Novel Method for Synthesis of γ-Lithium Vanadium Oxide as Cathode Materials in Lithium Ion Batteries

Jinxiang Dai,[†] Sam F. Y. Li,*[,†,‡] Zhiqiang Gao,[†] and Kok Siong Siow[†]

Department of Chemistry and Institute of Material Research and Engineering, National University of Singapore, 10 Kent Ridge Crescent, Republic of Singapore 119260

Received March 10, 1999. Revised Manuscript Received July 23, 1999

γ-$Li_xV_2O_5$ ($x = 0.9-1$) was synthesized at 350 °C. The material was characterized by X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FT-IR). The synthesis reactions were studied by thermogravimetric analysis (TGA). The composition of γ-$Li_xV_2O_5$ was determined by atomic absorption spectrophotometry (AAS) and inductively coupled plasma−atomic emission spectrophotometry (ICP-AES). Its electrochemical performance as cathode active materials was studied by galvanostatic charge−discharge and cycle voltammetry. γ-$Li_xV_2O_5$ could deintercalate lithium ion reversibly. The potential vs Li^+/Li electrode was from 2.6 to 4.0 V. γ-$Li_xV_2O_5$ has *potential* as starting electrode active material in lithium ion batteries.

Introduction

Vanadium oxides have been widely studied as cathode-active materials in lithium rechargeable batteries because of their low cost and low toxicity.[1−6] Some of them have been used in lithium rechargeable batteries. $V_2O_5-P_2O_5$ amorphous (a-V_2O_5) compounds can intercalate more than two lithium ions per formula. The cyclability is satisfactory when the potential window is 1.8−3.8 V.[4] Xerogel V_2O_5 (X-V_2O_5) can reversibly intercalate 1.8 lithium ions per formula corresponding to the quasi-reduction of vanadium from +5 to +4.[7] Both a-V_2O_5 and X-V_2O_5 cathode active materials are in the lithium deintercalated state. They cannot be used in lithium ion batteries in which carbon is used as anode-active materials. According to the "rocking-chair" mechanism the cathode-active materials must be lithium sources and carbon cathode-active materials must be lithium sinks.[8] The cathode-active materials must be in full lithiated state. Layered $Li_xV_2O_4$ synthesized by hydrothermal method[9] may be utilized as cathode material. However its reversible lithium ion deintercalation is less than 0.6 Li^+ per formula (95 (mA h)/g) in voltage of 2.5−4.1V. The available lithiated vanadium oxide is γ-$Li_xV_2O_5$ with two-dimensional layer structures. The orthorhombic lattice consists of VO_5 pyramids sharing edges and forming double ribbons parallel to the *b* axes. The ribbons are connected by pyramid corners to form puckered [V_2O_5] layers in the [010] plane as shown in Figure 1.[10−12] The electrochemical active γ-$Li_xV_2O_5$ has previously been obtained by electrochemical method (battery discharge method) and analyzed by XRD.[13] Although it can reversibly deintercalate and intercalate 0.9 lithium ion per formula in the voltage window of 2.8−3.8 V, it cannot be used in lithium ion batteries because its initial state is V_2O_5, the fully deintercalated state. For high-temperature synthesized γ-$Li_xV_2O_5$, only 0.5 lithium atom per V_2O_5 group can be deintercalated up to 3.8 V vs Li/Li^+ electrode.[14,15] For low-temperature prepared γ-$Li_xV_2O_5$ obtained by annealing δ-$Li_xV_2O_5$ at 350 °C, lithium can be deintercalated completely at 3.8

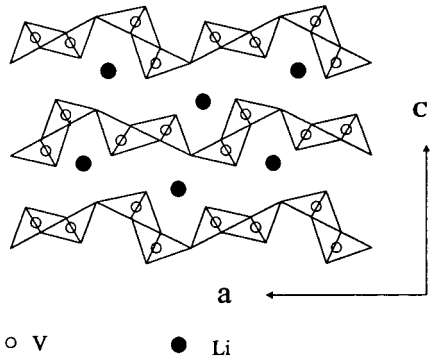

Figure 1. Structural description of γ-$Li_xV_2O_5$.

