

Hydrothermal ammoniated treatment of PAN-graphite felt for vanadium redox flow battery

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Received: 3 January 2011 / Revised: 12 March 2011 / Accepted: 16 March 2011 / Published online: 20 April 2011
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Abstract A novel method of hydrothermal ammoniated treatment on the polyacrylonitrile (PAN)-based graphite felt for vanadium redox flow battery was developed. The graphite felt was treated in a Teflon-lined stainless steel autoclave for different time at 180 °C. The content of nitrogen in the PAN graphite felt changed from 3.803% to 5.367% by adjusting treatment time to 15 h in ammonia solution, while FT-IR results indicated that nitrogenous groups were introduced. The electrochemical properties of these graphite felts were characterized by cyclic voltammetry, electrochemical impedance spectroscopy, as well as cell charge and discharge tests. The energy efficiency of the treated graphite felt reached 85% at a current density of 20 mA/cm². The corresponding coulombic efficiency and voltage efficiency were 95.3% and 75.1%, respectively. The improvement of the electrochemical properties for the treated graphite felt might be attributed to the increase of polar nitrogenous groups of carbon fiber surface, which facilitated charge transfer between electrode and vanadium ions.

Keywords Vanadium redox flow battery · Graphite felt · Ammonia treatment · Nitrogenous groups

Introduction

Vanadium Redox Battery (VRB) proposed by Skyllas-Kazacos et al. has emerged as one of the promising green

energy source for energy storage of intermittently renewable energy (wind energy, solar energy, etc.) due to its long cycle life, flexible design, fast response time, deep-discharge capability, low cost, and environmental friendship in energy storage [1–3]. All-vanadium redox flow battery employing V(IV)/V(V) as positive electrolyte and V(II)/V(III) as negative electrolyte has an open-circuit voltage of approximately 1.26 V at 100% state-of-charge [1, 4, 5]. Since sulfuric acid solution is used as the support electrolyte in VRB, polyacrylonitrile (PAN)-based graphite felts are preferably chosen as the electrodes because of their wide operation potential range, stability, and availability in high surface area at reasonable cost [6]. However, graphite felt electrodes showed poor kinetics reversibility. Thus, much attention has been paid to the modification of the electrodes for enhancing the electrochemical properties [7, 8]. Up to now, a variety of surface treatment methods have been reported for improving the electrochemical activity of graphite felt, such as heat treatment [9], electrochemical oxidation [10], acid treatment [11], modification with iridium ions [12]. These methods, however, are not advantageous to commercial application for the use of noble metal, dangerous concentrated acid or tedious treatment time.

Nitrogen-doped carbon nanostructured materials have shown higher electrocatalytic activity in many electrochemical devices than non-doped ones [13–19]. Recently, Shao et al. [20] found that the electrochemical redox behavior of V(IV)/V(V) couple showed much higher performance on N-MPC than that on the widely used graphite by preparing mesoporous carbon (MPC) by a soft-template method and doping with nitrogen by heat-treating MPC in NH₃ at 850 °C (N-MPC). This work opens up wider application of nitrogen-doped carbon materials and introduces a new way to modify carbon electrode materials for vanadium redox flow batteries. However, considering the high cost and

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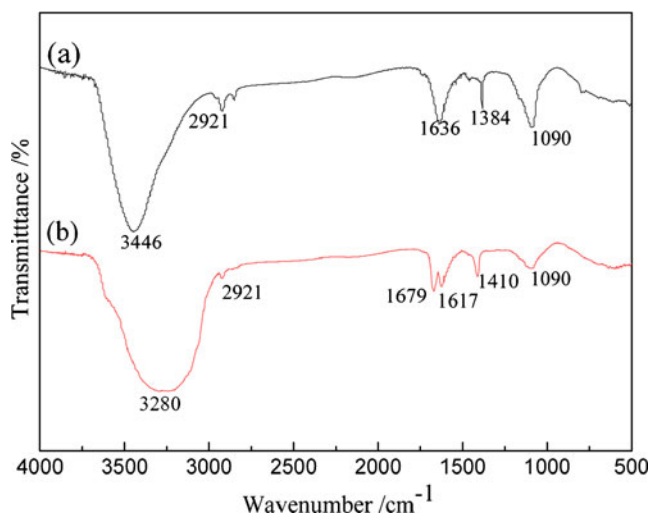


Fig. 1 FTIR spectra of untreated graphite felt (a) graphite felt treated 15 h in ammonia solution at 180 °C (b)

contamination in the process, an improvement of treating electrode in the similar way at mild conditions is needed with a view to practical commercial use.

