SUPPORTING INFORMATION

Rechargeable Sodium-ion Battery: High Capacity Ammonium Vanadate Cathode with Enhanced Stability at High Rate

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First-principles calculations are based on Density Functional Theory (DFT) as implemented in Vienna Ab-initio Simulation Package (VASP).[1] We use a generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE)[2] functional of the exchange and correlation energy. In the initial structure, the NH_4^+ ion lie between the layers and Na^+ ions, are present into the gallery space as well as within the layers.[3] All the structures are fully relaxed through minimization of energy till the magnitude of forces is smaller than 0.02 eV $Å^{-1}$ and pressure less than 0.01 Kbar. We used an energy cut-off of 500 eV on the plane wave basis set and k-mesh grids of 3x9x9 for sampling Brillouin Zone integrations. We used U = 3.0 eV (Hubbard parameter) to incorporate onsite correlations of electrons in d orbitals of V in all the calculations. We calculated average electrochemical potential from Nernst equation

$$V_{cell} = \frac{-\Delta G}{nF} \approx \frac{-\Delta E}{nF} = -(E_{in-Na} - E_{de-Na} - E_{Na})$$

where V_{cell} is the cell voltage, ΔG is change in Gibbs free energy per mole which is approximate equal to change in calculated total energy ΔE, n is the number of moles of electrons transferred and F is the Faraday constant. E_{in}-Na, E_{de}-Na and E_{Na} are total energy are the energies per formula unit of sodiated and de-sodiated structures of electrode and one mol of Na atom, respectively (Figure S2).

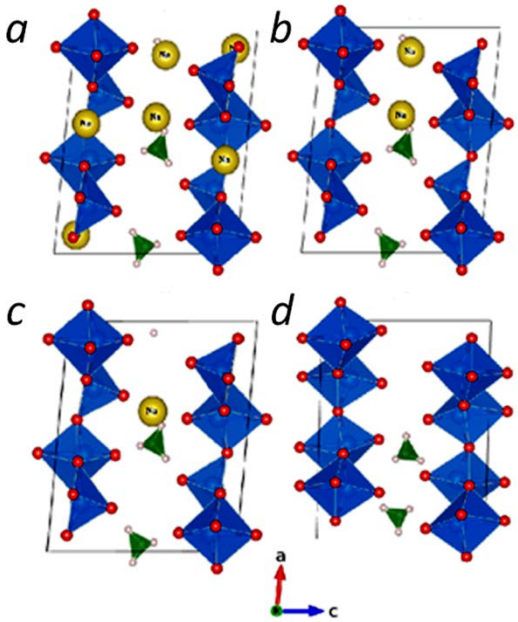

Figure S1. Configuration of the (a) $Na_3NH_4V_4O_{10}$. (b) $Na_1NH_4V_4O_{10}$. (c) $Na_{0.5}NH_4V_4O_{10}$. (d) $NH_4V_4O_{10}$.

Table S1. Magnetic moment of all the Vanadium atoms in $Na_xNH_4V_4O_{10}$ from DFT calculations.

	Magnetic moment							
$Na_xNH_4VO_{10}$	V1	V2	V3	V4	V5	V6	V7	V8
0	0.2	0	1	0	0	0.2	0	1
0.5	0.2	0.2	0.7	0.3	0.2	1	1	0.2
1	1	0.2	0.3	1	0.2	1	1	0.3
3	1.1	1.1	1.1	1.1	1.1	1.1	1.1	1.1

Table S2. Calculated lattice parameters and lattice volume at different concentration of Na in $NH_4V_4O_{10}$.

$Na_xNH_4V_4O_{10}$	Lattice parameter			Volume(Å ^{3})	
	a(Å)	b(Å)	c(Å)		
0	11.78(11.71[#])	3.74(3.66[#])	9.75(9.72[#])	428.91	
0.5	11.79	3.74	9.71	426.55	experimental lattice parameter
1	12.07	3.77	9.08	413.49	
3	12.51	3.94	9.85	484.4	

