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CIDEMAT
Centro de investigación, innovacion y desarrollo de Materiales

UNIVERSIDAD DE ANTIOQUIA
1803

Symposium: A04: Battery Student Slam 6

#A04-0556

(1-x) $Li_{1-y}Na_yM_{1-z}Ti_zO_2$ *x* $LiM_{2-z}Ti_zO_4$ Layered-Spinel Nanoparticles As Promising Dual Positive Electrode For Lithium-Ion Batteries And Sodium-Ion Batteries

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Content

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Introduction

Methodology

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Conclusions

Renewable sources - Storage systems

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↑ **Global energy demand**

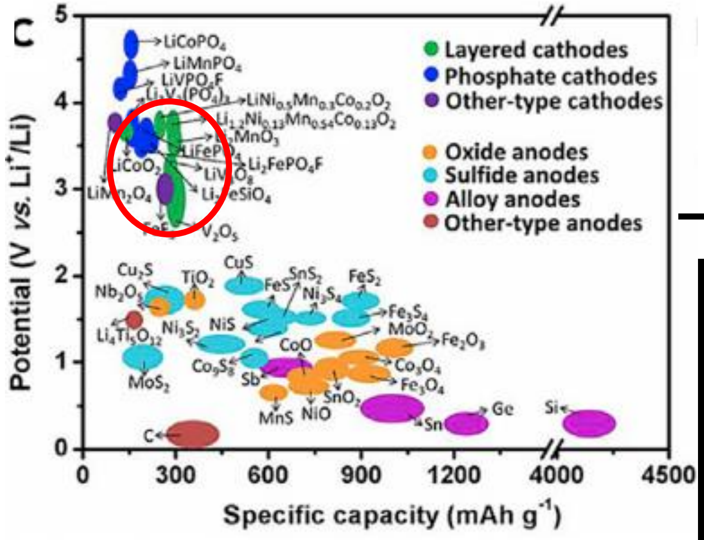
Projection

Generate → Renewable sources

Find → **Storage systems**

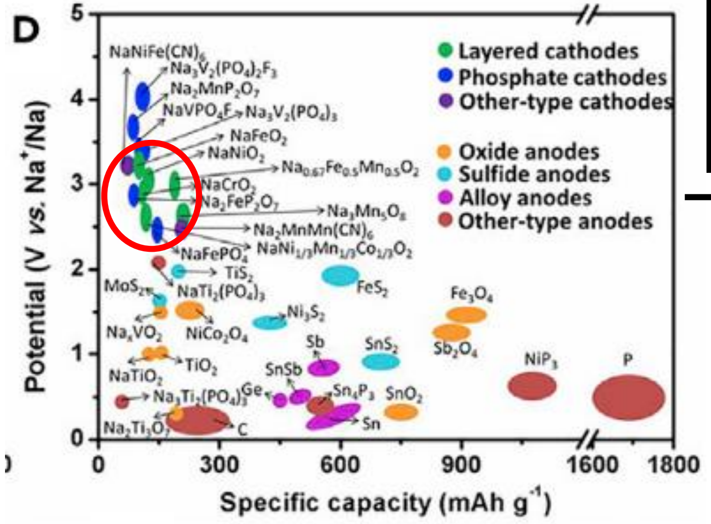
Li-Ion Batteries LIBs | **Na-ion batteries SIBs**

LIBs



- High voltage
- High Capacity

SIBs



- Low Price
- Abundant

Meng, Jiashen, et al. Joule, 2017, Vol. 1, 522.

¿Why the Li-ion and Na-ion batteries are still under develompent?

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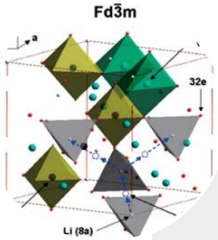
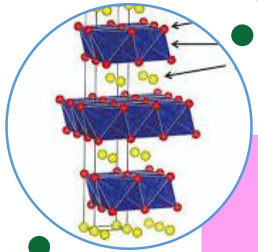
Cathode material →

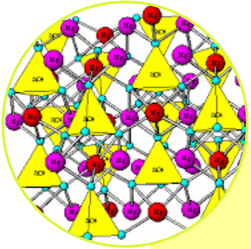
High energy capacity
Long life cycle
Lower Cost
Eco-friendly.
High coulombic efficiency



Spinel



Layered



Olivine

Layered-Spinel Heterostructre

Dual positive electrode

Application

- Lithium ion battery
- Sodium ion battery

Wang, Sihui et al, Journal of Power Sources, 245 (2014) 570-578.
Ngoc Hung Vua (2017)

Na:Spinel – Layered Heterostructure

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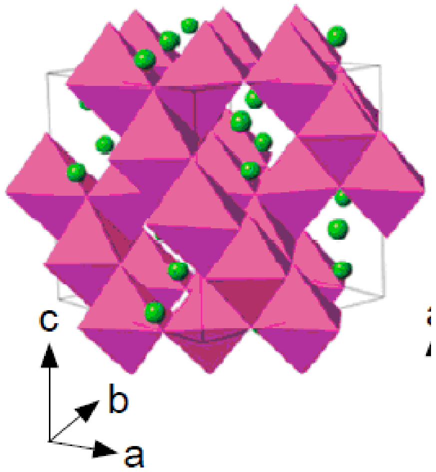


spinel $LiMn_2O_4$

3D

Faster ion and electron transport (3D)

