Carbon Coating for Improvements of Electrochemical Properties of Li_{1.1}V_{0.9}O_2 Anode Active Materials for Li Secondary Batteries

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ABSTRACT

Generally, Lithium Vanadium Oxide has a larger volumetric capacity anode active material than that of graphite. Unfortunately, LVO (Li_{1.1}V_{0.9}O_2) have some critical weak points, such as low cycle life, low rate capability, low electrical conductivity. To improve those of weakness of LVO, we prepared carbon coated LVO with sucrose successfully and evaluated their electrochemical properties, such as, relatively crystallinity, small particle size, and electrical conductivity. Furthermore, charge transfer resistance and lithium ion diffusivity was measured by EIS and GITT evaluations to understand relationship carbon layer thickness and electrochemical properties. From this result, it is necessary to consider the electrochemical parameters such as the electric conductivity, the charge transfer resistance, and the lithium ion diffusivity depending on the amount of the carbon layer in order to improve the electrochemical property by the carbon coating.

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Keywords : Lithium Vanadium Oxide, Carbon Coating, Anode, Li Secondary Battery

1. Introduction

Rechargeable Lithium Ion Batteries (LIB) have been attracting much attention as a power source for many electronic devices. Recently, power tools, stationary applications and EVs have been expanding in our life. However, the energy density of present LIB is not enough high to satisfy such applications. Therefore, it is necessary to develop a battery with higher energy density as a next generation battery. The anode active material is one of key factors for improving the capacity of lithium rechargeable batteries. Especially, graphite has been commonly used for the anode material in LIBs, because of its characteristic properties like high capacity density, low reaction voltage, low irreversibility and good electronic conductivity. However, its theoretical capacity (372 mAh g⁻¹) is almost fully utilized.1,2 Therefore, in order to increase the density of batteries, it is necessary to develop the new anode active material for higher energy density batteries.

As one of promising candidates, the research on lithium vanadium-based anode materials for lithium secondary batteries has been done due to its suitable properties for high capacity anode. Among many possible compositions of Li_{1+x}V_{1-x}O_2 vanadium-based oxide compounds, LVO (Li_{1.1}V_{0.9}O_2) has been investigated as a potential candidate to replace the conventional carbonaceous materials.3 LVO has two kinds of structures which are R3m at the initial state and Pm3 at the charged state. A reversible phase transitions during charge and discharge reaction with lithium has been observed. LVO has a theoretical gravimetric capacity of 314 mAh g⁻¹, which is close to gravimetric capacity of graphite of 372 mAh g⁻¹. However, LVO has a high theoretical density, meaning that the volumetric capacity is higher (1350 mAh cm⁻³). It is 30% higher than graphite (790 mAh cm⁻³).4-7

Pristine lithium vanadium oxide has a relatively low volume change (25%).8,9 It is much lower than other alternative anode materials, such as, Sn or Si based, and transition oxide anode materials. But drawbacks of lithium vanadium oxide lead to poor cycling life, such as, low electronic conductivity, partial surface cracks and fragmentations during lithiation or delithiation reaction.10,11 Some researches, such as carbon coating,9,12,13 metal ion doping14 and coupled with graphite,15 are employed to improve its cycling stability. To improve the properties of LVO for anode active materials, a carbon coating is one of the effective surface treatment methods for improvement of electrical conductivity of LVO. Lee et al. has already reported carbon coated lithium vanadium oxide. They showed 76% of initial efficiency, 330 mAh g⁻¹ and 250 mAh g⁻¹ of charge and discharge specific capacity, respectively, and 20 cycles of cycle life evaluation of prepared carbon coated LVO.9

In this study, we optimize the preparation of carbon coated LVO anode active material and investigate the physical and electrochemical properties to observe the difference in what between carbons coated LVO prepared by using sucrose as carbon source and pristine LVO through the more quantitative evaluation.

