Supplementary Information for

Efficient Pathways to Improve Electrode Performance of P'2 $Na_{2/3}MnO_2$ for Sodium Batteries

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Supporting Experimental Section

Electrochemical Characterization of P'2 $Na_{2/3}MnO_2$: The composite electrode consisting of active material (P'2 $Na_{2/3}MnO_2$ powder), acetylene black (AB, HS-100, Denka), and poly(vinylidene fluoride) (KF 1100; Kureha Co. Ltd.) was pasted onto Al foil as a current collector by slurry coating method, and then dried under vacuum and further heated at 120 °C in a vacuum for 2 h. The composition for the composite electrode is $Na_{2/3}MnO_2$:AB:PVdF = 80:10:10 in wt%, and the typical mass loading of the active material is 3 – 5 mg cm^{-2}. Metallic sodium (FUJIFILM Wako Pure Chemical) was used as a negative electrode. The electrolyte solution used was 1 M $NaPF_6$ in propylene carbonate (PC) (Kishida Chemical). A porous glass fiber filter (GB-100R, Advantec) was used as a separator placed between the positive and negative electrodes. The two-electrode cells were assembled in an Ar-filled glove box and cycled at room temperature.

Supporting Figures

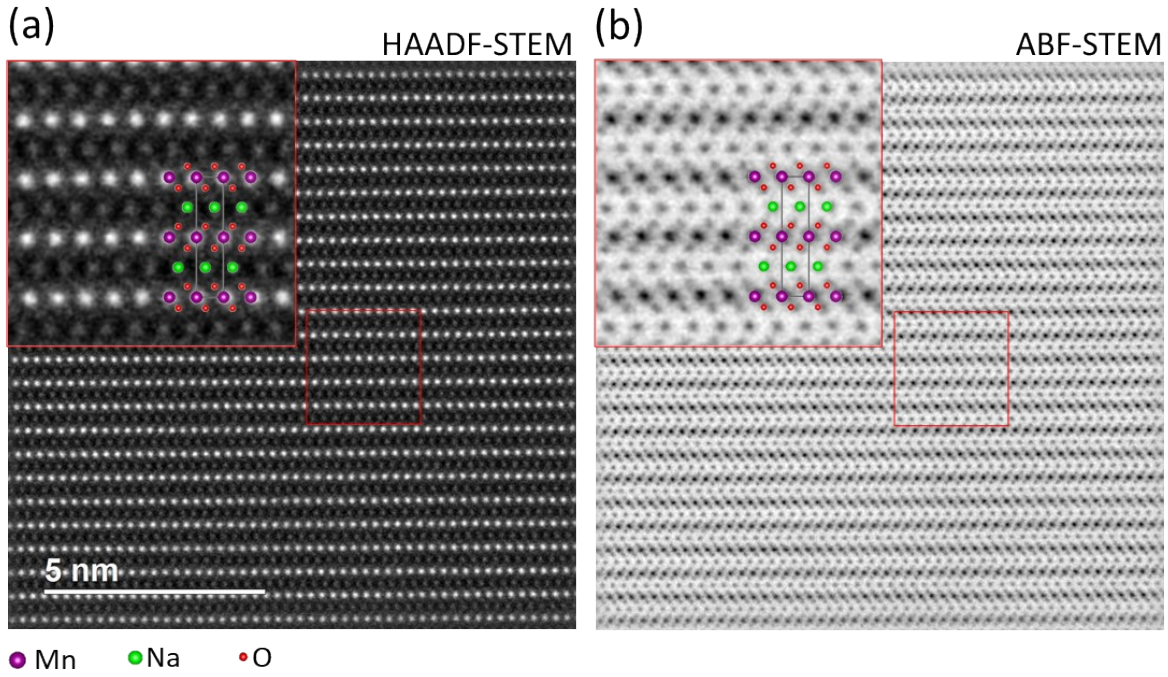

Figure S1. HAADF- and (e) ABF-STEM images along [100] of $Na_{2/3}MnO_2$.

