A NOVEL APPROACH TOWARDS THE SYNTHESIS OF $LiMVO_4$ (M=Ni, Mn) CATHODES

N.Kalaiselvi*, A.Ganesh Kumar, C.Sathya Kumar, V.R.P.Gokul, T.Thangaraj,
N.G.Renganathan and N.Muniyandi.

Central Electrochemical Research Institute, Karaikudi, Tamil Nadu-630 006,India.
Telephone no: (04565) 427550 to 427559 Fax no: (04565) 427779, 427713, 427205, 427206
e-mail: kalakanth@vsnl.com

ABSTRACT

An ideal low temperature synthetic route to prepare vanadates such as $LiMnVO_4$ and $LiNiVO_4$ with high purity, better morphology and good electrochemical behavior was attempted via, Self Propagating High Temperature (SPHT) method using an internal fuel. Conventional solid-state fusion method and acetate precursor method were also carried out at high temperatures such as 1073 K and 873 K respectively and the results were compared with that of SPHT method. Samples obtained from these three methods were examined for their FTIR spectra, XRD pattern, surface area, particle size analysis and SEM. Both the compounds viz. $LiMnVO_4$ with an orthorhombic spinel-related structure and $LiNiVO_4$ with an inverse spinel structure were found to be synthesized stoichiometrically at a lower temperature (573 K) through SPHT method. Charge-discharge studies carried out at a constant current drain (0.1mA) showed that these vanadates were electrochemically active. To understand the role of fuels in SPHT method, three fuels namely Urea (U) (FCV=6) and two other fuels with a high fuel calorific value viz. Glycine (FCV=9) and Pthalyl DiHydrazide (PDH) (FCV=37) were employed in the synthesis. Among the three fuels better products were obtained for Glycine and Pthalyl DiHydrazide (PDH) rather than Urea in terms of surface homogeneity and better morphology. Advantages of the SPHT method of synthesis and the role of fuels were discussed in detail.

KEYWORDS: $LiMnVO_4$, $LiNiVO_4$, low temperature synthesis, fuel, fuel calorific value.

INTRODUCTION

$LiNiVO_4$, a 4.8 V cathode material discovered by Fey et al [1] in 1993 initiated the search for other similar lithium metal vanadates, which resulted in the outcome of cathodes such as $LiCoVO_4$ and LiMnVO4. In addition to the existing promising 4V oxide candidates viz., $LiMn_2O_4$, $LiCoO_2$ & $LiNiO_2$, the inclusion of vanadium in the lithiated transition metal oxides structures resulted in the formation of lithiated ternary vanadates, an entirely different category of cathode materials which are found to have different structures according to the nature and the arrangement of the transition metals in terms of cation distribution. However, most of them are bestowed with better electrochemical behavior and therefore used as potential cathode materials. In this series challenging candidates of 4V and 5V category cathodes such as $LiMnVO_4$ and $LiNiVO_4$ respectively are gaining importance as they play a vital role in the lithium intercalation chemistry. The isostructural compounds $LiNiVO_4$ (4.8V) and $LiCoVO_4$ (4 V) differ considerably in their cell voltage, an implication that nickel atoms in the inverse spinel may play a critical role [1]. Similarly the orthorhombic type spinel related structure of $LiMnVO_4$ (4.2V) indicates that the spinel structure with edge sharing MnO_6 octahedral is quite similar to that of $LiMn_2O_4$ and hence is a 4.2V type of cathode material. Therefore in the vanadate series, it is only the other transition metal atom such as Mn, Ni, Co etc, which plays a vital role and decides the cell voltage via, structural arrangement. In the present study, two vanadates viz. $LiNiVO_4$ (inverse spinel) and $LiMnVO_4$ (spinel) were selected for synthesis through various routes. Since the effect of structure over the cell voltage and electrochemical behaviors was well attended already, the effect of synthesis over the performance of these cathode materials was studied in the present investigation. With this view, solid state carbonates fusion method, acetate precursor method and the novel SPHT (Self Propagating High Temperature) method with nitrate precursors were attempted with different heating temperature and duration accordingly. The products obtained from each method were analyzed thoroughly and a correlation was made between the method of preparation and the effect of the same towards the physico and electrochemical properties of the cathode.

