Alkali Ions Pre-intercalated Layered Vanadium Oxide Nanowires for Stable Magnesium Ions Storage

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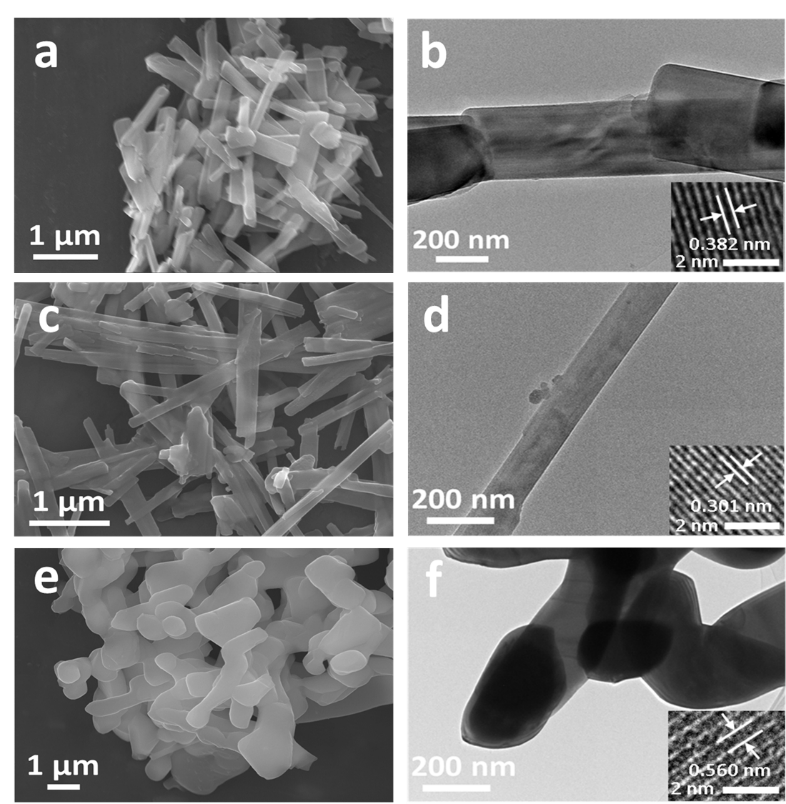
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**Support Information**

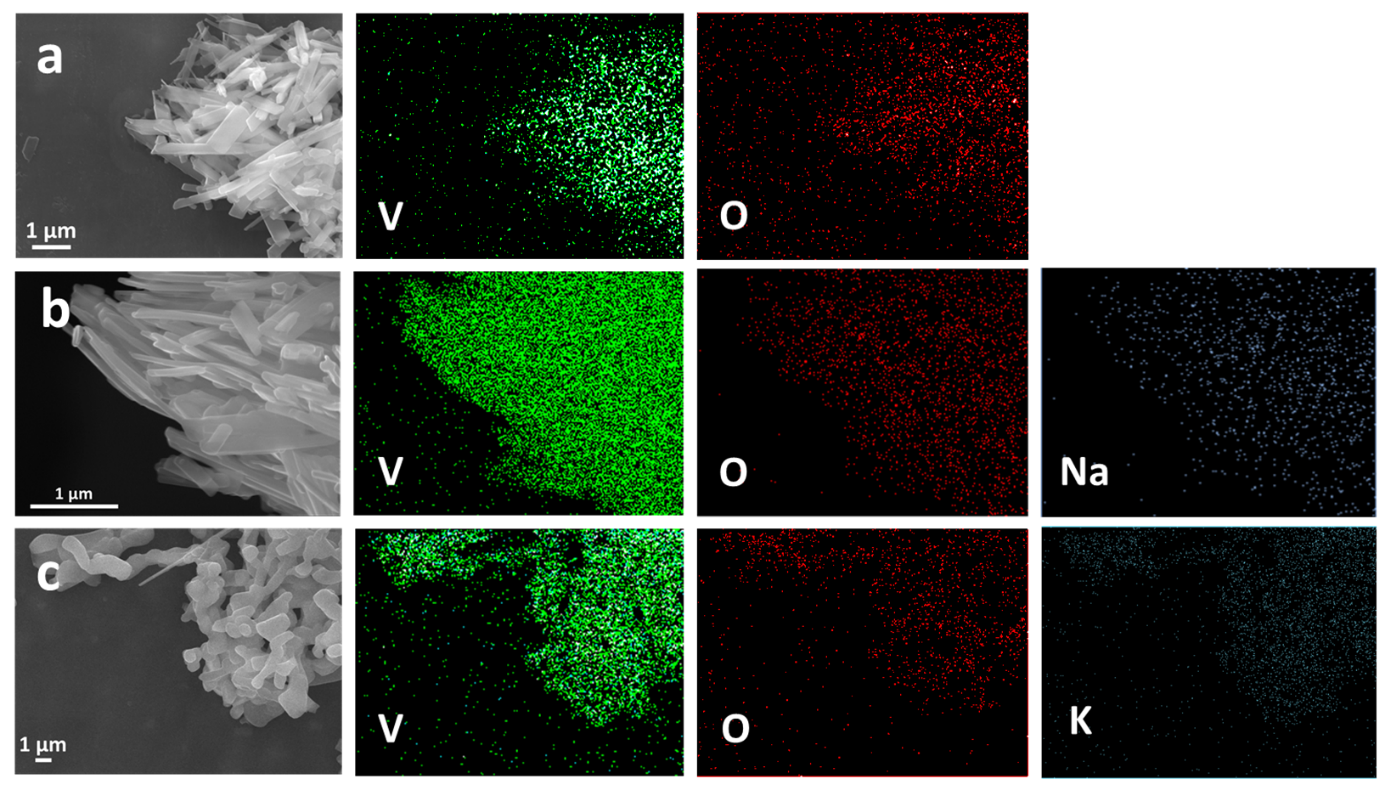
Density Functional Theory and Crystal Structure