Low structural stability

Modification

Ti^{4+}

$LiMn_{2-x}Ti_xO_4$

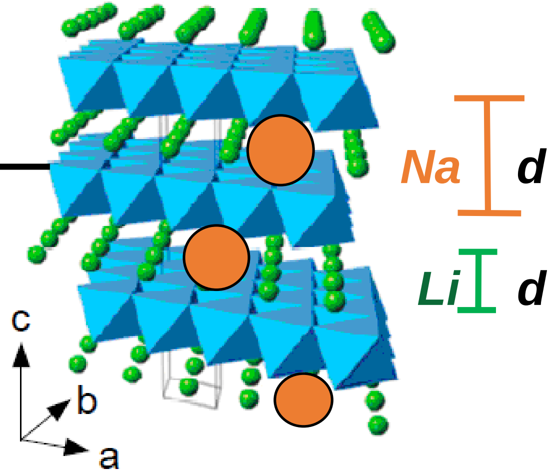
- Reduce Jahn-Teller effect – Mn^{3+}: Inducing a volume change
- Decrease dissolution of Mn^{2+} towards the electrolyte
- Improving the stability of the material

Specific theoretical capacity: 272 (137) ($mAhg^{-1}$)

Fast capacity fade at high current rates

Modification

Na^{+}



layered $LiCoO_2$

2D

$Li_{1-x}Na_xMn_{0.4}Ni_{0.5}Ti_{0.1}O_2$

- 1-D Li^{+}transport during discharge and charge

Li, Y. Wu, M. Ouyang, C. (2015).
Schmidt, et al. J. of Power Sources. 196 (2011) 5342.
Yinhua, Z. Xingyu, Z. Xu, Y. Le, Zhang, X. Chen, H. Yang, J.P.S. 321 (2016) 120–125.
J. Zheng et al. Advanced Energy Materials, 1601284 (2017) 1-25.

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Methodology

¿What is the Composition of Na^+ in the Layered-Spinel Heterostructures?

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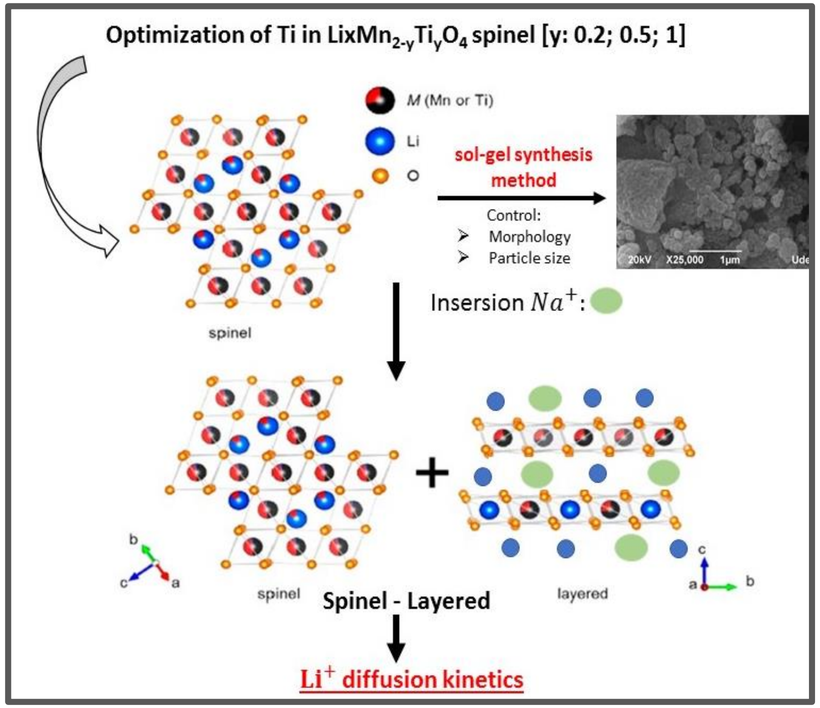
$$0.5\ Li_{1-y}Na_yMn_{0.4}Ni_{0.5}Ti_{0.1}O_2\ 0.5\ LiMn_{1.8}Ti_{0.2}O_4$$



Sol- gel synthesis method → Control: Morphology, Particle size

Application → **Na-Ion batteries**

Na^+ Composition

Y=0.5	Y=0.75	Y=1.0
$Na_{0.5}LMTO$	$Na_{0.75}LMTO$	$Na_{1.0}LMTO$

Li-Ion batteries → Characterization

Na^+ Composition

Y=0	Y=0.1	Y=0.2	Y=0.5
Na_0LMTO	$Na_{0.1}LMTO$	$Na_{0.2}LMTO$	$Na_{0.5}LMTO$

Characterization:

XRD
SEM
CV
Charge/ Discharge

RESULTS

Structural and morphological characterization

XRD

0,5 $Li_{1-y}Na_yMn_{0.4}Ni_{0.5}Ti_{0.1}O_2$ 0,5 $LiMn_{1.8}Ti_{.2}O_4$ [y=0, 0.1, 0.2 and 0.5]

