**Supporting Information**

Fast and stable Mg2+ intercalation in a high voltage NaV2O2(PO4)2F/rGO cathode material for magnesium-ion batteries

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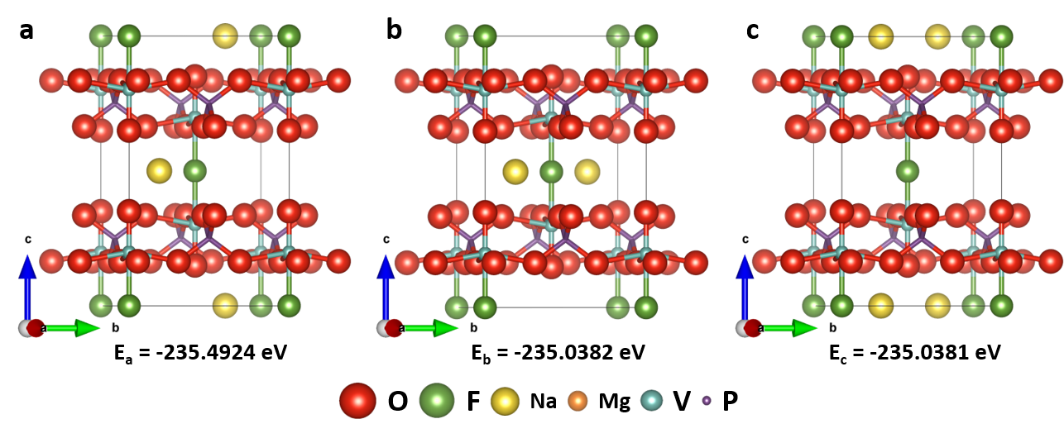


Figure S1. Three different alignment states of Na in NaV2O2(PO4)2F/rGO based on the refinement results in a unit cell. (a) One Nais inside the unit cell and the other Na is on the surface of the unit cell. (b) Two Naare inside the unit cell. (c) Two Na are on the surface of the unit cell.

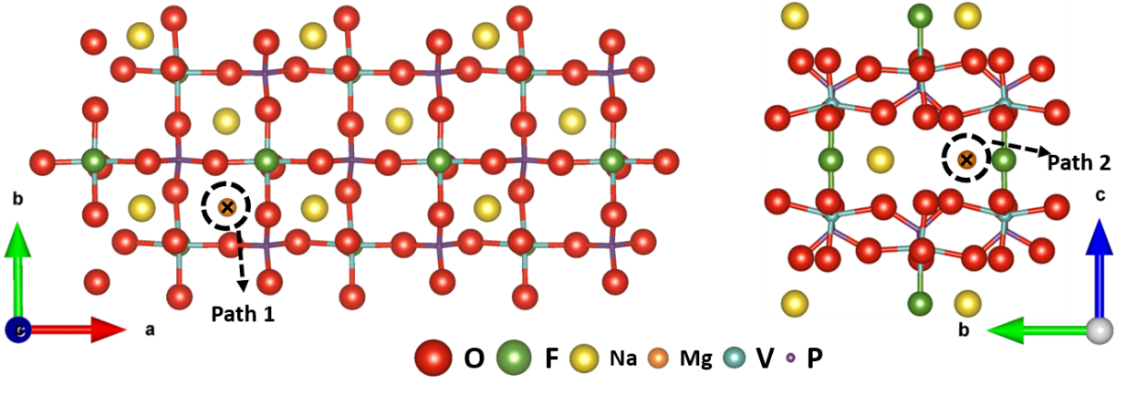


Figure S2. Diffusion profile of path 1 perpendicular to the *ab* plane (left) and path 2 parallel to the *ab* plane (right).

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Figure S3. XRD pattern of NVOPF, indicating that the pure phase of the NVOPF is synthesized.

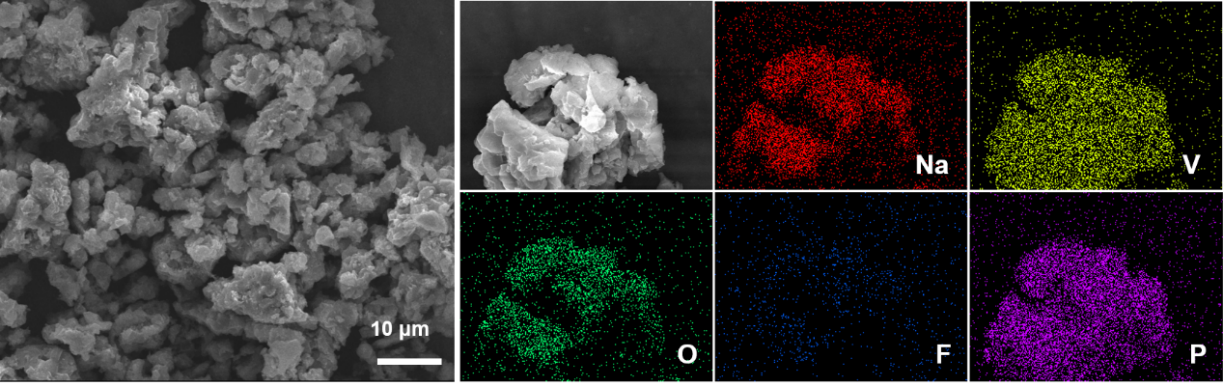


Figure S4. SEM image and elemental mapping images of NVOPF, which shows the morphology of the prepared NVOPF with micron size and the existence of Na, O, V, P, and F elements.