[†] Department of Chemistry.
[‡] Institute of Material Research and Engineering.

(1) Le, D. B.; Passerini, S.; Coustier, F.; Guo, J.; Soderstrom, T.; Cwens, B. B.; Smyrl, W. H. *Chem. Mater.* **1998**, *10*, 682.
(2) Okada, S.; Yamaki, J. Extended Abstracts of the 176th Meeting of the Electrochemical Society; Hollywood, CA, 15−20 Oct, 1989; P62.
(3) Cocciantell, J. M.; Menetrier, M.; Delmas, C.; Doumerc, J. P.; Pouchard, M.; Broussely, M.; Labat, J. *Solid State Ionics* **1995**, *78*, 143.
(4) Sakurai, Y.; Yamaki, J. I. *J. Electrochem. Soc.* **1988**, *135*, 791.
(5) Minett, M. G.; Owen, J. R. *J. Power Sources* **1990**, *32*, 81.
(6) Cocciantell, J. M.; Brousely, M.; Doumerc, J. P.; Labat, J.; Poachard, M. *J. Power Sources* **1991**, *34*, 103.
(7) West, K.; Chistiansen, B. Z.; Ostergard, M. J. L. *J. Power Sources* **1987**, *20*, 165.
(8) Scrosati, B. Insertion Compounds for Lithium Rocking Chair Batteries. In *The Electrochemistry of Novel Materials*; Lipkouski, J., Ross, P. N., Eds.; VCH: New York, NY, 1994; p 111.
(9) Chirayil, T.; Zavalij, P. Y.; Whittingham, M. S. *Chem. Mater.* **1998**, *10*, 2629.
(10) Galy, J.; Hardy, A. *Acta Crystallogr.* **1965**, *19*, 432.
(11) Hardy, A.; Galy, J.; Casalot, A.; Pouchard, M. *Bull. Soc. Chim. Fr.* **1965**, *4*, 1056.
(12) Ueda, Y. *Chem. Mater.* **1998**, *10*, 2653.
(13) Labat, J. (St Medard en Jalles); Cocciantelli, J.-M. (Talence) US Patent 5219677.
(14) Liaw, B.; Raistrick, I. D.; Huggins, R. A. *Solid State Ionics* **1986**, *18−19*, 828.
(15) Cocciantelli, J. M.; Ménétrier, M.; Delmas, C.; Doumerce, J. P.; Pouchard, M.; Hagenmuller, P. *Solid State Ionics* **1992**, *500*, 99.

10.1021/cm9901461 CCC: $18.00
Published on Web 10/09/1999

V vs Li/Li^+. However, δ-$Li_xV_2O_5$ has to be obtained by reaction of LiI (1.5 M in CH_3CN) with α-V_2O_5.[15,16] The high cost and sensitivity to moisture of LiI and CH_3CN make it not viable as a low cost and low toxicity cathode material. We used LiOH, CH_3COOH, and NH_4VO_3 as starting materials to synthesize γ-$Li_xV_2O_5$ ($x = 0.9-1$). It can reversibly deintercalate and intercalate 0.9 lithium ions per formula, corresponding to 120 (mA h)/g specific capacity. The voltage vs Li^+/Li electrode was 2.6−4.0 V. It may become a desirable cathode active material to be used in lithium ion batteries.

Experimental Section

Synthesis and Analysis of γ-$Li_xV_2O_5$. γ-$Li_xV_2O_5$ ($x = 0.9-1$) was synthesized by the reaction of NH_4VO_3, LiOH, and CH_3COOH.[17] The composition of the products was analyzed with atomic absorption spectrophotometry (AAS) and inductively coupled plasma−atomic emission spectrophotometry (ICP-AES). The solid mixture obtained after evaporation of water from blended solution of LiOH, CH_3COOH, and NH_4VO_3 and drying at 110 °C in an oven for 1 h was used in thermogravimetric analysis (TGA) experiments. The TGA was performed in an N_2 atmosphere with a Universal V1.10B system supplied by TA Instruments. The XRD patterns were obtained using a SIEMENS D5005 X-ray powder diffractometer. X-ray profiles were measured between 6° and 60° 2θ using a monochromatized Cu Kα radiation source ($\lambda = 1.5418$ Å). The morphologies of the sample particles were examined with a JEOL-JSM35CF scanning electron microscope. The IR absorption spectra of the prepared samples were obtained by KBr pellet method using a BIO-RAD FTS165 FT-IR spectrometer.

