Supporting Information

High-Efficiency Cathode Potassium Compensation and Interfacial Stability Improvement Enabled by Dipotassium Squarate for Potassium-ion Batteries

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Experimental Section

Synthesis of dipotassium squarate ($K_2C_4O_4$). 3,4-dihydroxy-3-cyclobutene-1,2-dione (Meryer Chemical Technology Co., Ltd.) and $K_2CO_3$ (Meryer Chemical Technology Co., Ltd.) were mixed with a molar ratio of 1:1 and then dissolved in deionized water, followed by constantly stirring for 12 h at room temperature. After removing the deionized water through a rotary evaporator, the obtained powder was washed with ethanol several times and dried under vacuum at 60 °C overnight.

Synthesis of P3-type $K_{0.5}MnO_2$ and soft carbon. P3-type $K_{0.5}MnO_2$ was synthesized via a solid-state calcination method. Stoichiometric amounts of MnO$_2$ (99%, Sigma–Aldrich) and $K_2CO_3$ (Meryer Chemical Technology Co., Ltd.) were ground and then calcinated at 900 °C for 12 h. After furnace cooling, the powder was kept at 200 °C and quickly transferred into an Ar-filled glovebox (oxygen and water levels less than 0.1 ppm) to prevent further contamination from moisture environment. Soft carbon was prepared by thermal pyrolysis of Perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA, Sigma–Aldrich) at 900 °C for 10 h at inert atmosphere.

Materials Characterization. The morphologies and microstructures of as-prepared materials were analyzed using field-emission scanning electron microscopy (FE-SEM, Zeiss SUPRA 55) and transmission electron microscopy (TEM, JEOL JEM-2010). High-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) images were acquired by a probe corrector at 300 kV. A Bruker D8 Discovery X-ray diffractometer with Cu Kα radiation (scan step = 0.02°, 2-Theta = 5°–80°) was employed to reveal the crystal structure of as-synthesized samples. Raman spectra were carried out via a Renishaw inVia Raman spectrometer system (Gloucestershire, UK) associated with a Leica DMLB microscope (Wetzlar, Germany) and a 17 mW Renishaw He-Ne laser source at 633 nm. X-ray
photoelectron spectroscopy (XPS) was performed through an ESCALAB-250 (Thermo Scientific, UK). For ex situ material characterizations, potassium half cells were dissembled in an Ar-filled glove box, and the cycled electrodes were thoroughly washed with diethyl carbonate (DEC) to remove impurities. These electrodes were directly used for ex situ XPS and TEM analysis.

**Electrochemical Measurements.** The $\text{K}_{0.5}\text{MnO}_2$ material, sacrificial salt $\text{K}_2\text{C}_2\text{O}_4$, Super P C65 and polyvinylidene difluoride (PVDF) with a weight ratio of 8:1:1:1 were dispersed in N-Methyl-2-pyrroldione (NMP) under vigorous stirring. The formed slurry was coated onto the aluminum current collector and dried under vacuum at 80 °C overnight. The mass loading of active materials is approximately 2–2.5 mg cm$^{-2}$. The electrochemical performances of as-prepared electrodes were evaluated by 2032-type coin cells (CR2032) assembled in a glove box filled with Ar. A piece of metallic potassium foil and a glass microfiber filter (Whatman, Grade GF/D) were employed as the counter electrode and the separator, respectively. The electrolyte was 0.8 M potassium hexafluorophosphate ($\text{KPF}_6$, DoDo Chem) in ethylene carbonate (EC) and diethyl carbonate (1:1 in volume, DoDo Chem). Cyclic voltammogram (CV) measurements were conducted on a CHI660E workstation (Shanghai Chenhua Co. Ltd., China). Galvanostatic charge and discharge (GCD) tests were recorded on a NEWARE™ battery tester (CT-4008T model). Electrochemical impedance spectra (EIS) were performed with a 5 mV amplitude ranging from 10 mHz to 100 kHz. For the Galvanostatic intermittent titration technique (GITT) test, all the potassium-ion half cells were pre-activated at 10 mA g$^{-1}$ for 5 cycles and then cycled with a pulse current of 10 mA g$^{-1}$ for 30 min, followed by a 6 h rest interval to reach the equilibrium potential state. Diffusion coefficients ($D_k$) were calculated based on the following equations (1):
\[ D_k = \frac{4}{\pi \tau} \left( \frac{m_n V_m}{S} \right)^2 \frac{\Delta E_s}{\Delta E_t} \]  

Wherein \( \Delta E_s \) and \( \Delta E_t \) are the change of equilibrium potential and variation of cell voltage at each current pulse step. \( n_m \) and \( V_m \) are the number of moles and molar volume (cm\(^3\)) of active materials. \( S \) and \( \tau \) represent the surface area of electrodes (cm\(^2\)) and duration of the pulse current. For the full cell, the mass ratio of cathode and anode materials is designed to be 4. Both of the two electrodes were directly used without pre-potassiation treatment.

