

LiNiM_xV_{1-x}O₄ (M = Co, Mg and Al) solid solutions – prospective cathode materials for rechargeable lithium batteries?

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Abstract

An ever first attempt to study the effects of cation substitution at the V sites of LiNiVO₄, especially upon the electrochemical activity of the same has been made in the present investigation. A series of compounds with the general formula viz., LiNiM_xV_{1-x}O₄ with M = Co, Mg and Al; $x=0.0, 0.1, 0.3$ and 0.5 has been synthesized by adopting a novel solution-based soft-chemical route namely the Starch-Assisted Combustion (SAC) method. Powder X-ray diffraction (PXRD) studies indicate the possible solubility limit of all the three selected cations viz., Co, Mg and Al with V in LiNiVO₄ matrix to a level of 10% and the rest of the compositions are observed to contain mixed phases. FTIR vibrational spectroscopic studies also confirm the above observation. SEM, particle size distribution, cyclic voltammetric (CV) and electrochemical cycling studies have also been carried out for these compounds with a view to gain more knowledge about the impact of added metal cations towards partial substitution of vanadium in the chosen LiNiVO₄ matrix. It is interesting to note that CV evidences high Li⁺ reversibility in the voltage region of 4–5 V for the three solid solutions with $x=0.1$. Based on the performance results of the electrochemical charge–discharge studies carried out on these compounds, only LiNiAl_{0.1}V_{0.9}O₄ seems to have a better chance as suitable cathode material for rechargeable lithium battery applications.

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Keywords: Cathode materials; LiNiM_xV_{1-x}O₄; Lithium batteries

1. Introduction

The last decade has seen a tremendous commercial success of 4 V rechargeable lithium-ion batteries employing cubic spinel (normal) LiMn₂O₄ phase [1] as cathode material. Nevertheless, a different class of inverse spinel compounds viz., LiNiVO₄ and LiCoVO₄ has also been inviting the interest of various lithium battery research groups via potential application as cathode materials for lithium batteries [2]. It is quite interesting to observe that among the two inverse spinel analogs, LiNiVO₄ is capable of exhibiting a higher voltage of 4.8 V versus Li (but with a lower capacity value of about 45 mAh g⁻²) while LiCoVO₄ exhibits only 4.2 V, implying that the presence, site occupancy [3] local symmetry and distribution of Ni atoms in the inverse spinels play a vital

role in promoting the voltage. Also it is reported that, since V^{3+/4+} redox reaction takes place around 3.5 and 4 V, V^{4+/5+} transformation is expected to occur at a quite high voltage, partially explaining the observed high voltage characteristics in these vanadates [4]. Hence, the physical as well as chemical aspects of these materials are particularly interesting both from fundamental and applied point of view [5] apart from the well attempted properties of LiNiVO₄ such as the crystal structure [6–8], magnetic properties [6], phase diagrams [9] and electronic conductivity [10]. However, certain other aspects of the compound like maintenance of structural integrity upon cycling, enhancement in the deliverable capacity, etc., need to be studied extensively. Despite the appreciable high cell voltage behavior, the compound LiNiVO₄ suffers from lower realizable capacity, compared to other potential cathodes that are recommended normally for practical lithium-ion battery applications [11]. Therefore attention needs to be paid towards the aspect of improving the electrochemical characteristics of LiNiVO₄ via, modification of the same through

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partial replacement of nickel or vanadium by suitable metal cations with an ultimate view to obtain better performing vanadate cathode material for lithium batteries.

Generally improvement in the electrochemical performance of any cathode material including LiMVO_4 category ($M = \text{Ni, Co and Mn}$ confirm) may be addressed either by adopting new synthesis strategies or by modifying the undoped matrix through the incorporation of suitable cations (dopants/substitution), especially at the transition metal sites. According to the earlier reports [12,13] both Li and M in LiMVO_4 occupy the O_h sites (16d, 1/2, 1/2) and V the T_d sites (8a, 1/4, 1/4, 1/4) in the oxygen (32e, x, x, x) lattice with the space group $\text{Fd-}3m$, which can be represented as $[\text{V}]_{\text{tet}}[\text{Li, M}]_{\text{oct}}\text{O}_4$. In LiMVO_4 , M and V are the available transition metal sites that can provide sites for substitution with other cations and therefore partial substitution for M and V by another transition (or non-transition) metal ions are expected to have some effects on its structure and electrochemistry of the parent compound. With regard to LiNiVO_4 , only few reports on the partial substitution of Ni in LiNiVO_4 are available till date and to mention a few, substitution with Mn [14], Co [15] for Ni in LiNiVO_4 (and Ni in LiCoVO_4 [16]) has been attempted. But attempts to introduce cations at the V sites of LiNiVO_4 have not yet been made so far and so it would be highly pertinent to investigate on these lines. Therefore the very focal theme of the present communication includes the adoption of fairly novel SAC synthesis methodology and a possible exploration of incorporation of Co, Mg and Al as dopants for V in LiNiVO_4 to yield a set of $\text{LiNiM}_x\text{V}_{1-x}\text{O}_4$ compounds as possible electrochemically active cathodes for use in rechargeable lithium-ion batteries.

