

## Supporting Information

### **P2-Na<sub>x</sub>Co<sub>0.7</sub>Mn<sub>0.3</sub>O<sub>2</sub> (x≈1.0) Cathode Material for Na-Ion Batteries with Superior Rate and Cycle Capability**

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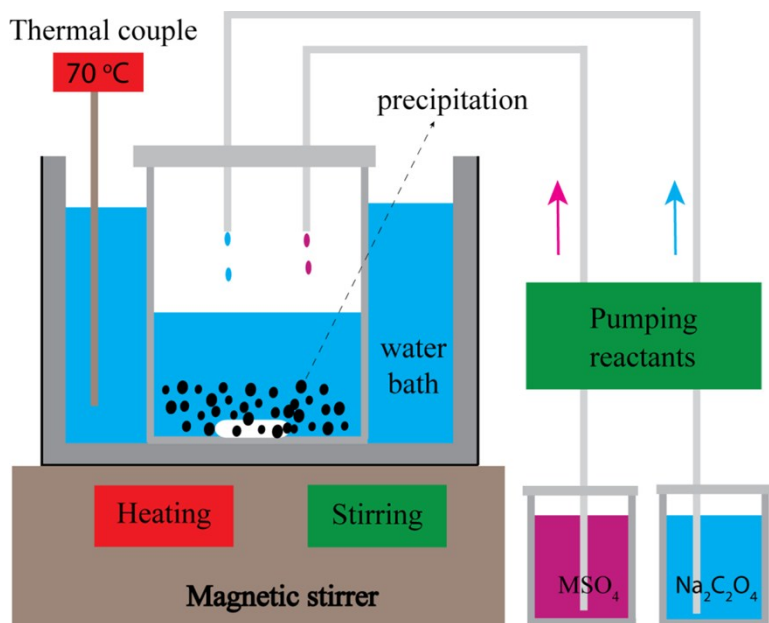
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## Synthesis setup



