Supplementary Information

Synergistic effect of multi-transition metal co-substitution in high cycle life performance of $Na_xCo_{0.5}Fe_{0.25}Mn_{0.25}O_2$ cathode for sodium-ion batteries

Jena Akash Kumar Satrughna[χ], Archana R. Kanwade[ψ], and Parasharam M. Shirage[*,ψ]

[χ]*Department of Physics, Indian Institute of Technology Indore, Indore-453552, MP, India*

[ψ]*Department of Metallurgical Engineering and Materials Science, Indian Institute of Technology Indore, Indore-453552, MP, India*

[*]***Corresponding author contact details:*** pmshirage@iiti.ac.in, paras.shirage@gmail.com

S1. CIF file of $Na_{0.6}CoO_2$ used for structural refinement of XRD peak indexing.

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#------------------------------------------------------------------------------
#$Date: 2016-02-13 21:28:24 +0200 (Sat, 13 Feb 2016) $
#$Revision: 176429 $
#$URL: file:///home/coder/svn-repositories/cod/cif/1/52/91/1529124.cif $
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#
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#
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data_1529124
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_publ_author_name
'Fouassier, C.'
'Matejka, G.'
'Reau, J.M.'
'Hagenmuller, P.'
_publ_section_title
;
 Sur de Nouveaux Bronzes Oxygenes de Formule Nax Co O2 (x below or equal
 to 1). Le Systeme Cobalt-Oxygene-Sodium
;
_journal_name_full              'Journal of Solid State Chemistry'
_journal_page_first             532
_journal_page_last              537
_journal_volume                 6
_journal_year                   1973
_chemical_formula_sum           'Co Na0.6 O2'
_chemical_name_systematic       'Na.60 Co O2'
_space_group_IT_number          160
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_symmetry_space_group_name_H-M   'R 3 m :H'
_cell_angle_alpha               90
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_cell_angle_gamma               120
_cell_formula_units_Z           3
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_cell_length_c                  16.53
_cell_volume                    114.732
_citation_journal_id_ASTM       JSSCBI
_cod_data_source_file           Fouassier_JSSCBI_1973_54.cif
_cod_data_source_block          Co1Na0.6O2
_cod_original_cell_volume       114.7317
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_cod_database_code 1529124
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-x+y,-x,z
-y,-x,z
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-y+2/3,x-y+1/3,z+1/3
-x+y+2/3,-x+1/3,z+1/3
-y+2/3,-x+1/3,z+1/3
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-x+y+2/3,y+1/3,z+1/3
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-y+1/3,x-y+2/3,z+2/3
-x+y+1/3,-x+2/3,z+2/3
-y+1/3,-x+2/3,z+2/3
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-x+y+1/3,y+2/3,z+2/3
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_atom_site_label
_atom_site_type_symbol
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
_atom_site_occupancy
_atom_site_U_iso_or_equiv
O2 O 0 0 0.618 1 0.0
O1 O 0 0 0.382 1 0.0
Co1 Co 0 0 0 1 0.0
Na1 Na 0 0 0.836 0.6 0.0

S2. CIF file of $NaMnO_2$ used for structural refinement of XRD peak indexing.

generated using pymatgen

data_NaMnO2

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_cell_length_b 3.09861044

_cell_length_c 10.89813200

_cell_angle_alpha 90.00000000

_cell_angle_beta 90.00000000

_cell_angle_gamma 120.00000000

_symmetry_Int_Tables_number 194

_chemical_formula_structural NaMnO2

_chemical_formula_sum 'Na2 Mn2 O4'

_cell_volume 90.61845555

_cell_formula_units_Z 2

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_symmetry_equiv_pos_site_id

_symmetry_equiv_pos_as_xyz

1 'x, y, z'

2 '-x, -y, -z'

3 'x-y, x, z+1/2'

4 '-x+y, -x, -z+1/2'

5 '-y, x-y, z'

6 'y, -x+y, -z'

7 '-x, -y, z+1/2'

8 'x, y, -z+1/2'

9 '-x+y, -x, z'

10 'x-y, x, -z'

11 'y, -x+y, z+1/2'

12 '-y, x-y, -z+1/2'

13 '-y, -x, -z+1/2'

14 'y, x, z+1/2'

15 '-x, -x+y, -z'

16 'x, x-y, z'

17 '-x+y, y, -z+1/2'

18 'x-y, -y, z+1/2'

19 'y, x, -z'

20 '-y, -x, z'

