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VANADIUM BASED LITHIUM NICKEL ALUMINIUMOXIDE SYSTEM WITH GOOD PERFORMANCE IN LITHIUM-ION BATTERIES

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Abstract

$LiNi_xV_{1-x-y}$ Al_yO_2, are cathode materials for lithium ion batteries which have been synthesized via carbon combustion method. Lithium nickel oxide derivatives are considered by the battery manufacturers to be very promising for application in 4V lithium-ion batteries. The objective of this study is, to successfully synthesize a lithium nickel vanadium aluminum oxide cathode which can show intercalation and de-intercalation process during cyclic voltammetry testing and a discharge capacity of above 50mAh/g. $LiNi_{1-x-y}V_xAl_yO_2$were synthesized by the carbon combustion method using acetylene carbon black as a binder. X-Ray Diffraction (XRD) reveals extra peaks related to Vanadium metal when it is added into $LiNiAlO_2$. The intensity peak of the spectrum increased when the V content is increased. Scanning Electron Microscopy (SEM) shows the grain particles become non-spherical and flakes when more vanadium substituted for nickel in the sample. Fourier Transform Infrared (FTIR) spectroscopy analysis and Energy dispersive analysis of X-Ray (EDAX) confirmed that NO^{3-} impurities are not present and composition in samples Galvanostatic charge/discharge data obtained illustrates a discharge capacity of 80.57mAh/g $LiNi_{0.8}V_{0.1}Al_{0.1}O_2$ and an average of 80.55mAh/g for 10 cycles whereas $LiNi_{0.6}V_{0.3}Al_{0.1}O_2$ highest discharge capacity is 80.52mAh/g and also an average of 80.53mAh/g for 10 cycles. Voltammographs of the $LiNi_{0.8}V_{0.1}Al_{0.1}O_2$, $LiNi_{0.7}V_{0.2}Al_{0.1}O_2$ and $LiNi_{0.6}V_{0.3}Al_{0.1}O_2$ materials showed good oxidation and reduction loop at 0.05mV/s and 1 mV/s scan rate.

Keywords: Lithium-ion batteries; Lithium Nickel Oxide;Cathode

Abstrak

$LiNi_xV_{1-x-y}$ Al_yO_2, adalah bahan katod bagi baterilitium ion yang telah disintesis melalui kaedah pembakaran karbon. Litium nikel oksida derivative menjadi pilihan oleh kebanyakan pengeluar bateri bagi aplikasi penggunaan 4 V bateri litium ion. Objektif kajian ini adalah, untuk mensintesis bahan katod litium nikel vanadium aluminium oksida yang boleh menunjukkan proses inter kalasidan de-inter kalasi semasa ujian cyclic voltam metri dan menghasilkan nilai kapasiti nyahcas 50mAh / g keatas. $LiNi_xV_{1-x-y}Al_yO_2$ telah disintesis oleh kaedah pembakaran karbon menggunakana setilena karbon hitam sebagai pemangkin. Pembelauan sinaran-X (XRD) menunjukkan pertambahan puncak spektrum yang berkaitan dengan logam vanadium apabila ia ditambah ke dalam $LiNiAlO_2$. Puncak keamatan spectrum semakin meningkat apabila kandungan vanadium bertambah. Scanning Electron Microscopy (SEM) menunjukkan zarah bijian menjadi tidak sfera dan berkepingan apabila kandungan vanadium meningkat digantikan dengan nikel di dalam sampel. Analisis Fourier Transform Infrared Spectroscopy (FTIR) dan Energy dispersive X-Ray (EDAX) mengesahkan bahawa bendasing NO3- wujud dalam sample dan komposisi bahan dalam sampel. Data galvano static diperolehi menunjukkan kapasiti nyahcas $LiNi_{0.8}V_{0.1}Al_{0.1}O_2$ adalah 80.57mAh/ g dan nilai purata adalah 80.55mAh / g selama 10 kitaran manakala nilai kapasiti nyah cas tertinggi adalah 80.52 mAh / g dan juga purata 80.53mAh / g selama 10 kitaran adalah dari bahan $LiNi_{0.6}V_{0.3}Al_{0.1}O_2$. Data Voltammographs daripada bahan $LiNi_{0.8}V_{0.1}Al_{0.1}O_2$, $LiNi_{0.7}V_{0.2}Al_{0.1}O_2$dan $LiNi_{0.6}V_{0.3}Al_{0.1}O_2$ menunjukkan gelung pengoksidaan dan pengurangan yang baik pada kadar imbasan 0.05mV/ s dan 1 mV /s.

