

Short communication

## Factors affecting the electrochemical performance of organic/ $V_2O_5$ hybrid cathode materials

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Received 20 November 2003; accepted 31 January 2004

Available online 12 April 2004

### Abstract

Polyaniline– $V_2O_5$  hybrid materials have been prepared by an oxidative intercalation reaction and the factors that affect their electrochemical discharge–charge performance have been investigated. The first discharge capacity of a sample produced from a nominal molar ratio of aniline:  $V_2O_5 = 3$  ( $V_2O_5$ –(AN)3.0) is higher than that of a sample prepared from the lower ratio of aniline:  $V_2O_5 = 0.5$  ( $V_2O_5$ –(AN)0.5). The  $V_2O_5$ –(AN)0.5 sample also shows better reversibility. Samples have been post-treated at different temperatures in air or oxygen. Post-treatment improves the electrochemical performance of  $V_2O_5$ –(AN)0.5 but degrades both the capacity and reversibility of  $V_2O_5$ –(AN)3.0. A  $V_2O_5$ –(AN)0.5 sample post-treated at 70 °C in air exhibits the best discharge–charge characteristics.

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**Keywords:** Lithium battery; Intercalation; Hybrid;  $V_2O_5$ ; Polyaniline; Post-treatment

### 1. Introduction

Inorganic–organic hybridization is capable of producing novel materials that have both inorganic and organic characteristics. Such hybrid materials can be produced by intercalation of organic molecules into a layered inorganic material. Recently, hybrid materials composed of conducting polymer and  $V_2O_5$  xerogel have been prepared [1–8] by oxidative intercalation reaction of non-conducting organic monomer, and have been applied as electrode materials in rechargeable lithium batteries. In the case of polyaniline (PANI)-intercalated  $V_2O_5$ , the discharge capacity of an as-prepared sample is not exceptional despite the fact both PANI and  $V_2O_5$  are active components for electrochemical lithium intercalation. A significant improvement has been achieved, however, by oxygen post-treatment at temperatures below 100 °C for less than 5 h [6], which indicates that several factors may have a significant influence on the capacity of PANI– $V_2O_5$  hybrid materials.

This study examines the factors that affect the electrochemical performance of PANI– $V_2O_5$  hybrid cathode materials using non-aqueous electrolyte cells. For this purpose, a comparison is made of the effects of PANI concentration, heat-treatment temperature, and post-treatment condition on the electrochemical lithium insertion characteristics of PANI intercalated– $V_2O_5$  compounds.

### 2. Experimental

#### 2.1. Preparation of $V_2O_5 \cdot yH_2O$ xerogel

$V_2O_5$  xerogels were prepared by the method described elsewhere [9]. The  $V_2O_5$  powder (3 g) was dissolved in 300 ml of 10%  $H_2O_2$  solution. An exothermic reaction takes place during a partial decomposition of  $H_2O_2$  and leads to the release of oxygen gas. A clear orange solution is formed after about 10 min and becomes a dark red gel after few hours. The red gel was aged for three days and then dried at 100 °C to produce a composition of  $V_2O_5 \cdot yH_2O$  ( $n \approx 1.6$ – $1.8$ ), where the water content was deduced from the observed interlayer distance ( $d \approx 11.8 \text{ \AA}$ ) from X-ray

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diffraction (XRD) analysis. The composition of the xerogel was consistent with published data [10,11].

## 2.2. Synthesis of $(\text{PANI})_x/\text{V}_2\text{O}_5$ hybrid materials

Intercalation of PANI into  $\text{V}_2\text{O}_5$  was performed by reacting  $\text{V}_2\text{O}_5$  xerogel with aniline (AN) in a  $\text{CH}_3\text{OH}:\text{H}_2\text{O}$  (80:20% (w/w)) solution, as described elsewhere [8]. A 0.5 g (2.34 mmol) sample of dried  $\text{V}_2\text{O}_5$  xerogel was mixed with 30 ml of  $\text{H}_2\text{O}$ . The resulting mixture was added to a 0.11 g (1.17 mmol; AN: $\text{V}_2\text{O}_5 = 0.5:1$ ) or a 0.69 g (7.02 mmol; AN: $\text{V}_2\text{O}_5 = 3:1$ ) sample of aniline solution dissolved in 240 ml of  $\text{CH}_3\text{OH}$ . The reaction mixture was stirred at room temperature for 36 h in air. The product was isolated by filtration, washed with  $\text{CH}_3\text{OH}$  and dried at ambient temperature under vacuum. The dried products were post-treated at 70 or 130 °C for 5 h under an air atmosphere or a constant flow of oxygen in a tubular furnace.

