

## Electronic Supporting Information

for

### Improved electrochemical performance of $\text{Na}_{0.67}\text{MnO}_2$ through Ni and Mg substitution

K. Hemalatha,<sup>ab‡</sup> M. Jayakumar,<sup>a‡</sup> Parthasarathi Bera<sup>c</sup> and A. S. Prakash<sup>a\*</sup>

<sup>a</sup> CSIR-Central Electrochemical Research Institute-Chennai unit, CSIR Madras Complex, Taramani, Chennai 600113, India

<sup>b</sup> Academy of Scientific and Innovative Research (AcSIR), CSIR- Central Electrochemical Research Institute-Chennai unit, CSIR Madras Complex, Chennai 600113, India

<sup>c</sup> Surface Engineering Division, CSIR-National Aerospace Laboratories, HAL Airport Road, Bangalore 560017, India

\* Corresponding Author

‡Equally contributing first authors

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#### Experimental details

$\text{P2-Na}_{0.67}\text{Ni}_{0.25}\text{Mg}_{0.1}\text{Mn}_{0.65}\text{O}_2$  was prepared by sol-gel method which was described in details elsewhere.<sup>1</sup> In brief, an aqueous solution of stoichiometric quantities of metal acetates of Na, Ni, Mg and Mn in the molar ratio of 0.67:0.25:0.1:0.65 were homogeneously mixed with citric acid which was used as a chelating agent. An excess of 5% sodium acetate was added to compensate the sodium evaporation loss at high temperatures. The solution was heated at 80 °C to form gel. The formed gel was decomposed and then reheated to 400 °C for 6 h and 900 °C for 12 h and cooled down to 200 °C at a slower rate to get the desired phase. The sample was stored in an argon filled glove box to prevent its exposure to air and moisture. For comparison,  $\text{Na}_{0.67}\text{Ni}_{0.34}\text{Mn}_{0.66}\text{O}_2$  and  $\text{Na}_{0.67}\text{MnO}_2$  were also prepared by adopting similar procedure. Powder X-ray diffraction pattern of the sample was recorded using Bruker D8 Advance Da Vinci diffractometer using  $\text{CuK}\alpha$  radiation. The crystal structure and lattice parameters were analyzed by Rietveld refinement<sup>2</sup> using the Fullprof program.<sup>3</sup> Scanning electron microscopy images were recorded with VEGA 3SBH TESCAN. Chemical composition of the sample was quantitatively estimated using Varian spectra 220 atomic absorption spectrophotometer. XPS of as-prepared, charged and discharged samples were recorded with Thermo Fischer Scientific Multilab 2000

spectrometer using non-monochromatic  $\text{AlK}_\alpha$  radiation (1486.6 eV) as an X-ray source operated at 150 W (12 kV, 12.5 mA).

Electrochemical tests were carried out on Swagelok type cells assembled in an argon filled glove box (MBRAUN Unilab).  $\text{P2-Na}_{0.67}\text{Ni}_{0.25}\text{Mg}_{0.1}\text{Mn}_{0.65}\text{O}_2$  was mixed with conducting carbon (80:15 wt%) and then ball milled using SPEX 800 miller for 20 min. The slurry was prepared by mixing this composite powder with 5 wt% poly(vinylidene fluoride) in N-ethyl pyrrolidone and coating onto a Al foil followed by drying in vacuum oven at 100 °C for at least 12 hours. This film was pressed and punched to serve as the working electrode (cathode) while metallic sodium acts as the anode. Typical sample loading was about 4-5 mg/cm<sup>2</sup>. The electrolyte solution used was 1 mol/L  $\text{NaPF}_6$  dissolved in a mixture of 1:1 volume percent of EC:PC and a glass fiber filter (Whatmann) was used as separator. The cell thus fabricated was cycled galvanostatically in the voltage range of 1.5 to 4.2 V and 2.0 to 4.2 V. All the electrochemical experiments were carried out using VMP3Z biologic multi-channel potentiostat/galvanostat. For *ex situ* XRD studies, the electrode materials after charging and discharging were transferred to the Argon filled glove box, disassembled, washed with suitable solvents, dried and sealed in suitable sample holder with Kapton film to avoid contact with atmosphere.

