



## Short communication

## Graphite–carbon nanotube composite electrodes for all vanadium redox flow battery

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## ABSTRACT

The voltammetric behaviors of graphite (GP) and its composites with carbon nanotube (CNT) were studied in 5 M H<sub>2</sub>SO<sub>4</sub> + 1 M VOSO<sub>4</sub> solution with cyclic voltammetry (CV), and the surface morphology of the composites was observed with scanning electron microscope (SEM). The results obtained from voltammetry show that the redox couples of V(IV)/V(V) and V(II)/V(III), as positive and negative electrodes of all vanadium flow liquid battery, respectively, have good reversibility but low current on the GP electrode, and the current can be improved by CNT. It is found from the observation of SEM that the CNT is dispersed evenly on the surface of sheet GP when they are mixed together. The best composition for the positive and the negative of all vanadium flow liquid battery determined by comparing voltammetric behavior of the composite electrodes with different content of CNT is 5:95 ( $w_{\text{CNT}}/w_{\text{GP}}$ ) for both positive and negative electrodes. The activity of the composite electrode can be affected by the heat treatment of CNT. CNT treated at 200 °C gives better activity to the composite electrode.

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## 1. Introduction

All vanadium redox flow battery (VRB) has attracted much attention due to its long cycle life, flexible design and high reliability [1]. It is believed that it is good for storing electricity produced by intermittently renewable energy sources such as wind and solar power. VRB employs V(IV)/V(V) and V(II)/V(III) redox couples as the positive and the negative half-cells, respectively, and has an open circuit voltage of approximately 1.26 V at 100% state of charge [2,3]. The typical electrode materials for VRB are metal and carbon electrodes, which are similar to the electrode materials for sodium polysulfide/bromide redox flow battery [4–6]. Metal electrodes such as gold and platinum are not practical because of their high cost. Carbon is cheap but its activity for VRB needs to be improved.

It has been found that graphite (GP) gives a good reversibility to electrode reactions [7]. Carbon nanotube (CNT) is a new kind carbon material that has special performances [8], especially has good electrical conductivity [9,10]. The purpose of this paper is to understand the performance of GP–CNT composite used for the electrodes in VRB.

## 2. Experimental

The composite electrodes were prepared by mixing GP and CNT (the mass ratios of GP to CNT in the composites were 99:1, 97:3, 95:5, 93:7, and 91:9, respectively) with 8% polyvinylidene fluoride (PVDF) dissolved in *N*-methyl-2-pyrrolidone, coating the mixture onto Pt, and being dried at 30 °C for 12 h. The diameter of GP was 10 μm and the outer diameter of CNT was 8–15 nm. The pure GP and CNT electrodes were also prepared in the same way for a comparison. All the electrodes had the same geometrical area (1.13 cm<sup>2</sup>). For the heat treatment, CNT was treated at different temperatures in air or vacuum for 12 h.

For electrochemical characterizations, a three-electrode cell was used with the GP–CNT composite electrode as working electrode, a Pt electrode as the counter electrode and a saturated calomel electrode as the reference electrode. The potentials reported in this paper are with respect to this reference. The electrolyte used is 5 M H<sub>2</sub>SO<sub>4</sub> + 1 M VOSO<sub>4</sub> solution. All the experiments were conducted under room temperature with an electrochemical instrument (PGSTAT-30, Autolab, Eco Chemie, B.V. Company).