## 2.3. Characterization

Powder X-ray diffraction analysis was performed using a Rigaku X-ray diffractometer in the  $2\theta$  range from 3 to 60° with Cu  $K\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ). Fourier transform infrared (FT-IR) spectra were recorded with KBr pellets and a MGNA-IR 560 spectrometer (Nicolet). Thermal analyses were performed by means of a SDT 2960 Simultaneous DTA-TGA (TA instruments) system at the heating rate of 10 °C/min in air.

Electrochemical studies were performed with a Macfile-II galvanostat system under a constant current density of 0.5 mA  $\text{cm}^{-2}$  in the 4–1.5 V range. Swage lock-type cells [12] were assembled in a dry room. A mixture of synthesized organic/ $\text{V}_2\text{O}_5$  material, Super P black (MMM Carbon Co.) and polytetrafluoroethylene (70:20:10% (w/w/w)) was used as the positive electrode (cathode), Li foil as the negative electrode (anode), and a 0.95 M solution of  $\text{LiPF}_6$  in ethylene carbonate/dimethyl carbonate (50:50% (v/v)) as the electrolyte.

## 3. Results and discussion

Thermogravimetric (TG) and differential scanning calorimetric (DSC) curves for an as-prepared sample that was produced by reacting 0.5 mol AN with 1 mol  $\text{V}_2\text{O}_5$  are shown in Fig. 1. Four distinct stages are observed in these curves. The first step, from ambient temperature to about 120 °C, corresponds to the removal of weakly-bound water. The second step up to 240 °C correlates with the loss of more strongly-bound water, which is in good agreement with the endothermic peak in the DSC curve. After removal of water, there is an abrupt weight loss at around 250 °C, which is attributed to decomposition and combustion of intercalated organic polymers. This combustion is confirmed by the exothermic peak in the DSC curves. The gain in weight

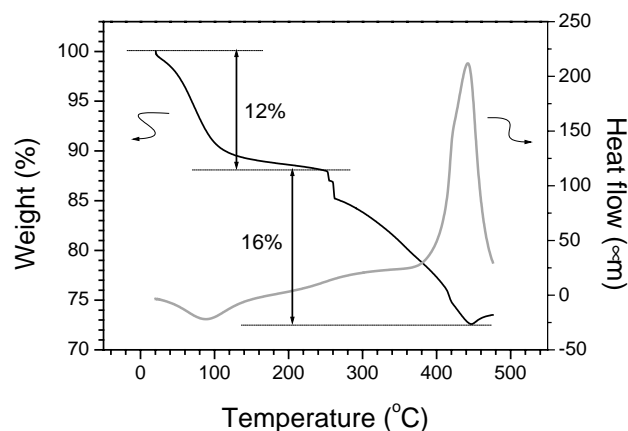


Fig. 1. TG–DSC curves for as-prepared  $\text{V}_2\text{O}_5\text{-(AN)}_{0.5}$ .

starting from 440 °C is probably due to the uptake of oxygen, which occurs together with the conversion of  $\text{V}^{4+}$  to  $\text{V}^{5+}$  [13]. The resulting TG–DSC curves of PANI– $\text{V}_2\text{O}_5$  are close to those for poly(thiophene)-derivatives intercalated in  $\text{V}_2\text{O}_5$  [14]. For the reaction product made with a molar ratio of AN: $\text{V}_2\text{O}_5 = 0.5:1$ , the composition is determined to be  $(\text{C}_6\text{H}_5\text{NH}_2)_{0.37}\text{V}_2\text{O}_5 \cdot 1.65\text{H}_2\text{O}$  based on the consecutive weight loss of water and polymer, i.e.  $(\text{C}_6\text{H}_5\text{NH}_2)_x\text{V}_2\text{O}_5 \cdot y\text{H}_2\text{O} \rightarrow (\text{C}_6\text{H}_5\text{NH}_2)_x\text{V}_2\text{O}_5 \rightarrow \text{V}_2\text{O}_5$ , where  $x$  and  $y$  are calculated from the following equations:

