

ADVANCED MATERIALS

Supporting Information

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Investigation of Potassium Storage in Layered P3-Type
 $\text{K}_{0.5}\text{MnO}_2$ Cathode

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Experimental section

Synthesis of P3-type $\text{K}_{0.5}\text{MnO}_2$

P3-type $\text{K}_{0.5}\text{MnO}_2$ was prepared using a conventional solid-state method. Stoichiometric amounts of K_2CO_3 (anhydrous, VWR) and Mn_2O_3 (99.9%, Sigma–Aldrich) were mixed and homogenized using a planetary ball-mill (Retsch PM200) at 300 rpm for 4 h. The resulting mixture was pelletized using uniaxial pressing and annealed at 800 °C for 12 h to crystallize the phase. After cooling, the sample was kept at 200 °C and transferred into an Ar-filled glovebox to prevent contamination from moisture.

Calculation details

All first-principles calculations were performed using the Vienna *ab initio* simulation package program^[1] with the spin-polarized GGA.^[2] We used the Perdew–Burke–Ernzerhof exchange-

correlation parameterization to density functional theory^[3] and the projector-augmented wave method.^[4] The GGA+ U approach^[5, 6] with a U value of 3.9 eV for Mn^[7] was used to correct the incomplete cancellation of the self-interaction in GGA. We used a kinetic cutoff energy of 520 eV and various k -point meshes with a grid density of 1000 per number of atoms in a supercell. All the possible K-vacancy orderings within O3-, P3-, and O1-K_xMnO₂ supercells up to nine formula units of K_xMnO₂ were created using an enumeration technique,^[8] and for each composition the 300 arrangements with the lowest electrostatic energies were calculated using GGA+ U . To describe the van der Waals interaction between oxide layers in K_xMnO₂ for the voltage prediction, the DFT-D3 scheme suggested by Grimme *et al.* was adopted.^[9]

Characterization

The structure of each sample was analyzed using XRD (Rigaku Miniflex 600) with Cu K α radiation, and the structural parameters were determined by the Rietveld method using a Highscore Plus software. The morphologies of the samples were verified using field-emission SEM (FE-SEM; Zeiss Gemini Ultra-55). The *in situ* XRD analysis was performed using a diffractometer equipped with a Mo source (Bruker D8) and a homemade *in situ* electrochemical cell with a Be window. The *in situ* cell was cycled galvanostatically using a potentiostat/galvanostat (Solartron 1287).

Electrochemical test

Electrodes were prepared by mixing as-synthesized K_{0.5}MnO₂ (80 wt%), Super P carbon black (Timcal, 10 wt%), and dry polytetrafluoroethylene (DuPont, 10 wt%) in an Ar-filled glovebox. Test cells were assembled into 2032 coin-cells in the glovebox with a two-electrode configuration using K metal counter electrodes. A separator of grade GF/F (Whatman, USA) and an electrolyte of 0.7 M KPF₆ in ethylene carbonate/diethyl carbonate (anhydrous, 1:1

volume ratio) were used. The electrochemical tests were performed on a battery testing station (Arbin Instruments) using cathode films with a loading density of $\sim 5.8 \text{ mg cm}^{-2}$.

References

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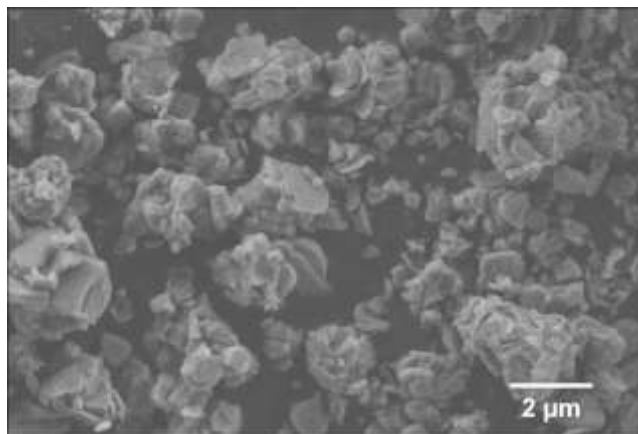


Figure S1. SEM image of P3-K_{0.5}MnO₂.

