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Application no.:	Sheet no.: 01

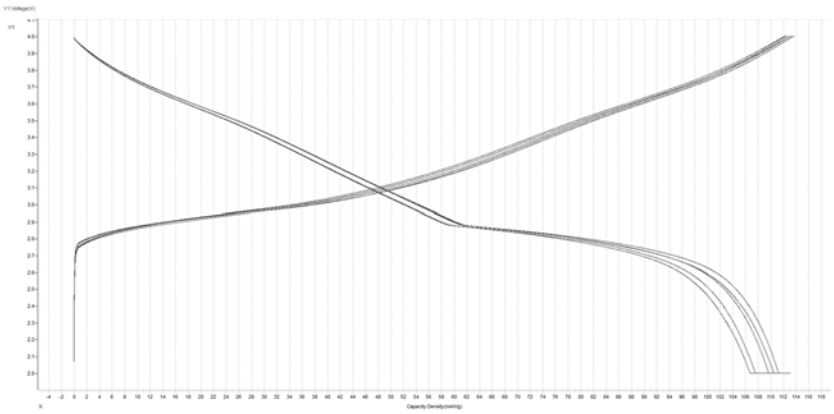


Figure 1(a)

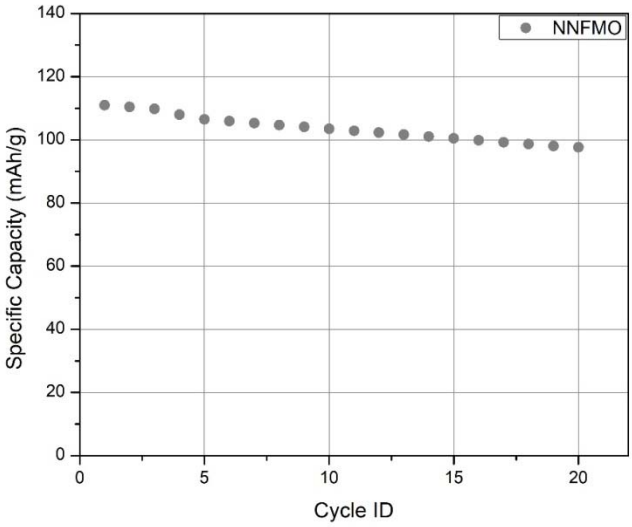


Figure 1(b)

Dr. P. Aruna Sree
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Agent for the Applicant

Applicant: GEGADYNE ENERGY LABS PRIVATE LIMITED	Total no. of Sheets: 04
Application no.:	Sheet no.: 02

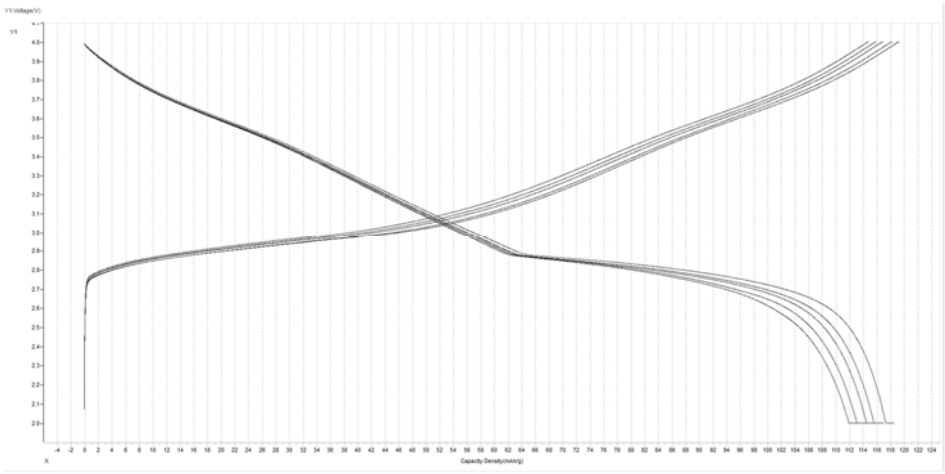


Figure 2(a)

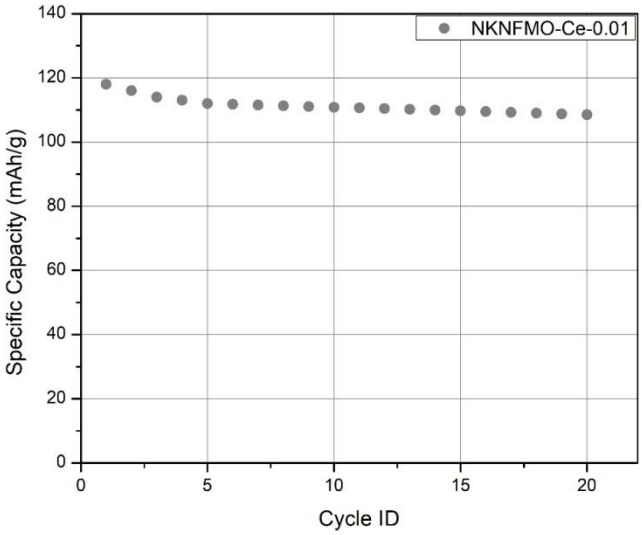


Figure 2(b)

Dr. P. Aruna Sree
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Applicant: GEGADYNE ENERGY LABS PRIVATE LIMITED	Total no. of Sheets: 04
Application no.:	Sheet no.: 03

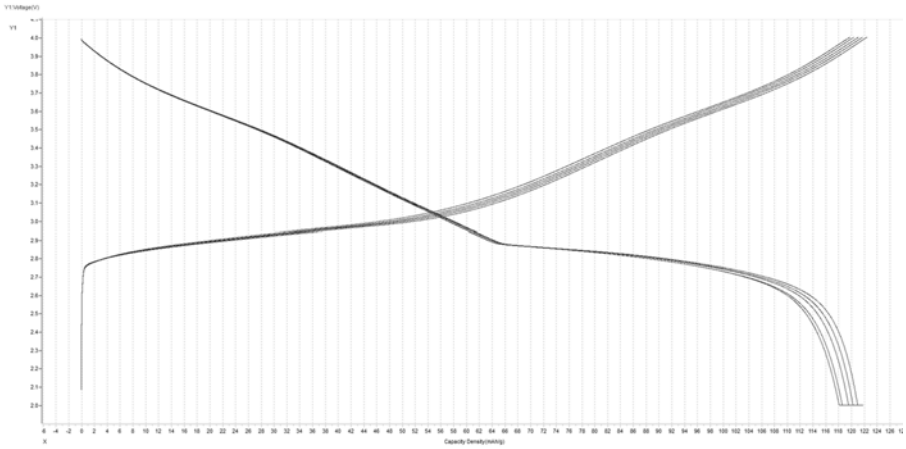


Figure 3(a)

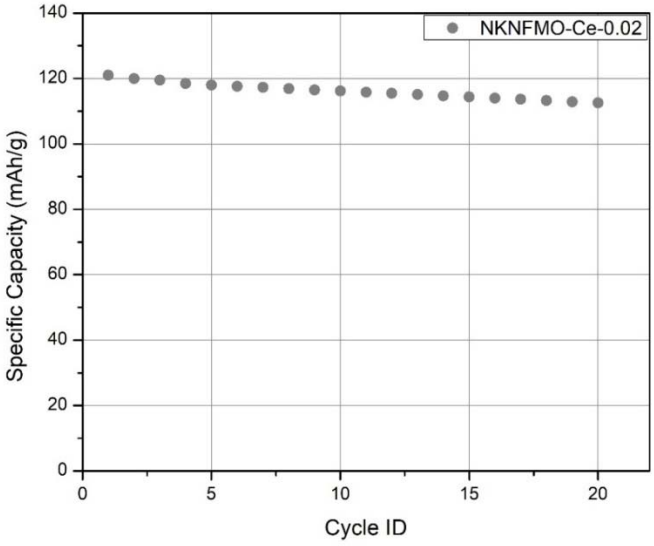


Figure 3(b)