$$\left[ \frac{18y}{181.9 + 93.13x + 18y} \right] = 0.12 \quad (1)$$

$$\left[ \frac{93.13x}{181.9 + 93.13x} \right] = 0.16 \quad (2)$$

Powder X-ray diffraction patterns for as-prepared and post-treated PANI-intercalated  $\text{V}_2\text{O}_5$  samples made with AN: $\text{V}_2\text{O}_5 = 0.5:1$  (denoted hereafter as  $\text{V}_2\text{O}_5\text{-(AN)}_{0.5}$ ) are presented in Fig. 2. The intercalation of organic polymers into the interlayers of the  $\text{V}_2\text{O}_5$  xerogel is confirmed by the shift in (001) reflections to lower angles. For the as-prepared sample, an interlayer expansion from 12.03 to 13.55 Å is observed. This expansion is the consequence of removing one layer of  $\text{H}_2\text{O}$  (approximately 2.8 Å) and inserting one monolayer of PANI. The net interlayer expansion can, thus, be calculated to be 4.32 Å, which suggests that parallel polymer chains lie between the  $\text{V}_2\text{O}_5$  slabs [15]. Post-treatment at 70 °C in air or oxygen does not alter the interlayer spacing (13.55 Å for 70 °C—air and 13.46 Å for 70 °C— $\text{O}_2$ ), but a slight contraction takes place with higher temperature treatment (13.30 Å for 130 °C—air and 12.95 Å for 130 °C— $\text{O}_2$ ).

The XRD patterns for as-prepared and post-treated PANI-intercalated  $\text{V}_2\text{O}_5$  samples made with AN: $\text{V}_2\text{O}_5 = 3:1$  (denoted hereafter as  $\text{V}_2\text{O}_5\text{-(AN)}_{3.0}$ ). An interlayer expansion from 12.03 to 15.33 Å is displayed by the as-prepared sample. Taking into account the 2.8 Å of vacant space left by water removal, an interlayer expansion

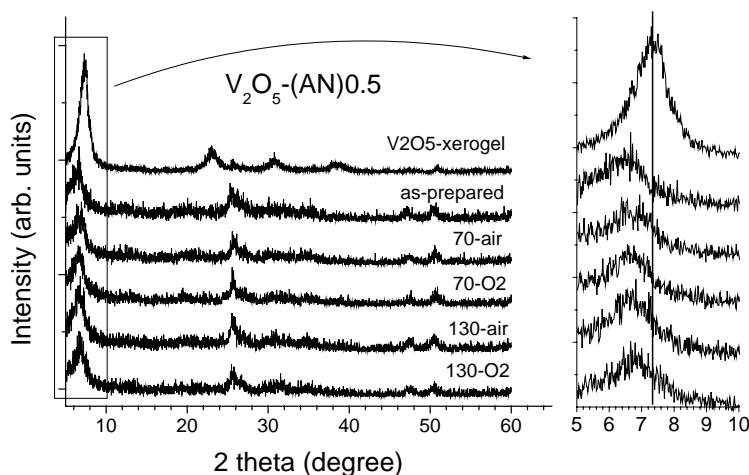


Fig. 2. Powder X-ray diffraction patterns for as-prepared and post-treated  $V_2O_5-(AN)0.5$ .

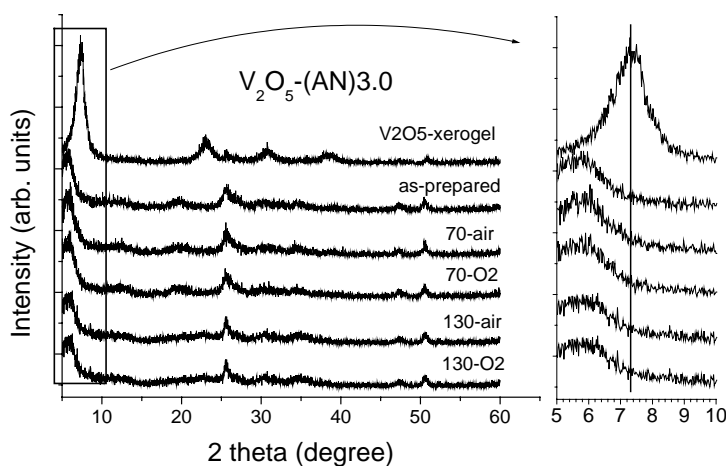


Fig. 3. Powder X-ray diffraction patterns for as-prepared and post-treated  $V_2O_5-(AN)3.0$ .

of 6.1 Å is estimated. This expansion is slightly larger than the thickness of the monolayer of PANI (5.3 Å) [15]. Post-treatment gives no significant change in the inter-layer spacing of  $V_2O_5-(AN)3.0$  samples, i.e. 70 °C—air (15.30 Å), 70 °C— $O_2$  (15.35 Å) and 130 °C—air and  $O_2$  (15.12 Å). The XRD analyses confirm that intercalated PANI is stable with respect to the applied post-treatment conditions, as expected from the TG–DSC analysis (Fig. 3).

