Increase in Discharge Capacity of Li Battery Assembled with Electrochemically Prepared V₂O₅/polypyrrole-composite-film Cathode†

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Flexible composite films of V₂O₅ and conductive polypyrrole (V₂O₅/PPy) were grown by facile electrochemical polymerization, wherein an anodization potential was applied to the substrate electrode in an electrolyte solution containing pyrrole monomer and dispersed V₂O₅ particles. The coating of polypyrrole (PPy) on the surface of V₂O₅ particles was induced by the oxidative catalytic action of V₂O₅ during the electrochemical polymerization of pyrrole. PPy in the composite film connects the isolated V₂O₅ particles. This results in the formation of conductive networks in the composite film cathode, thereby enhancing the Li⁺ ion diffusion to the surface of the isolated V₂O₅ particles and thus increasing the accessibility of the Li⁺ ions. The specific capacity tests of the Li rechargeable batteries revealed that the discharge capacity of this composite film cathode was higher, i.e., 497 mAhg⁻¹, than that of V₂O₅/PPy powder or pristine V₂O₅.

Key Words: Inorganic-organic composite film, Electrochemical preparation, Conducting polymer film, Li battery

Introduction

Layer-structured metal oxides have attracted much attention because of their potential application in lithium batteries owing to their outstanding structural flexibility with regard to lithium insertion/desertion.¹,² Vanadium pentoxide has been intensively studied as a cathode material in lithium batteries because of its structural reversibility, thermal stability, and high theoretical capacity in lithium intercalation/deintercalation.³,⁴ In order to exploit the nanoscale thin solid-phase layered structures for increasing the capacity of rechargeable lithium batteries, amorphous V₂O₅ materials such as aerogels or xerogels have been used as intercalation cathodes.⁵,⁶ However, the low crystallinity of V₂O₅ gels or the presence of water within the gels has often proved to be a major stumbling block in providing consistent electrochemical properties as battery materials. These adverse effects often offset the advantage of having an extremely high surface-to-volume ratio for amorphous V₂O₅ materials. In addition to the high surface to volume ratio, the specific capacities can be increased by enhancing the Li accessibility or by increasing the conductivity of the electrode materials. The kinetic barriers induced by the limited Li ion accessibility within cathodes can be minimized by embedding inorganic electrode materials in conductive organic materials. Conductive polymers are attractive electrode materials owing to their electrochemical activities;⁸,⁹ (i) they can be charged and discharged by a redox reaction involving lithium ions or counter anions of the electrolyte, (ii) they can be used to coat crystalline surfaces to enhance the electrical conductivity, and (iii) they can connect isolated crystalline particles with improved mechanical flexibility. Among various conductive polymers, PPy has been used extensively because of its high electrical conductivity, stability in electrochemical environments, and relatively easy preparation methods.¹⁰-¹² The composite powders of inorganic crystallites with polypyrrole have been investigated to overcome the inherently low electronic conductivity of inorganic crystallites and to obtain favorable electrochemical characteristics.¹³-¹⁷ In the present study, V₂O₅ and polypyrrole composite (V₂O₅/PPy) films were grown by an electrochemical polymerization method wherein an anodic potential was applied to a substrate electrode in a solution containing a pyrrole monomer and dispersed V₂O₅ particles. The use of these composite films increases the discharge capacity owing to their high conductivity, better Li⁺ ion accessibility, and improved diffusion pathways. Mechanically flexible V₂O₅ and polypyrrole composite films offer cyclic stability during the expanding and shrinking of V₂O₅ particles. Recently, there have been a few attempts to develop mechanically flexible rechargeable batteries containing only organic polymers, but the preparation of flexible electrodes containing inorganic oxide materials still remains a challenge.¹⁸,¹⁹ The strategy of this work involves facile formation of the composite films by electrochemical polymerization of the pyrrole monomer in the V₂O₅-dispersed electrolyte solution, thereby obtaining composite films with high capacity and stability.