**Electronic Supporting information ESI - 1.** Refined crystallographic parameters obtained from XRD Rietveld fit of as-prepared  $\text{Na}_{0.67}\text{Ni}_{0.25}\text{Mg}_{0.1}\text{Mn}_{0.65}\text{O}_2$  using Fullprof Suite

Atom	Wyckoff position	x	y	z	Occupancy
Mg1	2b	0	0	0	0.0608
Ni1	2b	0	0	0	0.9392
Mn1	2b	0	0	0	0.5112
Mg2	4d	1/3	2/3	0	0.2129
Ni2	4d	1/3	2/3	0	0.0550
Mn2	4d	1/3	2/3	0	1.2502
O1	12k	0.3352	0.3352	0.0938	1.4999
Na1	6g	0.2726	0	1/4	0.6584
Na2	2a	0	0	1/4	0.3545
Na3	4c	1/3	2/3	1/4	0.3652

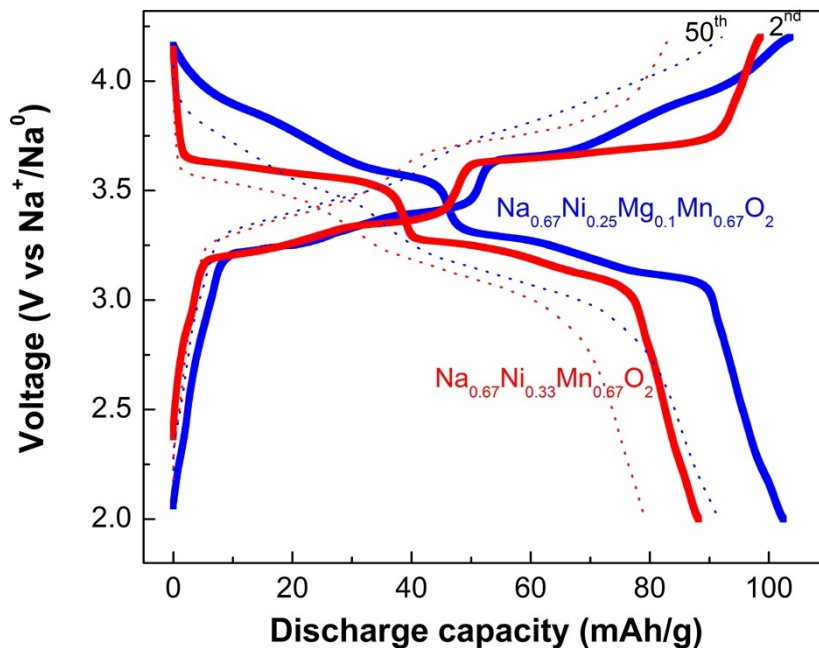
Lattice parameters :  $a(\text{Å})=b(\text{Å}) = 5.00285(4)$ ,  $c(\text{Å}) = 11.14097(3)$ , Space group :  $P6_3/mcm$  (No.193),  $R_p = 5.1$ ,  $R_{wp} = 7.3$ ,  $R_{exp} = 2.4$ ,  $\chi^2 (G^2) = 9.4$ , M–O bond lengths: 1.9754 (Å) x 6 (M1–O), 1.9645 (Å) x 6 (M2–O)

**Electronic Supporting information ESI-2: Summary of literature on  $\text{Na}_{0.67}\text{Ni}_{0.33}\text{Mn}_{0.67}\text{O}_2$  and  $\text{Na}_{0.67}\text{MnO}_2$ .**

Phase	1st discharge capacity in mAh/g at 0.1 C rate. Other rates given in parenthesis	Capacity retention at the end of 30th cycle in %	Voltage range	Reference
$\text{Na}_{0.67}\text{Ni}_{0.33}\text{Mn}_{0.67}\text{O}_2$	161	-	2-4.5 V	[4]
	88 (C/20 rate)	95	2.3-4.1 V	[5]
	134	64 (10th cycle)	2.3-4.5 V	
	153	-	2 – 4.5 V	[6]
	89	73 (10th cycle)	2-4 V	
	150	69	2-4.5 V	[7]
	150 (C/20)	67 (10th cycle)	2.5 – 4.5 V	[8]
	80 (C/20)	>95 (10th cycle)	2.5 – 4 V	
	140	~65	2 – 4.5 V	[9]
	86	>95	2 – 4 V	
	86*	-	2 – 4.2 V	[10]
	89	90	2 – 4.2 V	Present work
	$\text{Na}_{0.67}\text{MnO}_2$	~155 (0.1mA/cm <sup>2</sup> )	~40 (10 <sup>th</sup> cycle)	2.0-3.8V
161 (50mA/g)		75	1.5-3.8 V	[12]
140 (50mA/g)		62		
163 (40mA/g)		~68	2.0-4.5V	[13]
116 (0.1 C)		-	2.0-4.2 V	Present work
$\text{Na}_{0.67}\text{Ni}_{0.25}\text{Mg}_{0.1}\text{Mn}_{0.65}\text{O}_2$	140	89	1.5 – 4.2 V	Present work
	100	95	2 – 4.2 V	