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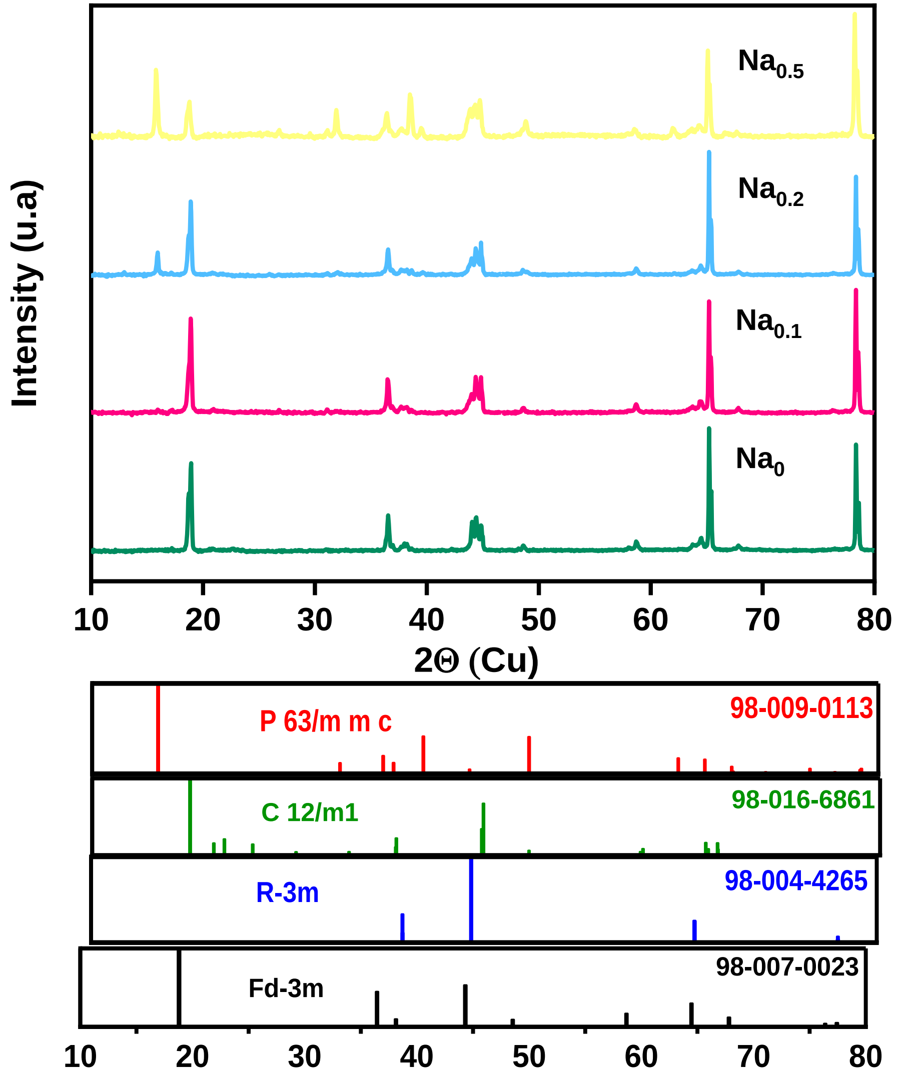

Figure. 1: XRD patterns of Layered-spinel-type [y = 0, 0.1, 0.2, 0.5, 1] powders.

Table 1: Rietveld Analysis

	Samples	Na_0	$Na_{0.1}$	$Na_{0.2}$	$Na_{0.5}$
Space group Fd-3m $Li_1Mn_{1.5}Ni_{0.5}O_4$	% Phase	29	34	25	19.2
	Lattice parameter	a=8,168 (2) b=8,168 (2) c=8,168 (2) Volume (Å) = 544.9 (2)	a=8,172 (2) b=8,172 (2) c=8,172 (2) Volume (Å) = 545.7 (2)	a=8,171 (2) b=8,171 (2) c=8,171 (2) Volume (Å) = 545.65 (2)	a=8,15 (2) b=8,15 (2) c=8,15 (2) Volume (Å) = 541.3 (2)
Space group R-3m $Li_{0.524}Ni_{1.476}O_2$	% Phase	26	10	16	15,2
	Lattice parameter	a=2,91 (2) b=2,91 (2) c=14,21 (3) Volume (Å) = 103,93 (3)	a=2,91 (2) b=2,91 (2) c=14,29 (3) Volume (Å) = 105,29 (3)	a=2,912 (2) b=2,912 (2) c=14,1 (2) Volume (Å) = 103,93 (2)	a=2,91 (2) b=2,91 (2) c=14,28 (3) Volume (Å) = 105,28 (3)
Space group C 12-m1 $Li_2Mn_1O_3$	% Phase	45	49	51	33
	Lattice parameter	a=4,95 (1) b=8,56 (1) c=4,99 (2) Volume (Å) = 199,06 (3)	a=4,97 (1) b=8,49 (1) c=5,14 (2) Volume (Å) = 203,017 (2)	a=4,929 (1) b=8,532 (2) c=5,025 (2) Volume (Å) = 199,4 (2)	a=4,93 (2) b=8,53 (2) c=5,03 (2) Volume (Å) = 199,4 (3)
Space group P 63-mmc $Na_{0.58}Mn_{0.667}Ni_{0.33}O_{1.95}$	% Phase	0	5	8	28,3
	Lattice parameter		a=2,88 (2) b=2,888 (2) c=11,15 (2) Volume (Å) = 80,41 (2)	a=2,862 (3) b=2,862 (3) c=11,21 (2) Volume (Å) = 79,55 (3)	a=2,862 (3) b=2,862 (3) c=11,21 (2) Volume (Å) = 79,53 (3)
Impurates Mn-Ni--O	% phase	0	2		4.2

