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# K<sub>3</sub>MnO<sub>4</sub>: a New Cathode Material for K-ion Batteries

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## Abstract

In the search for materials used as active species in cathodes for K-ion batteries, only few compositions of transition metal oxides or transition metal polyanionic frameworks have been proposed so far. In this work, we report for the first time the synthesis and study of the electrochemical activity an original  $K_3MnO_4$  polymorph. This phase is a 0D-type structure made of isolated  $MnO_4$  tetrahedra surrounded by  $K^+$  ions. A reversible charge capacity of almost one  $K^+$  per unit formula at the average voltage of 2.3 V vs.  $K^+/K$  is obtained, leading to the reversible formation of  $K_2MnO_4$  through a biphasic process.

One of the major challenges of the 21<sup>st</sup> century is the need to solve the problems related to the management of the energy requested by an ever-increasing consumption, demography and living standards. It is therefore imperative to anticipate this energy demand in a sustainable development context. Storage technologies are highly dependent on the materials used, and it is therefore necessary to search for new advanced materials that are also ecological and cheap. Despite the high performance of lithium-based systems, their production associated with environmental cost is pushing scientists to develop alternative systems based on sodium and potassium, which are abundant and evenly distributed over the Earth's crust. Therefore, in recent years, K-ion batteries (KIBs) have been proposed as a viable alternative. Indeed, this technology has many advantages such as the possibility to use graphite at the negative electrode, aluminum as the current collector and a redox potential of the  $K^+/K$  couple of -2.93 V vs. SHE, which could result in a higher energy density than in the case of sodium (-2.71 V), reaching values as high as 150 Wh/kg and 350 Wh/L.<sup>1</sup>

Many cathode materials, belonging to the same families of those already studied for Li-ion and Na-ion batteries (LIBs and NIBs, respectively) have been studied so far.<sup>2,3</sup> Among them, one could cite vanadium phosphates or Prussian Blue analogues<sup>4</sup> as well as transition metal (TM) oxides including those based on manganese<sup>5</sup>. Regarding the latter family, it is interesting to point out that in the system K-Mn-O, only layered phases with the general formula  $K_xMnO_2$  have been reported as a possible cathode material for KIBs. The layered  $K_xMnO_2$  family was first described by Delmas<sup>6,7</sup> and coworkers, and more recently Kubota<sup>8</sup> and co-workers. Compounds such as P2–

$\text{K}_{0.3}\text{MnO}_2$ <sup>9</sup> and  $\text{P3-K}_{0.5}\text{MnO}_2$ <sup>10</sup> were reported as efficient cathode materials for KIBs, with reversible capacities of 65 and 100 mAh/g in the potential windows 3.5-1.5 V and 3.9-1.5 V, respectively. However, the layered structure undergoes severe structural distortion and phase transition during  $\text{K}^+$  insertion/extraction, resulting in a rapid capacity fading and poor cycling stability. The use of water to expand the interlayer distance for  $\text{K}_{0.27}\text{Mn}_{0.98}\text{O}_2 \cdot 0.53\text{H}_2\text{O}$  produced an improvement in the kinetics of  $\text{K}^+$  ion diffusion and in rate capability.<sup>11</sup> However, as reported for Prussian blue analogues,<sup>12</sup> water molecules react at elevated potential<sup>13</sup> conducting to low columbic efficiency<sup>14</sup>. This lack of convincing performance triggered our exploration of alternative KIB cathode materials in the K-Mn-O system.