EXPERIMENTAL

Stochiometric amounts of carbonates of lithium and nickel or lithium and manganese were used along with NH_4VO_3 powder in the solid-state fusion method. The mixture of carbonates and vanadates was ground well and heat-treated to 673 K initially which was then heated to 1073 K subsequently with intermittent grinding. The heat treatment was carried out for at least 72 hours. The final product was ground well and subjected to further analysis. In the acetate precursor method, respective acetates of Li and Ni or Li and Mn were dissolved in water and NH_4VO_3 is added to the homogeneous solution separately. The resultant solution was evaporated for removal of water at 373 K and then heat treated to 873 K for about 48 hours. The residual powder obtained was analyzed systematically. Calculated amounts of nitrates of Li and Ni or Li and Mn along with NH_4VO_3 were mixed appropriately in triple distilled hot water followed by the addition of nitrogenous fuel in water. The ultimate homogeneous solution was directly heated to 573 K for about 3 hours. The fine powders obtained were taken for characterization studies. Urea, Glycine and PDH were used as internal fuels in this regard. Urea (FCV=6) was used in the preparation of both the vanadates. Glycine (FCV=9) was used for $LiMnVO_4$ and Pthalyl DiHydrazide (PDH) (FCV=37) was used for $LiNiVO_4$. The products resulted from both the high fuel calorific value fuels (Glycine & Pthalyl DiHydrazide (PDH)) were compared with that of Urea in both the cases of $LiNiVO_4$ and $LiMnVO_4$ so as to understand the effect of fuel calorific value (FCV) towards the SPHT method. The systematic analysis of the products obtained from carbonates, acetates and nitrates were compared finally with a view to understand the effect of synthetic methodology over the performance of cathode material. In this regard, the powders were analysed for FTIR spectra (Perkin –Elmer FTIR spectrometer), XRD (Jeol JDX – 8030 X-ray diffractometer), Particle size (Malvern Easy Particle size analyzer), Surface area (BET Method), SEM, impedance (EG&G) and cyclic voltametry studies (PAAR model No. 263A,Lock in amplifier model No.5210)

The various reactions carried out with different precursors at different reaction temperature and time are schematically represented in Fig (1).

$$\text{(a)}\ Li_2CO_{3\,(s)} + MCO_{3\,(s)} + NH_4V0_{3\,(s)} \xrightarrow[24h]{673\ K} \text{Intermediate product(s)} \xrightarrow[72\ h]{1073\ K} LiMVO_4 + Y$$

M=Mn and Ni
Y=gases such as CO_2, O_2 etc.,

$$\text{(b)}\ Li\,(OOCCH_3)_{(l)} + M(OOCCH_3)_{2\,(l)} + NH_4VO_{3\,(l)} + H_2O \xrightarrow[-\,H_2O]{373\ K}$$

$$\text{Intermediate product (solid mass)} \xrightarrow[48\ h]{873\ K} LiMVO_4 + Y$$

M=Mn and Ni
Y=gases such as CO_2, O_2 etc.,

$$\text{(c)}\ LiNO_{3\,(l)} + M(NO_3)_{2\,(l)} + NH_4VO_{3\,(l)} + x\,\underset{\text{Urea}}{(\,NH_2CONH_2)^{*}_{(l)}} + H_2O \xrightarrow[3\ h]{573\ K} LiMVO_4 + Y$$

M=Mn and Ni and Y=gases such as CO_2, O_2, N_2 etc.

