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Influence of Adipic Acid on Electrochemical Properties of $Li_3V_2(PO_4)_3$ as Cathode Material for Rechargeable Lithium-Ion Batteries

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Abstract: ***Monoclinic $Li_3V_2(PO_4)_3$ powders were synthesized with different calcination temperature of 800, 900 and 950 ^{0}C for 8 h in Ar atmosphere by solid state method using adipic acid as a chealting agent. The influence of calcination temperatures of carbon coated $Li_3V_2(PO_4)_3$ has been investigated using X-ray diffraction (XRD) and electrochemical methods. The crystalline phase formation was investigated using thermogravimetric-differential thermal analysis (TG-DTA). Among the optimized conditions, the sample prepared with 0.15 molar ratio of adipic acid to total metal ions at the calcination temperature of 900 ^{0}C showed a better electrochemical performance compared to other samples. The capacity retention of the $Li_3V_2(PO_4)_3$ + 0.15 molar ratio of adipic acid sample is 93% after 19 cycles, whereas it is only 85% for pure $Li_3V_2(PO_4)_3$ sample.***
Keyword: ***$Li_3V_2(PO_4)_3$, adipic acid, solid state route, Lithium-ion batteries, carbon-coating .***

I. INTRODUCTION

The frame work materials based on phosphate polyanion have been identified as potential electro active materials for lithium ion batteries since their initial report in 1997 [1, 2]. Lithium transition metal phosphates, such as $LiFePO_4$ [3], $LiCoPO_4$ [4], $LiMnPO_4$ [5], $LiNiPO_4$ [6], $Li_3Ti_2(PO_4)_3$ [7] and $Li_3V_2(PO_4)_3$ [8-14] have been focus of candidate as cathode materials. Among the phosphates above, monoclinic $Li_3V_2(PO_4)_3$ is a highly promising material proposed as a cathode for higher voltage rechargeable lithium-ion batteries because of their stable framework, good ion mobility and high reversible capacity. $Li_3V_2(PO_4)_3$ contains both mobile Li cations and redox-active metal sites occupied within a rigid phosphate structure. The theoretical capacity for $Li_3V_2(PO_4)_3$ is 197 mAh/g, while three Li ions are completely extracted at the voltage of 4.8 V, which is the highest for all phosphate [14]. In the monoclinic $Li_3V_2(PO_4)_3$ phase, the first charging an ordered Li phase of intermediate composition [$Li_{2.5}V_2(PO_4)_3$]; then the second stage (3.68 to 4.1 V) is related by the removal of Li-ions from the stable tetrahedral sites. Then, the final stage (4.1 to 4.5 V) is due to the change of the V^{3+}/V^{4+} redox couple to the $V^{4+/5+}$ [15].

Though, the above materials having an intrinsic drawback to practical applications because of poor conductivity even at very slow rates. In order to improve the method to prepare the electrodes by coating the particles with a thin carbon layer [16], adding conductive materials [17], or/and reducing the particle size [18]. In this, the coating technique has the advantage to enhance the electrode's electronic and ionic conductivity and consequently to promote higher capacities. The $LiFePO_4$ material has a capacity of 160 mAh/g when coated with 1 wt% of carbon material [19].

$Li_3V_2(PO_4)_3$ material is synthesized by reducing V^{5+} compound to V^{3+}. The reduction agent should be used, in order to reduce V^{5+} to V^{3+}. Many reduction and coating agents have been used as a carbon source so far, such as, hydrogen [12], glucose [20], sucrose [21], phenolic resin [22], carbon [14], citric acid [23] and humic acid [24]. For the first time, recently we have reported the adipic acid as a carbon source and as a chelate agent in $LiFePO_4$ material which was prepared by simple sol-gel and solid state route [25-27]. Adipic acid is in-expensive and affords successful control of the particle size, thus obviating the need for promote treatment for carbon coating. We found that, the carbon-coated $LiFePO_4$ material exhibited a better initial discharge capacity of 150 mAh/g and stable electrochemical performance, whereas it was only 127 mAh/g for pure $LiFePO_4$ material. This has motivated us to carry out the electrochemical properties of monoclinic $Li_3V_2(PO_4)_3$ sample.