In this system, a composition attracted our attention:  $\text{K}_3\text{MnO}_4$ . This phase, first reported by Hagemuller et al.,<sup>15</sup> could be described as a 0D-type structure built of isolated  $\text{MnO}_4$  tetrahedra surround by potassium ions. A magnetic study of  $\text{K}_3\text{MnO}_4$  was performed between 0 and 200 K, proving a paramagnetic behavior and the +V oxidation state of manganese. However, this material has not yet been studied regarding electrochemical potassium (de)insertion. In principle, up to two potassium ions can be removed from the structure, leading to  $\text{KMnO}_4$  with a theoretical capacity of 227 mAh/g. In addition, we expect also the possible insertion of two potassium ions leading to the composition  $\text{K}_5\text{MnO}_4$  (171 mAh/g), which does exist in the similar iron-based system ( $\text{K}_5\text{FeO}_4$ ).<sup>16</sup> It is also worth noting that in 2007, Saint et al.<sup>17,18</sup> reported the lithium insertion into the phase  $\alpha\text{-Li}_3\text{MnO}_4$ , which is the stable polymorph at low temperature, crystallizing in the wurtzite-type structure.<sup>19,20</sup> This polymorph shows a first discharge capacity of 80 mAh/g corresponding to the insertion of for 0.4 Li in the potential window 4.0-1.8 V.<sup>18</sup> Nevertheless, the capacity drops by 75% after 30 cycles compared to the first discharge value.<sup>21</sup>

Hagemuller and co-workers succeeded in preparing the two polymorphs of  $\text{K}_3\text{MnO}_4$  as single crystals by solid-state route from  $\text{K}_2\text{O}$  and  $\text{MnO}_2$  under different atmosphere. The high temperature polymorph  $\gamma\text{-K}_3\text{MnO}_4$  (obtained at 1100°C under  $\text{O}_2$ ) has a cubic symmetry (P213) with a disordered distribution of K and Mn in similar tetrahedral sites. The low temperature polymorph  $\beta\text{-K}_3\text{MnO}_4$ , can be prepared by annealing  $\gamma\text{-K}_3\text{MnO}_4$  at 300°C under argon. This polymorph has a tetragonal symmetry (I-42m) with ordered  $\text{MnO}_4$  tetrahedra. The manganese is reported at the edge and the center of the tetragonal mesh, every manganese is surrounded by four oxygen.

In this work,  $\text{K}_3\text{MnO}_4$  was prepared via a simple conventional solid-state method starting from of a 10 % excess of potassium superoxide  $\text{KO}_2$  (Acros Organic) and manganese oxide  $\text{MnO}$  (Sigma-Aldrich, 99%), following the chemical reaction:  $3\text{KO}_2 + \text{MnO} \rightarrow \text{K}_3\text{MnO}_4 + \text{O}_2$ . The required precursors were mixed together for 2 hours in a planetary ball mill and further heated at  $500^\circ\text{C}$  for 12 h in an alumina crucible under vacuum, producing a well-crystallized air sensitive blue colored compound (Fig.1 c)). Note that such color is common for manganese +V oxides.<sup>22</sup> SEM analysis shows large particles of about  $10\ \mu\text{m}$  in size (Fig.1 d)) without a particular shape. The corresponding X-ray powder diffraction (XRD) pattern was refined starting from the published cell parameters of the iron analogue  $\text{K}_3\text{FeO}_4$  (Fig.1 a)),<sup>23</sup> indicating the formation of a previously unknown  $\text{K}_3\text{MnO}_4$  polymorph. We propose to label this new polymorph  $\alpha\text{-K}_3\text{MnO}_4$ . This phase crystallizes in the orthorhombic space group  $\text{Pnma}$  with the following cell parameters:  $a=7.754(1)\ \text{\AA}$ ,  $b=8.960(1)\ \text{\AA}$ ,  $c=7.918(1)\ \text{\AA}$  and a volume of  $V = 550.998(1)\ \text{\AA}^3$ . For this polymorph,  $[\text{MnO}_4]$  tetrahedra are organized differently compared to the two other known polymorphs. As for the tetragonal structure, they are ordered but alternatively pointing to opposite directions (“zig-zag” arrangement) (Fig. 1b)).

