

# Electrochemical properties of VO–flyash composite for lithium polymer battery

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## Abstract

A VO–flyash composite electrode for a lithium/polymer battery (LPB) was developed. We investigated XRD diffraction and electrochemical properties of vanadium oxide (VO)–flyash composite with polyvinylidene (PVDF)/polyacrylonitrile (PAN)-based polymer electrolyte as a function of mixing ratio. The discharge capacity of VO–flyash with 50 wt.% V<sub>2</sub>O<sub>5</sub> in PVDF–PAN–PC<sub>5</sub>EC<sub>5</sub>iClO<sub>4</sub> electrolyte was 150 and 128 mAh/g at 1 and 10 cycles, respectively. The discharge capacity of VO–flyash with 85 wt.% V<sub>2</sub>O<sub>5</sub> was 195 mAh/g at 10 cycles. The capacity retention of VO–flyash anode with 3 wt.% V<sub>2</sub>O<sub>5</sub> was higher than that of VO–flyash cathode with 85 wt.% V<sub>2</sub>O<sub>5</sub>. The VO–flyash with 3 wt.% V<sub>2</sub>O<sub>5</sub> composite anode in PVDF/PAN-based electrolyte shows good capacity with cycling.

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**Keywords:** PVDF/PAN-based electrolyte; Lithium/polymer battery; VO–flyash composite

## 1. Introduction

Polymer electrolytes were discovered by Fenton et al. [1] in 1973. Wright [2] showed that complexes formed with PEO and alkali metal salts deliver high ionic conductivity. Subsequently these complexes were proposed by Armand et al. [3] as polymer electrolyte for solid-state battery and electrochemical device application. Polymer electrolytes have provided the attractive possibility of developing a new type of lithium battery, the so-called lithium/polymer battery (LPB) [4] with thin layers.

Carbon is known to be one of the anode materials for lithium rechargeable batteries. The capacity properties of carbon electrodes are based on the intercalation and deintercalation properties of the graphite structure [5]. Disordered carbon materials have attracted attention because of their high discharge capacity [6]. Cost reduction of LPB is essential to application such as power sources for portable electronic devices, electric vehicles and large-scale energy storage systems. Flyash finds reuse primarily in cementation products [7], stabilizing clay-based building materials [8]. A very large amount has been wasted of flyash in industry. Recycling of waste has become an issue for industries. The principal component of flyash is carbon. In recent publica-

tions, flyash have been regarded as an attractive alternative to carbon for use in lithium rechargeable batteries [9,10]. Wu et al. reported a method to improve the electrochemical properties of polymeric carbon by adding V<sub>2</sub>O<sub>5</sub> to the carbon precursors [11]. Also, they suggested that the added V<sub>2</sub>O<sub>5</sub> could form a nucleation agent, which results in an increased *d*<sub>002</sub> value and a modified carbon structure. We have studied a vanadium oxide (VO)–flyash composite with polymer electrolyte for lower price materials, not only for cathode active material but also for anode active material.

In this work, we investigated characteristics of charge/discharge cycling of VO–flyash composite as a function of addition of vanadium oxide with PVDF/PAN-based polymer electrolyte such as cathode and anode materials.

## 2. Experimental

Polyvinylidene-hexafluoropropylene (PVDF-HFP, Eif Atochem, Kynar 2801) and polyacrylonitrile (PAN, Aldrich) were dried under vacuum at 60 °C for 20 h. LiClO<sub>4</sub> (Aldrich) was dried under vacuum at 110 °C for 20 h before use. Propylene carbonate (PC) and ethylene carbonate (EC) were purchased from Aldrich. LiClO<sub>4</sub> was dissolved in PC–EC solutions. To PC–EC–LiClO<sub>4</sub> we added 10 wt.% PVDF-HFP and 10 wt.% PAN. The liquid electrolyte solution was homogeneously mixed by stirring. The polymer electrolyte film was prepared by casting and a rapid heating technique

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[12] at 110 °C for 10 min. The thickness of the electrolyte film was 100  $\mu\text{m}$ .

