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Supporting information

P3-type K_{0.33}Co_{0.53}Mn_{0.47}O₂·0.39H₂O: Novel Bifunctional Electrode

for Na-Ion Batteries

Experimental Section

Materials Synthesis: $K_{0.33}Co_{0.53}Mn_{0.47}O_2 \cdot 0.39H_2O$ (KCM) was prepared by a sol–gel method. 5 mmol Co(CH₃COO)₂·4H₂O, 5 mmol Mn(CH₃COO)₂·4H₂O, 10.4 mmol CH₃COOK and 40 mmol citric acid were added in 50 ml deionized water, respectively. After stirred uniformly, the transparent solution was transferred to a glass dish and heated at 90 °C for 12 hours. The damp-dry gel was separated from the glass dish and then became hardened at room temperature. The gel was first heated at 380 °C for 10 hours and further heated at 800 °C for another 10 hours in a muffle furnace. There was no temperature-fall period between the two heating process and the heating rates were all set to be 5 °C min⁻¹. After cooling down, the obtained ash was washed with deionized water and ethyl alcohol several times by centrifuging to remove the by-products. The final product was dried at 80 °C overnight.

Characterization: X-ray diffraction (XRD) measurements were performed on a Bruker D8 Focus Powder X-ray diffractometer with Cu Kα radiation (40 kV, 40 mA) and the Rietveld method (GSAS program suite) was used to refine the XRD data of the as-synthesized material. X-ray photoelectron spectroscopy (XPS) analysis was analyzed with an ESCALAB MK II. Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) measurement was performed on a Thermo Jarrell Ash (TJA) Atomscan Advantage instrument, and the characterization was operated on the solution of the dissolved sample in the mixed solvent of concentrated sulfuric acid, hydrochloric acid and nitric acid (volume ratio 5:3:1). Scanning electron microscopy (SEM) was performed on a field emission Hitachi S-4800 instrument. Transmission electron microscope (TEM), Selected area electron diffraction (SAED) and Elemental mapping were performed on a FEI Tecnai G₂ S-Twin instrument. Thermogravimetric analysis (TGA) was performed under air atmosphere from 25 to 500 °C at a heating rate of 10 °C min⁻¹ on a NETZSCH STA 449 F3 Simultaneous TGA-DSC Instrument. The *Ex situ* XRD patterns were collected from the KCM electrodes with different depths of charge or discharge that primarily sealed in sample holders with Kapton film windows in an argon atmosphere. The *Ex situ* XRD patterns were collected from the the primarily sealed in sample holders with Kapton film windows in an argon atmosphere. The *Ex situ* XRD patterns were collected from the the primarily sealed in sample holders with Kapton film windows in an argon atmosphere. The *Ex situ* XRD patterns were collected from the the primarily sealed in sample holders with Kapton film windows in an argon atmosphere.

Electrochemical evaluation: The active electrode materials, KCM, commercial Sb_2O_3 were separately mixed with acetylene black and CMC in a weight ratio of 7:2:1 with deionized water as medium to form slurry. Then a doctor blade was used to spread the slurry uniformly onto aluminum foil (KCM) or copper foil (Sb_2O_3), and the electrodes were dried at 80 °C overnight. The loading of the KCM and the Sb_2O_3 on the current collector is about 1 and 1.7 mg cm⁻², respectively. The electrodes were then cut into 12 mm diameter discs and assembled with Na metal as counter electrodes in 2025 coin-type cells in an argon-filled glove box. The electrolyte was 1 M NaPF₆ in EC/DEC (1:1 v/v) with 5% FEC and the separators were glass fibers. The specific capacity of KCM based full cell was calculated approximately based on the cathode mass before electrochemical activation (pre-charge). For preparing the second full cell, the Sb_2O_3 electrode was pre-sodiated to 0 V to get the workable anode containing Na-

Sb alloy and Na₂O, and no special treatment was made on the KCM cathode before assembling. Land CT2001A battery testing system (Land, China) was used for galvanostatic charge-discharge cycling and VMP3 electrochemical workstation (Bio-Logic, France) was used for cyclic voltammetry measurements and electrochemical impedance spectroscopy (EIS was conducted on a frequency range of 100 kHz–0.01 Hz).



Fig. S1 TGA curves of the KCM sample.