Preparation and Electrochemical Studies of Electrodes and Cells. The composite cathode consisted of 80% active material, 15% graphite, and 5% poly(vinylidene fluoride) (PVDF), which were blended in 1-methyl-2-pyrrolidone to form the slurry that was deposited on the aluminum disk. The lithium anodes were made by pressing the lithium foil on nickel disks. The separator was micropolypropylene membrane. A cell was prepared by assembling cathode, separator, and anode in a sandwich-like manner. The electrolyte was prepared by dissolving $LiClO_4$ (1 M) in a blended solvent of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 volumetric ratio). The galvanostatic charge−discharge and cycle voltammetry were performed by electrochemical test instrument Model-273 supplied by an EG&G Princeton Applied Research.

Results and Discussion

TGA Results and Preparation Reaction. According to the preparation process, NH_4VO_3, LiOH, and CH_3COOH in a molar ratio of 1:1.2:1.2 were dissolved in deionized water at boiling temperature. While the solution was kept a boiling, the pink solid mixture was obtained after evaporation of the water. The reaction can be expressed in following equation:

$$2NH_4VO_3 + 1.2LiOH + 1.2CH_3COOH \rightarrow 0.67NH_4V_3O_8\cdot H_2O + 1.2CH_3COOLi + 0.75NH_3 + 1.2H_2O \quad (1)$$

Equation 1 can be verified by comparing the weights of solid mixed products and the reactants. The pink solid mixture was also analyzed with powder X-ray diffraction, and $NH_4V_3O_8\cdot H_2O$ and CH_3COOLi was identified. The solid mixture can produce final the product of γ-$Li_xV_2O_5$ ($x = 0.9-1$) after heating at 300−500 °C in N_2 for 10 h. The TGA result of the solid mixed products is illustrated in Figure 2. The two weight loss steps can be explained by two reaction steps. The first weight loss begins at 120 °C and ends at 230 °C. The weight loss at 230 °C is 13.61%. In the fist step, the peak of differential curve is at 191.4 °C. The second step is from 230 to 312.0 °C. The weight loss at 312 °C is 21.12%, and residue weight is 65.33% of initial weight. The peak of differential curve is at 285.7 °C. There is no further weight loss until 800 °C. From the TGA results, the following reaction equations can be hypothesized:

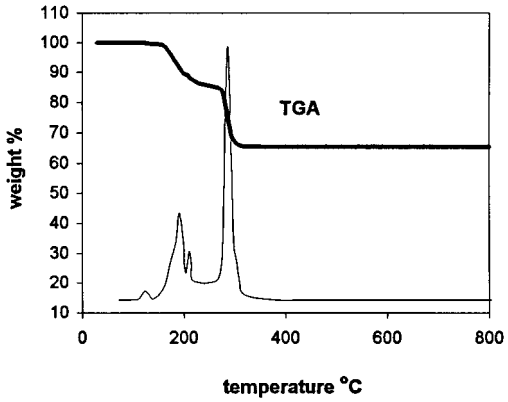

Figure 2. TGA of the solid mixture produced from mixed solution of NH_4VO_3, LiOH, and CH_3COOH.

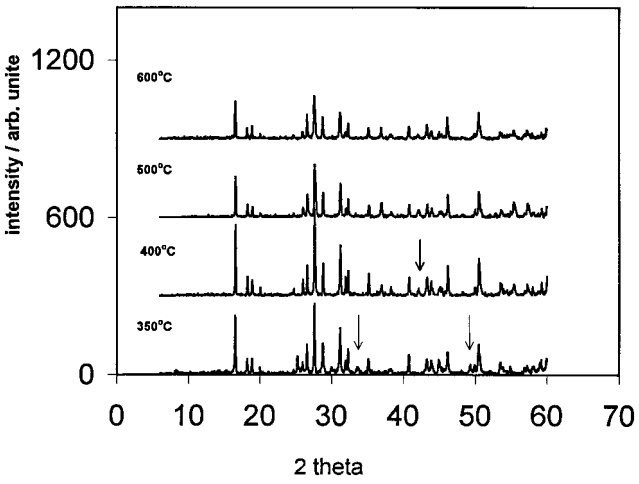

Figure 3. The XRD patterns of samples synthesized at different temperatures.