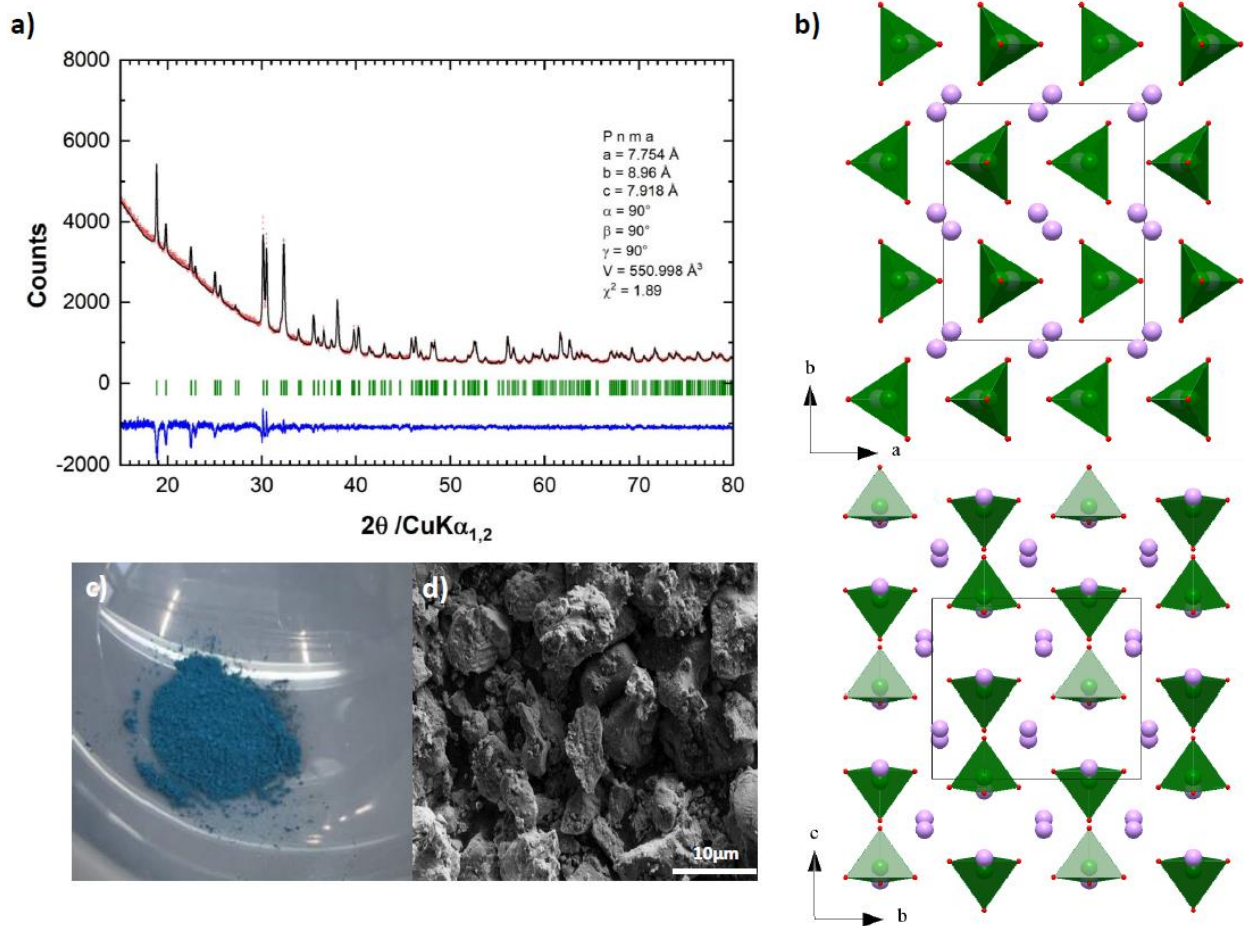


Figure 1 - (a) Rietveld refinement of as-prepared  $\alpha\text{-K}_3\text{MnO}_4$ : experimental ( $\circ$ ) and calculated (line) XRD pattern. The difference between experimental and calculated patterns,  $y_{\text{obs}} - y_{\text{cal}}$  is shown at the bottom. (b)  $\alpha\text{-K}_3\text{MnO}_4$  crystal structure following (001) and (100) axes; (c) Picture and (d) SEM image of as-prepared  $\alpha\text{-K}_3\text{MnO}_4$ .