Figure S5 shows the Rietveld refinement and crystal structure of NVOPF/rGO. The Rietveld refinement gives the following lattice parameters: *a* = *b* = 6.38850(7) Å and *c* =10.60779(0) Å. The other structural parameters are given in Table S1. This is consistent with previous reports.[1, 2] The refinement result meets low reliability factors of GOF=1.31, Rwp=4.44%, and Rp=3.35%.

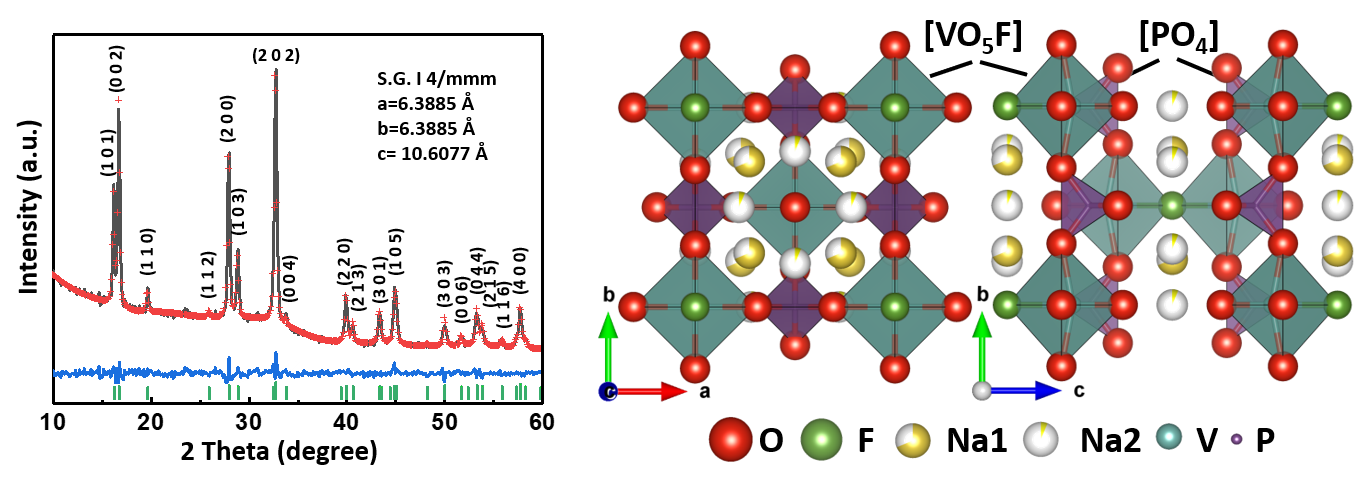


Figure S5. Rietveld refinement and crystal structure of NVOPF/rGO.

Table S1. Rietveld refinement atomic coordinates for NVOPF/rGO.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Atom | Site | Occupancy | x | y | z |
| Na1 | 8h | 0.688 | 0.2706 | 0.2706 | 0 |
| Na2 | 8j | 0.063 | 0.2193 | 0.5000 | 0 |
| V | 4e | 1.000 | 0 | 0 | 0.1984 |
| P | 4d | 1.000 | 0 | 0.5000 | 0.2500 |
| O1 | 16n | 1.000 | 0 | 0.3085 | 0.1648 |
| O2 | 4e | 1.000 | 0 | 0 | 0.3504 |
| F1 | 2a | 1.000 | 0 | 0 | 0 |
| F1 | 2a | 1.000 | 0 | 0 | 0 |

The HRTEM image (Figure S6, inset) shows an interplanar distance of 0.317 nm, corresponding to the (110) planes of tetragonal phase NVOPF/rGO. C element is evenly distributed on the surface of the NVOPF/rGO microspheres, indicating that the microspheres are encased in graphene. The presence of C element is also proven by the Raman pattern (Figure S7) and the carbon content is 4.33 wt%.

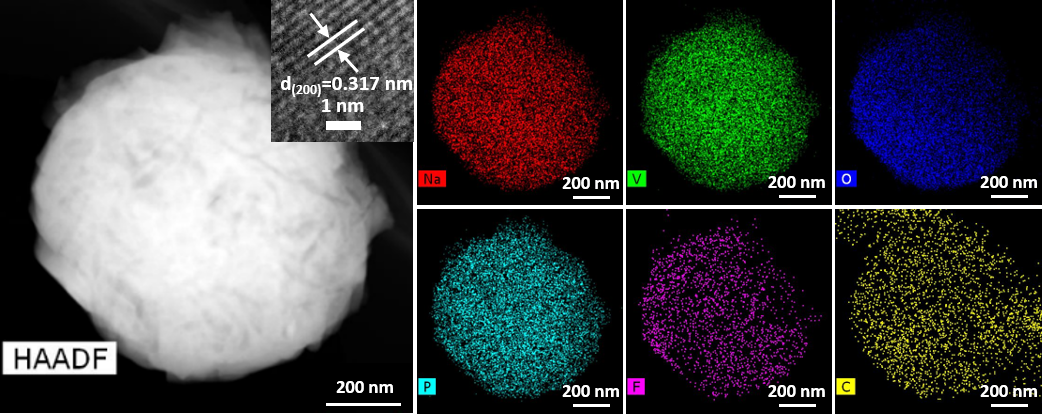


Figure S6. HAADF image with corresponding elemental maps of NVOPF/rGO and the inset is HRTEM image.

