An innovative soft-chemistry approach to synthesize LiNiVO$_4$

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Abstract

LiNiVO$_4$, a high voltage lithium intercalated cathode—first of its kind with an inverse spinel crystal structure has been synthesized by adopting "soft-chemistry" route, otherwise known as starch-assisted combustion method. Using nitrates as the starting materials, different heat treating conditions were employed with varying amounts of starch, which serves as fuel. Systematic PXRD studies carried out on these heat treated samples indicated monophase formation of LiNiVO$_4$ at a temperature as low as 400 °C without any impure phases, especially NiO. From the present investigation, the amount of starch sufficient for accomplishing good crystallinity with electrochemical activity has been optimized as 2 g for 0.01 M of the reactants. Mono-dispersed particles with an average grain size below 1.5 μ are notable from SEM and particle size analysis. The electrochemical activity of thus synthesized LiNiVO$_4$ powders has been examined in terms of charge/discharge cycle performance of Li//LiNiVO$_4$ assembly using 2016 type coin cells. Also, the reversibility of the material with respect to Li$^+$ has been verified through cyclic voltammetric studies. The novelty, flexibility and the significance of the starch-assisted methodology are highlighted.
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1. Introduction

Despite the existence of certain promising 4 V cathode materials viz., LiCoO$_2$ [1], LiNiO$_2$ [2] and LiMn$_2$O$_4$ [3], the recent discovery of both LiNiVO$_4$ and LiCoVO$_4$ [4] has paved way to the possible entrance of an entirely different category of inverse spinel cathode materials for secondary lithium batteries. Among these two inverse spinels, LiNiVO$_4$ is bestowed with a high voltage of 4.8 V vs Li$^+$ with a capacity of about 45 m A h g^{-1}. However the other analog viz., LiCoVO$_4$ is found to exhibit only 4.2 V, implying that the presence, site occupancy [5], local symmetry and distribution of Ni atoms in the inverse spinel plays a vital role in the stepping up of the voltage to 4.8 V. LiNiVO$_4$ is believed to have an equal and random occupation of octahedral sites by monovalent Li and bivalent Ni ions and with the tetrahedral site occupation by the pentavalent V ions [6,7] in the cubic close packed array of oxygens. Though adequate knowledge about its crystal structure [6,8,9], magnetic properties [6], vibrational spectroscopic data [10], phase diagrams [11] and electronic conductivity [7] has been acquired, the dispute over the presence/absence of three-dimensional tunnel structure (favoring Li$^+$ diffusion) is not settled yet. This compound is thus gaining popularity and is inviting the attention of researchers to probe various aspects of the compound, say on its observed high voltage performance, ambiguity in preservation of structural integrity during electrochemical cycling etc. Of late, attempts to obtain phase pure LiNiVO$_4$ are being made by various researchers since synthesis is the key step towards the successful development of materials with good physical as well as electrochemical properties. Hence maximum efforts need to be put forth in selecting techniques for the synthesis of better performing LiNiVO$_4$, so also any other cathode material of potential activity.

Conventionally adopted "solid-state" method, being non-economical and arduous in nature, is posing a serious problem towards the unavoidable association of undesirable impurities such as NiO, the presence of which degrades the electrochemical performance of the cathode active material [5]. Thus came the existence of the most preferred "soft-chemistry" route, a better alternative to the existing materials processing methodologies. Here again, combustion method involving the reaction mixture with an internal fuel is adopted normally. Being the very first of its kind, Prabaharan et al. [12] has used glycine (a nitrogenous fuel), and studied the electrochemical characteristics of LiNiVO$_4$ synthesized at 500 °C. Generally the soft-chemistry route, an economically viable course makes possible the atomic level of mixing of the ingredients thereby eliminating completely

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the possible impure phase contamination. Therefore, the present study was undertaken with a view to synthesize uncontaminated, highly crystalline cathode active LiNiVO$_4$ inverse spinel following soft-chemistry method using a carbonaceous fuel namely starch at a temperature of 400 °C. Besides being a low temperature and an easy-to-adopt methodology, the highlight of this method is that it yields phase pure LiNiVO$_4$ with better electrochemical activity in terms of acceptable capacity, good cyclability and better reversibility. Also we suggest that this processing route provides the basis for a low cost, low temperature method for the preparation of homogeneous sub-micron ceramics compared to any other existing methods.