**In situ Raman measurements.** The exclusively laboratory-made *in situ* potassium half-cell was assembled using a potassium metal foil as both the reference and counter electrodes, which was fixed on the glass slide as a negative part. A glass microfiber filter and 0.8 M KPF\(_6\) in EC and DEC (1:1 in volume) were used as the separator and electrolyte, respectively. The positive electrode was fabricated by coating the mixed slurry (the active material, sacrificial salt, Super P C65, and PVDF with a mass ratio of 8:1:1:1) onto the aluminum mesh. A piece of quartz window (0.5 mm in thickness) was placed on the top as an optical window to collect the laser signal. The whole assembly process was done in an argon-filled glovebox. The current density for the *in situ* Raman test was 20 mA g\(^{-1}\) with a cutoff potential from 1.5 V to 4.0 V.
Figure S1. a-c) SEM images of the as-synthesized $K_{0.5}MnO_2$ cathode material at different magnifications. The P3-type layered $K_{0.5}MnO_2$ was prepared via a solid-state calcination process and showed plate-like morphology with a particle size around 2 μm.
Figure S2. a, b) Low-resolution and c, d) high-resolution transmission electron microscopy (HRTEM) images of the as-synthesized $K_{0.5}MnO_2$ cathode material. HRTEM images demonstrate a lattice spacing of 0.3 nm between the adjacent layers, corresponding to the (002) plane of P3-type $K_{0.5}MnO_2$. 
Figure S3. a-d) TEM-EDS elemental maps for K, Mn and O in K$_{0.5}$MnO$_2$. High-angle annular dark field (HAADF) images show a uniform distribution of K, Mn, and O elements in the obtained material.
**Figure S4.** XRD pattern of the as-synthesized $K_{0.5}MnO_2$ cathode material. The XRD pattern of the as-prepared $K_{0.5}MnO_2$ can be indexed to a typical P3-type layered structure (R3m space group) with an ABBCCA stacking sequence.
Figure S5. a) Overall XPS survey and high-resolution XPS spectra of b) K 2p, c) Mn 2p and d) O 1s for $\text{K}_{0.5}\text{MnO}_2$. XPS results indicate the presence of Mn$^{4+}$ together with K and O in $\text{K}_{0.5}\text{MnO}_2$ (Figure S5a-d, Supporting information).
Figure S6. GCD curves of a) $K_2C_4O_4$, b) $K_2C_2O_4$ and c) $C_6H_5K_3O_7$ at the initial three cycles.
Figure S7. GCD curves of the KMO electrodes with different weight percentages of $\text{K}_2\text{C}_4\text{O}_4$ (6%, 9% and 12%) at the initial cycle.
Figure S8. Cycling performance of the as-prepared electrodes at 10 mA g\textsuperscript{-1} for 100 cycles between 1.5 and 4.2 V.
Figure S9. GCD curves of a) KMO and b) KCO@KMO at different cycles between 1.5 and 4.0 V (vs. $K^+/K$) at a current density of 10 mA g$^{-1}$. 
Figure S10. The comparison of initial Coulombic efficiency ($\eta = \frac{C_{\text{1st-discharge}}}{C_{\text{1st-charge}}}$) of different layered transition metal oxide cathodes.
Figure S11. The change of average working voltage between two electrodes during cycling.
Figure S12. GCD curves of a) KMO and b) KCO@KMO under different current densities between 1.5 and 4.0 V.
Figure S13. XRD pattern of the as-synthesized $K_{0.6}CrO_2$ cathode material.
Figure S14. Galvanostatic charge/discharge profiles of a) K$_{0.6}$CrO$_2$ and b) K$_2$C$_4$O$_4$@K$_{0.6}$CrO$_2$ electrodes in the first cycle. (c) Cycling performance of the as-prepared electrodes at 10 mA g$^{-1}$ for 50 cycles.
Figure S15. EIS measurements of a) KMO and b) KCO@KMO electrodes at different charged states.
Figure S16. The overall XPS survey spectra of a) KMO and b) KCO@KMO electrodes before and after charging.
Figure S17. High-resolution TEM image of the pristine KMO electrode.
**Figure S18.** a) XRD pattern and b) SEM image of the as-prepared soft carbon.
Figure S19. GCD curves of the soft carbon electrode at the initial three cycles.
Figure S20. CV profiles of KCO@KMO//SC at a) a scan rate of 0.1 mV s$^{-1}$ and b) at various scan rates between 0.5 and 4.0 V.
Figure S21. Rate capability of KCO@KMO||SC under different current densities between 0.5 and 4.0 V.
Figure S22. GCD curves of KCO@KMO//SC under different current densities between 0.5 and 4.0 V.
Figure S23. The energy density of KCO@KMO||SC and KMO||SC full cells after the first and 100th cycles.
Figure S24. Photograph of a portable timer powered by the KCO@KMO//SC full cells.