Electronic Supplementary Material (ESI) for Energy & Environmental Science.

Supplementary Information

Development of P3-$K_{0.69}CrO_2$ as an ultra-high-performance cathode material for K-ion batteries

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Experimental method

Synthesis of $NaCrO_2$ and K_xCrO_2 (x=0.3, 0.7, 1 and 1.5) using the solid-state method

$NaCrO_2$ powder was synthesized using the typical solid-state method from a stoichiometric ratio of Cr_2O_3 (Sigma–Aldrich, purity: 99%) and Na_2CO_3 (Sigma–Aldrich, purity: 99%) as starting materials. The mixture of the starting materials was calcined at 900 °C in an argon atmosphere for 10 h. Then, the produced $NaCrO_2$ powder was rapidly moved into an argon-filled glove box and quenched to room temperature to avoid contamination by moisture, which causes the formation of NaOH on the surface of the $NaCrO_2$. For comparison, K_xCrO_2 samples (x=0.3, 0.7, 1, and 1.5) were synthesized via the solid-state method from a stoichiometric ratio of Cr_2O_3 (Sigma–Aldrich, purity: 99%) and K_2CO_3 (Sigma–Aldrich, purity: 99%) as starting materials. The mixture of the starting materials was calcined at 900 °C in an argon and oxygen atmosphere for 10 h.

Electrochemical characterization

The cathodes were fabricated by blending the thermally sodiated $NaCrO_2$ active mass (85 wt.%), Super-P carbon black (10 wt.%), and polyvinylidene fluoride (5 wt.%). The resultant slurry was uniformly pasted onto aluminum foil using the doctor blade method and then carefully dried at 110 °C for 12 h under vacuum. The loading of the active mass on the foils was approximately 3.0–4.0 mg cm^{-2}. Electrochemical characterization was performed using 2032 coin half-cells. The electrolyte solutions used in this study were 0.5 M $NaPF_6$ in propylene carbonate (PC) with 2 vol.% fluoroethylene carbonate (FEC) for the Na cell and 0.5 M KPF_6 in ethylene carbonate (EC) and diethylene carbonate (DEC) (1:1 by v/v) for the K cell.

The fabricated cathodes and sodium/potassium metal anodes were separated by a glass fiber (Advantec) to prevent short-circuiting. All the cells were prepared in an argon-filled dry box. A typical galvanostatic charge–discharge test was performed in the range of 2.0–3.6 V vs. Na/Na^+ for the Na cell and 1.5–3.8 V vs. K/K^+ for the K cell, where 1C = 100 mA g^{-1}.

Preparation of $K_{0.69}CrO_2$ cathode

The $K_{0.69}CrO_2$ cathode was prepared using electrochemical ion-exchange of the $NaCrO_2$ compound. The $NaCrO_2$ compounds were extensively subjected to 300 cycles in the K-metal | 0.5 M KPF_6 in EC: DEC (1:1) | $NaCrO_2$ cell at a current density of 1C (100 mA g^{-1}) within the voltage range of 1.5–3.8 V. The resultant $KCrO_2$ was washed with diethylene carbonate (DMC) solution at least 10 times and dried at 80 °C for 3 h in a glove box.

Material Characterization

Powder X-ray diffraction (XRD) (Rigaku, Rint-2000) using Cu Kα radiation was employed to identify the crystalline phases of the powders. XRD data were obtained in the 2θ range of 10°–80° using a step size of 0.03°. To avoid exposure to air or moisture, we used a ketone-sealed apparatus for the XRD measurements. The morphologies of the powders were examined using scanning electron microscopy (SEM; JSM-6340F, JEOL). Transmission electron microscopy (TEM; JEM2010, JEOL) and energy-dispersive X-ray spectroscopy (EDX) mapping were used to determine the localized particle morphologies and confirm the stoichiometry of the $NaCrO_2$ compound and K_xCrO_2. The galvanostatic intermittent titration technique (GITT) was used at each 15-min step of charge (depotassiation)/discharge (potassiation) followed by a 1-h relaxation step.