Thus the present investigation has been carried out primarily to explore the possible existence of solid solutions containing cations such as Co, Mg and Al at the vanadium sites and to understand the influence of these dopants on the electrochemical behavior of LiNiVO_4 by synthesizing solid solutions of the type $\text{LiNiM}_x\text{V}_{1-x}\text{O}_4$, via Starch-Assisted Combustion (SAC) method. The results obtained mainly from PXRD, FTIR, CV and charge–discharge studies are analyzed and discussed in detail.

2. Experimental

2.1. Synthesis of $\text{LiNiM}_x\text{V}_{1-x}\text{O}_4$ series

A set of $\text{LiNiM}_x\text{V}_{1-x}\text{O}_4$ compounds with $M = \text{Co, Mg and Al}$ and $x = 0.0, 0.1, 0.3$ and 0.5 has been synthesized by adopting Starch-Assisted Combustion (SAC) method, the procedure of which has already been reported by the same authors related to the synthesis of LiNiVO_4 , LiMn_2O_4 and LiCoO_2 [17,18] cathode materials. In a typical synthesis, to a hot solution of starch (2 g in 100 ml distilled water), crystals of nitrates of lithium (0.01 M), nickel, cobalt, aluminum, magnesium (each being in the stoichiometric ratio) and ammonium meta vanadate (0.01 M) were added and dissolved to

get a homogeneous solution. The resultant mixture was oven dried initially at 110°C (24 h) to get the precursor in the form of foam. The dried foam was furnace heated at 300°C for 3 h followed by a thermal treatment at 700°C for 3 h for better crystallinity. The as-received fine powders were subjected to characterization studies, with a view to understand the effect of synthesis upon physical as well as electrochemical activity of the synthesized compounds.

3. Instrumentation

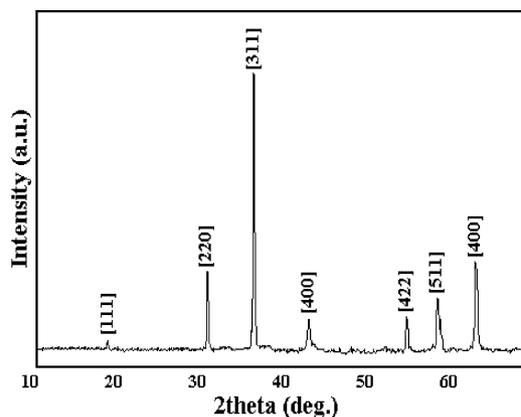
Phase characterization was done by powder X-ray diffraction technique using JEOL-JDX 8030 X-ray diffractometer using Ni filtered $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) in the 2θ range of $10\text{--}70^\circ$ at a scan rate of 0.1° s^{-1} . FTIR spectrum was recorded with Perkin Elmer Paragon-500 FTIR Spectrophotometer using KBr pellets in the region $400\text{--}1000 \text{ cm}^{-1}$. Surface morphology of the particles was examined from the scanning electron micrographs obtained on Hitachi S-3000 H scanning electron microscope and the particle size of the oxide materials was determined using Malvern Easy Particle sizer. Surface area of the synthesized powders was determined by BET adsorption method using low temperature nitrogen adsorption (Quanta Chrome Nova 1000, US).