$$0.67NH_4V_3O_8\cdot H_2O + 1.2CH_3COOLi \rightarrow 0.67NH_4V_3O_8 + 0.533CH_3COOLi + 0.67LiOH + 0.67CH_3COOH \quad (2)$$

$$0.67NH_4V_3O_8 + 0.533CH_3COOLi + 0.67LiOH \rightarrow LiV_2O_5 + 0.1Li_2O + G \quad (3)$$

"G" in eq 3 represents gas products evaporated in the second step reaction and they may be N_2H_4, $CH_3COOCOCH_3$, $CH_3COOOCOCH_3$, H_2O, and O_2, etc. From eq 2, CH_3COOH can be eliminated during the thermal treatment and the calculated weight loss should be 13.64%, agreeing with the TGA results of 13.61%. From eq 3, the calculated weight loss should be 20.91%,

(16) Murphy, D. W.; Christian, P. A.; Disalvo, F. J.; Waszczak, J. V. *Inorg. Chem.* **1979**, *18*, 2800.
(17) Li, S. F. Y.; Dai, J.; Gao, Z.; Siow, K. S. Singapore Patent Appl. No. 9801487-1.

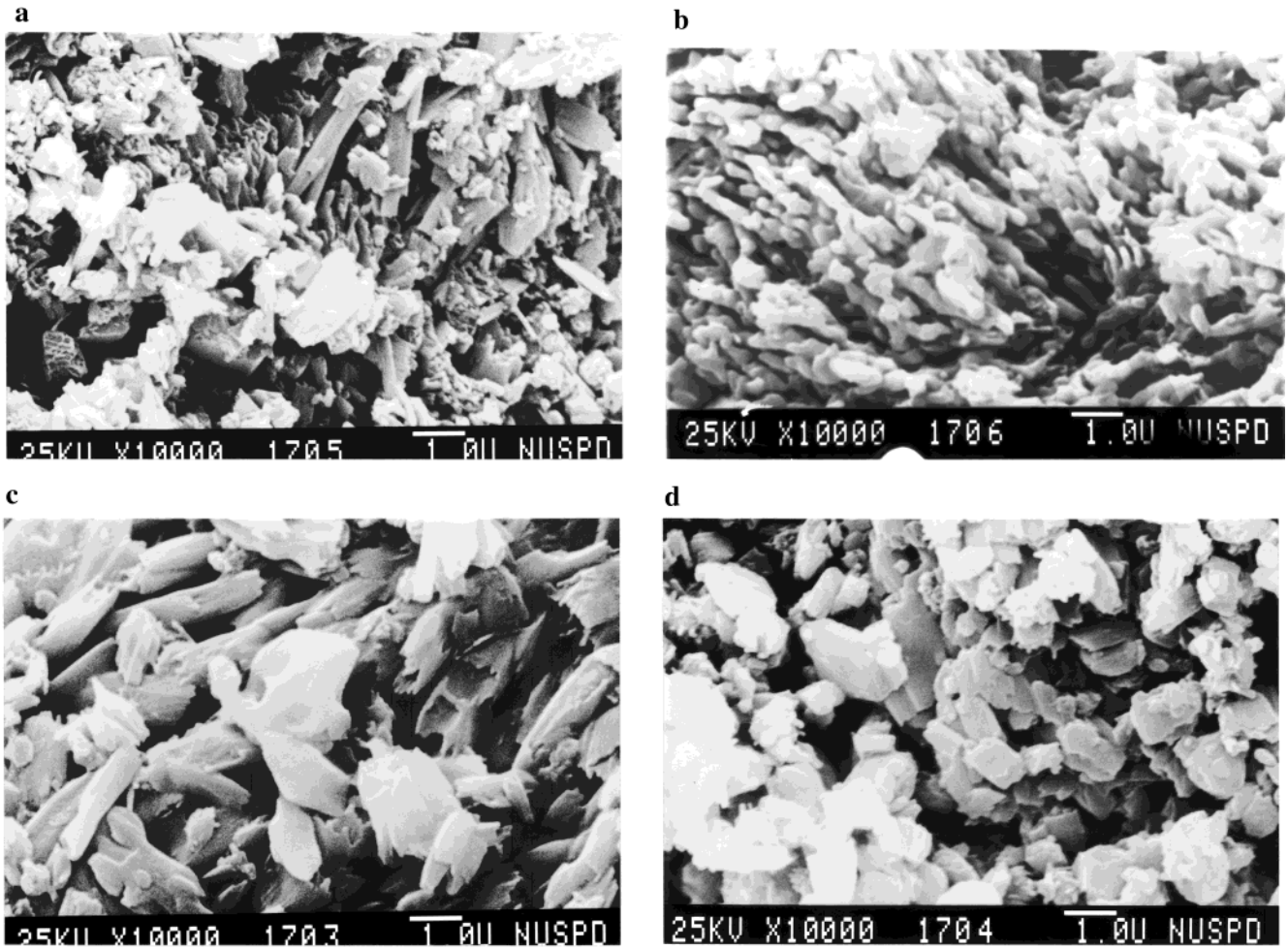

Figure 4. SEM picture of the samples synthesized at different temperatures.

agreeing with the TGA results of 21.12%. The calculated reaction product weight should be 65.4% weight of reactants, agreeing with the TGA result of 65.33%.

Composition and Elemental Analysis. $Li_xV_2O_5$ ($x = 0.9-1$) is produced in an N_2 atmosphere. The vanadium should be reduced from +5 to a lower valence state by NH_3 or acetate. The final valence is determined by the x value. When reactant molar ratio of NH_3VO_3/LiOH/CH_3COOH was 2:1.2:1.2, the composition of the product is $Li_{0.96}V_2O_{4.89}$, corresponding to +4.41 of vanadium. For simplicity, it is termed as $Li_xV_2O_5$ ($x = 0.9-1$). The elemental analysis results show that part of the lithium compounds could be washed out during the final wash step with water. The washed out lithium compounds should be Li_2O according to eq 3. The elemental analysis results agree with TGA results and proves that the wash with water is necessary.