Dr. P. Aruna Sree
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Applicant: GEGADYNE ENERGY LABS PRIVATE LIMITED	Total no. of Sheets: 04
Application no.:	Sheet no.: 04

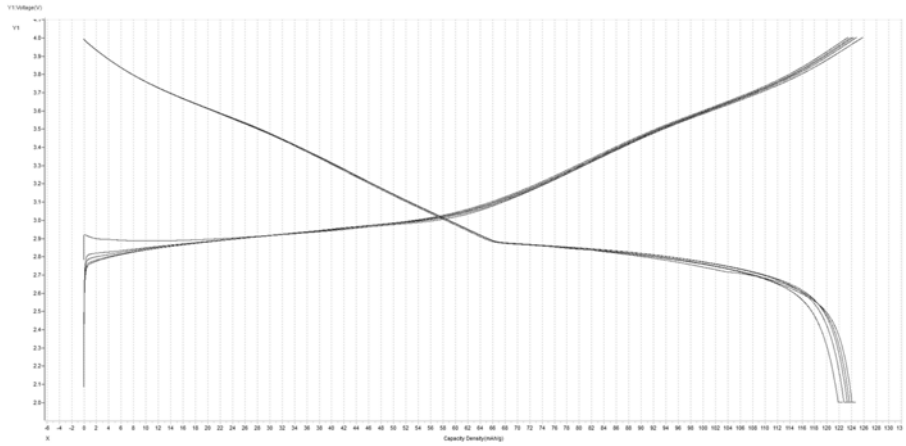


Figure 4(a)

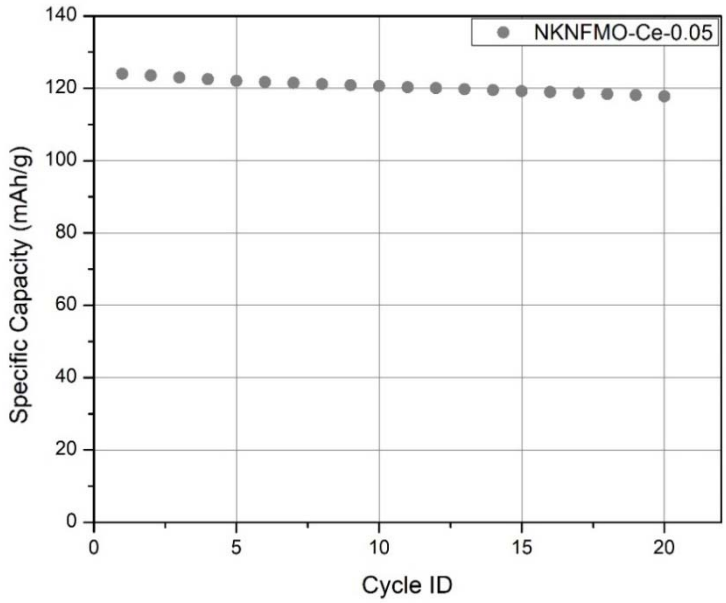


Figure 4(b)

Dr. P. Aruna Sree
(Regn.No.: IN/PA 998)
Agent for the Applicant

FORM 2

THE PATENTS ACT, 1970

(39 of 1970)

AND

The Patents Rules, 2003

COMPLETE SPECIFICATION

(See section 10 and rule 13)

1. TITLE OF THE INVENTION:

"CERIA DOPED MIXED CATIONIC CATHODE ACTIVE MATERIAL"

2. APPLICANT:

(a) NAME: GEGADYNE ENERGY LABS PRIVATE LIMITED

(b) NATIONALITY: Indian Company registered under the Companies Act, 2013

(c) ADDRESS: RH32, Pushpanjali, Opp Puranik City, Owala Naka, GB Road, Thane (West) - 400615, Maharashtra, India.

3. PREAMBLE TO THE DESCRIPTION:

The following specification particularly describes the invention and the manner in which it is to be performed.

FIELD OF INVENTION:

The present invention relates to ceria doped mixed cationic cathode active material of Formula (I) for energy devices. The cathode active material of the present invention shows high specific capacity with little or no fading on cycling, and can be recharged multiple times without losing the charge capacity.

BACKGROUND & PRIOR ART:

Alkali-ion batteries are analogous in many ways to the lithium-ion batteries that are in common use today; they are both reusable secondary batteries that comprise an anode (negative electrode), a cathode (positive electrode) and an electrolyte material, both are capable of storing energy, and they both charge and discharge via a similar reaction mechanism. When an alkali-ion (or lithium-ion) battery is charging, M^+ (or Li^+) ions de-intercalate from the cathode and insert into the anode. Meanwhile charge balancing electrons pass from the cathode through the external circuit containing the charger and into the anode of the battery. During discharge the same process occurs but in the opposite direction.

Lithium-ion battery technology has enjoyed a lot of attention in recent years and provides the preferred portable battery for most electronic devices in use today; however, lithium is not a cheap metal to source and is considered too expensive for use in large scale applications. By contrast, alternative alkali-ion based battery technology is still in its relative infancy but is seen as advantageous; metals like sodium and potassium are much more abundant than lithium and some researchers predict this will provide a cheaper and more durable way to store energy into the future, particularly for large scale applications such as storing energy on the electrical grid.

Metal oxides with the general formula A_XMO_2 (where A represents one or more alkali metal ions and M represents one or more metal ions at least one of which has several oxidation states, for example a transition metal) are known to crystallise in a number of different layered structures. This is described in detail

by C. Delmas et al in "Structural Classification and Properties of the Layered Oxides", Physica 99B (1980) 81-85. In summary, the structures are all made up of MOβ edge sharing octahedra which form $(MO_2)n$ sheets. These sheets are stacked one on top the other and are separated by the alkali metal atoms and the exact position of the alkali metal will dictate whether the overall structure of the metal oxide is to be described as octahedral (O), tetrahedral (T) or prismatic (P). In a lattice made up of hexagonal sheets, there are three possible positions for the oxygen atoms, conventionally named A, B and C. It is the order in which these sheets are packed together that leads to the O, T and P environments. The number 2 or 3 is also used to describe the number of alkali metal layers in the repeat unit perpendicular to the layering. For example, when the layers are packed in the order ABCABC, an O3 structure is obtained. This translates to 3 alkali metal layers in the repeat unit and each alkali metal being in an octahedral environment. Such materials are characterised by the alkali metal ions being in octahedral orientation and typical compounds of this structure are A_XMO2 ($x \leq 1$). The order ABAB with the alkali metal ions in tetrahedral orientation will yield a T1 structure which is typified by A_2MO_2 compounds. Packing the sheets in ABBA order gives a P2 structure in which one half of the prism shares edges with MO β octahedra and the other half shares the faces. Packing in ABBCCA order results in a P3 structure type in which all prisms share one face with one MO β octahedron and three edges with three MO β octahedra of the next sheet and the compounds are found to adopt the P3 structure. It will be noted that the amount of alkali metal present in the A_XMO_2 material has a direct bearing on the overall structure of the metal oxide.

Attempts are made in the art to dope alkaline batteries or lithium-ion batteries with active materials selected from alkali metals, transition metals, lanthanides to increase depth of discharge and to improve the cyclability.

US8475959 relates to a positive electrode active material for a lithium ion battery comprising a layered lithium doped lithium metal oxide composition

approximately represented by a formula $xLi_2MnO_3.(1-x)LiNi_{u+\Delta}Mn_{u-\Delta-d}Li_dCo_wA_yO_2$, x ranges from about 0.03 to about 0.55, d ranges from about 0.004 to about 0.05, 2u+w+y is approximately equal to 1, Δ ranges from about −0.0019 to about 0.0019, w ranges from about 0.2 to about 0.475, u ranges from about 0.2 to about 0.4, y ranges from 0 to about 0.1 with the proviso that both (u+Δ) and w are not both 0 and A is Mg, Sr, Ba, Cd, Zn, Al, Ga, B, Zr, Ti, Ca, Ce, Y, Nb, Cr, Fe, V, or combinations thereof.