Kata kunci : Baterilitium ion; Litium Nikel Oksida; Katod

1.0 INTRODUCTION

Lithium-ion batteries is attractive alternative as rechargeable batteries for market demand for power tools, electric vehicle (EV) and hybrid electric vehicle (HEV) applications compared the other rechargeable batteries.Lead acid battery technology is well proven and is more than a century old. However the lead acid battery shows low gravimetric and volumetric energy density. Nickel-metal hydride batteries provide reliable cyclability and are commonly used in hybrid vehicles. Their downside is a relatively low energy density and low cycle life and relatively high self-discharge rate up to 10% per month[1]. According *Diouf and Pode ,2015*, lithium ion batteries has a large potential for major energy storage in off-grid renewable energy especially in renewable energy sector such as electric vehicles, grid storage, consumer electronics, military and medical applications[2].

Technological improvement in rechargeable lithium ion batteries especially lithium ion batteries on layered lithium metal oxide material such as $LiCoO_2$, $LiNiO_2$[3]and spinel $LiMn_2O_4$ have been seriously prevented from extensive practical applications due underlying structural drawback[4]; [5]. Lithium nickel oxide ($LiNiO_2$) has been considered as a promising positive electrode material for high energy rechargeable batteries[6]; [7] $LiNiO_2$ has layered structure similar to $LiCoO_2$ and is cheaper than $LiCoO_2$ [8]; [9]; [10]. Although $LiNiO_2$ has high theoretical capacity, it is difficult to synthesis in its tendency of non-stoichiometric phase, and it is not easy to prepare on large scale, [10]; [11] due to its lower thermodynamic stability compare $LiCoO_2$ and the presence of excess nickel on Li sites. These anti sites in $LiNiO_2$ strongly affect the electrochemical properties of batteries [8].

In the case of partial substitution of Ni with other metals in $LiNi_{1-y}M_yO_2$ system there are still some possible improvement. Presently, some lithium nickel oxide derivatives are considered by the battery manufacturers to be very promising for application in 4V lithium-ion batteries. With the aim of finding new positive electrode materials for lithium-ion batteries, many research and development effort has been devoted towards $LiNiO_2$ and $LiNiO_2$ substituted materials. In order to inhibit the reduction of Ni^{4+} during cycling, doping with hetero atoms such as Al, Co or Li can also be employed to stabilize $LiNiO_2$ and to improve the electrochemical performance. *Albrecht et.al,* reported that aluminum doping enhance the cycling stability of lithium nickel cobalt mixed oxide.[12]The objective of this study are to determine the characteristic and performance lithium nickel oxide doped with vanadium and aluminum which can show intercalation and de-intercalation process during cyclic voltammetry testing and a discharge capacity of above 50mAh/g.

2.0 EXPERIMENTAL

Carbon combustion synthesis (CCS) is a modified combustion method was used to prepare cathode materials. A high purity lithium nitrate, $LiNO_3$(R&M 98% pure), Nickel (II) nitrate hexahydrate, $Ni(NO_3)_2.6H_2O$ (R & M 99% pure), Vanadium (V) oxide, V_2O_5(Merck 99% pure) and Aluminum nitrate nonahydrate, $Al(NO_3)_3.9H_2O$ (R&M 98.5% pure) with different proportions were packed into porcelain crucible. The materials were throughly mixed into a porcelain crucible with carbon (Acetylene Black) amount is 0.1 gram. All the mixtures were ignited and heated at 900°C for 5 hour in air. The sample was cooled at the ambient temperature. Finally the compound was ground with an agate mortar and pestle until it is become a fine powder. To prepare the cathode, acetylene black (AB) and poly (tetrafluoro ethylene) PTFE were mixed together at ratio 2:1 until the materials are not agglomerate. Active material (cathode) was weighted 100 milligram and put in agate mortar. The mixture of AB and PTFE were weighted 32 milligram and mixed together with active material until it form a film. All the film was putted on to the round shape 10mm diameter aluminum mesh grid. After drying at 180 ^{0}C for 4 hour in oven, the electrode were assemble into Teflon holder cell with Li electrode and electrolyte (1 M $LiPF_6$ in EC: EMC: DMC = 1:1:1 in volume) in an Ar- filled glove box.