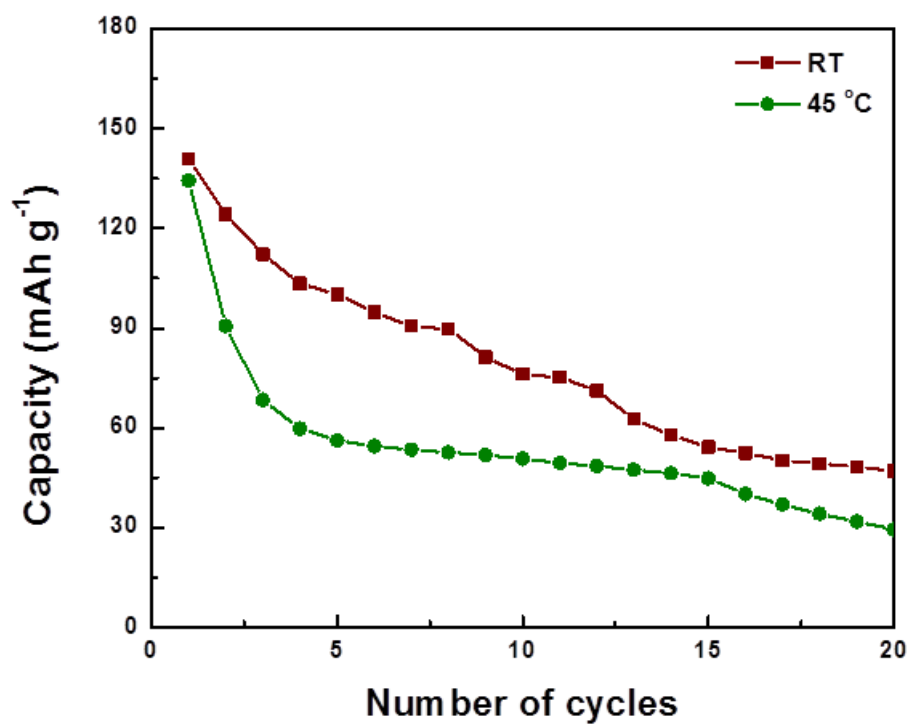


Figure S2. Discharge capacities of P3-type $\text{K}_{0.5}\text{MnO}_2$ over 20 cycles operated at RT and 40 °C at a current rate of 5 mA g^{-1} .

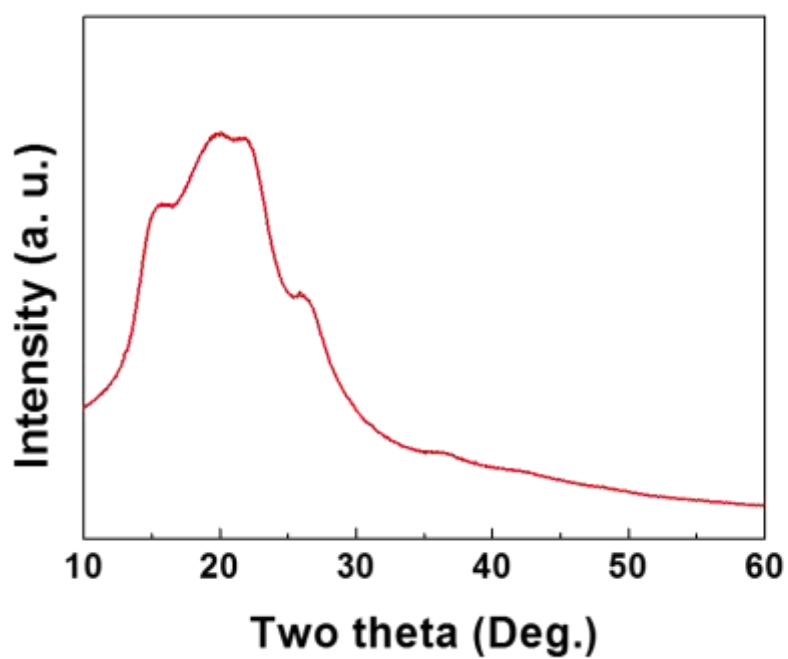


Figure S3. *Ex-situ* XRD of $K_{0.5}MnO_2$ after high voltage cycling. Note that the large background between 12° to 30° originates from the Kapton film used to seal the sample.



Figure S4. Glassfiber separator after 20 cycles.