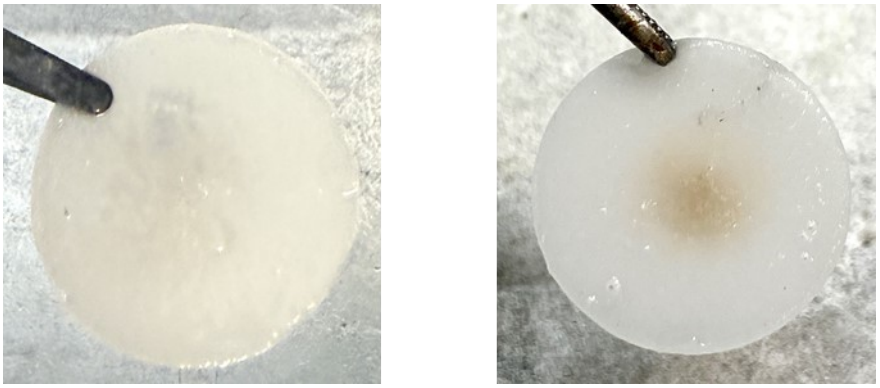

Figure S2. Photographs of the glass filters in Na/$Na_{2/3}MnO_2$ cells after 30 cycles in the voltage ranges of (left) 2.4–4.0 V and (right) 1.5–4.0 V at a rate of 10 mA g^{-1}.