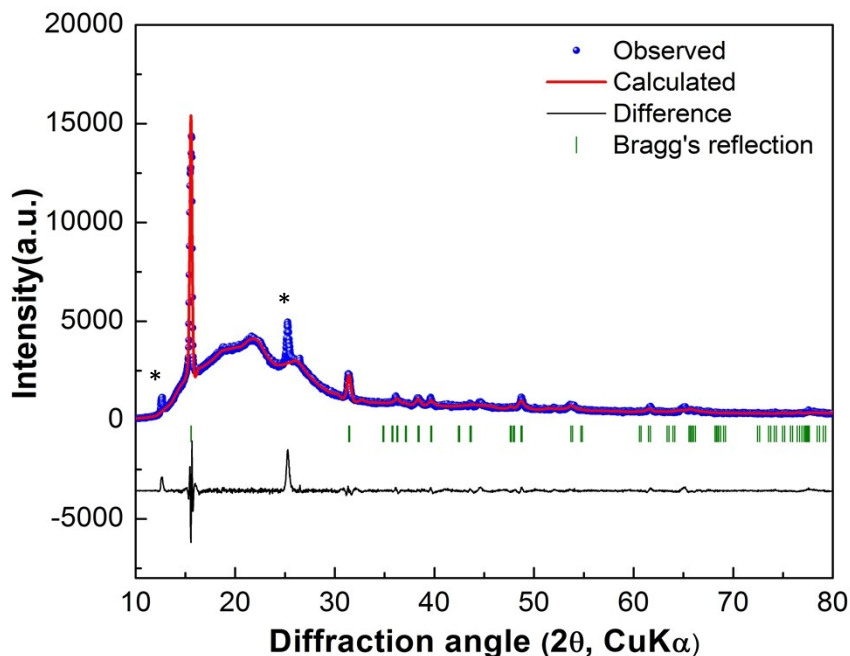
\*  $\text{Na}_{0.67}\text{Ni}_{0.33}\text{Mn}_{0.67}\text{O}_2$  / r-GO composite

**Electronic Supporting information ESI-3:** Cycling profiles and capacity retention plots of  $\text{Na}_{0.67}\text{Ni}_{0.25}\text{Mg}_{0.1}\text{Mn}_{0.65}\text{O}_2$  and  $\text{Na}_{0.67}\text{Ni}_{0.34}\text{Mn}_{0.66}\text{O}_2$  in the voltage range 2- 4.2V at 0.1C rate.



Cycling profile of  $\text{Na}_{0.67}\text{Ni}_{0.25}\text{Mg}_{0.1}\text{Mn}_{0.65}\text{O}_2$  is smooth compared to iso-structural  $\text{Na}_{0.67}\text{Ni}_{0.34}\text{Mn}_{0.66}\text{O}_2$  as seen in ESI-3.  $\text{Na}_{0.67}\text{Ni}_{0.25}\text{Mg}_{0.1}\text{Mn}_{0.65}\text{O}_2$  delivers a discharge capacity of about 100 mAh/g in the voltage range 2.0 – 4.2 V at 0.1C rate. On the other hand  $\text{Na}_{0.67}\text{Ni}_{0.33}\text{Mn}_{0.67}\text{O}_2$  delivers 89 mAh/g under similar conditions. By the end of 50 cycles, the capacity retained by  $\text{Na}_{0.67}\text{Ni}_{0.33}\text{Mn}_{0.67}\text{O}_2$  and  $\text{Na}_{0.67}\text{Ni}_{0.25}\text{Mg}_{0.1}\text{Mn}_{0.65}\text{O}_2$  are 79 mAh/g and 91 mAh/g, respectively.