Experimental

V₂O₅/PPy composite films were synthesized by an electrochemical polymerization of pyrrole on a stainless-steel (SS) gauze-electrode (SUS304-150 mesh, 90 μm thick, 17 mm diameter disk) in an electrolyte solution (0.1 M LiClO₄) containing both the pyrrole monomer (0.20 M) and well-dispersed V₂O₅ particles (14 mgmL⁻¹). Following the method outlined, the V₂O₅/PPy composite films were grown on the SS substrate.
istics of the V2O5/PPy composite electrodes with V2O5 powder in battery test mode. In order to compare the battery character-
tistics of these cathodes was tested using a battery test system (Maccor 3000) and a scanning electron microscope [SEM, JEOL JSM-6700F]. Cyclic voltammograms (CVs) were recorded using a Pine AFRDE4 Bi-potentiostat/galvanostat at a scan rate of 10 mVs⁻¹ in a potential limit from 1.5 to 4.5 V in a three-electrode cell system with a Li/Li⁺ reference electrode, an V2O5/PPy com-
posite film as working electrode, and a Pt-grid counter electrode. A 1.0 M lithium perchlorate in a propylene carbonate (PC) solution was used as the electrolyte; lithium perchlorate and PC were used after recrystallization and distillation, respecti-
vely. The batteries employed in this study were a series of the coin-type CR2032 lithium rechargeable batteries based on the cathodes of the V2O5/PPy composite film, V2O5/PPy composite powders, and V2O5 powder. They were assembled in a dry room. The other parts of the assembled batteries were a lithium-
metal plate as a negative electrode (anode) and a polypropylene (PP) separator soaked in a 1.0 M LiPF6 electrolyte solution in ethylene carbonate (EC)/dimethyl carbonate (DMC). The final composition and the morphology of the V2O5/PPy com-
posites were characterized by an FT-IR spectrophotometer [Nicolet iS10], a thermal gravity analyzer [Mac Science, MTC 1000], and a scanning electron microscope [SEM, JEOL JSM-6700F]. Cyclic voltammograms (CVs) were recorded using a Pine AFRDE4 Bi-potentiostat/galvanostat at a scan rate of 10 mVs⁻¹ in a potential limit from 1.5 to 4.5 V in a three-electrode cell system with a Li/Li⁺ reference electrode, an V2O5/PPy composite film as working electrode, and a Pt-grid counter electrode. A 1.0 M lithium perchlorate in a propylene carbonate (PC) solution was used as the electrolyte; lithium perchlorate and PC were used after recrystallization and distillation, respectively. The batteries employed in this study were a series of the coin-type CR2032 lithium rechargeable batteries based on the cathodes of the V2O5/PPy composite film, V2O5/PPy composite powders, and V2O5 powder. They were assembled in a dry room. The other parts of the assembled batteries were a lithium-
metal plate as a negative electrode (anode) and a polypropylene (PP) separator soaked in a 1.0 M LiPF6 electrolyte solution in ethylene carbonate (EC)/dimethyl carbonate (DMC). The final form of the positive electrode for the coin-type Li cell was prepared by rolling the pristine V2O5/PPy composite film on the SS gauze. The thickness of the positive electrode was approximately 180 μm including the SS gauze. The performance of these cathodes was tested using a battery test system (Maccor series 4000) and cycled galvanostatically in a multichannel battery test mode. In order to compare the battery characteristics of the V2O5/PPy composite electrodes with V2O5 powder electrodes, V2O5 powder was mixed with acetylene carbon black and polytetrafluoroethylene (PTFE) binder to make the V2O5 electrodes without any conducting polymer. For the powder materials, a thin pellet (approximately 90 μm thick after rolling) electrode was conventionally made using Doctor Blade method after slurrying in a solvent.

Results and Discussion

The V2O5/PPy composite films were grown on the electrode surfaces in a solution of pyrrole containing dispersed V2O5 particles using the electrochemical oxidative polymerization method previously described. It is well known that V2O5 has the ability to oxidize pyrrole and that the oxidation of pyrrole should take place on the surface of the V2O5 particles. Additionally, the V2O5/PPy composite powders were also produced from the same electrolyte solution. The V2O5 particles had dual functions: (i) as an oxidative catalyst for the polymerization of pyrrole in the electrolyte solution, and (ii) as an embedded particle component of the V2O5/PPy composite powders. All the composite films formed on the substrate-electrode and the composite powders formed in the electrolyte solution were in brownish-black color. This, coupled with SEM analysis, con-