In this work, the effect of hydrothermal ammoniated treatment on PAN-based graphite felts was investigated at 180 °C in a Teflon-lined stainless steel autoclave for different time. It was found that the nitrogenous group can be successfully introduced onto the surface of PAN-based graphite felt after the treatment. The electrochemical results of the hydrothermal ammoniated treated graphite felt toward the redox reactions of V(IV)/V(V) indicated a high catalytic activity of NH₃-treated graphite felt.

Experimental

Chemicals and materials

PAN-graphite felt (cubic electrical resistance 0.1 Ω/25 mm, thickness 6 mm produced by Shenhe carbon fiber Materials Co. Ltd., Liaoning China), which is made of PAN carbon fiber via needle-punching processing and subsequently graphitization above 2,000 °C, was treated thermally in a sealed 50 mL Teflon-lined stainless steel autoclave containing 15 mL 25% ammonia solution at 180 °C for different time. The treated samples were washed with deionized water until the pH of the rinsed water was neutral, and dried in vacuum oven at 110 °C for 5 h.

Electrochemical tests

For electrochemical characterizations, a three-electrode cell was used with the graphite felt (1 cm²) as the working electrode, a Pt electrode served as the counter electrode,

and a saturated calomel electrode served as the reference electrode (SCE). The electrolyte is 3 M H₂SO₄+0.1 M VOSO₄ solution. Cyclic voltammetry (CV) result was obtained with CHI 660 C workstation (Shanghai Chenhua Instruments, China) with a scan rate of 0.001 V/s over the voltage ranging from 0 to 1.6 V. Electrochemical impedance spectroscopy (EIS) was measured on Princeton workstation (PARSTAT2273, EG&G, US) by applying an alternating voltage of 5 mV over the frequency ranging from 10⁻² to 10⁵ Hz.

Cell performance of the different graphite felt (untreated and treated) was measured using an in-house designed static state cell system. The graphite felts were soaked in 1.5 M VOSO₄+3 M H₂SO₄ electrolyte prepared by electrochemical oxidation V₂O₅ (Changsha Asian Light Economic Trade Co. Ltd., 98.5–99%) in sulfuric acid for more than 1 day at an ambient temperature prior to cell assembly. The positive electrode compartment was separated from the negative electrode compartment with a PE-01 membrane (Zhejiang Qianqiu Group Co. Ltd., China) that was sealed with rubber washers. Constant-current charge–discharge tests are carried out with a battery test system CT2001C-10 V/2 A (Wuhan Land Co., China).

Materials characterization

The surface morphology of the samples was characterized with a scanning electron microscopy (JEOL, JSM-6380LV, Japan) at an acceleration voltage of 25 kV. Elemental analysis of graphite felt before and after treated was characterized with a Vario EL cube CHNOS carbon-sulfur analyzer (ELEMENTAR, Germany)

Adsorption character to vanadium ion

The dry graphite felts were weighed and immersed in 3 M H₂SO₄+1.6 M VOSO₄ solution at room temperature for 24 h. The electrolyte uptake was determined according to the following equation:

$$WI(\%) = \frac{W_w - W_d}{W_w} \times 100\%$$

Where W_d and W_w are the weight of graphite felts before and after electrolyte absorption, respectively.

Table 1 Element analysis results of graphite felt electrodes before and after ammonia treated

Sample	C (%)	S (%)	H (%)	N (%)	C/N
Untreated	94.53	0.912	0.523	3.803	24.86
Ammonia treated	91.96	0.713	0.407	5.367	17.13