**Electronic Supporting information ESI-4.** Rietveld fit of  $\text{Na}_{0.67}\text{Ni}_{0.25}\text{Mg}_{0.1}\text{Mn}_{0.65}\text{O}_2$  sample charged to 4.2 V for *Cmcm* model system and table of refined crystallographic parameters

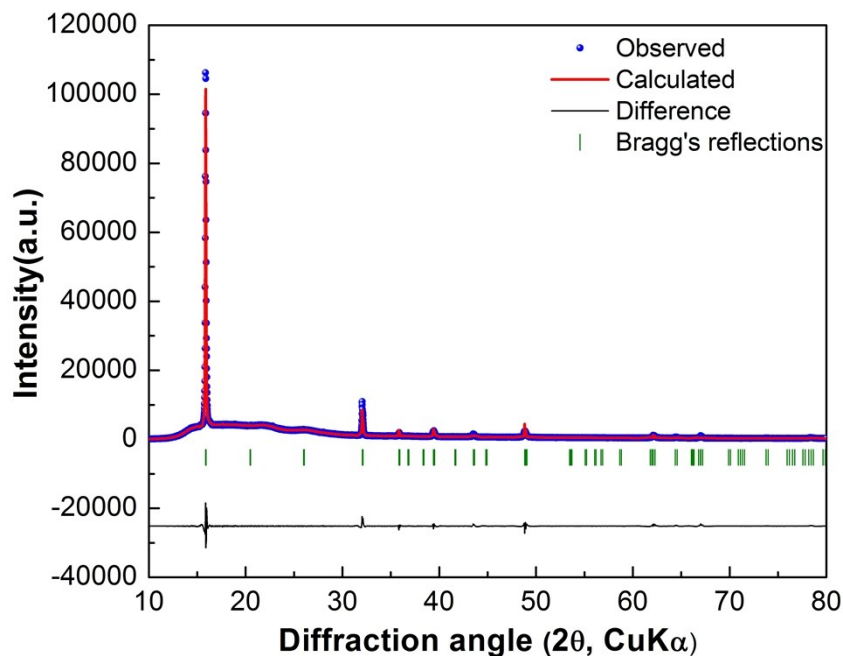


Peaks corresponding to hydrated phase were observed instantaneously during *ex situ* XRD measurements. The peaks are marked with \* and excluded during refinement.

Atom	Wyckoff position	x	y	z	Occupancy
Na1	4c	0	0.0320	1/4	0.2900
Na2	4c	0	0.0200	1/4	0.0100
Mg1	4a	0	0	0	0.1000
Ni1	4a	0	0	0	0.2577
Mn1	4a	0	0	0	0.6510
O	8f	0	0.5852	0.0834	1

Lattice parameters :  $a(\text{Å})=2.5716(2)$ ,  $b(\text{Å})=4.6318(1)$ ,  $c(\text{Å}) = 11.3889(3)$ , Space group : *Cmcm* (No.63),  $R_p = 4.6$ ,  $R_{wp} = 7.4$ ,  $R_{exp} = 2.9$ .  $\chi^2$  ( $G^2$ ) = 6.3. M–O bond lengths: 1.6465 (Å) x 4, 2.1424(Å) x 2.

**Electronic Supporting information ESI-5.** Rietveld fit of  $\text{Na}_{0.67}\text{Ni}_{0.25}\text{Mg}_{0.1}\text{Mn}_{0.65}\text{O}_2$  sample discharged up to 1.5 V using  $P6_3/mcm$  model system and table of refined crystallographic parameters



Atom	Wyckoff position	x	y	z	Occupancy
<b>Mg1</b>	2b	0	0	0	0.0608
<b>Ni1</b>	2b	0	0	0	0.9392
<b>Mn1</b>	2b	0	0	0	0.5115
<b>Mg2</b>	4d	1/3	2/3	0	0.2126
<b>Ni2</b>	4d	1/3	2/3	0	0.0550
<b>Mn2</b>	4d	1/3	2/3	0	1.2500
<b>O1</b>	12k	0.4447	0.4447	0.0421	1.4999
<b>Na1</b>	6g	0.1534	0	1/4	0.8172
<b>Na2</b>	2a	0	0	1/4	0.9920
<b>Na3</b>	4c	1/3	2/3	1/4	0.3680

Lattice parameters :  $a(\text{Å})=b(\text{Å}) = 5.0079(3)$ ,  $c(\text{Å}) = 11.1606(3)$ , Space group :  $P6_3/mcm$  (No.193),  $R_p = 4.8$ ,  $R_{wp} = 8.7$ ,  $R_{exp} = 2.7$ ,  $\chi^2 (G^2) = 10.7$ . M-O bond lengths: 2.2762 (Å) x 6 (M1-O), 1.5451 (Å) x 6 (M2-O)

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