$$\text{(d) } LiNO_{3\,(l)} + Mn(NO_3)_{2\,(l)} + NH_4VO_{3\,(l)} + x\,\underset{\text{Glycine}}{(NH_2CH_2COOH)^{*}_{(l)}} + H_2O \xrightarrow[3\ h]{573\ K} LiMnVO_4 + \underset{\text{Gases}}{(CO_2 + N_2 + H_2 + etc)}$$

$$\text{(e) } LiNO_{3\,(l)} + Ni(NO_3)_{2\,(l)} + x\,\underset{\text{PthalylDiHydrazide(PDH)}}{[C_6H_4(CONHNH_2)_2]^{*}_{(l)}} + NH_4VO_{3\,(l)} + H_2O \xrightarrow[3h]{573\ K} LiNiVO_4 + \underset{\text{Gases}}{(CO_2 + N_2 + H_2 + etc.)}$$

FOOTNOTE

x may have values according to the fuel calorific value (FCV) calculations [2]

* - Fuels

s – solid powder

l – liquid (solid dissolved in triple distilled water)

Fig .(1). Schematic representation of the synthesis of $LiMnVO_4$ compounds.

RESULTS AND DISCUSSION

(a) XRD and Atomic Absorption Spectroscopy (AAS) measurements:

Fig. (2) represents the XRD patterns observed for $LiNiVO_4$ resulted from carbonate, acetate and nitrate precursor methods. Though similar XRD pattern was observed invariably for all the products, common impurities such as $LiVO_3$ and NiO were found to be present in meager amounts in the carbonate and acetate precursor method. The same was found to be absent completely in the nitrate method irrespective of the fuel used. Hence sample purity and homogeneity were found to be satisfactorily good in the SPHT method comparatively. In spite of having treated at higher temperature for longer duration, the carbonate and acetate precursor methods suffered from the usual problem of association of VO_3 and NiO impurities encountered by many of the previous researchers, [3]. However, the peaks of SPHT method were found to be intense and accounted for better crystallinity.

The powder XRD pattern of $LiMnVO_4$ (Fig.3) derived from the SPHT method showed a structure close to those of $LiCuVO_4$ [5] and $CrVO_4$ [6]. This observation is found to be in good agreement with that of Sato et al [7]. Further the position of MnO_6 octahedra and VO_4 tetrahedra were confirmed by FT IR analysis, which will be discussed later. The XRD peak position and relative intensities of peaks observed for SPHT method (Fig.3) were quite similar with those of the reported ones. However products obtained from other two methods viz. Solid State Fusion and Acetate Precursor Method showed a slight change in both peak positions and intensity apart from the presence of impurity peaks as in the case of $LiNiVO_4$.

Also it is quite interesting to note that $LiMnVO_4$ and $LiNiVO_4$ derived from SPHT method via, the usage of higher fuel calorific value fuels such as glycine and Pthalyl DiHydrazide (PDH) respectively, showed a slight peak broadening with respect to the peaks observed for the product derived from urea. This an encouraging result that the peak broadening in general can be correlated to the better electrochemical behavior as it is reported to be due to the reduced size of the particles with a preferred distribution of particle [8].

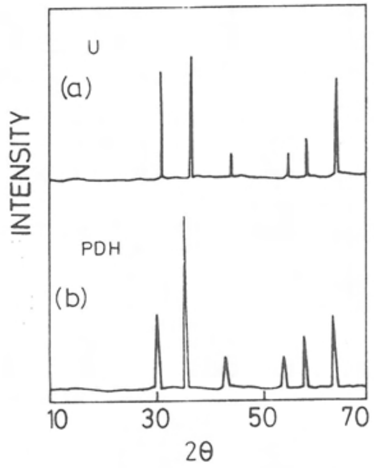


Fig 2. XRD pattern observed for $LiNiVO_4$ synthesized using (a) Urea as fuel (b) Pthalyl DiHydrazide (PDH) as fuel.