**Figure S1.** Overview of the experimental setup used for the oxalate co-precipitation.

## Precursor

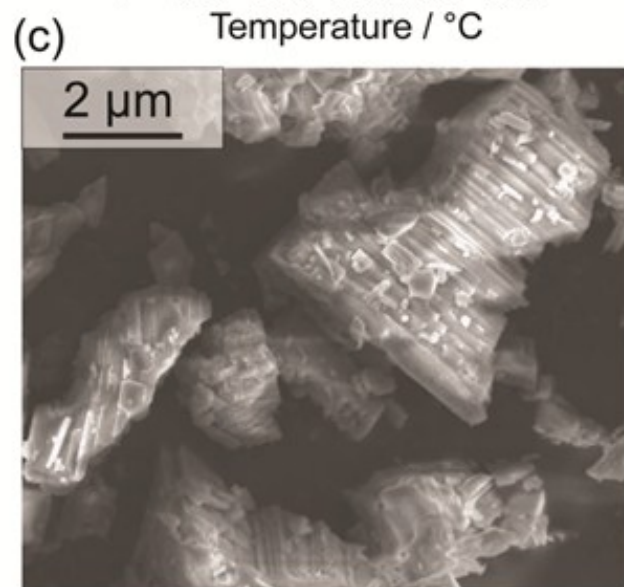
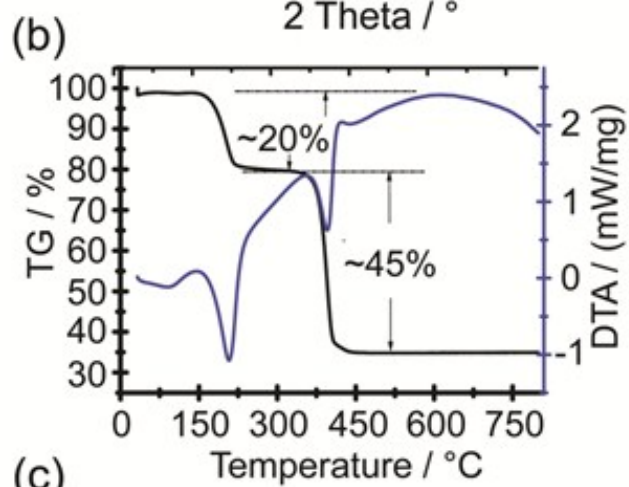
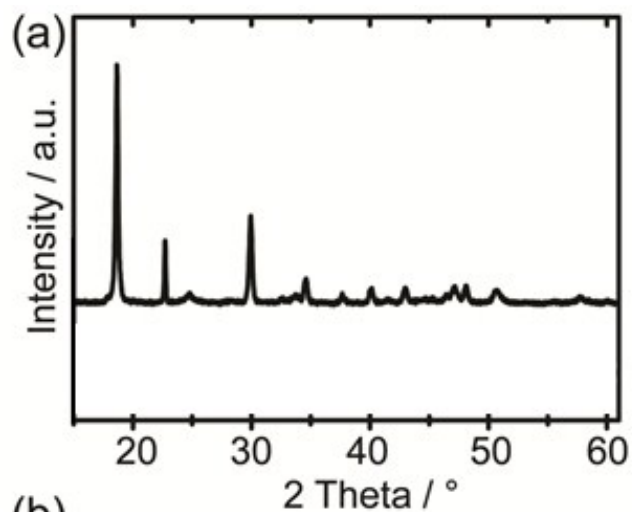
The  $\text{P2-Na}_x\text{Co}_{0.7}\text{Mn}_{0.3}\text{O}_2$  ( $x \approx 1.0$ ) material was prepared by solid state reaction between a Co/Mn-oxalate dihydrate precursor and  $\text{Na}_2\text{CO}_3$  (molar ratio Co/Mn:Na = 1:1.05). The pink powder ( $\text{Co}_{0.7}\text{Mn}_{0.3}\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ ) precursor material was prepared by a co-precipitation reaction, and it crystallized in the orthorhombic space group Cccm, as shown by PXRD in Figure S2a. Thermo-gravimetric analysis and differential thermal analysis (TGA-DTA) show a typical two step mass loss of the oxalate compound, corresponding to dehydration and decomposition processes, respectively (Figure S2b). The as-prepared  $\text{Co}_{0.7}\text{Mn}_{0.3}\text{O}_2 \cdot 2\text{H}_2\text{O}$  precursor material consists of a very dense stacking of platelet shaped crystals forming layered particles with a size of  $\sim 1\text{-}5 \mu\text{m}$  (Figure S2c).

The combination of the PXRD and TGA/DTA results confirm that Co and Mn form a solid solution within a single precursor phase. The composition is determined to be  $\beta\text{-Co}_{0.7}\text{Mn}_{0.3}\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  by inductively coupled plasma-optical emission spectrometry (ICP-OES) and TGA-DTA analysis, see figure S2b and table S1. Fourier transform infrared spectroscopy (FTIR) and PXRD of decomposition products after TGA-DTA analysis, see Figure S3, further supports the precursor is in fact an oxalate containing cobalt and manganese.