The charge-discharge profiles of  $\alpha\text{-K}_3\text{MnO}_4$  were measured by incremental galvanostatic cycling at C/20 (corresponding to the (de)insertion 1  $\text{K}^+$  per unit formula in 20 h) in the potential window 1.6–3.5 V versus  $\text{K}^+/\text{K}$  (Fig. 2a). Despite our attempts, we never succeeded in inserting potassium ions into the structure, probably due to the large size of  $\text{K}^+$  ions. Thus, starting from  $\text{K}_3\text{MnO}_4$ , one  $\text{K}^+$  could be removed during the oxidation process at 2.6 V vs.  $\text{K}^+/\text{K}$ , leading to the formation of  $\text{K}_2\text{MnO}_4$ . The potentiostatic intermittent titration (PITT) curve shown in Fig. 2c reveals a dominant bell shape-type response at 2.66 V, which characterizes a biphasic process, and a second similar but shorter process located at 2.8 V vs.  $\text{K}^+/\text{K}$ . The first biphasic process is also clearly observed (Fig. 2 b)) in the derivative curve showing half width length narrower than 50 mV (6 mV on charge

and 28mV on discharge), suggesting the formation of a new phase at the end of the oxidation with a composition close to  $\text{K}_2\text{MnO}_4^{24}$ .

As shown on the incremental galvanostatic curve, once the charge is extended above 3.1 V, the process is no longer reversible. A second irreversible phenomenon is observed and may be due to either the further oxidation of Mn, to an anionic redox process or electrolyte decomposition.

On discharge, a reduction plateau at 2.2 V vs  $\text{K}^+/\text{K}$  is observed, corresponding to the insertion of 0.7  $\text{K}^+$  per unit formula. This process, which corresponds to the first oxidation plateau, is reversible upon further cycling, and correspond to a capacity of 70 mAh/g with a Coulombic efficiency of 97.3%. The large polarization of about 400 mV observed between charge and discharge is probably due to the large size of the particles (10  $\mu\text{m}$  diameter).

The rate capacities of the synthesized material are shown in Fig. 2d, the charge capacity was taken at 3.1V ensuring our work in the reversible window potential of 1.6V – 3.1V. The plot of charge capacity indicate is reaching 70 mAh/g after 5 cycles for a C/20 rate. A slight increase in capacity is observed at higher rate, around 75 mAh/g at C/50 and 90 mAh/g at C/100. Nevertheless, it would be necessary to optimize the particle size to increase the capacity.