The structural of the sample was confirmed by X-Ray PANalytical's Empyrean X-ray diffractometer using Cu-Ka (1.54060 Å). The morphology of the particles was measured by Scanning Electron Microscopy (SEM) and Energy dispersive analysis of X-Ray (EDAX) was performed with a HITACHI model SU 8020. FTIR NEXUS Thermo 69000 Nicolet to determine the composition of the samples. Battery performance was tested by charge/ discharge characteristics and cyclic voltammetry experiments were done at room temperature using Li foil as the reference and counter electrode using AUTOLAB instrument. The working electrode was the Li-based intercalation material synthesized at 900^{0}C for 5hr synthesized by carbon combustion.

3.0 RESULTS AND DISCUSSION

3.1 X-Ray Diffraction

X-Ray Diffraction (XRD) was done in order to see the patterns that were obtained for the materials. A good XRD spectra should be similar with the JCPD data which show the material is isostructural to $LiNiO_2$ and therefore can be indexed as cubic spinel phase (space group Fd3m). The spectra of intensity against 2θ value for sample. $LiNiO_2$ Fig 1, samples shown the peak is narrow and sharp. The phase purity was achieved, and the narrowness of the diffraction lines indicates a good crystallinity of this material and suggests a homogeneous distribution of the cations within the structure. XRD spectra of intensity against 2θ value for $LiNi_{0.8}V_{0.1}Al_{0.1}O_2$,$LiNi_{0.7}V_{0.2}Al_{0.1}O_2$ and $LiNi_{0.6}V_{0.3}Al_{0.1}$ $O_2$is shown in Fig 2. The spectra of the $LiNi_{0.8}V_{0.1}Al_{0.1}$ O_2, $LiNi_{0.7}V_{0.2}Al_{0.1}O_2$ and $LiNi_{0.6}V_{0.3}Al_{0.1}$ O_2 materials seems to have undergone some changes from the pure $LiNiO_2$ XRD spectra. The refinements of the powder x-ray diffraction data of the samples were carried out in space group Fd3m.The intensity peak of the spectrum increased when the V content is increase. The small amount of NiO impurity are presented at 37.27^0, 43.31^0, 62.95^0 and 75.7^0 based on JCPDS data[13] XRD pattern shows that aluminum content increases a peak (101) and clear split *(108)*/*(110)*Bragg lines and narrowing of the diffraction peaks. According *Julien et.al*[14] should be possible that Al^{3+} substituted for Ni^{3+}.Substitution of Al for Ni results in slight changes the lattice parameter as demonstrated by *Ohzuku et.al*[19] Ionic radii of Al^{3+} in octahedral coordination in oxygen environment is suitable for the partial substitution of the nickel ions in lithium nickelate.

3.2 Scanning Electron Microscopy (SEM)

The morphology of pure and doped samples calcined with carbon was investigated by scanning electron microscopy (SEM).The SEM of $LiNiO_2$ and doped sample with were done at different magnification. Fig 3 show homogeneous distribution of particle at 25000x magnification. Sample A_1 material has facet cubic grain and uniform particle roundness which show good crystalline and sharp peak on the XRD pattern. Intercalation and de-intercalation occur along specific crystallographic planes and directions, so higher crystallinity improves electrode performance[9]. The micrograph sample A_2, A_3 and A_4 show the grain particles become non-spherical and flakes when more vanadium substituted for nickel inthe sample. Non-spherical for layered structures have been shown to improve performance which has been attributed to high tap density [15].