2. Experimental

2.1 Preparation of active materials

The anode material pristine LVO is prepared as solid state reaction. A stoichiometric amount of Li₂CO₃ (Wako Pure Chemical Industries, Ltd, 99.9%) and V₂O₅ (High Purity Materials, 99.9%) mixed in mortar during 20 min. The reactants were calcined at 1100°C for 8 h in 3% of H₂/Ar gas. Heating rate is 5°C min⁻¹. To prepare carbon coated LVO, the pristine LVO powder was immersed in an water solution containing 5 wt.% (LVO-A), 10 wt.% (LVO-B), and 15 wt.% (LVO-C) sucrose (Wako Pure Chemical Industries, Ltd) relative to weight of LVO, and the resulting samples was dried at 80°C. The sample was subsequently heat-treated under an argon atmosphere at 800°C for 12 h with a heating rate of 5°C min⁻¹.

2.2 Material characterizations

X-ray Diffraction patterns were collected with X-ray diffractometer (XRD, RINT-2000/PC, Rigaku Co.) with CuKα radiation in the 2θ range of 10° ≤ 2θ ≤ 70° to identify the crystal structures of the LVO samples. The morphologies were analyzed with Scanning Electron Microscope (SEM, JSM-7500F, JEOL Ltd.) and transmission electron microscopy (JEM-ARM200F, JEOL). In order to characterize the carbon on ratio of coated LVO samples, Raman
spectroscopy was carried out by Laser Raman spectrometer (NRS-1000, JASCO) and the thermogravimetric analysis (TGA, DTG-60H, Shimadzu Co.) data were obtained from 30 to 800°C at 5°C min⁻¹ in air condition. Plus, to observe difference of specific surface area by sucrose coating, specific surface area of the LVO samples was determined by N₂ adsorption using a specific surface area instrument (BELSORP-miniX).

2.3 Electrochemical evaluation

The electrode slurry was prepared by mixing the active materials (80 wt. %), with acetylene black (10 wt. %) and polyvinylidene fluoride (KF-L#1120, 10 wt. %) in 1-methyl-2-pyrrolidione organic solvent. The slurry was casted on Cu foil using a doctor blade and dried in a convection oven at 110°C for 2 hours, and then pressed using a rolling press machine. For electrochemical evaluation of the electrodes, the 2032 coin type cells were assembled with lithium foil and the electrodes, the 2032 coin type cells were assembled with lithium foil using a rolling press machine. For electrochemical evaluation of the electrodes, the 2032 coin type cells were assembled with lithium foil (Honjo Metal Co., Ltd.) electrode, microporous polypropylene separator, electrolyte 1 mol dm⁻³ LiPF₆ in organic solvent mixture of ethylene carbonate (EC) with ethyl methyl carbonate (EMC) (3:7 in volume, Kishida chemical Co., Ltd.) in argon filled glovebox.

The coin cell tests were conducted in the galvanostatic mode using a battery cycler (HJ1001SD8). The rate performance of LVO/Li half-cell was measured at room temperature with different current densities varying from 0.2 to 5 C, and by using the constant charging rate of 0.2 C. Cycle life evaluation was carried out at 0.5 C current conditions during 50 cycles. EIS evaluation was carried out at 10 mHz to 10 kHz frequency range with ±5 mV voltage. The state of charge was set at 100% and 80% by using 0.2 C discharges. After the charge or discharge followed by the relaxation time of 4 hours, EIS measurement was conducted.

Galvanostatic intermittent titration technique (GITT) technique was used to measure the Li⁺ ions diffusion in the electrode. The 2032 coin half cells were cycled at 0.1 C rate and then were fully charged at 0.1 C rate. At every 10% of full discharge capacity, GITT measurement was carried out with the relaxation time of 4 hours after each discharge. Plus, values of molar volume of discharge states were calculated by molar mass of Li₁₁ₓV₀.₉ₓO₂ and composite electrode density. The same procedure was continued until voltage reached 2.0 V (DOD 100%)

3. Results and Discussions

Figure 1 shows the result of XRD patterns which are the pristine LVO and carbon coated LVO samples (LVO-A, LVO-B, LVO-C). The observed LVO samples had the R3m space group in hexagonal structure and it is similar with others previous studies. In addition, there are no impurities in other carbon coated LVO samples. In order to compare the crystallinity of each sample, we calculated the crystal size according to Scherrer equation. The crystalline size of pristine LVO, LVO-A, LVO-B and LVO-C were estimated to be 128.7 nm, 127.4 nm, 126.9 nm, 118.4 nm, respectively. As increasing coating carbon amount, the size of crystalline was decreased. Figure 2 shows SEM images for each LVO powder samples. The size of LVO particles was approximately 5–15 μm. The pristine LVO has different surface form other carbon coated LVO samples.

