

## Supporting information

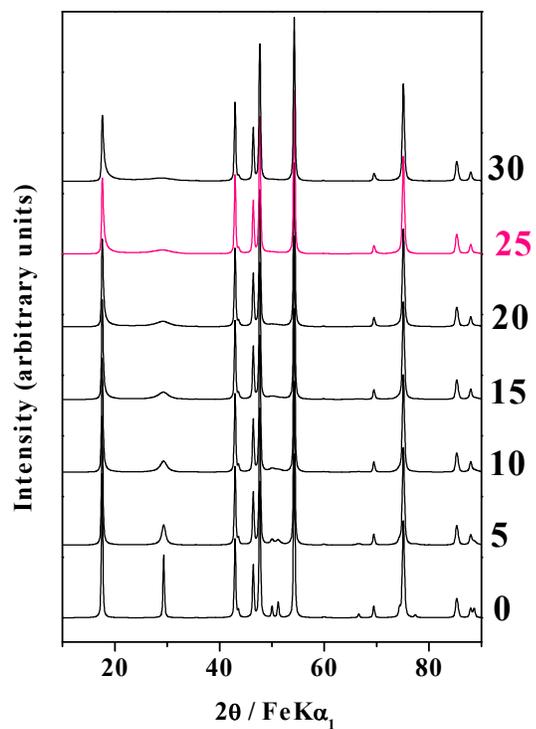
### $\beta$ -NaMnO<sub>2</sub> : a High Performance Cathode for Sodium-Ion Batteries

**AUTHORS:** Juliette Billaud, Raphaële J. Clément, A. Robert Armstrong, Jesús Canales-Vázquez, Patrick Rozier, Clare P. Grey and Peter G. Bruce

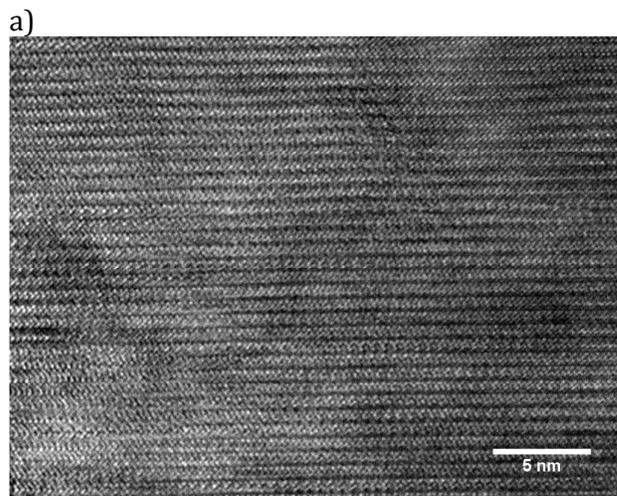
**CORRESPONDING AUTHOR:** Peter G. Bruce, email: peter.bruce@materials.ox.ac.uk

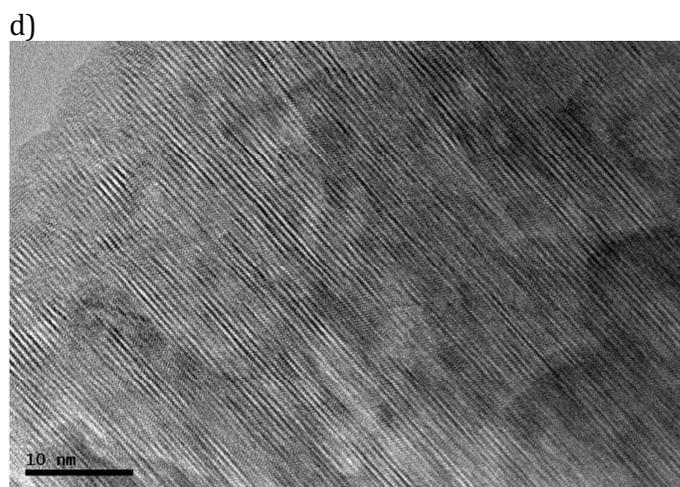
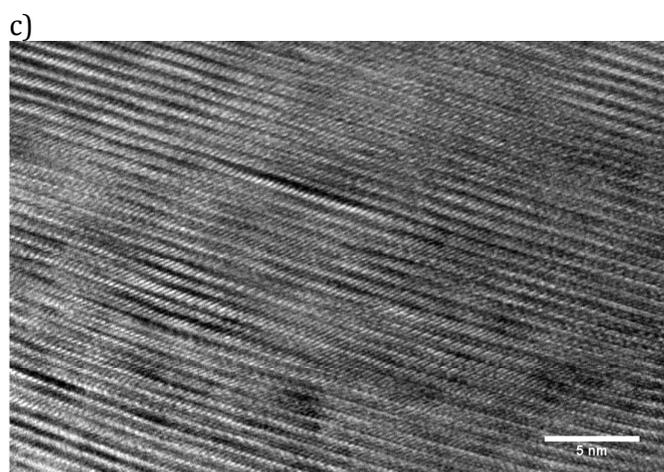
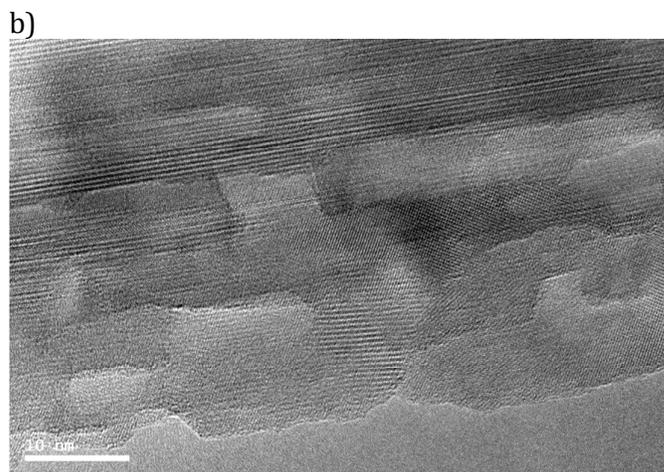
#### TABLE OF CONTENTS:

