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$Na_{0.67}Mn_{1-x}Mg_xO_2$ ($0 \leq x \leq 0.2$): A High-Capacity Cathode for Sodium Ion Batteries

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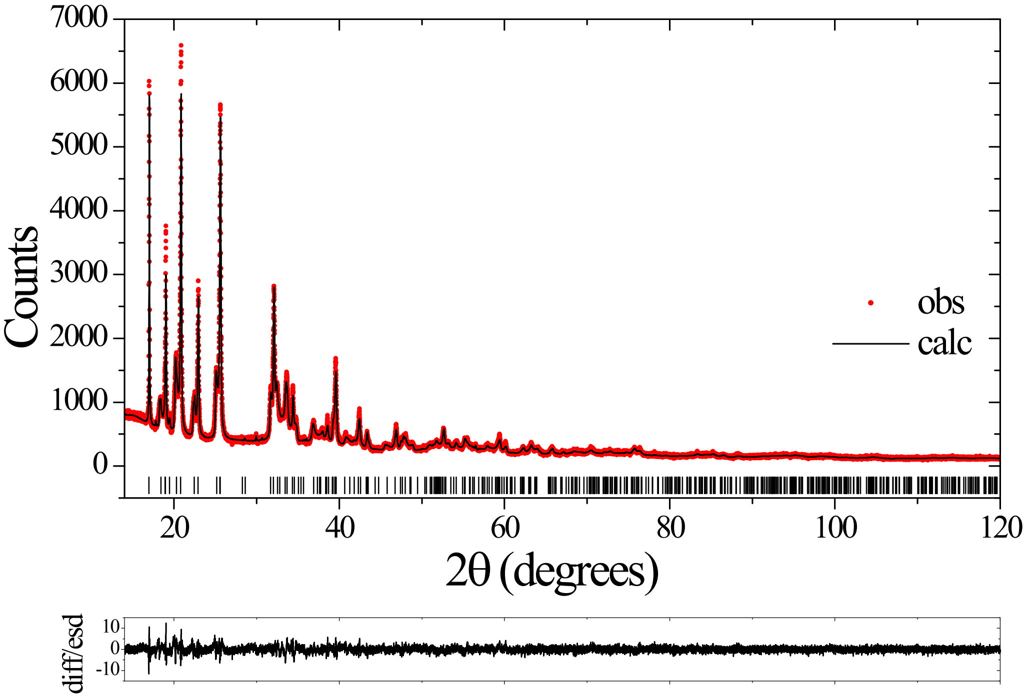
Experimental :

Samples of $Na_{0.67}Mn_{1-x}Mg_xO_2$ (x = 0, 0.05, 0.1 and 0.2) were synthesized by two methods: conventional solid-state synthesis and a solution route. The solid-state route involved mixing together the precursors viz. Na_2CO_3 (Sigma Aldrich, anhydrous ≥ 99.5%), Mn_2O_3 (Alfa Aesar, 98%) and MgO (Alfa Aesar, 99%) in appropriate ratios using ball milling for 1h. Milled powder samples were compressed in the form of pellets and calcined at 900 ^oC for 15 h in air followed by quenching and/or furnace cooling. After the heat treatment pellets were ground and stored in an Ar-filled glove box. The solution route involved dissolving appropriate molar ratios of manganese acetate and magnesium acetate tetrahydrates (both Aldrich) in distilled water. Separately, a solution of Na_2CO_3 (Fisher) dissolved in H_2O was prepared. Co-precipitation was performed by adding the acetate mixture dropwise to the Na_2CO_3 (under intensive stirring). H_2O was removed by evaporation and the resulting solid was dried overnight at 300^oC. The powders were pelletized and calcined at 600 ^oC for 15 hours, quenched, ground and pelletized again. The final calcination was performed at 800 ^oC for 15 hours in air followed either by a quench or furnace cooling to room temperature. The samples were then transferred to an Ar-filled glovebox.

