

Supplementary Information

Structural Enhancement of $\text{Na}_3\text{V}_2(\text{PO}_4)_3/\text{C}$ Composite Cathode Materials by Pillar Ion Doping for High Power and Long Cycle Life Sodium-ion Batteries

Sung-Jin Lim^a, Dong-Wook Han^a, Do-Hwan Nam^a, Kyung-Sik Hong^a, Ji-Yong Eom^b,
Won-Hee Ryu^{a,c,*}, and Hyuk-Sang Kwon^{a,*}

^a Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology (KAIST), 291 Daehak-ro, Yuseong-Gu, Daejeon, 305-701, Republic of Korea

^b Clean & Energy Materials R&D Center, Korea Automotive Technology Institute, Cheonan-si, Chungnam 330-912, Republic of Korea

^c Department of Chemical and Environmental Engineering, Yale University, New Haven, Connecticut 06520-8286, United States

* Corresponding author.

E-mail: hskwon@kaist.ac.kr (Hyun-Sang Kwon), wonhee.ryu@yale.edu (Won-Hee Ryu)

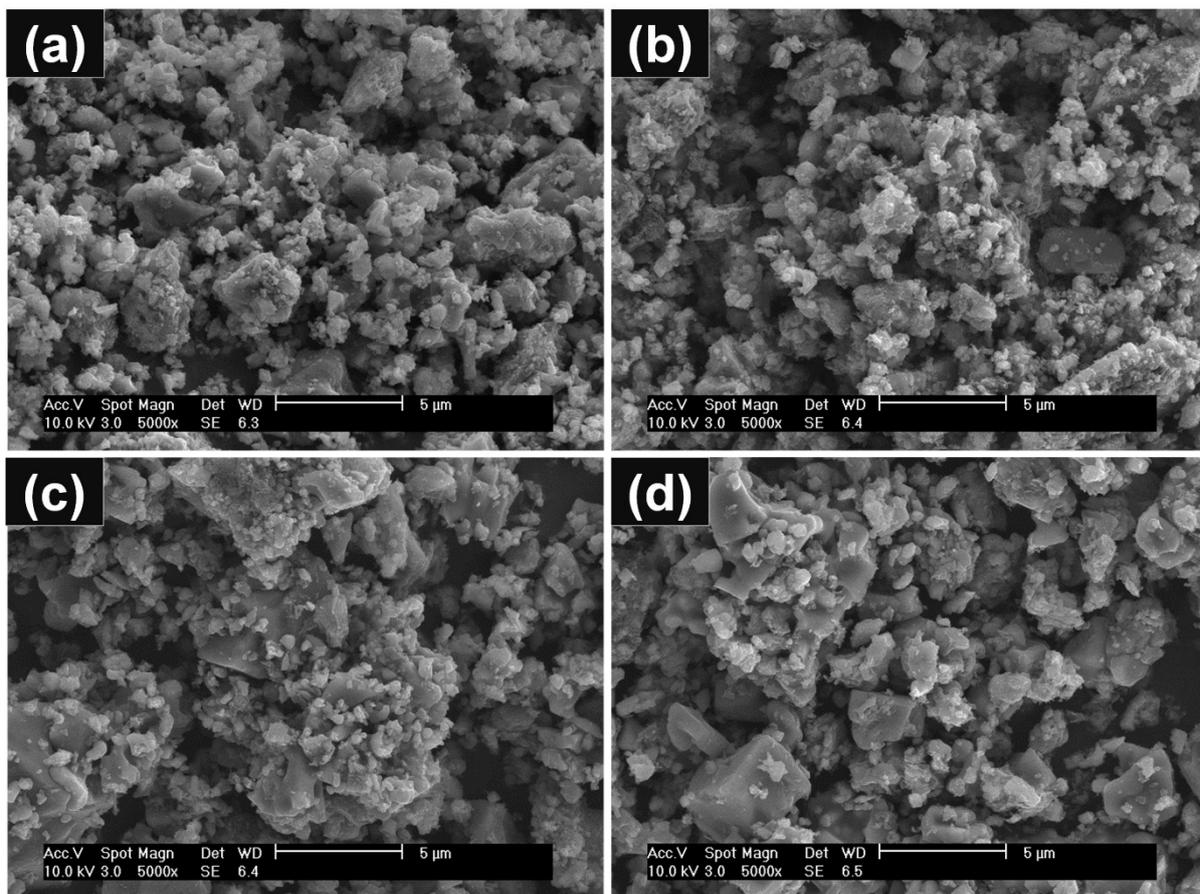


Figure S1. SEM images of (a) the undoped-NVP/C, (b) K0.04-NVP/C, (c) K0.09-NVP/C, and (d) K0.12-NVP/C.