XRD

0,5 $Li_{1-y}Na_yMn_{0.4}Ni_{0.5}Ti_{0.1}O_2$ 0,5 $LiMn_{1.8}Ti_{.2}O_4$ [y=0.5, 0.75 and 1.0]

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Table 2: Rietveld Analysis

	Samples	$Na_{0.5}$	$Na_{0.75}$	$Na_{1.0}$
Space group Fd-3m $Li_1Mn_{1.5}Ni_{0.5}O_4$	**% Phase**	**19.2**	**14.1**	**15.5**
	Lattice parameter	a=8,15 (2) b=8,15 (2) c=8,15 (2) Volume (Å) = 541.3 (2)	a=8,174 (2) b=8,174 (2) c=8,174 (2) Volume (Å) = 543.7 (2)	a=8,175 (2) b=8,175 (2) c=8,175 (2) Volume (Å) = 546.75 (2)
Space group R-3m $Li_{0.524}Ni_{1.476}O_2$	**% Phase**	**15.2**	**2.2**	**1.1**
	Lattice parameter	a=2,91 (2) b=2,91 (2) c=14,28 (3) Volume (Å) = 105,28 (3)	a=2,93 (2) b=2,93 (2) c=14,31 (3) Volume (Å) = 105,29 (3)	a=2,94 (2) b=2,94 (2) c=14,33 (2) Volume (Å) = 103,93 (2)
Space group C 12-m1 $Li_2Mn_1O_3$	**% Phase**	**33**	**5.0**	**1.3**
	Lattice parameter	a=4,95 (1) b=8,56 (1) c=4,99 (2) Volume (Å) = 199,06 (3)	a=4,96 (1) b=8,50 (1) c=5,16 (2) Volume (Å) = 199,2 (2)	a=4,929 (1) b=8,534 (3) c=5,25 (3) Volume (Å) = 199,47(2)
Space group P 63-mmc $Na_{0.58}Mn_{0.667}Ni_{0.33}O_{1.95}$	**% Phase**	**28.3**	**74.1**	**81**
	Lattice parameter	a=2,862 (3) b=2,862 (3) c=11,21 (2) Volume (Å) = 79,53 (3)	a=2,87 (2) b=2,87 (2) c=11,15 (2) Volume (Å) = 80,41 (2)	a=2,88 (3) b=2,88 (3) c=11,91 (2) Volume (Å) = 82,3 (3)
Impurates Mn-Ni--O	**% phase**	**4.2**	**4.6**	**1.1**

SEM

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0,5 $Li_{1-y}Na_yMn_{0.4}Ni_{0.5}Ti_{0.1}O_2$ 0,5 $LiMn_{1.8}Ti_{.2}O_4$ [y=0, 0.1, 0.2, 0.5, 0.75 and 0.5]

