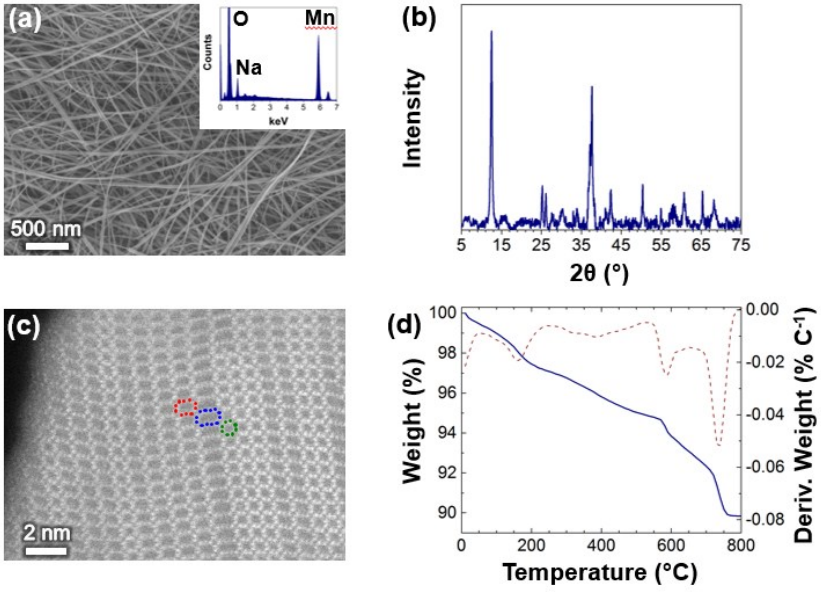
Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information:

Synthesized 2xn-MnO_2

Electrochemical experiments were performed using working electrodes of the 2xn-MnO_2 (Fig S1) consisting of rectangular structural tunnels of two by two, two by three, and two by four octahedra on each side,[30] with a distribution of 37.8%, 36.7%, and 25.5%, respectively. In this work, the simulated systems contain tunnels of two by three octahedra, as this configuration is found in similar amounts to two by two tunnels, and the two by three tunnel most closely represents the average tunnel dimension in a nanowire. Slight differences in tunnel size in the computational model and experimentally synthesized material, as well as the nanowire morphology of the 2x3-$Na_{0.20}MnO_2 \cdot n(H_2O)$ phase, can account for the differences in experimentally measured and simulated (theoretically predicted) electrochemical parameters, but the trends predicted by our model are observed in experiment. Water content was controlled via annealing at various temperatures according to the TGA curve in Figure S1d.



Supplementary Figure 1. (a) SEM image of 2xn-MnO_2 nanowires with EDX spectrum shown in the inset, (b) XRD pattern of 2xn-MnO_2 nanowires, (c) cross-section STEM image of 2xn-

MnO_2 nanowires with green, red, and blue circles denoting 2x2, 2x3, and 2x4 octahedra tunnels, respectively, and (d) TGA and derivative of 2xn-MnO_2 nanowires.

	Pristine	Discharge Only	Discharge + Charge
Test 1	0.18	0.62	0.27
Test 2	0.18	0.52	0.27

Supplementary Table 1. Na:Mn ratios of 2xn-MnO_2 electrodes before cycling (pristine), after first discharge, and after one discharge + charge cycle. Na:Mn ratio are calculated from EDX measurements of electrodes removed from cycled cells. The concentration of structural Na^+ ions is never significantly reduced below 0.20.