## Supporting Information of "P2- and P3-K<sub>x</sub>CoO<sub>2</sub> as Electrochemical Potassium Intercalation Host"

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**Fig. S1** (a) XRD patterns of  $K_x \text{CoO}_2$  before and after washing. SEM images of  $K_x \text{CoO}_2$  (b) before and (c) after washing.



**Fig. S2** XRD patterns of P2-K<sub>0.41</sub>CoO<sub>2</sub>; (a) pristine, after exposure to humid air for (b) 1 h, (c) 1 day, (d) 2 days and subsequent drying (e) at 80 °C for 12 h and (f) at 150 °C for 12 h.

After exposure to humid air, new peaks at about 13 and 27° are observed in Figs. S2 b-d and even after drying at 80 °C. These peaks are indexed as  $002_{hyd}$  and  $004_{hyd}$  of a hydrated phase. Although the peaks disappear after drying at 150 °C, the lattice parameters are different from those of the pristine sample. These results confirm that P2-K<sub>0.41</sub>CoO<sub>2</sub> is sensitive to moisture and the sample has to be handled in Ar atmosphere.



**Fig. S3** (a) Synthesis procedure of  $K_{2/3}CoO_2$ . (b) XRD pattern and (c) SEM image of P2- $K_{2/3}CoO_2$ . (d) Charge and discharge curves and (e) capacity retention of the K // P2- $K_{2/3}CoO_2$  cell in the voltage range of 2.0 – 3.9 V at a current density of 11.5 mA g<sup>-1</sup>.



**Fig. S4** *Operando* X-ray diffraction patterns of a Na // P2-Na<sub>2/3</sub>CoO<sub>2</sub> cell with 1 mol dm<sup>-3</sup> NaPF<sub>6</sub>/PC in the voltage range of 2.0 - 4.45 V. Diffraction peaks of all the patterns can be indexed as a P2-type phase with space group of  $P6_3/mmc$ .