The FT-IR spectra of as-prepared and post-treated samples of  $V_2O_5-(AN)0.5$  and  $V_2O_5-(AN)3.0$  are given in Figs. 4 and 5, respectively. The bands in the 1000–1800  $cm^{-1}$  range correspond to the typical PANI pattern [15], which confirms that an emeraldine form of PANI is formed by the oxidative intercalation reaction. These peaks are little affected by post-treatment, even at 130 °C. This is an indicative of almost no change in the emeraldine form. The three strong bands below 1000  $cm^{-1}$  are the characteristics of vanadium–oxygen stretching [16]. The vanadyl V=O vibration band at around 1015  $cm^{-1}$  in the  $V_2O_5$  xerogel, which is likely to be sensitive to the out-of-plane chemical environment, shifts down to 1000  $cm^{-1}$  upon intercalation of PANI into  $V_2O_5$ . This red

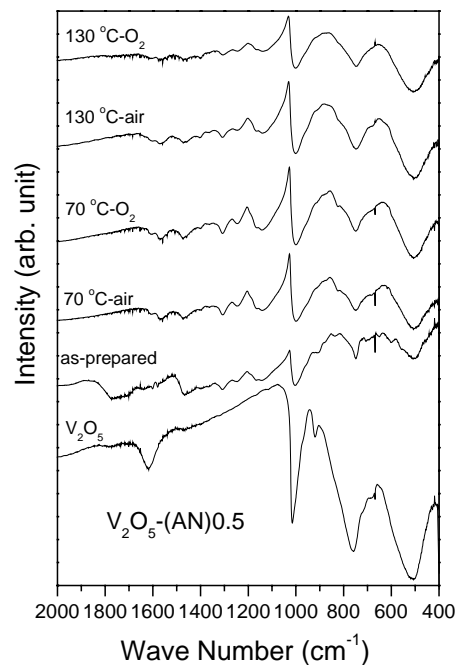


Fig. 4. FT-IR spectra for as-prepared and post-treated  $V_2O_5-(AN)0.5$ .

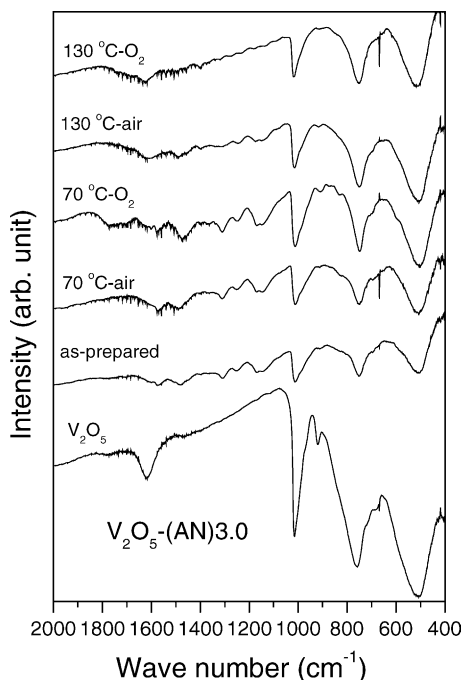


Fig. 5. FT-IR spectra for as-prepared and post-treated  $V_2O_5-(AN)3.0$ .

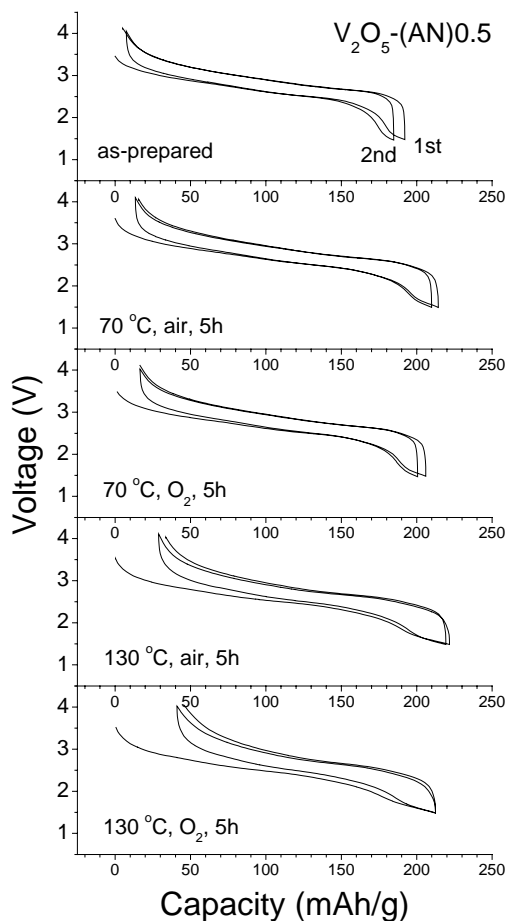


Fig. 6. Discharge-charge curves for as-prepared and post-treated  $V_2O_5-(AN)0.5$ . Data are collected under a constant current density of  $0.5 \text{ mA cm}^{-2}$  in 4–1.5 V range.