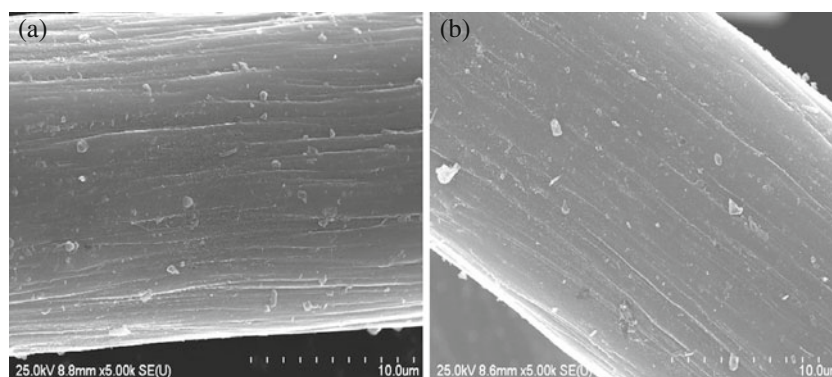


Fig. 2 SEM images of untreated graphite felt (a) and treated for 15 h in ammonia solution at 180 °C (b)

Results and discussions

FTIR analysis

Frustrated total internal reflection (FTIR) spectra of graphite felts untreated and treated for 15 h are recorded in the range of 4,000–500 cm^{-1} in transmittance mode, which is shown in Fig. 1. As for untreated sample, the peaks at 1,636 and 3,446 cm^{-1} are attributed to carboxylic C=O and O–H stretching vibration, respectively [21]. The peaks at 1,384 and 1,090 cm^{-1} are assigned to O–H bending vibration and C–O stretching vibration, respectively [22]. After ammonia treatment, the spectrum of graphite felt sample still possesses C–O and C–H stretching vibration, which appears at 2,915 cm^{-1} [23]. The prominent lump within 3,100–3,500 cm^{-1} for graphite felt sample is due to the NH_2 stretch of the amine group overlapped with O–H stretching vibration. The presence of new bands at 1,617 and 1,410 cm^{-1} , correspond to N–H in-plane and C–N bond stretching vibration, respectively [24]. The carbonyl (C=O) peak shifts to 1,679 cm^{-1} due to the formation of

amide group C(=O) NH_2 [22]. On the basis of the FTIR analysis, oxygen-containing groups such as carboxylic acid on the carbon fiber surface have converted to nitrogenous groups which may exist as the form of amides, aromatic amines, lactams, imids ect after the ammonia treatment [25, 26].

Elemental analysis

The elements content of the untreated and treated graphite felts are listed in Table 1. As shown in Table 1, after the treatment for 15 h, the N content and C/N ratio of the untreated sample increase from 3.803% and 24.86 to 5.367% and 17.13, respectively, with a decreasing contents of C, H, and S after the treatment for 15 h. The oxygen content in graphite felt also decreases after NH_3 treatment. From the FTIR analysis, this variation is due to the decomposition of oxygen-containing groups and sulfur-containing groups at high temperature [27, 28] and the reaction between NH_3 and oxygen-containing groups, produced nitrogenous groups like amides, aromatic amines, lactams, imids ect [25, 26].

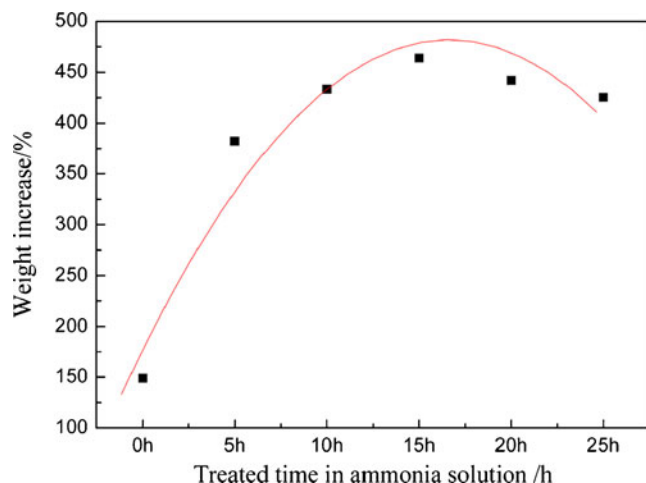


Fig. 3 Relation between weight increase of graphite felts and treated time in ammonia solution