Powder X-ray diffraction (XRD) was performed using a Bruker D8 Advance diffractometer, with a Cu anode, $\lambda = 1.541$ Å. A Kapton® foil was used to cover the samples in order to prevent moisture ingress. Powder X-ray diffraction on charged samples was performed on a Stoe STADI/P diffractometer operating in capillary mode with $FeK\alpha_1$ radiation ($\lambda = 1.936$ Å) to eliminate Fe fluorescence. The morphology of all samples was examined using a FEI scanning electron microscope (SEM) Quanta 200FEG operated at 30 keV and equipped with an Apollo 10 SSD EDX detector. Synchrotron powder X-ray diffraction was obtained in capillaries on the I11 diffractometer at the Diamond Light Source, UK. Rietveld refinements of the structures were carried out using the program Topas Academic [1].

For the electrochemical characterization powder samples were coated on an aluminum foil after mixing with carbon black (CB) and polyvinylidene fluoride (PVDF) in the wt % ratio, active material: CB : PVDF = 75 : 15 : 10 followed by slurry formation in N-methyl-2-pyrrolidinone (NMP). Coated foils were dried overnight at 80 ^{o}C under vacuum. Electrodes were punched out and used as cathodes in coin cells with sodium metal as anode and glass microfiber (Whatman, GF/A) as separator. Electrode loadings were typically 3-5 mgcm^{-2}. 1M $NaClO_4$ in EC : PC :: 1:1 by wt% was used as the electrolyte. Cells were assembled in the glove box and tested at room temperature using a multichannel Maccor® battery tester Series 4000. In order to obtain material for powder X-ray diffraction at the end of charge the electrode was removed, washed with dry dimethyl carbonate and dried. The resulting powder was then transferred to a 0.5mm capillary and sealed.

a)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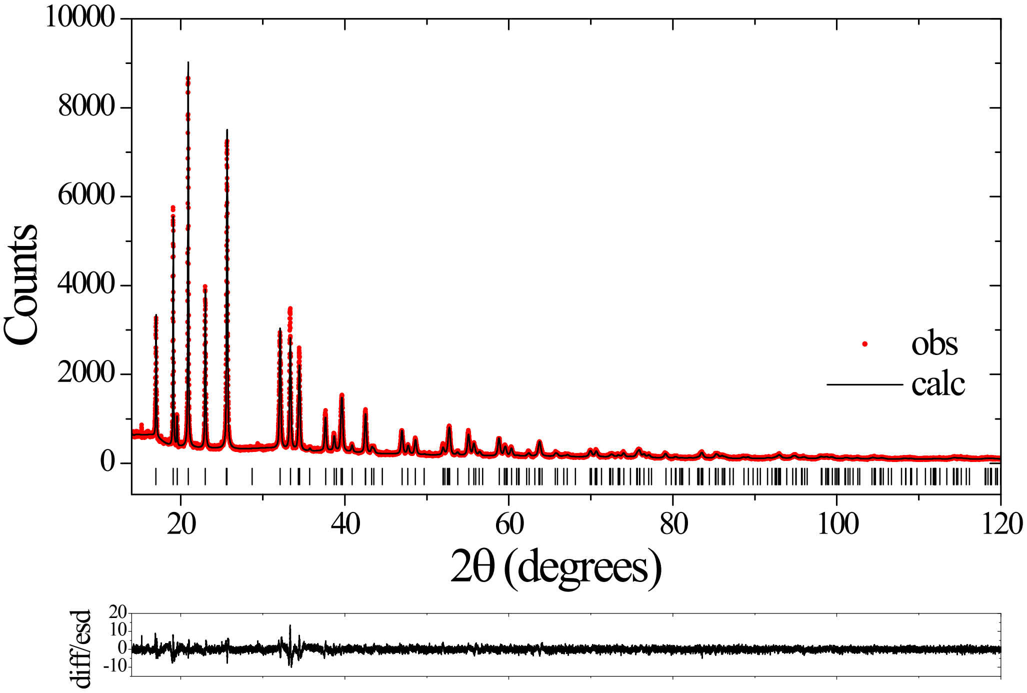
b)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10
0
-10

Fig. S1. Refined synchrotron powder X-ray diffraction patterns of $Na_{0.67}Mn_{0.9}Mg_{0.1}O_2$ for (a) quenched and (b) furnace cooled samples. Dots represent observed data and solid line the calculated pattern. The lower line is the difference/esd.

