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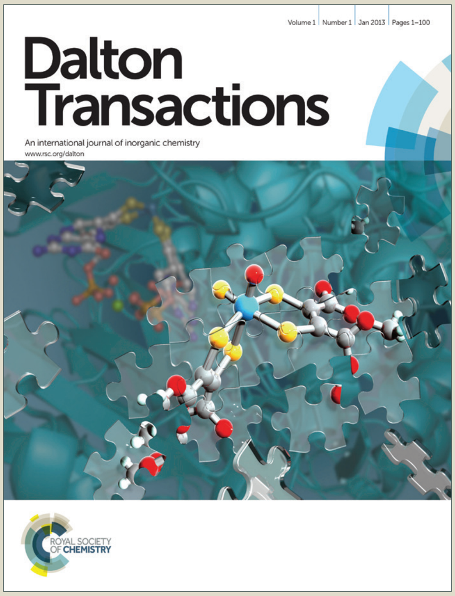

ROYAL SOCIETY OF CHEMISTRY

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Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Facile synthesis of graphite nitrate-like ammonium vanadium bronzes and their graphene composites for sodium-ion battery cathodes

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Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

A simple and versatile method for preparation of new crystalline graphite nitrate-like ammonium vanadium bronze $(NH_4)_{0.19}V_2O_5\cdot 0.44H_2O$ nano-microstructures is developed via a simple hydrothermal route following heat treatment. $(NH_4)_{0.19}V_2O_5\cdot 0.44H_2O$ platelets are tested as a novel high-energy cathode material for sodium-ion batteries. The enhancement of electrochemical performance for $(NH_4)_{0.19}V_2O_5\cdot 0.44H_2O$ platelets electrode is offered in addition of graphene and using graphite nitrate-like ammonium vanadium bronze microflowers. Graphene-based graphite nitrate-like vanadium bronze microflowers composite shows a higher discharge capacity of 208.9 Ahg^{-1} for the second cycle between a 1.5 - 3.4 V voltage limit at a discharge current density of 20 mAg^{-1}. The reversible capacity of 141.5 Ahg^{-1} is remained after 40 cycles.

1. Introduction

Nowadays, there is a remarkable demand for rechargeable batteries with reversible and efficient electrochemical energy storage and conversion in the field of portable electronic consumer devices, electric vehicles, and large-scale electricity storage in smart and intelligent grids [1]. Sodium-ion battery is one of the promising rechargeable batteries for its huge abundant and low cost sodium resources [2]. The current concerns are leading to an increasing interest in low cost, high safety electrode materials for sodium-ion batteries with a long cycle life and high energy-density. Now researchers in growing numbers are coming to pay attention to the electrochemical properties of various electrode materials, for example, a Nasicon-type structured $Na_3V_2(PO_4)_3$ [3], layered Na_2FePO_4F and olivine Na(Fe, Mn) PO_4 [4], $Na_4Mn_9O_{18}$ nanowires [5], $Na_x[Fe_{1/2}Mn_{1/2}]O_2$ [6], Prussian blue analogues [7, 8], amorphous phosphorus-carbon composite [9, 10], WS_2 [11], and organic sodium-ion batteries [12].

Vanadium oxides and bronzes offer the advantages of being cheap, easy to synthesize, plenty of the earth and high-energy density. Therefore, they have attracted many interests in energy conversion and storage [13]. However, few interests were attracted to study vanadium oxide and bronze electrode materials for sodium-ion batteries. Hamani et al. reported the electrochemical properties vs. Na of the layered Na_xVO_2 phases having either octahedral or trigonal prismatic symmetries, which could reversibly insert 0.5 Na atoms per unit formula leading to sustain a reversible capacity of 120 $mAhg^{-1}$ [14]. NaV_6O_{15} nanorods also displayed stable sodium-ion insertion-deinsertion reversibility and delivered 142 $mAhg^{-1}$ sodium ions when they worked at a current density of 0.02 Ag^{-1} [15]. NaV_3O_8 nanowires show a discharge capacity of 169.6 $mAhg^{-1}$ at a low current density [16]. V_6O_{13} has showed high stability, good reversibility and high capacity as a cathode material for sodium-ion batteries, indicating cell feasibility and good cycling efficiency [17, 18]. Recently, a nanoscale ordered bilayered V_2O_5 cathode material was operated at room temperature and it showed the theoretical capacity of 250 $mAhg^{-1}$ for small diffusion length and large surface area tested from a 1.0 V voltage [19]. Double-layer single crystalline V_2O_5 nanobelts also exhibited a high capacity of 231.4 $mAhg^{-1}$. It corresponds to the theoretical capacity to form $Na_2V_2O_5$ on Na-ion insertion [20]. Hollow VOOH microspheres presented a capacity of 150 $mAhg^{-1}$ [21]. However, few people paid full attention to ammonium vanadium oxide cathode materials for lithium-ion and sodium-ion batteries [22-25].