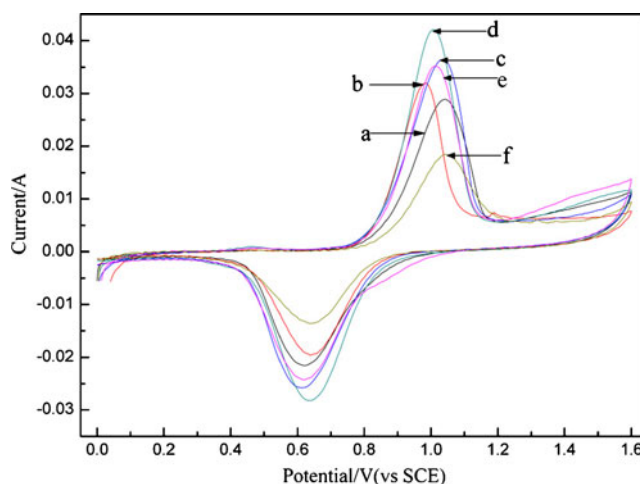


Fig. 4 CV curves recorded at 0.001 V/s in 0.1 M H_2SO_4 solution of untreated graphite felt electrode (a), and treated in ammonia solution for b 5, c 10, d 15, e 20, and f 25 h at 180 °C

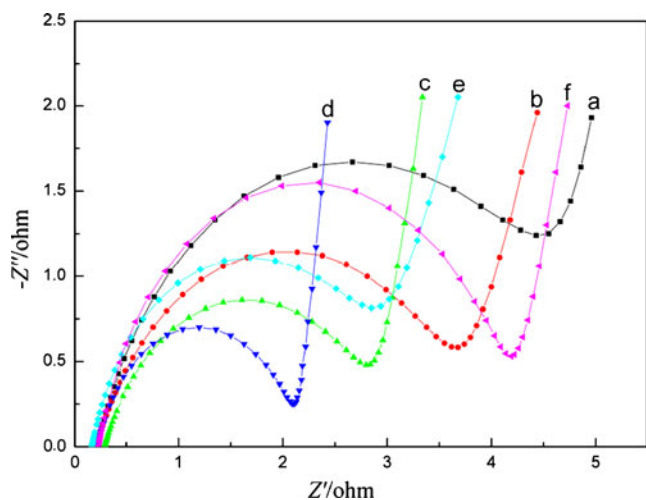


Fig. 5 Nyquist plots of different graphite felt electrodes in 0.1 M $VOSO_4 + 3 M H_2SO_4$ solution at open-circuit potential. Untreated graphite felt (a) and treated graphite felt in ammonia solution for b 5, c 10, d 15, e 20, and f 25 h at 180 °C

SEM image

The surface morphology of graphite felt samples is presented in Fig. 2a, b. As shown in Fig. 2, there is no obvious change on the surface morphology of the graphite felts before and after ammonia treatment. But the surfaces of the treated graphite felt are cleaner than that of the untreated one. This phenomenon can be caused by the weak reaction between NH_3 and carbon fiber and removing the surface contaminants or any inhibitory layer that may hinder electron transfer [11]. Thus, compared with electrochemical oxidation treatment [10], ammonia treatment does not affect the smoothness of the carbon fiber surface, neither does it weaken the carbon fiber's mechanical property.

Adsorption character to vanadium ion

Relation between weight increase of graphite felts and treated time in ammonia solution are measured and presented in Fig. 3. It can be seen that a maximum value of weight increase at 15 h is obtained as extension of treated time in ammonia solution, which is consistent with

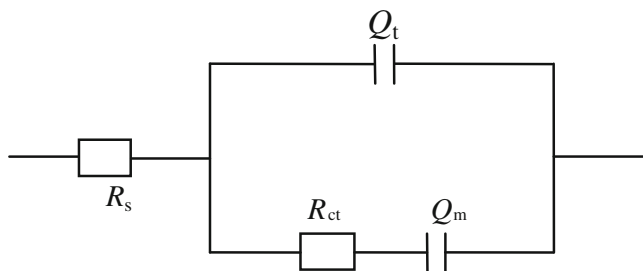


Fig. 6 Equivalent circuit for graphite felt electrodes

variation of CV results latter. Variation of absorbability is mainly attributed to variation of surface area and functional group of carbon fiber. And the change of the surface condition of the treated and untreated samples could be neglected (as Fig. 3 show). Thus, the improvement of adsorbability may be due to increase of nitrogenous groups, especially amide group.