In the case of carbon coated samples, there are amorphous carbon layer by decomposition of sucrose. In order to observe the deposited carbon on LVO surface, TGA and Raman spectroscopy were carried out. First, TGA data was obtained for each LVO sample, as shown in Fig. 3(a). In the temperature range of 100–600°C, the weight loss appeared due to the residual carbon, and then the increasing mass appears due to the oxidation of vanadium. 

Residual carbon of LVO-A, LVO-B and LVO-C, as measured by the reduced mass, was 2.7 wt.%, 4.4 wt.% and 5.9 wt.%. Figure 3(b) show the results of Raman spectroscopy of pristine LVO and carbon coated LVO samples. There are two distinct bands in Raman spectrum (1000–1800 cm⁻¹), indicating the presence of the coated carbon layers in carbon coated LVO. It is generally supposed that the bands at 1380 cm⁻¹ and 1589 cm⁻¹ can be ascribed to the characteristic D band (disordered carbon) and G band (graphitic carbon), respectively. In addition, heights of carbon peak intensity were increased by inserted amount of carbon. Nevertheless, there are no crystalline peak of carbon in the wide-angle XRD patterns. Furthermore, transmission electron microscopy (TEM) has also been used to...
provide deeper insight into characterization of carbon coated LVO samples.

Figure 4 shows HRTEM images of LVO-A, LVO-B and LVO-C. In the TEM images, we can confirm lattice layer spacing of 0.49 nm matching with the d-spacing of (003) plane of LiVO₂ in core part of sample LVO-A and LVO-B. And, commonly observed, all the samples have outer shell which enwrapped by a thin and homogeneous coating layer, which is composed of the graphitized carbon microcrystalline and amorphous carbon. The carbon layer thickness of LVO-A, LVO-B and LVO-C, as measured, was 3.06 nm, 6.63 nm and 6.82 nm. Case of LVO-C, there some thicker carbon layer around 23.75–28.68 nm. The large amount of carbon coated sample corresponds to thicker carbon layer and presence of more stacking graphitic layers, distinctly.

To compare the electronic conductivity of each samples, the resistivity meters (MCP-T700, Mitsubishi) was used for pellet samples (diameter: 16 mm, thickness: 1 mm), as shown in Fig. 5. The measured electronic conductivity were 3.62 × 10⁻⁵ S cm⁻¹ (pristine LVO), 1.33 × 10⁻³ S cm⁻¹ (LVO-A), 2.88 × 10⁻³ S cm⁻¹ (LVO-B), 2.94 × 10⁻³ S cm⁻¹ (LVO-C) (standard deviation of every conductivities results was 9.39 × 10⁻⁶ S cm⁻¹). All the coated LVO samples have 2 orders higher than that of pristine LVO sample. It can be confirmed that coated carbon materials have higher electronic conductivity.