![Figure 1. FT-IR spectra of (a) V2O5/PPy composite powder, (b) V2O5/PPy composite film prepared by electrochemical method, (c) PPy-only powder prepared using catalyst (FeCl3), and (d) PPy-only film prepared by electrochemical method using LiClO4 electrolyte solution.](image)

firms the coating of PPy on the surface of the yellow colored V2O5 particles, i.e., PPy-coated V2O5. The structural, composi-
tional, and morphological characterization of the V2O5/PPy composites has afforded insight into their electrochemical be-
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such as FeCl₃ or ammonium persulfate, in a solution which contains no electrolyte. The relative intensities of the IR absorption bands corresponding to V₂O₅ and PPy indicate the relative amounts of each component in the V₂O₅/PPy composites prepared. The relative absorption-band intensity of V₂O₅ to PPy of the composites is larger in the powder forms than in the film forms. The weight ratio of the V₂O₅/PPy composites was determined by thermogravimetric analysis (TGA). Since the combustion of the polymer is normally completed below 500 °C, the V₂O₅ content in the composites is estimated from the TGA data, as shown in Fig. 2. The composition of the V₂O₅/PPy powders obtained from the electrolyte solution corresponded to the amount of each component initially added to the solution; 80 (± 0.5) wt % of V₂O₅. In the electrochemically prepared composite film, a V₂O₅ particle content of 37 (± 5) wt % was obtained. The V₂O₅ content in the composite film electrodes prepared in this work was normally lower than that of the composite powders formed from the electrolyte.

SEM images of the V₂O₅/PPy composites are shown in Fig. 3. The irregular- or sphere-shape morphology of the V₂O₅/PPy composite films (Figs. 3(a) and 3(b)) is similar to the original irregular- or sphere-shape morphology of V₂O₅ (Figs. 3(c) and 3(d)). We did not observe any cauliflower-shaped or other shaped PPy lumps in the V₂O₅/PPy composite films. As shown in Fig. 3(e), the morphology of PPy film grown from pyrrole only typically shows a cauliflower-like shape. This work demonstrates that one can electrochemically synthesize composite films of conductive PPy with embedded V₂O₅ without employing an elaborate template or catalyst. Moreover, the V₂O₅/PPy composite powders can also be obtained from the electrolyte solution.

A series of cyclic voltammetric tests were performed on the composite films in an effort to evaluate the electrochemical properties of thus prepared V₂O₅/PPy composite films. Fig. 4 shows cyclic voltammograms (CVs) of the V₂O₅/PPy composite film in the potential range of 1.5 and 4.5 V versus Li/Li⁺ reference electrode in 1.0 M LiClO₄ propylene carbonate solution. The CVs obtained from the V₂O₅/PPy composite films exhibit
broad anodic waves at approximately 3.2 and 3.8 V during the anodic scan from 1.5 to 4.0 V, and cathodic waves at approximately 3.7 and 2.5 V during the cathodic scan from 4.0 to 1.5 V. These two anodic waves correspond to two consecutive Li$^+$ insertions into the composite film electrode. Similarly, the two cathodic waves can be attributed to two consecutive Li$^+$ insertions into the composite film electrode. This cyclic voltammogram confirms that the lithium ion can be quasi-reversibly intercalated (inserted) into and deintercalated from the vanadium oxide lattice, according to the following equation: V$_2$O$_5$ + xLi$^+$ + xe$^-$ ⇌ Li$_x$V$_2$O$_5$, at amounts of two equivalents (x = 2) per V$_2$O$_5$, as previously reported.\textsuperscript{1-3} The CV of the PPy-only film electrode is also shown in Fig. 4(b) for a comparison. The PPy-only film reveals reversible anodic and cathodic waves at approximately 3 V with fairly low current.

The performance of the V$_2$O$_5$/PPy composite film as a cathode for a Li battery was tested and compared with those of the V$_2$O$_5$/PPy composite powder and pristine V$_2$O$_5$ powder by assembling coin-type Li cells with a battery test system. During these tests, for the purpose of initial conditioning, the initial charge-discharge cycle was at a slow rate, 0.2 C, and the following two cycles were at 0.5 C rate. The remaining 45 charge-discharge cycles were performed at 1.0 C rate (295 mAg$^{-1}$). Fig. 5 shows these initial discharge curves of the lithium batteries assembled with cathodes of (a) the V$_2$O$_5$/PPy composite film, (b) the V$_2$O$_5$/PPy composite powder pellet, and (c) pristine V$_2$O$_5$ powder pellet. All these curves show multiple distinctive voltage plateaus, which are known to be related to the structural modifications of V$_2$O$_5$ induced by the lithium insertion during the discharging process.\textsuperscript{1,2,20} The voltage plateaus appearing at above 3 V correspond to the structural modifications from potential plateaus that appear at the lower voltage levels are attributed to the structural modifications related to Li$^+$ insertion of greater than one equivalent. The plateaus in the vicinity of 2.3 V for the (a) V$_2$O$_5$/PPy composite film, (b) V$_2$O$_5$/PPy composite powder pellet, and (c) pristine V$_2$O$_5$ powder pellet are extended to the specific capacity values of approximately 292, 270, and 235 mAhg$^{-1}$, respectively. Considering that the theoretical limits of the specific capacities of V$_2$O$_5$ for one equivalent and two equivalents of Li$^+$ intercalation are 147 and 295 mAhg$^{-1}$ respectively, it is worth mentioning that the V$_2$O$_5$/PPy composite film case is reaching the theoretical limits in both one and two equivalents. Further discharge of the batteries leads to another plateau at approximately 2.0 V with an electrochemical insertion above two equivalents of Li$^+$ into the lattices and the ensuing the formation of Li$_3$V$_2$O$_5$ (x = 3 for Li$_x$V$_2$O$_5$) during the first discharging process to the extended potential range. As shown in Fig. 5 for three initial discharge curves (a) and (b) and (c), the plateaus in the vicinity of 2.0 V are extended to the specific capacity values of approximately 497, 418, and 368 mAhg$^{-1}$, respectively. The specific capacities for the composite cases of (a) and (b) and (c) are significantly higher than the values reported in Refs. 1-3, 20-23, which reported 400 mAhg$^{-1}$ as the highest discharge specific capacity for cathodes comprising of various forms of V$_2$O$_5$.