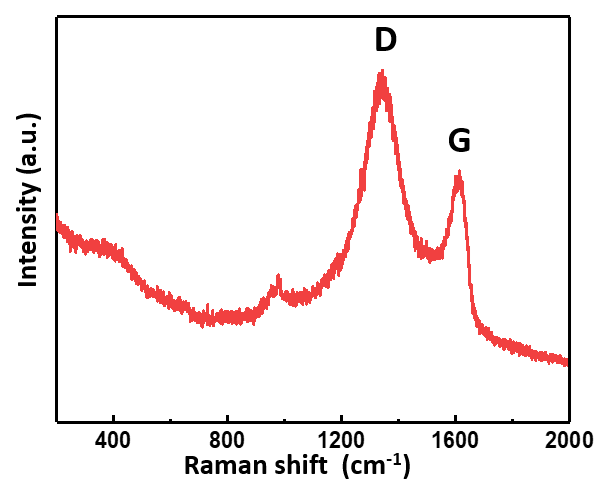


Figure S7. Raman spectrum of NVOPF/rGO.

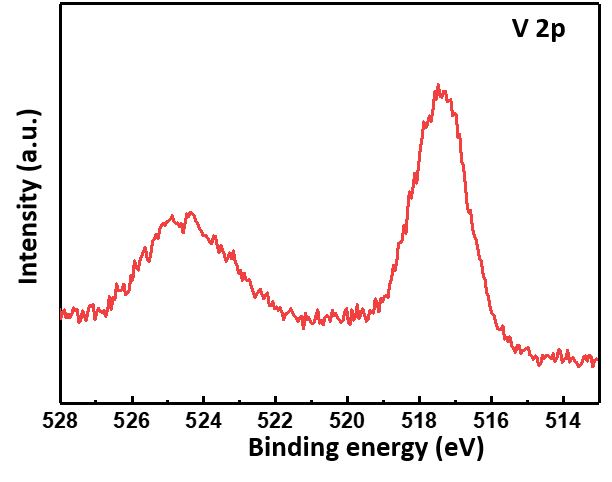


Figure S8. XPS spectrum of NVOPF/rGO.

Table S2. Rietveld refinement atomic coordinates for NaV2O2(PO4)2F/rGO.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Atom | Site | Occupancy | x | y | z |
| Na1 | 8h | 0.256 | 0.2974 | 0.2974 | 0 |
| V | 4e | 1.000 | 0 | 0 | 0.1926 |
| P | 4d | 1.000 | 0 | 0.5000 | 0.2500 |
| O1 | 16n | 1.000 | 0 | 0.3085 | 0.1628 |
| O2 | 4e | 1.000 | 0 | 0 | 0.3460 |
| F1 | 2a | 1.000 | 0 | 0 | 0 |
| F1 | 2a | 1.000 | 0 | 0 | 0 |

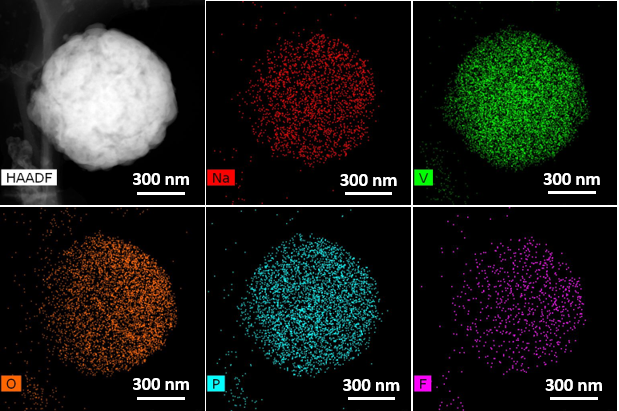


Figure S9. HAADF image with corresponding elemental maps of NaV2O2(PO4)2F/rGO.

Figure S10 (left) presents the GITT curves including discharge and charge processes at a current density of 0.02 A g-1. NaV2O2(PO4)2F/rGO delivers a discharge capacity of 118.3 mAh g-1 and two discharge plateaus. The Mg2+ diffusion coefficient (DGITT) can be calculated according to the GITT curves by the following equation:[3]

(1)

where the DGITT (cm2 s-1) is Mg2+ diffusion coefficient, mB, MB, VM, and τ are the mass, molar mass, molar volume of NaV2O2(PO4)2F/rGO and constant current pulse time, respectively, *S* is electrode–electrolyte contact area. In Figure S10 (right), the ΔEt refers to the voltage changes during a constant current pulse without the IR drop and the ΔEs is the potential difference during the open circuit period.