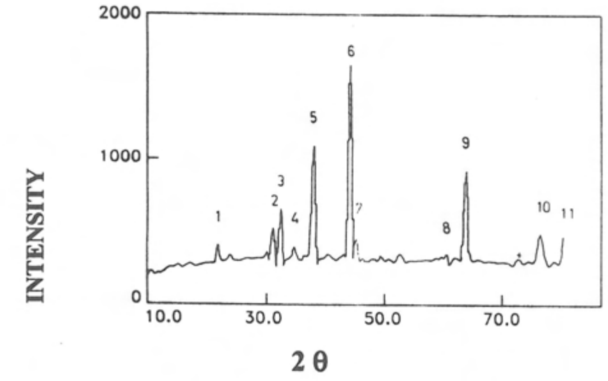


Fig 3. XRD pattern observed for $LiMnVO_4$ (SPHT Method) synthesized using Glycine as fuel

The stoichiometry of $LiNiVO_4$ obtained from all the three methods were verified through Atomic Absorption Spectroscopy (AAS) measurements. A discrepancy with respect to the contents Li and Ni was observed for products derived from carbonate and acetate precursor method compared to that of SPHT method. Similarly, Atomic Absorption Spectroscopy (AAS) measurement results of $LiMnVO_4$ also favored SPHT method as it showed the stoichiometry as $Li_{0.99}\ Mn_{0.98}\ V_{0.99}\ O_4$. The carbonate and acetate precursor methods gave products with the stoichiometry of Mn and V < 0.95. The results are tabulated (Table1).

Table 1. Comparison of $LiMnVO_4$ & $LiNiVO_4$ stoichiometry results derived from Atomic Absorption Spectroscopy (AAS) measurements.

	$LiMnVO_4$			$LiNiVO_4$		
Methods of Preparation	Li	Mn	V	Li	Ni	V
Carbonate method	0.99	0.89	0.91	0.97	0.92	0.98
Acetate method	0.98	0.90	0.94	0.94	0.96	0.97
SPHT Urea	0.98	0.98	0.98	0.98	0.99	0.99
SPHT Glycine	0.99	0.98	0.99	0.99	0.99	0.99

Therefore, SPHT method in general was found to give better stoichiometry with purity for both the cathodes viz. $LiNiVO_4$ and $LiMnVO_4$, as evident from the Atomic Absorption Spectroscopy (AAS) measurements.

(b) FT IR spectra:

Despite the medium frequency region of FTIR spectra [4], the bands observed for various vibrations (Fig.4) are tabulated (Table 2) for the product $LiNiVO_4$ obtained from SPHT method. However, additional peaks corresponding to γ V=O and Ni-O around 1020 cm^{-1} and 585 cm^{-1} were found to be present in the products of carbonates and acetate methods.

Table 2. FT IR frequencies observed for $LiNiVO_4$ (SPHT method)

REGION	ASSIGNMENT
810.41,849.95 cm^{-1}	V-O Bond of VO_4 Tetrahedron
440.10,660.32 cm^{-1}	Li-O-Ni stretching
419.99 cm^{-1}	Li-O stretching