2. Experimental

2.1. Synthesis of LiNiVO$_4$

Initially, the amount of starch required for the formation of stoichiometric LiNiVO$_4$ with the expected properties has been studied extensively based upon the results obtained especially from the PXRD and charge/discharge studies. Calculated amount of 'water soluble' starch was dissolved in 20 ml of hot distilled water. To the hot starch solution was added stoichiometric amounts of nitrates of Li, Ni and ammonium meta vanadate. The solution was stirred gently to ensure complete dissolution of the added salts. The resulting solution was allowed to dry at 110 °C to get yellow foam, called as the precursor. Subsequently, the precursor was heat treated to various temperatures ranging from 300 to 800 °C for 3 h individually. The resulting powders of

LiNiVO$_4$ were collected and subjected to physical and electrochemical characterization. The schematic approach of the starch-assisted route is clearly depicted in the flowchart (Fig. 1).

2.2. Instruments

Thermal studies were carried out in air at a heating rate of 10 °C min^{-1} using Simultaneous TG/DTA Thermal Analyzer (Model No: STA 1500, PL Thermal Sciences, UK). Powder X-ray diffraction studies were carried out on a JEOL-JDX 8030 X-ray diffractometer using Ni filtered Cu Kα radiation ($\lambda = 1.5405$ Å) in the 2θ range of 10–80° at a scan rate of 0.1° s^{-1}). FTIR spectra were recorded with Perkin Elmer Paragon-500 FTIR Spectrophotometer using KBr pellets in the region 400–1000 cm^{-1}. Surface morphology of the particles was examined from the SEM micrographs obtained from Hitachi S-3000 H Scanning Electron Microscope and the particle size of the materials was determined using Malvern Easy Particle Sizer. The characterized LiNiVO$_4$ powders of preferred crystal structure and surface morphology were subjected to electrochemical characterization. Charge/discharge studies were carried out using an in-house cell testing assembly. Cyclic voltammogram was recorded using 'AUTOLAB' software governed by an IBM compatible PC.

3. Results and discussion

In order to optimize the amount of starch to be used, products obtained from the usage of varying amounts of
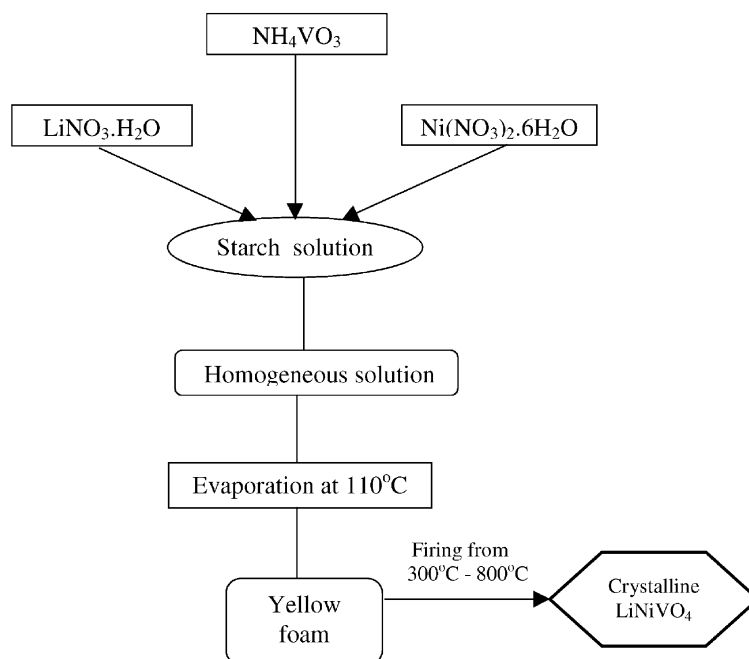

Fig. 1. Flowchart showing various steps involved in the starch-assisted combustion synthesis of LiNiVO$_4$.

starch with similar heat treating conditions were attempted. The fuel calorific value (FCV) of starch is determined to be around $4\,kcal\,g^{-1}$ (Van Nostrand's Scientific Encyclopedia, NY, II Edition). However FCV/fuel equivalence ratio has not been used in optimizing the amount of fuel that is required for the synthesis. Unlike glycine, a molar correlation in terms of a chemical equation may not be possible in the case of starch. Because being a polysaccharide $(C_6H_{10}O_5)_n$ starch does not have a definite *n* value. Hence attempts were made based on trial and error method only. When 1 g of starch was used, deliquescent product formation was observed which on further heating yielded an over sintered product. However, the usage of 4 g of starch resulted in the formation of a product, quite similar to those obtained from 2 and 3 g of starch. Therefore it was understood that the ideal amount of starch required for the formation of a stable and a crystalline phase pure product lie in the range 2–3 g. The same has been verified through electrochemical studies also, as the excess of starch (4 g) led to no spectacular enhancement of electrochemical property. Moreover, using the optimized amount of starch, a temperature as low as 400 °C has been realized as the essential calcination temperature of formation of pure and crystalline $LiNiVO_4$.