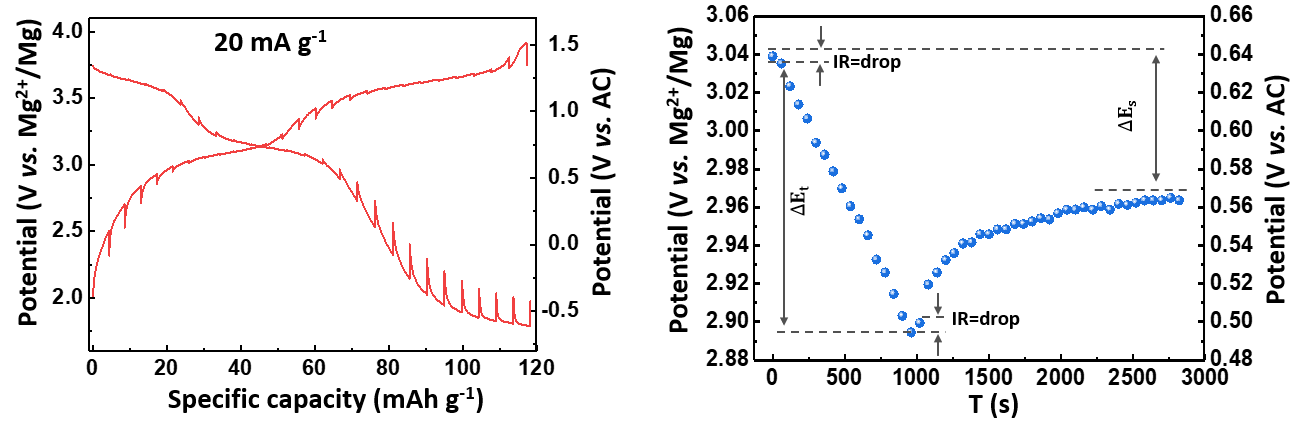


Figure S10. GITT curve of NaV2O2(PO4)2F/rGO electrode (left) and GITT potential response curve with time (right). The test was carried out at constant current pulse of 20 mA g-1 for 15 min and a relaxation period of 30 min.

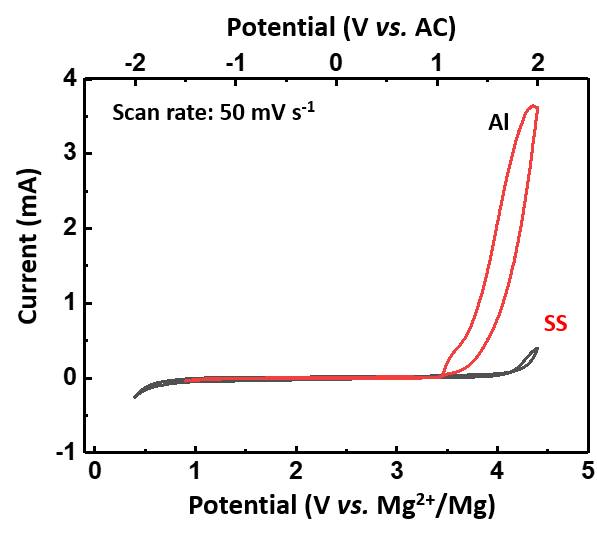


Figure S11. CV curves of stainless steel (SS) and aluminum (Al) was used as a working electrode at Mg(TFSI)2/AN electrolyte with a scan rate 50 mV s-1.

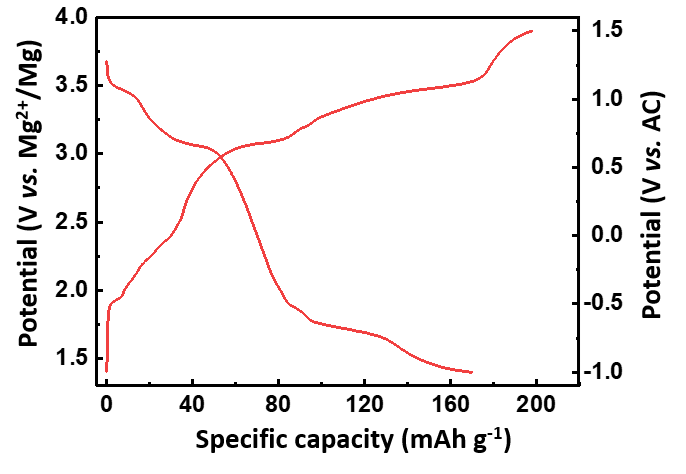


Figure S12. GCD curve of the NaV2O2(PO4)2F/rGO electrode by using three electrodes system cell.

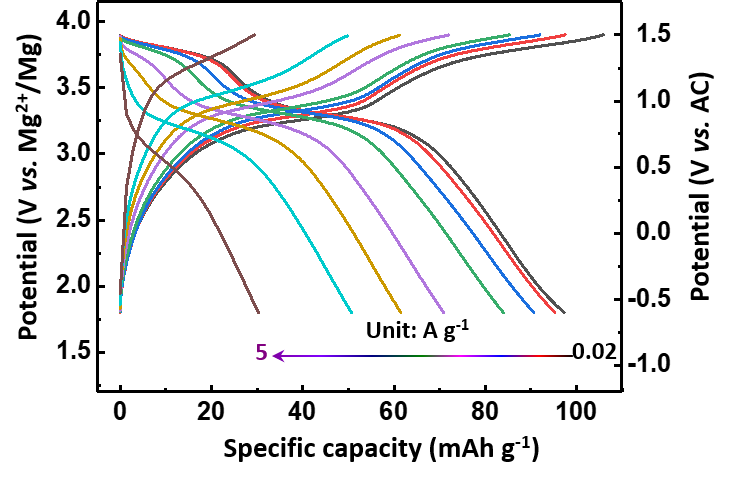


Figure S13. GCD curves of the NaV2O2(PO4)2F/rGO electrode at different current densities.