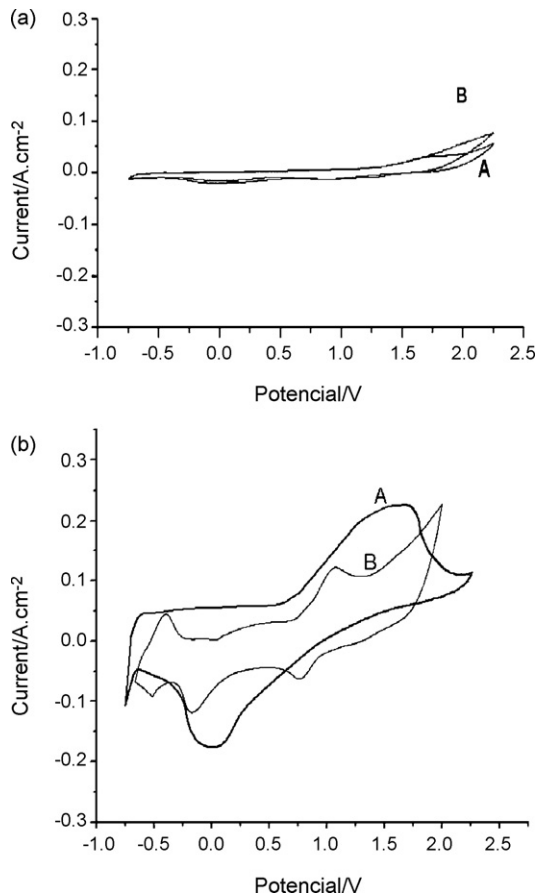
## 3. Results and discussion

## 3.1. CVs of CNT and GP

The cyclic voltammograms of CNT and GP electrodes in 5 M H<sub>2</sub>SO<sub>4</sub> solution are shown in Fig. 1a. No faradaic current can be

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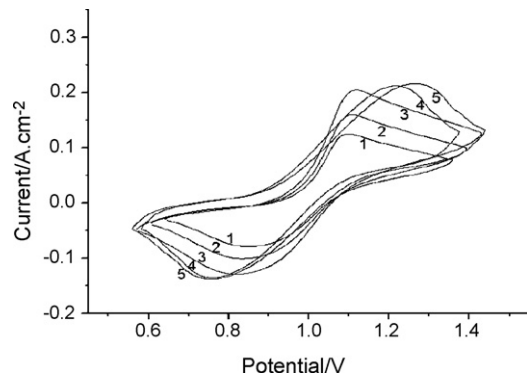


**Fig. 1.** Cyclic voltammograms of CNT electrode (A) and GP electrode (B) in 5 M H<sub>2</sub>SO<sub>4</sub> (a) and 5 M H<sub>2</sub>SO<sub>4</sub> + 1 M VOSO<sub>4</sub> (b) solutions. Scan rate: 20 mV s<sup>-1</sup>.

observed for the potentials from -0.75 V to 1.70 V. At the potential higher than 1.70 V, the increasing current with the increase of the potential can be observed. This should be ascribed to the decomposition of water to oxygen or carbon oxide on the electrodes.

Fig. 1b shows the cyclic voltammograms of CNT and GP electrodes in 5 M H<sub>2</sub>SO<sub>4</sub> + 1 M VOSO<sub>4</sub> solution. For GP, the oxidation and reduction related to vanadium from V(V) to V(II) can be distinguished from its voltammogram: the oxidation and reduction currents at the potentials between -0.75 V and -0.25 V, -0.25 V and 0.75 V, and 0.75 V and 1.50 V, are corresponding to the transformations between V(II) and V(III), V(III) and V(IV), and V(IV) and V(V), respectively. The reduction peak for the transformation of V(IV) to V(III) appears at about -0.2 V but the corresponding oxidation peak is insignificant, indicating that the transformation between V(IV) and V(III) is not reversible. The anodic and cathodic peaks associated with the couple V(IV)/V(V) appear at approximately 1.05 V and 0.85 V, respectively, and the peaks associated with the couple V(II)/V(III) appear at approximately -0.5 V and -0.4 V for the reduction and oxidation, respectively. This indicates that both V(IV)/V(V) and V(II)/V(III) are quite reversible on GP. However, different voltammogram appears for CNT electrode, as shown in Fig. 1b. Only one couple of oxidation and reduction peaks can be observed for the CNT electrode, and the difference in peak potentials is about 1.64 V. This suggests that the oxidation and reduction reactions related to vanadium of different valence on CNT are not reversible as good as those on GP. This might be ascribed to the poor activity of CNT toward the oxidation and reduction of vanadium.

On the other hand, the current on the CNT is far larger than that on the GP. This should be ascribed to the high electrical conductivity



**Fig. 2.** Cyclic voltammograms of GP-CNT composite electrodes in 5 M H<sub>2</sub>SO<sub>4</sub> + 1 M VOSO<sub>4</sub> solution, with CNT content of (1) 1 wt.%, (2) 3 wt.%, (3) 5 wt.%, (4) 7 wt.%, and (5) 9 wt.%. Scan rate: 20 mV s<sup>-1</sup>.

and high surface area of CNT. Thus, CNT is not suitable to be used as the electrode for VRB by itself. GP can be used as the positive and the negative electrodes for VRB, but its current for the oxidation and reduction should be improved.