Table S1a. Crystallographic parameters for quenched $Na_{0.67}Mn_{0.9}Mg_{0.1}O_2$.

Cmcm. a = 2.8445(1) Å, b = 5.2264(3) Å, c = 11.1802(5) Å.

Atom	Wyckoff symbol	x/a	y/b	z/c	B_{iso}	occupancy
Na1	4c	0.0	0.3208(14)	0.25	4.4(3)	0.48(1)
Na2	4c	0.0	0.020(4)	0.25	3.5(5)	0.18(1)
Mn1/Mg1	4a	0.0	0.0	0.0	0.64(2)	0.9/0.1
O1	8f	0.0	0.6524(6)	0.0912(2)	0.88(4)	1

R-factors: R_{exp} = 2.56%, R_{wp} = 6.71%, R_p = 5.28%

Table S1b. Crystallographic parameters for slow cooled $Na_{0.67}Mn_{0.9}Mg_{0.1}O_2$.

$P6_3/mcm$. a = 2.88093(6) Å, c = 11.2148(4) Å.

Atom	Wyckoff symbol	x/a	y/b	z/c	B_{iso}	occupancy
Na1	2a	0.0	0.0	0.25	7.6(4)	0.26(1)
Na2	4c	0.3333	0.6667	0.25	5.5(2)	0.39(1)
Mn1/Mg1	2b	0.0	0.0	0.0	0.599(7)	0.853/0.096(2)
O1	4e	0.3333	0.6667	0.0903(2)	0.94(3)	1

R-factors: R_{exp} = 2.79%, R_{wp} = 7.44%, R_p = 5.69%

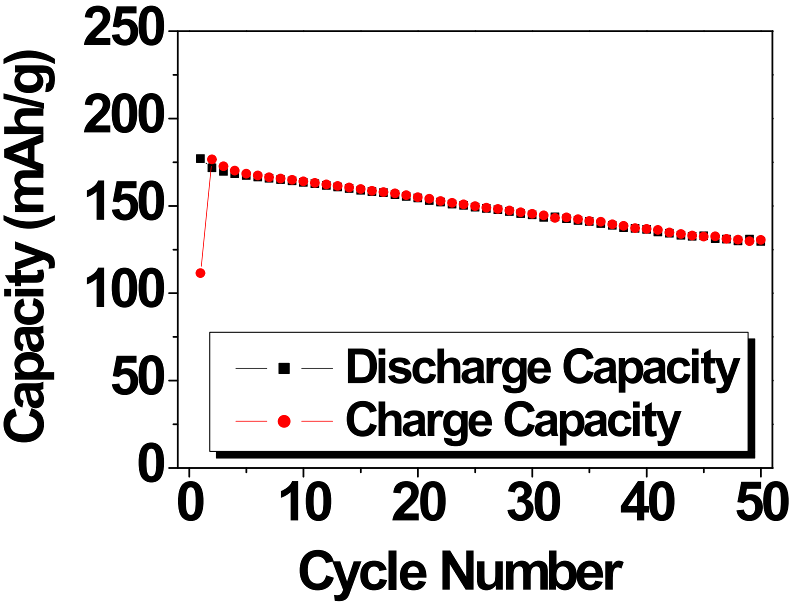

Fig. S2. Cycling performance for quenched $Na_{0.67}Mn_{0.95}Mg_{0.05}O_2$ up to 50 cycles.

[1] A. A. Coelho, *J. Appl. Cryst.*, 2000 **33** 899.