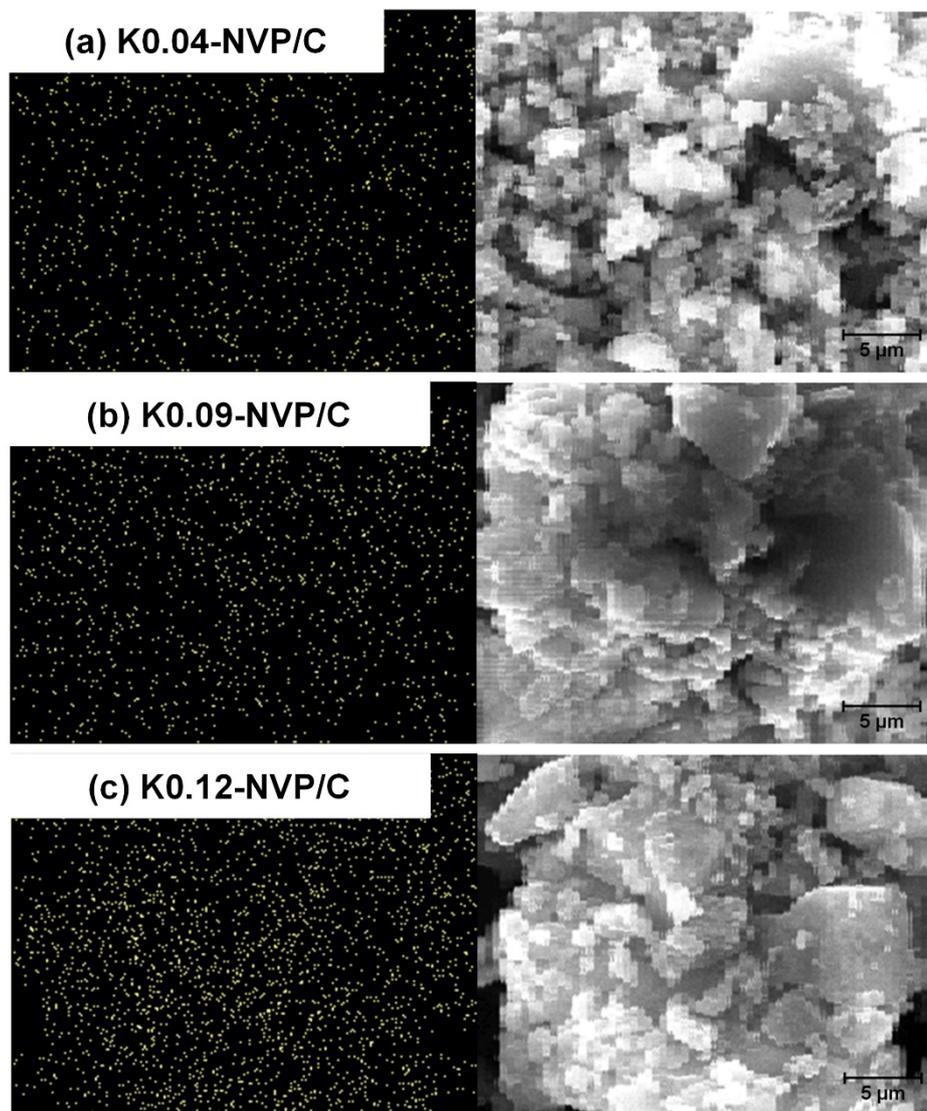


Figure S2. Atomic distribution of K (left) analyzed from the SEM images (right); (a) K0.04-NVP/C, (b) K0.09-NVP/C, and (c) K0.12-NVP/C. The results indicate that the K atoms were uniformly distributed in each particle without segregation.

