higher Al contents, a weak exothermic event is witnessed at around 500°C, corresponding to a weight loss of ~10%. This may be attributed to the decomposition of aluminum nitrates.

X-ray diffraction.—The phase purity and homogeneity of LiNiVO_4 is a necessary criterion for cathode activity in lithium-ion batteries. Figure 3 shows the XRD patterns of LiNiVO_4 calcined at different temperatures, viz., 250, 450, 650, and 850°C. All the peaks match those of JCPDS card no. 38-1395, confirming the formation of single-phase inverse spinel structured compound without any impurity, even with the samples calcined at 250°C. This observation is in contrast to that of Fey et al.,² who suggested that a temperature of at least 700°C was necessary to obtain satisfactory crystallinity in LiNiVO_4 powder by the conventional solid-state reaction process. Furthermore, LiNiVO_4 prepared by the solid-state fusion method involves long reaction times. Additionally, carbonate and nitrate precursors employed in the solid-state fusion method add VO_3 and NiO impurities, as has been observed by several researchers.³ However, in the present method, product formation takes place at 250°C. It can be seen from Fig. 3 that the intensity of the XRD pattern increases with increasing calcination temperature. The high-intensity reflections observed with LiNiVO_4 samples calcined at 850°C indicate a high degree of crystallinity for these samples. The XRD fingerprints of LiNiVO_4 possess striking similarity with those of LiCuVO_4 .^{11,12} Nevertheless, the XRD pattern of LiNiVO_4 calcined at 250 and 450°C show fairly weak reflections, indicating the amorphous nature of the compounds. Additionally, the positions of the tetrahedral and octahedral $[\text{MO}_6]$ units in the structure were corroborated by FTIR analysis.

Figure 5 depicts the XRD patterns of $\text{LiAl}_x\text{Ni}_{1-x}\text{VO}_4$ at different Al-doping levels, viz., 0.05, 0.1, 0.25, and 0.5 calcined at 850°C. The peak signatures of the pattern are in agreement with that of inverse spinel (JCPDS card no. 38-1395). The presence of an additional peak in the (111) plane is ascribed to the incorporation of aluminum and is probably due to the tendency toward the structural transformation from truly inverse spinel-to-spinel structure. The high degree reflection of plane (311) indicates the highly crystalline state of the particles.