CV in $VOSO_4$ solution

Cyclic voltammograms of different electrodes in 0.1 M $VOSO_4 + 3 M H_2SO_4$ solution are shown in Fig. 4. The anodic peak associated with the oxidation of V(IV) to V(V) and the corresponding reduction peaks appear at 0.9–1.1 V and 0.6–0.7 V (vs. SCE), respectively. Both the oxidation peak current (I_{pa}) and the reduction peak current (I_{pc}) initially increase with the increase of ammoniating treatment time and then decrease before the sample treated for 20 h, indicating that the sample treated for 15 h exhibited the best electrochemical activity for V(IV)/V(V) redox reaction. This phenomenon can be explained as follows. For one thing, lone-pair electron on nitrogenous groups such as amides, aromatic amines, and lactams can enhance the basicity of carbon fiber and the electrical conductivity of ammoniated carbon fiber. For another, according to the results of density functional theory calculations, carbon atoms adjacent to nitrogen dopants possessed a substantially high positive charge density to counterbalance the strong electronic affinity of the nitrogen atom [15], the “positively charged” carbon atoms work as the active sites. Thus, the electron transfer between graphite felt electrode and vanadium ions is improved. At the same time, improvement of adsorption to vanadium ion resulted from the higher nitrogenous group content on graphite felt electrode causes higher surface vanadium ion concentration. Therefore, a larger reaction current of the treated samples is obtained, and the sample with higher surface concentration of nitrogenous groups exhibits higher activity toward V(IV)/V(V) redox reaction. The sample treated longer than 15 h exhibits poorer activity than the sample treated for 15 h, because the deteriorated mechanical property of the samples reduces the effective area for V(IV)/V(V) redox reaction [29]. When the samples was treated longer than 15 h, some carbon fibers shed from the felty body, the conductive network of graphite felts was destroyed, the effective area and the activated point for the electrochemical reaction reduces, so the poorer electrochemical activity was obtained.

EIS analysis

In order to gain additional supporting evidence, the EIS characteristic of the graphite felt electrodes in 0.1 M

Table 2 Parameters obtained from fitting the impedance plots of Fig. 5 with the equivalent circuit of Fig. 6

Sample	$R_s/\Omega\text{cm}^2$	Q_t		$R_{ct}/\Omega\text{cm}^2$	Q_m	
		$Y_{0,1}$	n		$Y_{0,2}$	n
Untreated	0.2156	0.05077	0.7735	4.757	2.116	0.8646
180 °C 5 h	0.1988	0.0563	0.7223	3.559	4.158	0.7021
180 °C 10 h	0.2812	0.06489	0.7187	2.704	6.92	0.8728
180 °C 15 h	0.2158	0.07686	0.796	1.943	11.11	0.8995
180 °C 20 h	0.1684	0.05187	0.8057	2.957	7.847	0.7748
180 °C 25 h	0.228	0.03685	0.8338	4.025	5.435	0.8338

VOSO₄+3 M H₂SO₄ solution at the open-circuit potential has been investigated and the corresponding Nyquist plot is shown in Fig. 5. A semi-circle and a linear part are observed in the frequency range from 10⁵ to 10⁻² Hz, indicating that the V(IV)/V(V) redox reaction is mix-controlled by charge transfer and diffusion steps. The semicircle part at high frequencies reflects the charge-transfer process and the linear part at low frequencies reflects the diffusion processes in pore channel of graphite felt [12, 30]. Thus, the spectrum is fitted with an equivalent circuit shown in Fig. 6. In the equivalent circuit, R_s stands for the solution resistance, R_{ct} represents the charge-transfer resistance across electrode/solution interface, Q_t is the constant-phase element, which represents the electric double-layer capacitance of electrode/solution interface, and Q_m is the constant-phase element relevant to vanadium ions adsorption and diffusion in pore channel of the graphite felt electrodes [31]. The parameters are obtained and listed in Table 2. One parameter of constant-phase elements Y_0 ($Y_{0,1}$ and $Y_{0,2}$) and the charge-transfer resistance R_{ct} strongly depend on the treatment time, which

decrease with the increase of the treatment time when the sample is treated no more than 15 h. This should be ascribed to increase of nitrogenous groups on the surfaces of the treated graphite felts. For $Y_{0,1}$ and $Y_{0,2}$, more vanadium ions are adsorbed on the surface of graphite felt electrodes, which result in thickness decrease of dispersion layer, value increase of electrode capacitance according to Stern double layer theory. Lone-pair electron on nitrogenous groups can enhance the electrical conductivity and facilitate the charge-transfer reaction. And this can explain the change of the charge-transfer resistance R_{ct} . Parameters of samples treated longer than 15 h get worse than the sample treated for 15 h. This can be caused by the deteriorated mechanical property and the destroyed of the conductive network of graphite felts electrodes, which is ascribed to shedding of carbon fibers from the felty body and consequently decrease of the effective area for V(IV)/V(V) redox reaction