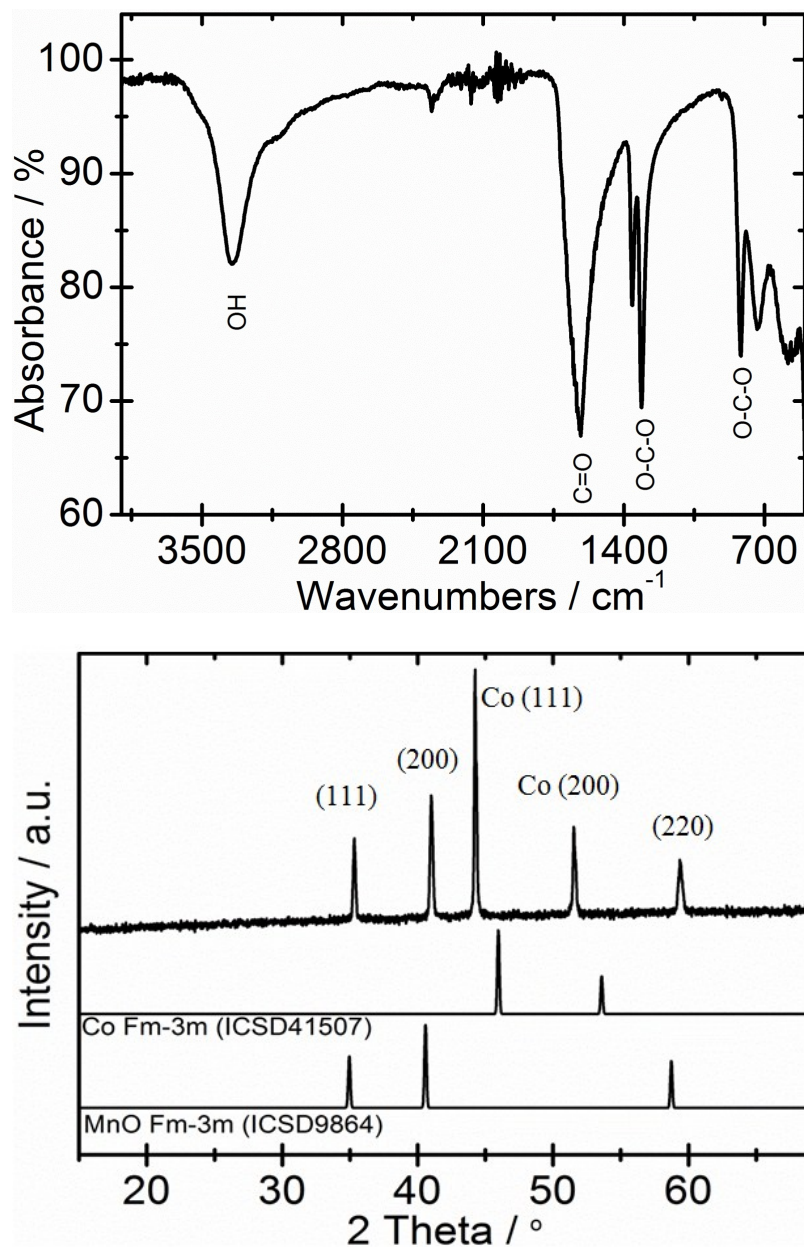
**Table S1.** ICP measured result of the  $\text{Co}_x\text{Mn}_{1-x}\text{O}_2 \cdot 2\text{H}_2\text{O}$  sample.

Element	Measured (mg/L)	Calculated (atomic ratio)
Co	0.681	0.697

Mn	0.276	0.303
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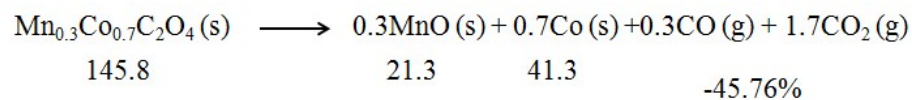
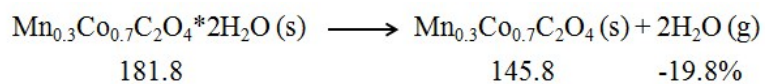
**Figure S2** Crystal structure, thermal stability performance, and morphological properties of the as-prepared  $\beta$ - $\text{Co}_{0.7}\text{Mn}_{0.3}\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  precursor: (a) PXRD pattern of the  $\beta$ - $\text{Co}_{0.7}\text{Mn}_{0.3}\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$  precursor, (b) TGA-DTA data measured by heating the precursor in Ar/O<sub>2</sub> atmosphere from room temperature to 800 °C at 5 °C/min, and (c) SEM image of the precursor sample.



**Figure S3.** (Top) FTIR results of as-prepared precursor (bottom) PXRD pattern of the product of as-prepared precursor after TG-DTA.