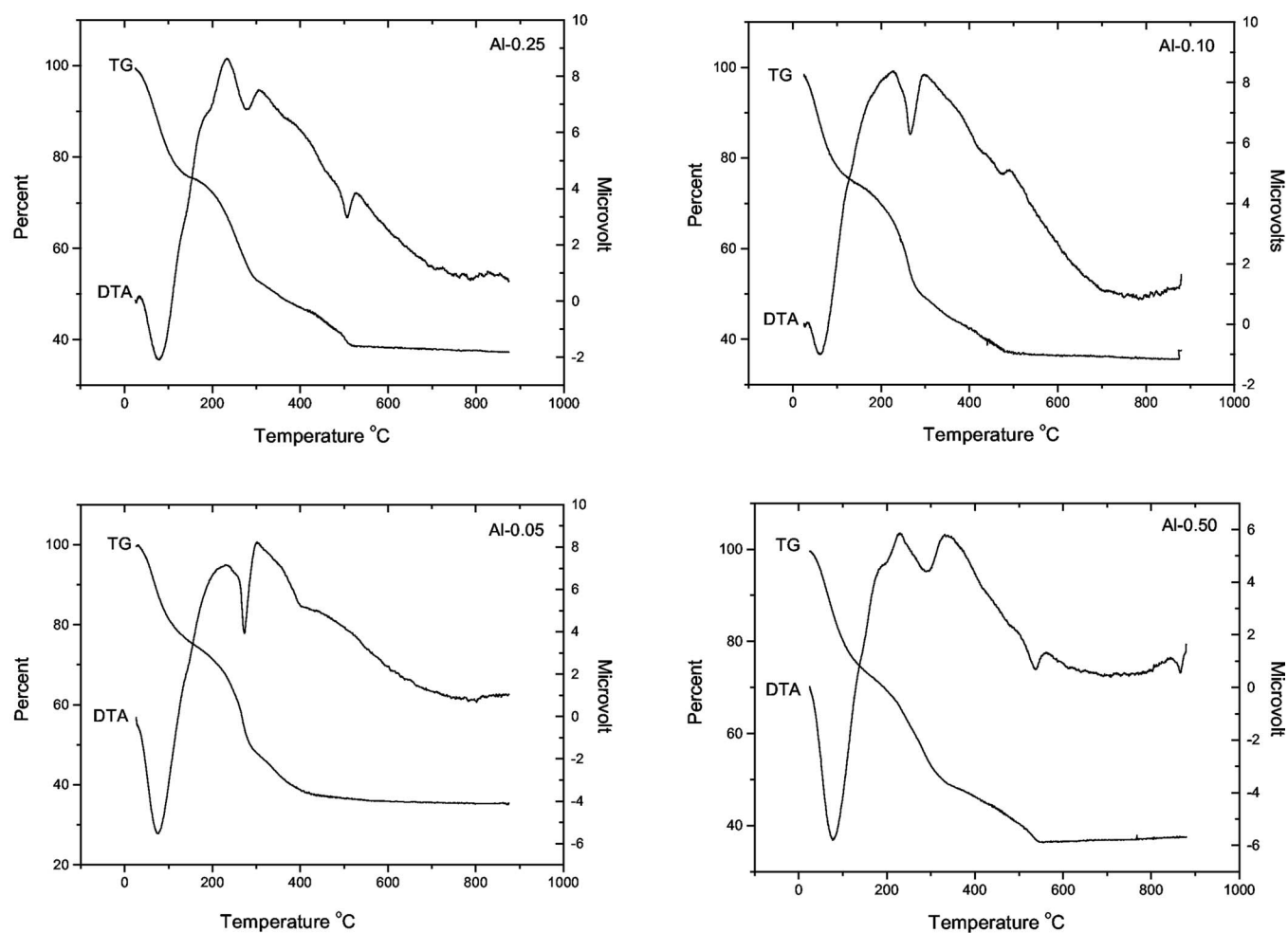


Figure 4. TG and DTA curves of $\text{LiAl}_x\text{Ni}_{1-x}\text{VO}_4$ precursor.

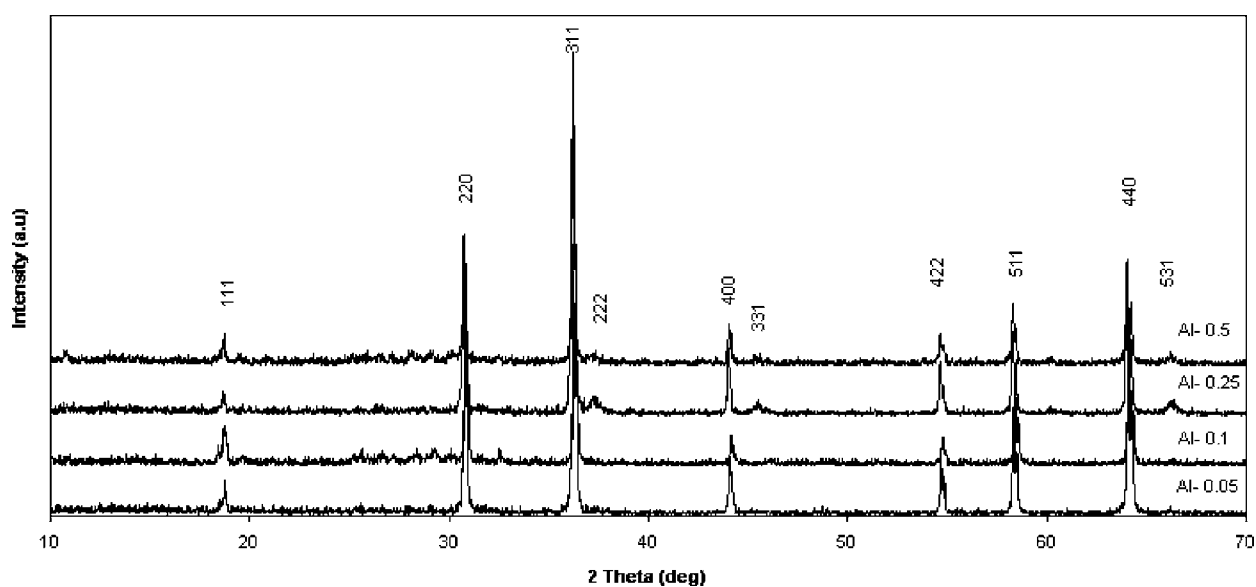


Figure 5. XRD patterns of the sol-gel-derived $\text{LiAl}_x\text{Ni}_{1-x}\text{VO}_4$ powders calcined at 850 $^{\circ}\text{C}$.

