

# **$\beta$ -NaVO<sub>3</sub> as Pseudocapacitive Anode Material for Sodium-Ion batteries**

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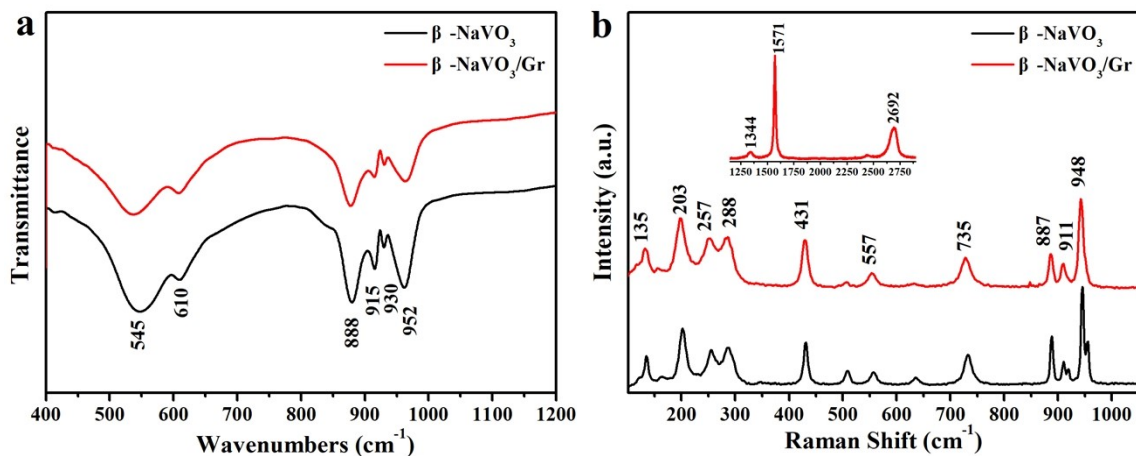
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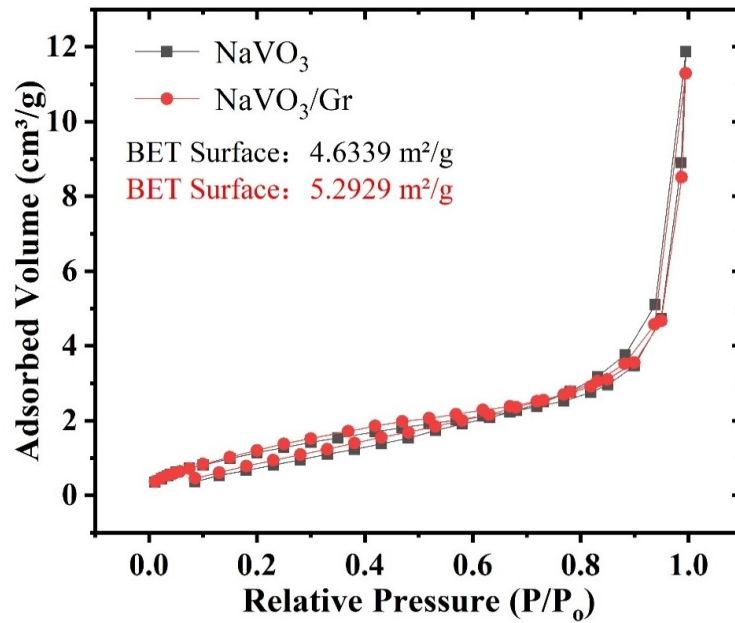
## Figures and Tables