Electrochemical performance of the synthesized cathode materials was evaluated by assembling cathode-limited 2016 lithium coin cells. Cathodes were fabricated by slurring the cathode powders with 10% graphite and 2% PVdF as binder in *N*-methyl 2-pyrrolidone (NMP) as solvent and coating the mixture over Al foil (serves as current collector). After drying at 110°C overnight, the discs were pressed in a hydraulic press by applying a pressure of about $10\text{--}12 \text{ kg cm}^{-2}$ for perfect adherence of the coated material over the surface of the Al current collector. Discs of 1.6 cm diameter were punched out and typical cathodes were found to have an average active material weight of about $10\text{--}15 \text{ mg}$ per disc. Electrolyte consisted of 1 M LiAsF_6 dissolved in equal volumes of EC and DMC and the separator used was polypropylene cloth. Charge–discharge studies were performed using an in-house cell-testing unit.

4. Results and discussion

4.1. Physical appearance of the $\text{LiNiM}_x\text{V}_{1-x}\text{O}_4$ compounds

It is interesting to observe that depending upon the nature and the extent of cations substituted, color of the $\text{LiNiM}_x\text{V}_{1-x}\text{O}_4$ compounds also changes in the range from light yellow to coffee brown. Also, the color of the compounds is found to get intensified with the increasing amount of dopant as follows: $\text{LiNiCo}_{0.1}\text{V}_{0.9}\text{O}_4$ – light brown; $\text{LiNiCo}_{0.5}\text{V}_{0.5}\text{O}_4$ – coffee brown; $\text{LiNiMg}_{0.1}\text{V}_{0.9}\text{O}_4$ – dull brownish yellow; $\text{LiNiMg}_{0.5}\text{V}_{0.5}\text{O}_4$ – black;

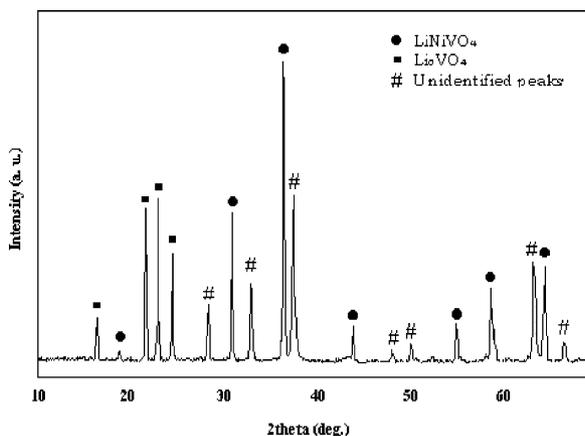
Fig. 1. XRD of $\text{LiNiAl}_{0.1}\text{V}_{0.9}\text{O}_4$.

$\text{LiNiAl}_{0.1}\text{V}_{0.9}\text{O}_4$ – yellow and $\text{LiNiAl}_{0.5}\text{V}_{0.5}\text{O}_4$ – light brownish yellow. This simple observation in the color change may also be taken as a qualitative measure to substantiate the incorporation of dopants into the crystal lattice of the parent vanadate.

4.2. Phase analysis by PXRD

Since the powder X-ray diffractograms of $\text{LiNiM}_x\text{V}_{1-x}\text{O}_4$ series with $\text{M} = \text{Co}$, Al and Mg ($x = 0.0$ and 0.1) are all found to be similar, only PXRD of aluminum-substituted nickel vanadate with $x = 0.1$ viz., $\text{LiNiAl}_{0.1}\text{V}_{0.9}\text{O}_4$ is depicted in Fig. 1. The sharp and highly intense XRD peak pattern indicates the formation of pure $\text{LiNiAl}_{0.1}\text{V}_{0.9}\text{O}_4$ phase (so also of $\text{M} = \text{Co}$ and Mg) with a high degree of crystallinity. Also the result is in favor of the fact that the cubic spinel structure is well preserved in these compounds when the cations were substituted to a level of 10%, thereby confirming the possible existence of solid solutions of $\text{LiNiM}_x\text{V}_{1-x}\text{O}_4$ [$\text{M} = \text{Co}$, Mg and Al] compounds up to 10% dopant concentration.