Table I. FTIR frequencies peaks observed for sol-gel synthesized LiNiVO₄.

No.	Temperature (°C)	Wavelength (cm ⁻¹)	Assignment
1	250	814.99	V—O bond of VO ₄
		951.89	VO ₄ tetrahedron
		731.52	Li—O—Ni stretching
		644.38	Li—O stretching
2	450	815.99	V—O bond of VO ₄
		955.28	VO ₄ tetrahedron
		731.83	Li—O—Ni stretching
		646.90	Li—O stretching
3	650	878.33	V—O bond of VO ₄
		947.34	VO ₄ tetrahedron
		727.36	Li—O—Ni stretching
4	850	938.47	VO ₄ tetrahedron

FTIR spectroscopy.— The FTIR spectra of LiNiVO₄ calcined at different temperatures (250, 450, 650, and 850°C) were recorded and the absorption peaks of the various stretching and bending vibrations are listed in Table I. The peaks for V=O and Ni—O are around 951.89 and 814.99 cm⁻¹, respectively. The bands between 900 and 600 cm⁻¹ are associated with the stretching vibrations of V—O bonds of VO₄ tetrahedra in LiNiVO₄.¹³⁻¹⁵ Some evidence for the presence of a little residual carbonyl and nitrate moieties (450–525 cm⁻¹) in the product at low calcination temperature are also reflected in the spectrum. As the calcination temperature is increased, the absorption peaks of the carbonyl group slowly vanish, leaving only the absorption bands of the V—O bonds.¹⁶ This indicates the complete decomposition of the precursors and the formation of pure, single-phase LiNiVO₄. Richardson and Ross¹⁷ reported that the FTIR peaks for LiNiVO₄ were similar to those of a related compound LiMnVO₄ and those of the orthorhombic C_mC_m-type CrVO₄. Touboul and Toledano¹⁸ and Lytle¹⁹ reported that the spinel-

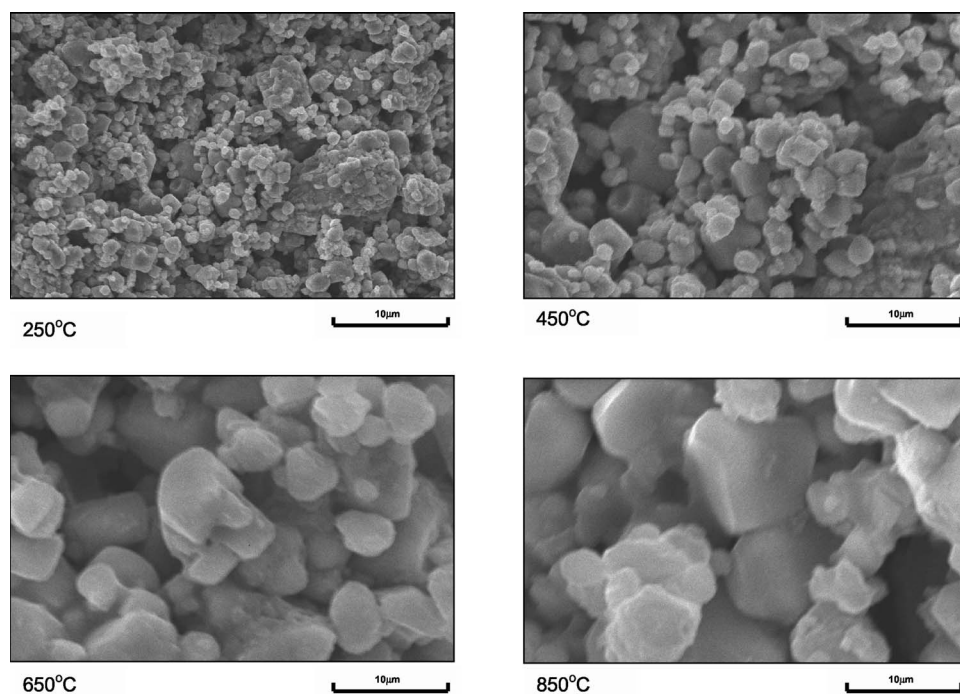
Table II. FTIR frequencies peaks observed for sol-gel synthesized LiAl_xNi_{1-x}VO₄.