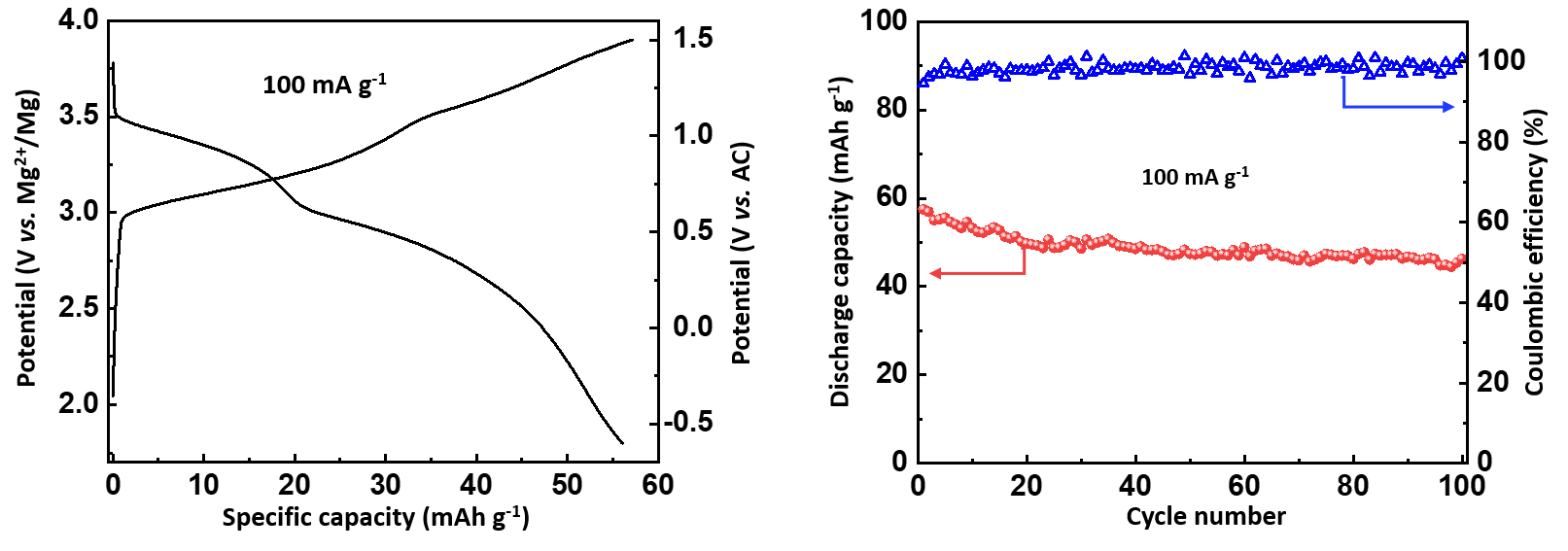


Figure S14. GCD curve (left) and cycling performances (right) of NaV2O2(PO4)2F electrode at 100 mA g-1.

Table S3. Summary of the reported cathode materials with voltages exceeding 2 V for MIBs.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Materials | Voltage *vs.* Mg2+/Mg (V) | Rate (mAh g-1/ mA g-1) | Cycles/ mA g-1 | Capacity retention （%） | Reference |
| NaV2O2(PO4)2F | ~3.3 | 106/20 61.5/1000 30.3/5000 | 280/20 1000/100 9500/500 | 98.7 97.5 76.0 | present study |
| NiHCF | ~3.0 | 52/10 41/100 32/500 | 2000/250 | 65.0 | [4] |
| V2(PO4)3 | ~2.7 | 197/9.85(55 °C) | 5/9.85 | 100.0 | [5] |
| MgCoSiO4 | ~2.7 | 73/6.2 | 30/6.2 | 85.7 | [6] |
| Mn2O4 | ~2.6 | 190/13.5 | 1/13.5 | - | [7] |
| NaV2(PO4)3 | ~2.5 | 88/20 | 100/20 | 81.0% | [8] |
| MgCo2O4 | ~2.3 | 200/5.2(150 °C) 198/13(150 °C) 170/26(150 °C) | 1/5.2 1/13 2/26 | - - 73.5 | [9] |
| V2O5 | ~2.3 | 153/0.5 μA cm-2 | 36/0.5 μA cm-2 | 83.3 | [10] |
| MnO2 | ~2.3 | 140/100 | 20/100 | 66.7 | [11] |
| Mo2.5+yVO9+δ | ~2.1 | 397/2 114/4 114/10 | 15/2 25/4 25/10 | 62.5 100.0 75.0 | [12] |
| Mg0.3V2O5.1.1H2O | ~2.1 | 162/100 120/1000 50/4000 | 500/100 3000/500 10000/2000 | 100.0 100.0 80.0 | [13] |
| NH4V4O10 | ~2.1 | 175/42 108/211 68.9/421.2 | 100/211 | 100.0 | [14] |
| V2O5.1.42H2O | ~2.1 | 320/50 150/500 100/2000 | 30/100 200/1000 | 89.1 81.0 | [15] |