The XRD and the Structure of $Li_xV_2O_5$. The XRD of the products synthesized at different temperatures are illustrated in Figure 3. From XRD patterns of the products and JCPDS data,[18] it can be seen that the as-synthesized products are γ-$Li_xV_2O_5$. There are not significant differences between the products synthesized at different temperatures. However, if the patterns are analyzed further, the slight differences can be found between the 350 °C sample and other samples. There are some small diffraction peaks in the 350 °C diffraction pattern, which are not found in the other diffraction patterns, such as those labeled with arrows. The difference may be caused by phase impurity in the 350 °C sample. TGA results have revealed that the reaction can be completed at a temperature higher than 320 °C, and the weight does not change any further after 320 °C. However small amounts of of other phases of $Li_xV_2O_5$ can change to γ-$Li_xV_2O_5$ only at a temperature higher than 350 °C.

The Morphology of the Synthesized γ-$Li_xV_2O_5$. The SEM micrographs of the synthesized γ-$Li_xV_2O_5$, at different temperatures, are illustrated in Figure 4. Figure 4a is the picture of the 350 °C sample. It can be seen that the particles in the sample are highly irregular. Neither size nor the form of the particles is even. It can be explained by the low crystallinity and the defects in the crystallites. Figure 4b is the micrograph of the 400 °C sample. Comparing to that of the 350 °C sample, the particles of the 400 °C sample are much more regular in form. Most of the particles are ellipsoidal, and their dimensions are ~1 μm. Figure 4c is the micrograph of the 500 °C sample. The particles are in the form of a bar or a tube. Most of their dimensions are in the 2−5 μm range. Figure 4d is the micrograph of the 600 °C sample. The particles appear as pellets with dimensions in the 2−4 μm range. From the analysis of the morphology of γ-$Li_xV_2O_5$ synthesized at different temperatures, it is evident that the particle morphology changes significantly with temperature. The

(18) JCPDS, PDF 18-756.