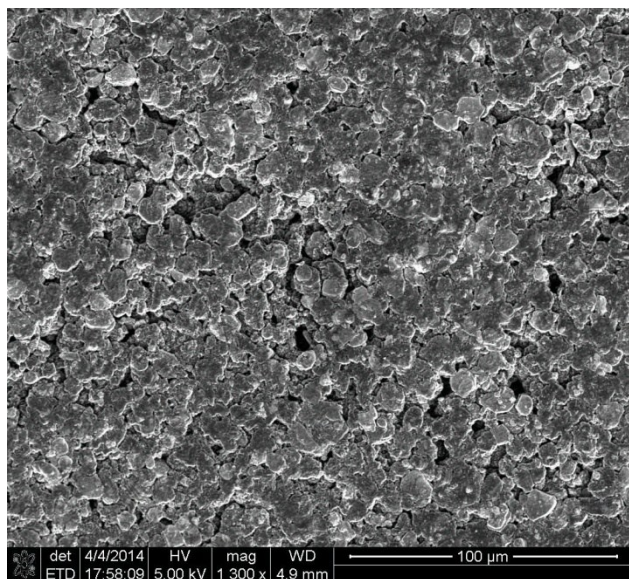


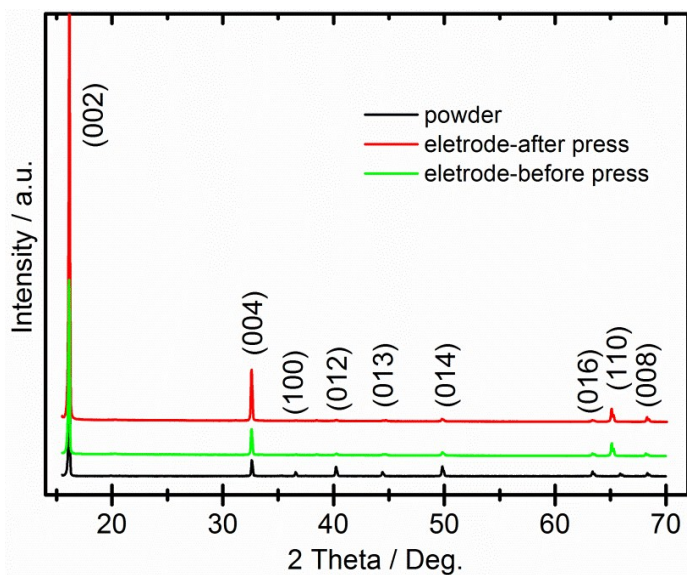
According to table S1 and Figure S3 the proposed reaction is:



## Preferred orientation

After coating the powder on an Al current collector, almost only the peaks at the [001] planes can be observed with lab X-ray source. As the PXRD patterns in figure S4 reveal the preferred orientation is obtained before pressing of the electrode and is not affected by it.

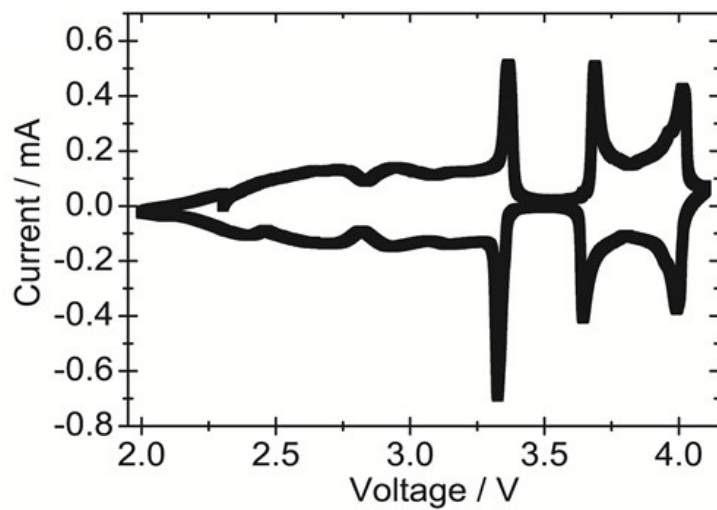




**Figure S4.** (Top) SEM image of the electrode, (Bottom) XRD pattern of the electrode.

## Cyclic voltammetry

Cyclic voltammetry measurement was conducted on the Na/P2-Na<sub>x</sub>Co<sub>0.7</sub>Mn<sub>0.3</sub>O<sub>2</sub> (x≈1.0) cell to obtain more information about the electrochemical properties of the as-prepared material.