A VO-flyash composite was synthesized by the reaction of an intimately mixed preparation of  $\text{V}_2\text{O}_5$  (Aldrich) and flyash in various mass ratios. The flyash was collected from a power plant firing heavy oil at 1400–1600 °C. The amount of  $\text{V}_2\text{O}_5$  is reported as a mass percentage mass. The mixture was heated in the Ar at 800 °C for 2 h and cooled slowly in the furnace.

A composite slurry was prepared by mixing VO-flyash powder with carbon (SP270) and PVDF in NMP solution. The mixture slurry was stirred for 3 h. The composite films were prepared by coating this slurry on Cu and Al foil current collector. After solvent evaporation, the composite films were vacuum-dried at 110 °C for 24 h. The electrochemical behavior of the composite films was investigated in three-electrode cells with polymer electrolyte. The composite films were used as working electrode. Pure lithium metal was used as the counter and reference electrodes. PVDF-PAN-PC-EC-LiClO<sub>4</sub> was used as the electrolyte and separator. The components of test cell were stacked in polypropylene film. The size of each cell was 2 cm  $\times$  1 cm. The current density of charge/discharge cycling was 0.1 mA/cm<sup>2</sup>. Preparation and testing of cells were carried out in argon-filled glove box.

### 3. Results and discussion

Fig. 1 shows XRD pattern of the VO-flyash prepared by heating a reaction mixture of  $\text{V}_2\text{O}_5$  and flyash as a function of mass ratio at 800 °C in Ar. The VO-flyash with 3 and 50 wt.%  $\text{V}_2\text{O}_5$  can be indexed by assuming an amorphous mixture.

The first charge/discharge curve of VO-flyash cathode with 50 wt.%  $\text{V}_2\text{O}_5$  electrode in PVDF-PAN-PC<sub>5</sub>EC<sub>5</sub>LiClO<sub>4</sub> electrolyte at room temperature is shown in Fig. 2. The charge/discharge cycling was carried out between 4.0

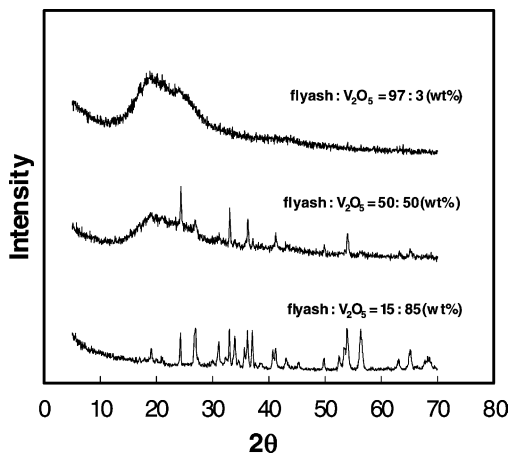


Fig. 1. XRD pattern of the VO-flyash prepared by heating method as a function of mass ratio at 800 °C in Ar.

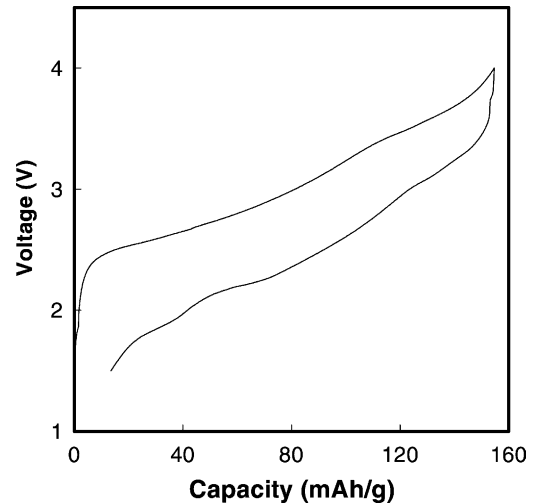


Fig. 2. Charge/discharge curve of VO-flyash with 50 wt.% /Li cell in PVDF-PAN-PC<sub>5</sub>EC<sub>5</sub>LiClO<sub>4</sub>.

and 1.5 V with a current density of 0.1 mA/cm<sup>2</sup>. At the charging process, the charge voltage plateau does not appear. The first charge capacity of VO-flyash with 50 wt.%  $\text{V}_2\text{O}_5$  was 155 mAh/g. The profile of the charge/discharge curve of VO-flyash with 85 wt.%  $\text{V}_2\text{O}_5$  electrode was identical. But the capacity of each charge/discharge was different.