The charge and discharge tests were carried out with reasonable electrode condition at current of 0.1 C (1 C = 250 mAh g⁻¹). The composite electrode were 2.5–2.55 g cm⁻³ of density and 3.8–4.3 mg cm⁻² of loading level. Figure 6 shows the voltage curves of each sample during stabilized cycles, (a) initial cycle and (b) second cycle. In the initial cycle, all the LVO samples have the irreversible charge with potential plateau at −0.5 V, which is observed during the initial charging process. In this potential plateau, the SEI may be formed. The similar phenomena were identified during initial charge process in previous LVO studies.8–11 But, irreversible capacities of all carbon coated samples were increased. In fact, the initial coulombic efficiency of pristine LVO was 78.2%. The initial coulombic efficiencies of carbon coated LVO samples were 75.5% (LVO-A), 73.2% (LVO-B), 74.2% (LVO-C). Combined with the results of the BET surface area, the specific surface area of LVO samples were 0.45 m² g⁻¹ (LVO pristine), 0.52 m² g⁻¹ (LVO-A),
All the carbon coated LVO samples have increased specific surface area. Therefore, initial efficiencies of all of carbon coated LVO samples are decreased. Figure 6(c) shows change in the discharge capacities of the LVO samples during 50 cycles at 0.5 C current conditions. The discharge capacities of all samples were increased during 15 cycles. It may be due to the “electrochemical grinding”. This phenomenon has been observed in the MoO2 type powder which breaks down to the smaller particles in high concentration of Li intercalation process. From this result, it can be said that the carbon coating has no effect on the protection for “electrochemical grinding” by Y. Liang et al.21 The first delivered discharge capacity of each samples were 276.9 mAh g⁻¹ (pristine LVO), 294.1 mAh g⁻¹ (LVO-A), 300.4 mAh g⁻¹ (LVO-B), 293.6 mAh g⁻¹ (LVO-C). The capacity retention after 50 cycles for each sample was 47.4% (pristine LVO), 53.8% (LVO-A), 57.5% (LVO-B), 53.8% (LVO-C), respectively. The carbon coating improved the cycle performance of LVO samples during 50 cycles. Especially, LVO-B had 10% higher capacity retention. Evaluation of rate capabilities was carried out, as shown in Fig. 6(e) and Fig. 6(f). In order to realize the same conditions of every discharge measurements, all LVO electrodes were firstly charged at 0.2 C-rate of constant current. Even at 5 C-rate (within 12 min.), the discharge capacity of 10 wt.% carbon coated LVO was 225.1 mAh g⁻¹. The rate capability of 5 C versus 0.2 C was 76%. In addition, 10 wt.% carbon coated LVO showed excellent discharge rate capability over 75% up to 5 C-rate, indicating that the carbon coating can be attributed to improvement of the rate capability. All the carbon coated LVO samples have improved electrochemical properties. As pristine LVO and three kinds of LVO samples resemble in particle size, difference of their electrochemical performance would be mainly related to the different amount of the coating carbon. However, the inclusion of 15 wt.% of carbon sample shows a negligible effect in reducing the electrode polarization, suggesting that over-coating of carbon is unfavorable for the electrode performance of carbon coated LVO samples.

For more quantitative measurements, impedance evaluations were carried out to understand the effect of carbon coating on the surface of LVO samples. Figure 7(a)–(d) show the Nyquist plots of pristine LVO and carbon coated LVO composite electrodes at several DOD states, from DOD 20% to DOD 100%. The Nyquist plots for all samples were similar each other. There are two kinds of components in the semicircle in the middle-high frequency region. The intercept at Z’ axis in high frequency refers to electrolyte solution resistance. In the low frequency zone, the semicircle relates the charge transfer resistance for lithium ion’s migration through the solid electrolyte interface film formed on the surface of LVO.21–26
In order to estimate a diffusivity of lithium ion, GITT (Galvanostatic Intermittent Titration Technique) was employed. From the GITT measurement, the quantitative lithium ion diffusion coefficients at each DOD state of LVO samples were obtained. Figure 9(a) shows the potential profile on process of GITT evaluation. When the diffusivity equation in the material is assumed to obey Fick’s diffusion equations as follows (1), the diffusion coefficient of lithium ion can be described,\(^27,28\)

\[
D = \frac{4}{\pi} \left( \frac{V_m}{FS} \right)^2 \left( \frac{dE}{dx} \right)^2 \left( \frac{t}{L^2} \right)
\]

where \(D\) is diffusion coefficient (cm\(^2\) s\(^{-1}\)), \(V_m\) is molar volume of active material (cm\(^3\) mole\(^{-1}\)), \(F\) is the Faraday constant (C mole\(^{-1}\)), \(I_o\) is applied current (A), \(S\) is surface area of the electrode (cm\(^2\)), \(L\) is the thickness of the electrode (cm), \(dE/dx\) is the dependence of electrode potential on the stoichiometry of the inserted lithium ions, \(dE/dt\) is transient voltage change as a function of the square root of time.

Figure 9(b) shows the calculated diffusion coefficient of each DOD state of LVO samples. Every result has a similar shape of variation with one minima diffusivity in discharge process. A similar minimum in the chemical diffusion coefficient is commonly observed in LVO anode active materials which show a phase transition due to strong attractive interactions between the intercalation species and the host matrix or some order–disorder transition during charging and discharge process.\(^29,30\) The diffusion coefficients of carbon coated LVO samples are larger than pristine LVO. Obviously, carbon coating can enhance the Li ion conductivity. Furthermore, case of coated samples, diffusivity of the 10 wt.% carbon coated LVO (LVO-B) sample is larger than that of the LVO-A (5 wt.% ) and LVO-C (15 wt.% ) samples.