**Figure S5.** Cyclic voltammetry result measured between 2.0 V and 4.2 V at 0.02 mV/s.

## Relationship of EIS and voltage of a cell

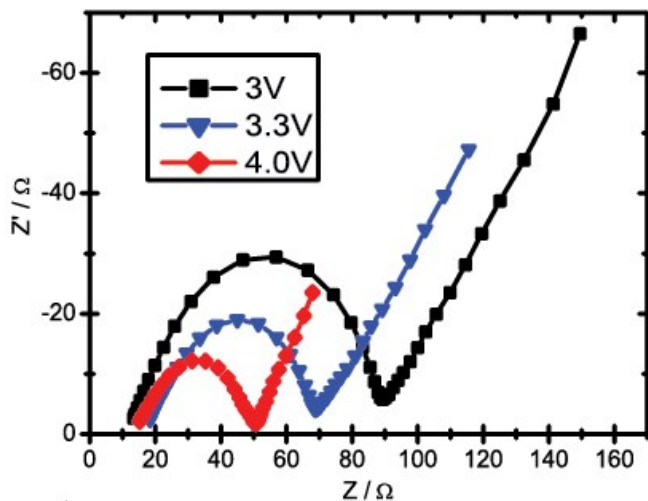


Figure S6. Relationship of EIS and voltage of a cell.

## Coulombic efficiency

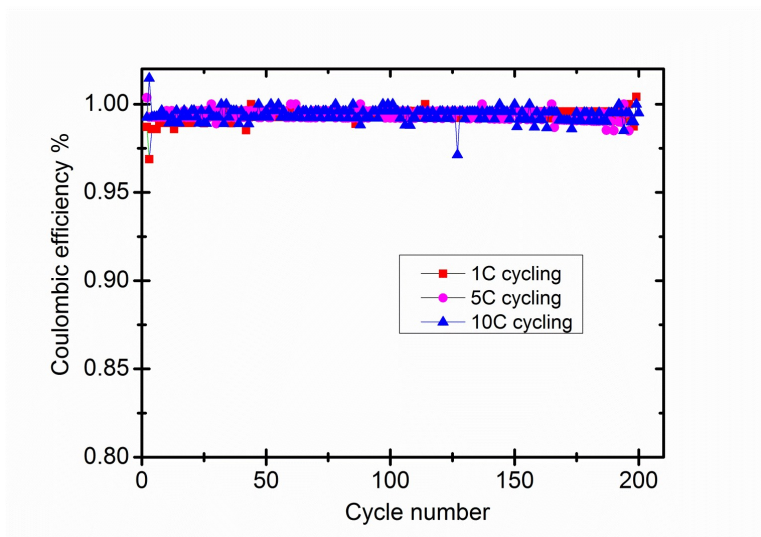


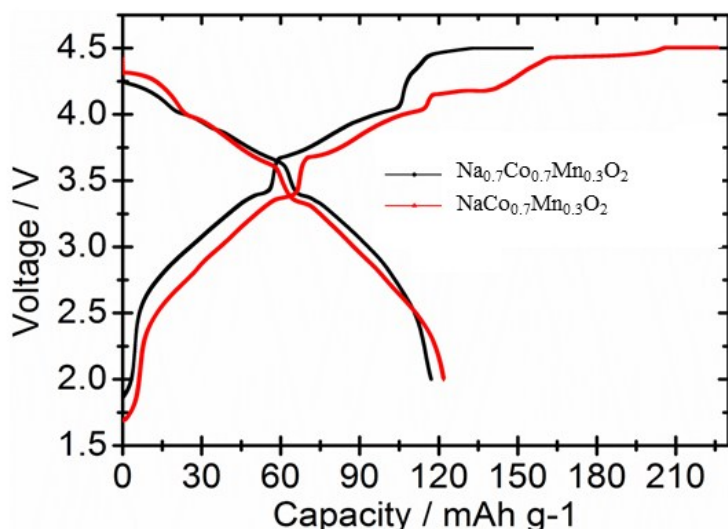
Figure S7. Coulombic efficiency of  $P2-Na_xCo_{0.7}Mn_{0.3}O_2$  ( $x \approx 1.0$ ) at different current densities during long term cycling.