Herein, we firstly report the synthesis of new crystalline graphite nitrate-like ammonium vanadium bronze via a simple hydrothermal method requiring low cost manufacturing and ultra-low power consumption. Graphite nitrate-like ammonium vanadium bronze was prepared with controlled phase structure and morphology. When they were used as cathode materials for sodium-ion batteries, graphene based graphite nitrate-like ammonium vanadium bronze composites showed better cycling stability and higher discharge capacity.

2. Experimental

Graphite nitrate-like ammonium vanadium bronze square platelets were prepared according to the following procedure. 0.16 g oxalic acid and 0.2 g ammonium metavanadate (NH_4VO_3) were dissolved in 30 ml deionized water under stirring at room temperature for 2 hours. After that, the mixture was transferred to a 50-ml Teflon-lined stainless autoclave, sealed, kept at 200 ^OC for 24 hours, cooled to room temperature, washed with deionized water and dried at 200 ^OC for 5 days (Marked with Sample v1-g0). Under the same procedure, graphite nitrate-like ammonium vanadium bronze platelets were prepared with 1.28 g oxalic acid, 0.59 g ammonium metavanadate (NH_4VO_3) and 0.4 g ammonium nitrate (Marked with Sample v2-g0). Their composites based on graphene were prepared with an addition of 3 mg graphene under identical conditions (The two samples are marked with Sample v1-g3 and v2-g3, respectively.).

The morphological characteristics of the as-synthesized materials were observed with a Hitachi S-4800 field emission scanning electron microscope (SEM). Transmission electron microscopy (TEM) was carried out on a FEI Tecnai G20 electron microscopy instrument. X-ray diffraction (XRD) patterns were recorded on a diffractometer (Co Kα, PANalytical, and X'Pert). XPS measurements were performed with a Kratos Axis Ultra DLD spectrometer employing a monochromated Al-Kα X-ray source (hυ = 1486.6 eV). A pass energy of 160 eV was used for recording the survey spectrum, while 40 eV pass energy was used for high-resolution measurements. A Vario EL elemental analyzer from German Elementar Analysen Systeme GmbH and Optima 8000 ICP-OES from American Perkin-Elmer were used for elemental analysis of nitrogen, carbon and vanadium, respectively. Thermal analysis measurements were performed with an American Perkin-Elmer TGA7 analyzer. Raman spectra were recorded at room temperature using a Micro-Raman spectrometer from English renishawn. An Nd: YAG laser (532 nm) was used as the excitation source. A Land CT2001A battery tester was used to measure the electrode activities at room temperature.

The graphite nitrate-like ammonium vanadium bronzes and their composites based on graphene were tested as cathode materials for sodium-ion batteries. The composite of positive electrode material was consisted of the active material, a conductive material (super-pure carbon) and binder polyvinylidene difluoride (PVDF) in a weight ratio of 7/2/1. The Na metal was used as the counter electrode. The electrolyte was 1 M $NaClO_4$ dissolved in propylene carbonate (PC) solvent. The cells were charged and discharged between a 1.5 - 3.4 V voltage limit at a current density of 20 mAg^{-1}. A 1 M $NaClO_4$ dissolved in PC solvent with an addition of 5% weight fluoroethylene carbonate (FEC) was also used as an electrolyte for sodium-ion batteries.