3.1. Thermal analysis of LiNiVO4

The TG/DTA plots of the $LiNiVO_4$ precursor are shown in Fig. 2. As is evident from the thermogram, the formation of $LiNiVO_4$ is accompanied by a single exothermic peak. An expected endothermic peak around 100–120 °C however is not evident in the present investigation, as the precursor (yellow foam) has been subjected to the thermal analysis only after the complete removal of water. The other exothermic transformation that has been observed with a mass loss of about 40% may be attributed to the decomposition of

starch. This decomposition of starch occurs around 300 °C may be taken as an indication of phase formation and crystallization by way of initiating the reaction between the reactants. Therefore it is understood that a temperature as low as 300–350 °C is sufficient for the formation of the final product, as the combustion of starch supplies enormously high amount of exothermic heat energy facilitating the process of crystallization of vanadate. The same has further been supported by the fact that no more mass loss has been observed beyond this temperature range and the product formed is found to be stable at least up to 800 °C. The crystallinity and stability of thus formed product has also been substantiated by XRD results.

3.2. X-ray diffraction analysis of LiNiVO4

The parts a–f of Fig. 3 are the PXRD patterns of the heat treated samples from 300 to 800 °C. The part a of Fig. 3 shows the presence of carbon impurity peaks together with the peaks corresponding to the vanadate phase for the sample treated at 300 °C. Formation of single-phase and well-crystallized product even at 400 °C is evidenced from the part b of Fig. 3. Moreover, for samples treated between 400 and 800 °C, no significant change in the *d* values were noticed as indicated by the constant *a* values. However, an improvement in degree of crystallinity is observed as calcination temperature increased. Therefore, it is believed that a temperature as low as 400 °C is the minimum temperature required for the formation of single-phase