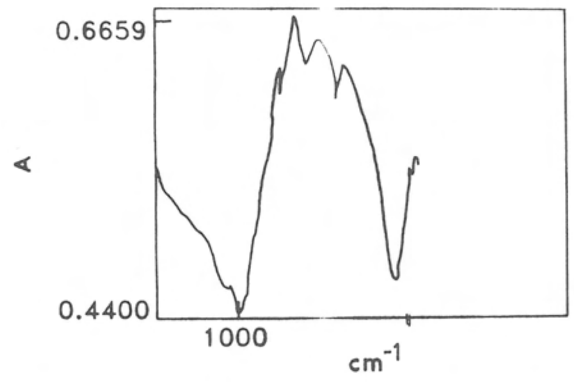


Fig 4. FT IR spectrum of $LiMnVO_4$

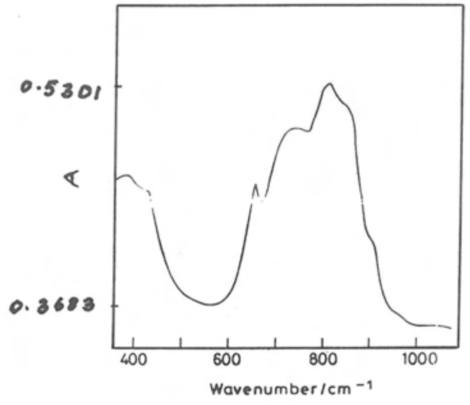


Fig 5. FT IR spectrum of $LiNiVO_4$

A study on the foamy $LiMnVO_4$ product from the SPHT method showed the FT IR peaks similar to those of a spinel $LiMn_2O_4$ [9] and the orthorhombic CmCm type of $CrVO_4$ compound [6]. Due to the shorter bond lengths of V-O, the absorption bands around 925, 880, 720 and 640 cm^{-1} may be assigned to the stretching vibrations of V-O bonds (Fig.5). Hence, the structure of $LiMnVO_4$, an orthorhombic spinel type of compound synthesized in the present study will also have MnO_6 octahedra and cation distributed $LiVO_4$ and VO_4 tetrahedra, which in turn may share the corners of the tetrahedra with the octahedral MnO_6 chain ([10] And [11]).

(c) Surface Morphology Studies:

The surface morphology was verified through SEM, Particle Size Analysis (PSA) and Surface Area Analysis (SAA) for both $LiNiVO_4$ and $LiMnVO_4$.The particle size and surface analysis results of $LiNiVO_4$ obtained from various methods were tabulated (Table3).

Table 3. Particulars of Particle size and Surface area observed for $LiNiVO_4$

Method of synthesis	PSA (µm)	SAA (m^2/g)
Carbonate method	18	4.3
Acetate method	10	5.9
SPHT method		
With Urea	4	6.9
With PDH	1	7.3

The PSA and SAA measurements results of $LiMnVO_4$ derived from various methods were graphically represented. (Fig.6). From the table and the graph it is evident that the reduction in particle size and increase in surface area were noted for SPHT method irrespective of the cathode material synthesized. Also, fuels with higher FCV (glycine in the case of $LiMnVO_4$ and Pthalyl DiHydrazide (PDH) in the case of $LiNiVO_4$) gave much better results both in terms of particle size and surface area analysis invariably. Probable reason may be that the suppression in grain growth has occurred and the possible agglomeration has very well been controlled by SPHT method via, the usage of fuels even at a temperature as low as 300°C. Among fuels, the higher FCV fuel was found to have better control over grain growth and hence resulted in finer particles of lowest particle size. The reduction in particle size can be correlated with a slight broadening of peaks observed in the XRD pattern obtained for the products derived from higher fuel calorific value fuels such as Glycine (FCV=9) and Pthalyl DiHydrazide (PDH) (FCV=37) which was in good agreement with the observations made