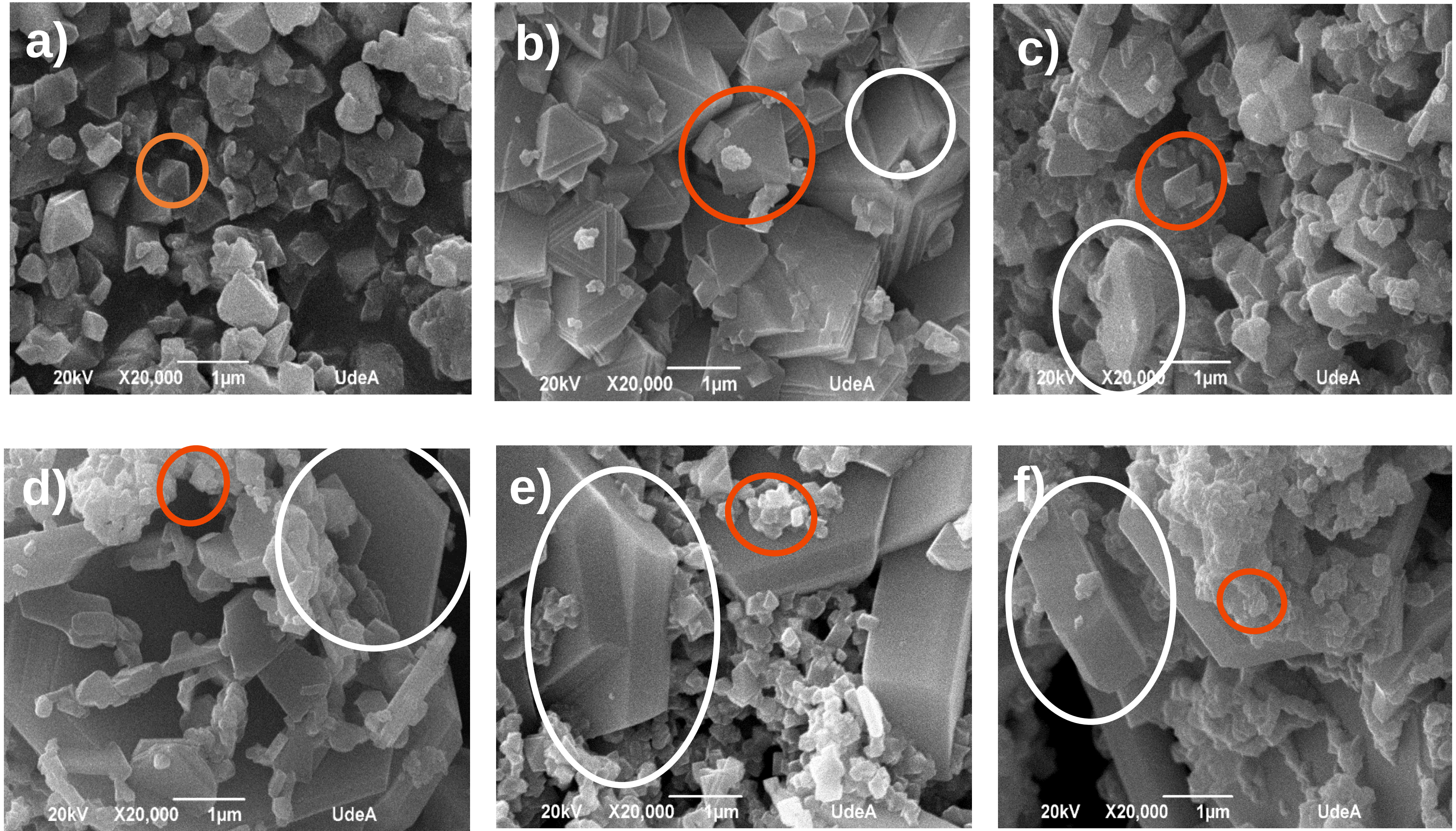

Figure. 2. SEM images of cathode materials (a) Na_0 (b)$Na_{0.1}$; (c)$Na_{0.2}$; (c)$Na_{0.5}$; (d)$Na_{0.75}$; (e)$Na_{1.0}$

RESULTS

Electrochemical characterization

Li-Ion batteries (LIB)

Na-Ion batteries (SIB)

Li-Ion batteries

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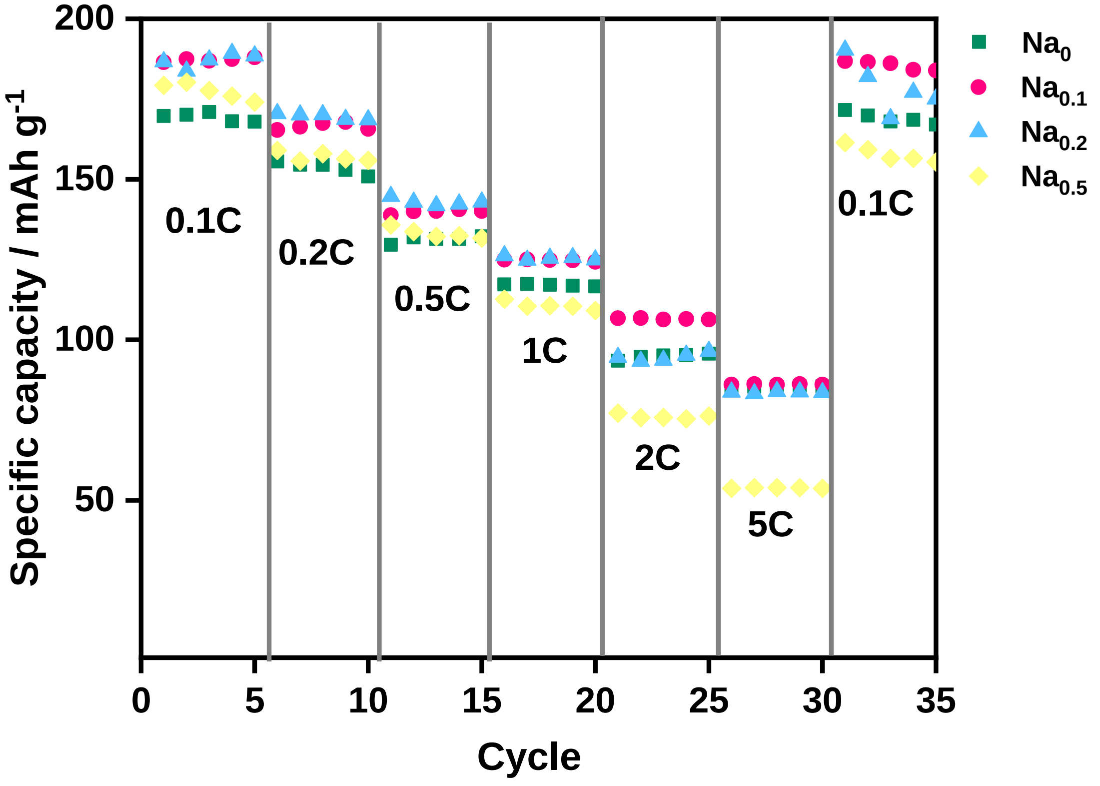
Discharge capacities at different C rates of the active materials: 0,5 $Li_{1-y}Na_yMn_{0.4}Ni_{0.5}Ti_{0.1}O_2$ 0,5 $LiMn_{1.8}Ti_{.2}O_4$ [y=0, 0.1, 0.2 and 0.5]



Excellent response the layered-spinel: $Na_{0.1}$ at high C.R

$Na_{0.5}$ composition showed the worst C.R

Figure. 3: Discharge capacities of the active materials: Na_0; $Na_{0.1}$; $Na_{0.2}$; $Na_{0.5}$ at different C rates between 4.9 and 2.0 V vs. Li|Li$^+$.