Figure S15 shows the XRD pattern of hexagonal structure of NaTi2(PO4)3 (PDF#33-1296), indicating that the pure phase of the NTP/C is synthesized. The SEM image of the NTP/C shows the microflower morphology of the prepared NTP/C with a size of about 10 um (Figure S16). Figure S17 displays the CV curve of NTP/C electrode within 1~2.4 V *vs.* Mg2+/Mg at a scan rate of 0.1 mV s-1. There is a pair of obvious redox peaks, which is corresponding to the redox of Ti4+/Ti3+.[16, 17]

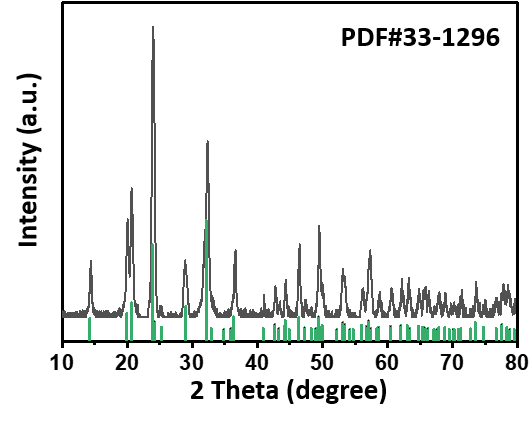


Figure S15. XRD pattern of NTP/C.

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Figure S16. SEM image of NTP/C.

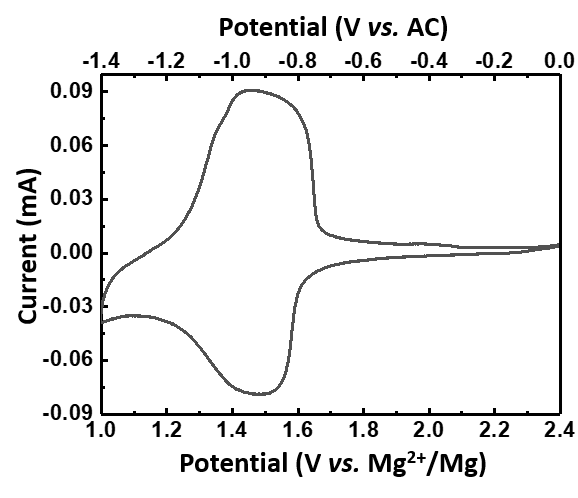


Figure S17. CV curve of NTP/C electrode within 1~2.4 V *vs.* Mg2+/Mg at a scan rate of 0.1 mV s-1.

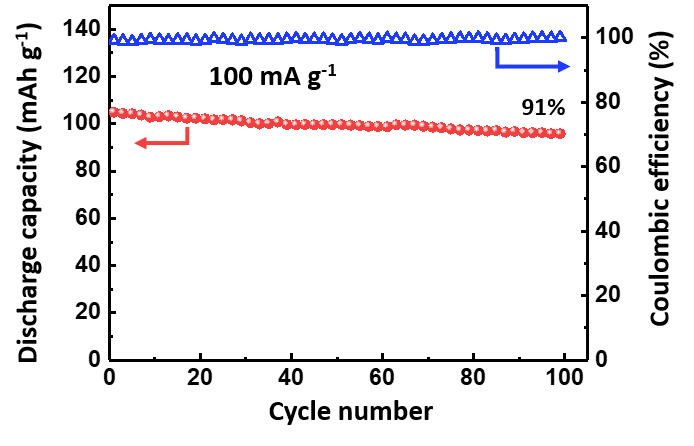


Figure S18. Cycling performances of NTP/C electrode at 100 mA g-1.