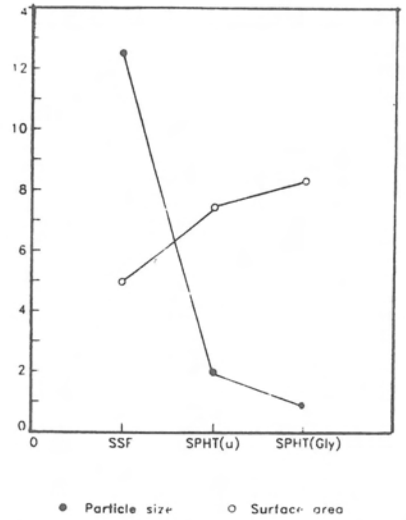


Fig 6. Particle size and surface area of $LiMnVO_4$ derived from various methods

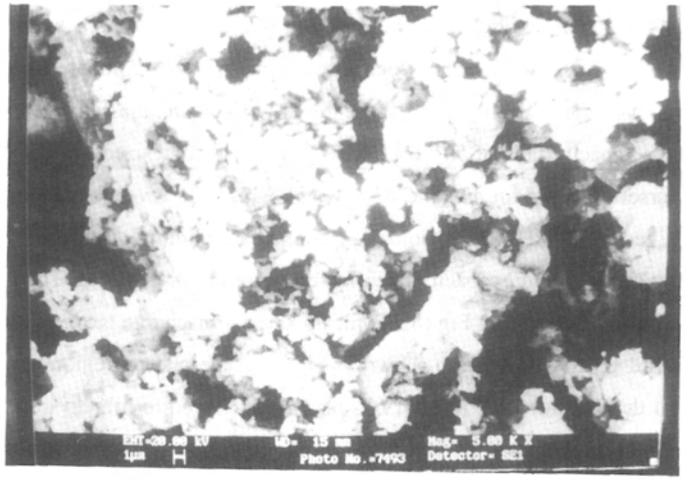
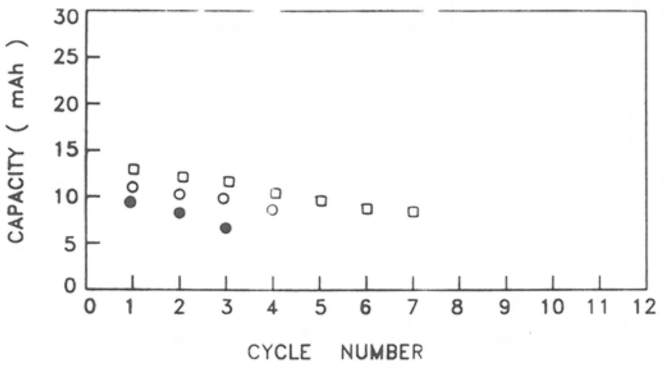


Fig 7. SEM photograph of $LiMnVO_4$

by Gover et al [8]. The physical grain size of $LiNiVO_4$ size has been examined through SEM analysis. The sub micronic (1µm) spherical grains were observed for $LiNiVO_4$ powders synthesized from SPHT product whereas grain size in the order of 10 µm and 20 µm were observed for acetate and carbonate precursor methods respectively. Similarly pore free state sub micron sized particles of 1µm (Fig.7) were observed in the SEM photographs of $LiMnVO_4$ derived from fuel-based synthesis using urea and glycine. The agglomerated particles resulted due to the fusion of solid or solute particles with the larger grain size resulted from the carbonate or acetate method. Therefore the preferred morphology with a well connected lowest grain size particles were realized through SPHT method irrespective of the nature of the cathode material being synthesized. In spite of the lowest reaction temperature, the grain size growth has been controlled considerably in SPHT method, thus resulted in sub micronic level ultra fine powders.

ELECTROCHEMICAL STUDIES

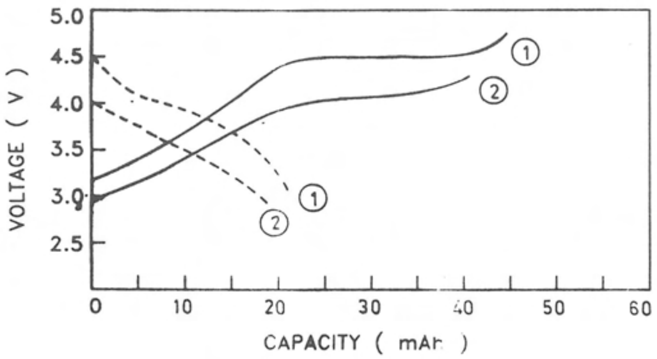
In contrary to the results of Sato et al [7], $LiMnVO_4$ was found to have electrochemical activity in terms of lithium intercalation – deintercalation process. The OCV was found to be 3.2V for the fabricated cell, which remained constant without any fluctuation. The 2016 coin cell when charged at 0.1 mA current drain had shown a capacity of 80mAh/g, which on discharge showed 50mAh/g of capacity. First four cycles were exhibited with out much capacity fade and the remaining four cycles encountered the capacity loss up to 50%. Therefore in $LiMnVO_4$, both the cations, viz. the high valent V^{5+} ion and the divalent Mn^{2+} ions, in spite of it's lower valency, would have involved in redox reaction, due to which the inherent electrochemical activity had been realized. Similarly, $LiNiVO_4$ synthesized from SPHT method showed satisfactory electrochemical behavior when compared to the products from other two methods. Keeping 4.7V as the initial DC voltage, the cells were cycled with out exceeding a capacity fade of 50%. $LiNiVO_4$ powders synthesized from carbonates and acetates precursors showed an average of 3 cycles with 80% reversible capacity whereas products obtained from SPHT methodology performed a minimum of at least 7 cycles.PDH based products showed better capacity retention compared to that of urea. The effect of fuel over the cycle life is depicted in Fig (8). Typical charge – discharge curve pattern observed for $LiNiVO_4$ and $LiMnVO_4$ are also shown in Fig. (9). The plateau region around 3.8V in $LiMnVO_4$ and that around 4.5V in $LiNiVO_4$ may be attributed to lithium intercalation and deintercalation process. Thus both the inverse spinel $LiNiVO_4$ and spinel related $LiMnVO_4$ were found to be bestowed with appreciable electrochemical behavior so as to say that these compounds are also potential cathode materials for rechargeable lithium batteries.