Article titled "A Manganese-Doped Barium Carbonate Cathode for Alkaline Batteries' by Benjamin Hertzberg et.al published in Journal of The Electrochemical Society,**161** (6) A835-A840 (2014) discloses substitution of manganese in the Witherite crystal structure of $BaCO_3$ to provide $BaMn_{0.51}C_{0.49}O_3$whichcreates a high degree of electrochemical activity, superior rate capability and cyclability. The article further provides synthesis of Manganese-doped Witherite via a one-step hydrothermal process.

The article by Su Cheol Han et.al titled 'Ca-doped $NaxCoO_2$ for improved cyclability in sodium ion batteries' published in Journal of Power Sources 277 (2015) 9e16 provides multi-valent cation substitution for Na^+ as cathode material to improve the cyclability of sodium ion batteries (SIBs) since calcium has no movement in the electrolyte and does not come out of the lattice during charging. The article discloses $Na_xCa_yCoO_2$ ($0.45 \leq x \leq 0.64$, $0.02 \leq y \leq 0.10$) cathode material synthesized via a solid-state method.

A Ni-doped Magnesium manganese oxide as the cathode via a conventional hydrothermal method, which help to improve conductivity and solve defects derived from pure manganese oxide with nickel doping is reported in the article titled "Ni-doped magnesium manganese oxide as a cathode and its application in aqueous magnesium-ion batteries with high rate performance" by Hongyu Zhang et.al in *J. Name*., 2013, **00**, 1-3.

US8835041 discloses an electrode suitable for use as a cathode in a sodium electrochemical cell or battery, the electrode comprising a layered material of formula $Na_cLi_dNi_eMn_fM_zO_b$, wherein M comprises one or more metal cation, $0.24 \leqq c/b \leqq 0.5$, $0 \leqq d/b < 0.23$, $0 \leqq e/b \leqq 0.45$, $0 \leqq f/b \leqq 0.45$, $0 \leqq z/b \leqq 0.45$, the combined average oxidation state of the metallic components Na, Li, Ni, Mn, and M is in the range of about 3.9 to 5.2, and b is equal to (c+d+Ve+Xf+Yz)/2, wherein V is the average oxidation state of the Ni, X is the average oxidation state of the Mn, and Y is the average oxidation state of the M; and wherein a combined positive charge of the metallic components is balanced by a combined negative charge of the oxygen anions, the Na is predominately present in a sodium layer, and the Mn, Ni, and M are predominately present in a transition metal layer.

The recent research by Li Yang et.al in Journal of Electronic Materials published in 2018, The Minerals, Metals & Materials Society titled "Effect of Cu Doping on the Structural and Electrochemical Performance of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ Cathode Materials has demonstrated that the Cu-doped material exhibits better galvanostatic charge/discharge cycling performance arising from an enlarged Li layer spacing and a reduced degree of cation mixing.

Improvements are made in the art to prevent cation mixing, oxygen evolution and structural collapse in layered cathode materials by doping with anionic elements such as F, Cl, and S into the oxygen sites of layered cathode materials to effectively enhance the electrochemical performance.

In the article titled "Fluorine-Doped $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ Cathode for High-Performance Lithium-Ion Batteries" by Hyeona Kim et.al published in Energies **2020**, 13, 4808; the oxygen atoms in the NCM are replaced with F- ions to produce a F-doped NCM structure in lithium-ion batteries, LiNixCoyMnzO2 (x + y + z = 1) (NCM) cathode materials.

The article titled “Superior cyclability of Ce-doped P2–Na0.67Co0.20Mn0.80O2 cathode for sodium storage” published on January 2021; discloses the effects of cerium doping on the active cathode material. P2-type Na0.67Co0.20Mn0.79Ce0.01O2 oxide were synthesized by solid-state method. The article provides P2 type sodium deficient cathode wherein the substitution is at Mn site.

CN107732178 relates to Nickel cobalt aluminum cathode material for lithium-ion batteries of cerium doping and a preparation method thereof. The molecular formula of the nickel cobalt aluminium anode material for lithium-ion batteries of cerium doping is LiaNixCoyAlzCebO2, wherein, b is 4/3 a/3 x y z, $1 \leq a \leq 1.2, 0.3 \leq x \leq 0.98, 0.01 \leq y \leq 0.6, 0.001 \leq z \leq 0.1, 0.00001 \leq b \leq 0.05$.

CN108550810 relates to a preparation method of a cerium-doped and carbon-coated modified ternary cathode material. However, CN’810 involves carbon coating of the activated precursor material.

US9882206 discloses dual doped layered cathode material, comprising Lithium cobalt oxide of general formula $LiMxNyCo1-x-yO2$ ($0.01 \leqq x, y \leqq 0.2$) wherein M is a divalent alkaline earth metal cation and N is a divalent transition metal cation.

With the increasing demand of renewable energy sources such as rechargeable batteries or other energy devices, cost is a significant factor to widespread adoption of doped Li-ion batteries along with overall cycle life and energy density. Therefore the current inventors observed that there is a scope to provide an improved doped cathode active material for energy storage devices or alkali-ion electrochemical cell which is capable of delivering high specific capacity with little or no fading on cycling, and yet being cost effective. This remains the objective of the present invention.

SUMMARY OF INVENTION:

In an aspect, the present invention provides mixed cation doped cathode active material of formula (I) for energy devices with little or no fading on cycling, comprising;

$$A_{(1-b)}B_b[Ni_{0.33}Fe_{0.33}Mn_{0.33}]_{(1-x)}Ce_xO_2 \quad \textbf{(Formula I)}$$

wherein

'A' comprises one or more alkali metals selected from lithium, sodium, potassium and cesium;

'B' comprises one or more alkali metals selected from lithium, sodium, potassium and cesium;

Ni is nickel in oxidation state 2+,

Fe is iron in oxidation state 3+,

Mn is manganese in oxidation state 4+,

Ce is ceria in oxidation state 3+, and

wherein

$0.01 \leq b \leq 0.4$, preferably $0.01 \leq b \leq 0.25$, further preferably $0.01 \leq b \leq 0.1$,

$0.01 \leq x \leq 0.25$, preferably $0.01 \leq x \leq 0.15$ and ideally $0.01 \leq x \leq 0.1$; and

wherein the said cathode active material possesses high specific capacity with little or no fading on cycling.

In another aspect, the doped cathode active material of Formula (I) comprises:

(i) $Na_{0.95}K_{0.05}Ni_{0.327}Fe_{0.327}Mn_{0.327}Ce_{0.01}O_2$,

(ii) $Na_{0.95}K_{0.05}Ni_{0.323}Fe_{0.323}Mn_{0.323}Ce_{0.02}O_2$,

(iii) $Na_{0.95}K_{0.05}Ni_{0.313}Fe_{0.313}Mn_{0.313}Ce_{0.05}O_2$.

In an aspect, the cathode active material with optimized stoichiometry is provided such that the O3 structure of the cathode doped with+3 ceria results in enlarged interlayer spacing, providing larger channels for ion movement. It also reinforces the structural stability because of significantly higher "Ce-O" bond energy [790 kJ/mol] compared to bond energies of "Fe-O"[407 kJ/mol], "Mn-O" [362 ± 25

kJ/mol], “Ni-O” [366±30 kJ/mol] and prohibits phase transitions which otherwise would lead to degradation over multiple cycles.

In yet another aspect, the present invention provides a process for preparation of the cathode active material of Formula (I) comprising co-precipitating a ternary hydroxide of the base transition metal elements and further mixing with stoichiometric ratios of respective A, B and Ceria (Ce) and heating in order to facilitate proper compound formation. Such a process may be conveniently performed in the presence of air, but it may also be performed under an inert atmosphere.

