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An overview of bio-interface electrolyte and Li_2FePO_4F as cathode in Li-ion batteries

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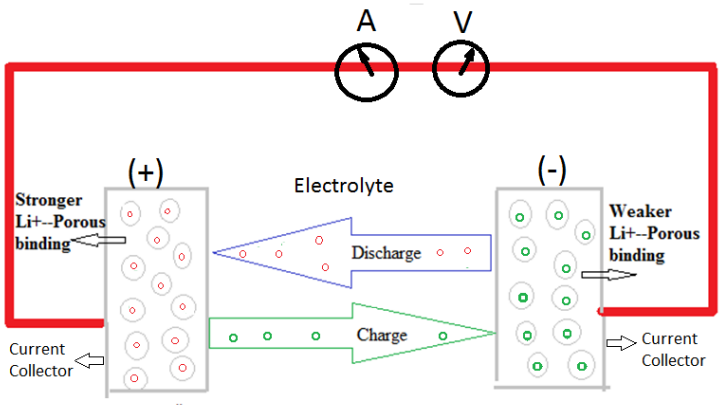
ABSTRACT

Composites of {[(1-x-y) $LiFe_{0.333}Ni_{0.333}Co_{0.333}]PO_4$}, xLi_2FePO_4F and $yLiCoPO_4$system were synthesized using the sol-gel method. Stoichiometric weights of the mole-fraction of LiOH, $FeCl_2{\cdot}4H_2O$ and H_3PO_4, LiCl, $Ni(NO_3)_2{\cdot}6H_2O$, $Co(Ac)_2{\cdot}4H_2O$, as starting materials of lithium, Iron, Nickel , and Cobalt, in 7 samples of the system, respectively. We exhibited $Li_{1.167}Ni_{0.222}Co_{0.389}Fe_{0.388}PO_4$ is the best composition for cathode material in this study. Obviously, the used weight of cobalt in these samples is lower compared with $LiCoO_2$ that is an advantage in view point of cost in this study. Charge-discharge characteristics of the mentioned cathode materials were investigated by performing cycle tests in the range of 2.4–3.8 V (versus Li/Li+). Our results confirmed, although these kind systems can help for removing the disadvantage of cobalt which mainly is its cost and toxic, the performance of these kind systems are similar to the commercial cathode materials in Lithium Ion batteries (LIBs).

Keywords: *lithium ion battery, $LiCoPO_4$, Li_2FePO_4F, sol-gel method, cathode materials*.

1. INTRODUCTION

Among the all batteries, some of theme, such as NIMH (nickel metal hydride) and lithium ion batteries (LIBs) have the most efficiency for electric vehicles (EVs), hybrid electric vehicles (HEVs) and so on. Although the vehicle bazar is dominated by NiMH market, the LIBs have received centralized research and progress due to its high energy density, cathode materials diversity, long and stable cycle life, suitable initial charge and discharge, high voltage and excellent environmental friendly [1-3]. Structure of various Li-ion batteries basically requires the optimum estimation for conductivities and diffusivities, in order to both predicting and designing of several improved materials. So far, lithium ion batteries have been mostly applied in a wide range of portable, cell phones, cameras and many other smart devices [4, 5]. For HEVs and EVs systems, however, the efficiency of LIBs, especially their energy densities, cost, voltage and safety must be improved yet. LIBs are combined of three major sections including, anodic Li+ intercalation, cathode, and the electrolytes-separator. During charging, lithium Cations via the electrolyte-separator section move from the cathode to the anode side and back when discharging, meanwhile the electrons flow out of the external circuit for providing the electrical power (Scheme1). Although the performance of LIBs depends on several items, basically the efficiency strongly relies on the composition of the electrolyte substance and property of the cathode material structures [6-8]. As instance for $LiMO_2$ (M=Co, Mn, Ni,..) as cathode materials there is two directions, in first item during charging, lithium ions move from positive side to negative electrode and electrons are removed from cathode by an external field and then are transferred to anode. In the second item, during discharge, anode provides the ions to electrolyte and electrons to the external circuit where the ions intercalate into cathode materials and electrons from the external circuit for charge restoration as following reactions. In Positive electrodes $LiMO_2 \rightleftarrows Li_{1-x}MO_2 + x\ Li^+ + x\ e^-$ and the negative electrode reaction as: $xC_6 + x\ Li^+ + x\ e^- \rightleftarrows xLiC_6$ with the whole reaction as: $LiMO_2 + xC_6 \rightleftarrows Li_{1-x}MO_2 + xLiC_6$.