We prepared the $Li_3V_2(PO_4)_3$ sample using adipic acid-assisted, solid state route with the different molar ratio of adipic acid to total metal ions such as 0.05, 0.1 and 0.15.The structural, physical and electrochemical properties of the materials were investigated. The results showed that, the material prepared with the 0.15 molar ratio adipic acid $Li_3V_2(PO_4)_3$ sample exhibited better electrochemical performance compared to other samples.

II. EXPERIMENTAL

The pure $Li_3V_2(PO_4)_3$ was prepared using the conventional solid-state route. High purity $LiCO_3$ (Wako, Japan), V_2O_5 (Sigma-Aldrich, USA), $(NH_4)_2HPO_4$ (Sigma-Aldrich, USA) and $C_6H_{10}O_4$ (Sigma-Aldrich, USA) were used as a starting materials. The stoichiometric ratios of the starting materials without and with adipic acid (molar ratio of adipic acid to total metal ions was 0.05, 0.1 and 0.15) were used for the pure $Li_3V_2(PO_4)_3$ and carbon-coated $Li_3V_2(PO_4)_3$ synthesis, respectively. Adipic acid was used here as a carbon source. The starting materials were thoroughly ground in an agate mortar and precalcined at 300 ^{0}C for 4 h in Ar atmosphere. The resultant compound has been ground thoroughly again and sintered at 850, 900, 950 ^{0}C for 8 h under Ar atmosphere using tubular furnace to obtain $Li_3V_2(PO_4)_3$ samples. Stoichiometric amounts of starting materials without and with adipic acid (molar ratio of adipic acid to total metal ions were 0.05, 0.1 and 0.15) were used for the pure $Li_3V_2(PO_4)_3$ and $Li_3V_2(PO_4)_3$ +ad 0.05, $Li_3V_2(PO_4)_3$ +ad 0.1 and $Li_3V_2(PO_4)_3$ +ad 0.15, respectively. The crystallographic phase analysis for the samples was carried out using x-ray diffraction analysis (XRD, Rint 1000, Rigaku, Japan). The diffraction data are collected over 2θ ranging from 10 to 80 at each 0.01^0 step width. Thermal studies were carried out by means of thermogravimetric-differential analysis (TG-DTA) using a thermal analyzer system (STA 1640, Stanton Redcroft Inc., UK). The electrochemical charge-discharge performance of the samples is evaluated in CR2032 coin-type cell. The cathode was made-up with 20 mg of active material, 3 mg of Ketzen black and 3 mg of conductive binder (TAB). The test cell was made of a cathode and a lithium metal anode which are separated by a porous polypropylene film (Celgard 3401). 1M $LiPF_6$ in EC:DMC = 1:1 (Techno Semichem Co., Ltd., Korea) was used as the electrolyte. This composite was pressed on 200 mm^2 stainless steel mesh which was used as the current collector under a pressure of 300 kg/cm^2 and dried at 160 ^{0}C for 4 h in vacuum oven. The cells were assembled in a glove box under an argon atmosphere. The charge/discharge current density was 0.1 mA/cm^2, and the cut-off voltage is controlled at the range of 3.0 to 4.8 V.

III. RESULTS AND DISCUSSION

Figure 1 shows the thermogravimetric-differential thermal (TG-DTA) curves of pure $Li_3V_2(PO_4)_3$ sample. From the figure, it can seen that the endothermic events starts nearby at 159 ^{0}C and ends at 400 ^{0}C, which is attributed due to evaporation of moisture (including water absorbed during sample loading). After 400 ^{0}C, the anhydrous $Li_3V_2(PO_4)_3$ began to oxidize in the air, when the temperature reached at 640 ^{0}C, the mass of the sample approached a fixed value. Therefore, according to TG-DTA analysis, the precursor was heat-treated at temperatures above 640 ^{0}C for the synthesis of $Li_3V_2(PO_4)_3$ sample.