Accordingly, the process for preparation of the cathode active material of Formula (I) comprises the steps of;

i. Preparing separately the solution of the base metal Ni, Fe and Mn salts in their respective stoichiometric ratios and the solution of mixture of ammonium hydroxide and alkali hydroxide;
ii. Mixing the above two solutions simultaneously into a fixed volume stirred reactor at suitable feed rates to maintain a pH of 10.5 to 11.5 and temperature between 45 to 55^{o}C followed by ageing under stirred condition to allow homogenous particle formation of the precipitated ternary hydroxides and drying to obtain the precursor powder;
iii. Intimately mixing together the obtained precursor powder of step (ii)with stoichiometric quantities of alkali salts and ceria and pressing into a pellet;
iv. Heating the resulting mixture in a furnace under a suitable atmosphere and temperature until reaction product forms; and optionally
v. Allowing the product to cool before grinding it to a powder.

In an aspect, the active material of Formula (I) is used as an electrode preferably a positive electrode (cathode), in conjunction with a counter electrode and one or more electrolyte materials in alkali ion-cell and in energy storage devices or electrochemical cell.

In another aspect, the present invention provides alkali-ion electrochemical cell comprising;

(i) the cathode consisting of ceria doped mixed cation active material of the formula (I);

$$A_{(1-b)}B_b[Ni_{0.33}Fe_{0.33}Mn_{0.33}]_{(1-x)}\,Ce_xO_2 \quad \textbf{(Formula I)}$$

wherein

'A' comprises one or more alkali metals selected from lithium, sodium, potassium and cesium;

'B' comprises one or more alkali metals selected from lithium, sodium, potassium and cesium;

Ni is nickel in oxidation state 2+,

Fe is iron in oxidation state 3+,

Mn is manganese in oxidation state 4+,

Ce is ceria in oxidation state 3+, and

wherein

$0.01 \leq b \leq 0.4$, preferably $0.01 \leq b \leq 0.25$, further preferably $0.01 \leq b \leq 0.1$,

$0.01 \leq x \leq 0.25$, preferably $0.01 \leq x \leq 0.15$ and ideally $0.01 \leq x \leq 0.1$;

(ii) the anode consisting of hard anode;

(iii) a separator; and

(iv) the non-aqueous electrolyte selected from 0.5M solution of $NaPF_6$ and 0.3M solution of KPF_6 in a mixture of Ethyl Methyl Carbonate, Propylene Carbonate and Fluoroethylene Carbonate (EMC:PC:FEC) in a ratio of 1:1:0.1.

In an aspect, the present invention provides electrode active material of Formula (I)is in conjunction with a counter electrode and one or more electrolyte materials in energy storage devices.

In another aspect, the charge-discharge profile of the present electrode active material of Formula (I) exhibits smooth discharging curve from 4V to 2V when used as the cathode in energy storage devices comprising hard carbon as anode and the electrolyte comprising of 0.5M solution of $NaPF_6$ and 0.3M solution of KPF_6 in a mixture of Ethyl Methyl Carbonate, Propylene Carbonate and Fluoroethylene Carbonate (EMC:PC:FEC) in a ratio of 1.2:0.8:0.15.

The ceria doped mixed cation cathode active material of Formula (I) of the present invention find application in alkali ion-cell, in energy storage devices such as batteries, rechargeable batteries, electrochemical devices and electrochromic devices. The cathodes of the present invention show an improvement in specific capacity and consequently, the energy density of devices made from them, over undoped cathodes.

Various aspects and features of the present invention will become apparent from the description of preferred embodiments, which are taken in conjunction with the appended drawings.

BRIEF DESCRIPTION OF DRAWINGS:

FIGURE 1 (a) shows schematic representation of cell voltage profile for the first 5 charge/discharge cycles of the cell having hard carbon as anode material and $Na_1Ni_{0.333}Fe_{0.333}Mn_{0.333}O_2$ as cathode active material;

FIGURE 1(b)illustrates the Constant current cycling (CC/CV) of a full cell with hard carbon as anode material and $Na_1Ni_{0.333}Fe_{0.333}Mn_{0.333}O_2$ in the voltage range 2 - 4V at 25°C in 0.5M NaPF6 in EC:DEC:FEC and PP used as a separator;

FIGURE 2(a) shows the cell voltage profile for the first 5 charge/discharge cyclings of the cell having $Na_{0.95}K_{0.05}Ni_{0.327}Fe_{0.327}Mn_{0.327}Ce_{0.01}O_2$ as cathode active material;

FIGURE 2(b) shows the constant current cycling (CC/CV) of a cell with $Na_{0.95}K_{0.05}Ni_{0.327}Fe_{0.327}Mn_{0.327}Ce_{0.01}O_2$ as cathode active material in the voltage range 2 - 4V at 25°C in 0.5M NaPF6 and 0.3M KPF6 in EMC:PC:FEC and PP used as a separator;

FIGURE 3(a) shows the cell voltage profile for the first 5 charge/discharge cycles of the cell having$Na_{0.95}K_{0.05}Ni_{0.323}Fe_{0.323}Mn_{0.323}Ce_{0.02}O_2$ cell;

FIGURE 3(b) shows the constant current cycling (CC/CV) of a cell having$Na_{0.95}K_{0.05}Ni_{0.323}Fe_{0.323}Mn_{0.323}Ce_{0.02}O_2$ as cathode active material in the voltage range 2 - 4V at 25°C in 0.5M NaPF6 and 0.3M KPF6 in EC:DEC:FEC and PP used as a separator;

FIGURE 4(a) shows the graph with plots ofcell voltage profile for the first five charge/discharge cycles of the cell having$Na_{0.95}K_{0.05}Ni_{0.313}Fe_{0.313}Mn_{0.313}Ce_{0.05}O_2$ as cathode active material;

FIGURE 4(b) shows the constant current cycling (CC/CV) of a cell having$Na_{0.95}K_{0.05}Ni_{0.313}Fe_{0.313}Mn_{0.313}Ce_{0.05}O_2$ as cathode active material in the voltage range 2 - 4V at 25°C in 0.5M NaPF6 and 0.3M KPF6 in EMC:PC:FEC and PP used as a separator;

DETAILED DESCRIPTION OF INVENTION:

The features of the present invention are described below in the various preferred and optional embodiments, however, should not be construed as limiting the scope of the invention.

Abbreviations:

EMC: Ethyl Methyl Carbonate

PC: Propylene Carbonate

FEC: Fluoroethylene Carbonate

PP: Polypropylene

In order to provide a clear and consistent understanding of the terms used in the present specification, a number of definitions are provided below. Moreover, unless defined otherwise, all technical and scientific terms as used herein have the same meaning as commonly understood by the person of ordinary skill in the art to which this invention pertains.

The word "element" used in the present invention refers to a member of the periodic table and has the suitable oxidation state when the element is used in combination with other members of the periodic table.

The present invention relates to a mixed cation ceria doped cathode active material with optimized stoichiometry such that the O3 structure of the formed cathode is doped with larger alkali ions as well as cerium ions and results in enlarged interlayer spacing, providing larger channels for ion movement. The +3 doped ceria also reinforces the structural stability because of significantly higher "Ce-O" bond energy [790 kJ/mol] compared to bond energies of "Fe-O"[407 kJ/mol], "Mn-O" [362 ± 25 kJ/mol], "Ni-O" [366±30 kJ/mol] and prohibits phase transitions which may lead to degradation over multiple repeated cycles.

In an embodiment, the present invention describes ceria doped mixed cation cathode active material, with little or no fading on cycling, for energy devices, having the formula (I),

$$A_{(1-b)}B_b[Ni_{0.33}Fe_{0.33}Mn_{0.33}]_{(1-x)}Ce_xO2 \textbf{(Formula I)}$$

wherein

'A' comprises one or more alkali metals selected from lithium, sodium, potassium and cesium;

'B' comprises one or more alkali metals selected from lithium, sodium, potassium and cesium;

Ni is nickel in oxidation state 2+,

Fe is iron in oxidation state 3+,

Mn is manganese in oxidation state 4+,

Ce is ceria in oxidation state 3+, and

wherein

$0.01 \leq b \leq 0.4$, preferably $0.01 \leq b \leq 0.25$, further preferably $0.01 \leq b \leq 0.1$,

$0.01 \leq x \leq 0.25$, preferably $0.01 \leq x \leq 0.15$ and ideally $0.01 \leq x \leq 0.1$; and

wherein the said cathode active material possesses high specific capacity with little or no fading on cycling.