3. Results and discussion

Ammonium vanadium bronzes and their composites based on graphene were prepared by a two-step method, as described in Experimental section. The reaction conditions of the products are summarized in Table 1. X-ray diffraction was performed to identify the crystalline structure of samples prepared without NH_4NO_3 at 200 ^OC for 5 days in Fig. 1a (Sample v1-g0), which has the same crystalline structure as graphite nitrate (JCPDS 74-2328, rhombohedral, space group: R-3m, space group number: 166). It has a strong diffraction peak at 7.90^o with a d-spacing of 11.18 Å. The diffraction peaks of graphene based composite prepared without NH_4NO_3 can also be ascribed to graphite nitrate (JCPDS 74-2328) in Fig. 1b (Sample v1-g3). When NH_4NO_3 was added, the as-synthesized two samples (Sample v2-g0, Sample v2-g3) both can be ascribed to graphite nitrate (JCPDS 74-2328) in Fig. 1c and d, respectively. Therefore, a series of graphite nitrate-like vanadium compounds and their composites based on graphene were firstly prepared by a facile two-step method. It was also reported that hollow fullerene-like V_2O_5 nanoparticles could be prepared via crystallization of lower density amorphous nanoparticles under laser ablation condition [26]. It implies that it is possible to prepare other carbon-like vanadium oxide with proper vanadium precursors under certain conditions.

Table 1 the reaction conditions of ammonium vanadium bronze and their composites based on graphene

Samples and reaction conditions	V1-g0	V1-g3	V2-g0	V2-g3
NH_4VO_3 (g)	0.2	0.2	0.59	0.59
NH_4NO_3 (g)	-	-	0.4	0.4
graphene (mg)	-	3	-	3
oxalic acid (g)	0.16	0.16	1.28	1.28
water (ml)	30	30	30	30
reaction time (h)	24	24	24	24
heat treatments (day)	5	5	5	5

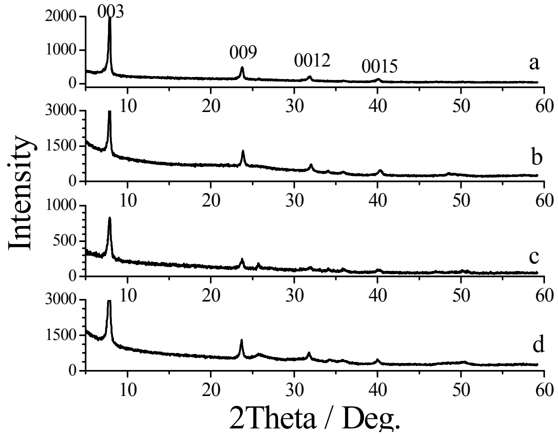

Fig. 1 Wide-angle powder XRD patterns of (a) ammonium vanadium bronze prepared without NH_4NO_3 (Sample V1-g0), (b) graphene based composites with (a), (c) ammonium vanadium bronze prepared with NH_4NO_3 and (d) graphene based composites with (c).

SEM observations show that the as-synthesized sample without an addition of ammonium nitrate is square platelets (Sample v1-g0), as shown in Fig. 2a. The magnified SEM image confirms that the length and width of a square platelet are both around 800 nm in Fig. 2b. As some graphene was added, big blocks were obtained, as shown in Fig. 2c, d (Sample v1-g3). Short brick-like particles were prepared with NH_4NO_3 (sample v2-g0), as shown in Fig. 2e. The magnified SEM image shows that the brick-like particle is about 150 nm thick and 820 nm long (Fig. 2f). The magnified SEM image displays that these blocks were composed of thin platelets in Fig. 2d. Microflower-like particles consisting of superimposed platelets prepared with NH_4NO_3 and graphene are observed and displayed in Fig. 2g (Sample v2-g3). The diameter of microflower-like particles could be up to 18 μm. The thickness of platelets is less than 50 nm as estimated from the magnified SEM image in Fig. 2h. NH_4NO_3 plays a great role in controlling the morphology and crystalline structure of vanadium precursors by affecting nucleation of vanadium precursors. In the absence of NH_4NO_3, an unknown block-like phase would be formed [27], while $NH_4V_4O_{10}$ will be formed with NH_4NO_3 under hydrothermal condition [30].