The present calculations were carried out by using the projector augmented wave (PAW) method within DFT, as implemented in the Vienna ab initio simulation package (VASP). The generalized gradient approximation (GGA) in the form of the Perdew-Burke-Ernzerhof (PBE) was used to treat the exchange-correlation energy. A kinetic energy cutoff of 500 eV was used for wave functions expanded in the plane wave basis. All atoms were allowed to relax until the forces were less than 0.05 eV Å−1. For the Brillouin-zone sampling, 6×6×6 k-points were adopted to ensure convergence of the total energy. Ultrasoft pseudopotentials were used to describe the interactions of the ionic core and valence electrons. The valence states considered in this study were V 3d34s2, O 2s22p4, Li 1s22s1, Na 2p63s1, K 3p64s1 and Mg 2p63s2. A unit cell of A-V3O8 (A= Li, Na, K) crystal with a periodic structure were used in the DFT calculations. The A-V3O8 (A= Li, Na, K) crystal had a monoclinic structure and belonged to the space group P21/m. DFT calculations were performed to identify the most suitable host site for Mg2+ ions intercalation in the A-V3O8 (A=Li, Na, K) crystal (space group: P21/m). During the discharge process, the most favorable geometry-optimized high-symmetry intercalation sites for 0.5 Mg2+ ions per unit formula in the A-V3O8 (A=Li, Na, K) cell were considered theoretically (Fig. S4). The Mg2+ ions intercalation energy (Ei) is defined as , where are the total energies (Etotal) of the Mg2+-intercalated A-V3O8 (A=Li, Na, K) unit cell and are the pristine energies (Epristine) of A-V3O8 (A=Li, Na, K) unit cell, while EMg is the energy of isolated Mg. The corresponding Epristine, Etotal and Ei are listed in Table S1. DFT calculations were also performed to investigate the pre-intercalated alkali cations (Li+, Na+, K+) diffusion dynamics between V3O8 layers.

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**Fig. S1** SEM images, TEM images and HRTEM image (inset) of LiV3O8 (a-b), NaV3O8 (c-d), KV3O8 (e-f).