Fig. 2 represents the PXRD of $\text{LiNiAl}_{0.3}\text{V}_{0.7}\text{O}_4$, which indicates the presence of mixed phases like Li_3VO_4 and LiAlO_2 together with some other unknown phases. $\text{LiNiAl}_{0.5}\text{V}_{0.5}\text{O}_4$

Fig. 2. XRD of $\text{LiNiAl}_{0.3}\text{V}_{0.7}\text{O}_4$.

also exhibits similar XRD patterns with the co-existence of undesirable impurities and so it is not reproduced here, i.e., peaks corresponding to the vanadate phase are observed along with impurity peaks in the $\text{LiNiM}_x\text{V}_{1-x}\text{O}_4$ compounds, especially when $x > 0.1$, for the entire set of compounds chosen for the study. Generally, Co_3O_4 , MgO and Li_3VO_4 (together with some unidentified peaks) are the respective common impurities that are found to be present in the Co and Mg doped vanadates with 30 and 50% dopants levels [viz., $\text{LiNiCo}_{0.3}\text{V}_{0.7}\text{O}_4$, $\text{LiNiCo}_{0.5}\text{V}_{0.5}\text{O}_4$, $\text{LiNiMg}_{0.3}\text{V}_{0.7}\text{O}_4$ and $\text{LiNiMg}_{0.5}\text{V}_{0.5}\text{O}_4$]. Thus, from the XRD studies performed on $\text{LiNiM}_x\text{V}_{1-x}\text{O}_4$ series, it is understood that the amount of M that replaces V may have variation only in the range $0 \leq x \leq 0.1$, with out affecting the original cubic structure, phase purity, and crystallinity. In other words, existence of solid solutions is possible only when the dopant level is well within 10%, irrespective of the type and nature of dopant being incorporated in to the $\text{LiNiM}_x\text{V}_{1-x}\text{O}_4$ matrix. It may also be reasonable to assume that the solubility of the selected cations with vanadium may have an upper limit of 20%. However, complete elimination of NiO and Li_3VO_4 impurities has been realized by Starch-Assisted Combustion method, resulting in the formation of solid solutions of the composition $\text{LiNiM}_x\text{V}_{1-x}\text{O}_4$ especially with $x = 0.0$ and 0.1 . Thus the deployment of solution assisted combustion method has been found to be successful in producing phase pure and better performing $\text{LiNiM}_x\text{V}_{1-x}\text{O}_4$ cathodes also.

Since $\text{LiNiM}_{0.3}\text{V}_{0.7}\text{O}_4$ and $\text{LiNiM}_{0.5}\text{V}_{0.5}\text{O}_4$ compounds with higher dopant concentration are found to be XRD impure, they have not been considered for further characterization studies. As a result, the study has been restricted with the $\text{LiNiM}_x\text{V}_{1-x}\text{O}_4$ solid solutions containing 10% of Co , Al and Mg dopants.

When the integrated intensity ratio of (2 2 0) and (3 1 1) peaks was considered for $\text{LiNiM}_x\text{V}_{1-x}\text{O}_4$ compounds, $I_{(220)}/I_{(311)} = 0.5$ is observed, which is similar to the reported results of Chitra et al. [19] and the same has been taken as a qualitative measure of high crystallinity of the sample. The introduction of dopants at the V sites in LiNiVO_4 has resulted in the variation of crystal lattice parameters, as evidenced from Table 1. The crystal constants viz., ‘ a ’, and cell volume of the parent LiNiVO_4 and $\text{LiNiM}_x\text{V}_{1-x}\text{O}_4$ compounds determined by an iterative least squares refinement method using the indexed ‘ h, k, l ’ values are included in the table.

Since $\text{LiNiCo}_{0.1}\text{V}_{0.9}\text{O}_4$ and $\text{LiNiMg}_{0.1}\text{V}_{0.9}\text{O}_4$ exhibited similar kind of results which are comparable with that of $\text{LiNiAl}_{0.1}\text{V}_{0.9}\text{O}_4$, characterization results of FTIR, SEM,

Table 1
Crystal constants of $\text{LiNiM}_{0.1}\text{V}_{0.9}\text{O}_4$ compounds

M in $\text{LiNiM}_{0.1}\text{V}_{0.9}\text{O}_4$	Cell constants	
	a (Å)	Cell volume (Å) ³
Co	8.231	557.6
Mg	8.229	557.2
Al	8.225	556.4
LiNiVO_4	8.217	554.8

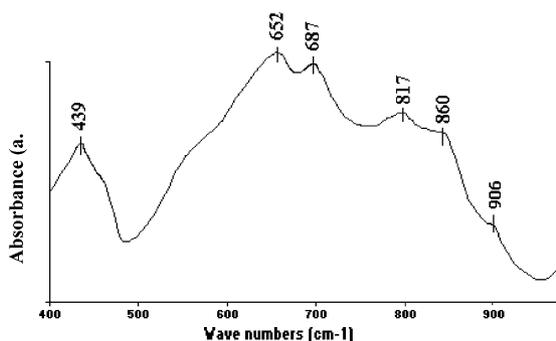


Fig. 3. FTIR spectra of $\text{LiNiAl}_{0.1}\text{V}_{0.9}\text{O}_4$.