The phase identification of the $Li_3V_2(PO_4)_3$ samples were conducted using an X-ray powder diffractometer as shown in figure 2 which was prepared in 950 ^{0}C for 8h under Ar atmosphere, respectively. All the diffraction patterns could be indexed well to monoclinic $Li_3V_2(PO_4)_3$ with the space group of *P2$_1$/n*. Moreover, the diffraction peaks of the sample shows a single-phase without any impurities such as Li_2O and Li_3VO_4 [22].

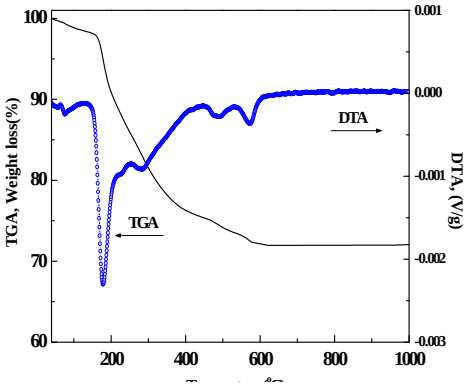

Fig.1.TG-DTA analysis of starting material of pure $Li_3V_2(PO_4)_3$

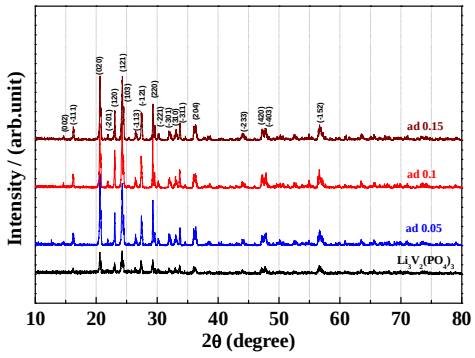

Fig.2. XRD patterns of pure and carbon coated $Li_3V_2(PO_4)_3$ samples

Charge/discharge curves of $Li_3V_2(PO_4)_3$ samples was prepared in three different calcination temperatures such as 850, 900, 950 ^{0}C for 8h under Ar atmosphere at the current density of 0.1 mA/cm^2, and the cut-off voltage is controlled at the range of 3.0 to 4.8 V as shown in figure 3. As shown in Fig., the initial charge and discharge capacities of $Li_3V_2(PO_4)_3$ + ad 0.15 sample (calcination temperature 850 ^{0}C for 8 h) are 184 and 146 mAh/g, respectively, so the columbic efficiency is 79.3 %. The fig 4b shows the initial

charge and discharge capacities of $Li_3V_2(PO_4)_3$ + ad 0.15 sample (calcination temperature 900 ^{0}C for 8 h) are 203 and 171 mAh/g, respectively, so the columbic efficiency is 84.2 %. Moreover, the initial discharge capacity value of 171 mAh/g for $Li_3V_2(PO_4)_3$ + ad 0.15 sample (calcination temperature 900 ^{0}C for 8 h) is higher compared to other calcination temperatures.

The cycling performance of the $Li_3V_2(PO_4)_3$ sample which was calcinated in the temperature 900 ^{0}C for 8 h as shown in the figure 4. The increasing capacity and stable trend has observed for $Li_3V_2(PO_4)_3$ + ad 0.15 sample compared to pure $Li_3V_2(PO_4)_3$ sample. The initial discharge capacities of 171 and 158 mAh/g were observed for $Li_3V_2(PO_4)_3$ + ad 0.15 and pure $Li_3V_2(PO_4)_3$ sample, respectively. Moreover, the capacity retention after 19th cycle for $Li_3V_2(PO_4)_3$ + ad 0.15 sample is 93 % of of the initial discharge capacity, whereas it is only 85 % for pure $Li_3V_2(PO_4)_3$ sample. The reason for the poor initial discharge capacity of pure $Li_3V_2(PO_4)_3$ sample is due to a little dissolved under relative higher voltage, because a better carbon coating can keep off the of $Li_3V_2(PO_4)_3$ with electrolyte. Moreover, the electron/L^+ location and transport within this lattice, the conductivity of pure $Li_3V_2(PO_4)_3$ sample without carbon coating might be increased during the extraction/reinsertion process which consequences in the poor cycleability.