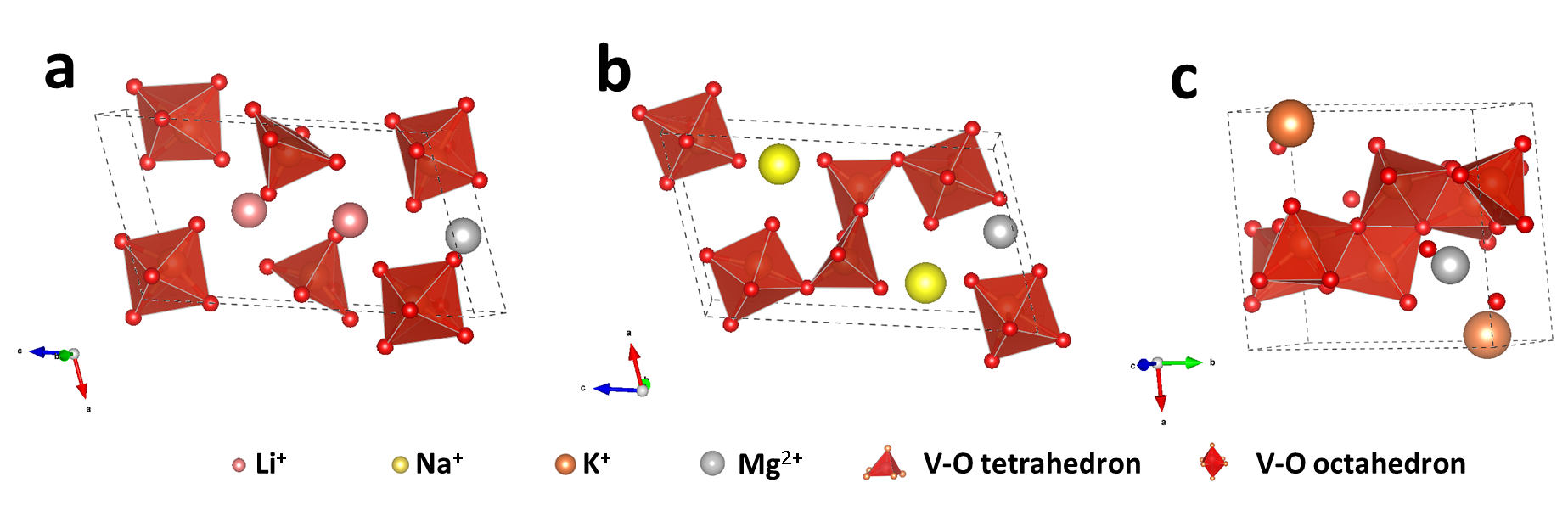
The morphology of LiV3O8 is similar to that of NaV3O8. Both of them are nanowires with a length of two or three micrometers (Fig. S1a, c). From TEM pattern (Fig. S1b, d), the diameter of LiV3O8 nanowire (~260 nm) is larger than NaV3O8 (~170 nm). Additionally, the lattice fringe with the spacing of 0.382 nm (matches well with (003) plane of LiV3O8) and 0.301 nm (matches well with (222) plane of NaV3O8) is revealed by HRTEM, respectively (inset of Fig. S1b, d). Fig. S1e and Fig. S1f show that the as-synthesized KV3O8 are nanoplate with the width about 200 nm. The HRTEM image (inset of Fig. S1f) shows the lattice fringes of 0.560 nm, which matches well with the (110) plane of KV3O8.



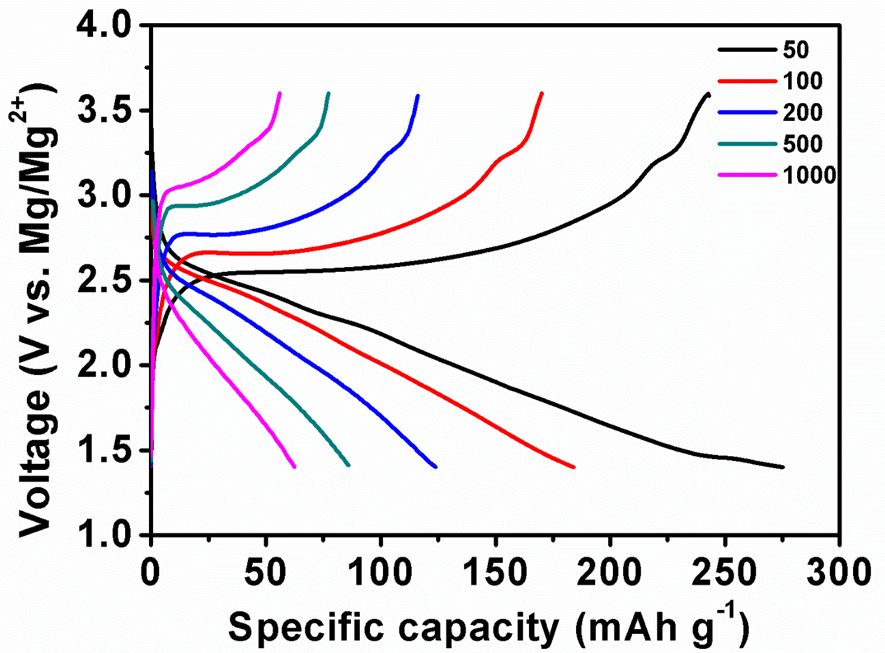
**Fig. S2** (a-c) EDS-mapping of A-V3O8 (A=Li, Na, K).