- Figure S1.** Simulation of  $\beta$ -NaMnO<sub>2</sub> with various percentages of stacking faults (from 0% to 30%)
- Figure S2.** HRTEM images of  $\beta$ -NaMnO<sub>2</sub>
- Figure S3.** Comparison of the <sup>23</sup>Na NMR spectra acquired on the  $\beta$ -NaMnO<sub>2</sub> pristine phase and after the 5<sup>th</sup> discharge
- Figure S4.** *Ex situ* <sup>23</sup>Na spin echo NMR spectra obtained on the pristine  $\alpha$ -NaMnO<sub>2</sub> phase
- Figure S5.** Continuous cycling at equal charge and discharge rates
- Figure S6.** Load curves at high and low rate obtained on cycle 5 between 2-4.2 V vs. Na<sup>+</sup>/Na
- Figure S7.** Results from the Galvanostatic Intermittent Titration Technique between 2-4.2 V vs. Na<sup>+</sup>/Na

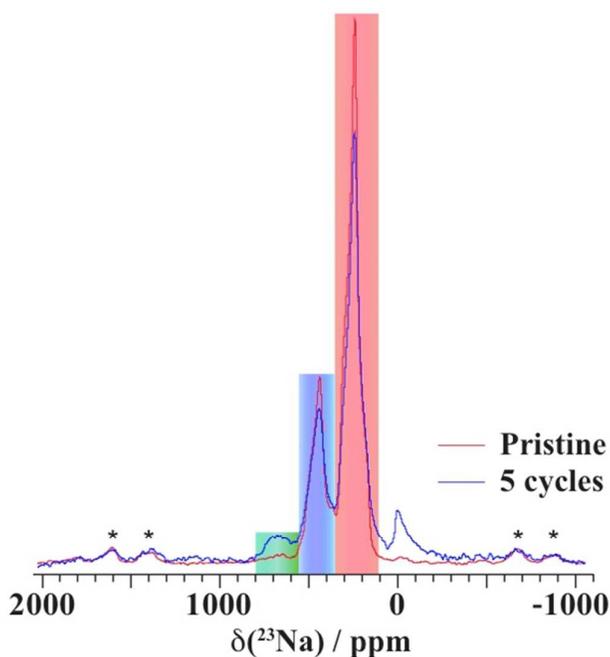


**Figure S1.** Simulation of  $\beta$ - $\text{NaMnO}_2$  with various percentages of stacking faults (from 0% to 30%). The pink pattern represents the simulation closest to the experimental pattern