## Voltage curve and sodium content

As shown in Figure S7, two samples with different sodium content but the same electrolyte show different voltage curves; the voltage plateau at  $\sim 4.2$  V cannot be found (and plateau at  $\sim 4.5$  V is negligible) in the P2-



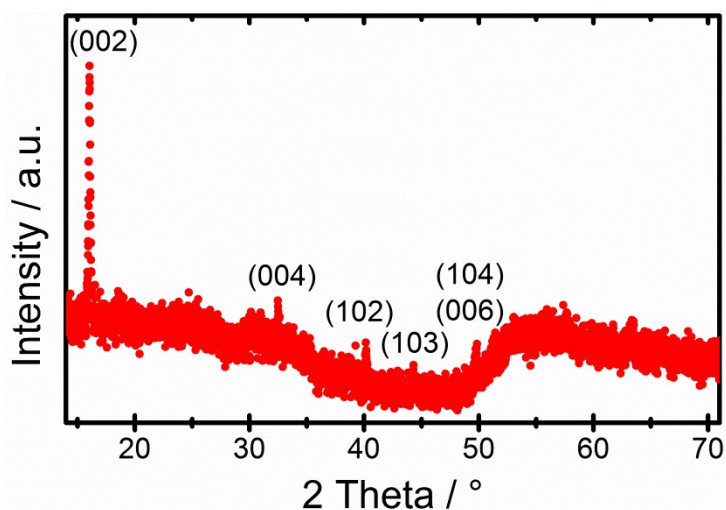
$\text{Na}_{0.7}\text{Co}_{0.7}\text{Mn}_{0.3}\text{O}_2$  sample which with lower sodium content but same electrolyte. These samples are from a different synthesis batch.



**Figure S8.** Voltage profiles from the first cycle at 0.1C between 2.0 V and 4.5 V. (red)  $\text{P2-Na}_x\text{Co}_{0.7}\text{Mn}_{0.3}\text{O}_2$  ( $x \approx 1.0$ ), (black)  $\text{Na}_{0.7}\text{Co}_{0.7}\text{Mn}_{0.3}\text{O}_2$ .

### PXRD of electrode material cycled 300 times between 4.5-2.0V

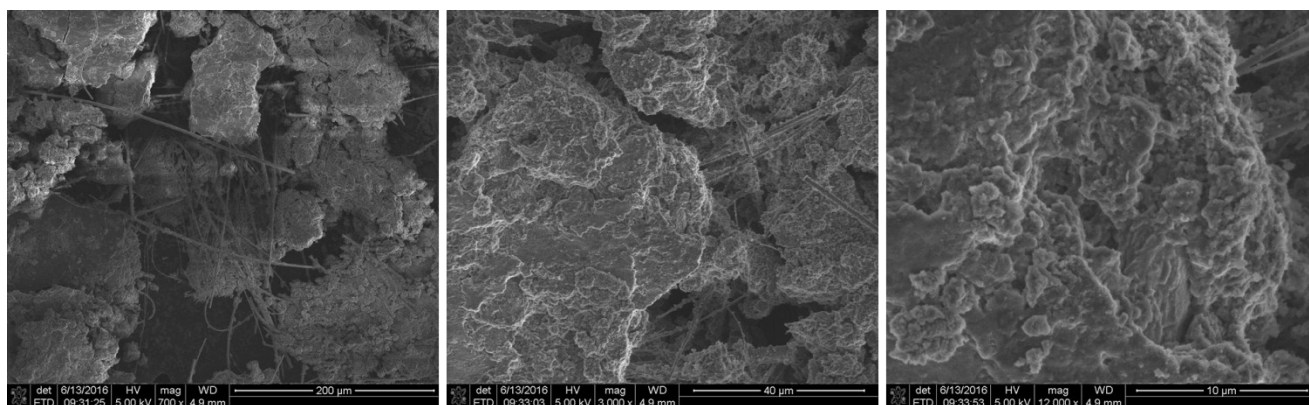
PXRD of  $\text{P2-Na}_x\text{Co}_{0.7}\text{Mn}_{0.3}\text{O}_2$  ( $x \approx 1.0$ ) cycled between 4.5-2.0V for 300 cycles at 1C. Qualitatively it can be seen that the P2 crystalline phase is still present in the electrode (see indexed peaks) but due to low data quality no conclusions about structural distortion can be made. Sample was obtained by opening a cell containing electrodes from a different synthesis batch that had finished cycling a few months earlier. The data quality is low due to the fact only very small amount of material could be recovered (typical active material loading is 3-4 mg) and the active material is now mixed with acetylene black and PVdF.