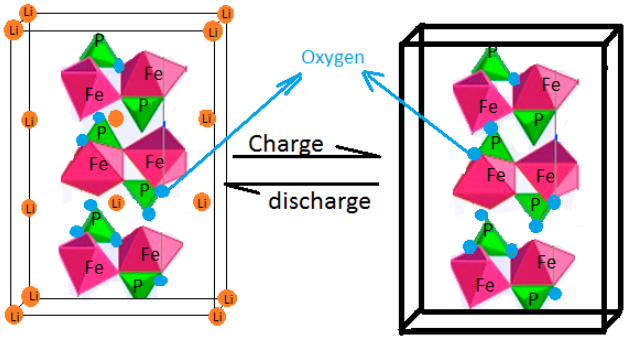
Scheme 1. The spheres are the active particles of the two porous electrodes in which Li^+ ions; can be stored. The voids between particles and between the electrodes are filled with an electrolyte in which Li^+ diffuse and migrate thermodynamically.

Initially, in 1991 the Sony Corporation focused on LiCoO2 materials as an important layered structure [9-12]. Then the other layered structure such as $LiNiO_2$ has been applied [13-15]. This layered cathode material displayed favorable specific capacities, but safety reasons and structural instability prevented further development. The other layered structures such as $LiMnO_2$ and $LiFeO_2$ were selected due to redox couples advantages of Fe^{4+}/Fe^{3+} and Mn^{4+}/Mn^{3+}. Unfortunately the preparing of electrochemically active $LiFeO_2$ phases was not possible and for $LiMnO_2$, though easy to prepare had problem about the structural instability due to the layered phase reversing to spinel $LiMn_2O_4$ during cycling [16,17].

1.1 Cathode material.

Many commercial batteries have been made of cathode materials with two kind classification first, some cathode material such as $LiTiS_2$ consist of anions close-packed which the alternate layers are localized between the anion plates and are occupied with the redox-active transition metals, while Li inserts into the empty remaining layers., followed. Second, a Large series of (+) materials have been investigated and are applied commercially in LIBs as cathode materials which can generally be categorized based on structure types such as olivine structure ($LiFePO_4$), layered structure ($LiCoO_2$, $LiNiO_2$, Li_2MnO_3, LiNi1-x$CoxO_2$, $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$) and spinel structure ($LiMn_2O_4$) which have a three dimensional framework shape.

1.1.1 Olivine structure. $LiFePO_4$ [18] can be applied at 95% of its theoretical capacities and 160mAh/g with suitable rate capabilities which is currently being selected as a candidate cathode material for next generation Li-ion batteries [19]. $LiFePO_4$ has an olivine structure (scheme.2) which is very different from the layered and spinel structures of other lithium-ion chemistries. The intercalation mechanism is also different, involving phase changes. $LiFePO_4$ has a specific capacity about 160mAhg^{-1} and an average voltage around 3.40V [18-21]. $LiFePO_4$ has more advantage due to inexpensive and environmentally friendly. In recent decades there have been centralized researches in improving the performance of Li-ion batteries in viewpoints of cathode materials. The cathode materials in the second group of Mendeleev's table have large tunnel structures, such as vanadium oxides, manganese dioxide, and transition-metal phosphates which potentially has la ower cost (olivine $LiFePO_4$) [22].