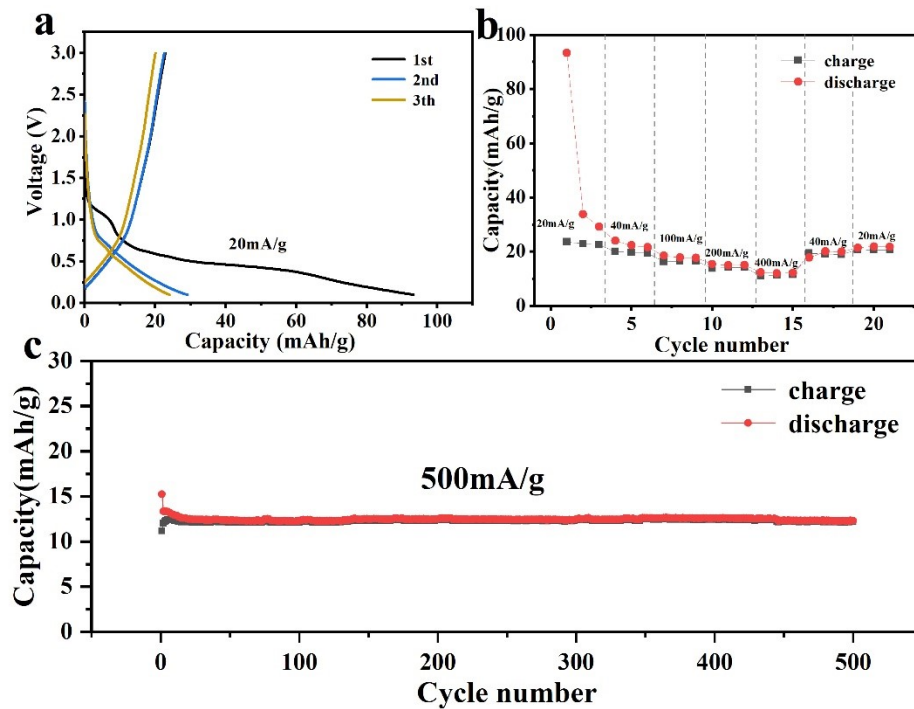
**Figure S1.** Infrared spectra (a) and Raman spectra (b) of  $\beta$ -NaVO<sub>3</sub> and  $\beta$ -NaVO<sub>3</sub>/Gr.

The Infrared spectra of  $\beta$ -NaVO<sub>3</sub> and  $\beta$ -NaVO<sub>3</sub>/Gr powder showed absorption bands at 545, 610, 888, 915, 930 and 952 cm<sup>-1</sup>, which are consistent with the previous report [1].

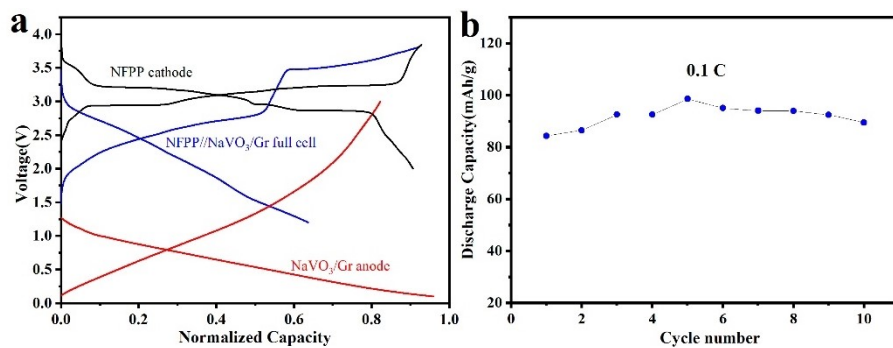
To be rigorous, electrodes for *ex-situ* Raman are different from electrodes tested in *ex-situ* XRD. As seen in **Fig. S1b**, Raman spectra of the two samples have similar peaks, and they are consistent with spectra detected by other investigators at room temperature and ambient pressure, which prove the as-prepared samples are NaVO<sub>3</sub> with orthorhombic structure [1, 2].