particle size analysis, particle size distribution and surface area of $\text{LiNiAl}_{0.1}\text{V}_{0.9}\text{O}_4$ alone has been furnished in this paper. However for electrochemical characterization, all the three solid solutions viz., $\text{LiNiM}_{0.1}\text{V}_{0.9}\text{O}_4$ with $M = \text{Co}, \text{Al}$ and Mg have been considered individually and the results are incorporated and discussed in the respective sections.

4.3. Vibrational spectra of $\text{LiNiAl}_{0.1}\text{V}_{0.9}\text{O}_4$

Fig. 3 shows the room temperature FTIR spectrum of $\text{LiNiAl}_{0.1}\text{V}_{0.9}\text{O}_4$ synthesized by SAC method at 700°C for 3 h. FTIR signatures observed for $\text{LiNiAl}_{0.1}\text{V}_{0.9}\text{O}_4$ in the $400\text{--}750\text{ cm}^{-1}$ region are largely associated either with the bending vibrations of the VO_4 tetrahedron or with the vibrations of NiO_6 and LiO_6 octahedral units. The possible bonding of Li and Ni with each oxygen atom in the VO_4 tetrahedra brings about some asymmetry but is likely to occur without distorting the cubic symmetry of the fundamental unit cell as evidenced from the simple IR spectrum. Hence broad bands observed around 815 and 860 cm^{-1} are tentatively assigned to the asymmetrical stretching modes of distorted VO_4 units [20]. Also, the vibrations due to NiO_6 bending modes, i.e. $\nu(\text{Ni-O-Li})$ are observed around 650 and 685 cm^{-1} and a weak band around 439 cm^{-1} may therefore be assigned to the asymmetric stretching of Li-O in LiO_6 environments [21,22]. Further bands in the high frequency region are assigned to the vibration between oxygen and the highest valent cation. As a result, the weak band around 905 cm^{-1} is assigned to the symmetric stretching in VO_4 [21]. Generally, FTIR bands of $\text{LiNiM}_{0.1}\text{V}_{0.9}\text{O}_4$ ($M = \text{Co}, \text{Al}$ and Mg) compounds are found to be present at slightly higher wave numbers than that of the undoped LiNiVO_4 . This may be attributed to the incorporation of the dopants in the LiNiVO_4 matrix and therefore it is substantiated from FTIR studies also that the select dopants got incorporated at the V sites of LiNiVO_4 to produce the series of solid solutions.

4.4. Microstructure, particle size, distribution and surface area (BET) of $\text{LiNiAl}_{0.1}\text{V}_{0.9}\text{O}_4$

Fig. 4a represents the SEM of $\text{LiNiAl}_{0.1}\text{V}_{0.9}\text{O}_4$ captured under a magnification of 2 K. The micrograph reveals

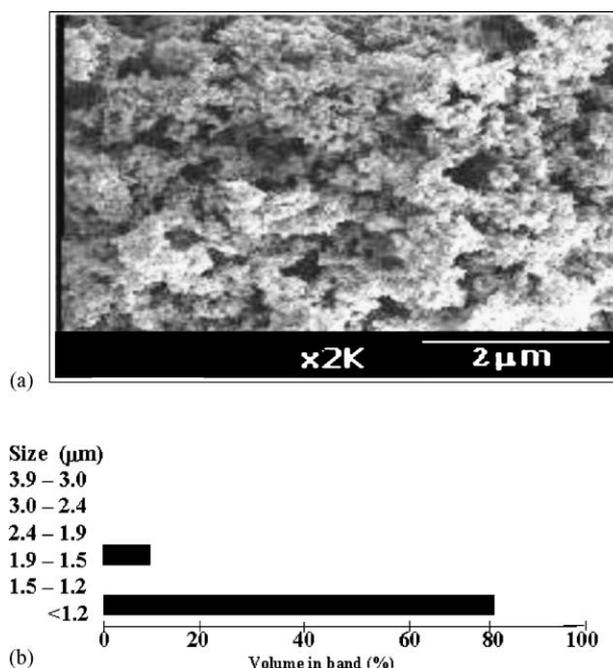


Fig. 4. (a) SEM of $\text{LiNiAl}_{0.1}\text{V}_{0.9}\text{O}_4$. (b) Particle size distribution of $\text{LiNiAl}_{0.1}\text{V}_{0.9}\text{O}_4$.