21 'x, x-y, -z+1/2'

22 '-x, -x+y, z+1/2'

23 'x-y, -y, -z'

24 '-x+y, y, z'

loop_

_atom_type_symbol

_atom_type_oxidation_number

Na+ 1.0

Mn3+ 3.0

O2- -2.0

loop_

_atom_site_type_symbol

_atom_site_label

_atom_site_symmetry_multiplicity

_atom_site_fract_x

_atom_site_fract_y

_atom_site_fract_z

_atom_site_occupancy

Na+ Na0 2 0.33333333 0.66666667 0.75000000 1

Mn3+ Mn1 2 0.00000000 0.00000000 0.00000000 1

O2- O2 4 0.33333333 0.66666667 0.40169600 1

S3. CIF file of $Na_{0.61}CoO_2$ used for structural refinement of XRD peak indexing.

#--

#$Date: 2016-02-13 21:28:24 +0200 (Sat, 13 Feb 2016) $

#$Revision: 176429 $

#$URL: file:///home/coder/svn-repositories/cod/cif/1/53/29/1532937.cif $

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_publ_author_name
'Jorgensen, J.D.'
'Avdeev, M.'
'Hinks, D.G.'
'Short, S.'
'Burley, J.C.'
_publ_section_title
;
 Crystal structure of the sodium cobaltate deuterate superconductor Nax Co
 O2 * 4x(D2 O)
;
_journal_name_full
'Physical Review, Serie 3. B - Condensed Matter (18,1978-)'
_journal_page_first             214517-1
_journal_page_last              214517-10
_journal_volume                 68
_journal_year                   2003
_chemical_formula_sum           'Co Na0.61 O2'
_chemical_name_systematic       'Na0.61 (Co O2)'
_space_group_IT_number          194
_symmetry_space_group_name_Hall  '-P 6c 2c'
_symmetry_space_group_name_H-M   'P 63/m m c'
_cell_angle_alpha               90
_cell_angle_beta                90
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_cell_angle_gamma 120

_cell_formula_units_Z 2

_cell_length_a 2.83176

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_cell_length_c 10.8431

_cell_volume 75.300

_citation_journal_id_ASTM PRBMDO

_cod_data_source_file Jorgensen_PRBMDO_2003_1978.cif

_cod_data_source_block Co1Na0.61O2

_cod_original_cell_volume 75.30034

_cod_original_formula_sum 'Co1 Na0.61 O2'

_cod_database_code 1532937

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_symmetry_equiv_pos_as_xyz

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x-y,x,z+1/2

-y,x-y,z

-x,-y,z+1/2

-x+y,-x,z

y,-x+y,z+1/2

-y,-x,-z+1/2

x-y,-y,-z

x,x-y,-z+1/2

y,x,-z

-x+y,y,-z+1/2

-x,-x+y,-z

-x,-y,-z

-x+y,-x,-z-1/2

y,-x+y,-z

x,y,-z-1/2

x-y,x,-z

-y,x-y,-z-1/2

y,x,z-1/2

-x+y,y,z

-x,-x+y,z-1/2

-y,-x,z

x-y,-y,z-1/2

x,x-y,z

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_atom_site_fract_x

_atom_site_fract_y

_atom_site_fract_z

_atom_site_occupancy

_atom_site_U_iso_or_equiv

Na2 Na+1 0 0 0.25 0.171 0.0

Co1 Co+3 0 0 0 1 0.0

O1 O-2 0.3333 0.6667 0.09057 1 0.0

Na1 Na+1 0.577 0.2885 0.25 0.146 0.0

S4. CIF file of $Na_xCo_{0.5}Fe_{0.25}Mn_{0.25}O_2$ from structural refinement.

```
#======================================================================

# CRYSTAL DATA

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_chemical_name_common                  'sir '
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_cell_length_c                         16.633499
_cell_angle_alpha                      90.000000
_cell_angle_beta                       90.000000
_cell_angle_gamma                      120.000000
_cell_volume                           116.198316
_space_group_name_H-M_alt              'R 3 m'
_space_group_IT_number                 160


loop_
_space_group_symop_operation_xyz
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   '-y, x-y, z'
   '-x+y, -x, z'
   '-y, -x, z'
   '-x+y, y, z'
   'x, x-y, z'
   'x+2/3, y+1/3, z+1/3'
   '-y+2/3, x-y+1/3, z+1/3'
   '-x+y+2/3, -x+1/3, z+1/3'
   '-y+2/3, -x+1/3, z+1/3'
   '-x+y+2/3, y+1/3, z+1/3'
   'x+2/3, x-y+1/3, z+1/3'
   'x+1/3, y+2/3, z+2/3'
   '-y+1/3, x-y+2/3, z+2/3'
```