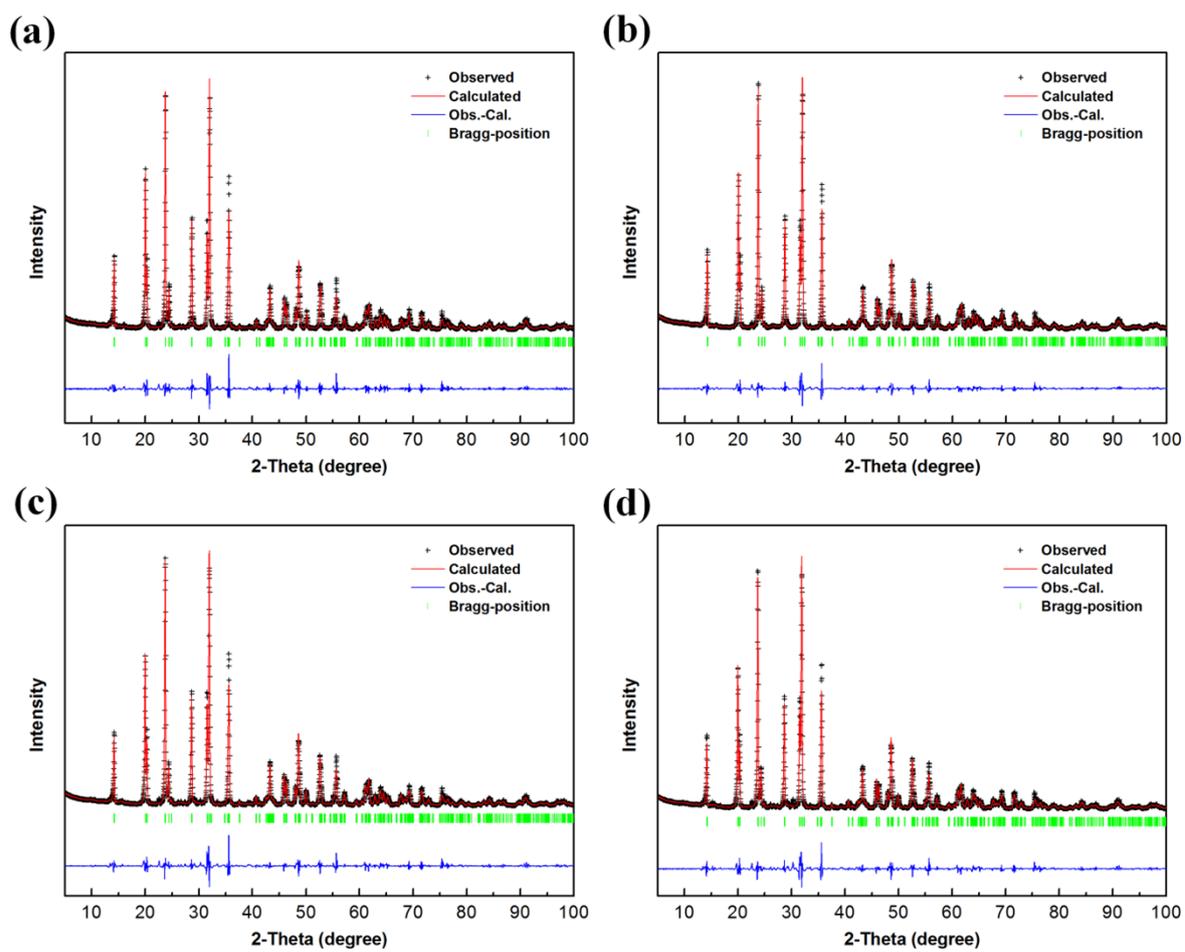


Figure S3. Rietveld refinement patterns of (a) the undoped-NVP/C, (b) K0.04-NVP/C, (c) K0.09-NVP/C, and (d) K0.12-NVP/C; R_{wp} values were 16.2, 12.8, 15.5, and 15.9, respectively.