Li-Ion batteries

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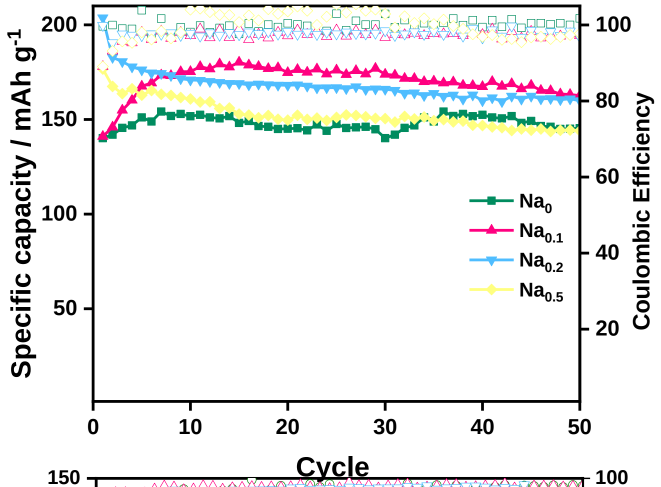
Discharge specific capacity of 0,5 $Li_{1-y}Na_yMn_{0.4}Ni_{0.5}Ti_{0.1}O_2$ 0,5 $LiMn_{1.8}Ti_{.2}O_4$ [y=0, 0.1, 0.2 and 0.5]

a)

0.1C →



→

Table 3: Specific capacity of the cathode Materials at 0.1C

Materials	Specific capacity/mA h g-1		%Retention
	Cycle 1	Cycle Max	Cycle 50
Na_0	140	154/Cycle 8	93
$Na_{0.1}$	142	180/Cycle 15	95
$Na_{0.2}$	204	204/Cycle 1	86
$Na_{0.5}$	177	177/Cycle 1	81

b)

1C →

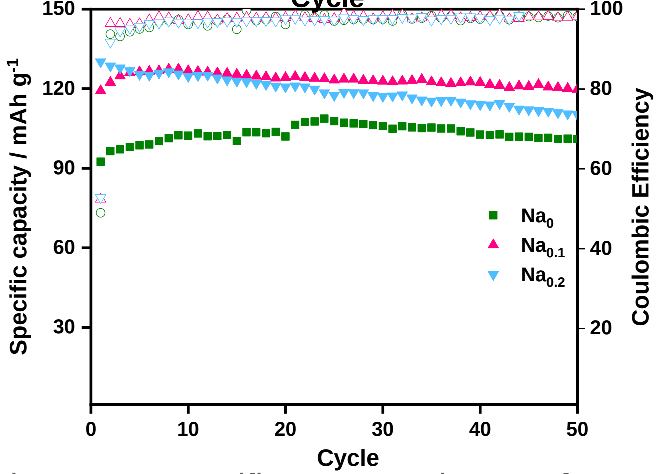


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Table 4: Specific capacity of the cathode Materials at 1C

Materials	Specific capacity/mA h g-1		
	Cycle 1	Cycle Max	%Retention/cycle 50
Na_0	92	109/Cycle 24	92
$Na_{0.1}$	119	127/Cycle 15	95
$Na_{0.2}$	130	130/Cycle 1	85

Figure 4. Discharge specific capacity of active material $0.5Li_{1-y}Na_yMn_{0.4}Ni_{0.5}Ti_{0.1}O_2 0.5LiMn_{1.8}Ti_{0.2}O_4$ [*y* = 0; 0,1; 0.2, 0.5] a) at a constant current of 23.9 mA g^{-1} (0.1C) b) at a constant current of 23.9 mA g^{-1} (1C) between 4.9 and 2.0 V vs. $Li|Li^+$.

Li-Ion batteries

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Charge/discharge curves of cathode materials: 0,5 $Li_{1-y}Na_yMn_{0.4}Ni_{0.5}Ti_{0.1}O_2$ 0,5 $LiMn_{1.8}Ti_{.2}O_4$ [y=0, 0.1, 0.2 and 0.5]