The specific capacity of VO-flyash/Li cells as a function of addition ratio of  $\text{V}_2\text{O}_5$  is shown in Fig. 3. The charge/discharge cycling was carried out between 4.0 and 1.5 V with a current density of 0.1 mA/cm<sup>2</sup>. The discharge capacity of VO-flyash with 50 wt.%  $\text{V}_2\text{O}_5$  in PVDF-PAN-PC<sub>5</sub>EC<sub>5</sub>LiClO<sub>4</sub> electrolyte was 150 and 128 mAh/g at 1 and 10 cycles at room temperature, respectively. The discharge capacity decreased with charge/discharge cycling. However, the capacity retention of VO-flyash with 85 wt.%

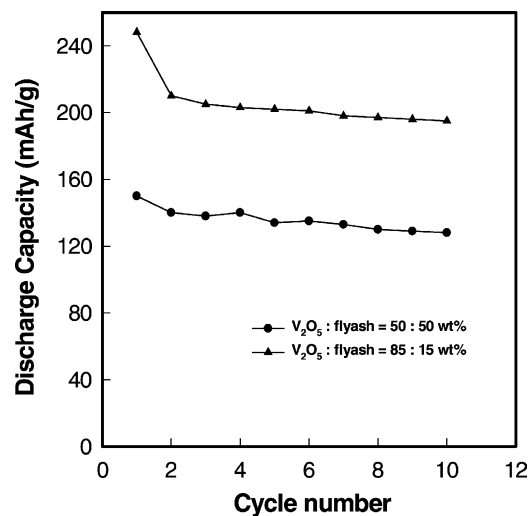


Fig. 3. Specific capacity of VO-flyash with 85 and 50 wt.% cathode in PVDF-PAN-PC<sub>5</sub>EC<sub>5</sub>LiClO<sub>4</sub>.

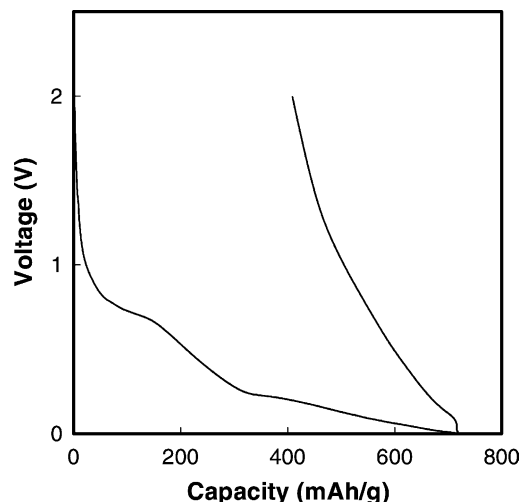


Fig. 4. Charge/discharge curve of VO-flyash with 3 wt.%/Li cell in PVDF-PAN-PC<sub>5</sub>EC<sub>5</sub>LiClO<sub>4</sub>.

V<sub>2</sub>O<sub>5</sub> was higher than that of VO-flyash with 50 wt.% V<sub>2</sub>O<sub>5</sub>. This difference of the discharge capacity was 52%. After the fourth cycling, the fading in capacity of VO-flyash with 85 wt.% V<sub>2</sub>O<sub>5</sub> was less than that of VO-flyash with 50 wt.% V<sub>2</sub>O<sub>5</sub>. Also, the charge/discharge efficiency was above 96% after the fourth cycle. The discharge capacity of VO-flyash with 85 wt.% V<sub>2</sub>O<sub>5</sub> was 195 mAh/g at 10 cycles. The capacity of the VO-flyash cathode is significantly affected by using a different mass ratio of flyash. From these results, we can conclude that VO-flyash cathode with 85 wt.% V<sub>2</sub>O<sub>5</sub> showed good capacity with cycling.