In a preferred embodiment, the ceria doped mixed cation cathode active material of Formula (I) comprises;

(i) $Na_{0.95}K_{0.05}Ni_{0.327}Fe_{0.327}Mn_{0.327}Ce_{0.01}O_2$,

(ii) $Na_{0.95}K_{0.05}Ni_{0.323}Fe_{0.323}Mn_{0.323}Ce_{0.02}O_2$,

(iii) $Na_{0.95}K_{0.05}Ni_{0.313}Fe_{0.313}Mn_{0.313}Ce_{0.05}O_2$,

In another embodiment, the present invention discloses a method for preparation of said cathode active material of Formula (I), the method comprising:

i. Preparing separately the solution of the base metal Ni, Fe and Mn salts in their respective stoichiometric ratios and the solution of mixture of ammonium hydroxide and alkali hydroxide selected from the group consisting of sodium hydroxide, lithium hydroxide, potassium hydroxide, or mixtures thereof;

ii. Mixing the above two solutions simultaneously into a fixed volume stirred reactor at suitable feed rates adjusted to maintain a pH of 10.5 to 11.5 and temperature between 45°C to 55°C followed by ageing under stirred condition to allow homogenous particle formation of the precipitated ternary hydroxides and drying to obtain the precursor powder;

iii. Intimately mixing together the obtained precursor powder of step (ii) with stoichiometric quantities of alkali salts and ceria and pressing into a pellet;

iv. Heating the resulting mixture in a furnace under a suitable atmosphere comprising ambient air, or under the atmosphere of pure oxygen, wherein the gas may be flowing, if desired, at a single temperature or over a range of temperatures between 450°C and 900°C until reaction product forms; and optionally

v. Allowing the product to cool before grinding it to a powder.

In an embodiment, the preferred alkali metal hydroxide is sodium hydroxide which is cheap and adds to the cost effectiveness of the process.

The Table 1 below lists the starting materials and experimental conditions used to prepare a known (comparative) composition (Example 1) and the Target Active Materials of the present invention (Examples 2 to 4).

Table 1:

1	$Na_1Ni_{0.333}Fe_{0.333}Mn_{0.333}O_2$	1 NaOH 0.333 NiO, 0.333Fe_2O_3, 0.333 $MnCO_3$	850°C, Oxygen Dwell: 12 Hrs Ramp Rate: 10°C/min
2	$Na_{0.95}K_{0.05}Ni_{0.327}Fe_{0.327}Mn_{0.327}Ce_{0.01}O_2$	0.475 Na_2CO_3, 0.025 K_2CO_3, 0.327$NiSO_4$, 0.327FeSO4, 0.327 MnSO4, 0.01 CeO_2	850°C, Oxygen Dwell: 12 Hrs Ramp Rate: 10°C/min
3	$Na_{0.95}K_{0.05}Ni_{0.323}Fe_{0.323}Mn_{0.323}Ce_{0.02}O_2$	0.475 Na_2CO_3, 0.025 K_2CO_3, 0.323 $NiSO_4$, 0.323 FeSO4, 0.323 MnSO4,	850°C, Oxygen Dwell: 12 Hrs Ramp Rate: 10°C/min

		$0.02CeO_2$	
4	$Na_{0.95}K_{0.05}Ni_{0.313}Fe_{0.313}Mn_{0.313}Ce_{0.05}O_2$	0.475 Na_2CO_3, 0.025 K_2CO_3, 0.313 $NiSO_4$, 0.313 FeSO4, 0.313 MnSO4, 0.05 CeO_2	850°C, Oxygen Dwell: 12 Hrs Ramp Rate: 10°C/min

In another embodiment, the present invention describes cathode active material of Formula (I), in conjunction with a counter electrode and one or more electrolytes in energy storage devices.

In another embodiment, the present invention provides alkali-ion electrochemical cell comprising;

(i) the cathode consisting of ceria doped mixed cation active material of the formula (I);

$$A_{(1-b)}B_b[Ni_{0.33}Fe_{0.33}Mn_{0.33}]_{(1-x)}Ce_xO_2$$ (**Formula I)**

wherein

'A' comprises one or more alkali metals selected from lithium, sodium, potassium and cesium;

'B' comprises one or more alkali metals selected from lithium, sodium, potassium and cesium;

Ni is nickel in oxidation state 2+,

Fe is iron in oxidation state 3+,

Mn is manganese in oxidation state 4+,

Ce is ceria in oxidation state 3+, and

wherein

$0.01 \leq b \leq 0.4$, preferably $0.01 \leq b \leq 0.25$, further preferably $0.01 \leq b \leq 0.1$,

$0.01 \leq x \leq 0.25$, preferably $0.01 \leq x \leq 0.15$ and ideally $0.01 \leq x \leq 0.1$;

(ii) the anode consisting of hard anode ;

(iii) the separator; and

(iv) the non-aqueous electrolyte selected from 0.5M solution of $NaPF_6$ and 0.3M solution of KPF_6 in a mixture of Ethyl Methyl Carbonate, Propylene Carbonate and Fluoroethylene Carbonate (EMC:PC:FEC) in a ratio of1.2:0.8:0.1.

In an embodiment, the ceria doped mixed cation cathode active material in said electrochemical cell comprises the O3 structure of the formed compound doped with larger alkali ions that results in enlarged interlayer spacing, providing larger channels for ion movement; the +3 doped ceria reinforce the structure and prohibits phase transitions and the degradation over multiple cycles.

In yet another embodiment, the charge-discharge profile of the present electrode active material of Formula (I) exhibits smooth discharging curve from 4V to 2V when used as the cathode in energy storage devices comprising hard carbon as anode and the electrolyte comprising of 0.5M solution of $NaPF_6$ and 0.3M solution of KPF_6 in a mixture of Ethyl Methyl Carbonate, Propylene Carbonate and Fluoroethylene Carbonate (EMC:PC:FEC) in a ratio of 1:1:0.1.

Accordingly, during cell charging process, host ions comprising the larger alkali metal ions migrate from the electrolyte and cathode, and are inserted into the Hard Carbon anode, increasing the gallery height of the said carbon anode layers, thereby helping in unimpeded movement of the smaller host ions, leading to better capacity retention across multiple cycles in the cell comprising the said cathode, a standard anode, and an electrolyte. The nickel ions are oxidized from +2 to +4oxidation state when the cations are deintercalated from the cathode along with a small contribution from the Fe3+ to Fe4+oxidation state during charging and are responsible for majority of the capacity. The capacity contribution of Manganese is insignificant and is only seen below 3V as a sloping curve. During the

subsequent discharge process, said host ions are extracted from the Hard Carbon and re-inserted into the cathode active material.

In yet another embodiment, the voltage profile of the present electrode material of Formula (I) shows a smooth linear curve from 4V to 2V with a slight plateau around 2.9V, which is repeatable between voltage cutoffs of about 2.0V to about 4.0V indicating that the active material of Formula (I) retains its structure during the entire charge –discharge cycles.

In an embodiment, the ceria doped mixed cationic cathode active material of the present invention shows the specific capacity of about 125mAh/gm and is stable up to about 20 cycles at 2 to4V.

In a preferred embodiment, the present invention discloses the alkali ion-electrochemical cell with little or no fading cycling comprising;

(i) $Na_{0.95}K_{0.05}Ni_{0.323}Fe_{0.323}Mn_{0.323}Ce_{0.02}O_2$ as cathode active material;

(ii) Hard Carbon as anode material;

(iii) A separator between the positive electrode and negative electrode; and

(iv) 0.5 M solution of $NaPF_6$ and 0.3 M solution of KPF_6 in a mixture of Ethyl Methyl Carbonate, Propylene Carbonate and Fluoroethylene Carbonate (EC: DEC:FEC) in a ratio of 1.2:0.8:0.1 as electrolyte.