The EIS results and GITT evaluations show that electrical conductivity, charge transfer resistance and ionic diffusivity greatly affect the electrode performance of pristine LVO and carbon coated LVO samples. Basically, the charge-transfer reaction carries out at the LVO electrode when accepting lithium ion and electrons concurrently. In the case of pristine LVO, the particle surface is more easily reachable by lithium ion, with the lack of electrical

**Figure 7.** Each discharge steps of impedance results (a) DOD 20%, (b) DOD 40%, (c) DOD 60%, (d) DOD 80%.

**Figure 8.** Each calculated resistance value solution resistance (a), \(R_{sol}\) (b), and charge transfer resistance (c) and used (d) equivalent circuits for understanding.

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\(v\)
conductivity. Electron conductivity and charge transfer resistance are improved by carbon coating. The thin carbon layer (LVO-A, LVO-B) with improved electron conductivity condition provides a favorable way to reach the LVO particle surface. On the other hand, LVO-B) with improved electron conductivity condition provides a balance between the electronic conductivity and ionic diffusivity. Electron conductivity and charge transfer resistance are improved by carbon coating. The thin carbon layer (LVO-A, LVO-C (15 wt.% sucrose added carbon coated LVO), as measured by the reduced mass by TGA, was 2.7 wt.%, 4.4 wt.% and 5.9 wt.%. We also observe thickness of carbon layer by TEM. No impurity was confirmed and the similar crystal structure of all carbon coated samples, and pristine LVO in XRD pattern. Through the evaluation of electronic conductivity, the coated LVO samples had 2 orders higher than that of pristine LVO. In addition, rate capabilities of all carbon coated LVO samples were significantly improved in the high rate discharge of the coin cell. Especially, LVO-B sample prepared with 10 wt.% sucrose had the largest capacity and remarkable rate capability. EIS evaluation and GITT were carried out to understand the high rate capability of the carbon coated LVOs about several DOD states. The charge transfer resistance and lithium ion diffusivity of all of carbon coated LVO samples were improved. EIS results show the charge transfer resistance decreased with increasing amount of residual carbon coating. So, LVO-C have the lowest charge transfer resistance values. However, LVO-D had the highest value of lithium diffusion coefficient on all of DOD states. Consequently, a balance of electrochemical characters, such as electronic conductivity, charge transfer and lithium ion diffusivity, are indispensable to optimize for best electric performance about carbon coating LVO sample.

4. Conclusion

In this study, to overcome disadvantages of LVO anode active material, we synthesized carbon coated LVO anode active material by using sucrose and proceeded with physical and electrochemical analyses. To confirm the effects of the carbon coating on LVO, surface morphology of each carbon coated LVO samples was observed by SEM image. Residual carbon of LVO-A, LVO-B and LVO-C, as measured by the reduced mass by TGA, was 2.7 wt.%, 4.4 wt.% and 5.9 wt.%. We also observe thickness of carbon layer by TEM. No impurity was confirmed and the similar crystal structure of all carbon coated samples, and pristine LVO in XRD pattern. Through the evaluation of electronic conductivity, the coated LVO samples had 2 orders higher than that of pristine LVO. In addition, rate capabilities of all carbon coated LVO samples were significantly improved in the high rate discharge of the coin cell. Especially, LVO-B sample prepared with 10 wt.% sucrose had the largest capacity and remarkable rate capability. EIS evaluation and GITT were carried out to understand the high rate capability of the carbon coated LVOs about several DOD states. The charge transfer resistance and lithium ion diffusivity of all of carbon coated LVO samples were improved. EIS results show the charge transfer resistance decreased with increasing amount of residual carbon coating. So, LVO-C have the lowest charge transfer resistance values. However, LVO-D had the highest value of lithium diffusion coefficient on all of DOD states. Consequently, a balance of electrochemical characters, such as electronic conductivity, charge transfer and lithium ion diffusivity, are indispensable to optimize for best electric performance about carbon coating LVO sample.

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