Computational Details

Density functional theory (DFT) calculations were performed using the Vienna Ab initio Simulation Package (VASP).[S1] We used projector-augmented wave (PAW) pseudopotentials[S2] with a plane-wave basis set, as implemented in VASP. Perdew−Burke−Ernzerhof (PBE) parametrization of the generalized gradient approximation (GGA) was used for the exchange-correlation function.[S3] The GGA+U method[S4] was adopted to address the localization of the *d*-orbital in the V ions, with a U value of 3.5 eV, which was previously determined from the self-consistent calculation of $NaCrO_2$.[S5] All the calculations were performed with an energy cutoff of 500 eV until the remaining force in the system converged to less than 0.05 eV/Å per unit cell. Nudged elastic band (NEB) calculations[S6] were performed to determine the activation barrier of the K^+ ion diffusion in the $K_{0.69}CrO_2$ structure. A unit cell created by four formulaic units of $K_{0.69}CrO_2$ was used, with one vacancy generated to model the K^+ ionic diffusion. We considered five intermediate states between the first and final images of a single K^+ diffusion event. During the NEB calculation, all the structures were allowed to relax within the fixed lattice parameters.

Reference

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S6. G. Henkelman. *J. Chem. Phys.*, 2000, **113**, 9901−9904

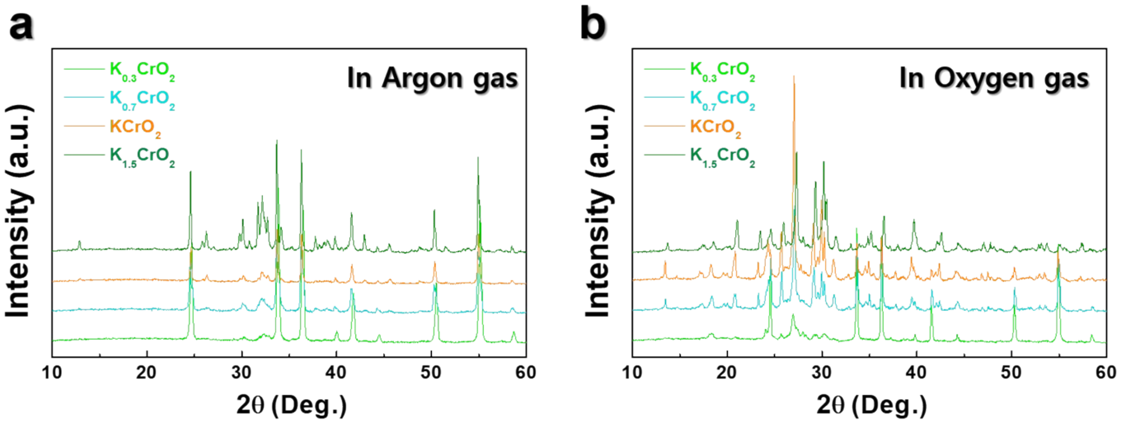

Fig. S1 XRD patterns of as-prepared K_xCrO_2 samples (x=0.3, 0.7, 1, and 1.5) synthesized using the solid-state method: (a) under argon gas and (b) under oxygen gas.

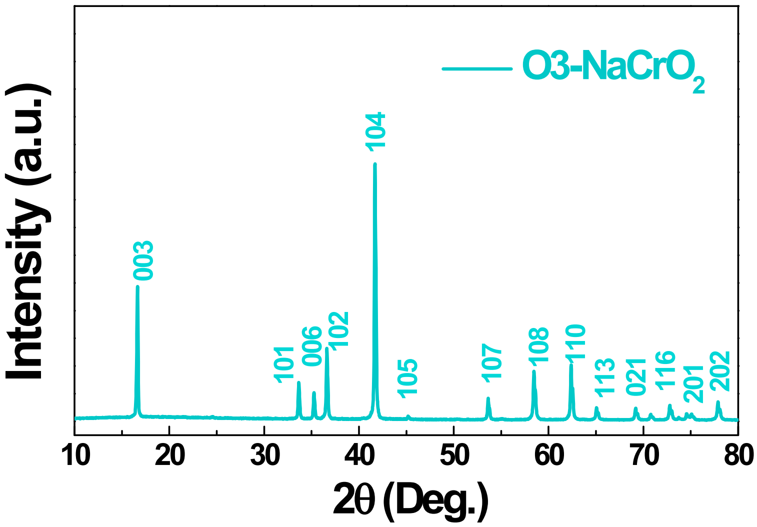

Fig. S2 XRD patterns of O3-$NaCrO_2$ cathode.