the presence of well-connected particles of porous nature. In addition to this feature, the presence of uniformly distributed sub-micron particles, which is desirable for any cathode material in view of better electrochemical behavior is also evident from Fig. 4a. Further, presence of a narrow band (Fig. 4b) in the particle size range of $1.2\text{--}1.6\text{ }\mu\text{m}$ has been observed, which is in favor of uniform distribution and the presence of size-reduced particles of the doped derivatives of $\text{LiNiM}_x\text{V}_{1-x}\text{O}_4$ category. About 10% of the particles could be present well below $1.2\text{ }\mu\text{m}$ size and a small percentage of $\text{LiNiAl}_{0.1}\text{V}_{0.9}\text{O}_4$ particles are found to fall under $2\text{ }\mu\text{m}$, as seen from Fig. 4b. A similarity in the particle morphology and the distribution pattern of particles has been observed for $\text{LiNiCo}_{0.1}\text{V}_{0.9}\text{O}_4$ and $\text{LiNiMg}_{0.1}\text{V}_{0.9}\text{O}_4$ compounds with that of $\text{LiNiAl}_{0.1}\text{V}_{0.9}\text{O}_4$ cathode. Average surface area of $\text{LiNiM}_{0.1}\text{V}_{0.9}\text{O}_4$ ($M = \text{Co}, \text{Al}$ and Mg) solid solutions as determined by BET (N_2 adsorption) method was found to be in the range of $25\text{--}28\text{ m}^2\text{ g}^{-1}$. Thus the presence of size-reduced particles with larger surface area has been made possible by employing the soft-chemical based Starch-Assisted Combustion method, which is the highlight of the selected method. Also, since the precursor solution has initially been subjected to slow rate of heating adhered throughout the calcination process, it is believed that the possible agglomeration of particles at high calcination temperature has very well been controlled. More precisely, the actual size of the particles and the pattern of distribution of particles are seen to be present very much in the preferred range of particle size analysis graph (Fig. 4).

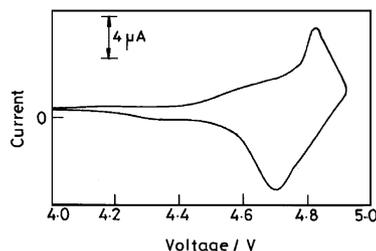


Fig. 5. Cyclic voltammogram of Li//LiNiAl_{0.1}V_{0.9}O₄ cell.

5. Electrochemical studies

5.1. Cyclic voltammetry studies

Fig. 5 shows the cyclic voltammogram of LiNiAl_{0.1}V_{0.9}O₄ cell in the voltage range of 4.0–4.9 V at a sweep rate fixed as 1 mV s⁻¹. The voltage scan has been limited to 4.9 V in the forward scan to avoid electrolyte decomposition, despite the usage of electrolyte solution consisting of 1 M LiAsF₆ in equal volumes of EC and DMC.

The CV features a pair of oxidation–reduction peaks in the range of 4.70–4.85 V, which are largely associated with a single electron transfer process during lithium intercalation–deintercalation process. The CV response also infers that the voltage difference between the Li⁺ intercalation–deintercalation processes is less, thus accounting for the high degree of reversibility in Li⁺ intercalation–deintercalation process. The electrochemical reversibility of LiNiAl_{0.1}V_{0.9}O₄ process is further demonstrated by charge–discharge cycling studies, which is presented in the following section.