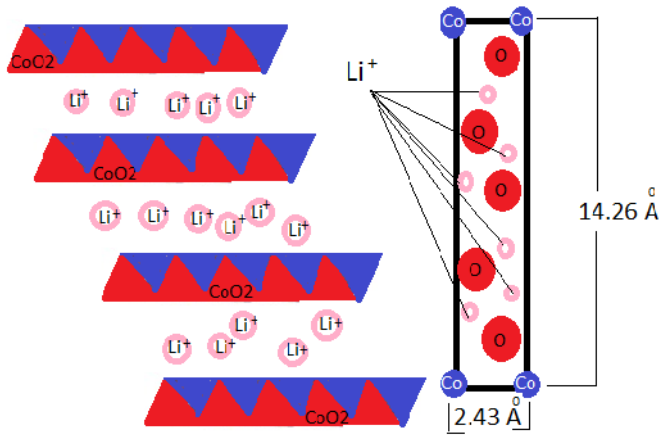


Scheme 2. $LiFePO_4$ during charge and discharge.

The tunnel structure of $LiFePO_4$ (where errant Fe ions in the Li sites) can reduce reactivity and diffusion of lithium. For $LiFePO_4$, the discharge potential is about 3.5 V vs. lithium and no explicit capacities fading were appeared even after a couple hundred cycles and its capacity (175 Ahkg^{-1}) is higher than commercial $LiCoO_2$ with high stabilizing even more than $LiNiO_2$ [23]. $LiFePO_4$ can be synthesized through hydrothermal conditions, or by sol-gel experiments [23].

The structure $LiFePO_4$ is consist of about 6.5% iron atoms in the lithium site with lattice parameters of *a:* 10.38 Å, *b:* 6.011 Å, and *c:* 4.71 Å compared with those for ordered $LiFePO_4$ of *a:* 10.33 Å, *b:* 6.012 Å, and *c:* 4.69 Å. Therefor the Fe atoms basically block diffusion of the Li^+, while diffusion effect along the tunnel is faster [23, 24] (scheme 2).

1.1.2 Layered structure. This structure generally has layered similar α-$NaFeO_2$ shape, that is a distorted rock-salt while the cations replaced in alternating (1 1 1) planes. In this structure the oxygen is placed in a centered cubic close-packed arrangement with the metal oxide, and the lithium ions would reside in the spaces among the oxygen layers. These kind structures help the intercalation process that the lithium cations are alternately diffused and removed from the structures during charge and discharge cycles [25]. The LIBs commercially is overmatched by an important layered structure as known "$LiCoO_2$", which firstly prepared by Sony's company in 1991. $LiCoO_2$ has α-$NaFeO_2$ position with oxygen atoms which are replaced in a cubic arrangement, as soon as Li atoms are completely removed; the oxygen layers rearranged themselves for giving hexagonal close packing in form of CoO_2 (Scheme.3). This cathode material exhibits an initial discharge capacity around "145mAhg^{-1}" with an expectation voltage of "3.75 V". Also improvements were demonstrated in the cycle-ability for this material when doped with transition metal such as Mg or Al. As $LiCoO_2$ is suitable material for commercial batteries several compositions are being studied via a solid solution with $LiCoO_2$ including, "Li_2MnO_3-$LiCoO_2$-$LiNiO_2$ [26], $LiCoO_2$-Li_2MnO_3 [27], $LiNi_{1/2}Mn_{1/2}O_2$-Li_2MnO_3-$LiCoO_2$ [28, 29] and $LiNiO_2$-$LiCoO_2$ [30].



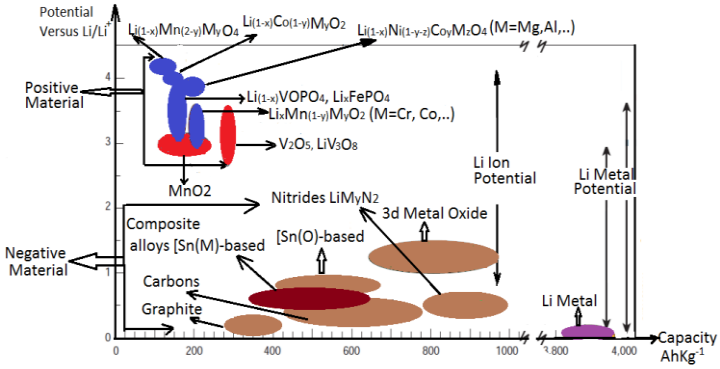
Scheme 3. Models of the layered $LiCoO_2$.