Also, the formation of pure monoclinic $Li_3V_2(PO_4)_3$ coated carbon particles with relatively high specific surface area, and an important factor for the capacity fading of cathode materials is the dissolution of the transition metal in electrolyte. The vanadium dissolution from $LiVP_2O_7$ was reported by Patoux [28]. So, it is projected that the vanadium in $Li_3V_2(PO_4)_3$ could also dissolve in the electrolyte with cycling [29].

Since the dissolution of transition metals occurs at the interface between material particles and electrolyte, the above result indicates that the carbon coated ($Li_3V_2(PO_4)_3$ + ad 0.15) sample could considerably prevent the vanadium dissolution from $Li_3V_2(PO_4)_3$. Therefore, to our experimental results, it is suggested that the better performance of monoclinic $Li_3V_2(PO_4)_3$ + ad 0.15 can be obtained at an optimal calcination temperature of 900 ^{0}C for 8 h.

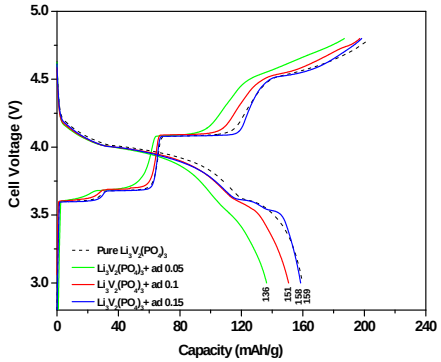

Fig.3. Charge/discharge profiles of pure and carbon coated $Li_3V_2(PO_4)_3$ sample

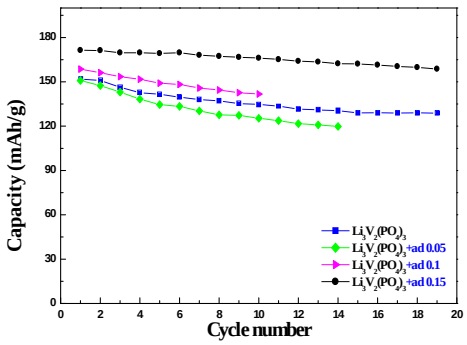

Fig.4. Cycling performance of pure and carbon coated $Li_3V_2(PO_4)_3$ samples, calcinated at 950 C/8h

IV. CONCLUSION

In summary, we prepared a pure and carbon coated $Li_3V_2(PO_4)_3$ powders with different calcination temperature of 800, 900 and 950 ^{0}C for 8 h in Ar atmosphere by solid state method. Moreover, the stoichiometric amounts of starting materials with adipic acid (molar ratio of adipic acid to total metal ions were 0.05, 0.1 and 0.15) were used for carbon coated $Li_3V_2(PO_4)_3$ samples. Among the above, the optimized conditions of the sample prepared with 0.15 molar ratio of adipic acid to total metal ions at the calcination temperature of 900 ^{0}C exhibited a better electrochemical performance compared to others. The initial discharge capacities of 171 and 158 mAh/g were observed for $Li_3V_2(PO_4)_3$ + ad 0.15 and pure $Li_3V_2(PO_4)_3$ sample, respectively. The rate capability study exposed an capacity retention of the $Li_3V_2(PO_4)_3$ + 0.15 molar ratio of adipic acid sample is 93% after 19 cycles, whereas it is only 85% for pure $Li_3V_2(PO_4)_3$ sample.