In an embodiment, the cathode active material of Formula (I) of the present invention find application in alkali ion-cell, in energy storage devices such as batteries, rechargeable batteries, electrochemical devices and electrochromic devices, with said cathode active material of Formula (I) arranged in series, parallel, or both.

Examples:

The following examples which include the preferred embodiments of the invention, will serve to illustrate the practice of this invention, it being understood that the particulars shown are by way of example and for purpose of illustrative discussion of preferred embodiments of the invention and are therefore not to be construed to be limiting the scope of the invention. The results obtained in the experimental examples are confirmed by way of analysis as depicted in the drawings, namely, figure 1 to figure 4.

The present invention and the advantages of the present invention are illustrated by way of experimental examples.

Example 1:Composites of $Na_1Ni_{0.333}Fe_{0.333}Mn_{0.333}O_2$

The composite $Na_1Ni_{0.333}Fe_{0.333}Mn_{0.333}O_2$ was used as a cathode active material, along with hard carbon as anode material. Further, 0.5M solution of $NaPF_6$ in a mixture of ethyl methyl carbonate, propylene carbonate and fluoroethylene carbonate (EMC:PC:FEC) in a ratio of 1.2:0.8:0.1 was employed as electrolyte.

The cells were formed at 0.1C rate and post formation, were run at 0.5C rate. To ensure that the cell was fully charged, the cell was potentiostatically held at 4 V at the end of the constant current charging process for 1 hour during the formation cycling. For the rest of the tests after the formation cycling, cells were only held for 1 minute potentiostatically at 4V to ensure full desaturation of the cathode. The testing was carried out at 25°C.

During the cell charging process, sodium ions were extracted from the cathode active material, and inserted into the Hard Carbon anode. During the subsequent discharge process, sodium ions were extracted from the Hard Carbon and re-inserted into the cathode active material.

The constant current cycling graphs are plotted in **Figure 1(a)** and **Figure 1(b)**.

Figure 1 (a) illustrates the cell voltage profile. The graphical illustration in Figure 1(a) shows cellvoltage (V) versus cathode specific capacity [mAh/g]) for the first five charge/discharge cycles of the cell having $Na_1Ni_{0.333}Fe_{0.333}Mn_{0.333}O_2$ used as cathode active material, and hard carbon as anode material.

Figure 1 (b) shows the constant current cycle life profile, i.e. the relationship between cathode specific capacity for discharge (mAh/g) and cycle number for hard carbon as anode material and$Na_1Ni_{0.333}Fe_{0.333}Mn_{0.333}O_2$ as cathode material. For the first cycle, the discharge specific capacity for the cathode is about 111mAh/g. For the twentieth cycle, the discharge specific capacity for the cathode is about 97 mAh/g. Therefore, it is evident that there occurs a capacity fade of about 12.6 % over 20 cycles, or an average of 0.63 % per cycle. The cathode material of this example demonstrates relatively poor capacity retention behavior.

Example 2: Composites $Na_{0.95}K_{0.05}Ni_{0.327}Fe_{0.327}Mn_{0.327}Ce_{0.01}O_2$ as cathode material

In this example, the cathode active material composite is selected as $Na_{0.95}K_{0.05}Ni_{0.327}Fe_{0.327}Mn_{0.327}Ce_{0.01}O_2$ whereas the anode material is hard carbon. The electrolyte used is a 0.5M solution of $NaPF_6$ and 0.3M solution of KPF_6 in a mixture of Ethyl Methyl Carbonate, Propylene Carbonate and Fluoroethylene Carbonate (EMC:PC:FEC) in a ratio of 1.2:0.8:0.1.The cells were formed at 0.1C rate and post formation, were run at 0.5C rate. To ensure that the cell was fully charged, the cell was potentiostatically held at 4 V at the end of the constant current charging process for 1 hour during the formation cycle. For the rest of the tests after the formation cycle, cells were only held for 1 minute potentiostatically at 4V to ensure full desaturation of the cathode. The testing was carried out at 25°C.During the cell charging process, host cations i.e., sodium and potassium are extracted from the cathode active material and inserted into the anode made of hard carbon. During the subsequent discharge process, said host ions are extracted from the hard carbon and re-inserted into the cathode active material.

Figure 2 (a) shows the cell voltage profile, which is a graph of cell voltage (V) versus cathode specific capacity (mAh/g) for the first five charge/discharge cycles of the cathode active material composite and anode material of the present example.

Figure 2 (b) shows the constant current cycle life profile, which is a graphical relationship between cathode specific capacity for discharge (mAh/g) and cycle number for the cell having composite as mentioned herein. For cycle 1, the discharge specific capacity for the cathode is about118 mAh/g. For cycle 20, the discharge specific capacity for the cathode is about 108 mAh/g. This represents a capacity fade of about 8 % over 20 cycles or an average of 0.4% per cycle. The cathode material under test clearly demonstrates relatively better capacity retention behavior.

Example 3: Composite of $Na_{0.95}K_{0.05}Ni_{0.323}Fe_{0.323}Mn_{0.323}Ce_{0.02}O_2$as cathode active material

In the present example, the composite of $Na_{0.95}K_{0.05}Ni_{0.323}Fe_{0.323}Mn_{0.323}Ce_{0.02}O_2$ is used as cathode active material, whereas hard carbon is used as anode material. The electrolyte used was a 0.5M solution of $NaPF_6$ and 0.3M solution of KPF_6 in a mixture of Ethyl Methyl Carbonate, Propylene Carbonate and Fluoroethylene Carbonate (EMC:PC:FEC) in a ratio of 1.2:0.8:0.1. The cells were formed at 0.1C rate and post formation, were run at 0.5C rate. To ensure that the cell was fully charged, the cell was potentiostatically held at 4 V at the end of the constant current charging process for 1 hour during the formation cycle. For the rest of the tests after the formation cycle, cells were only held for 1 minute potentiostatically at 4V to ensure full desaturation of the cathode. The testing was carried out at 25°C.

During the cell charging process, the host ions are extracted from the cathode active material and inserted into the hard carbon anode. During the subsequent

discharge process, host ions are extracted from the hard carbon and re-inserted into the cathode active material.

Figure 3 (a) shows the cell voltage profile, which is a graphical representation of cell voltage (V) versus cathode specific capacity (mAh/g) for the first five charge/discharge cycles of the cell with the present composites.

Figure 3 (b) shows the constant current cyclelife profile, which shows the relationship between cathode specific capacity for discharge (mAh/g) and cycle number for the cell having composites of the present example. For cycle 1, the discharge specific capacity for the cathode is about 121mAh/g. For cycle 20, the discharge specific capacity for the cathode is about 112.5mAh/g. This represents a capacity fade of about 7 % over 20 cycles or an average of 0.35% per cycle. It may be concluded that the cell having cathode active material of the present example demonstrates relatively better capacity retention behavior.

Example 4: Composite of $Na_{0.95}K_{0.05}Ni_{0.313}Fe_{0.313}Mn_{0.313}Ce_{0.05}O_2$as cathode active material

In this example, $Na_{0.95}K_{0.05}Ni_{0.313}Fe_{0.313}Mn_{0.313}Ce_{0.05}O_2$ is employed as cathode active material whereas hard carbon is employed as anode material. The electrolyte used was a 0.5M solution of $NaPF_6$ and 0.3M solution of KPF_6 in a mixture of Ethyl Methyl Carbonate, Propylene Carbonate and Fluoroethylene Carbonate (EMC:PC:FEC) in a ratio of 1.2:0.8:0.1. The cells were formed at 0.1C rate and post formation, were run at 0.5C rate. To ensure that the cell was fully charged, the cell was potentiostatically held at 4V at the end of the constant current charging process for 1 hour during the formation cycle. For the rest of the tests after the formation cycle, cells were only held for 1 minute potentiostatically at 4V to ensure full desaturation of the cathode. The testing was carried out at 25°C.