5.2. Charge–discharge studies

Charge–discharge studies were carried out with Li//LiNiM_{0.1}V_{0.9}O₄ cells (M = Co, Mg and Al) at a current density of 0.1 mA cm⁻² from 3 to 4.9 V. The cyclability curves of Li//LiNiM_{0.1}V_{0.9}O₄ cells are shown in Fig. 6 and Table 2

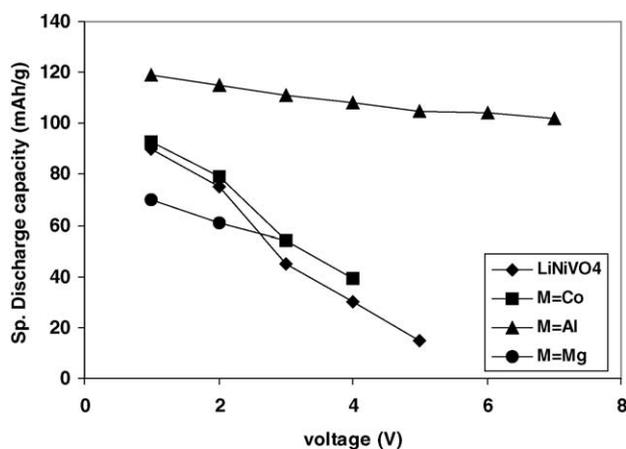


Fig. 6. Cyclability of Li//LiNiM_xV_{1-x}O₄ cells.

Table 2
Cyclability trend of Li//LiNiM_xV_{1-x}O₄ cells

Cycle no.	Discharge capacity of LiNiM _{0.1} V _{0.9} O ₄ (mAh g ⁻¹)			
	LiNiVO ₄	M = Co	M = Al	M = Mg
1	90	93	119	70
2	75	79	115	61
3	45	54	111	54
4	30	39	108	–
5	15	–	105	–
6	–	–	104	–
7	–	–	102	–

shows the observed variation of discharge capacity of these cells with the cycle number.

From the table, it is obvious that all the doped compounds of LiNiVO₄ exhibit good electrochemical behavior up to a minimum of 10 cycles, i.e., the doped derivatives of LiNiVO₄ are found to perform better than the parent LiNiVO₄ compound with respect to capacity retention and cyclability. With an exception of Mg as substituent, both the Co and Al substituted vanadates showed enhanced specific capacity values along with a considerable reversible capacity values, i.e., the magnitude of irreversible capacity loss is found to get reduced remarkably (<5%) in the case of LiNiAl_{0.1}V_{0.9}O₄ compound, even upon extended cycling. Similarly, LiNiCo_{0.1}V_{0.9}O₄ also exhibits acceptable reversible capacity values upon progressive cycling (~40 mAh g⁻¹) compared to the undoped LiNiVO₄ (<20 mAh g⁻¹). One interesting fact about the LiNiAl_{0.1}V_{0.9}O₄ cathode is that it gets stabilized from fourth cycle onwards, despite the slightly reduced initial discharge capacity *va*. Further, the maximum capacity is realized around 4.7 V via, flat discharge profile exhibited by LiNiAl_{0.1}V_{0.9}O₄ cathode. Also, it is interesting to observe that a moderate initial capacity of around 120 mAh g⁻¹ has been obtained from the first discharge, against the theoretical capacity of 148 mAh g⁻¹, which is an encouraging result realized through the partial substitution of V by Al (10%) in the LiNiM_xV_{1-x}O₄ matrix.

It is worth to recall now that Al when used as a dopant in LiCoO₂, etc., is reported to force more electronic exchange between lithium and the oxygen network [23,24]. Therefore, the possibility of similar exchange is expected to occur in the present case of LiNiAl_{0.1}V_{0.9}O₄ also and the same is believed to be the reason for the increased the cell voltage up to 4.7 V. Moreover, since Al cannot be oxidized or reduced beyond 3+ state, the maximum amount of intercalated or deintercalated lithium can also be limited, depending upon the Al content. Hence partial substitution of Al offers over charge stability to the lithium cell generally and thereby improves cyclability and cell safety by preventing the electrolyte decomposition, gassing, etc., as in the case of LiCoO₂ or LiNiO₂. However, a nominal amount of 10% Al substitution in LiNiM_xV_{1-x}O₄ may only be acceptable to exhibit a stable and better electrochemical performance, which is understood from the present investigation. It is also known that cathode which gives rise to a higher charge or discharge voltage shows

lower cycle efficiency and may support sample disintegration during cycling [24]. The same is considered to be responsible for the gradually reducing capacity values exhibited by $\text{LiNiAl}_{0.1}\text{V}_{0.9}\text{O}_4$ cathode upon extended cycling.