product. Though the crystallization of the product has been well initiated at 400 °C, it is felt that the improved crystallinity is expected for samples prepared at high temperature say 800 °C. However, samples treated between 400 and 700 °C have been considered for a separate study to understand the effect of temperature over the electrochemical behavior.
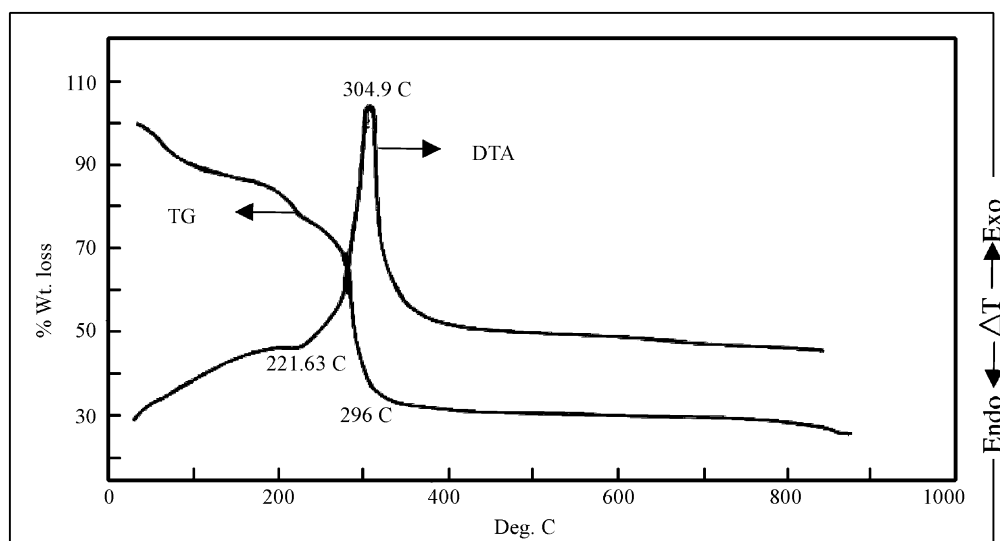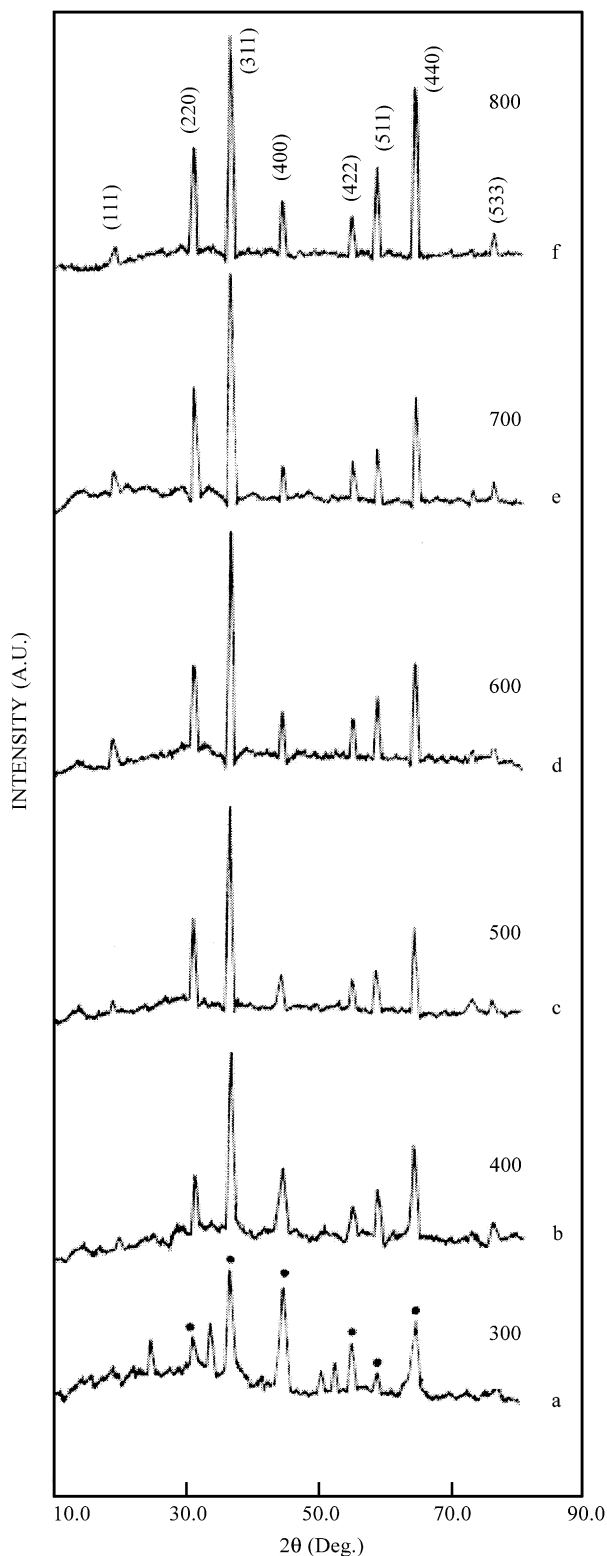

Fig. 2. TG/DTA of $LiNiVO_4$ precursor.

Fig. 3. PXRD patterns of LiNiVO$_4$; (•) denotes peaks of LiNiVO$_4$.

All the XRD peaks in the parts a–f of Fig. 3 are index-able under cubic lattice (Sp. Gr. Fd3m—O$_h^7$). The XRD pattern observed for various heat treating temperatures show the presence of weak (1 1 1) Bragg line and a strong (2 2 0)

line, a feature which is indicative of the inverse spinel structure of LiNiVO$_4$. Hence the presence of vanadium on the tetrahedral 8a site has been confirmed which in principle causes the increase in intensity of the (2 2 0) line at the expense of (1 1 1) line [4] (Wyckoff positions: 8a for V, 16d for Li and Ni, and 32e for O). The possible contamination of NiO (peak at $2\theta = 43.3°$) impurities is absolutely absent for all the samples heat treated from 400 to 800 °C. Thus the exclusion of NiO contaminant in the final compound as observed by Prabaharan et al. has been made possible through the usage of carbonaceous fuel also. Peaks corresponding to Li$_3$VO$_4$ phase ($2\theta = 16.2°$, $21.5°$, $22.8°$ and $24.3°$) were also found to be absent. As suggested by Chitra et al. [13], an intensity ratio $I_{(2 2 0)}/I_{(3 1 1)} = 0.5$ is taken as a qualitative measure of high crystallinity of the sample. Thus the phase purity, inverse spinel structure and the crystalline nature of LiNiVO$_4$ synthesized at different temperatures were confirmed by the room temperature PXRD measurements. Lattice constant for the samples were refined using a least squares fitting procedure. The observed a value of 8.217 Å coincides well with the standard value of 8.219 Å [14].