1.1.3 Spinel structure. The spinel cathode material such as $LiMn_2O_4$ has discussed by Thackeray et al and has been widely investigated by the Bellcor labs, and Amatucci [31]. The anion contains cubic close-packed oxygen and although is similar to the R-$NaFeO_2$ layer structure, there is a difference only in the distribution of the cation among the free sits of octahedral and tetrahedral position. The spinels might be imaged as a special form where the transition-metal cation is placed in all the layers therefore there are more open structures (like vanadium oxides) and also tunnel compounds of manganese dioxide or the transition-metal phosphates, such as the olivine $LiFePO_4$. The various potential cathode materials versus Li/Li^+ related to their applied capacities are presented in the scheme 4.

1.2. Solvent-Interface Materials & Electrolytes.

LIBs contain an anode, a cathode, and an electrolyte. The electrolyte is necessary for separating two major components of ionic and electronic transporting. In an ideal battery the Li^+ transport number will be unit in the electrolyte and the potential

can be estimated through the difference between the standard chemical As mentioned, the Li^+ flow via the electrolyte and separators, while the electrons move through the external circuit in system. Obviously, both of electrodes should allow for flow the Li^+ through suitable ionic and electron conductors. Potentials of the lithium in the negative and positive electrodes $\Delta G = n E F$.



Scheme 4. Various potential cathode materials versus Li/Li^+.

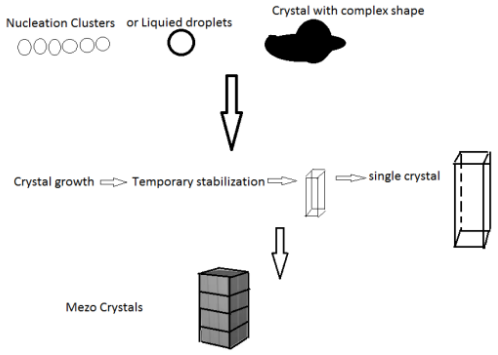
It is important to consider many electro-chemical activated materials are not suitable electronic conductors, so it is needed for adding the sensitive electronic conductive material such as carbon. For any mechanical holding of the electrodes together, a strong binder is also needed. The electrolyte solutions generally comprise Li salt dissolved in a liquid of organic solvent such as LiPF6 or Li-BOB (BOB is an anion including two boron which is coordinated with two oxalate groups) in an ethylene carbonate/dimethyl carbonate solvent. Although Biopolymers including Li^+ have been applied in recent years as electrolytes, their conductivities are still so much important item for any investigation of the efficiency in LIBs. Therefore they are only applied during the related liquids are added for giving a plasticized state. In addition, some solid electrolyte has been considered for several specialized electrolytes. Although the Li^+ flow inside the various electrolytes, the two electrodes should be separated for preventing an electrical short. It is done with using various porous separator materials. An important research [32], confirmed the excellent results of surfaces coating. This mechanism is depended on minimization in the reactivates of Co4+ with HF in electrolytes which is related to the interaction of moisture with those electrolyte's salts such as LiPF6.