No.	Temperature (°C)	Wavelength (cm ⁻¹)	Assignment
1	250	500	Li—O—Al stretching
		650	Li—O stretching
		725	Li—O—Ni stretching
		896	V—O bond of VO ₄
		915	VO ₄ tetrahedron
		950	Al—O—Ni stretching
2	450	500	Li—O—Al stretching
		650	Li—O stretching
		725	Li—O—Ni stretching
		897	V—O bond of VO ₄
		918	VO ₄ tetrahedron
		950	Al—O—Ni stretching
3	650	897	V—O bond of VO ₄
		917	VO ₄ tetrahedron
		950	Al—O—Ni stretching
4	850	902	VO ₄ tetrahedron
		950	Al—O—Ni stretching

related LiMnVO₄ compound would have [MnO₆] octahedra where cation distributed LiVO₄ and VO₄ tetrahedra, which may neutralize the corners of tetrahedra with octahedral MnO₆.¹⁵

FTIR spectra of LiAl_xNi_{1-x}VO₄ at different temperatures, viz., 250, 450, 650, and 850°C, were recorded and the absorption peaks of the various stretching and bending vibrations are listed in Table II. The peaks for Li—O—Al, V—O, Ni—O, and Li—O are seen between 500 and 918 cm⁻¹. The disappearance of the peaks between 450 and 525 cm⁻¹ in the samples calcined at 650 and 850°C are due to decomposition of carbonate salt of aluminum at higher temperature.

SEM analysis.— The electrochemical activity of cathode materials is influenced by the surface morphology of the particles. SEM images of the LiNiVO₄ inverse spinel calcined at different tempera-

**Figure 6.** SEM images of LiNiVO₄ particles calcined at different temperatures.

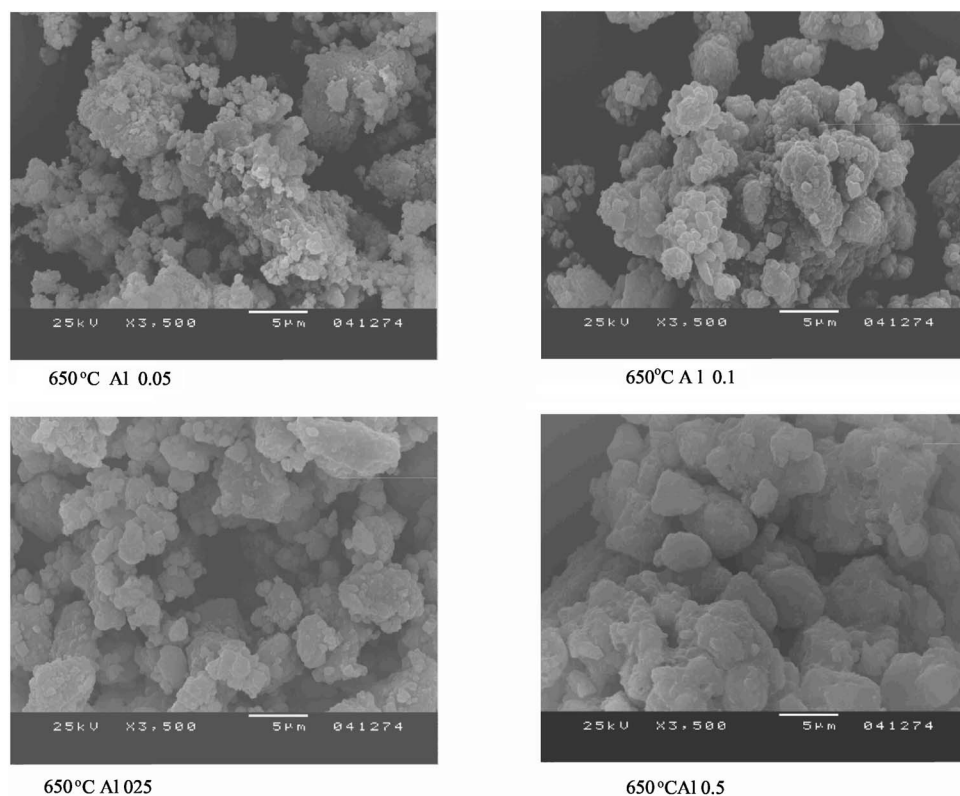


Figure 7. SEM images of different dopant level of $\text{LiAl}_x\text{Ni}_{1-x}\text{VO}_4$ particles calcined at 650°C .