V. ACKNOWLEDGEMENTS

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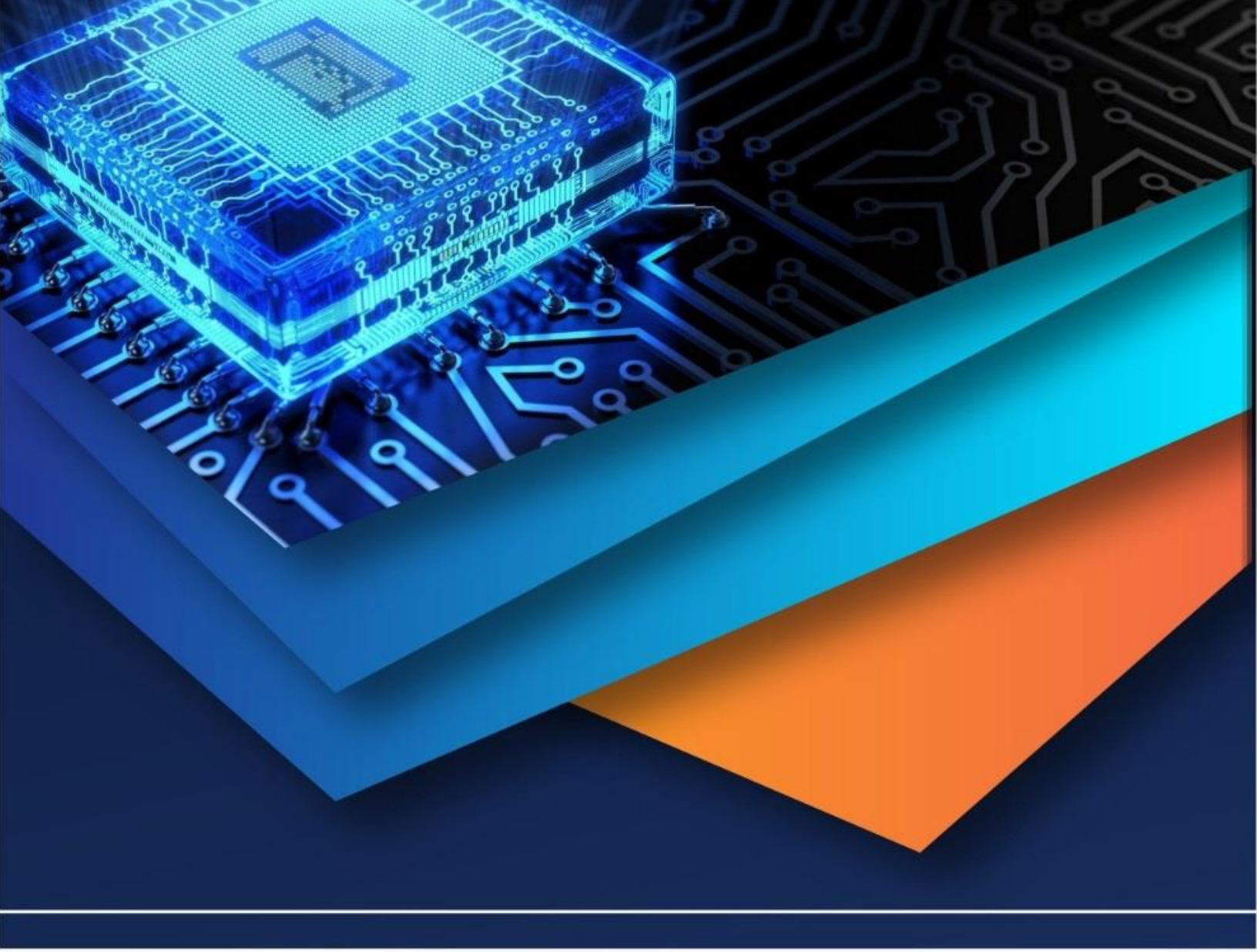

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