**Figure S9.** PXRD of  $P2-Na_xCo_{0.7}Mn_{0.3}O_2$  ( $x \approx 1.0$ ) cycled between 4.5-2.0V for 300 cycles at 1C.

### SEM of electrode material cycled 300 times between 4.1-2.0V

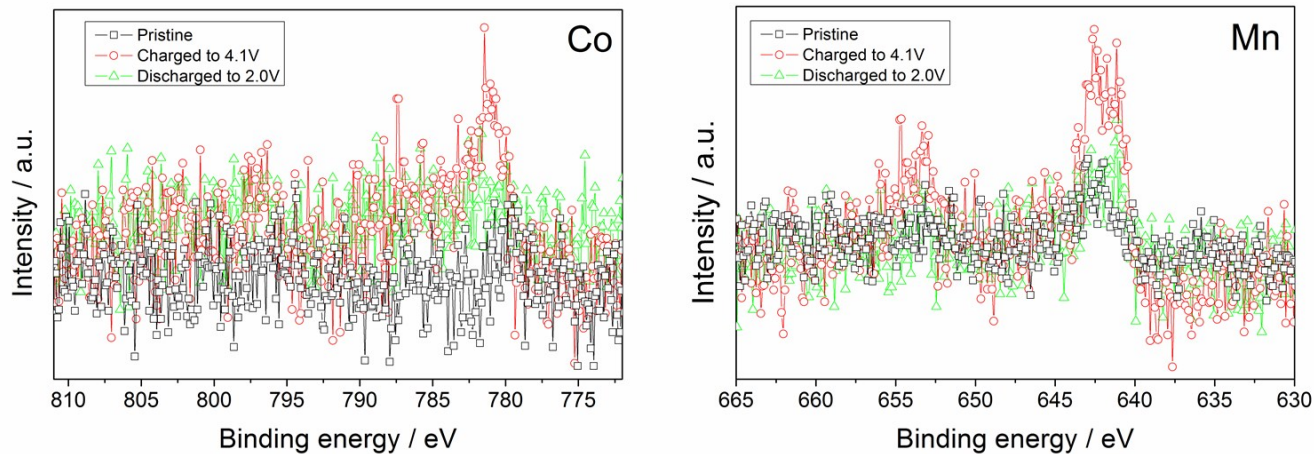
SEM pictures of  $P2-Na_xCo_{0.7}Mn_{0.3}O_2$  ( $x \approx 1.0$ ) cycled between 4.1-2.0V for 300 cycles at 1C. Sample was obtained by opening a cell containing electrodes from a different synthesis batch that had finished cycling a few months earlier. Note that needle like particles are glass fibres from the separator in the battery assembly and small secondary particles are acetylene black and PVdF. The SEM pictures show evidence of cracking. The layered morphology of the P2 particles is still visible after cycling although to a lesser extent. Both these results might contribute in part to the capacity fade of the electrode material but it is not clear that morphological changes are the major cause of the capacity fading.



**Figure S10.** SEM pictures of  $P2-Na_xCo_{0.7}Mn_{0.3}O_2$  ( $x \approx 1.0$ ) cycled between 4.1-2.0V for 300 cycles at 1C.

## Electrochemical activity

High resolution X-ray Photoelectron Spectroscopy (XPS) for cobalt and manganese of pristine P2- $\text{Na}_x\text{Co}_{0.7}\text{Mn}_{0.3}\text{O}_2$  ( $x \approx 1.0$ ), after first charge to 4.1V and first discharge to 2.0V. Measurement done on electrodes resulting in low signal to noise ratio. Changes in signals from pristine to charged to discharged sample show qualitatively that both cobalt and manganese are electrochemically active in the potential range 4.1-2.0V.



**Figure S11.** High resolution XPS for cobalt and manganese of pristine P2- $\text{Na}_x\text{Co}_{0.7}\text{Mn}_{0.3}\text{O}_2$  ( $x \approx 1.0$ ), after first charge and first discharge.