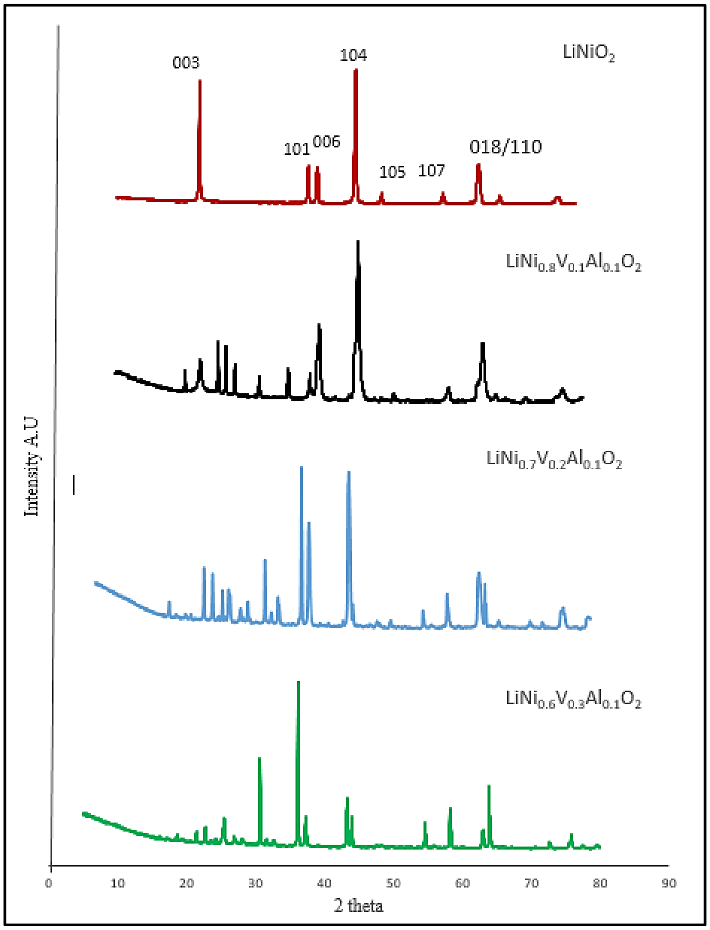

Figure 1 XRD pattern of $LiNiO_2$ and $LiNi_xV_{1-x-y}Al_yO_2$ cathode materials

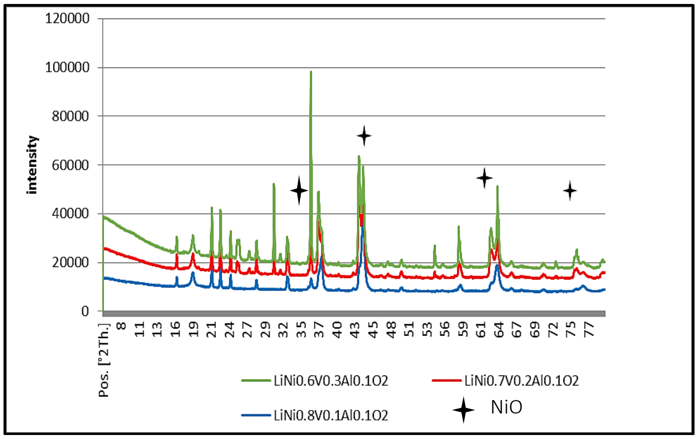

Figure 2 XRD pattern of cathode material synthesized at 900^0C for 5 hour

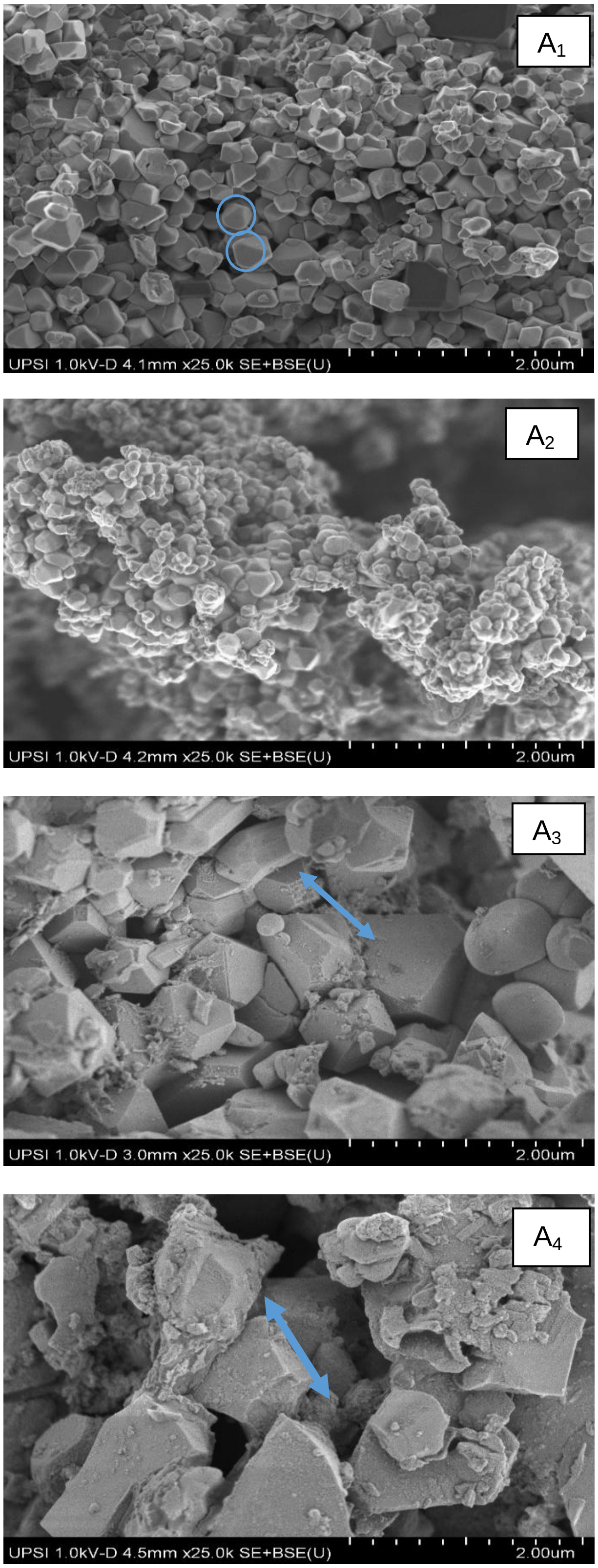

Figure 3 Scanning electron micrograph with 25,000 x Magnification of sample; A1)$LiNiO_2$, A2)$LiNi_{0.8}V_{0.1}Al_{0.1}O_2$, A3) $LiNi_{0.7}V_{0.2}Al_{0.1}O_2$, A4) $LiNi_{0.6}V_{0.3}Al_{0.1}O_2$

3.3 Fourier Transform Infrared Spectroscopy (FTIR)

Infrared spectroscopy IR was done to the samples to determine the purity of the samples. The samples were calcinalced at 900^{0}C for 5 hour with carbon as fuel for combustion synthesis. Spectrums in figure 3,4 and 5 show that there were peaks existed at around 630 cm^{-1} to 800 cm^{-1} , 1200 cm^{-1} to 1500 cm^{-1} and 1480 cm^{-1} to 3800cm^{-1}. These results confirm the existence of impurities in the sample. Ionic NO_3^- stretch can appear at 1325-1450cm^{-1} for strong peak and 800-870cm^{-1} for medium peaks. Ionic NO_3^- particle are existed in the spectrum[16]. These results show that the process an exothermic reaction between carbon as a binder is not sufficient generates the heat although the materials were heated at 900^{0}C.Figure show that FTIR signatures observed in range 475 -790 cm^{-1} region. According *Kalyani et.al*, the region largely associated either with the bending vibration of the VO_4 tetrahedron or the vibration of NiO_6 and LiO_6octhahedral units. The weak band at 1643 cm^{-1} and 3472 cm^{-1} are attributed to the bending and stretching vibrations of water molecules respectively. The characteristic peak at 1429.5 cm^{-1} are contributed to CO_3^{2-} vibration [18].