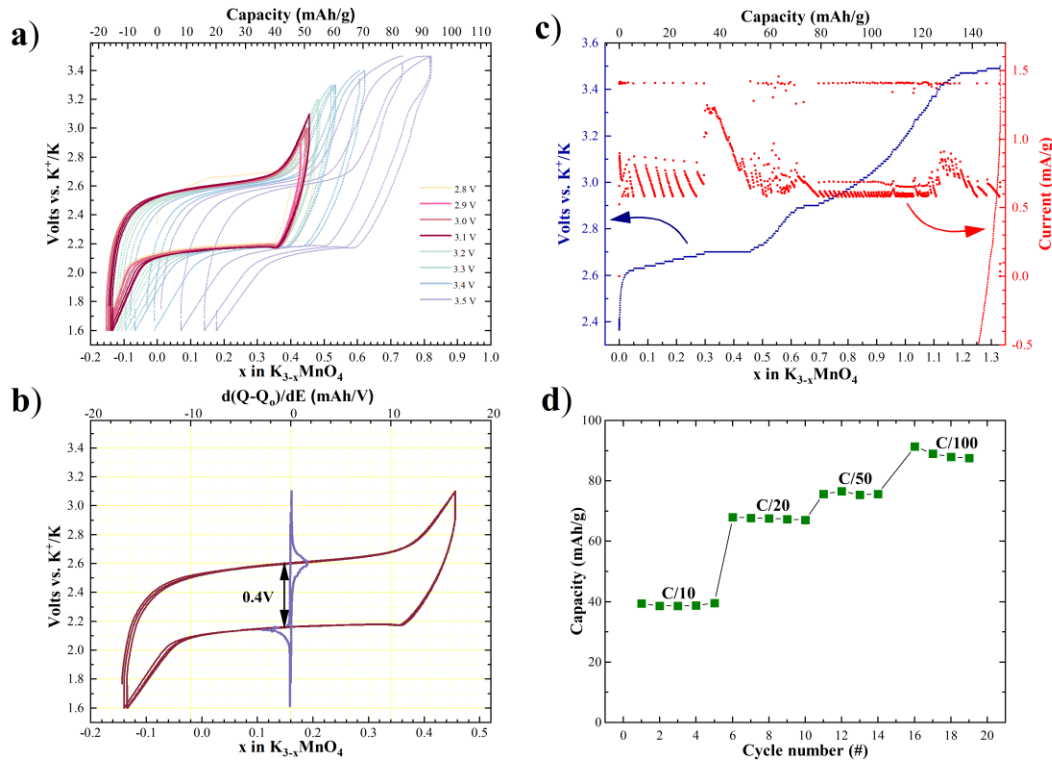


Figure 2. Electrochemical behavior of  $\alpha$ - $K_3MnO_4$ . (a) Incremental voltage vs. composition curves for  $K_3MnO_4$  at C/20 rate in the potential window 3.5V-1.6 V; (b) First galvanostatic curve at C/20 in the potential window 1.6-3.1V vs  $K^+/K$  and corresponding derivative curves  $|dQ/dE|$  versus voltage; (c) PITT curve during the first cycle of  $K_3MnO_4$  in the range of 3.5-2.4 V vs.  $K^+/K$  using 5 mV steps for 1 hour and current limitation equivalent to a galvanic current  $I_{limit} = I_{C/20}$ ; (d) and rate capability for the charge capacity at 3.1V versus cycle number.

To have a better insight on the structural changes occurring in the course of the electrochemical process, *operando* XRD patterns were recorded for two full cycles, the first one with limiting the oxidation potential to 3.1 V to highlight the reversibility of the first redox plateau, and the second up to 3.5 V to follow the irreversible process at higher potential (Fig. 3). For the first charge, 0.92  $K^+$  per unit formula could be deinserted, corresponding to a capacity of 70.4 mAh/g. In the diffraction pattern, the typical diffraction pattern of  $K_2MnO_4$  is observed, in addition to some remaining  $K_3MnO_4$ . During this experiment, only 0.92  $K^+$  per unit formula could be inserted in the following discharge. However, only the XRD peaks of  $K_3MnO_4$  are visible at the end of the discharge, indicating the full reversibility of the process-