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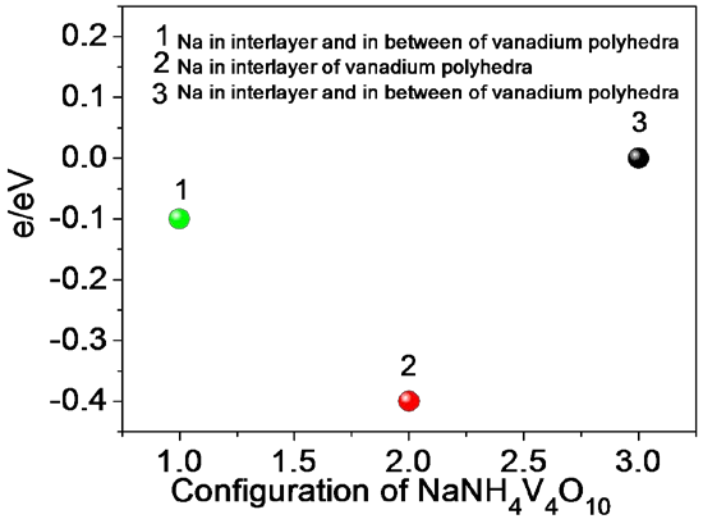

Figure S2. The calculated formation energies of $NH_4V_4O_{10}$ structure with Na in gallery space and within the layer.

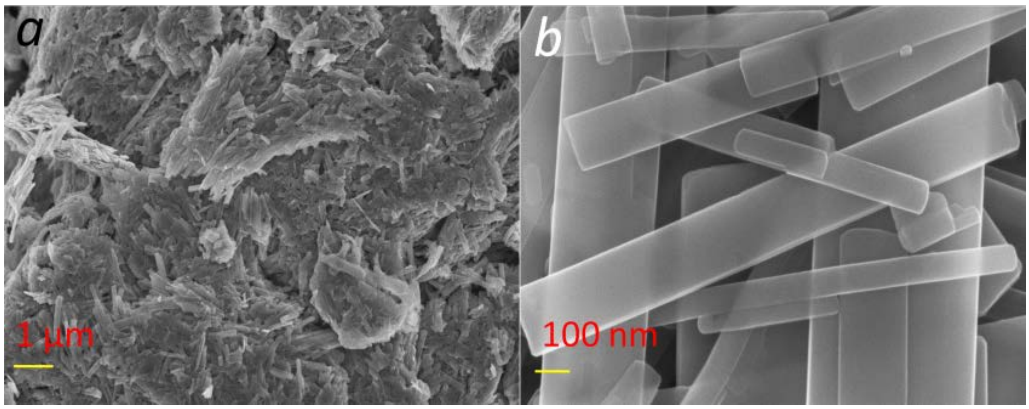

Figure S3. (a-b) FEG-SEM image of $NH_4V_4O_{10}$ nano-belts.

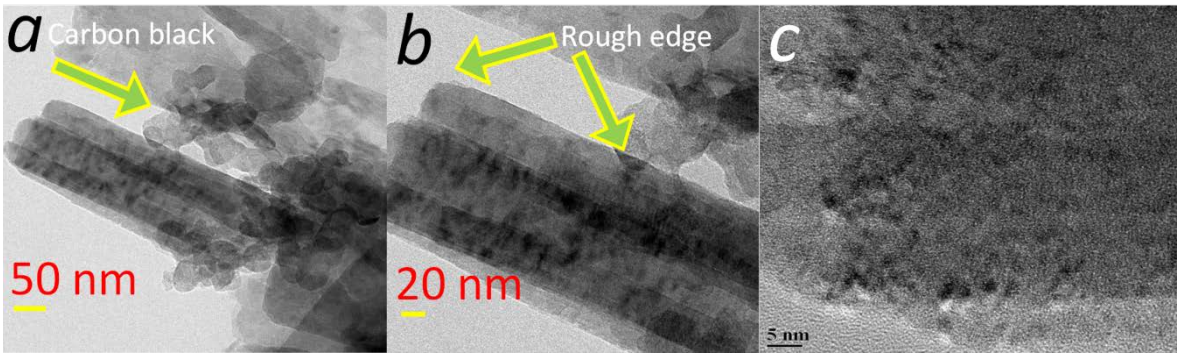

Figure S4. (a-b) FEG-TEM image. (c) HR-TEM image of $NH_4V_4O_{10}$ material (after 25thcycle).