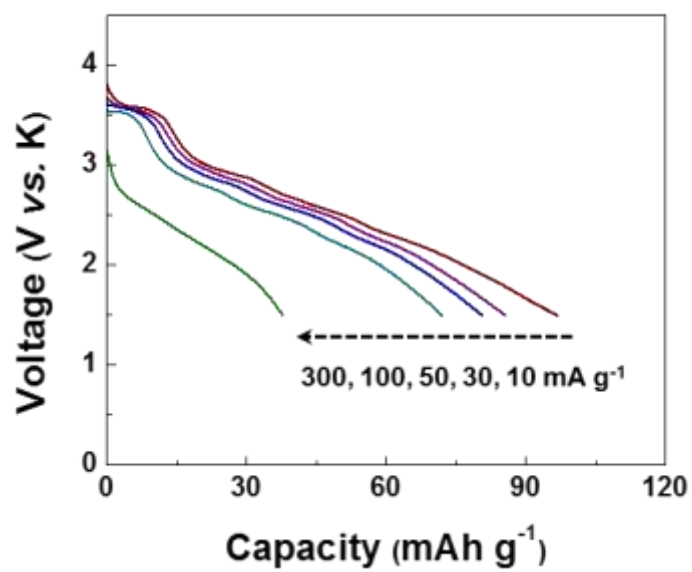


Figure S5. Rate capability of P3-type $K_{0.5}MnO_2$.

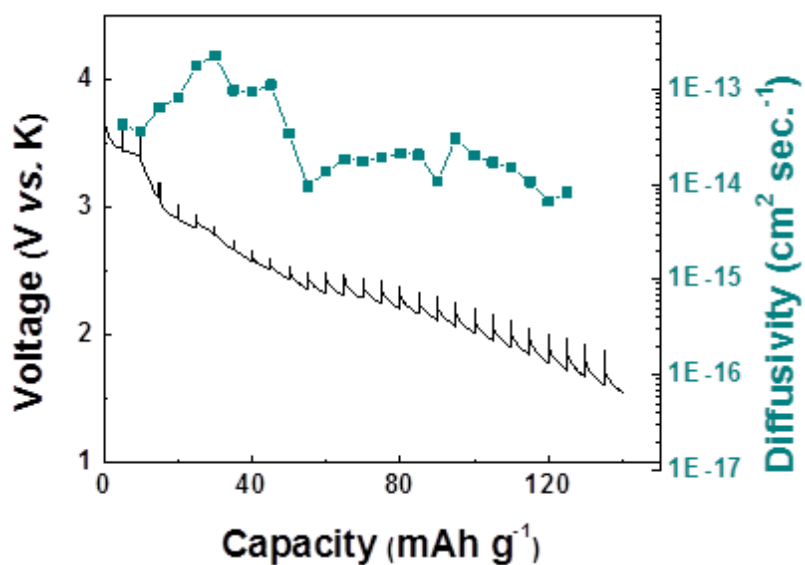


Figure S6. Galvanostatic intermittent titration technique (GITT) analysis. The GITT is performed at a current rate of 5 mA g⁻¹ with a 2-h relaxation time. The diffusivity is calculated from GITT analysis.