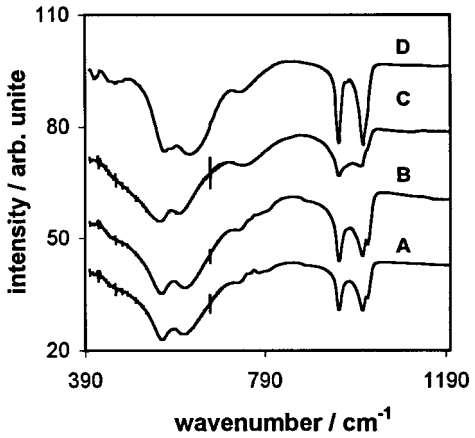

Figure 5. The IR curve of $Li_xV_2O_5$ synthesized at different temperatures.

significant changes in morphology may result from the increase in crystallinity. However, the increase in crystallinity is not easily observed in XRD.

IR of the Synthesized γ-$Li_xV_2O_5$. The IR spectra of the γ-$Li_xV_2O_5$ synthesized at different temperatures are illustrated in Figure 5. Curve A is the IR spectrum of the 350 °C sample. It contains the following main absorption peaks: 561.3, 611.0, 736.8, 777.4, 951.4, 1007.4, and 1018.0 cm^{-1}. Curve B is the IR spectrum of the 400 °C sample. It contains the following main absorption peaks: 553.6, 612.4, 732.0, 954.8, 1005.9, and 1019.4 cm^{-1}. It is similar to that of the 350 °C sample. The major difference is that there is no corresponding 777.4 cm^{-1} peak as in that of the 350 °C sample. But a shoulder at 792.8 cm^{-1} can be seen. Curve C is the IR spectrum of the 500 °C sample. It contains the following main absorption peaks: 552.2, 597.5, 741.2, 952.9, and 1005.9 cm^{-1}. Comparing to curves A and curve B, the major differences are (I) only two peaks are found in the 900−110 cm^{-1} range of wavenumber and (II) only one peak can be found between 700 and 800 cm^{-1}. Curve D is the IR spectrum of the 600 °C sample. It is similar to curve C and contains only five main peaks. The differences from curve C are that the two peaks between 500 and 650 cm^{-1} shift to higher wavenumbers and the two peaks between 900 and 1100 cm^{-1} become sharper. The changes from curve A to curve D can be explained by the increase in crystallinity of the γ-$Li_xV_2O_5$ with the increase of the synthesizing temperature. The higher crystallinity can result in less irregular positions of the V and O atoms and less diversities in the bonds between V and O atoms.

Electrochemical Performance of the γ-$Li_xV_2O_5$ Synthesized at Different Temperatures. Figure 6 is the cyclic voltammograms of γ-$Li_xV_2O_5$ and α-V_2O_5. Curve 1 is the cyclic voltammogram of α-V_2O_5 and curve 2 is the cyclic votammogram of γ-$Li_xV_2O_5$ synthesized at 350 °C. The positive current is discharge current and the negative current is charge current. The discharge peaks of curve 1 are at 3.143 and 3.354 V. The discharge peaks of curve 2 are at 3.434 and 3.552 V. They are 0.3 and 0.2 V higher than that of curve 1, respectively. The two main charge peaks of curve 1 are at 3.34 and 3.475 V, respectively. The two main charge peaks of curve 2 are at 3.553 and 3.671 V, respectively. They are 0.21 and 0.20 V higher than that of curve 1, respectively.

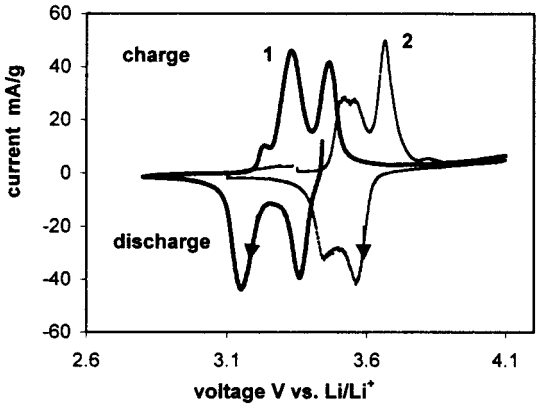

Figure 6. Cyclic voltammograms of γ-$Li_xV_2O_5$ and α-V_2O_5: (1) α-V_2O_5; (2) γ-$Li_xV_2O_5$. Scanning rate: 0.02 mV/s.