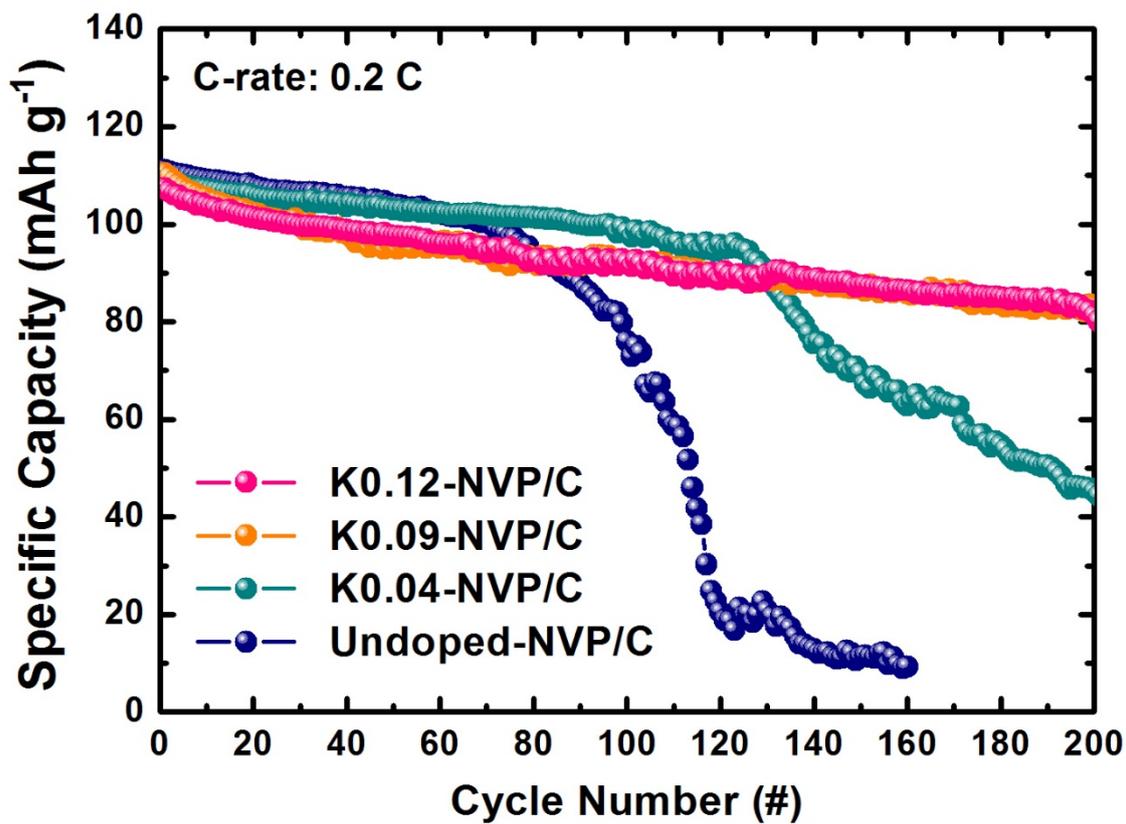


Figure S4. Cycle performance of $\text{Na}_{3-x}\text{K}_x\text{V}_2(\text{PO}_4)_3/\text{C}$ tested at 0.2 C in a voltage window between 3.8 and 2.5 V. The trend of these cycling results is consistent with the cycling data obtained at 1 C as shown in Figure 3a.