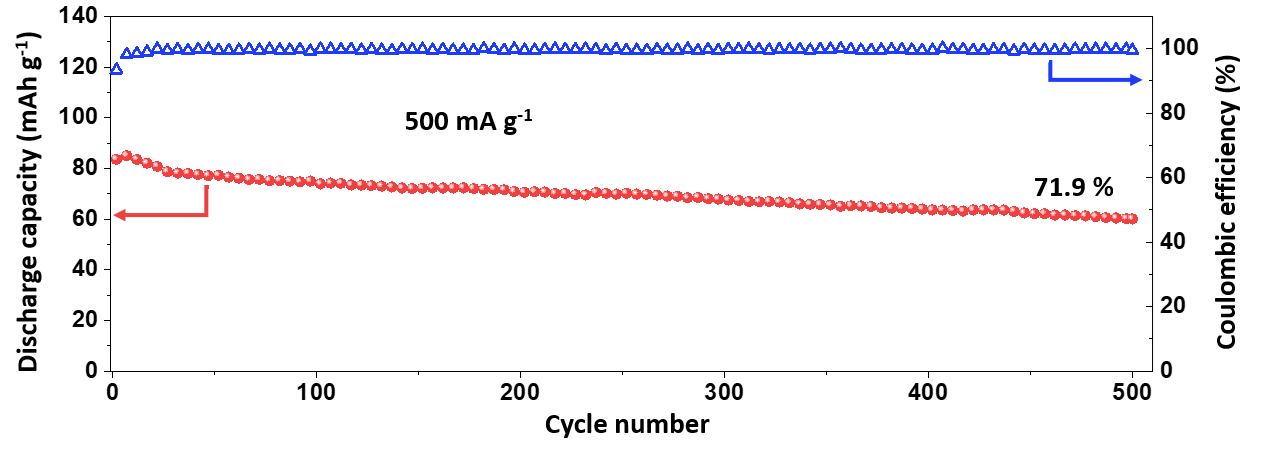


Figure S19. Cycling performances of NTP/C electrode at 500 mA g-1.

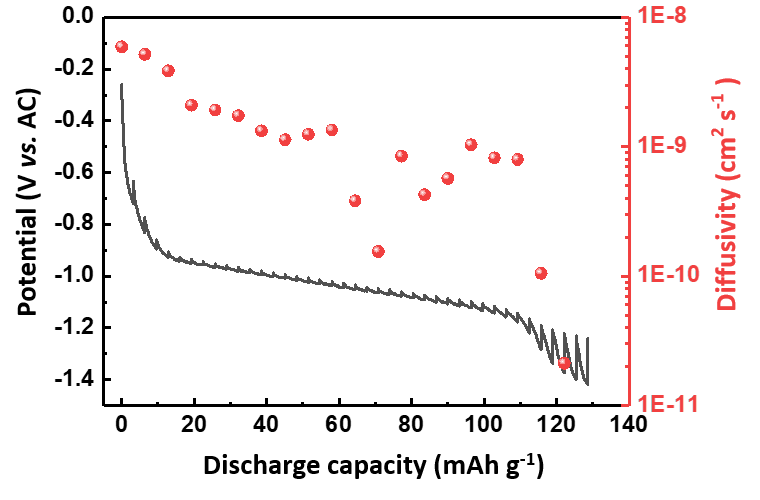


Figure S20. GITT curve of NTP/C electrode and diffusivity versus state of discharge.

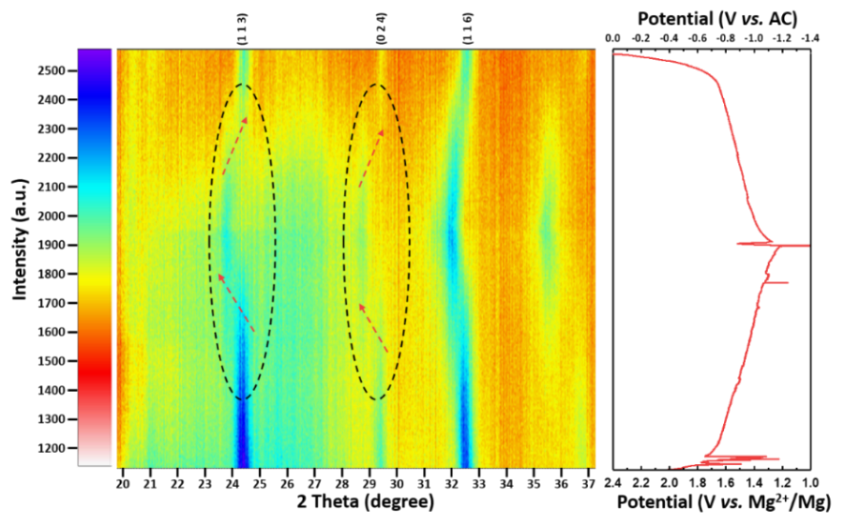


Figure S21. *In situ* XRD patterns and the corresponding charge/discharge curves of NTP/C electrode. The unsmooth charge-discharge curve may be due to the poor sealing and conductivity of the *in situ* mold cell.

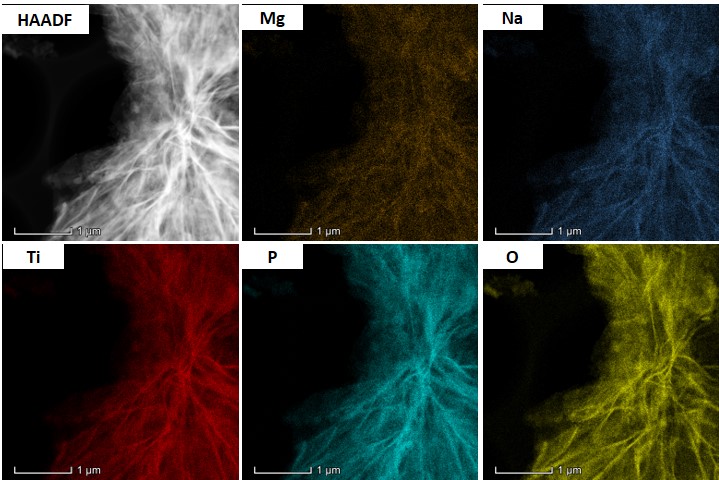


Figure S22. The HAADF image of discharged NTP/C and corresponding elemental maps

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Figure S23. Discharge curves and cycling performances of NaV2O2(PO4)2F/rGO electrode at Mg-HMDS based electrolyte.