No.	20	h	k	1	D-spacing (Å)	Intensity
1	13.048	0	0	-3	6.7795	343957.1
2	26.27	0	0	-6	3.3898	76110.07
3	36.916	-1	1	1	2.4329	42275.52
4	37.73	0	1	2	2.3823	27385.66
5	39.859	0	0	-9	2.2598	3340.57
6	40.845	-1	1	4	2.2075	13204.66
7	43.058	0	1	5	2.0991	19622.58
8	48.562	-1	1	7	1.8732	7267.09
9	51.773	0	1	8	1.7643	2425.07
10	54.064	0	0	-12	1.6949	1060.31
11	58.969	-1	1	10	1.565	663.04
12	62.919	0	1	11	1.476	497.9
13	65.975	-1	2	0	1.4148	352.82
14	67.584	-1	2	3	1.385	211.05
15	69.237	0	0	-15	1.3559	26.57
16	71.485	-1	1	13	1.3187	110.64
17	72.31	-1	2	6	1.3057	216.54
18	76.108	0	1	14	1.2497	32.64
19	78.074	0	2	1	1.223	32.86
20	78.577	-2	2	2	1.2165	20.47
21	79.935	-1	2	9	1.1992	24.5
22	80.583	0	2	4	1.1912	14.15
23	82.079	-2	2	5	1.1732	16.03
24	85.958	0	0	-18	1.1299	3.15
25	86.046	0	2	7	1.129	8.2
26	86.103	-1	1	16	1.1284	5.32
27	88.515	-2	2	8	1.1038	3.77

 Table S1. The calculated lattice reflections and interplanar distances of KCM by
 Rietveld refinement.

Atoms	X	У	Z	Occupancy
Κ	0	0	0.834369	0.33
Со	0	0	0.000000	0.53
Mn	0	0	0.000000	0.47
0	0	0	0.409998	1.00
0	0	0	0.590002	1.00
O _(H2O)	0	0	0.834369	0.39

 Table S2. Rietveld refinement parameters and results obtained for KCM.



Fig. S2 (a) Co 2p, (b) Mn 2p XPS spectra of KCM.



Fig. S3 (a) The Co 2p XPS spectra of the commercial Co_3O_4 . (b) The Mn 2p XPS spectra of the commercial MnO_2 .

The two major peaks of standard Co_3O_4 are located at 795.4 and 780.0 eV, after fitting it can be seen that the peaks of Co^{2+} locate at 796.36 and 781.16 eV (Peak 1, 2), and that of Co^{3+} at 794.81 and 779.80 eV (Peak 2, 3). These values are close to that of KCM. The two major peaks (653.8 and 642.0 eV) of standard MnO₂ are also close those of the KCM (653.9 and 642.3 eV).

As $K_{0.33}Co_{0.53}Mn_{0.47}O_2$ is an analogue to Na_xCoO_2 , and we should note that massive experimental data for the physical properties have been interpreted assuming that Na_xCoO_2 samples studied are totally oxygen stoichiometric. Actually, the assumption of stoichiometric oxygen content is valid only for Na-rich samples, whereas low-Nacontent samples inevitably possess oxygen vacancies, the concentration of which increases with decreasing Na content x.^{1,2} Thus, there should be some oxygen vacancies in the crystal structure that are responsible for maintaining electro-neutrality. Meanwhile, the instrumental error should also be responsible for the deviation. From the XPS fitting result of KCM, the mole ratio of Co^{2+} : Co^{3+} is about 1.05:1 and the valence cobalt is 2.55⁺. It's worth stressing that the valence states doesn't affect the refinement results.^{3, 4}



Fig. S4 (a) K 2p XPS spectrum of KCM. (b) O 1s XPS spectrum of KCM. (c) SEM image of KCM with a low magnification. (d) TEM images of KCM.



Fig. S5 Nyquist plots of a typical KCM electrode after different cycles prepared at 100 mA g^{-1} between 1.6 and 4.6 V.