1.2.1. Molten Salt Systems. Occasionally, LIBs batteries used the molten salts as electrolyte which acted at around 500 °C. Although the first cells applied both molten lithium and sulfur as two electrodes, the problems with interface of electrolyte – electrodes reaction appeared in the cell. Although it is a goal for developing a cell based on the lithium/sulfur, a system at low temperatures around -35 °C in electrolyte solvents of di-oxolane and di-methoxy-ethane has been investigated [33]. This cell with its liquid poly-sulfides cathodes has produced specific power 745 W/kg at 24 °C. Recently, the lithium anode from the reactive poly-sulfides is to coat it with the single-ion conducting glasses. One of the most important electrolytic behaviors is Na1+*x*Al11O17, which has been used as the electrolyte for a battery including molten sodium as anode and molten sulfur as cathode at 310 °C which mixed vanadium oxide (Li-Li*x*V2O5) also applied as electrodes for both NIBs and LIBs[33].

2. MATERIALS AND METHODS

2.1. Synthesis of $LiFePO_4$.

Meso-crystal structures [34-37] have 3D- superstructures which their morphologies are composed of a few to hundreds of nano-scaled primary units (around 1-900 nm) [34]. Meso-crystal has been initially demonstrated in bio-minerals. The formation of meso-crystals has been accomplished via a processing such as parallel crystallization, colloidal assemblies and controlled structure formation from nanoparticle building units [38] (scheme.5).



Scheme 5. Presentations of different crystallization pathways leading to the formation of meso crystals.

The morphology of the $LiFePO_4$ is of primary importance for the electrochemical properties, as the rate performance, conductivities and capacities of the of lithium-ion battery cells. The application of $LiFePO_4$ Meso-crystalline needs the poly (vinyl pyro-lidone) or other surfactants as growth-directing agents during the synthesis.

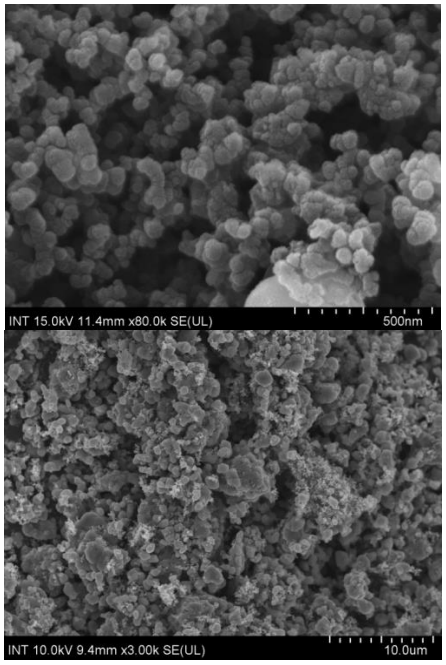


Figure 1. SEM of $LiFePO_4$.

The cells were charged and discharged at room temperature in the voltage range of 2.4–3.8 V (versus Li/Li+).

Scheme 6. The glove Box model kk-011AD in institute for nanotechnology, Vietnam National University-Ho Chi Minh City

$LiFePO_4$ Meso-crystals can be synthesized through low-temperature solvent-thermal reaction as follows. The initial solutions were prepared via dissolving stoichiometric mole-fraction of LiOH, $FeCl_2{\cdot}4H_2O$ and H_3PO_4 in 25 milliliter ethanol under strong mechanical stirring for an hour. The prepared, clear green solution has been covered in a glass of a Teflon autoclave which was then heated up in an oven to 250 °C and high pressure for overnight. $LiFePO_4$ Meso-crystals took place inside the autoclave during solvent-thermal processing, and also the reactor was allowed for cooling down up to 25 °C with water bath. The collected green precipitate has been washed completely with water and was dried under vacuum at 70 °C. Carbon coating on the surface of $LiFePO_4$ Meso-crystals, N-acety-lglucos-amine ($C_5H_{15}NO_6$, 0.2 g) was added in the precursor solution before the autoclave treatment. For increasing the crystal stabilities of material and also the conductivities of the carbon layers, Glove-Box model of kk-011AD (serial No: kk-1760) have been used at it is atmosphere (scheme.6). The final pristine $LiFePO_4$ powder was very pure and green and also the final $LiFePO_4$ carbon/meso-crystal composites were black in color in Fig.1 the SEM of $LiFePO_4$ are shown.