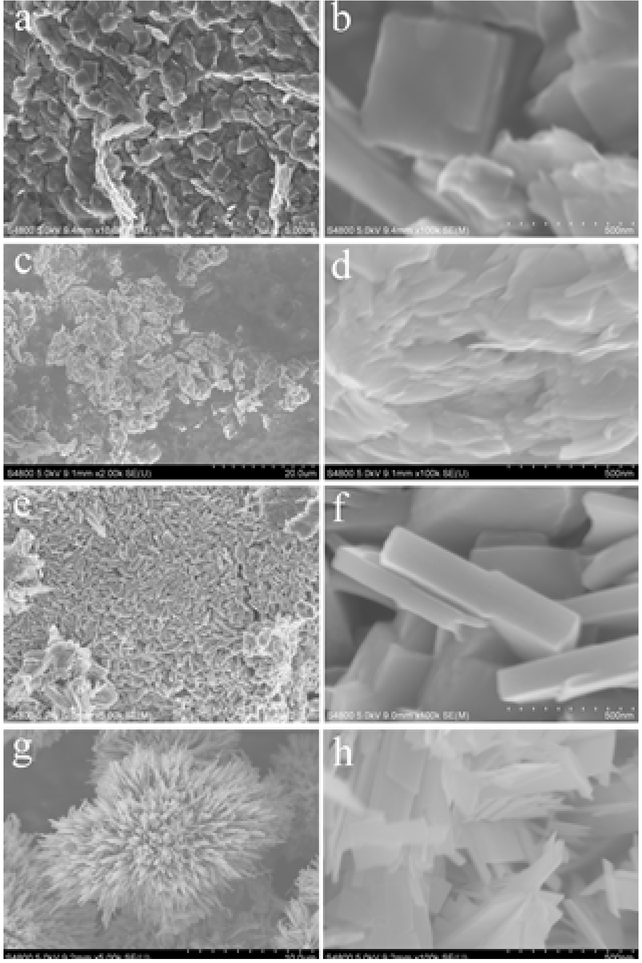

Fig. 2 SEM images of samples after heat treatment prepared without (a, b) or with NH_4NO_3 (e, f), and their corresponding composites based on graphene (c, d) and (g, h), respectively.

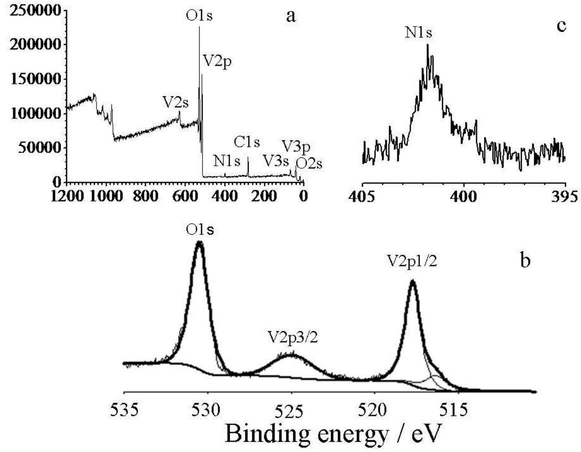

Fig. 3 Wide survey XPS spectrum (a) and high-resolution XPS spectra of graphite nitrate-like ammonium vanadium bronze prepared without NH_4NO_3 (b) O1s, V2p and (c) N1s.

X-ray photoelectron spectroscopy (XPS) was performed to identify the elemental composition of Sample v1-g0. Wide survey XPS spectrum shows that the surface of ammonium vanadium bronze is composed of N, V and O in Fig. 3a. The XPS spectrum of the V2p3/2 peak is composed of two peaks at 517.7 and 516.6 eV, corresponding to V (V) and V (Ⅳ) in Fig. 3b, respectively [24]. The average oxidation number of V is +4.9 calculated from X-ray photoelectron spectroscopy (XPS) data by their peak area ratios. Fig. 3c shows that the binding energy of N1s is at 401.4 eV, which is ascribed to NH_4^+ [28]. TG curves (Fig. 4) show that there is a weight loss of 4.8% from 200 to 440 ^{o}C, due to the release of NH_3. Element analysis (EA) and inductively coupled plasma spectroscopy (ICP) were performed to analyze the content of N and V, respectively. The results show the weight content of N is 1.17%, while 44.5% for V. Based on the above analysis, the formula of graphite nitrate-like ammonium vanadium bronze (Sample v1-g0) can be expressed as $(NH_4)_{0.19}V_2O_5 \bullet 0.44H_2O$.