It can be seen in Fig. 5 that, compared to the pristine V$_2$O$_5$, the V$_2$O$_5$/PPy composite powder has the higher specific capacity throughout the whole initial discharge curves. Conductive PPy polymer in the V$_2$O$_5$/PPy composite powder electrode evidently has aided with the Li$^+$ insertion into the Li$_3$V$_2$O$_5$ lattice of the composite electrode, by improving both the accessibility of Li$^+$ ion and the electrical conductivity. Conductive polymers in the composite films can connect the isolated V$_2$O$_5$ particles and give rise to valid conductive networks in the electrodes. Furthermore, the V$_2$O$_5$/PPy composite film possesses the greatest specific capacity, indicating that the conductive PPy polymer film formed by the electrochemical method is even more effi-
the battery assembled with the V2O5/PPy composite film can be concluded that the contribution to the capacity from the oxidation and reduction of polypyrrole itself to the redox current of the composite electrode is small when compared to the contribution of V2O5 in the V2O5/PPy composite films. Rather, the mechanically flexible, electrically conductive, and electrochemically active organic polymers enhance the specific capacities by connecting isolated V2O5 particles thus, creating valid conductive networks for lithium ions and/or counter anions of the electrolyte for the electrode. This enables increased activation of the isolated V2O5 particles and allows them to be employed for the lithium intercalation/deintercalation in the composite film during the battery cycling. In addition, the polypyrrole itself is also oxidized and reduced involving lithium ions or counter anions of the electrolyte. Owing to the synergistic effect (discussed above) between the inorganic and organic components of the composite films, the V2O5/PPy composites possess significantly larger specific capacities compared to the simple algebraic summation of the specific capacities of the pristine V2O5 and PPy. This synergistic effect is evidently further emphasized in the case of the electrochemically formed film as shown in Figs. 5(a) and 7(a), compared to the case of the powder as shown in Figs. 5(b) and 7(b). This interesting phenomenon is initially attributed to the enhanced diffusion of lithium to the surface of the isolated V2O5 particles and increased the accessibility of the lithium ion. However, further investigations are underway in this work.

Conclusions

In this work, V2O5/PPy composite films have been synthesized by an electrochemical method. Charge/discharge cycling data of a rechargeable Li battery have shown that the V2O5/PPy composite films can be potentially used as high-capacity cathode materials with an initial discharging capacity of 497 mAh g⁻¹ (at 0.1 C rate) and a 48th discharging capacity of 221 mAh g⁻¹ (at 1 C rate). The composites consisting of a layer-structured metal oxide and a conducting polymer result in a synergistic interaction between the inorganic and organic components. The V2O5/PPy composite electrodes have higher specific capacities than the V2O5 electrode for Li batteries owing to the improved electronic conductivity and the enhanced lithium-ion accessibility in the cathode. The conductive polymers in the composites efficiently connect the isolated V2O5 particles, resulting in the formation of conductive networks in the electrode. Thus, a synergistic interaction between the inorganic and organic components of the V2O5/PPy composites is evident.

Figure 7: Specific capacities of lithium batteries assembled with cathode of (a) V2O5/PPy composite film, (b) V2O5/PPy composite powder, (c) pristine V2O5 powder, and (d) PPy-only film. For the purpose of initial conditioning, the first charge-discharge cycle was at 0.2 C rate and the following two cycles at 0.5 C rate. The remaining 45 cycles were all at 1C rate (295 mAg⁻¹).
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