'-x+y+1/3, -x+2/3, z+2/3'

'-y+1/3, -x+2/3, z+2/3'

'-x+y+1/3, y+2/3, z+2/3'

'x+1/3, x-y+2/3, z+2/3'

loop_

_atom_site_label

_atom_site_occupancy

_atom_site_fract_x

_atom_site_fract_y

_atom_site_fract_z

_atom_site_adp_type

_atom_site_U_iso_or_equiv

_atom_site_type_symbol

O2 1.0 0.000000 0.000000 0.618000 Uiso 0.063320 O

O1 0.9264 0.000000 0.000000 0.382000 Uiso 0.063320 O

Co1 0.5016 0.000000 0.000000 0.000000 Uiso 0.063320 Co

Mn1 0.2506 0.000000 0.000000 0.000000 Uiso 0.063320 Mn

Fe1 0.2413 0.000000 0.000000 0.000000 Uiso 0.063320 Fe

Na1 0.6522 0.000000 0.000000 0.843800 Uiso 0.063320 Na

#==

CRYSTAL DATA

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_cell_angle_gamma 120.000000

_cell_volume 91.494279

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_space_group_IT_number                 194

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_space_group_symop_operation_xyz
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   '-x, -y, -z'
   '-y, x-y, z'
   'y, -x+y, -z'
   '-x+y, -x, z'
   'x-y, x, -z'
   '-x, -y, z+1/2'
   'x, y, -z+1/2'
   'y, -x+y, z+1/2'
   '-y, x-y, -z+1/2'
   'x-y, x, z+1/2'
   '-x+y, -x, -z+1/2'
   'y, x, -z'
   '-y, -x, z'
   'x-y, -y, -z'
   '-x+y, y, z'
   '-x, -x+y, -z'
   'x, x-y, z'
   '-y, -x, -z+1/2'
   'y, x, z+1/2'
   '-x+y, y, -z+1/2'
   'x-y, -y, z+1/2'
   'x, x-y, -z+1/2'
   '-x, -x+y, z+1/2'

loop_
   _atom_site_label
   _atom_site_occupancy
   _atom_site_fract_x
```

```
  _atom_site_fract_y
  _atom_site_fract_z
  _atom_site_adp_type
  _atom_site_U_iso_or_equiv
  _atom_site_type_symbol
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  Mn1       0.0368  0.000000     0.000000     0.000000    Uiso  0.106240 Mn
  Co1       0.0650  0.000000     0.000000     0.000000    Uiso  0.106240 Co
  Fe1       -0.0204 0.000000     0.000000     0.000000    Uiso  0.106240 Fe
  O2        1.0561  0.333333     0.666667     0.401700    Uiso  0.106240 O
#=============================================================================
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_cell_length_b                         2.839500
_cell_length_c                         10.761900
_cell_angle_alpha                      90.000000
_cell_angle_beta                       90.000000
_cell_angle_gamma                      120.000000
_cell_volume                           75.145558
_space_group_name_H-M_alt              'P 63/m m c'
_space_group_IT_number                 194