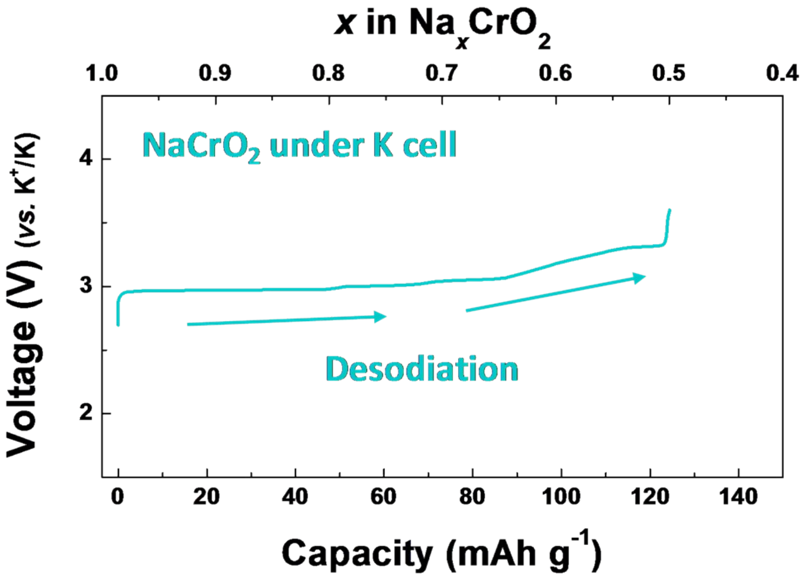

Fig. S3 Initial desodiation process of O3-NaCrO$_2$ cathode under K metal | 0.5 M KPF$_6$ in an EC:DEC = 1:1 (v/v) | NaCrO$_2$ cell.

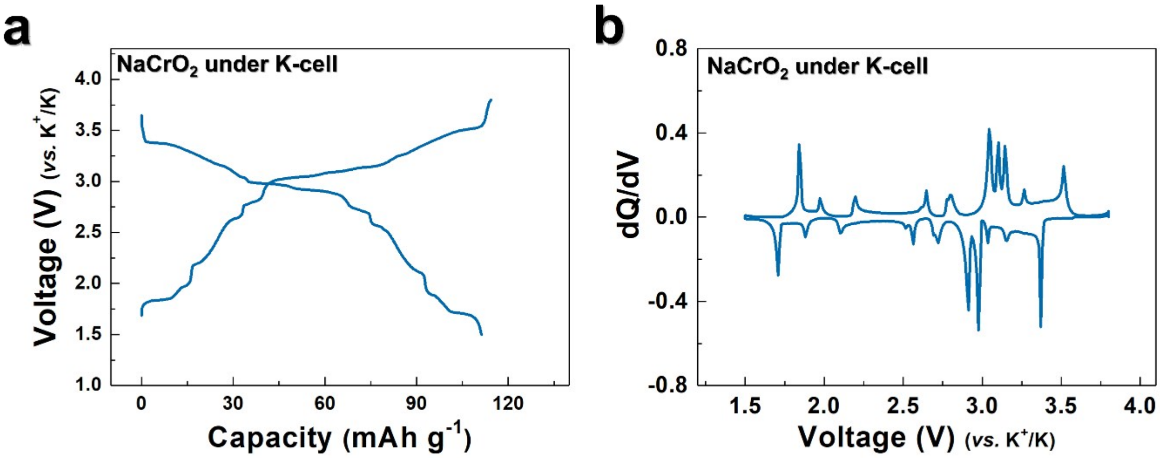

Fig. S4 (a) Charge–discharge curve and (b) dQ dV^{-1} of O3-$NaCrO_2$ under K metal | 0.5 M KPF_6 in an EC:DEC = 1:1 (v/v) | $NaCrO_2$ cell.

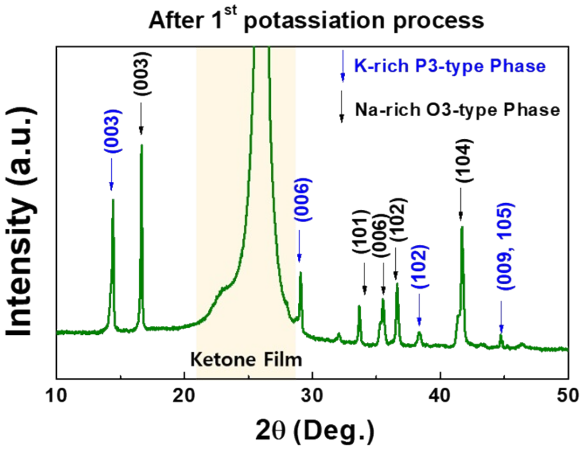

Fig. S5 XRD patterns of $Na_{0.5}CrO_2$ electrode after 1st potassiation process.