The composites were synthesized using the sol-gel method due to simple chemical reaction with a low temperature and a high degree of homogeneity. For fabrication of cathodes, the prepared products were first mixed with acetylene black and poly-vinylidene fluoride in N-methyl-pyrrolidone (NMP).

3. RESULTS

The purpose of this study is to find a ternary solid solution of Li-based cathode material that is an advantageous replacement for $LiCoPO_4$ which is expensive and toxic (based on our previous works)[40-68]. Therefore a combination of ternary composition diagram including {[(1-x-y) $LiFe_{0.333}Ni_{0.333}$ $Co_{0.333}$] PO_4}, xLi2$FePO_4F$ and y$LiCoPO_4$ composite have been considered. In viewpoint of electrochemical behavior which indicates manganese is +4, which remain without Jahn-Teller distortion with the +3 valance (Mn^{+3}). Solid solutions were basically elected in terms of obtaining a cathode composition with superior efficiency of cycle-ability, capacity and structural stabilities also with costs low. By a few works the solid solutions have been applied as cathode material including both binary and ternary systems. It is notable that the initial crystal structures of the cathode material not only specifies the initial characteristic capacity, but also imply to the stability. The consistency of de-lithiated cathode materials is substantial for any increase of the cycle life. So through substituting some atoms of Mn with Fe atoms the total metal-oxygen bonding of the material is going to be stronger than the cathodes because the 3d state of Mn^{4+} is $3d^3$ ($t_{2g}^3 e_{2g}^0$).

This investigation is used for finding the best cathode material compositions of {[(1-x-y) $LiFe_{0.333}Mn_{0.333}$ $Co_{0.333}$] PO_4}, xLi_2FePO_4F and y$LiCoPO_4$ with high initial discharge capacity, grate cycle-ability and inexpensive cost compared to current lithium-ion cathode materials. Therefore, initially, 28 different composition points according to using the lever rule, stoichiometric weights and mole-fractions were chosen in order to find an optimized material with good electrochemical performance. These 28 points were extracted through the triangle phase diagram of the defined system [Fig.2 and table 1&2] and synthesis through sol-gel method.

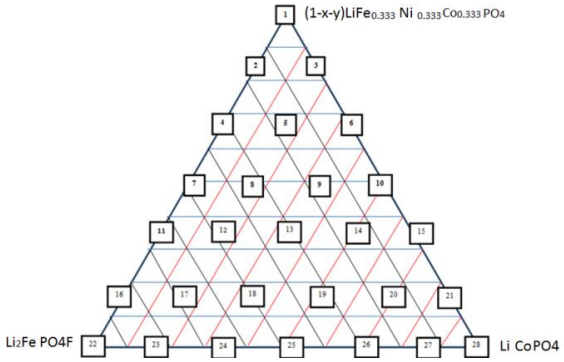


Figure 2. Binary and Ternary diagram of [(1-x-y) $LiFe_{0.333}Ni_{0.333}Co_{0.333}$] PO_4, X Li2$FePO_4F$ and y$LiCoPO_4$ compositions.

Ni and Co amount are decreased towards down direction of triangle; meanwhile the Iron is increased. High Fe value is found at sample 7 and its content decreases at the opposite endpoints of the triangle.

Table 2. 10 different composition points according to using the lever rule, stoichiometric weights and mole-fractions of the triangle diagram.

Sample	Composition
1	$LiNi_{0.333}Co_{0.333}Fe_{0.333}PO_4$
2	$Li_{1.167}Ni_{0.278}Co_{0.278}Fe_{0.444}PO_4$
3	$LiNi_{0.278}Co_{0.278}Fe_{0.278}Co_{0.167}PO_4$
4	$Li_{1.333}Ni_{0.222}Co_{0.222}Fe_{0.555}PO_4$
5	$Li_{1.167}Ni_{0.222}Co_{0.389}Fe_{0.388}PO_4$
6	$LiNi_{0.222}Co_{0.555}Fe_{0.222}PO_4$
7	$Li_{1.5}Ni_{0.167}Co_{0.167}Fe_{0.667}PO_4$

Table 3. Summary capacity and cycle-ability for 10 samples, of the system [(1-x-y) $LiFe_{0.333}Ni_{0.333}Co_{0.333}]$ PO_4, X Li_2FePO_4F and y$LiCoPO_4$ compositions.