3.3. FTIR of LiNiVO$_4$

Fig. 4 shows the room temperature FTIR spectrum of LiNiVO$_4$ treated at 800 °C. FTIR signatures observed for LiNiVO$_4$ in the 400–750 cm^{-1} region are largely associated either with the bending vibrations of the VO$_4$ tetrahedron or 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 without distorting the cubic symmetry of the fundamental unit cell. Hence broad bands around 810 and 850 cm^{-1} are tentatively assigned to the asymmetrical stretching modes in distorted VO$_4$ units [15]. Also, the vibrations due to NiO$_6$ bending modes i.e., $\nu[(Ni–O–Li)]$ are observed around 650 cm^{-1} and two weak bands around 440 and 420 cm^{-1} may therefore be assigned to asymmetric stretching of Li–O in LiO$_6$ environments [10,12]. Also, the 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 900 cm^{-1} is assigned to the symmetric stretching in VO$_4$ [12].

3.4. Microstructure, particle size and distribution of LiNiVO$_4$

SEM analysis reveals the nature, shape, approximate grain size and surface morphology of the particles with respect to the method of synthesis. The formation of mono-dispersed spherical particles with the clearly seen crystal facets is an indication of preferred surface morphology of a cathode material that has been synthesized. In comparison with the previous report [12], it is evident from the observed SEM of LiNiVO$_4$ (Fig. 5a) that the usage of carbonaceous fuel (starch) at a low temperature as 400 °C plays a vital role towards the restricted agglomeration of particles, suppressed
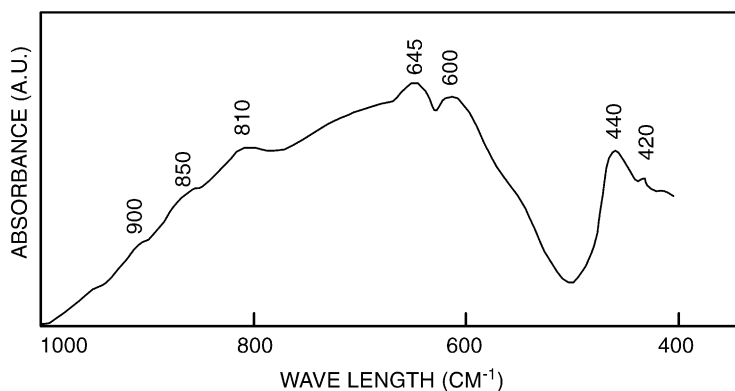
Fig. 4. Room temperature FTIR spectrum of LiNiVO$_4$.

grain growth and in particular, formation of independent particles of uniform size. Interestingly, the same has been observed in the SEM of LiNiVO$_4$ (Fig. 5a) with almost spherical size. The possible agglomeration of particles expected at high calcination temperature (800 °C) has not occurred in the present study. In addition to these features, the presence of uniformly distributed submicron particles is desirable for any cathode material in view of better electrochemical behavior. It is noteworthy to mention here that