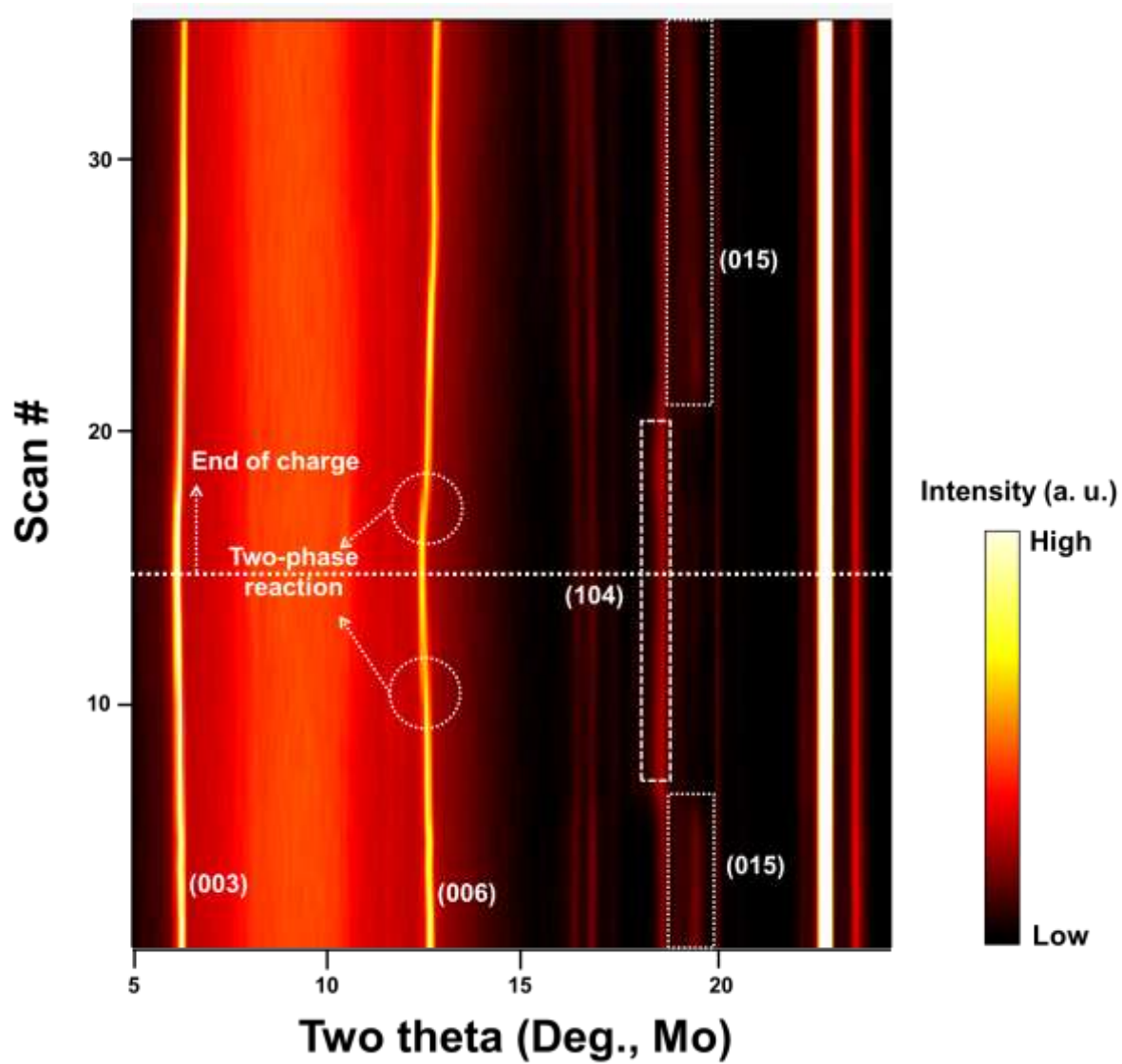


Figure S7. 2D plot of *in situ* XRD characterization.