### 3.2. Composites for the positive electrode

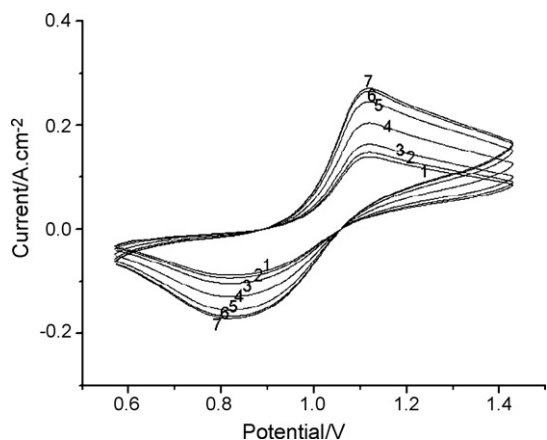
#### 3.2.1. CVs of GP-CNT composite electrodes with different contents of CNT

Fig. 2 shows the cyclic voltammograms of GP-CNT composite electrodes with different contents of CNT in 5 M H<sub>2</sub>SO<sub>4</sub> + 1 M VOSO<sub>4</sub>. It can be seen from Fig. 2 that the peak potentials for the oxidation of V(IV) to V(V) and the reduction of V(V) to V(IV) keep unchanged and the peak currents of these reactions increase with increasing the content of CNT, when the content of CNT is from 1 wt.% to 5 wt.%. However, as the content of CNT increases further, the peak potential for the oxidation of V(IV) to V(V) becomes more positive and that for the reduction of V(V) to V(IV) becomes more negative, and the currents for these reactions have less change. This phenomenon should be ascribed to balance between activity and electrical conductivity. Apparently, the current for the transformation reaction between V(IV) and V(V) can be improved by the composite of GP with small amount of CNT, equal to or less than 5 wt.%.

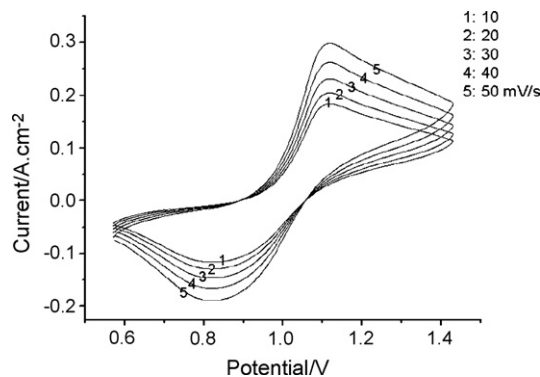
#### 3.2.2. Effect of heat treatment

Fig. 3 shows the cyclic voltammograms of GP-CNT (95:5, w/w) composite electrodes in 5 M H<sub>2</sub>SO<sub>4</sub> + 1 M VOSO<sub>4</sub> solution. Before the preparation of composite electrode, CNT was treated under different conditions. It can be seen from Fig. 3 that the current for transformation reactions between V(V) and V(IV) is influenced by the heat treatment conditions on CNT. The current for the reactions decreases with increasing the treatment temperature for the electrodes with CNT treated in air, indicating that the heat treatment of CNT in air gives poor activity to the composite electrode. This might be related to the lower conductivity of CNT with carbon oxide formed in air at high temperature. Controversially, when the temperature is lower than 200 °C, the current for the reactions increases with increasing the treatment temperature for the electrodes with CNT treated in vacuum. When the temperature increases further, the current for the reactions keeps almost unchanged. This indicates that the heat treatment of CNT in vacuum improves the activity of the composite electrode and the better treatment temperature is 200 °C.