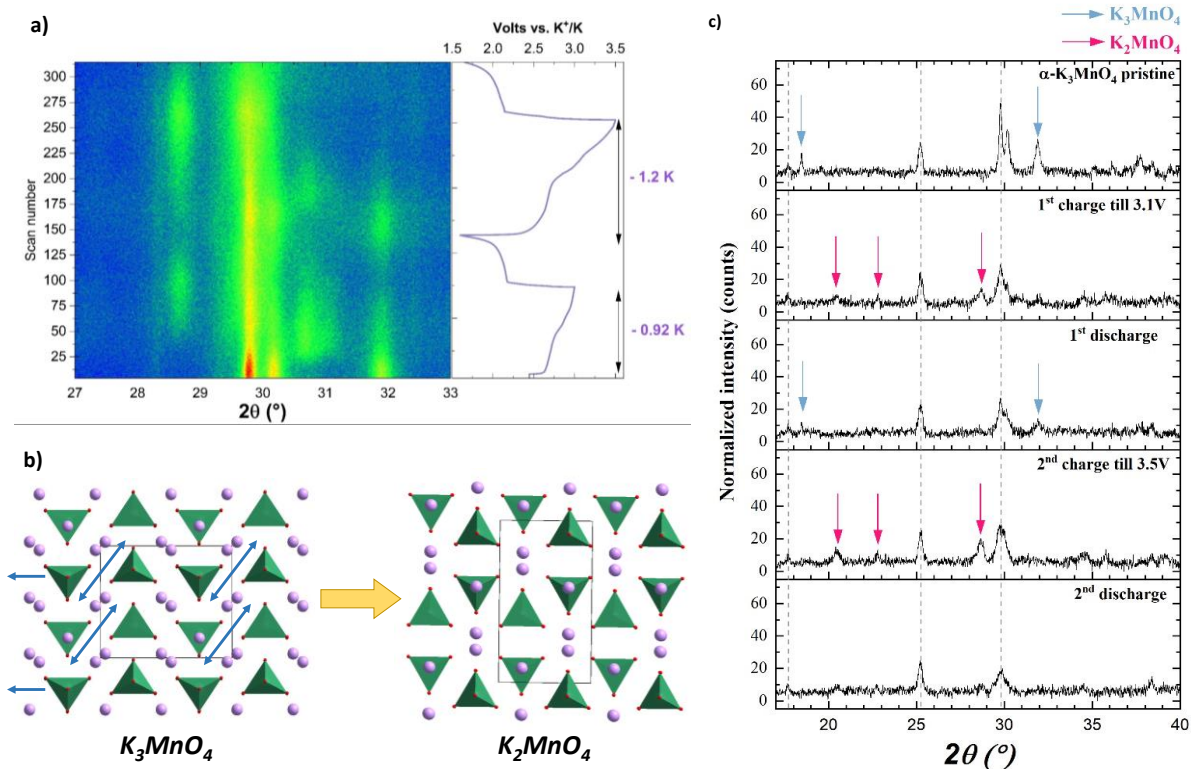


Figure 3. Structural evolution of  $\alpha$ - $K_3MnO_4$  upon potassium ion extraction-insertion. (a) operando XRD analysis during the two first charge-discharge process in a K half-cell at a current rate of  $C/20$  between 1.6-3V for the first cycle and 1.6V-3.5V vs  $K^+/K$  for the second cycle. XRD patterns were collected every hour, corresponding to an exchange of 0.05  $K^+$  per pattern. (b) Structural view along the  $c$  axis of orthorhombic  $K_3MnO_4$  and  $K_2MnO_4$ . (c) XRD powder patterns of  $\alpha$ - $K_3MnO_4$  during operando measurement after the different charge and discharged. Reflection attributable to  $K_3MnO_4$  and  $K_2MnO_4$  phase are indicated with blue and red arrows, respectively. Dotted lines correspond to the common peaks between the two phases.

For the second charge, 1.2  $K^+$  ions per unit formula could be deinserted, corresponding to a capacity of 93.7 mAh/g. During the whole operando measurement, a decrease in intensity and a broadening of the diffraction peaks is observed, indicating the gradual decrease in crystallinity of the different phases. However, while  $K_2MnO_4$  peaks ( $20.45^\circ$ ,  $22.72^\circ$  and  $28.66^\circ$ ) are observed at the end of both first and second charge, those of  $K_3MnO_4$  ( $18.49^\circ$  and  $31.97^\circ$ ) are not recovered at the end of the second discharge, indicating the total and irreversible amorphization of the material

during oxidation above 3.5V vs K<sup>+</sup>/K. Nevertheless, the low signal-to-noise ratio of the *operando* XRD patterns makes it difficult to fully characterize the structure of these materials, and synchrotron XRD, possibly combined with neutron diffraction should be performed to better characterize the structure of these phases, in particular that of the intermediate phase that seems to form half-way through the first and second charge (Figure 3 a). Given the paramagnetic nature of K<sub>3</sub>MnO<sub>4</sub>, a study of its magnetic properties was carried out as well as that of the fully oxidized one obtained at 3.5 V vs. K<sup>+</sup>/K. From the dependence of the magnetization on the temperature, one can estimate the manganese oxidation state using the Curie-Weiss law. For the pristine material, (without carbon black), an average manganese oxidation state of +4.4 is obtained. After one charge up to 3.5 V, the oxidation state of Mn is +5.8, very close to Mn<sup>+VI</sup>, which would correspond to the formation of K<sub>2</sub>MnO<sub>4</sub>.