During the cell charging process, the host ions are extracted from the cathode active material, and inserted into the hard carbon anode. During the subsequent discharge process, the host ions were extracted from the hard carbon and re-inserted into the cathode active material.

Figure 4 (a) shows the cell voltage profile, that is graphical representation ofcell voltage (V) versus cathode specific capacity (mAh/g) for the first five charge/discharge cycles of the composites of the example 4.

Figure 4 (b) shows the relationship between cathode specific capacity for discharge (mAh/g) and cycle number for the composites of the present example. For cycle 1, the discharge specific capacity for the cathode is about 124 mAh/g. For cycle 20, the discharge specific capacity for the cathode is about118 mAh/g. This represents a capacity fade of about 5 % over 20 cycles or an average of 0.25% per cycle. The aforesaid cathode active material exhibits much better capacity retention behavior than the previous composites.

Although the invention has been described in detail in the foregoing for the purpose of illustration, it is to be understood that such detail is solely for that purpose and that variations can be made therein by those skilled in the art without departing from the spirit and scope of the invention except as it may be limited by the claims.

We claim,

1. Ceria doped mixed cationic cathode active material of formula (I)

$$A_{(1-b)}B_b[Ni_{0.33}Fe_{0.33}Mn_{0.33}]_{(1-x)}Ce_xO_2 \quad \textbf{(Formula I)}$$

wherein

'A' comprises one or more alkali metals selected from lithium, sodium, potassium and cesium;

'B' comprises one or more alkali metals selected from lithium, sodium, potassium and cesium;

Ni is nickel in oxidation state 2+,

Fe is iron in oxidation state 3+,

Mn is manganese in oxidation state 4+,

Ce is ceria in oxidation state 3+, and

wherein

$0.01 \leq b \leq 0.4$, preferably $0.01 \leq b \leq 0.25$, further preferably $0.01 \leq b \leq 0.1$,

$0.01 \leq x \leq 0.25$, preferably $0.01 \leq x \leq 0.15$ and ideally $0.01 \leq x \leq 0.1$, and

wherein the said cathode active material possesses high specific capacity with little or no fading on cycling.

2. The ceria doped cathode active material as claimed in claim 1 comprising;

$Na_{0.95}K_{0.05}Ni_{0.327}Fe_{0.327}Mn_{0.327}Ce_{0.01}O_2$,

$Na_{0.95}K_{0.05}Ni_{0.323}Fe_{0.323}Mn_{0.323}Ce_{0.02}O_2$,

$Na_{0.95}K_{0.05}Ni_{0.313}Fe_{0.313}Mn_{0.313}Ce_{0.05}O_2$.

3. The ceria doped cathode active material as claimed in claim 1, wherein said active material is prepared by the process comprising:

   i. Preparing separately the solution of the base metal Ni, Fe and Mn salts in their respective stoichiometric ratios and the solution of mixture of ammonium hydroxide and alkali hydroxide selected from the group consisting of sodium hydroxide, lithium hydroxide, potassium hydroxide, or mixtures thereof;

ii. Mixing the above two solutions simultaneously into a fixed volume stirred reactor at suitable feed rates adjusted to maintain a pH of 10.5 to 11.5 and temperature between 45 to 55ºC followed by ageing under stirred condition to allow homogenous particle formation of the precipitated ternary hydroxides and drying to obtain the precursor powder;

iii. Intimately mixing together the precursor powder of step (iv) with stoichiometric quantities of alkali salts and ceria and pressing into a pellet;

iv. Heating the resulting mixture in a furnace under a suitable atmosphere comprising ambient air, or under the atmosphere of pure oxygen, wherein the gas may be flowing, at a single temperature or over a range of temperatures between 450°C and 900°C until reaction product forms; and optionally;

v. Allowing the product to cool before grinding it to a powder.

4. The ceria doped cathode active material as claimed in any of the claims 1 to 3, wherein said cathode active material is in conjunction with a counter electrode and one or more electrolytes in energy storage devices.

5. The ceria doped cathode active material as claimed in any of the claims 1 to 4 for use in alkali ion-cell, in energy storage devices such as batteries, rechargeable batteries, electrochemical devices and electrochromic devices.

6. An alkali-ion electrochemical cell with high specific capacity and with little or no fading on cyclingcomprising:

(i) hard carbon as an anode;

(ii) a cathode containing the ceria doped mixed cation active material of Formula (I) as claimed in any of the claims 1 to 5;

(iii) a separator comprising polypropylene; and

(iv) an electrolyte comprising 0.5 M solution of $NaPF_6$ and 0.3 M solution of KPF_6 in a mixture of Ethyl Methyl Carbonate, Propylene Carbonate and Fluoroethylene Carbonate (EMC:PC:FEC) in a ratio of 1.2:0.8:0.1.

Dated this 28th day of June, 2022

Dr. P. Aruna Sree
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Agent for the Applicant
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CERIA DOPED MIXED CATIONIC CATHODE ACTIVE MATERIAL

ABSTRACT:

The present invention relates to ceria doped mixed cationic cathodes for energy devices notably non-aqueous re-chargeable alkali-ion electrochemical cells and batteries and to the process of preparation thereof. More particularly, the present invention relates to doped cathode active materials of Formula (I) that shows little or no fading on cycling, which is able to be recharged multiple times without significant loss in charge capacity.

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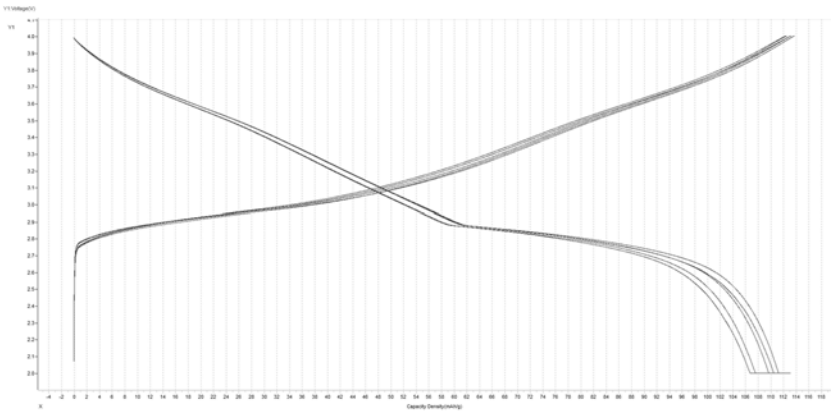


Figure 1(a)

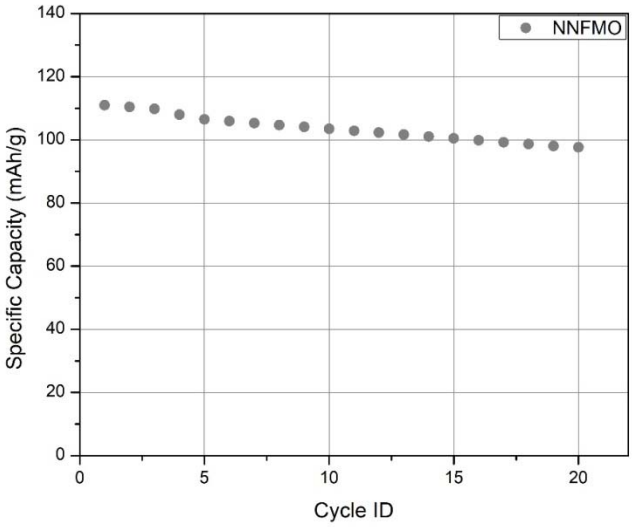


Figure 1(b)