On the other hand, $\text{Li//LiNiCo}_{0.1}\text{V}_{0.9}\text{O}_4$ and $\text{Li//LiNiMg}_{0.1}\text{V}_{0.9}\text{O}_4$ cells exhibited poor electrochemical performance and displayed severe capacity degradation within a minimum of five cycles compared to the respective Al doped derivative. It is well known that Mg also cannot be oxidized or reduced beyond 2+ state (as in the case of Al substitution), and hence it is expected that the maximum amount of intercalated or deintercalated lithium can be limited in $\text{LiNiMg}_x\text{V}_{1-x}\text{O}_4$ compound also. Nevertheless, no improvement in the electrochemical performance has been observed. On the other hand, the co-doped derivatives exhibited a lower working voltage of about 4.2 V (comparable with Li//LiNiVO_4 cell synthesized by SAC method), despite the deintercalation peak which appears at 4.7 V in the cyclic voltammogram of $\text{Li//LiNi}_{0.7}\text{Co}_{0.3}\text{VO}_4$ cell. Probable reasons for these observations may generally be deduced as follows:

- (A) The upper voltage limit (4.9 V) selected for performing the charge–discharge studies (in the present study) may be too high, as the very selection of higher voltage limit has resulted in fairly lesser capacity values and lower cycling efficiency. However, the same behavior is acceptable only as similar trends are already reported in the literature [24].
- (B) Factors such as possibility of loss of structural integrity or morphological changes upon cycling and the dissolution of cathode material upon cycling, etc., may not be ignored completely, as the same may also be partially responsible for the less encouraging cycleability behavior of doped derivatives of $\text{LiNiM}_x\text{V}_{1-x}\text{O}_4$ compounds.
- (C) With the higher dopant concentration, migration of dopants is also possible, which in turn may tend to deteriorate the overall electrochemical performance of the compounds. In the present study also, the chosen level of dopant concentration such as 10–50% may be little high to allow possible migration of dopant. Hence attempts to use less than 10% dopant level are recommended for exploration of better electrochemical activity in the $\text{LiNiM}_x\text{V}_{1-x}\text{O}_4$ category cathodes in future.

In short, the present study triggers and implies favorably upon one fact that realization of modified/improved electrochemical properties is possible in the $\text{LiNiM}_x\text{V}_{1-x}\text{O}_4$ variety cathodes also, provided the upper charging voltage limit is fixed below 4.5 V (in order to realize improved cycle life with high specific capacity values). Work towards this direction has been reserved for future study along with a consideration to carry out the incorporation of dopants from the lowest possible concentration level.

6. Conclusion

By adopting Starch-Assisted Combustion (SAC) method, an unique attempt, a set of solid solutions viz., $\text{LiNiCo}_x\text{V}_{1-x}\text{O}_4$, $\text{LiNiAl}_x\text{V}_{1-x}\text{O}_4$ and $\text{LiNiMg}_x\text{V}_{1-x}\text{O}_4$ ($x = 0.0, 0.1, 0.3$ and 0.5) has been prepared by incorporating the select category cations at the V sites of LiNiVO_4 . As evidenced from the XRD studies, substituted phase pure compounds (solid solutions) of $\text{LiNiM}_x\text{V}_{1-x}\text{O}_4$ are obtained only when $x = 0.0$ and 0.1 , whereas in the $0.2 \leq x \leq 0.5$ range, impurity peaks corresponding to Co_3O_4 , MgO , LiAlO_2 , Li_3VO_4 phases are observed with respect to Co, Al, and Mg dopants. Thus solubility limit of the dopants with V to yield solid solutions may lie probably below 20%. Cyclic voltammogram recorded for $\text{LiNiAl}_{0.1}\text{V}_{0.9}\text{O}_4$ reveals high lithium reversibility, thereby suggesting better electrochemical performance possibilities. Among the three cations investigated, Al substitution in $\text{LiNiAl}_{0.1}\text{V}_{0.9}\text{O}_4$ exhibited overall better cyclability and capacity compared to both the undoped and doped derivatives of LiNiVO_4 compound. Based on this major reason $\text{LiNiAl}_{0.1}\text{V}_{0.9}\text{O}_4$ had been evaluated as prospective cathode material for use in the rechargeable lithium batteries from the list of compounds chosen for the present study. However, possibilities are still wide open to evaluate and recommend $\text{LiNiM}_x\text{V}_{1-x}\text{O}_4$ ($M = \text{Mg}$ and Co) compounds also for use in practical lithium battery applications, which needs specific attempts oriented towards critical issues such as selection of dopant level from the lowest possible limit, fixing a nominal charging voltage limit, etc.

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