Fig. 4 shows the first charge/discharge curves of VO-flyash anode prepared by heating with 3 wt.% V<sub>2</sub>O<sub>5</sub> and Li electrode in PVDF-PAN-PC<sub>5</sub>EC<sub>5</sub>LiClO<sub>4</sub> electrolyte. The charge/discharge cycling was carried out between 2.0 and 0.0 V with current density of 0.1 mA/cm<sup>2</sup>. The initial open circuit voltage (OCV) of VO-flyash/Li cell was 3.1 V. The first discharge capacity of VO-flyash with 3 wt.% V<sub>2</sub>O<sub>5</sub> was 718 mAh/g. The profile of the charge/discharge curve seems to be that of hard carbon. This implies that added VO material does not achieve reaction of Li intercalation between 2.0 and 0.0 V.

Fig. 5 shows the specific capacity of VO-flyash with a 3 wt.% V<sub>2</sub>O<sub>5</sub> anode in PVDF-PAN-PC<sub>5</sub>EC<sub>5</sub>LiClO<sub>4</sub> at room temperature. The capacity retention of VO-flyash anode with 3 wt.% V<sub>2</sub>O<sub>5</sub> was higher than that of VO-flyash cathode with 85 wt.% V<sub>2</sub>O<sub>5</sub>. A large irreversible capacity is observed on the first cycle. The irreversible capacity of VO-flyash anode is 410 mAh/g. However, the irreversible capacities become much smaller than that of the first cycle. This means that the electrochemical behavior of VO-flyash with 3 wt.% V<sub>2</sub>O<sub>5</sub> is same that with disordered carbon. The charge/discharge efficiency was above 98% after the fifth cycle. The discharge capacity of VO-flyash composite was 264 mAh/g at 12 cycles. The optimization of VO-flyash composite in polymer

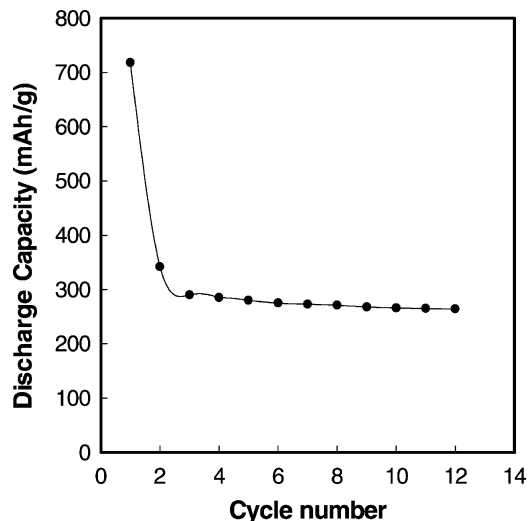


Fig. 5. Specific capacity of VO-flyash with 3 wt.%/Li cell in PVDF-PAN-PC<sub>5</sub>EC<sub>5</sub>LiClO<sub>4</sub>.

electrolyte is now on test in our laboratory. In these results, we suggest that the VO-flyash with 3 wt.% V<sub>2</sub>O<sub>5</sub> composite anode in PVDF/PAN-based electrolyte shows good capacity with cycling.

#### 4. Conclusions

On the basis of the results described above, we can come to the following conclusions; the discharge capacity of VO-flyash with 85 wt.% V<sub>2</sub>O<sub>5</sub> in PVDF-PAN-PC<sub>5</sub>EC<sub>5</sub>LiClO<sub>4</sub> electrolyte was 195 mAh/g at 10 cycle. VO-flyash cathode with 85 wt.% V<sub>2</sub>O<sub>5</sub> showed good capacity with cycling. The capacity retention of VO-flyash anode with 3 wt.% V<sub>2</sub>O<sub>5</sub> was higher than that of VO-flyash cathode with 85 wt.% V<sub>2</sub>O<sub>5</sub>. The electrochemical behavior of VO-flyash with 3 wt.% V<sub>2</sub>O<sub>5</sub> is same that with disordered carbon. The VO-flyash with 3 wt.% V<sub>2</sub>O<sub>5</sub> composite anode in PVDF/PAN-based electrolyte shows good capacity with cycling. These results suggest that VO-flyash can use low-cost material such as cathode and anode materials for lithium/polymer batteries.

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