tures are depicted in Fig. 6. It is evident that the particles of the product obtained by calcination at 250°C are of micrometer-sized spherical grains. In fact, the products obtained by calcination at 250 and 450°C are agglomerates of finer particles. In general, good agglomeration and interparticle contact is useful in enhancing electrochemical activity. The samples calcined at 650 and 850°C had an ice-cube-like morphology. Further, a growth in the particle size is

apparent with increasing calcination temperature. The SEM images of LiNiVO_4 calcined at 450 , 650 , and 850°C show particles of size around 1.0 , 1.5 , and $2.5 \mu\text{m}$, respectively.

Figure 7 shows the SEM pictures of LiNiVO_4 with different levels of aluminum calcined at 250°C . It is evident that the surface morphology of the doped samples is similar to that of undoped samples at 250°C . However, a reduction in the particle size is observed at lower dopant levels. The growth in the particle size is seen as the aluminum content is increased.

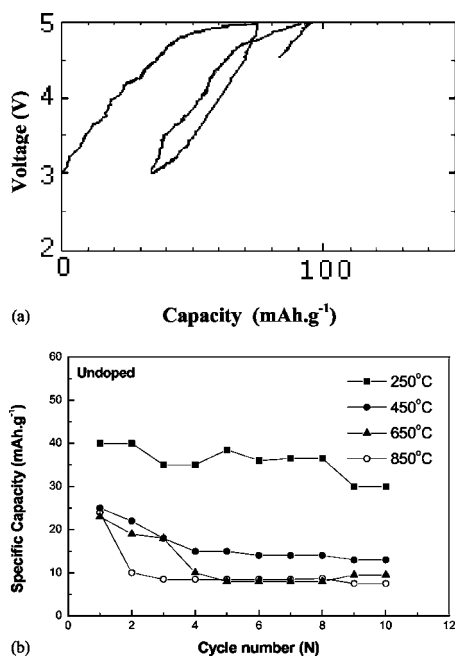


Figure 8. (a) Typical charge-discharge behavior of LiNiVO_4 calcined at 250°C . (b) Cycle number vs capacity behavior of LiNiVO_4 calcined at different temperatures.

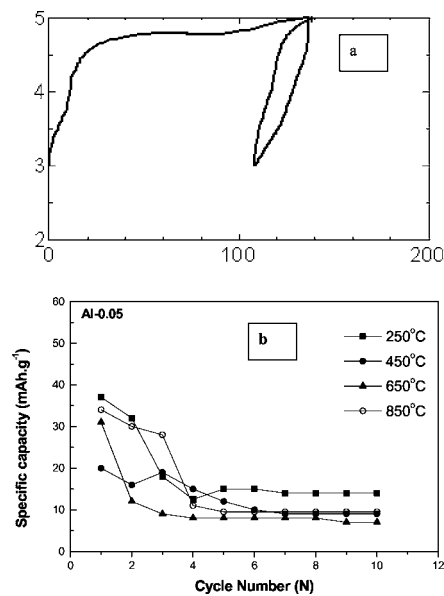


Figure 9. (a) Typical charge-discharge behavior of $\text{LiAl}_{0.05}\text{Ni}_{0.95}\text{VO}_4$ calcined at 250°C . (b) Cycle number vs capacity behavior of $\text{LiAl}_{0.05}\text{Ni}_{0.95}\text{VO}_4$ calcined at different temperatures.