Charge–discharge test

A typical charge and discharge curve for a vanadium redox cell, employing untreated graphite felt and treated in ammonia solution for different time at 180 °C, is shown

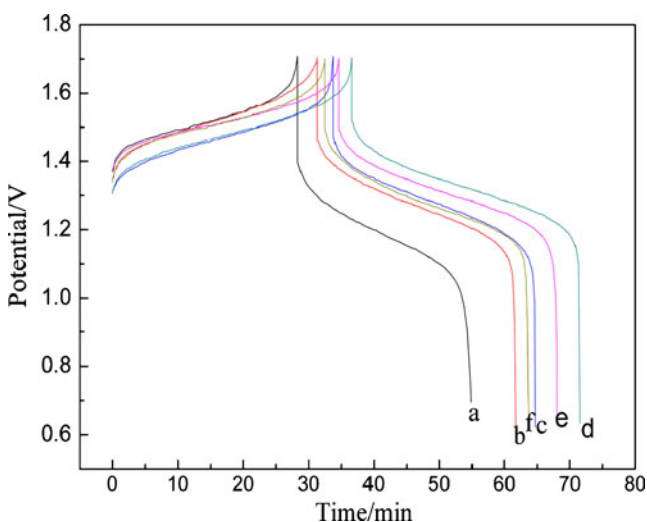


Fig. 7 The 20th charge–discharge curves of the cells using different graphite felt electrodes at a current density of 20 mA/cm². Untreated graphite felt (a) and graphite felt treated in ammonia solution for b 5, c 10, d 15, e 20, and f 25 h at 180 °C

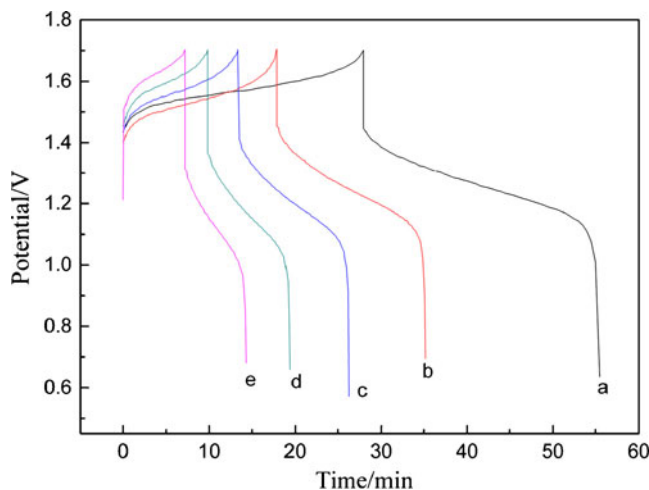


Fig. 8 Charge–discharge curves of the cell employing the untreated graphite felt electrodes at the rate of a 20, b 30, c 40, d 50 and f 60 mA/cm²

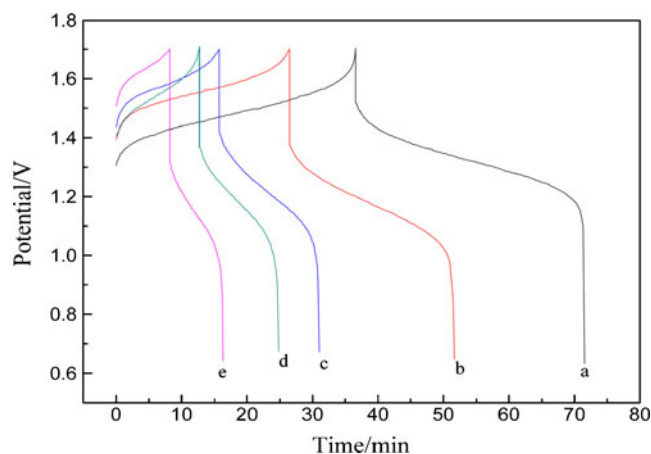


Fig. 9 Charge–discharge curves of the cell employing the graphite felt electrodes treated in ammonia solution for 15 h at 180 °C at the rate of **a** 20, **b** 30, **c** 40, **d** 50, and **e** 60 mA/cm²

in Fig. 7. All of the batteries are charged to 1.7 V and discharged to 0.7 V at a constant current density of 20 mA/cm². As Fig. 7 demonstrated, the capacity of the cells increase with the increase of the treatment time except for the battery using the sample treated for 15 h, which is related to the activity of the samples toward two electrode reactions and is consistent with the CV results.