Sample	Blend	Li_2FePO_4F	$LiCoPO_4$
1	Pure	0	0
2	Binary	0.167	0
3	Binary	0	0.167
4	Binary	0.333	0
5	Ternary	0.167	0.167
6	Binary	0	0.333
7	Binary	0.500	0
Sample	$LiNi_{0.333}Co_{0.333}Fe_{0.333}$ PO_4	First discharge Capacity	Cycle-ability
1	1	132.5	46
2	0.833	141.4	45
3	0.833	110.3	55
4	0.667	100.5	50
5	0.667	126.4	60
6	0.667	111.5	60
7	0.500	112.6	80

High Cobalt value is found in sample 1 and its percentage is found in a wide region in the triangle. It is predicted which capacities and cycle-ability of the compositions are directly related to the amount of Fe, Co and Ni. It is notable, specific capacity is determined as the number of energies which can be a reserve in volume or mass (Ah), while the rate capability (which are related to their design and varies considerably between different manufactures), can be determined as the rate at which the cell is being charged. Therefore the C-rate is the capacity of the battery divided by the hourly charging rate. The discharge capacity curves of this work have been compared with 18650-type "C/$LiCoO_2$ Sony battery" result which is modified by Ehrlich [69]. Since $LiCoO_2$ cathode has an initial discharge capacity around145mAh/g [39], therefore any materials of these compositions with initial capacities more than this amount (of course with a suitable cycle-ability) might be considered. The samples were tested via a cycler (Arbin BT 2000 battery testing system), between 2.4V and 3.8V with low C-rate of C/10. The initial results indicate of a wide range and irregular of cycle-ability and capacities. The initial discharge capacities varied from 100.5 to 141.4 "$mAhg^{-1}$". Both capacity and cycle-ability increase from $LiFe_{0.333}Ni_{0.333}Co_{0.333}PO_4$ towards the binary compositions.

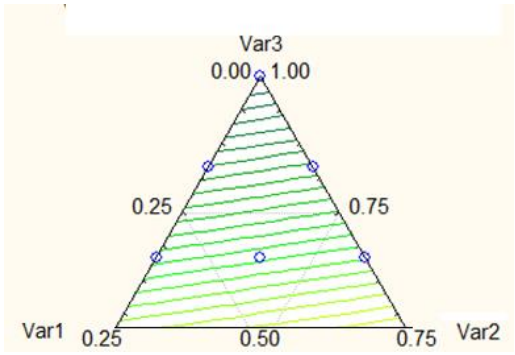


Figure 3. Ternary of capacity versus Var_1, Var_2 and Var_3 for 28 samples of {[(1-x-y) $LiFe_{0.333}Ni_{0.333}Co_{0.333}]$ PO_4}, xLi_2FePO_4F and y$LiCoPO_4$ composites.

Although sample 2 shows high capacity of "141.4" $mAhg^{-1}$, it contains of a low cycle-ability compare to sample 5. The samples 1, 2 and 5 exhibits suitable capacities but only sample 5 is acceptable due to high cycle-ability. Although these kinds of data are not sufficient for determining a suitable cathode material in viewpoint of capacity and cycle-ability amount, the statistical analysis can be useful for finding the region of the best item from the data of the 7 compositions. Therefore a few testing with both capacity and cycle-ability relation in viewpoint of the triangle regions is needed (Figs. 3, 4). In this work the SATISTICA software has been used for analyzing the data which Var_1, Var_2, Var_3, are Li_2FePO_4, $LiCoPO_4$ and $LiFe_{0.333}Ni_{0.333}$ $Co_{0.333}]$ PO_4respectively while the Var_4 alternately, are the capacity and cycle-ability.