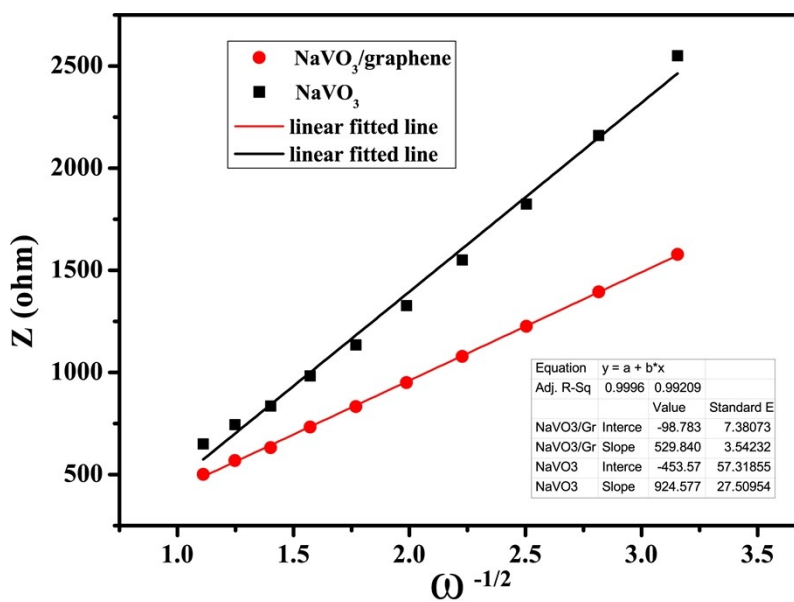
**Figure S2.** The  $N_2$  adsorption-desorption isotherms (BET) of  $\beta$ - $NaVO_3$  and  $\beta$ - $NaVO_3/Gr$ .



**Figure S3.** (a) Charge-discharge curves of graphene, (b) Rate performance of graphene, (c) Cycle performance of graphene.



**Figure S4.** Typical charge/discharge profiles of the full cell ( $\beta$ -NaVO<sub>3</sub>/Gr/NFPP) and the corresponding NFPP cathode and  $\beta$ -NaVO<sub>3</sub>/Gr anode in half cell (a), Cycle performance of the full cell at 0.1C (b).



**Figure S5.** Linear fitting of  $Z'$  vs  $\omega^{-1/2}$  relationship.

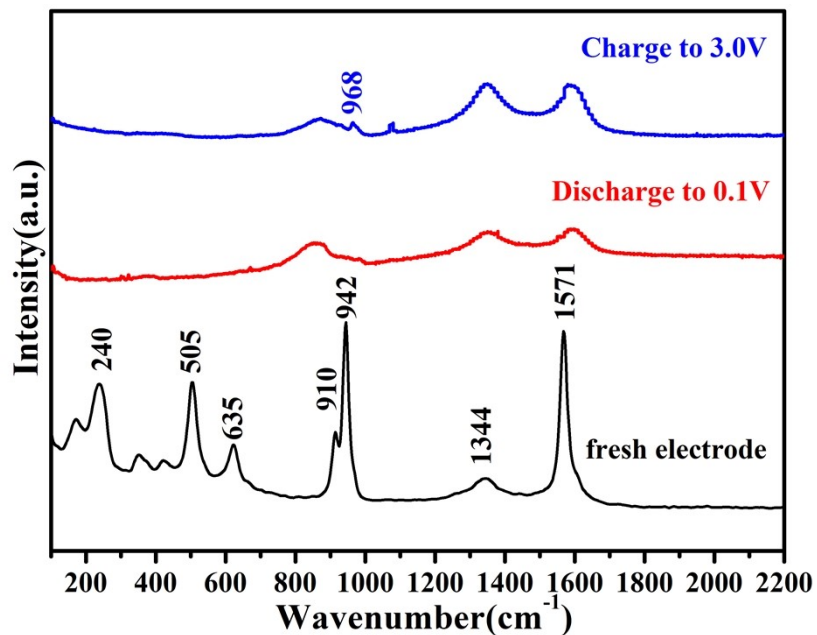
$D_{Na}$  in  $\beta$ -NaVO<sub>3</sub> and  $\beta$ -NaVO<sub>3</sub>/Gr can be calculated from the sloping line in Nyquist plots by