loop_
_space_group_symop_operation_xyz
  'x, y, z'
  '-x, -y, -z'
  '-y, x-y, z'
  'y, -x+y, -z'
  '-x+y, -x, z'
  'x-y, x, -z'
```

'-x, -y, z+1/2'

'x, y, -z+1/2'

'y, -x+y, z+1/2'

'-y, x-y, -z+1/2'

'x-y, x, z+1/2'

'-x+y, -x, -z+1/2'

'y, x, -z'

'-y, -x, z'

'x-y, -y, -z'

'-x+y, y, z'

'-x, -x+y, -z'

'x, x-y, z'

'-y, -x, -z+1/2'

'y, x, z+1/2'

'-x+y, y, -z+1/2'

'x-y, -y, z+1/2'

'x, x-y, -z+1/2'

'-x, -x+y, z+1/2'

loop_

_atom_site_label

_atom_site_occupancy

_atom_site_fract_x

_atom_site_fract_y

_atom_site_fract_z

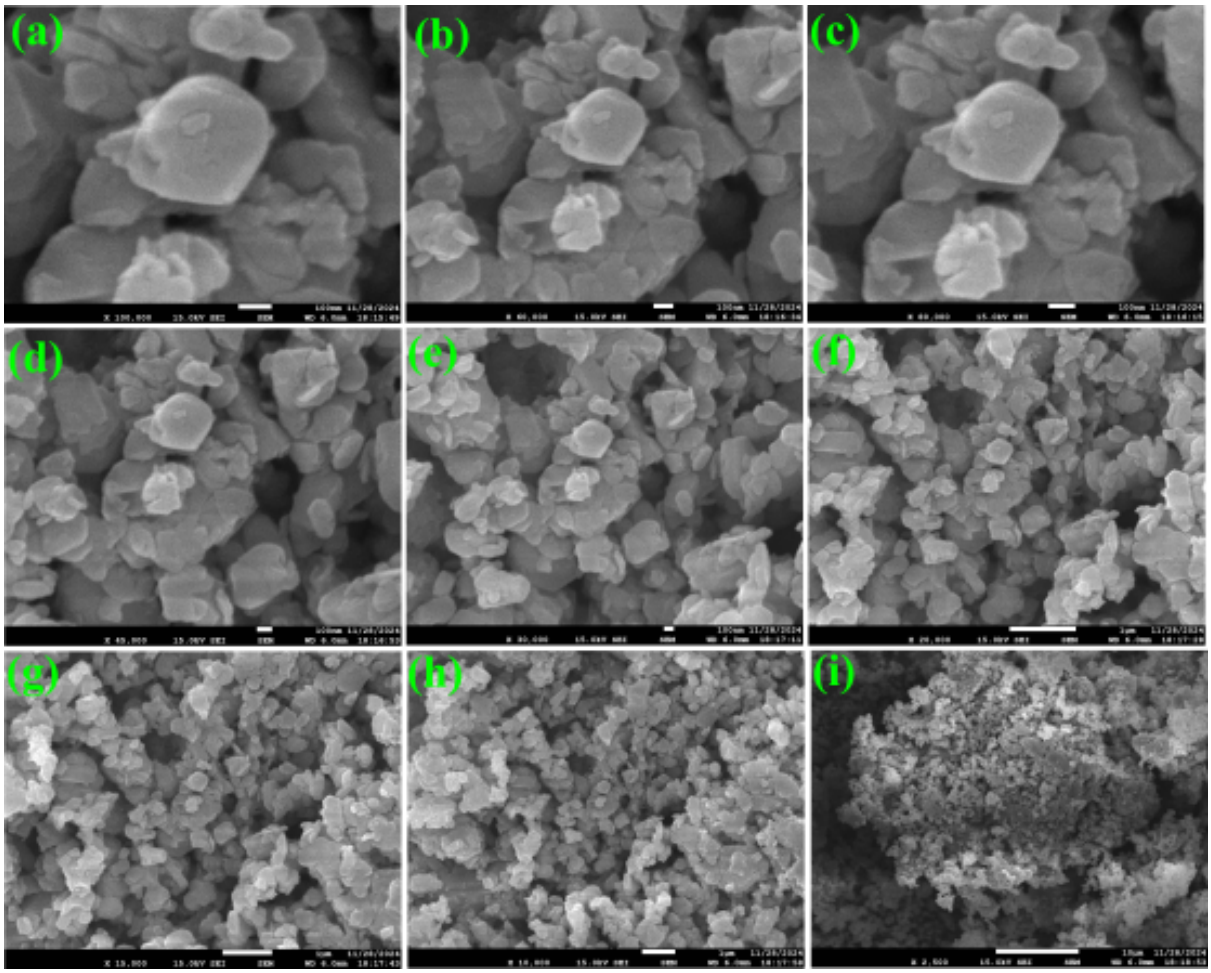
_atom_site_adp_type

_atom_site_U_iso_or_equiv