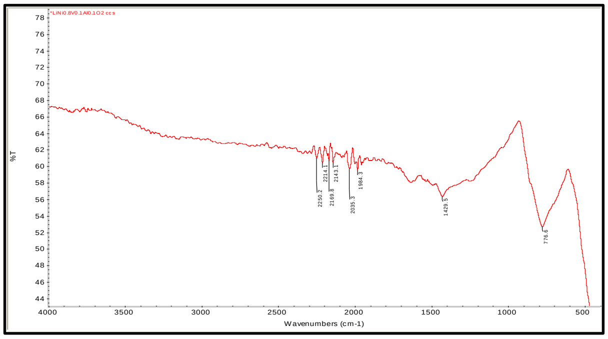

Figure 4 Infrared spectrum of $LiNi_{0.8}V_{0.1}Al_{0.1}O_2$ material

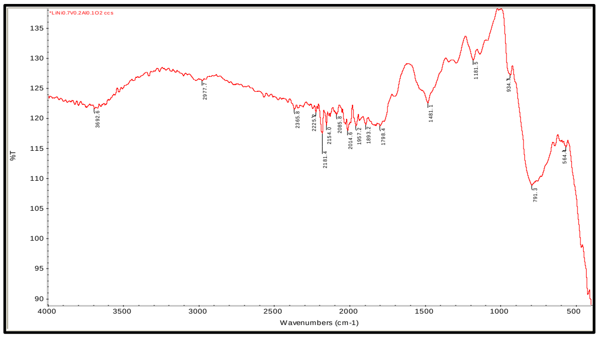

Figure 5 Infrared spectrum of $LiNi_{0.7}V_{0.2}Al_{0.1}O_2$ material

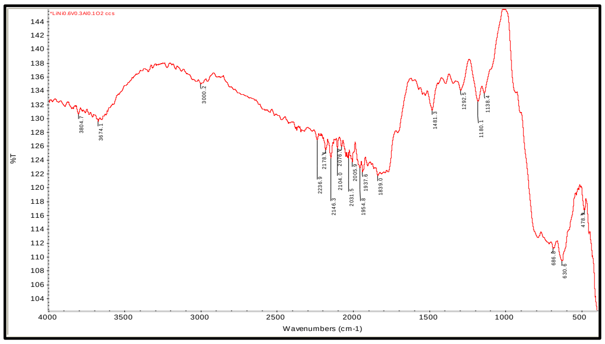

Figure 6 Infrared spectrum of $LiNi_{0.6}V_{0.3}Al_{0.1}O_2$material

3.4 Energy Dispersive X-Ray Spectroscopy (EDAX)

EDAX analysis was done to the cathode materials to determine the ratio starting material. EDAX result was than compared with the amount of the chemicals/starting materials were used during the preparation of the material From the Table 1 lithium element is not detected in the measurement because limitation of instrument. The obtained data revealed that Ni, Al, V and C presence in the element measurement.The data value are different depend on their mole ratio of the metals used to synthesized. Figure 7, shows the EDAX spectra of the samples of 3 elements used in the preparation of cathode material. The peaks in the samples are those assigned to nickel, aluminum, vanadium and oxygen atoms.

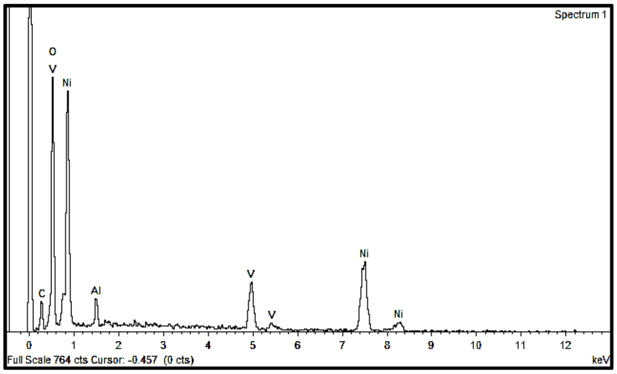

Figure 7 Energy Dispersive analysis of X-Ray spectra of $LiNi_{0.8}V_{0.1}Al_{0.1}O_2$

3.5 Charge/discharge and Cyclic Voltammetry

Galvanostatic charge/discharge was done to the 3 sample to study its performance. The cycling data for 10 cycles at a charge/discharge between 2.4 V and 4.2 V. These materials were charged and discharged at a voltage of 4.2 V – 2.2 V Discharge capacity of $LiNi_{0.8}V_{0.1}Al_{0.1}O_2$ is 80.57mAh/g in the first cycle and an average of 80.55mAh/g for 10 cycle. Discharge capacity $LiNi_{0.7}V_{0.2}Al_{0.1}O_2$ is 10.42 mAh/g for 10 cycle. $LiNi_{0.6}V_{0.3}Al_{0.1}O_2$ shown highest discharge capacity is 80.52mAh/g and also an average of 80.53mAh/g for 10 cycles (Figure 8). Al-doped and V doped $LiNiO_2$ improved cycling stability. According *Gaoet.a,)* doping withmultiple ions in $LiNi_{1-y}Co_yO_2$ solid solution shown improve cyclibility and thermal stability[20].