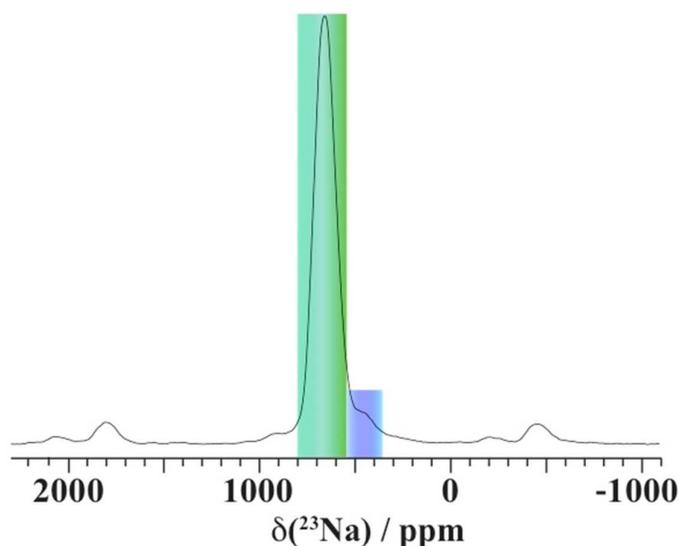




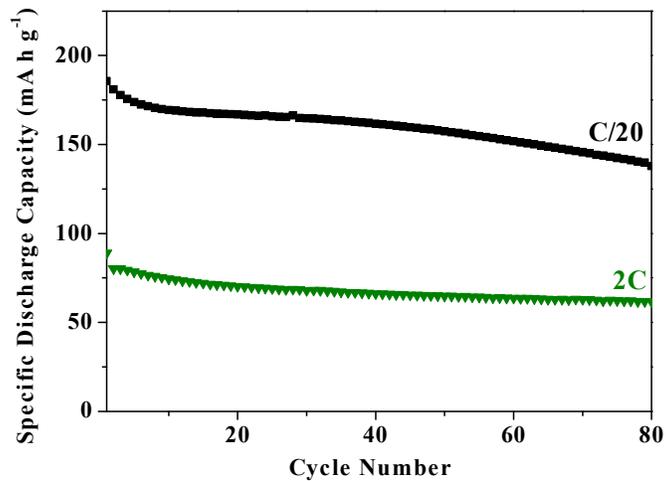
**Figure S2.** HRTEM images of  $\beta$ - $\text{NaMnO}_2$ : a) as-prepared; b) at the end of charge, at 4.2 V vs.  $\text{Na}^+/\text{Na}$ ; c) at the end of discharge, at 2V vs.  $\text{Na}^+/\text{Na}$ ; d) after 5 full charge/discharge cycles.



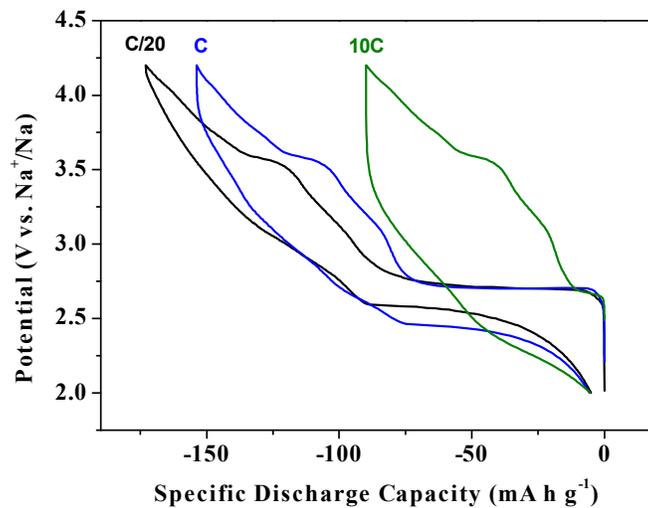
**Figure S3.** Comparison of the  $^{23}\text{Na}$  NMR spectra acquired on the  $\beta\text{-NaMnO}_2$  pristine phase and after the 5<sup>th</sup> discharge. Spinning sidebands are denoted with (\*). The three regions containing the resonances of Na atoms in a pure  $\alpha$  environment, in a pure  $\beta$  environment, and in the vicinity of a stacking fault are highlighted in green, red, and blue, respectively. The peak near 0 ppm is due to  $\text{Na}^+$  in a diamagnetic environment, most probably from residual electrolyte or its decomposition products formed during cycling.



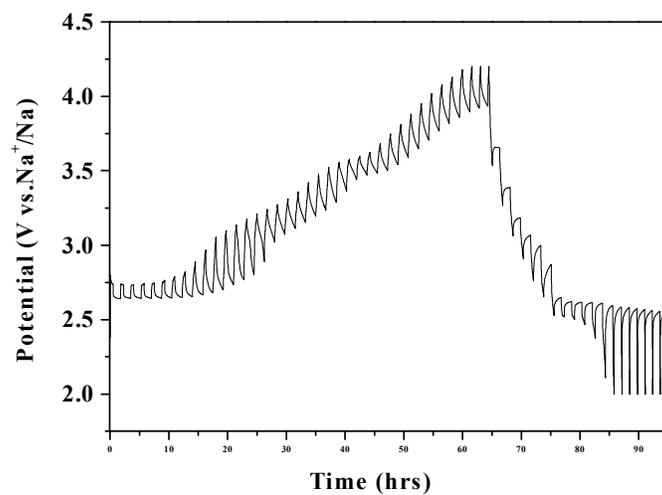
**Figure S4.** *Ex situ*  $^{23}\text{Na}$  spin echo NMR spectra obtained on the pristine  $\alpha\text{-NaMnO}_2$  phase under an external field of 200 MHz and at a spinning frequency of 60 kHz. The two regions containing the resonances of Na atoms in a pure  $\alpha$  environment and in the vicinity of a stacking fault are highlighted in green and blue, respectively



**Figure S5.** Values of specific discharge capacities for  $\beta$ -NaMnO<sub>2</sub> cycled between 2 and 4.2 V vs. Na<sup>+</sup>/Na at room temperature. 80 cycles are presented for each rate. Charge and discharge rates were identical. Black symbols correspond to a rate of C/20 and green symbols to 2C.



**Figure S6.** Load curves at high and low rate obtained on cycle 5 between 2-4.2 V vs. Na<sup>+</sup>/Na. The cycling rate is indicated on the corresponding load curve.



**Figure S7.** Results from the Galvanostatic Intermittent Titration Technique between 2-4.2 V vs. Na<sup>+</sup>/Na. A current of 20 mA g<sup>-1</sup> was applied for 30 min followed by a resting period of 75 min.