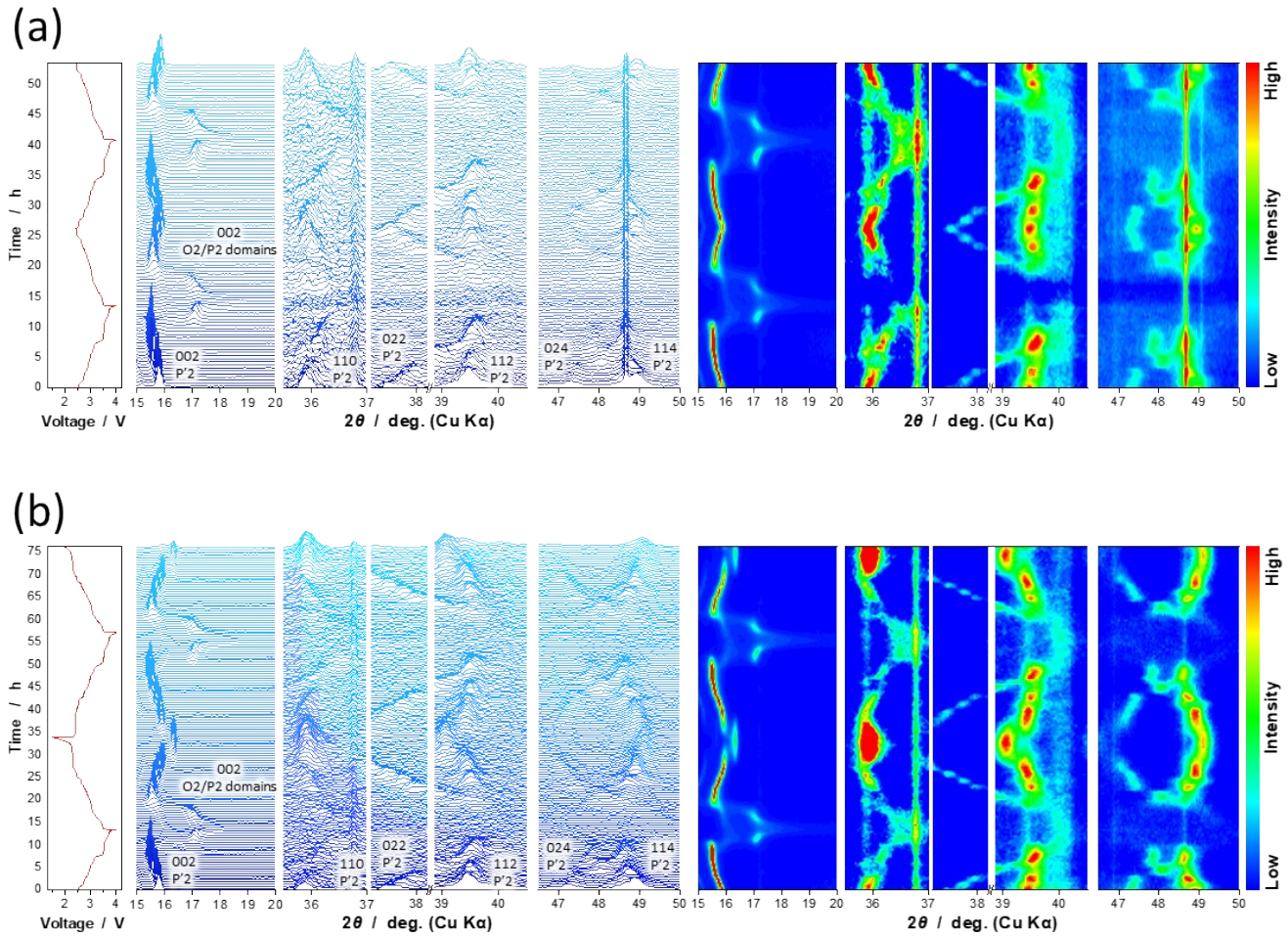

Figure S3. *In-situ* XRD patterns and corresponding contour plots of P'2 $Na_{2/3}MnO_2$ during the initial two cycles in the voltage ranges of (a) 2.4–4.0 V and (b) 1.5–4.0 V at a rate of 10 mA g^{-1}.

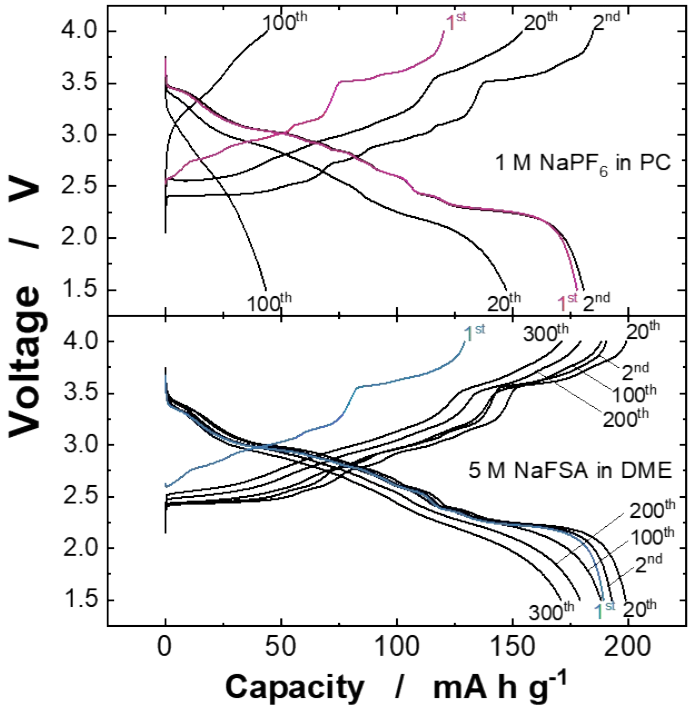

Figure S4. Charge/discharge curves of P'2 $Na_{2/3}MnO_2$ cycled with 1 M $NaPF_6$ in PC and 5 M NaFSA in DME electrolytes in the voltage range of 1.5–4.0 V at a rate of 50 mA g^{-1}.

Figure S5. A photograph of the glass filter in a Na/$Na_{2/3}MnO_2$ cell with 5 M NaFSA in DME electrolyte after 200 cycles in the voltage range of 1.5–4.0 V at a rate of 50 mA g^{-1}.