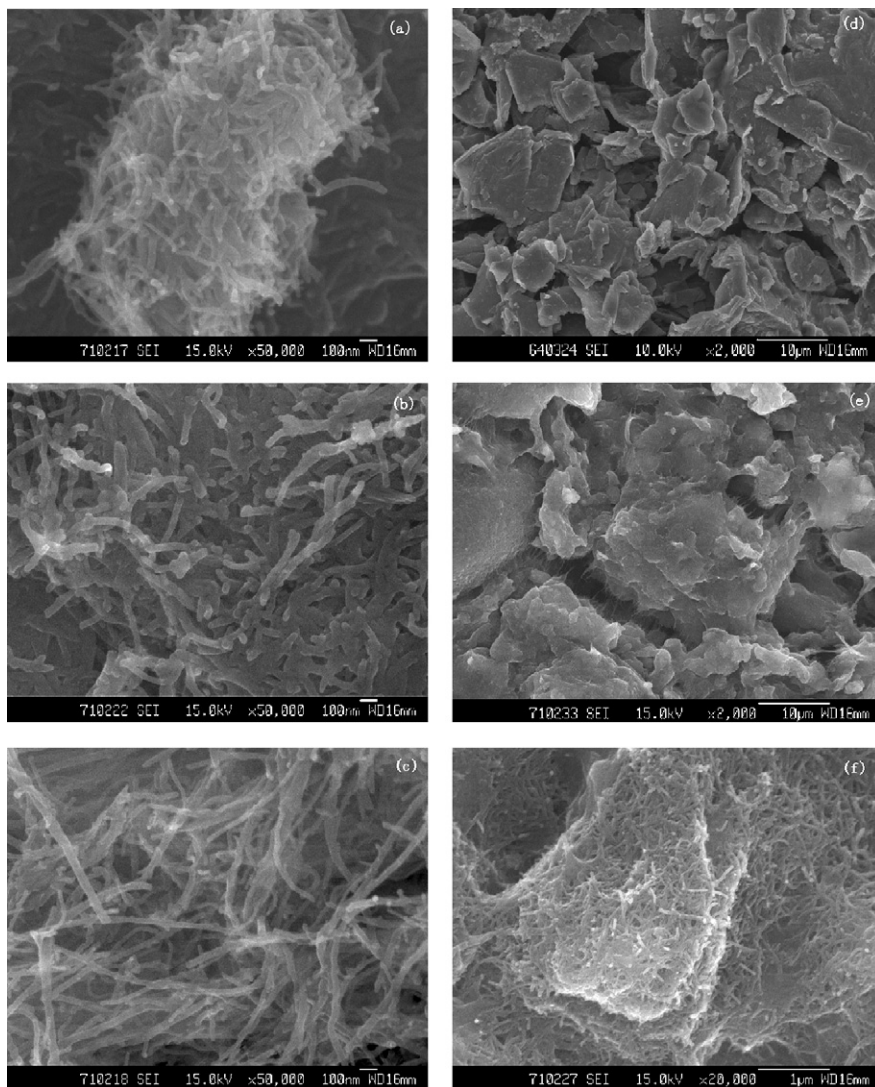
Fig. 4 shows the cyclic voltammograms of the composite electrode with 5 wt.% CNT treated at 200 °C in vacuum under different scan rate in 5 M H<sub>2</sub>SO<sub>4</sub> + 1 M VOSO<sub>4</sub> solution. It can be seen from



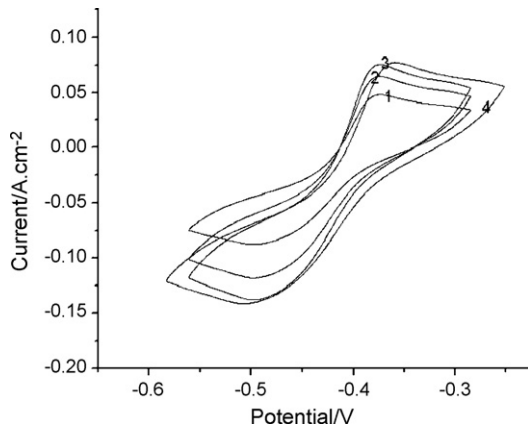
**Fig. 3.** Cyclic voltammograms of GP-CNT (95:5, w/w) composite electrodes in 5 M H<sub>2</sub>SO<sub>4</sub> + 1 M VOSO<sub>4</sub> solution, with CNT treated by (1) annealing at 300 °C in air, (2) at 200 °C in air, (3) at 100 °C in air, (4) no annealing, (5) annealing at 100 °C in vacuum, (6) at 200 °C in vacuum, and (7): at 300 °C in vacuum. Scan rate: 20 mV s<sup>-1</sup>.