o SPHT (Urea) • Solid State Fusion Method

□ SPHT (Pthalyl DiHydrazide PDH)

Fig 8. Effect of fuel vs. cycle life and capacity of $LiNiVO_4$



____________ Charging Curve - - - - - - - - - - - Discharge Curve

Fig 9. Charge –Discharge behavior of (1) $LiNiVO_4$ and (2) $LiMnVO_4$

CONCLUSION

Self Propagating High Temperature (SPHT) method using an internal fuel resulted in the stoichiometrically satisfactory cathode materials ($LiNiVO_4$ and $LiMnVO_4$) with better purity and crystallinity. Despite the lowest temperature (573 K) and minimum time adopted for the heat treatment, the products obtained from the fuel based synthesis (SPHT) showed growth controlled sub micronic particles with larger surface area .The electrochemical behavior of both the cathodes was found to be better for the products obtained from SPHT method compared to those of carbonate and acetate precursor methods. Also, higher fuel calorific value fuels in SPHT method yielded products that exhibited enhanced cycle life without much capacity fade.

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Solute-Solvent Interactions in the Acidic Dissociation of Protonated Indicator Bases Containing Nitrogen in Water / 1,2 Dimethoxyethane Binary Mixtures at Different Temperatures from emf Measurements

H. Sadek, A.A. Taha*, A.A. El Harakany and A.A. Mahmoud.

Department of Chemistry, Faculty of Science, University of Alexandria, Alexandria, Egypt

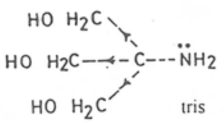
ABSTRACT:

The acidic dissociation constants of the protonated form of 2-amino-(2-hydroxymethyl)-propane-1,3-diol (tris) and 2-amino-2-methylpropane-1,3-diol (bis) in a series of water/1,2 dimethoxy ethane mixtures at 5 °C temperature intervals from 25 to 45 °C are determined using a cell without liquid junction potential. The corresponding thermodynamic parameters (ΔG^o, ΔH^o, and ΔS^o) of the protonated form of these buffer indicators in the various solvent mixtures are evaluated. The variation of the standard free energy change of transfer with solvent compositions for both indicators indicates a characteristic minimum which is attributed to selective solvation of the individual species participating in the equilibrium process. Solubility measurements of these indicators at different temperatures are determined in order to evaluate the thermodynamic functions of the transfer of the free bases which may provide a better insight on the nature of the ion-solvent interactions and the relative basicity of the solvent.

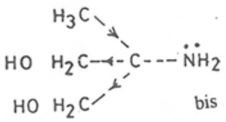
Key words: Acidic dissociation, tris, bis, 1,2 dimethoxyethane, solubility, solvent effect, ion-solvent interactions.

INTRODUCTION

As part of extensive studies[1-5] on the dissociation equilibria in different aquo-organic mixtures, we report the results of measurements of the dissociation constants for protonated forms of 2-amino-(2-hydroxymethyl) propane-1,3-diol (tris) and 2-Amino-2-methyl propane-1,3-diol (bis) in a binary 1,2-dimethoxyethane (DME)/water mixtures. Their molecular structures are:



tris



bis

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[*] Author to whom correspondence should be addressed.

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