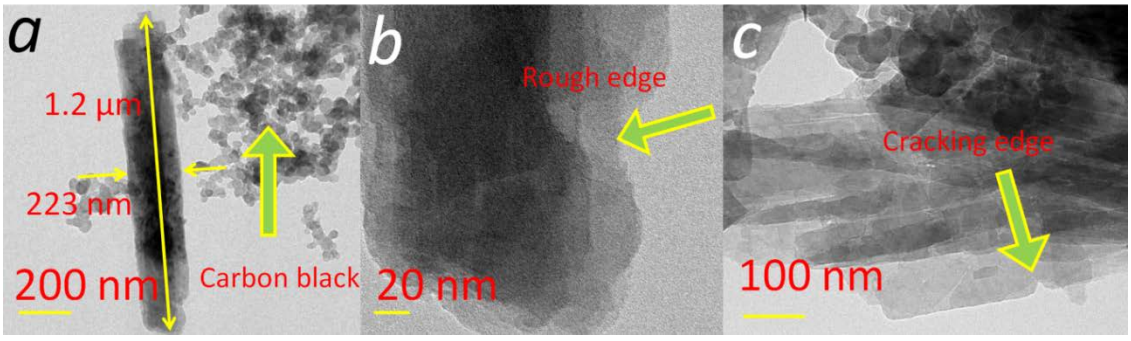

Figure S5. (a-c) FEG-TEM image of $NH_4V_4O_{10}$ material (after 32th cycle).

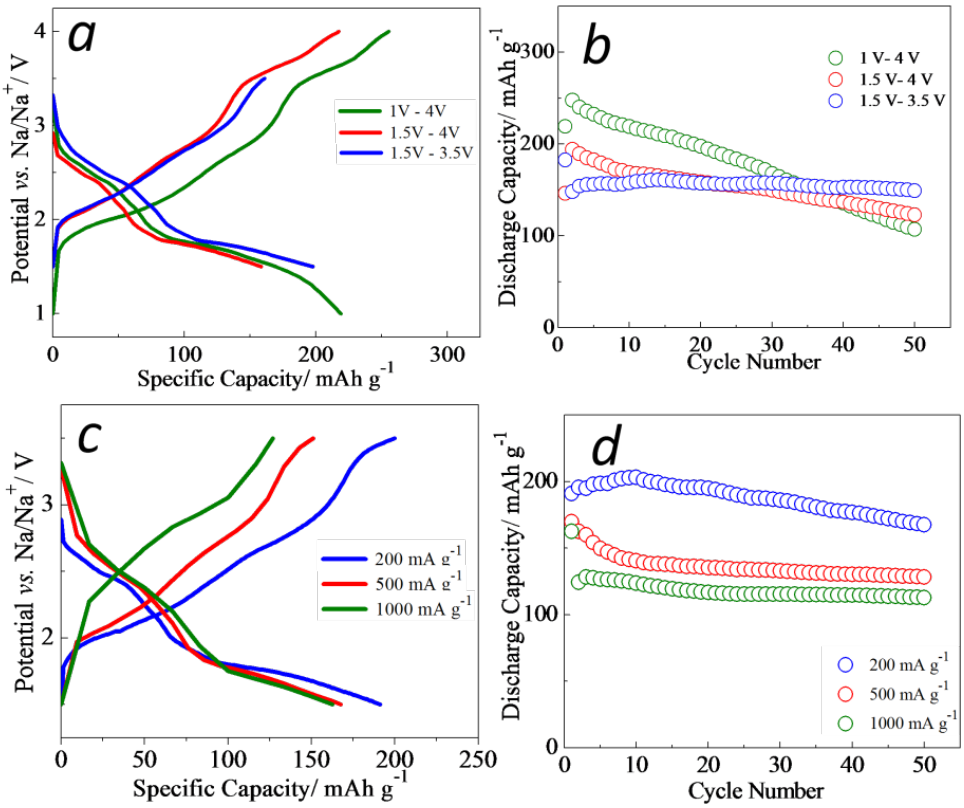

Figure S6. (a) 1st charge/discharge profile of $NH_4V_4O_{10}$ cathode material between varying potential (bare Al-current collector). (b) Discharge capacity vs. cycle number (bare Al-current collector), (c) 1st charge/discharge of $NH_4V_4O_{10}$ cathode material between 1.5-3.5 V at varying current rate with carbon coated Al-current collector. (d) Discharge capacity vs. cycle number between 1.5-3.5 V at varying current rate with carbon coated Al-current collector.