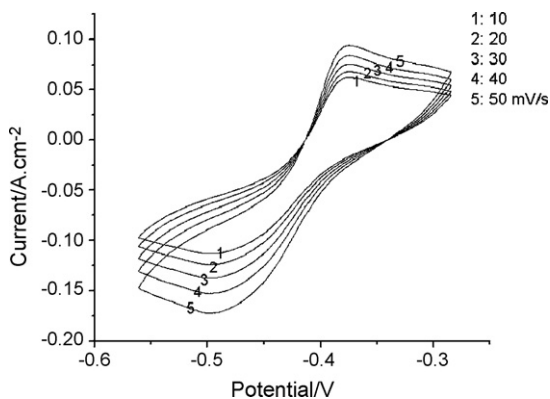
**Fig. 4.** Cyclic voltammograms of the composite electrode with 5 wt.% CNT treated at 200 °C in vacuum under different scan rates in 5 M H<sub>2</sub>SO<sub>4</sub> + 1 M VOSO<sub>4</sub> solution.



**Fig. 5.** Morphological images of GP, CNT and their composite, (a) CNT as received, (b) CNT treated at 200 °C in air, (c) CNT treated at 200 °C in vacuum, (d) GP, and (e and f) GP-CNT composite with 5 wt.% CNT treated at 200 °C in vacuum.



**Fig. 6.** Cyclic voltammograms of composite electrodes at the potentials for the transformation between V(III) and V(II) in 5 M H<sub>2</sub>SO<sub>4</sub> + 1 M VOSO<sub>4</sub> solution, with CNT content of (1) 1 wt.%, (2) 3 wt.%, (3) 5 wt.%, and (4) 7 wt.%. Scan rate 20 mV s<sup>-1</sup>.



**Fig. 7.** Cyclic voltammograms of CNT-GP composite electrode with 5 wt.% CNT under different scan rates in 5 M H<sub>2</sub>SO<sub>4</sub> + 1 M VOSO<sub>4</sub> solution.

Fig. 4 that the peak potentials for the oxidation of V(IV) and the reduction of V(V) keep almost unchanged with scan rate, indicating that the transformation reaction between V(IV) and V(V) is quite reversible.

### 3.2.3. Morphology of GP, CNT and their composite

Fig. 5 shows the surface morphology of GP, CNT and their composite. The CNT is tangled together before treated, as shown in Fig. 5a. The CNT is still tangled together when treated at 200 °C in air but more loosely than those before treated, as shown in Fig. 5b. However, when CNT is treated at 200 °C in vacuum, the CNT becomes straight and independent of each other, as shown in Fig. 5c. The change of CNT morphology caused by heat treatment in vacuum can be ascribed to the purification of CNT under vacuum [11,12].

Fig. 5d shows the surface morphology of GP, Fig. 5e and f show that of the composite of GP with 5 wt.% CNT treated at 200 °C in vacuum. It can be seen that GP has a layered structure and CNT can be dispersed evenly on it. The activity improvement of GP by its composite with CNT should be related to the dispersion of CNT on

GP. The dispersed CNT increases electrical conductivity and thus the active sites of GP for the transformation between V(IV) and V(V). However, when the content of CNT in the composite is larger than 5 wt.%, the GP is covered completely by CNT and the composite behaves like CNT.

### 3.3. Composites for the negative electrode

Fig. 6 shows the cyclic voltammograms of GP-CNT composite electrodes with different contents of CNT at the potentials for the transformation between V(III) and V(II) in 5 M H<sub>2</sub>SO<sub>4</sub> + 1 M VOSO<sub>4</sub>. It can be seen from Fig. 6 that similar phenomena as those observed for the transformation between V(IV) and V(V) appear for the transformation between V(III) and V(II). The CNT in the composite improves the current on GP when CNT content is lower than 5 wt.%, but keeps unchanged when CNT content is higher.

The oxidation of V(II) and the reduction of V(III) on the composite electrode with 5 wt.% CNT are also quite reversible, because the peak potentials for these reactions is independent of scan rate, as shown in Fig. 7. Therefore, the composite of GP with 5 wt.% CNT is not only good for the positive but also for the negative electrodes for all vanadium battery.

## 4. Conclusion

The transformation reactions for all vanadium battery are quite reversible on graphite but not on carbon nanotube. However, the currents for the reactions are low on graphite. The low currents can be improved by the composite of graphite with carbon nanotube, especially when carbon nanotube is treated at 200 °C in vacuum. The improvement is best when the content of carbon nanotube is 5 wt.%. This improvement can be ascribed to the high electrical conductivity of carbon nanotube.

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