In conclusion, these results confirm the deinsertion of one K<sup>+</sup> per unit formula from the new polymorph  $\alpha$ -K<sub>3</sub>MnO<sub>4</sub> through a biphasic phenomenon at 2.66 V, which accompanies the oxidation of manganese from Mn<sup>+V</sup> to Mn<sup>+VI</sup>. This oxidation goes along with a decrease of the cell volume by 15% between K<sub>3</sub>MnO<sub>4</sub> and K<sub>2</sub>MnO<sub>4</sub>. This process corresponds to a reversible capacity of 70 mAh/g at C/20 with a relatively large polarization (400 mV), which can in principle be improved by optimizing the electrode formulation and the particle size of the material. Above this potential, the further extraction of K<sup>+</sup> gives rise to an irreversible process, which corresponds to a progressive amorphization of the system. It is important to underline that this material, non-toxic and inexpensive, is in addition very easy to prepare. This finding confirms the interest of the exploration of the K–Mn–O system for the discovery of alternative electrode materials for KIBs.

## EXPERIMENTAL METHOD

The compounds were characterized by XRD using a SMARTLAB (Rigaku) diffractometer with Bragg-Brentano geometry (CuK <sub>$\alpha$ 1,2</sub> radiation). Note that due to their instability in air, XRD patterns were registered using 0.4 mm diameter quartz capillary. The *operando* XRD measurement was carried out on a MiniFlex (Rigaku) diffractometer with Bragg-Brentano geometry (CuK <sub>$\alpha$ 1,2</sub> radiation). For the electrochemistry measurement, a SP-50 potentiostat (Biologic SA, Claix, France) couple with electrochemical cell with a Beryllium window was used.

*Operando* analyses were performed with an homemade cell described in a previous paper.<sup>25</sup> In this study, a beryllium window is used, a cathode material of about 15 mg was made with K<sub>3</sub>MnO<sub>4</sub> (70 wt%) PTFE (10wt%) and black carbon (20w%). The material was cycled at C/20 and XRD scans were continuously measured between 5° and 50°. Each XRD scan had a duration of about 10 min. A scanning electron microscope (SEM) Zeiss Field Effect Gun (FEG) XL-30 with a resolution of about 1 nm was used to study the sample morphology, while the elemental compositions were confirmed by energy dispersive spectroscopy (EDS) on a Link-Isis analyzer (ATW 6650 detector). Magnetic measurements were carried out with a SQUID magnetometer (MPMS, Quantum Design). For each sample the zero-field-cooled (ZFC) and field-cooled (FC) data were collected with an applied field of 1000 Oe. The magnetic susceptibility was calculated by dividing the magnetization by the magnetic field value. The field-dependent magnetic moment values were collected at 5 K. The Curie–Weiss fitting  $\chi = \frac{N_A \mu_B^2 (\mu_{eff}^2)}{3kT}$  of the  $\chi$  (T) curve for 250K < T < 350K yields to calculated effective paramagnetic moment with  $\mu_B = 9.274 \cdot 10^{-24}$  erg/G,  $k = 1.381 \cdot 10^{-16}$  erg/K,  $N_A = 6.022 \cdot 10^{23}$  mol<sup>-1</sup> and the  $\mu_{eff}^2 = 2 * \sqrt{S(S + 1)}$ <sup>26</sup>. The experimental effective magnetic moment for the two composition were  $\mu_{eff}(K_3MnO_4) = 3.5\mu_B$  and  $\mu_{eff}(K_2MnO_4) = 2.63\mu_B$ . The electrochemical characterization was performed in Swagelok-type cells with a solution 0.8M KPF<sub>6</sub> in EC:DEC as the electrolyte and metallic potassium as the counter-electrode. The working electrode was prepared from a mixture of K<sub>3</sub>MnO<sub>4</sub> with acetylene black in a weight ratio of 50:50. The electrochemical cells were cycled at constant current between 1.6-3.5 V on a BCS potentiostat/galvanostat (Biologic SA, Claix, France) at room temperature. Potentiostatic intermittent titration technique (PITT) measurements were conducted using potential steps of 5 mV limited by a mini-mum current equivalent to a C/100 galvanostatic rate.

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## Notes

“The authors declare no competing financial interest.”

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## TOC GRAPHICS