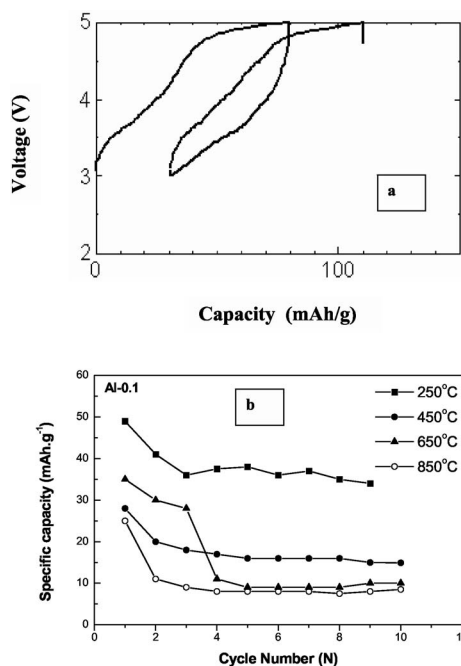


Figure 10. (a) Typical charge–discharge behavior of $\text{LiAl}_{0.10}\text{Ni}_{0.90}\text{VO}_4$ calcined at 250°C . (b) Cycle number vs capacity behavior of $\text{LiAl}_{0.10}\text{Ni}_{0.90}\text{VO}_4$ calcined at different temperatures.

Charge–discharge studies.—Typical charge–discharge characteristics of LiNiVO_4 calcined at 250°C and the cycling performance of LiNiVO_4 calcined at different temperatures, viz., 250, 450, 650, and 850°C , are presented in Fig. 8a and b, respectively. It can be seen that undoped LiNiVO_4 calcined at 250°C delivers 40 mAh g^{-1} during the first cycle and stabilizes at around 35 mAh g^{-1} . Samples calcined at higher temperatures show a negative trend in discharge capacity. After a few cycles, the capacity of the compound gradually decreases. Hence, it can be concluded that calcination at 250°C in

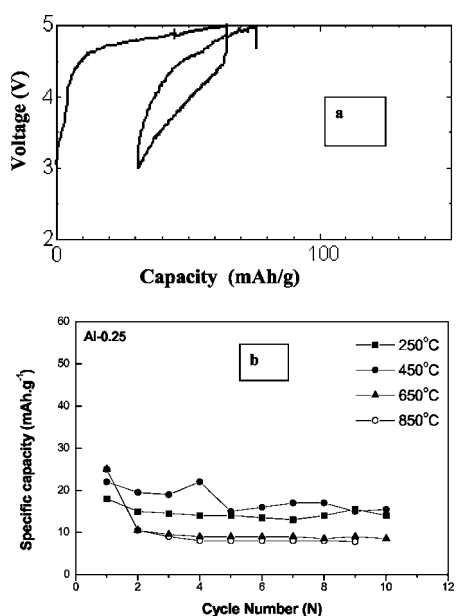


Figure 11. (a) Typical charge–discharge behavior of $\text{LiAl}_{0.25}\text{Ni}_{0.75}\text{VO}_4$ calcined at 250°C . (b) Cycle number vs capacity behavior of $\text{LiAl}_{0.25}\text{Ni}_{0.75}\text{VO}_4$ calcined at different temperatures.

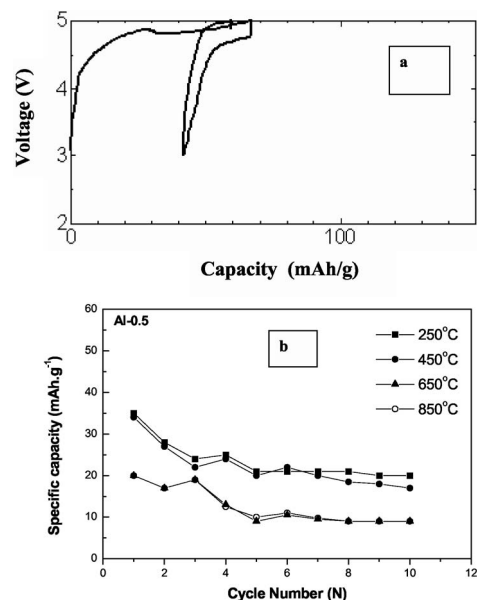


Figure 12. (a) Typical charge–discharge behavior of $\text{LiAl}_{0.50}\text{Ni}_{0.50}\text{VO}_4$ calcined at 250°C . (b) Cycle number vs capacity behavior of $\text{LiAl}_{0.50}\text{Ni}_{0.50}\text{VO}_4$ calcined at different temperatures.

the case of LiNiVO_4 has better electrochemical activity compared to that obtained from the compounds synthesized at higher temperature.