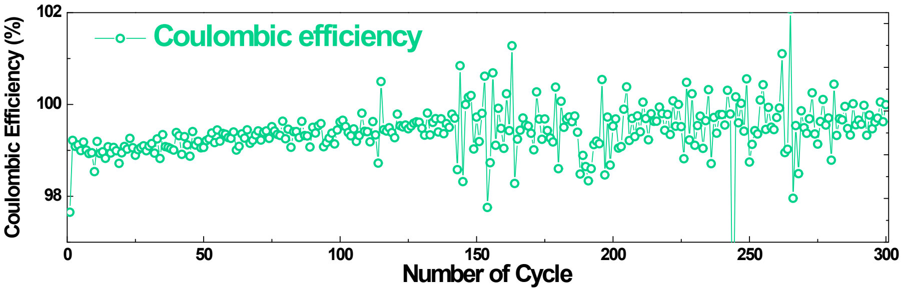

Fig. S6 Electrochemical ion-exchange process: Coulombic efficiency of K metal | 0.5 M KPF_6 in a EC : DEC = 1:1 (v/v) | $NaCrO_2$ cell during 300 cycles.

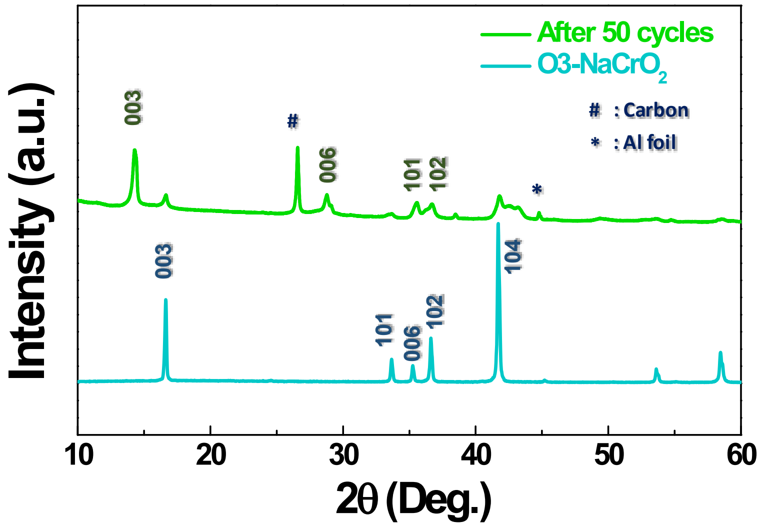

Fig. S7 XRD patterns of O3-$NaCrO_2$ and cycled K_xCrO_2 electrode after 50 cycles.