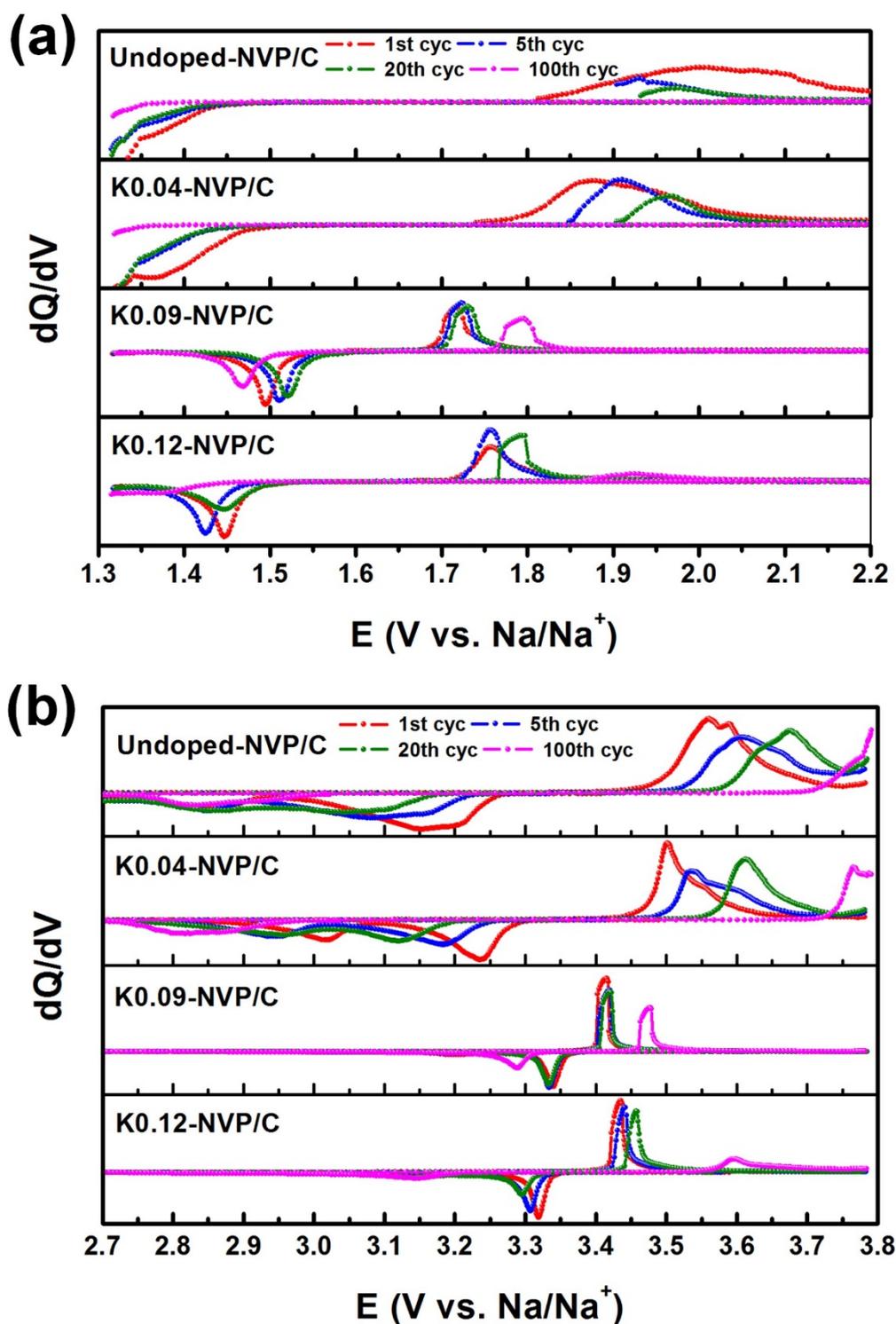


Figure S5. dQ/dV plots of $\text{Na}_{3-x}\text{K}_x\text{V}_2(\text{PO}_4)_3/\text{C}$ for the 1st, 10th, 50th, and 100th cycles obtained from the cycling test at 1 C in a voltage window between 3.8 and 1.3 V; (a) between 2.2 and 1.3 V and (b) between 3.8 and 2.7 V. The voltage difference of each oxidation/reduction peak gradually increased and peak broadening was observed with repeated cycling, indicating that the electrochemical and structural stabilities of the undoped-NVP/C and K0.04-NVP/C (small doping amount) were decreased due to the difficulty of the reversible reaction with large Na-ions. On the other hand, the sharp oxidation/reduction peaks of the K0.09-NVP/C and K0.12-NVP/C were effectively maintained after the 100th cycle without any shifting or peak broadening because the structure was stabilized by pillar ions.

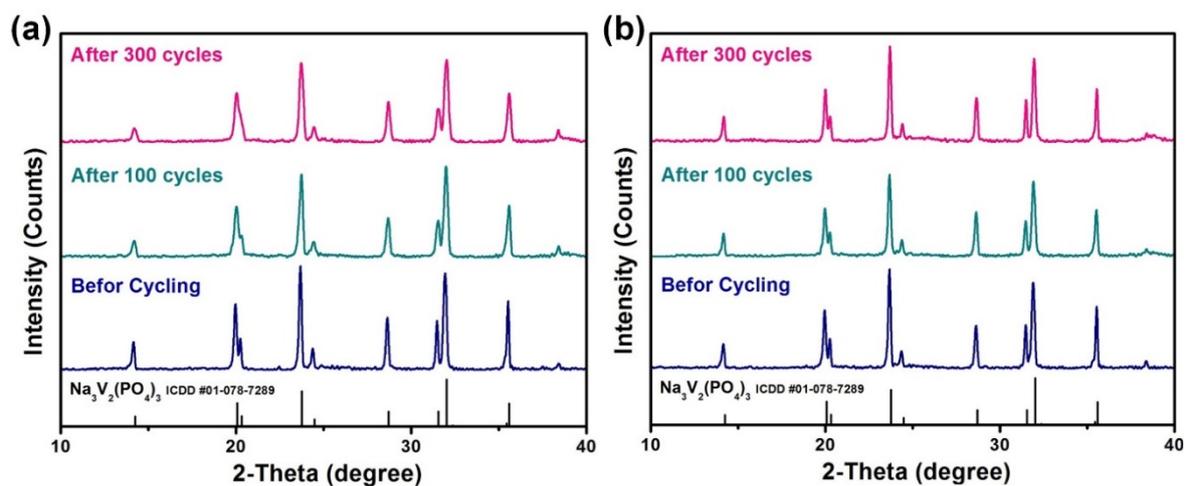


Figure S6. *Ex-situ* XRD patterns of (a) the undoped-NVP/C and (b) K0.09-NVP/C collected before cycling, after 100 cycles, and after 300 cycles.