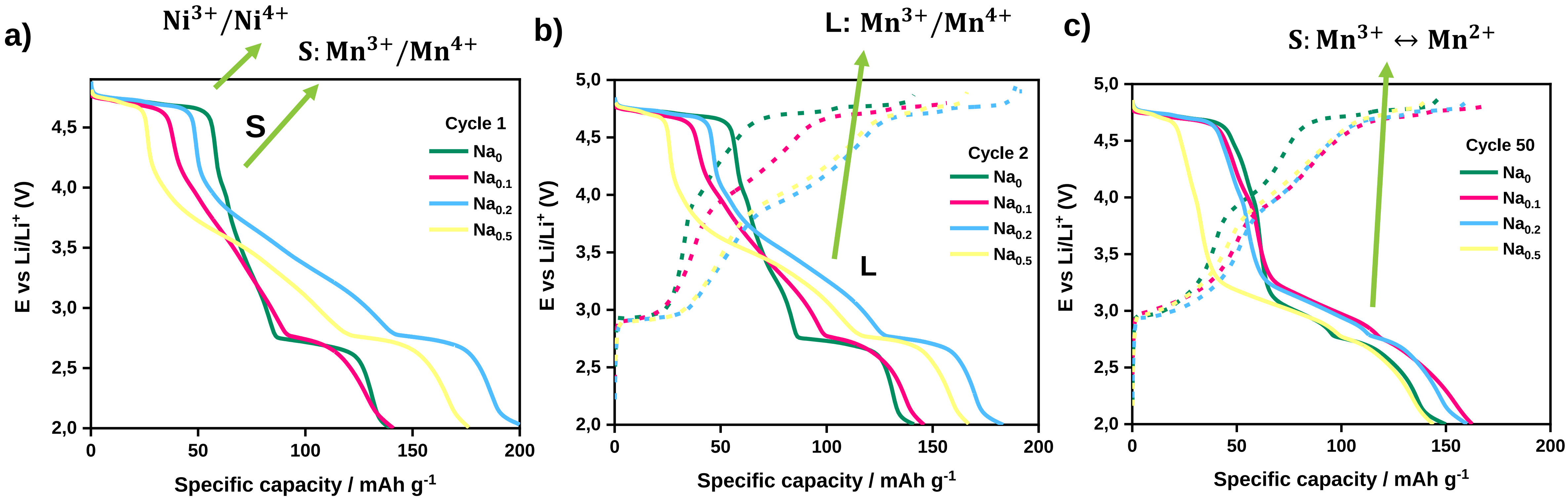

Figure 5. Charge/discharge curves of cathode materials corresponding to cycle numbers (a) 1st; (b)2th and (c) 50th. The tests were performed at 29.3 mA g^{-1} (0.1 C-rate) in a voltage range of 2.0 - 4.9 V vs. Li|Li^+ in a 1.2 mol L^{-1} $LiPF_6$ EC: DMC electrolyte.

Na-Ion batteries

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Charge/discharge curves of cathode materials: 0,5 $Li_{1-y}Na_yMn_{0.4}Ni_{0.5}Ti_{0.1}O_2$ 0,5 $LiMn_{1.8}Ti_{.2}O_4$ [y=0.5, 0.75 and 1.0]

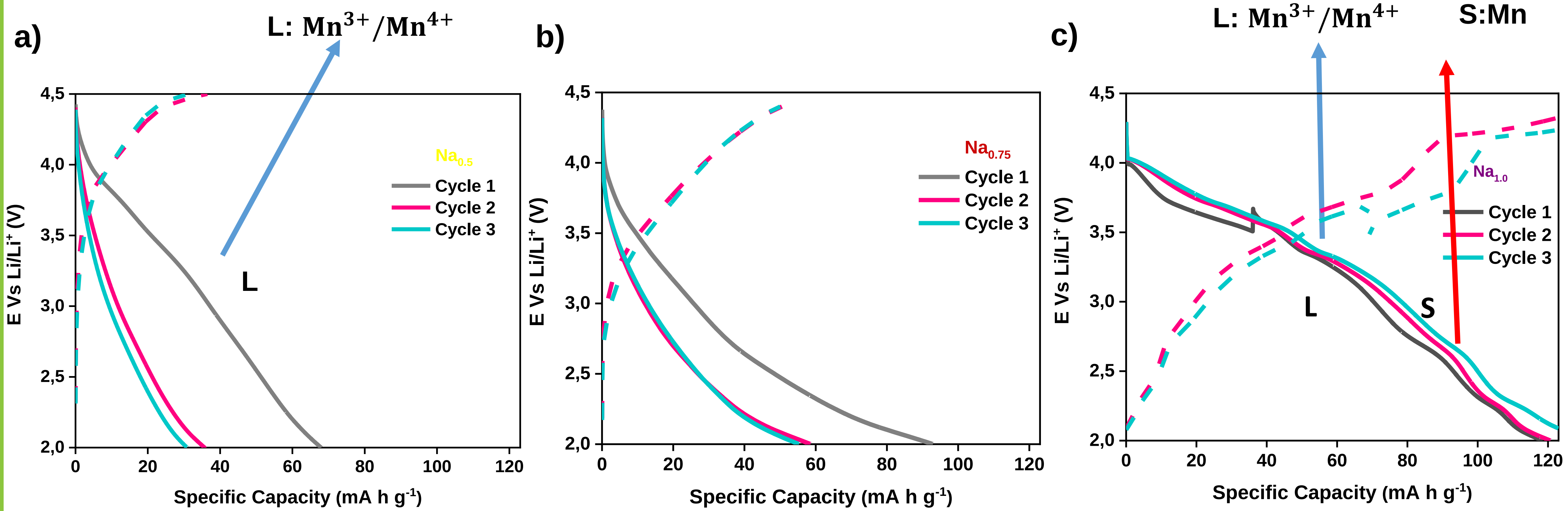

Figure 6. Charge/discharge curves corresponding to cycle numbers 1st; 2th and 10th of cathode materials a) **$Na_{0.5}$**; b) **$Na_{0.75}$** c) **$Na_{1.0}$** The tests were performed at 10.0 mA g^{-1} (0.1 C-rate) in a voltage range of 2.0 - 4.4 V vs. Na|Na^+ in a 1.0 mol L^{-1} $NaPF_6$ EC: DMC electrolyte.