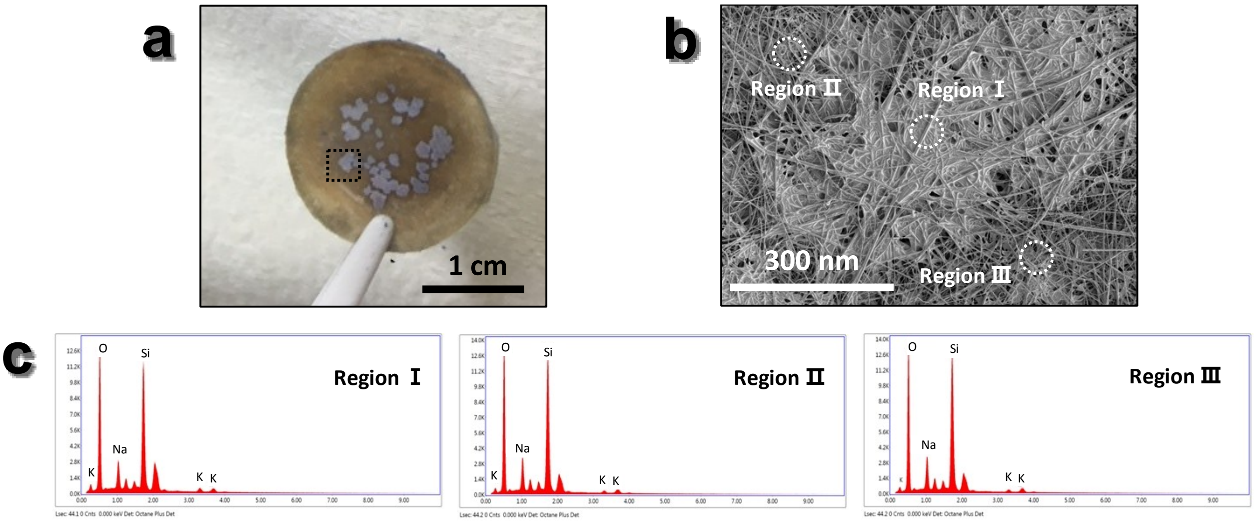

Fig. S8 (a) Digital photograph of cycled separator (after 300 cycles) collected from K | 0.5 M KPF_6 in an EC:DEC = 1:1 | $NaCrO_2$ cell. (b) SEM image of region outlined by square box in (a) and (c) corresponding elemental analysis of Regions I, II, and III.

Table S1. Elemental analysis of cycled separator shown in Fig. S6b.

Element	Atomic % (Region I)	Atomic % (Region II)	Atomic % (Region III)
*O (K)	59.00	53.23	57.17
*Si (K)	30.66	36.88	9.45
Na (K)	8.43	8.22	32.18
K (K)	1.91	1.67	1.20

*Si and O elements were detected because of the use of glass fiber separators.

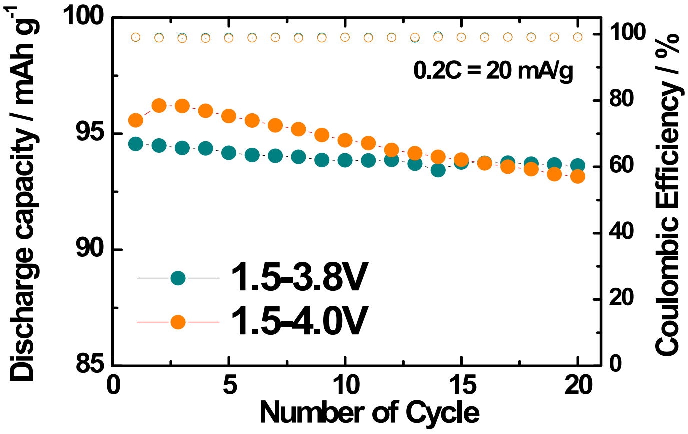

Fig. S9 Cycle life test of $K_{0.69}CrO_2$ cathode at 0.2 C with different charge cut-off potentials.

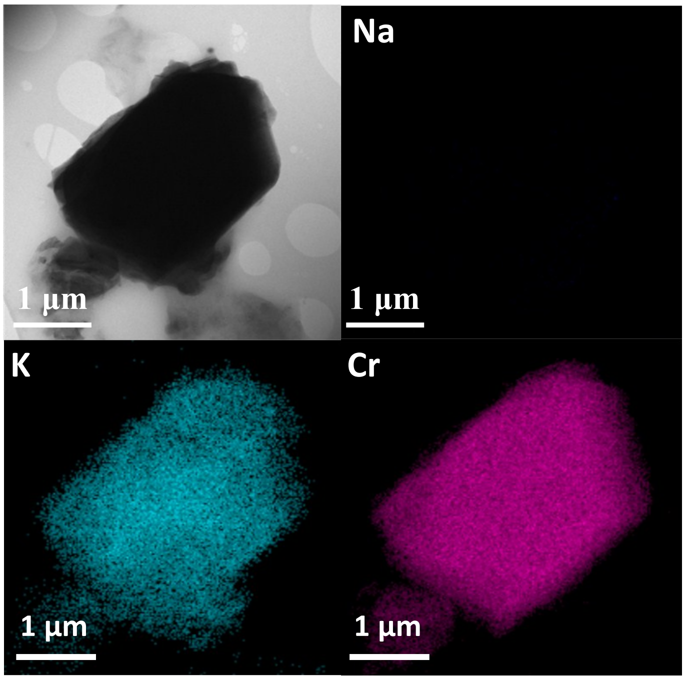

Fig. S10 TEM image and corresponding EDX mapping of cycled P3-$K_{0.69}CrO_2$ cathode after 1000 cycles.