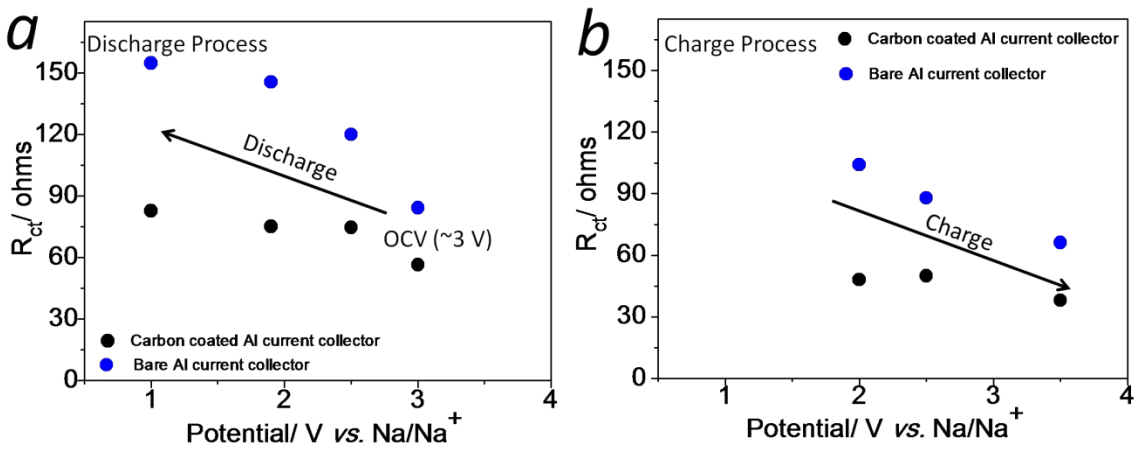

Figure S7. R_{ct} of Carbon coated and bare Al current collector during (a) Discharge process. (b) Charge process.

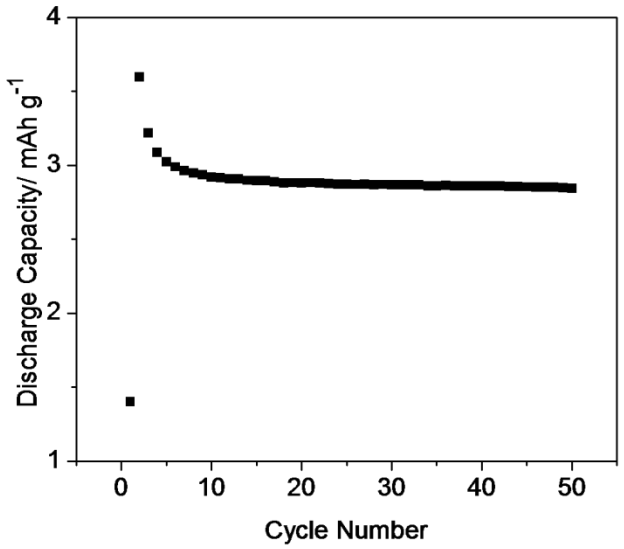

Figure S8. Discharge capacity of carbon at 200 mA g^{-1} current rate between potential window 1.5 V-3.5 V.

The capacity contribution from conductive carbon is shown in Figure S8 which is ~3 mAh g^{-1} at 200 mA g^{-1} current rate (experiment done only with conductive carbon) between potential window of 1.5 V-3.5 V. Moreover, Na^+ storage in conductive carbon was negligible compared to the $NH_4V_4O_{10}$ cathode material with and with-out carbon coated Al current collector.

REFERENCES

1. Kresse, G.; Furthmuller, J. Efficiency of Ab-initio Total Energy Calculations for Metals and Semiconductors Using a Plane-wave Basis Set. *Comput. Mater. Sci.* **1996**, *6*, 15-50.

2. Perdew, J.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865-3868.

3. Kim, H.; Kim, D. Y.; Kim, Y.; Lee, S.; Park, K. Na Insertion Mechanisms in Vanadium Oxide Nanotubes for Na-Ion Batteries. *ACS Appl. Mater. Interfaces* **2015**, *7*, 1477-1485.