Supporting Information

**Fig. S1.** 3D packing diagram of KNaV$_{10}$ with a spacefill style along $\alpha$ axis.
Fig. S2. The TGA curve of MgV$_{10}$. 
Fig. S3. The experimental and simulated XRD patterns of KNaV$_{10}$. 
Fig. S4. The experimental and simulated XRD patterns of MgV$_{10}$. 

Intensity (a.u.)

2θ

MgV$_{10}$
MgV$_{10}$ Simulated
Fig. S5. TEM images of MgV$_{10}$ collected at different amplifications.
Fig. S6. Cyclic voltammograms of KNaV_{10} with a scan rate of 0.1 mV s^{-1} at the potential range of 3.8 -1.0 V.
Fig. S7. SEM images of KNaV$_{10}$ in the stage of (a) pristine, (b) discharged, (c) charged and MgV$_{10}$ in the stage of (d) pristine, (e) discharged, (f) charged.
Fig. S8. FTIR spectra of KNaV$_{10}$ in the stage of pristine, discharged and charged.
Fig. S9. FTIR spectra of MgV$_{10}$ in the stage of pristine, discharged and charged.
Fig. S10. Cycling performance of KNaNi$_{10}$ at 50 mA g$^{-1}$. 
Fig. S11. Rate capability of MgV$_{10}$ and KNaV$_{10}$. 
Fig. S12. The evolutions of the electron number of MgV$_{10}$ and KNAV$_{10}$ upon on battery cycling.