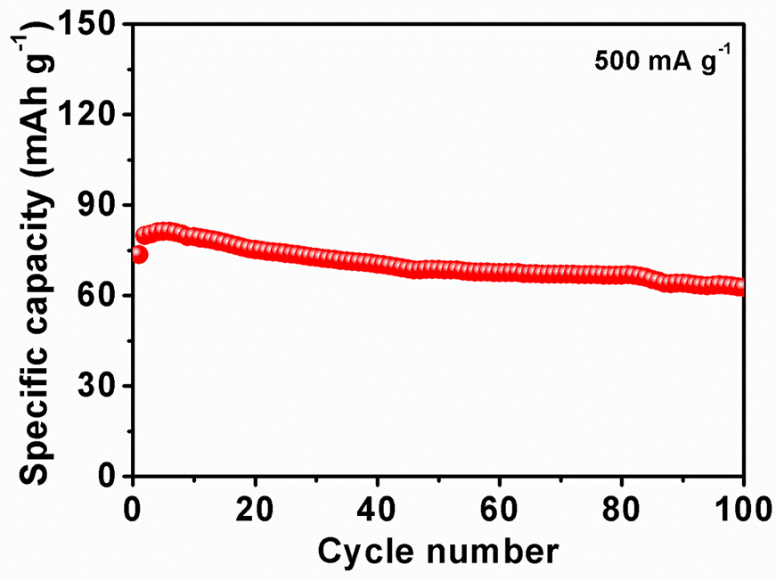
**Fig. S3** Nyquist plots of A-V3O8 (A=Li, Na, K) after 1 cycle.



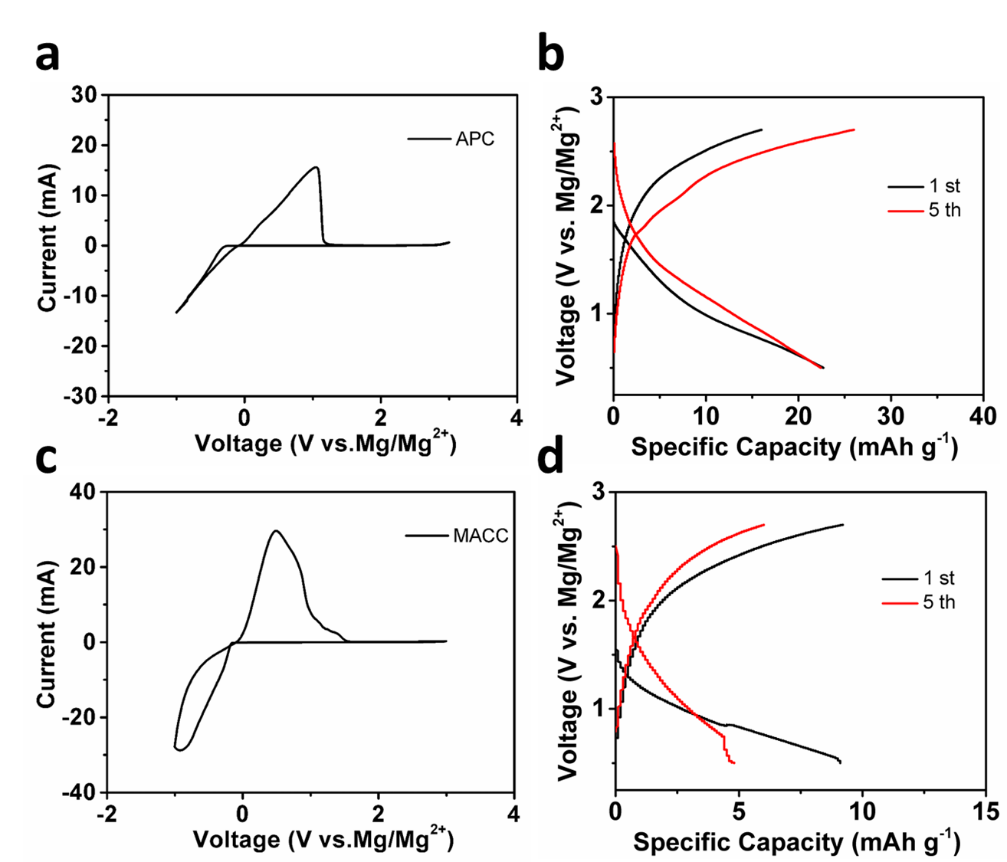
**Fig. S4** (a-c) Illustration of the crystal structure of A-V3O8 (A=Li, Na, K) after Mg2+ ions intercalated.