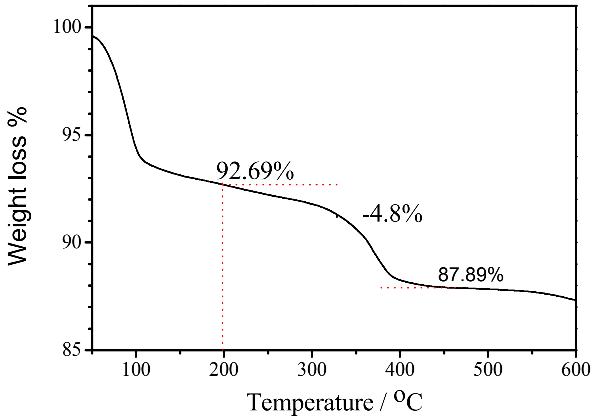

Fig. 4 TG curve of graphite nitrate-like ammonium vanadium bronze prepared without NH_4NO_3 (Sample V1-g0).

Raman spectra of graphene based graphite nitrate-like ammonium vanadium bronze composite (Sample v1-g3 and v2-g3) exhibits a series of bands at 142, 194, 281, 405, 520, 689, 990, 1351 and 1589 cm^{-1} same to those of V_2O_5 in Fig. 5a and b, respectively. The peak at 990 cm^{-1} is characteristic of the V=O bond, implying that there is a V_2O_5 unit in the formula of ammonium vanadium bronze. The band at 1351 cm^{-1} is called the D band [28], which is a disorder induced band [29]. The band at 1589 cm^{-1} is ascribed to the G band due to the symmetry of the hexagonal lattice, which allows only one first order Raman band for graphene [29]. Therefore, Raman spectra show that there are at least two kinds of carbon (disorder carbon and graphene) in the two graphene based composites (Sample v1-g3 and v2-g3). Element analysis (EA) was used to analyze the content of graphene. There is 2.006% graphene for Sample v1-g3, while 1.466 % graphene for Sample v2-g3. Transmission electron microscopy (TEM) was further performed to study graphene based composites. Square platelet-like particles were observed and displayed in Fig. 6a (Sample v1-g3). The magnified TEM image shows that there is a thin grey graphene platelet on the surface of graphite nitrate-like ammonium vanadium bronze platelets in Fig. 6b. For Sample v2-g3, TEM image shows that there are many thin graphene platelets around the black graphite nitrate-like ammonium vanadium bronze particles in Fig. 6c. The magnified TEM image shows that much graphene was dispersed on the surface of graphite nitrate-like particles in Fig. 6d. There is also some isolated graphene.

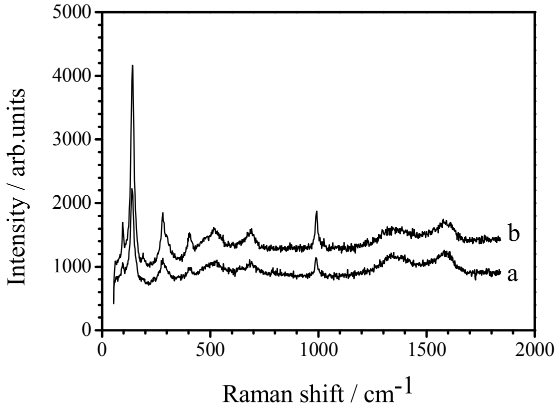

Fig. 5 Raman spectra of graphite nitrate-like ammonium vanadium bronze based graphene composites (a) prepared without NH_4NO_3 (Sample V1-g3) and (b) with NH_4NO_3 (Sample V2-g3).

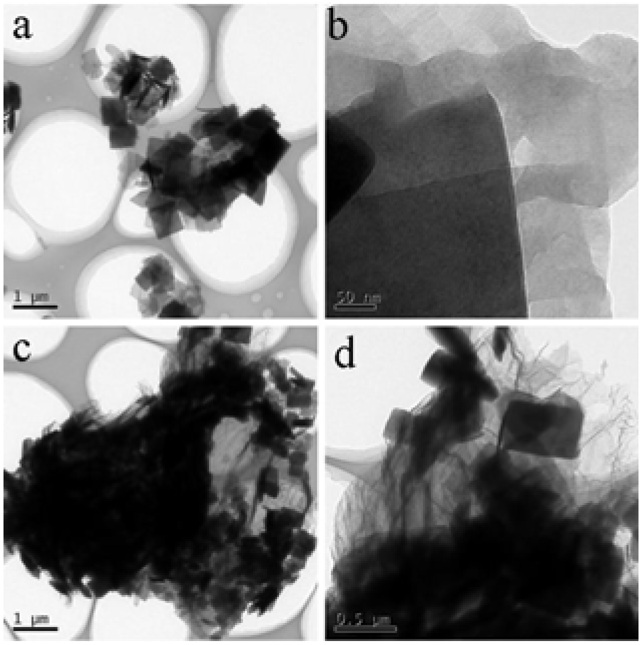

Fig. 6 TEM images of ammonium vanadium bronze based graphene composites prepared without NH_4NO_3 (a, b) (Sample V1-g3) and with NH_4NO_3 (c, d) (Sample V2-g3).