shift can be attributed to a bonding interaction between polyaniline and the inorganic lattice, via  $N-H \cdots O=V$  [2]. Post-treatment of  $V_2O_5-(AN)0.5$  has little influence on both the PANI peaks and the vanadyl vibration wavenumber. This shows that the chemical interaction between PANI and  $V_2O_5$  is maintained (Fig. 4). For  $V_2O_5-(AN)3.0$  samples, the intercalated PANI is little influenced by post-treatment at least at  $70^\circ\text{C}$  under both air and oxygen conditions, as can be seen in Fig. 5. Increase in temperature up to  $130^\circ\text{C}$  deteriorates the PANI structure, which is expected to exert an adverse effect on the electrochemical performance.

The influence of post-treatment conditions on the first and second discharge-charge characteristics of  $V_2O_5-(AN)0.5$  samples is demonstrated in Fig. 6. The discharge capacity is improved after post-treatment at  $70^\circ\text{C}$ , regardless of the chosen gas atmosphere, and there is good reversibility. With post-treatment at  $130^\circ\text{C}$ , the first discharge capacities are enhanced but are decreased on the second cycle. The  $V_2O_5-(AN)0.5$  sample post-treated at  $70^\circ\text{C}$  in air for 5 h exhibits the best performance.

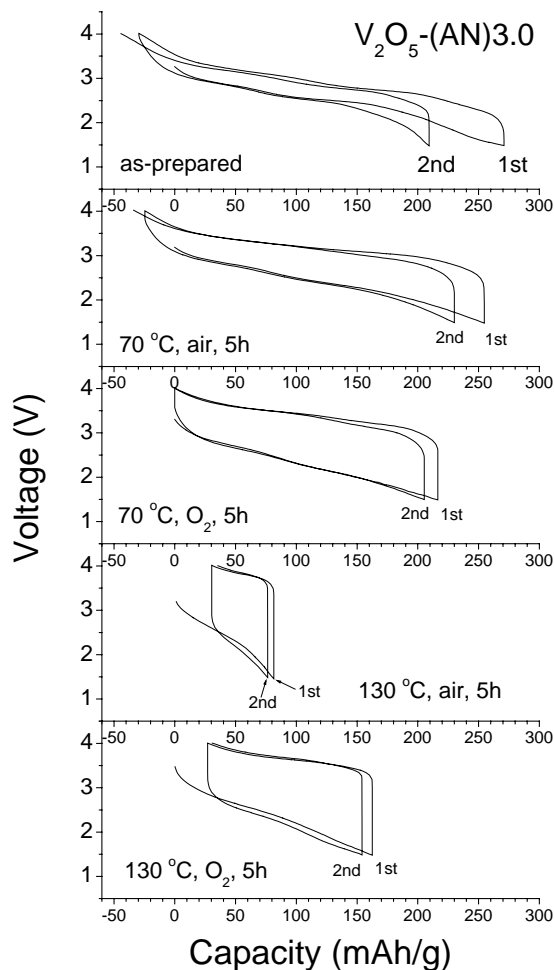


Fig. 7. Discharge-charge curves for as-prepared and post-treated  $V_2O_5-(AN)3.0$ . Data are collected under a constant current density of  $0.5 \text{ mA cm}^{-2}$  in 4–1.5 V range.

The first and second discharge–charge characteristics for the  $V_2O_5-(AN)_{3.0}$  samples before and after post-treatment are presented in Fig. 7. The discharge capacity and reversibility are not as good as those for the  $V_2O_5-(AN)_{0.5}$  samples, although the first discharge capacity is substantially improved for the as-prepared sample. After post-treatment, even at a low temperature of 70 °C, the discharge capacities are poor. There is serious polarization behaviour after heat-treatment at 130 °C which is due to the structural instability mentioned above.

#### 4. Conclusions

Factors that affect the discharge–charge performance of PANI-intercalated  $V_2O_5$  are investigated. The important conclusions are as follows:

- (i) In terms of the composition, the sample prepared by reacting 0.5 mol aniline with 1 mol  $V_2O_5$  is better than that obtained by reaction of 3 mol aniline with 1 mol  $V_2O_5$ .
- (ii) For the temperature used in post-treatment, 70 °C is better than 130 °C.
- (iii) For the atmosphere used in post-treatment at 70 °C, oxygen is not superior to air.

#### Acknowledgements

This work was supported by the Ministry of Information and Communication of Korea.

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