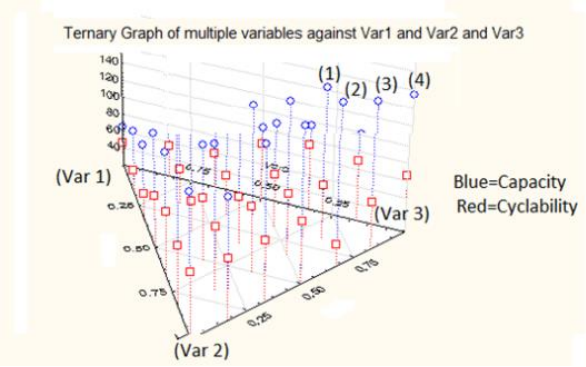


Figure 4. {[(1-x-y) $LiFe_{0.333}Ni_{0.333}Co_{0.333}]$ PO_4}, xLi_2FePO_4F and y$LiCoPO_4$ composites with high precisionist of capacity and cycle-ability Var_1, Var_2 and Var_3.

Recently a few works have been investigated for increasing the efficiency of cathode materials in LIBs [70-85]. By this work various compositions are used for exploring the novel cathode materials with two-dimensional layered structure through the ternary composition's diagram among Iso-structural materials. Through an analyzing among these compositions, two samples were chosen and subsequently synthesized, characterized and tested consequently with high precisionist. Via initial discharge capacity and some extra results number 5 as $Li_{1.167}$ $Ni_{0.222}$ $Co_{0.389}$ $Fe_{0.388}$ PO_4 is indicated as the suitable cathode material among those structures. Obviously, the used weight of cobalt in these samples is lower compared with $LiCoO_2$ that is an advantage in viewpoint of cost and toxic in this study. The repeat of samples was made into T-Cells and subjected to electrochemical testing using the original conditions and the cycling was accomplished between 2.4 - 3.8V with constant C-rate of C/10 at room temperature (Fig. 5).

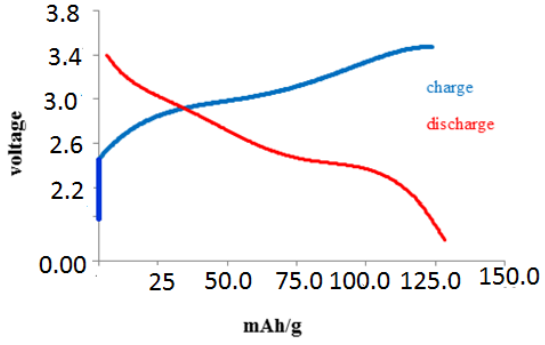


Figure 5. Charge and discharge capacity of $Li_{1.167}$ $Ni_{0.222}$ $Co_{0.389}$ $Fe_{0.388}$ PO_4.

The repeat sample exhibits better charge and discharge capacities and this improvement in the capacities is attributed to the synthesis conditions.

4. CONCLUSIONS

{[(1-x-y) $LiFe_{0.333}Ni_{0.333}$ $Co_{0.333}$] PO_4}, xLi_2FePO_4F and $yLiCoPO_4$ composite system of cathodes with submicron particles have been successfully synthesized by a sol-gel method. The structural and electrochemical properties have been systemically investigated to examine the effects of charge/discharge capacities and also capacity retention. The results show that the prepared "$Li_{1.167}$ $Ni_{0.222}$ $Co_{0.389}$ $Fe_{0.388}$ PO_4" type layered structure regardless of the nickel content and Fe, improve the capacity retention significantly. In addition, the percentage of nickel and cobalt exhibit good performance. Although these kind systems can help for removing the disadvantage of cobalt which mainly is its cost and toxic, the performance of these kind systems is similar to $LiCoO_2$ cathode material. Therefore fabrication of lithium-ion batteries using a few more transition elements such as Ni, Fe and Mn is suggested for any further research.

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