The electrochemical performance of graphite-like nitrate ammonium vanadium bronze platelets (Sample V1-g0) and its graphene composite (Sample V1-g3) were evaluated with an electrolyte of 1 M $NaClO_4$ dissolved in PC solvent. Fig. 7a and b show the first and second charge-discharge profiles of Sample V1-g0 and Sample V1-g3 between 1.5 and 3.4 V at a current density of 20 mAg^{-1}. It can be observed that Fig. 7a has steeper charge-discharge profiles than Fig. 7b. When 5% FEC was added to the electrolyte, the similar charge-discharge profiles were obtained for Sample V1-g3 in Fig.7c. The similar first and second charge-discharge profiles of Sample V2-g0 and its composite based on graphene (Sample V2-g3) were also obtained with an electrolyte of 1 M $NaClO_4$ dissolved in PC solvent in Fig. 7d and e, respectively. Graphene based ammonium vanadium bronze (Sample V2-g3) composite also has similar charge-discharge profiles with an addition of FEC in Fig. 7f. But the discharge capacity of the graphene based graphite nitrate-like microflower composite (Sample V2-g3) is dramatically raised with or without an addition of FEC. It can be found that graphene based graphite nitrate-like ammonium vanadium bronze microflower composite is a kind of cathode materials with a high discharge capacity for Na-ion batteries.

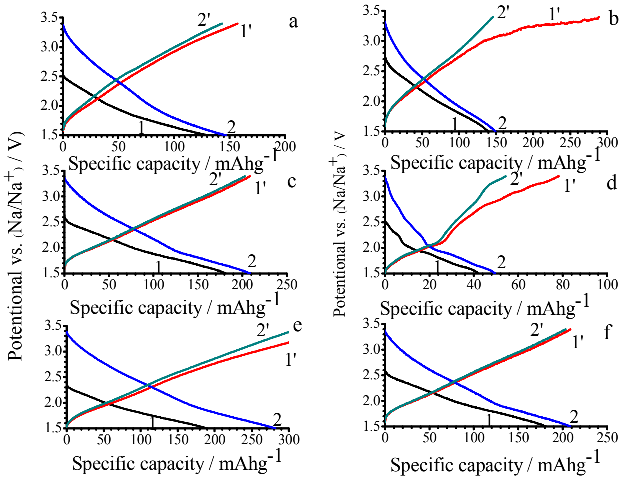

Fig. 7 The first and second charge-discharge profiles of (a) ammonium vanadium bronze (Sample V1-g0) , (b) graphene based composite without an addition of FEC (Sample V1-g3) and (c) with an addition of FEC (Sample V1-g3), (d) ammonium vanadium bronze (Sample V2-g0), (e) graphene based composite without an addition of FEC (Sample V2-g3) and (f) with an addition of FEC (Sample V2-g3).

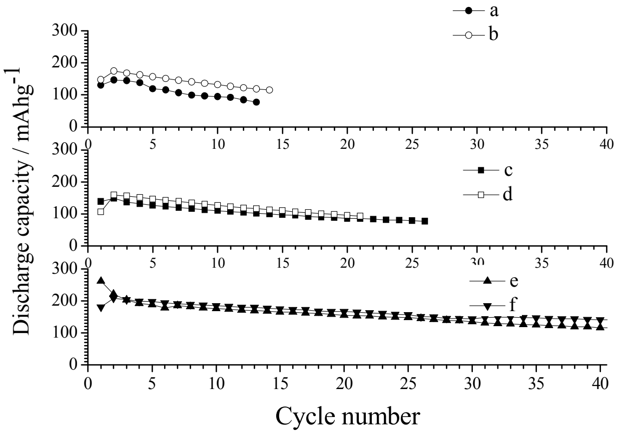

Fig. 8 The cycling performance of ammonium vanadium bronzes (a) Sample V1-g0 and (b) Sample V2-g0, the graphene based ammonium vanadium bronze composites without an addition of FEC (c) Sample V1-g3 and (d) Sample V2-g3 and with an addition of FEC (e) Sample V1-g3 and (f) Sample V2-g3.