Na-Ion batteries

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Discharge specific capacity of 0,5 $Li_{1-y}Na_yMn_{0.4}Ni_{0.5}Ti_{0.1}O_2$ 0,5 $LiMn_{1.8}Ti_{.2}O_4$ [y=0.5, 0.75 and 1.0]

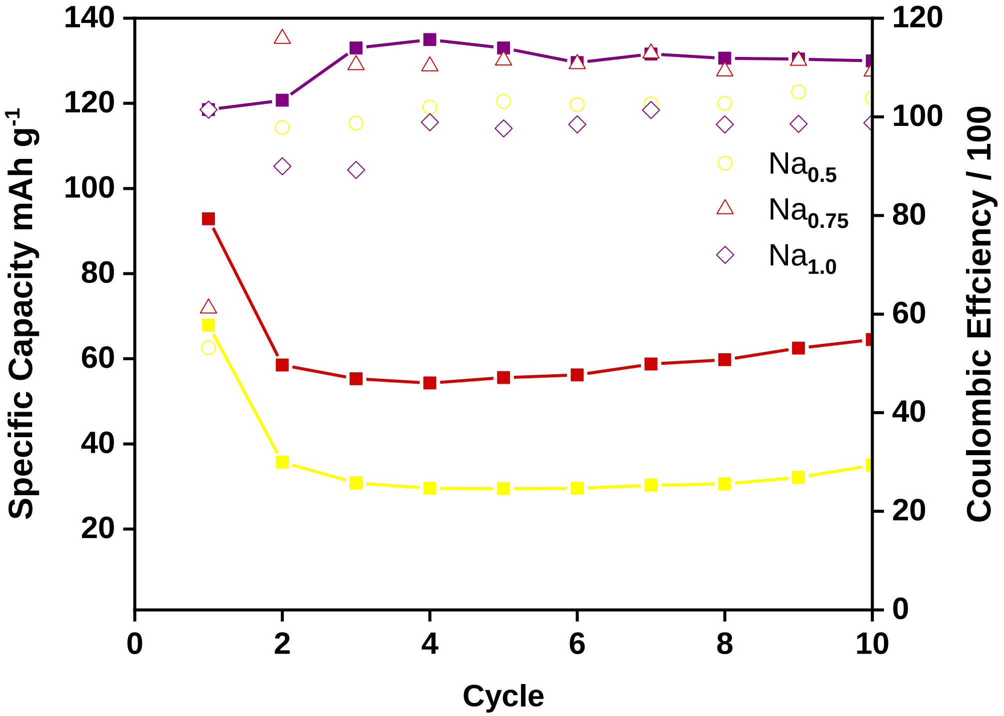

Figure 7. Discharge specific capacity of active material $0.5Li_{1-y}Na_yMn_{0.4}Ni_{0.5}Ti_{0.1}O_2 0.5LiMn_{1.8}Ti_{0.2}O_4$ [y = 0.5; 0.75; 1.0] at a constant current of 15.0 mA g^{-1} (0.1C-rate) between 4.4 and 2.0 V vs. Na|Na^+ in a 1.0 mol L^{-1} $NaPF_6$ EC: DMC electrolyte.

Conclusions

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- For LIB cycling the stoichiometry $0,5Li_{0.9}Na_{0.1}Mn_{0.4}Ni_{0.5}Ti_{0.1}O_{2}0,5LiMn_{1.8}Ti_{0.2}O_{4}$ showed at a constant current of 23.9 mA g^{-1} (0.1C-rate) a maximum specific capacity, ca 180.4 mA h g^{-1} a mild decrease of the specific capacity during cycling was evident, it where maintains 95% of its charge capacity after 50 cycles compared with undoped $0,5Li_{1}Mn_{0.4}Ni_{0.5}Ti_{0.1}0,5LiMn_{1.8}Ti_{0.2}O_{4}$ which was ca. 154 mA h g^{-1} and maintains 93% of its charge capacity after 50 cycle.

- For SIB cycling the stoichiometry $0,5Li_{0}Na_{1.0}Mn_{0.4}Ni_{0.5}Ti_{0.1}O_{2}0,5LiMn_{1.8}Ti_{0.2}O_{4}$ showed an initial specific capacity, ca 135.0 mA h g^{-1}, at a constant current of 150.0 mAg^{-1}, equivalent to 0.1 C-rate could be a potential cathode for the development of rechargeable Na-ion batteries.

- By possessing interesting properties electrochemical we believe that these materials could be a potential electrode for the development of high-power rechargeable Li-ion batteries and Na-ion batteries.

References

- Wang, Sihui et al, Journal of Power Sources, 245 (2014) 570-578.
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- J. Zheng et al. Advanced Energy Materials, 1601284 (2017) 1-25.

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