In Fig. S5, the diameters of the semi-circles at high-frequency region are approximately equal to the value of charge transfer impedance (Rct) which are estimated by ZView-Impedance software and the values are listed in Table S3. It's found that the Rct gradually decreases from 1422 to 385.5 Ω which should be related to the further infiltration of the electrolyte that could cause the activation of KCM. The linear plots at low-frequency region are relevant to the diffusion of Na⁺ ions in the materials. The sodium ion diffusion coefficient (D) is calculated by the mathematical formula: D= R²T²/A²n⁴F⁴C²\sigma², where R is the gas constant, T is the absolute temperature, A is the surface area of the electrode, n is the number of electrons per molecule during oxidization, F is Faraday's constant, C is the concentration of sodium ions, and σ is the Warburg factor related to Z': Z'= R_D + R_L+ $\sigma\omega^{-1/2}$.²⁶ As shown in Table

S3, from 1st to 50th cycle, the diffusion coefficient of Na ions gradually increases from 3.76×10^{-13} to 2.54×10^{-12} cm² s⁻¹, and this phenomenon might be related to the gradual replacement of K ions by Na ions which could provide more channels for easy movement of Na ions.

Parameter	Pristine	1st	5th	10th	50th
Rct (Ω)	1422	867.5	758.5	439.8	385.5
D (cm ² s ⁻¹)	-	3.76×10 ⁻¹³	9.88×10 ⁻¹³	2.14×10 ⁻¹²	2.54×10 ⁻¹²

 Table S3. Impedance parameters and Na ion diffusion coefficients of KCM after

 different cycle.

It's noticed that the activation phenomenon of the cathode has already disappeared at the 50th cycle, and it should be inferred that after certain cycles some degree of electrode degradation would play a certain role which could counteract the decrease of charge transfer impedance and the increase of diffusion coefficient.



Fig. S6 (a) Co 2p (Peak 1, 2 for Co²⁺, Peak 3, 4 for Co³⁺) (b) Mn 2p XPS spectra of KCM in different states as cathode (Peak 1, 2 for Mn⁴⁺, Peak 3, 4 for Mn³⁺ and Peak 5, 6 for Mn²⁺).

The *ex situ* XPS method was utilized to evaluate the valence changes of Co and Mn as shown in Fig. S6a, b. As the electrode is charged to 4.6 V, the peak intensity of Co^{2+} decreases and that of the Co^{3+} increases, also the Co^{2+} is not fully oxidized to Co^{3+} .⁵ And the appearing of Mn³⁺ might be caused by the reduction of O²⁻ accompanying by some mirror decomposition of the electrolyte forming the cathode electrolyte interface (CEI) film.⁶⁻⁸ Thus we inspect the charge progress involved the oxidation of Co^{2+} to Co^{3+} , the activation of Mn⁴⁺ to Mn³⁺, the forming of CEI film and so on. When the electrode is discharged to 1.6 V, the peak intensity of Co^{3+} decreases and that of the co²⁺ increases. At the same time, the Mn³⁺ is reduced to Mn²⁺ which also results in the capacity attribution in the discharge progress.



Fig. S7 (a) Co 2p (Peak 1, 2 for Co²⁺, Peak 3, 4 for Co³⁺ and Peak 5, 6, 7, 8 originate from Mental Co) (b) Mn 2p XPS spectra of KCM in different states as anode (Peak 1, 2 for Mn⁴⁺, Peak 3, 4 for Mn³⁺ and Peak 5, 6 for Mn²⁺).

As the electrode is discharged to 0 V, the peaks of Co^{2+} and Co^{3+} vanish and four peaks at 792.8, 779.3, 791.0 and 776.2 eV (Peak 5, 6, 7, 8) appear (Fig. S7a). According to the report on the sodium storage ability of Co_3O_4 and the result presented here we interpret preliminarily that the conversion reaction from Co^{2+}/Co^{3+} to mental Co is realizable.⁹ Peak 7 and 8 with such low binding energies should attributed to the mental cobalt in a sodium-around surrounding, and Peak 5 and 6 should be attributed to the satellite peaks of Peak 7 and 8. Different from the cobalt, the change of Mn 2p XPS spectra is easier to understood (Fig. S7b), after discharged to 0 V, we can see the Mn⁴⁺ vanish and a mixture of Mn³⁺ and Mn²⁺ is presented. Except the formation of SEI film, the valence changes of cobalt and manganese contribute partial capacity in the initial discharge that are responsible for the capacity discrepancy from theoretical estimate. As the electrode is charged to 2 V, only the peaks of Co 2p3/2 are detectable (Peak 4, 8), and we could deduce that the conversion from mental Co to Co³⁺ is realized. Meanwhile, the Mn²⁺ is partially oxidized to Mn³⁺.