SEM analysis has been carried out mainly to discuss the morphology of the synthesized compound. SEM, which is the magnification of the selected portion of the sample, represents the averaged out size of the particles. However, particle size analysis results give the entire picture of the pattern in which the particles are being distributed in the bulk. Accordingly, a single and a narrow band (Fig. 5b) observed in the particle size range (1.2–1.6 μm) is an evidence for the uniform distribution of the reduced sized particles.
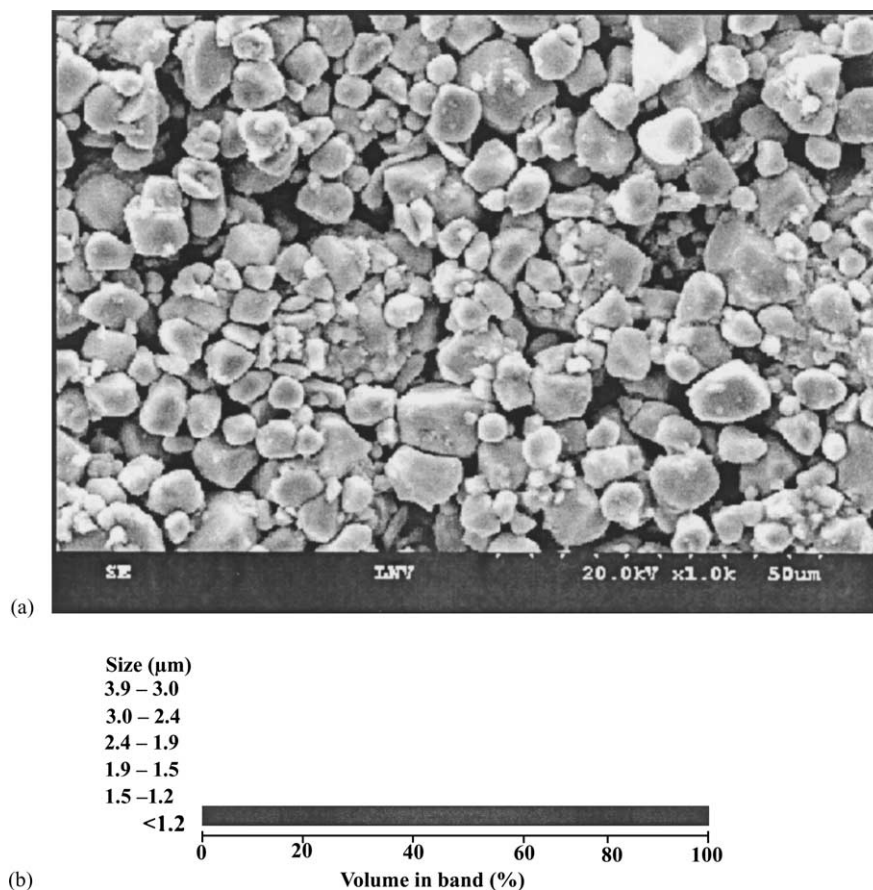

Fig. 5. (a) Scanning electron micrograph of LiNiVO$_4$; (b) particle size distribution in LiNiVO$_4$.

3.5. Electrochemical studies

Electrochemical studies were performed with cathode limited 2016 coin cells using lithium metal foil (Cyprus Foote Mineral, USA) as anode. Cathode was fabricated by making a slurry with 88% LiNiVO$_4$ powder, 10% graphite and 2% PVdF binder in N-methyl-2-pyrrolidone medium. The slurry was then coated as a thin film of uniform thickness over pure aluminum current collector. The coated foil was dried in an air oven at 110 °C for 12 h and pressed in a hydraulic press (10 ton) for uniform film adherence. Discs of 1.8 cm diameter were punched out from the foil and used as cathodes. A solution of 1 M LiAsF$_6$ in 1:1 v/v EC:DMC was used as the electrolyte with a polypropylene separator.

The electrochemical discharge characteristics (between 3 and 4.9 V) of the cells fabricated using the synthesized LiNiVO$_4$ powder (800 °C) against lithium metal anode at a constant current drain of 0.05 mA is presented in Fig. 6. Concentration polarization is expected to be less, since the reduced grain size of the uniformly distributed particles of larger surface area is expected to enhance the kinetics of Li$^+$ diffusion. Interestingly the same has been observed in the present study, as evident from the charge/discharge studies. The cells discharged at 0.05 mA showed a defined voltage plateau around 4.4 V, corresponding to the Li insertion during the first cycle. However, the same has been found to get diminished subsequently, an indication of possible capacity fade expected for the successive cycles. Despite this fact, the first discharge cell capacity was found to be 90 mA h g^{-1} against the theoretical value of 148 mA h g^{-1}. At the first glance, this smaller value of discharge capacity may seem to be far behind the theoretical value but it is better than the values reported by Fey et al. [4,16]. Probably, the improved morphological features of the cathode material may be thought of as the reason for the observed high first discharge capacity. Moreover, as the discharge capacity has only a lower bound over the available capacity of the cathode active material, it may be due to the possible oxidation of the electrolyte [4] in
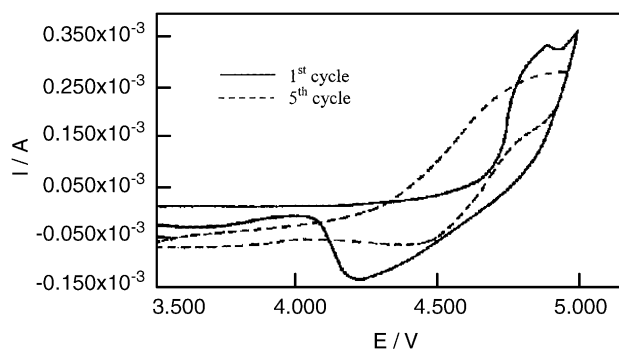