The charge–discharge curves of battery employing graphite felt untreated and treated in ammonia solution for 15 h (marked cell A, cell B, respectively) at different current densities are presented in Figs. 8 and 9. The coulombic efficiency (CE), voltage efficiency (VE), and overall energy efficiency (EE) values of cell A and cell B are summarized in Table 3. As long as the cell geometry and membrane kept constant for all the tests, the changes in

energy efficiency would reflect changes in electrode activity. As Figs. 8, 9 and Table 3 show, cell B showed better charge–discharge performance than cell A at any current density. Also, VE and EE values of cell B were higher than that of cell A with the variation of current density. It is proved that the performance of VRB using ammoniated treatment felt as electrode improve evidently compared with batteries employing raw felt. As Table 3 show, the CE of batteries increase with the increasing of current density, while the VE show the completely opposite trend for the two batteries. The former is caused by the shorter charge–discharge time at high current densities, which can reduce the crossover of vanadium ions and a higher CE is obtained. And the variation of VE is due to the increase of ohmic resistance and the overpotentials led by the increase of current densities. The CE, VE and EE of cell B at the current density of 20 mA/cm² are 95.3%, 89.5%, and 85.3%, respectively. When the current density increases to 60 mA/cm², the values of CE, VE, and EE decrease slightly. Therefore, the battery succeeds in maintaining almost cell efficiencies at different charge–discharge current densities.

Conclusions

A new method based on hydrothermal ammoniated treatment has been employed to optimize the electrochemical activity of graphite felt. The sample treated at 180 °C for 15 h exhibited the best adsorption character to vanadium ion and electrochemical activity for V(IV)/V(V) redox reaction, leading to a significant improvement in VRB

Table 3 Vanadium redox cell efficiency values for batteries employing graphite felt electrodes untreated (cell A) and treated in ammonia solution for 15 h at 180 °C (cell B) under various current densities

Current density (mA/cm ²)	Cycle number	Cell A efficiency (%)			Cell B efficiency (%)		
		CE/%	VE/%	EE/%	CE/%	VE/%	EE/%
20	1	96.2	83.4	80.2	95.3	89.5	85.3
	20	96.3	82.9	79.9	95.4	89.0	84.9
	40	95.9	83.7	80.3	95.5	89.0	85.0
30	1	96.6	77.4	74.8	95.6	81.5	77.9
	20	96.3	78.0	75.1	95.8	80.5	77.1
	40	96.8	77.8	75.3	95.7	81.1	77.6
40	1	97.3	74.2	72.2	97.3	76.6	74.5
	20	97.4	73.5	71.6	97.3	76.5	74.5
	40	97.2	73.4	71.4	97.5	76.0	74.1
50	1	97.6	72.1	70.4	97.3	75.7	73.6
	20	97.6	71.4	69.7	97.9	75.8	74.2
	40	97.5	71.3	69.5	97.7	75.5	73.8
60	1	97.6	67.4	65.8	98.6	70.2	69.2
	20	97.7	66.7	65.2	97.9	69.0	67.6
	40	97.5	65.9	64.3	98.0	69.7	68.3

efficiencies. EE of 85% was obtained after treatment at a current density of 20 mA/cm², the corresponding CE and VE were 95.3% and 75.1%, respectively. Charge–discharge performance of the battery remained stable when the current density varied from 20 to 60 mA/cm². The increase in the activity of electrode is attributed to the increase and formation of surface-active nitrogenous groups, which facilitates charge-transfer between electrode and vanadium ions. The results demonstrated a new approach for improving electrode material activity for VRB. This treatment method can also be applied for other electrode materials used in previous VRB studies such as carbon paper [30], carbon felt [12], and carbon cloth [32].

Acknowledgments This work was financially supported by the Major State Basic Research Development Program of China (973 Program) (No. 2010CB227201) and National Natural Science Foundation of China (No. 50972165).

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