Table 1 Amount of chemical, Atomic % of metal and ratio between in Lithium Nickel Oxide and lithium Nickel Vanadium Aluminum oxide system for carbon combustion synthesis

Lithium intercalate materials	Element	Amount used to synthesize (g)	Mole ratio of the metal	Atomic percentage shown in EDAX (%)	Atomic ratio (%)
$LiNi_{0.8}V_{0.1}Al_{0.1}O_2$	Li	2.298	1.0	-	-
	Ni	7.755	0.8	44.14	18.83
	V	0.606	0.1	9.15	4.50
	Al	1.250	0.1	1.99	1.84
	C	0.100	-	9.22	19.23
	O		-	35.50	55.59
$LiNi_{0.7}V_{0.2}Al_{0.1}O_2$	Li	2.298	1.0	-	-
	Ni	6.786	0.7	40.43	17.86
	V	1.213	0.2	14.15	7.20
	Al	1.250	0.1	3.22	3.10
	C	0.100	-	6.38	13.77
	O		-	35.82	58.06
$LiNi_{0.6}V_{0.3}Al_{0.1}O_2$	Li	2.298	1.0	-	-
	Ni	5.816	0.6	23.51	11.04
	V	1.8187	0.3	37.50	20.29
	Al	1.250	0.1	1.51	1.54
	C	0.100	-	4.54	10.41
	O		-	32.93	56.72

Cyclic voltammetry experiments were done at room temperature using Li foil as the reference and counter electrode. The working electrode was the Li-based intercalation material synthesized at 900^0C for 5hr synthesized by carbon combustion. All thematerials was scanned at 1 mVs^{-1} and 0.05mVs^{-1}. Oxidation and reduction peaks in the voltammogram suggesting intercalation and de-intercalation had occurred in the material. Figure 9, 10 and 11 shows the cyclic voltammogram of samples cell in the voltage range of 2.0-5.0V at 0.05mVs^{-1} scan rate. The CV features a pair oxidation- reduction peak $LiNi_{0.8}V_{0.1}Al_{0.1}O_2$ range 2.7V-4.8V and has broader oxidation reduction loop. The voltammogram for $LiNi_{0.7}V_{0.2}Al_{0.1}O_2$material, show oxidation peak at 4.9V and reduction peak 3.3V. The voltammogram for $LiNi_{0.6}V_{0.3}Al_{0.1}O_2$ material show oxidation peak at 4.5V and reduction peak 3.6V. Voltammographs of the $LiNi_{0.8}V_{0.1}Al_{0.1}O_2$,$LiNi_{0.7}V_{0.2}Al_{0.1}O_2$ and $LiNi_{0.6}V_{0.3}Al_{0.1}O_2$ materials showed good oxidation and reduction loop. These results indicate that good materials would produce an oxidation loop at potential more than 4.0 V[16].

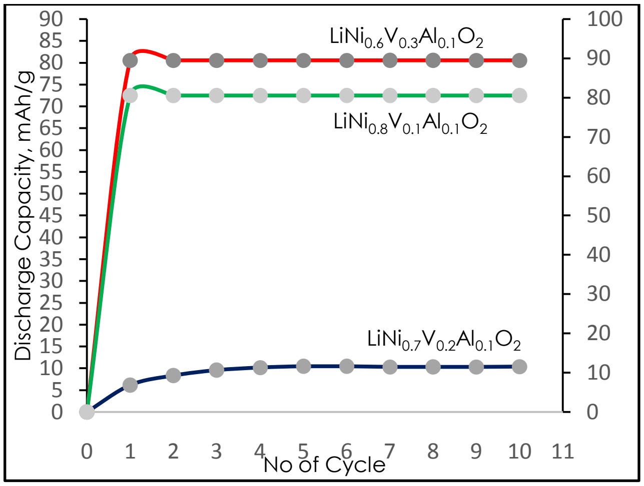

Figure 8 Discharge capacity vs No of cycle of of $LiNi_{0.8}V_{0.1}Al_{0.1}O_2$, $LiNi_{0.7}V_{0.2}Al_{0.1}O_2$ and $LiNi_{0.6}V_{0.3}Al_{0.1}O_2$