Fig. S8 (a) CV curves of KCM at 0.1 mV s⁻¹ between 1.6 and 4.6 V. (b) 0 and 2 V.

Fig. S8a shows the CV curves of KCM *vs.* Na⁺/Na at a scan rate of 0.1 mV s⁻¹ between 1.6 and 4.6 V. The initial anodic scan from open circuit potential to 4.6 V exhibits distinct characters that the two peaks at 4.30 and 4.54 V are closely related to the desertion of the interplanar ions and molecules accompanied by the movement of the MeO₆ sheets. The insertion-desertion of Na ions starts from the initial cathodic scan and four obvious peaks at 4.3, 3.9, 3.4 and 1.68 V are observed. The Na ions are

preferable to insert to the sheets than the small amounts of K ions during the discharge process in view of the smaller radius and less relative molecular weight.¹⁰ The peak at 4.3 V has been speculated to the desertion of the electrolyte solvent at a higher voltage.^{11, 12} The two cathodic peaks at 3.9 and 3.4 V might originate from the reduction of Co³⁺ which is supported by the several found reaction voltages in sodium-combat-oxygen compounds, the peak at 1.68 V originates from the reaction of Mn⁴⁺ to Mn^{3+, 13-} ¹⁵ After the first cathodic scan, regularity is found between the redox peaks. The four anodic peaks at 2.3, 3.75, 4.2, and 4.55 V pairs with the cathodic peaks at 1.68, 3.4, 3.9 and 4.3V, respectively. Since the second reduction process, the three reduction peaks above 3.0 V tend to merge into one broad peak at 4.0 V, this phenomenon might be caused by the increased polarization. Although some peak shifts and broadenings occur during the following scans, overall shapes of the curves maintain, this indicates the structural reversibility in the electrochemical process.

Material	Discharge/c -harge capacity	Rate	Average potential	Voltage range	Cycle	Ref.	
Na ₃ V ₂ (PO4) ₃ /C	93 mAh g ⁻¹	0.05 C	3.40 V	2.7–3.8 V	-	16	
	66.3 mAh g ⁻	0.025 C	1.63 V	1-3V	50		
P2-	about 68 mA h g ⁻¹	9 mA g ⁻¹	over 3.5 V	2-4.2 V	30		
Na _{2/3} N1 _{1/3} T1 _{2/} ₃ O ₂	about 78 mA h g ⁻¹	C/5	0.7 V	0.2-3 V	25	17	
P2- Na0.6[Cr0.6 Ti0.4]O2	74 mAh g ⁻¹	7.6 mA g ⁻¹	3.5 V	2.5-3.8 V	200	10	
	105 mAh g- 1	11.2 mA g ⁻¹	0.8 v	0.5-2.5V	200	19	
O3-type Na _{0.8} Ni _{0.4} Ti _{0.6} O ₂	63 mA h g ⁻¹	63 mA h g ⁻¹	3.5 V	2-4 V	250	2	
	62 mA h g ⁻¹	62 mA g ⁻¹	0.75 V	0-2.5 V	250	3	
This work	114 mA h g- 1	100 mA g ⁻¹	over 3 V	1.6-4.6 V	130		
	174 mAh g- 1	100/50 -0 mA g ⁻¹	0.53 V	0-2 V	200/950	-	

Table S3. Summary of the typical "bi-functional" matterials for NIBs.



Fig. S9 (a) XRD patterns of the KCM as cathode at end-states in the 2nd and 20th cycle(b) XRD patterns of the electrodes as cathodes with other depths of charge and discharge as cathode in the 2nd cycle.



Fig. S10 XRD patterns of the electrodes at end-states as anodes in the 2nd cycle.



Fig. S11 (a) The 100th and 200th charge-discharge curves of the as-assembled KCMbased full cell. (b, c) The rate ability of the KCM-based cell (The mass loadings before activation are 1.15 mg and 1.21 mg for the cathode and anode, respectively). (d) CV curves of KCM (half cell) and KCM-based full cell.