Fig. 8 shows the cycling performance of ammonium vanadium bronzes and their composites based on graphene at a current density of 20 mAg^{-1} evacuated with two kinds of electrolytes. The graphite nitrate-like ammonium vanadium bronze microflowers electrode without an addition of FEC shows an enhanced cycling performance compared to graphite nitrate-like ammonium vanadium bronze platelets, as shown in Fig. 8a and b, respectively. The microflower-like graphite nitrate electrode delivers an initial discharge capacity of 147.5 mAhg^{-1}. A reversible capacity of 114.7 mAhg^{-1} is remained after 14 cycles. The better cycling performance is most likely that microflower microstructures may reduce solid state interface layer resistance, which will favor fast Li-ion transfer rate [31]. For graphene based ammonium vanadium bronze composites (Sample V1-g3 and V2-g3), the cycling numbers are increased. Sample V1-g3 and V2-g3 both show similar cycling performance in Fig. 8c and d, respectively. FEC was further added to the electrolyte of 1 M $NaClO_4$ dissolved in PC solvent for cycling test for Sample V1-g3 and V2-g3 electrodes in Fig. 8e and f. The discharge capacity and cycling performance were improved dramatically. Sample V1-g3 and V2-g3 electrode delivers a discharge capacity of 220.8 and 208.9 mAhg^{-1} for the second cycle. A reversible capacity of 116.6 and 141.5 mAhg^{-1} is remained after 40 cycles. The order of electrochemical performance is as follows: Sample V2-g3 > Sample V1-g3 > Sample V2-g0 > Sample V1-g0. The effects of FEC additives may be attributed to the improvement of the Na-ion insertion and extraction rate [30].

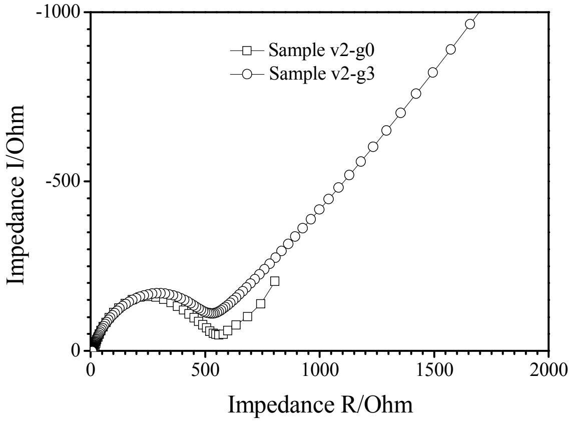

Fig. 9 Nyquist-diagram of samples after heat treatment prepared with NH_4NO_3 (□), and its graphene composite (○) after discharging and charging for 1 cycle.

The electrochemical impedance measurements were performed to elucidate the difference in electrochemical properties of ammonium vanadium bronze prepared with NH_4NO_3 (□), and its composites based on graphene (○) in Fig. 9. It can be found that graphene based composite has smaller total impedance, which may be attributed to improve the electrochemistry performance.

4. Conclusions

Graphite nitrate-like ammonium vanadium bronzes $(NH_4)_{0.19}V_2O_5 \cdot 0.44H_2O$) platelets, micro-flowers and their composites based on graphene were prepared with cheap reagents at a large scale via a facile template-free method. The enhancement of electrochemical performance for $(NH_4)_{0.19}V_2O_5 \cdot 0.44H_2O$ platelets is offered in addition of graphene, FEC to the electrolyte and using graphite nitrate-like ammonium vanadium bronze microflowers as cathode materials, which may be attributed to the improvement of electrode electrical conductivity, the reaction kinetics and Na-ion transfer rate. This facile two-step method is significant to fabricate other novel crystalline ammonium vanadium bronzes.

Acknowledgments

The project was supported by the National Natural Science Foundation of China (Grant No. 51204058) and the fund (JA12037).

Notes and references

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Novel graphite nitrate-like ammonium vanadium bronze cathode material for sodium-ion batteries delivers high capacity.