Fig. 7. CV of Li/LiNiVO$_4$ cell (scan rate = 1 mV s^{-1}).

the electrochemical window especially at this high voltage region.

Similar to the observations of Fey et al. [4], a significant irreversible capacity decline is observed from the second cycle and the same is found to be very prominent at the end of the 5th cycle. Hence the role of the oxidation of electrolyte at this electrochemical window is understood as one of the prime reasons towards the observed capacity fade. Although, the possibility of loss of structural integrity/morphological changes upon cycling cannot be neglected as the experimental conditions are in favor of the higher deliverable voltage and optimum cyclability. Nevertheless, the mode of electrolyte decomposition and capacity failure could be explained only after the introduction of oxidation resistant electrolyte.

Fig. 7 shows the cyclic voltammogram (1st and 5th cycle) of the Li//LiNiVO$_4$ cell in the voltage range 3.5–4.9 V at a sweep rate of 1 mV s^{-1}. The CV features a pair of oxidation–reduction peaks, which are associated with the single electron transfer process in lithium intercalation/deintercalation. Though the decomposition of electrolyte is not obvious from CV studies, the effect of the same on the capacity fade cannot be neglected based on the above arguments. Nevertheless, charge/discharge behavior remains almost unchanged and confirms the considerable reversibility for lithium insertion/extraction.
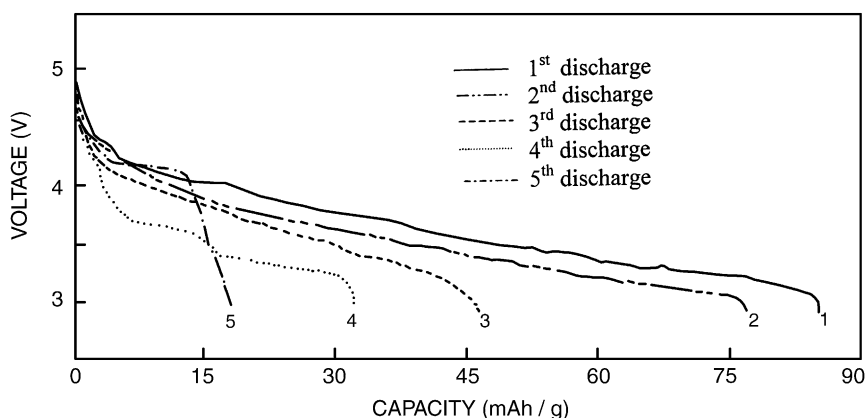

Fig. 6. Voltage vs discharge capacity plot of Li/LiNiVO$_4$ cell (drain = 0.05 mA).

4. Conclusion

Single-phase $LiNiVO_4$ with particles of average grain size less than $2\,\mu m$ has been synthesized through starch-assisted combustion method using an optimum amount ($2\,g$) of starch. A product yield over 95% achieved through this route is the highlight of the soft-chemistry approach. The flexibility of this method has been extended towards the successful synthesis of the technologically important cathodes like $LiMn_2O_4$ and $LiCoO_2$ (the results of which are to be communicated). Though the formation of nickel vanadate begins around $300\,°C$, phase purity and crystallinity are achieved around $350\,°C$, thus paves way to make use of the low temperature synthesis technology towards the synthesis of the promising cathode material. SEM indicates mono-dispersed particles with almost spherical morphology. The intercalation/deintercalation of Li^+ into the crystal lattice has been manifested from CV studies. From electrochemical charge/discharge cycling studies, it is obvious that the vanadate prepared by this method has a better chance as a cathode active material in lithium batteries. As surmised by previous workers, with the proper choice of the electrolyte combination, the cell capacity degradation could be offset only when a thorough knowledge about the crystal chemistry and in particular the local symmetry of nickel is acquired.

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