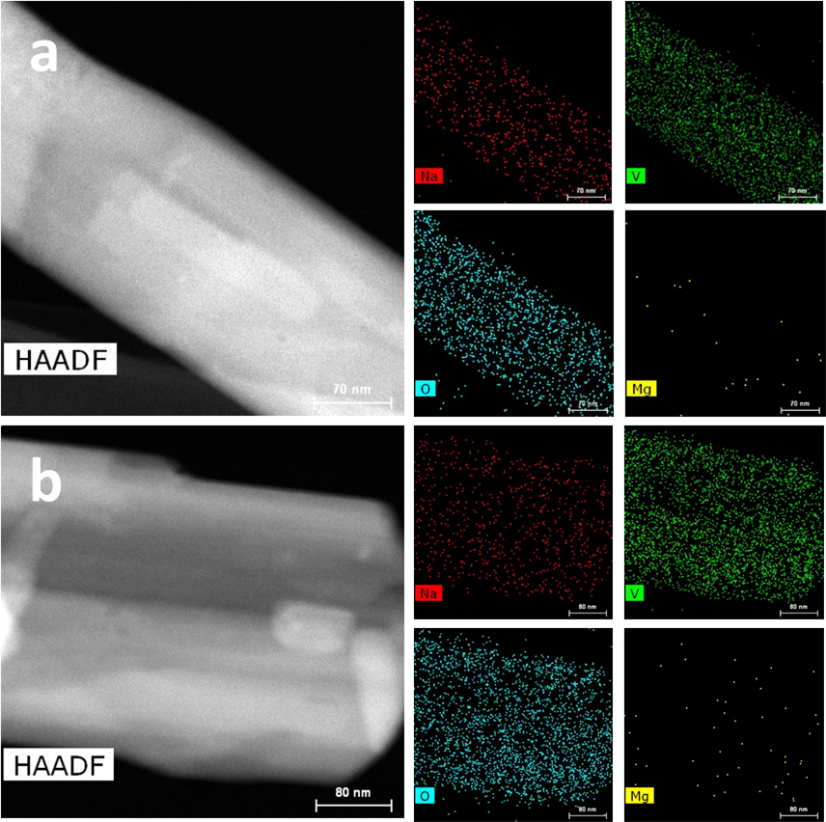
**Fig. S5** Charge/discharge curves of NaV3O8 at the current density of 50,100, 200, 500 and 1000 mA g-1.

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**Fig. S6** Cycling performance of NaV3O8 at the current density of 500 mA g-1.



**Fig. S7** (a) CV curves of APC at scan rate of 100 mV s-1. (b) Charge/discharge curves of NaV3O8 at 1st and 5th cycle in APC. (c) CV curves of MACC at scan rate of 100 mV s-1. (d) Charge/discharge curves of NaV3O8 at 1st and 5th cycle in MACC.

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**Fig. S8** HAADF image and EDS elemental mappings of NaV3O8 at (a) initial, (b) charge state.

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**Fig. S9** GITT potential feedback curve with time.

**Table S1.** The intercalation energy (Ei) of Mg2+ ions in A-V3O8 (A=Li, Na, K) and the coordinate of the intercalated Mg2+ ions.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| Pristine | Epristine | Intercalation of Mg2+ | The coordinate of Mg2+ | | | Etotal | Ei |
| XMg2+ | YMg2+ | ZMg2+ |
| Li2V6O16 | -190.32 | MgLi2V6O16 | 0.58 | 0.25 | 0.05 | -195.95 | -5.63 |
| Na2V6O16 | -189.31 | MgNa2V6O16 | 0.52 | 0.25 | 0.05 | -194.72 | -5.40 |
| K2V6O16 | -189.02 | MgK2V6O16 | 0.66 | 0.75 | 0.57 | -193.76 | -4.74 |

**Table S2.** The ICP result of the NaV3O8 electrode at different states.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| NaV3O8 | Mg(%) | V(%) | Weight ratio  (mMg/mV) | Molar ratio  (MMg/MV) |
| Initial state | 0.14 | 21.75 | 0.00644 | 0.01368 |
| Discharge state | 3.28 | 17.14 | 0.19136 | 0.40665 |
| Charged state | 0.16 | 22.23 | 0.00720 | 0.01530 |

**Table S3.** The AAS result of the electrolyte at different cycles when NaV3O8 act as cathode.

|  |  |  |  |
| --- | --- | --- | --- |
| Electrolyte | Na (mg L-1) | Na (mmol L-1) | Na:V in cathode |
| Initial state | 12.660 | 0.550 | 1:3 |
| 10th (charge state) | 13.660 | 0.594 | 0.934:3 |

**Scheme 1.**τ is the constant current pulse time, mB is mass of active materials, VM refers to molar volume of H2V3O8, MB is themolar mass of H2V3O8, S is the electrode–electrolyte interface, ΔES is the voltage difference during the open circuit time, and ΔEτ is the total change of battery voltage during a constant current pulse without the IR drop.