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Applicant: GEGADYNE ENERGY LABS PRIVATE LIMITED	Total no. of Sheets: 04
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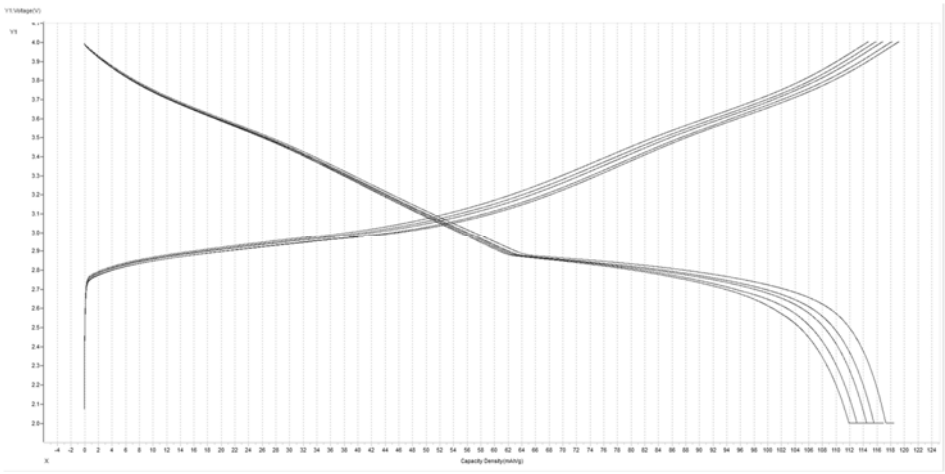


Figure 2(a)

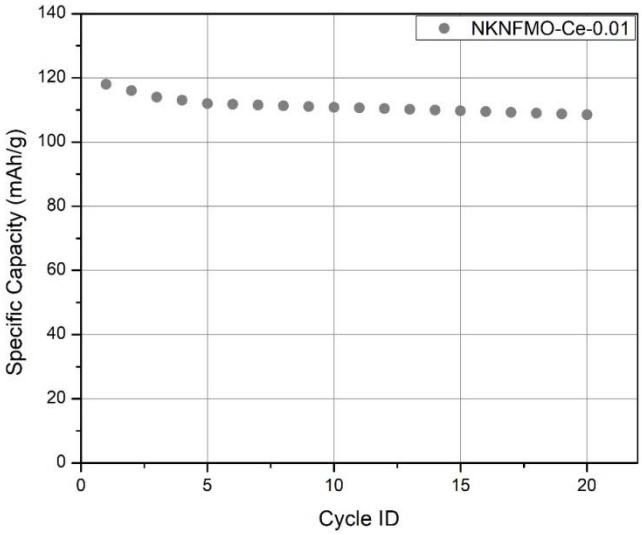


Figure 2(b)

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Applicant: GEGADYNE ENERGY LABS PRIVATE LIMITED	Total no. of Sheets: 04
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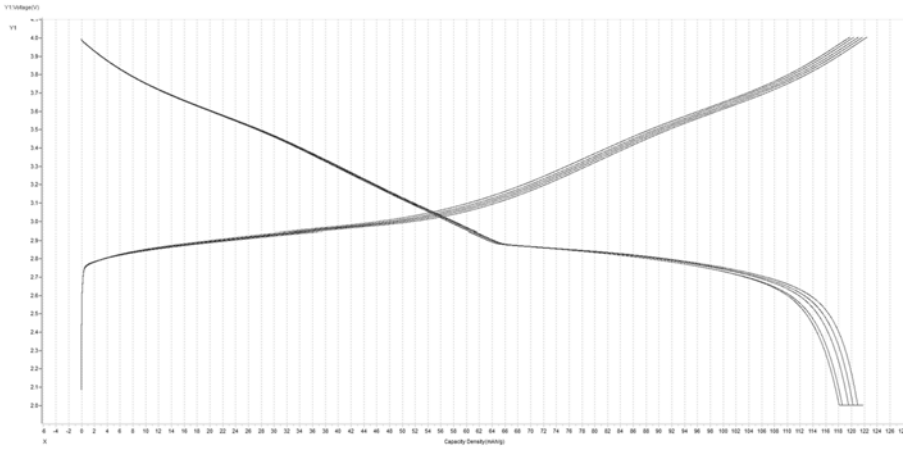


Figure 3(a)

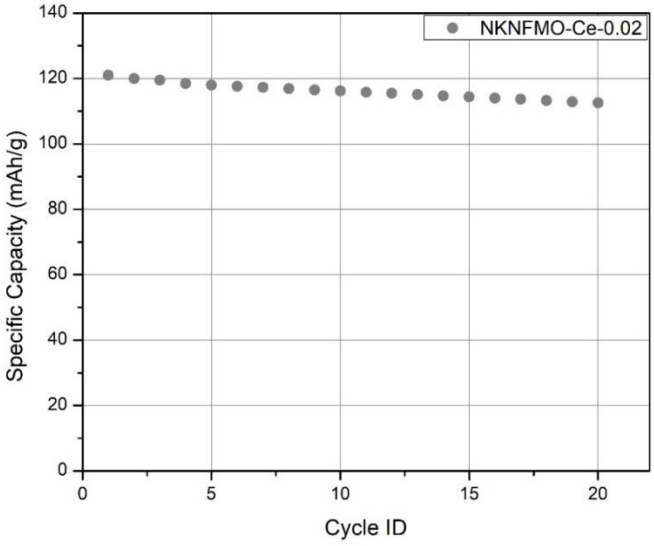


Figure 3(b)

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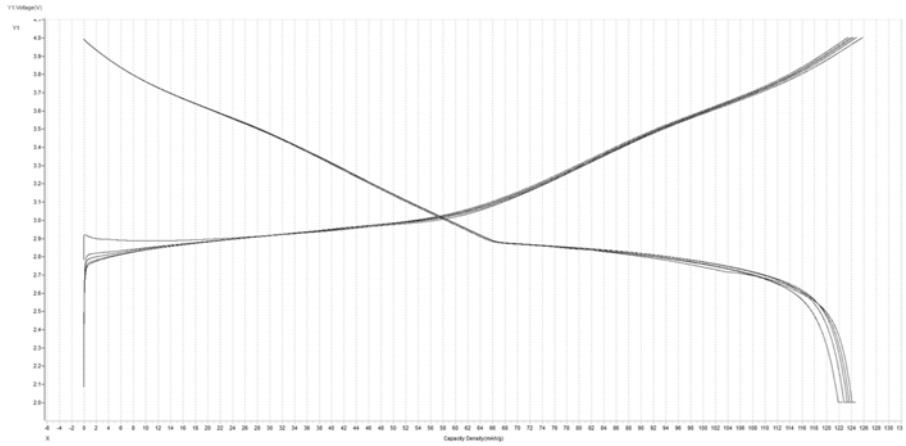


Figure 4(a)

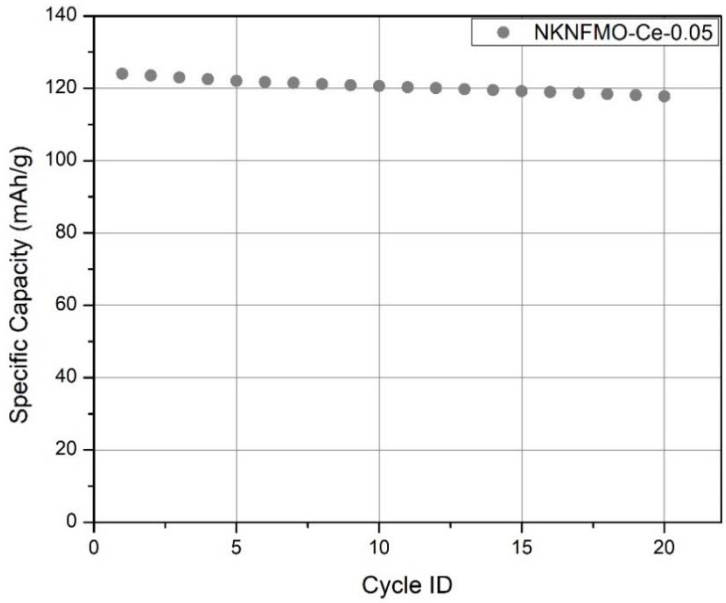


Figure 4(b)

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