Al-doped LiNiVO_4 samples were prepared with different concentrations, viz., 0.05, 0.10, 0.25, and 0.50, and calcined at different temperatures, viz., 250, 450, 650, and 850°C . It was observed that the discharge capacity decreases with an increase in calcination temperature, irrespective of the dopant concentration. The calcination temperature of 250°C is quite satisfactory for better performance. These observations are in good agreement with that of pristine LiNiVO_4 . Typical charge–discharge behavior and the cycling performance of $\text{LiAl}_x\text{Ni}_{1-x}\text{VO}_4$ ($x = 0.05, 0.10, 0.25, \text{ and } 0.50$) calcined at 250°C are presented in Fig. 9–12. Cycling studies of these materials indicate that the $\text{LiAl}_{0.1}\text{Ni}_{0.9}\text{VO}_4$ sample calcined at 250°C shows better performance. Further, $\text{LiAl}_{0.1}\text{Ni}_{0.9}\text{VO}_4$ exhibits a stable discharge capacity of 35 mAh g^{-1} over the investigated ten cycles. These results are superior to the earlier studies reported by Prabaharan et al.¹⁰ involving a low-temperature synthesis and characterization of LiNiVO_4 for Li-ion batteries. Further, Chitra et al.²⁰ reported that calcination of LiNiVO_4 at 800°C delivers a discharge capacity of 90 mAh/g in the 1st cycle vs the theoretical value of 148 mAh g^{-1} . However, after five cycles the capacity dropped to 15 mAh g^{-1} , which was claimed to be superior to the result obtained by Fey and Wu.⁸ A comparison of these results with our present studies indicate that the results obtained by us are superior, i.e., the undoped sample calcined at 250°C exhibits higher capacity retention of 30 mAh g^{-1} , even up to ten cycles. Further, all the samples calcined at higher temperature (850°C) suffer with severe capacity fade upon cycling. Thus, it is evident that calcination at higher temperature beyond 250°C for the synthesis of LiNiVO_4 results in severe capacity loss upon cycling. It is seen from the discharge curves (Fig. 8–12) that the discharge capacities of Al-doped vanadate are slightly higher than that of pristine LiNiVO_4 . It is interesting to note from Fig. 10b that the first discharge capacity of $\text{LiAl}_{0.1}\text{Ni}_{0.9}\text{VO}_4$ calcined at 250°C is around 50 mAh g^{-1} resulting in a coulombic efficiency of 80%. However, upon cycling the discharge capacity of $\text{LiAl}_{0.1}\text{Ni}_{0.9}\text{VO}_4$ stabilizes at around 35 mAh g^{-1} , corresponding to a coulombic efficiency of 60%. The coulombic efficiency was calculated using the ratio between the stable capacity of 35 mAh g^{-1} and the first charge capacity. Further, with increasing aluminum con-

tent beyond 0.1, poor discharge capacities result. This may be due to the tendency of Al-doped samples toward structural transformation from truly inverse spinel-to-spinel structure, as observed in the XRD pattern (Fig. 5). Thus, low levels of aluminum doping coupled with low-temperature calcination results in enhanced electrochemical performance of LiNiVO_4 . Finally, it can be said that aluminum appears in the 3^+ valency state, replacing nickel ions in $\text{LiAl}_x\text{Ni}_{1-x}\text{VO}_4$, thereby changing oxidation state of vanadium from 5^+ to 4^+ , equivalent to the amount of aluminum added. Thus, it is expected that the plateau of vanadium oxidation from 4^+ to 5^+ could appear in the first discharge curve and this plateau should vanish with increasing aluminum content. This tendency is observed in the case of $\text{LiAl}_{0.05}\text{Ni}_{0.95}\text{VO}_4$ and $\text{LiAl}_{0.1}\text{Ni}_{0.90}\text{VO}_4$, but the plateau rapidly decreases at higher aluminum content, viz., 0.25 and 0.5. This behavior could probably be attributed to the change in structure from inverse spinel to spinel structure.

Conclusions

High-purity, micrometer-sized, monophasic LiNiVO_4 particles have been successfully synthesized by a glycine-assisted sol-gel combustion method at temperatures as low as 250°C as confirmed by XRD and FTIR spectral studies. SEM images of the product show agglomerates of crystals of cubic morphology. It is demonstrated that the sol-gel combustion method can greatly lower the formation temperature. A low amount of aluminum and a low calcination temperature is found to be beneficial for enhanced electrochemical performance of LiNiVO_4 . The discharge capacity and cycling performance of the $\text{LiAl}_{0.1}\text{Ni}_{0.9}\text{VO}_4$ are superior at a calcination temperature of 250°C .

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