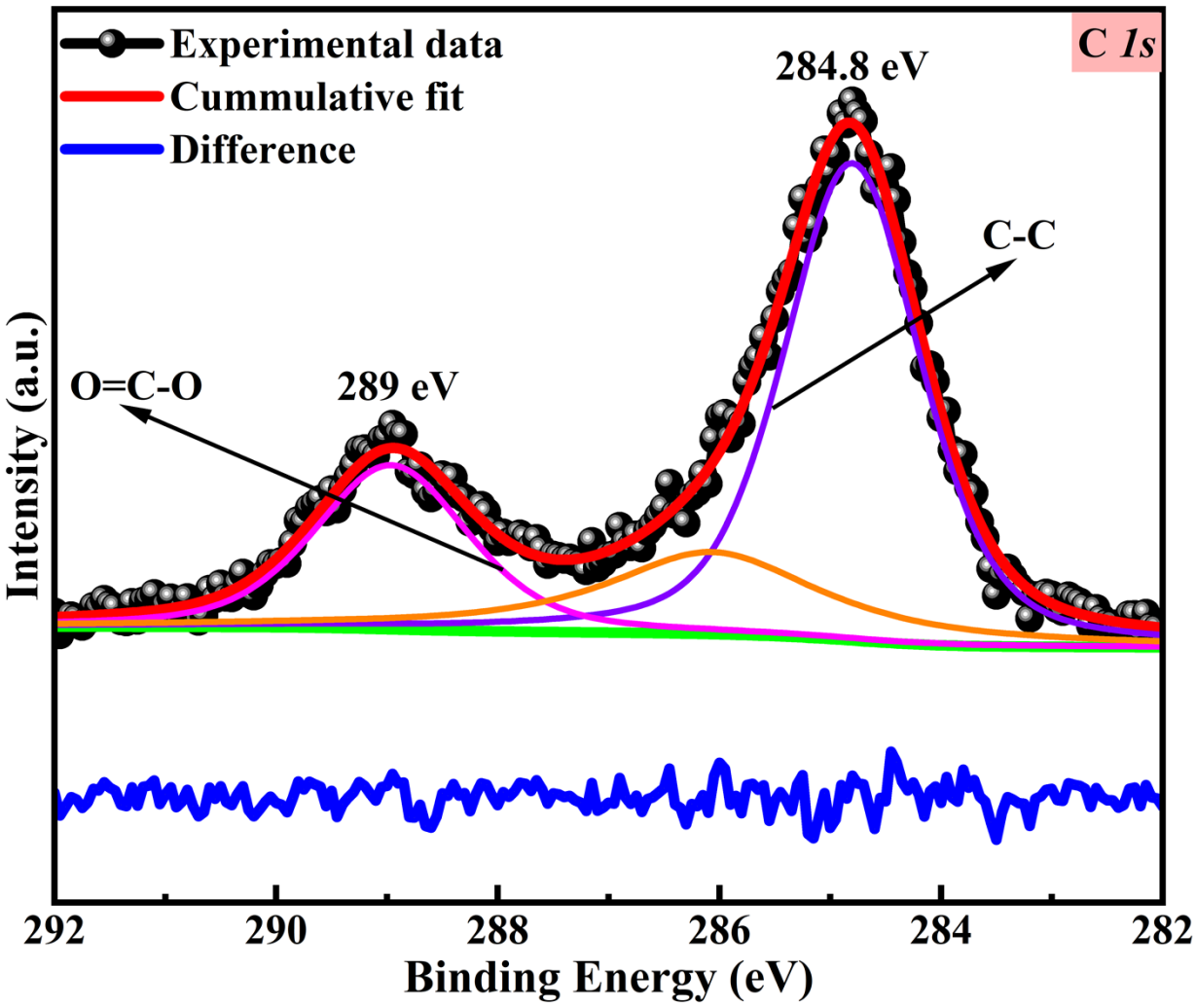
_atom_site_type_symbol

Co1	0.6675	0.000000	0.000000	0.000000	Uiso	0.030930 Co
Mn1	0.3325	0.000000	0.000000	0.000000	Uiso	0.030930 Mn
Fe1	0.5540	0.000000	0.000000	0.000000	Uiso	0.030930 Fe
Na2	0.2275	0.000000	0.000000	0.250000	Uiso	0.030930 Na
O1	0.8806	0.333333	0.666667	0.090570	Uiso	0.030930 O
Na1	0.6913	0.577000	0.288500	0.250000	Uiso	0.030930 Na

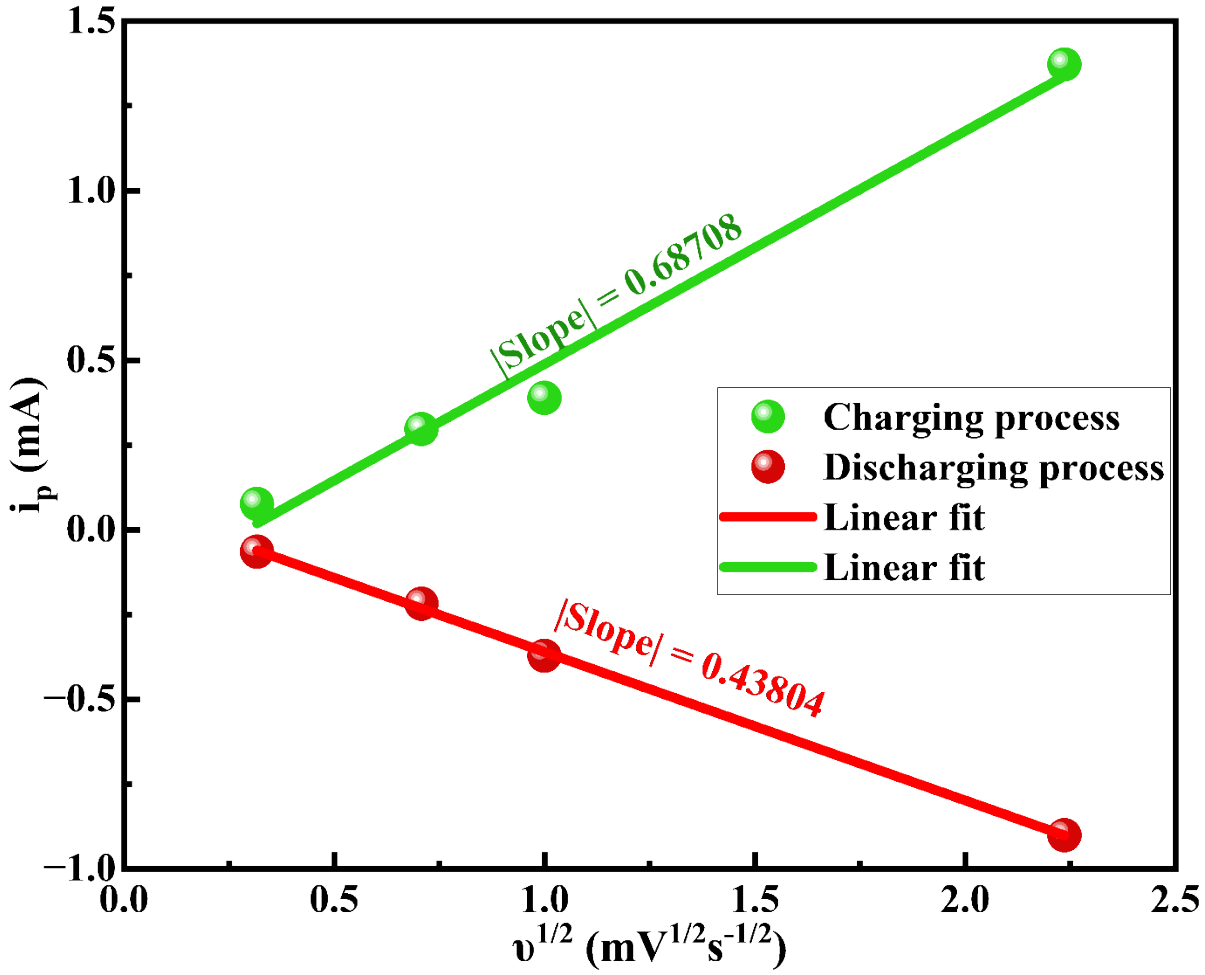
S5. Other FESEM images of $Na_xCo_{0.5}Fe_{0.25}Mn_{0.25}O_2$.



S6. XPS image of C-*1s* orbital.



S7. Graph resenting linear relation between peak current (i_p) and square of scan rate ($\upsilon^{1/2}$).



S8. Calculation of concentration of Na^+-ions in the electrode of $Na_xCo_{0.5}Fe_{0.25}Mn_{0.25}O_2$ for the calculation of sodium-ion diffusion constant.

(1) By considering x=1, the molar mass of $NaCo_{0.5}Fe_{0.25}Mn_{0.25}O_2$,

$$M = 112.1525 \text{ g/mol}$$

(2) Number of sodium ions per formula unit,

$$N = 1$$

(3) Density of $NaCo_{0.5}Fe_{0.25}Mn_{0.25}O_2$ unit cell,

$$\rho = 7.497 \text{ g/cm}^3$$

(4) The concentration of sodium ions,

$$C = \frac{N\ x\ \rho}{M} = \frac{1\ x\ 7.497 \frac{g}{cm^3}}{112.1525\ \frac{g}{mol}} = 0.06684648 \frac{mol}{cm^3}$$