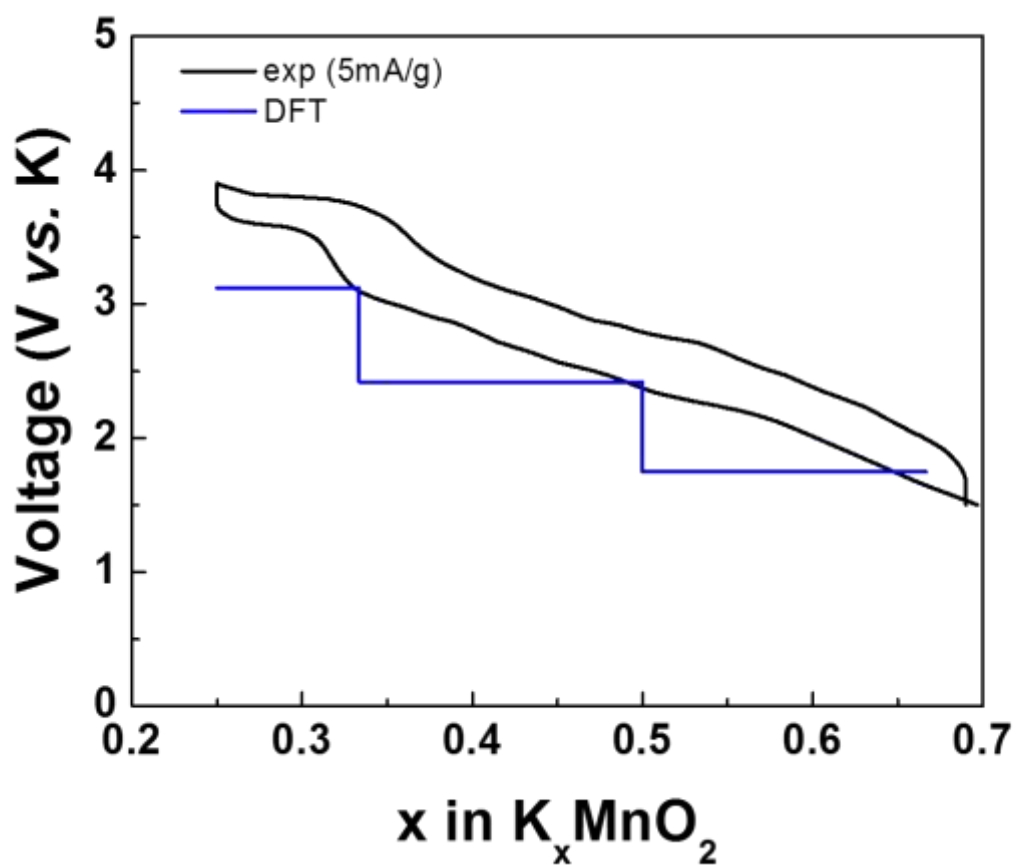


Figure S8. Calculated voltage plot (DFT) compared with experimentally obtained charge/discharge profiles.

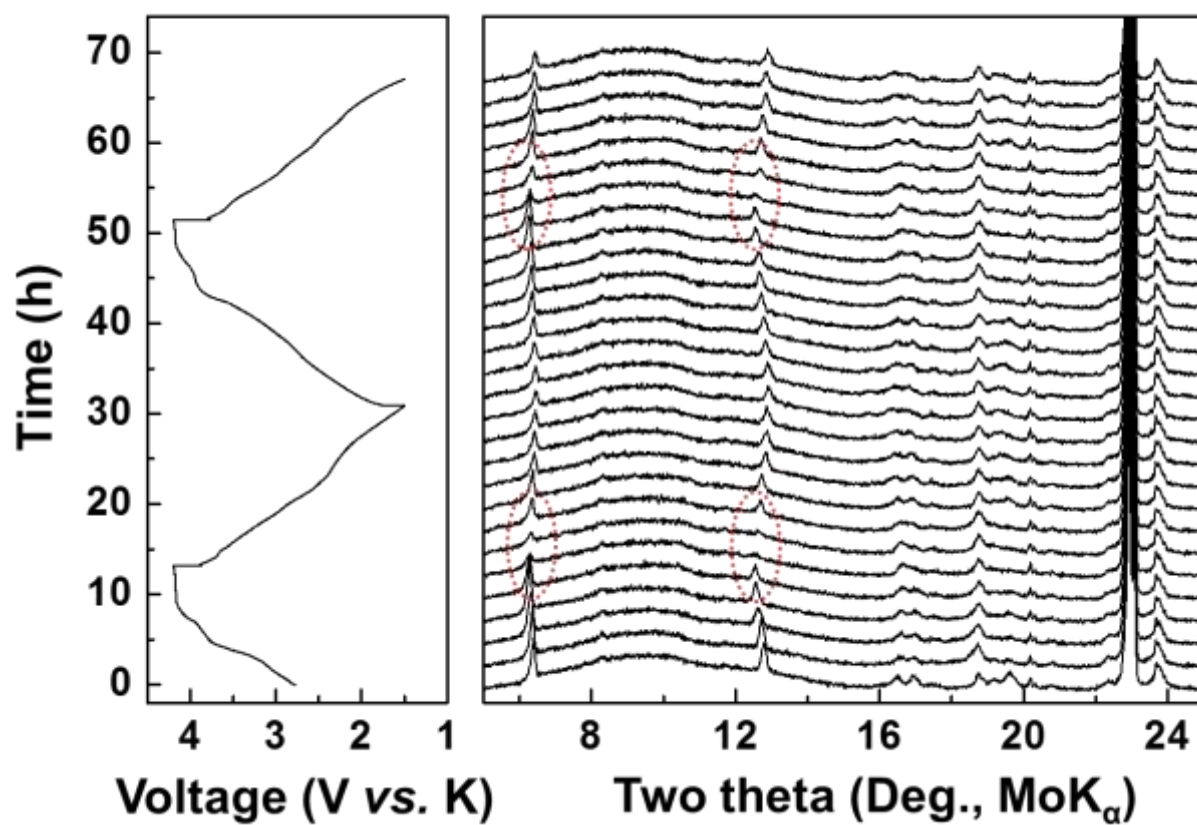


Figure S9. Typical charge/discharge profiles of P3-type $K_{0.5}MnO_2$ at a current rate of 7 mA g^{-1} between 1.5-4.2 V and corresponding *in situ* XRD patterns.