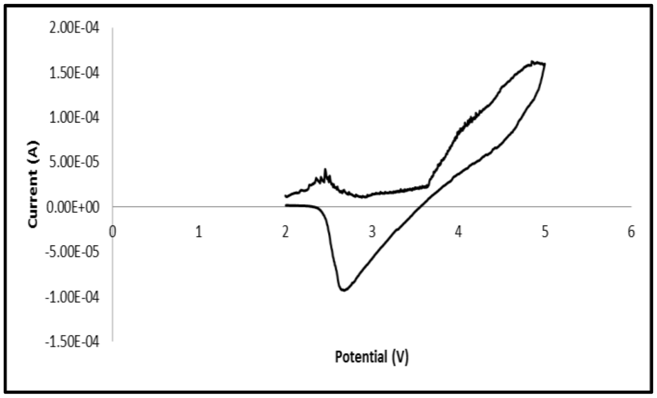

Figure 9 Cyclic Voltammogram I/V of $LiNi_{0.8}V_{0.1}Al_{0.1}O_2$ material for scan rate 0.05mVs^{-1}

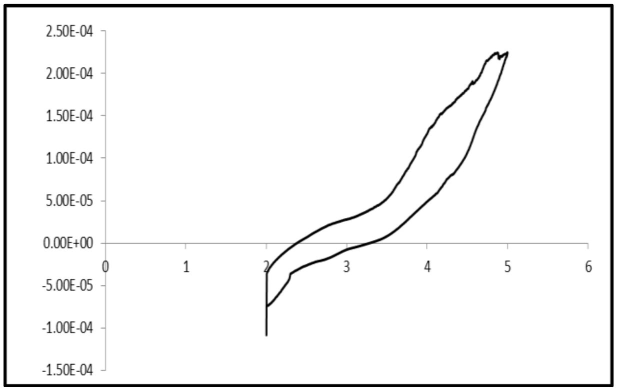

Figure 10 Cyclic Voltammogram I/V of $LiNi_{0.7}V_{0.2}Al_{0.1}O_2$ material for scan rate 0.05mVs^{-1}

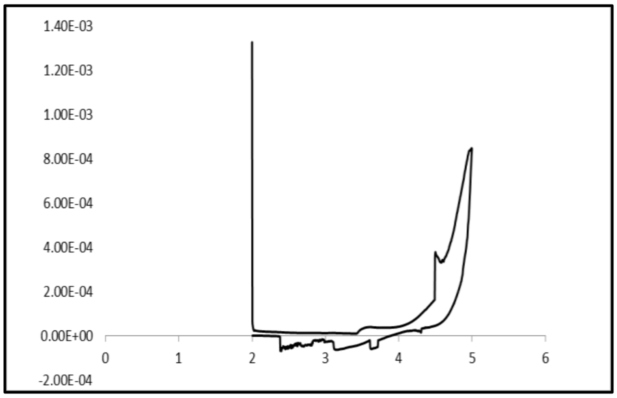

Figure 11 Cyclic Voltammogram I/V of $LiNi_{0.6}V_{0.3}Al_{0.1}O_2$ material for scan rate 0.05mVs^{-1}

4.0 CONCLUSION

$LiNi_{0.8}V_{0.1}Al_{0.1}O_2$, $LiNi_{0.7}V_{0.2}Al_{0.1}O_2$ and $LiNi_{0.6}V_{0.3}Al_{0.1}O_2$ were successful synthesized by a carbon combustion method. The refinements of the powder XRD data of the samples were carried out in space group Fd3m.The intensity peak of the spectrum increased when the V content is increase. The small amount of NiO impurity are present at 37.27^0, 43.31^0, 62.95^0 and 75.7^0 based on JCPDS data. SEM shown the homogeneous distribution of particle at 25 000 x magnification. The $LiNiO_2$ samples material have facet cubic grain and uniform particle roundness The doped materials show the grain particles become non-spherical and flakes when more vanadium substituted for nickel in the sample The Al and V-doped $LiNio_2$ cathode material was effective to maintained the cycle performance based on the charge/discharge capacity. Discharge capacity of $LiNi_{0.8}V_{0.1}Al_{0.1}O_2$ is 80.57 mAh/g and an average of 80.55mAh/g for 10 cycle. $LiNi_{0.6}V_{0.3}Al\ _{0.1}O_2$ shown highest discharge capacity is 80.52mAh/g and also an average of 80.53 mAh/g for 10 cycles. Voltammographs of the $LiNi_{0.8}V_{0.1}Al_{0.1}O_2$, $LiNi_{0.7}V_{0.2}Al_{0.1}O_2$ and $LiNi_{0.6}V_{0.3}Al_{0.1}O_2$materials showed good oxidation and reduction loop at 0.05mv/s and 1 mv/s scan rate. It shows that the cathode materials can intercalation and de-intercalation during cyclic voltammetry testing.

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