As shown in Fig. S11b, c, the cell demonstrates discharge capacities of 67.7, 57.3, 42.6, 31.9 mAh g⁻¹ at current densities of 100, 200, 500, 1000 mA g⁻¹, respectively.

Based on the discharge-charge curves, the full cell looks like a capacitor instead of a battery. The CV curves of the KCM (half cell) and KCM-based full cell are further compared that it is found that two curves show the simialr shape (Fig. S11d). It is should be emphasized that the CV curve records change of working electrode, and the working electrode of the two cells are all KCM. In CV test, the difference between the two cells

is the counter electrode which also acts the reference electrode (namely, mental Na for the half cell, KCM for full cell). The selected obvious anodic and cathodic peaks (marked with blue and red arrows) in the half cell looks obvious which should be distinctive characters of a battery. And it can be found that they shift to lower voltage in the full cell as the average working potential of activated KCM is higher than mental Na. Thus, it is deduced that the full cell is not a capactor, but a battery even the anodic and cathodic peaks are not so obvious. This extraordinary phenonemnon is also found in other battery system and should be caused by the large particle size and the slow kinetics for the migration of alkalis in the structural lattice.^{20,21}

Full Cell	Working Voltage (V)	Theoretical energy density (Wh·kg ⁻¹)	Ref.
Activated carbon- NaMnO ₂	1	19.5	22
Activated carbon- Na _{0.44} MnO ₂	1	20	23
NaTi ₂ (PO ₄) ₃ - Na $0_{.44}$ MnO ₂	1.1	33	24
NaTi ₂ (PO ₄) ₃ - Na ₂ NiFe(CN) ₆	1.27	43	25
This work	2.5	91	-

Table S4. Comparison between KCM-based full cell and some existing Na-ion battery systems.



Fig. S12 (a, b) Charge-discharge curves of a 2025 coin-type full cell using KCM as cathode and sodiated Sb_2O_3 as anode. The cell is a cathode-limited type and cycles at 100 mA g⁻¹. (c) The cycle performance of the full cell at 100 mA g⁻¹.

The mixture of Na-Sb and Na₂O prepared through sodiation of commercial Sb₂O₃ is selected as the working anode and no special treatment was made on the KCM cathode.¹⁸ During the initial charge progress, the K ions leave the cathode to the anode and react with Na-Sb forming ternary K-Na-Sb alloy in the electronic environment. K-Na-Sb alloy and Na₂O from the anode donate Na and K ions in the follow discharge progress. In the initial five cycles the full cell shows a gradually-increased discharge capacity over 83 mAh g⁻¹ with an average voltage of 2.2 V in the voltage range of 0.6 to 4.0 V (Fig. S12a). The discharge capacity increases to a maximum value of 99 mAh g⁻¹ in the 29th cycle, a discharge capacity of 70 mAh g⁻¹ and an average voltage of 2.2 V still remain after 100 cycles (Fig. S12b, c). After the first cycle, the balanced coulombic efficiency is around 98% indicating the excellent reversibility of the full cell and the successful coupling between the sodiated Sb₂O₃ anode and the KCM cathode. The SEM images and electrochemical performance of the commercial Sb₂O₃ are given in Fig. S13 and Fig.S14.



Fig. S13 SEM images of the commercial Sb_2O_3 .



Fig. S14 (a) Discharge-charge curves of commertial Sb_2O_3 at 100 mA g⁻¹ between 0 and 3 V. (b) Cycle performance of commertial Sb_2O_3 at 100 mA g⁻¹ between 0 and 3 V.



Fig. S15 (a, c) charge–discharge curves, (b, d) cycle performance of KCM between 1.6 and 4.6 V or 0 and 2 V with 1 M NaPF₆ in EC/DEC (1:1 v/v) without FEC additive.

To further explore the efficacy of KCM, the electrochemical performance of the material with FEC-free electrolyte was tested for comparison. However, the KCM shows poor electrochemical performance both as cathode and anode. As cathode, the KCM demonstrates a low discharge capacity of 69 mAh g⁻¹ at 100 mA g⁻¹ together with a low coulombic efficiency below 90% (Fig. S15a, b). As anode, although the capacities in the initial cycles are comparable to that of the FEC-added ones, the KCM delivers a poor cycle performance with a capacity of 76 mAh g⁻¹ at 100 mA g⁻¹ after 140 cycles (Fig. S15c, d).

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