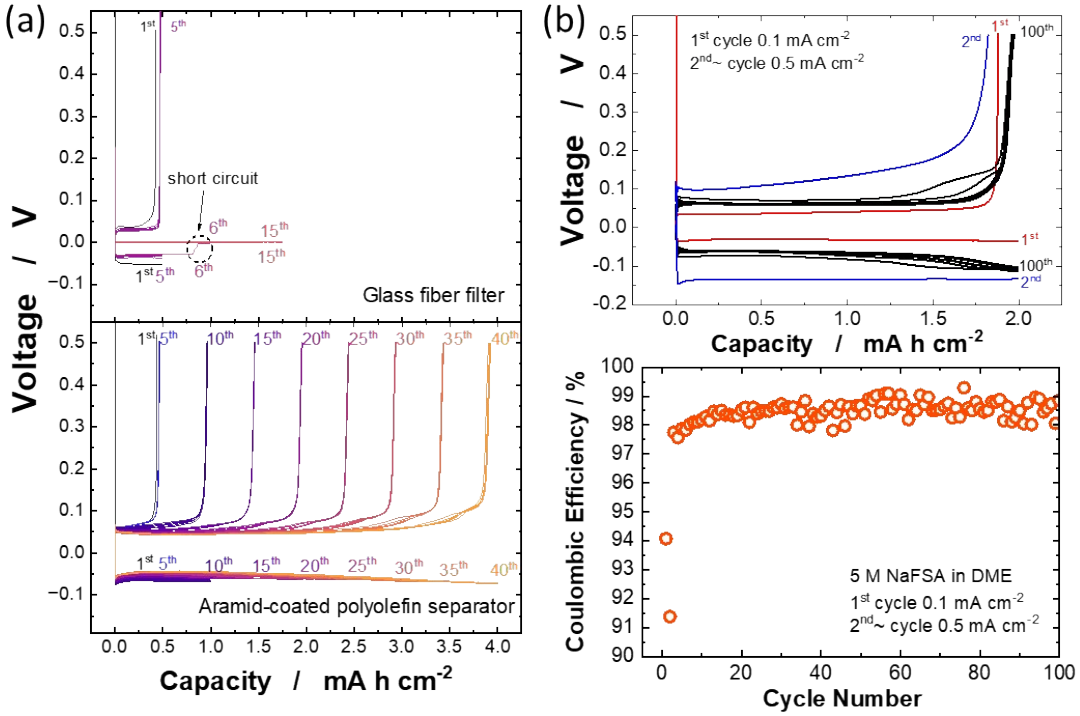

Figure S6. (a) Chronopotentiometric curves of Na deposition/stripping in Na/Cu cells with a glass fiber filter and aramid-coated polyolefin separator measured at various Na disposition capacities at a current density of 0.5 mA cm^{-2}. (b) Cycle performance of the Na/Cu cell with the aramid-coated polyolefin membrane cycled at 0.5 mA cm^{-2} after an initial cycle at 0.1 mA cm^{-2}. 5 M NaFSA in DME electrolyte was used as an electrolyte solution.

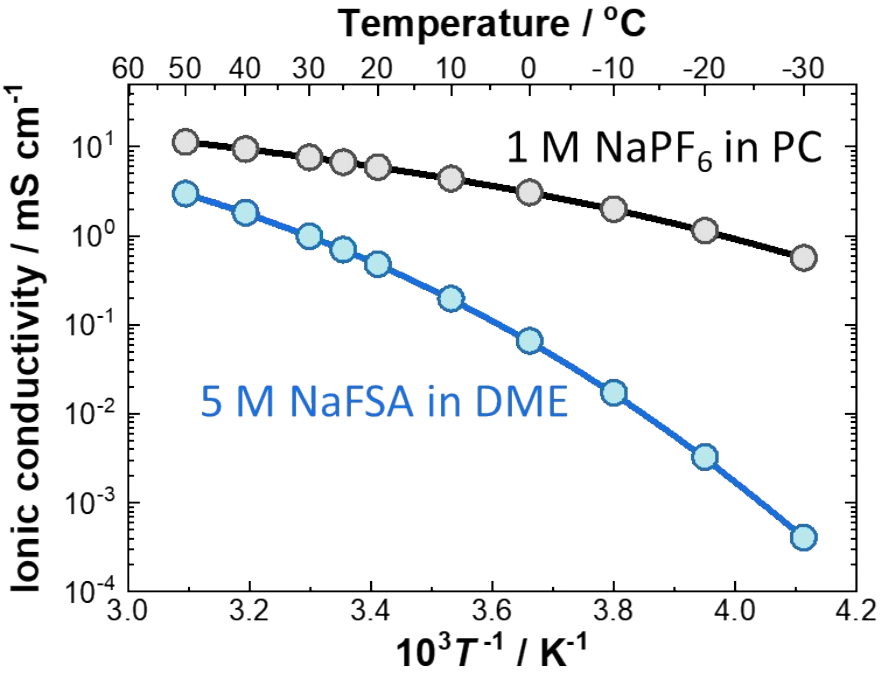

Figure S7. Arrhenius plots of ionic conductivity of 1 M $NaPF_6$ in PC and 5 M NaFSA in DME electrolytes.