$$D_{Na} = \frac{R^2 T^2}{2A^2 C^2 F^4 \sigma^2 n^4} \quad (1)$$

where  $T$  is the absolute temperature,  $R$  the gas constant,  $A$  the surface area (0.625

cm<sup>2</sup>),  $C$  the concentration of sodium ions in the active material ( $2.4 \times 10^{-2}$  mol cm<sup>-3</sup>),  $F$  the Faraday's constant,  $n$  the number of electrodes associated with the reaction, and  $\sigma$  the Warburg factor that is the slope of the lines in Fig.S4. The calculated  $D_{\text{Na}}$  is  $1.8 \times 10^{-16}$  cm<sup>2</sup> s<sup>-1</sup> for  $\beta$ -NaVO<sub>3</sub>, and  $5.99 \times 10^{-16}$  cm<sup>2</sup> s<sup>-1</sup> for  $\beta$ -NaVO<sub>3</sub>/Gr. The  $D_{\text{Na}}$  in  $\beta$ -NaVO<sub>3</sub>/Gr is higher than that in  $\beta$ -NaVO<sub>3</sub>.

Additionally,  $D_{\text{Na}}$ s calculated from GITT are much higher than those obtained from EIS. This difference probably originates from the different signal-collection patterns of GITT and EIS. In GITT measurements, a short current pulse with enough relaxation time (100 mins) is applied to eliminate parasitic background current contribution, resulting in a more accurate measurement. In contrast, high-frequency data collection for the EIS measurement could cause polarization in the sample, resulting in sluggish ion diffusion. Similar phenomena have been observed in materials with low conductivity.



**Figure S6.** *Ex-situ* Raman spectra of  $\beta$ -NaVO<sub>3</sub>/Gr electrodes at different states

The peaks located in the region of 100-700 cm<sup>-1</sup> can be assigned to the vibration of the VO<sub>5</sub> group, which are strongly related to double chain structure<sup>[1, 2]</sup>. The inconspicuous peak located at 859 cm<sup>-1</sup> is the fluorescence signal of Na<sub>3</sub>VO<sub>4</sub>. Furthermore, a weak peak located at 968 cm<sup>-1</sup> in the spectrum of electrode charged to 3.0 V can be assigned to V=O1(apex oxygen) stretching mode in Na<sub>x</sub>V<sub>2</sub>O<sub>5</sub><sup>[3]</sup>.

**Table S1. Atomic percentage variation of electrodes before and after cycling**

Element	Before cycling (Atomic percentage%)	After cycling (Atomic percentage%)
Na in $\beta$ -NaVO <sub>3</sub>	17.16	25.12
Na in $\beta$ -NaVO <sub>3</sub> /Gr	16.77	26.29
V in $\beta$ -NaVO <sub>3</sub>	21.12	11.97
V in $\beta$ -NaVO <sub>3</sub> /Gr	18.91	19.95

## References

1. S. Seetharaman, H. L. Bhat, P. S. Narayanan, Raman Spectroscopic Studies on Sodium Metavanadate, *Journal of Raman Spectroscopy* 14 (1983) 401-405.
2. M. H. Kuok, S. H. Tang, Z. X. Shen, C. W. Ong, Raman spectroscopic studies of  $\alpha$ -NaVO<sub>3</sub>,  $\beta$ -NaVO<sub>3</sub> and NaVO<sub>3</sub>·2H<sub>2</sub>O, *Journal of Raman Spectroscopy* 26 (1995) 301-30650.
3. I. Loa, K. Syassen, R. K. Kremer, Vibrational properties of NaV<sub>2</sub>O<sub>5</sub> under high pressure studied by Raman spectroscopy, *Solid State Communications* 112 (1999) 681-685.