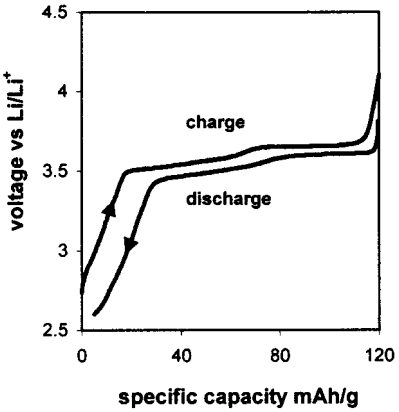

Figure 7. The discharge−charge curves of the $Li_xV_2O_5$. Discharge: 0.4 mA/cm^2, 0.2 °C; charge: 0.2 mA/cm^2, 0.1 °C.

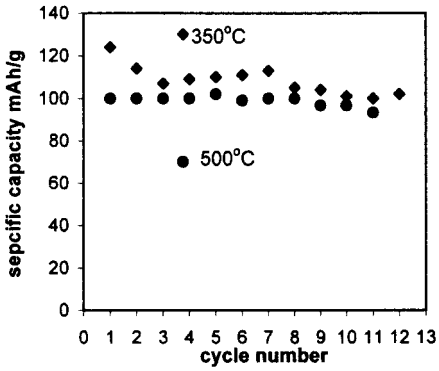

Figure 8. The cycle performance of the cell with γ-$Li_xV_2O_5$ synthesized at different temperature as cathode active material. Charge: 0.1 C. Discharge: 0.2 C. Voltage window: 2.6−4.0 V.

The total areas under discharge and charge parts of the curves are nearly equal in value for both curves, showing the reversibility of the γ-$Li_xV_2O_5$ and α-V_2O_5 in lithium ion intercalation−deintercalation. The results agree with those previously reported and show that the synthesized γ-$Li_xV_2O_5$ is the same as that prepared by low temperature and electrochemistry methods, in terms of electrochemical performance.[13−16]

The charge−discharge curves of the cell with γ-$Li_xV_2O_5$ synthesized at 350 °C are illustrated in Figure 7. After assembly, the open-circuit voltage of the cell was 2.6−2.9 V. From the charge curve, we can see two plateaus, consistent with the two major peaks in the cyclic voltammogram of the cell. At the beginning of the

charge, the voltage increases slowly, corresponding to the small peak in the cyclic voltammogram. At the end of the charge, the voltage increases suddenly, showing that no lithium ion can be deintercalated further. The discharge curve also contains two corresponding discharge plateaus. At the end of the discharge, the voltage decreases slowly, corresponding to the first part of the charge curve. The discharge capacity is nearly the same as the charge capacity. Therefore, the lithium deintercalation is reversible. The cycle performance of the cell with γ-$Li_xV_2O_5$ as cathode material is illustrated in Figure 8. The specific capacity of the cell with γ-$Li_xV_2O_5$ synthesized at 350 °C is higher than that of the cell with 500 °C γ-$Li_xV_2O_5$. The maintained capacity of the 350 °C γ-$Li_xV_2O_5$ is 102 (mA h)/g after12 cycles and that of the 500 °C γ-$Li_xV_2O_5$ is 94 (mA h)/g after 11 cycles.

Conclusion

The γ-V_2O_5 synthesized by the proposed method using LiOH, NH_4VO_3, and CH_3COOH can reversibly deintercalate and intercalate lithium ions. Its specific capacity is 120 (mA h)/g. The average voltage vs lithium metal electrode is 3.6 V. Combined with carbon anode, γ-$Li_xV_2O_5$ has potentiality to be used as cathode material in lithium ion batteries. Further research work should be focused on increasing the specific capacity and the cycleability.

CM9901461