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Figure S24. SEM images of NaV2O2(PO4)2F/rGO after 280 cycles.

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Figure S25. *Ex situ* XRD patterns for different states.



Figure S26. Rietveld refinement and crystal structure of discharged NaV2O2(PO4)2F/rGO.

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Figure S27.Distribution of Mg2+ in NaV2O2(PO4)2F/rGO crystal structure for 1.8 V.

Table S4. Rietveld refinement atomic coordinates for discharged NaV2O2(PO4)2F/rGO.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Atom | Site | Occupancy | x | y | z |
| Na1 | 8h | 0.268 | 0.2697 | 0.2697 | 0 |
| Mg1 | 8h | 0.144 | 0.2697 | 0.2697 | 0 |
| Mg2 | 8j | 0.170 | 0.2901 | 0.5000 | 0 |
| V | 4e | 1.000 | 0 | 0 | 0.1997 |
| P | 4d | 1.000 | 0 | 0.5000 | 0.2500 |
| O1 | 16n | 1.000 | 0 | 0.3222 | 0.1666 |
| O2 | 4e | 1.000 | 0 | 0 | 0.3192 |
| F1 | 2a | 1.000 | 0 | 0 | 0 |
| F1 | 2a | 1.000 | 0 | 0 | 0 |

To reveal the variation of vanadium oxidation state and magnesium in NaV2O2(PO4)2F/rGO at 1.8 V and 3.9 V, *ex situ* XPS patterns of Mg 1s and V 2p were collected as shown in Figure S28. The peak of Mg 1s at 1.8 V is apparent, and the peak of Mg 1s at 3.9 V almost disappear. The results of *ex situ* XPS indicate that the insertion and extraction of Mg2+ ions occur during discharge and charging. Compared to the raw NaV2O2(PO4)2F/rGO, the binding energy of V 2p at 1.8 V is significantly shifted to low energy, which indicates that the average valence state of vanadium decreases when Mg2+ ions are inserted into NaV2O2(PO4)2F/rGO. Conversely, the binding energy of V 2p at 3.9 V shifts to high energy, proving that the average valence state of vanadium increases when Mg2+ ions are removed from NaV2O2(PO4)2F/rGO.

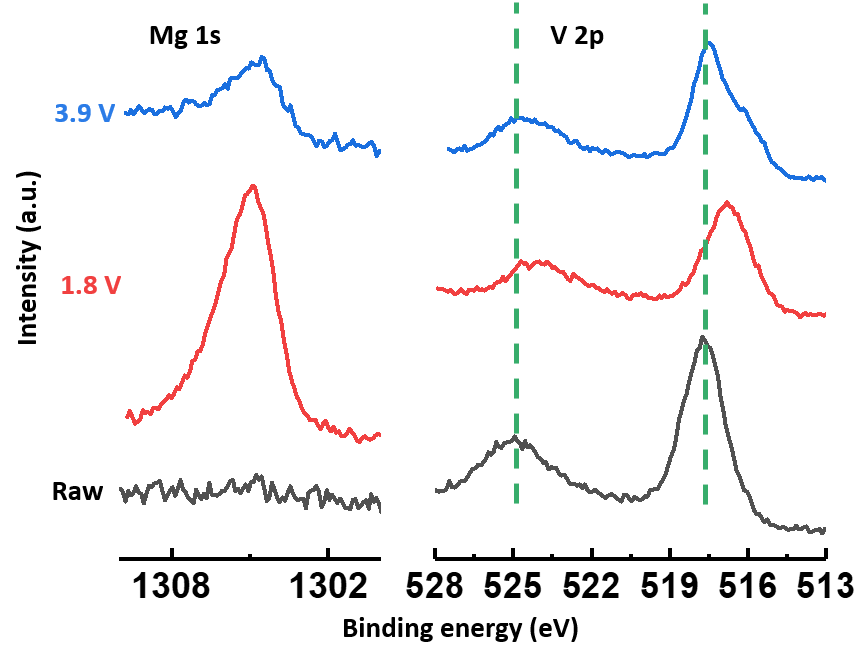


Figure S28. *Ex situ* XPS spectra of Mg 1s and V 2p of NaV2O2(PO4)2F/rGO in different states.

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Figure S29. HAADF image with corresponding elemental maps of NaV2O2(PO4)2F/rGO at 1.8 V.

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Figure S30.EDX spectrum for Area #1 in Figure S29 and percentage of atoms for corresponding elements.

Table S5. The ICP results of the NaV2O2(PO4)2F/rGO electrodes at different states.

|  |  |  |  |
| --- | --- | --- | --- |
| State | Elements | Concentration (mg/mL) | Molar ratio  (Mg:Na:V) |
| Blank control | Mg | 0.0129 |  |
| Na | 0.0167 |
| V | 0.0926 |
| Raw | Mg | 0.0791 | 0.0239:1.1021:2 |
| Na | 2.8845 |
| V | 11.6174 |
| 1.8 V | Mg | 1.6939 | 0.6250:1.0886:2 |
| Na | 2.7877 |
| V | 11.3685 |

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