



Short communication

Enhanced cycleability of LiCoO₂ coated with vanadium oxidesJae-Won Lee^{a,*}, Sun-Min Park^a, Hae-Jin Kim^b^a KICET, 233-5 Gasan-dong, Guemcheon-Gu, Seoul 153-801, Republic of Korea^b KBSI, 113 Gwahangno, Yuseong-gu, Daejeon 305-333, Republic of Korea

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ABSTRACT

Vanadium oxide (V₂O₅/V₂O₅ hydrates) sol-gel coatings on lithium cobalt oxide (LiCoO₂) are investigated as a means are prepared to improve the cycleability at a high-charge cut-off voltage. The V₂O₅ sol was prepared by a melt-quenching method. The crystal structure and morphology of the samples are examined by X-ray diffraction, scanning electron microscopy and transmission electron microscopy. The charge and discharge characteristics, including cycleability, are measured at room temperature, and the electrochemical properties of bare and coated LiCoO₂ are compared. Overall, a vanadium oxide coating on LiCoO₂ improves the cycleability at a high-charge cut-off voltage.

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1. Introduction

LiCoO₂ is the most widely used positive electrode (cathode) material in lithium rechargeable batteries on account of its excellent performance. The theoretical capacity of LiCoO₂ is approximately 274 mAh g⁻¹ when fully delithiated but the practical capacity is limited to almost half the theoretical value due to a monoclinic to hexagonal phase transformation upon charging between 4.15 and 4.2 V [1]. The dissolution of cobalt ions (Co⁴⁺) has also been reported as a reason for the deterioration of the crystal structure [2]. In order to prevent phase instability, the substitution of metal elements for Co in LiCoO₂ or a surface coating has been suggested [3–7]. Various metal oxides (e.g., MgO, Al₂O₃, ZnO) and metal phosphates (e.g., AlPO₄, FePO₄) have been coated on the surface of LiCoO₂ and reported to improve the cycleability of LiCoO₂ [8–12] at an increased charge cut-off voltage.

Vanadium pentoxide (V₂O₅) is one of the promising cathode materials for lithium rechargeable batteries. It has a theoretical capacity higher than 400 mAh g⁻¹ and is electrochemically active between 1.8 and 3.8 V [13]. V₂O₅ hydrates (V₂O₅·xH₂O) have been also studied extensively for battery applications. Giorgetti et al. [14] reported a fibrous V₂O₅·xH₂O xerogel with a sufficiently high lithium insertion capacity to make it attractive as an electrode material in lithium rechargeable batteries. In this sense, coating with vanadium oxide may not reduce the capacity of LiCoO₂, as

do other coatings with electrochemically inactive oxides. Furthermore, a V₂O₅ sol can be prepared simply by just melting V₂O₅ at high temperatures (above the melting point of V₂O₅—690 °C) and quenching the melt in water, which makes it easy to coat particles of other cathode materials.

In this study, V₂O₅ is coated on LiCoO₂ for the first time using a sol-gel process, and the effect of the coating on electrochemical performance, including high-voltage cycleability, is examined.

2. Experimental

Commercial LiCoO₂ was coated with V₂O₅ using a sol-gel process. A V₂O₅ sol was prepared via a melt-quenching method [15]. The crystalline V₂O₅ powder was melted at 800 °C in an electric furnace. After holding for 20 min at this temperature, the melt was quenched rapidly in distilled water with vigorous stirring. A brownish sol was obtained after 2 h and the appropriate amount of LiCoO₂ was dipped into the sol. The mixture was stirred continuously at 40 °C and finally the sol was changed to a gel. The gel on LiCoO₂ was dried at 70 °C in a convection oven for 8 h and then heat treated at 400 °C (designated as V-400) and 600 °C (designated as V-600) for 12 h in air.

The crystal structure of the resulting powder was analyzed by powder X-ray diffraction (XRD, Rigaku D/Max-2500/PC, Japan) with a Cu K α radiation source. The particle size and shape of the samples were investigated by means of field emission scanning microscopy (FE-SEM, S-800, Hitachi, Japan). The coating status of the sample was observed by transmission electron microscopy (TEM, JEM 2000EX, JEOL, Japan).

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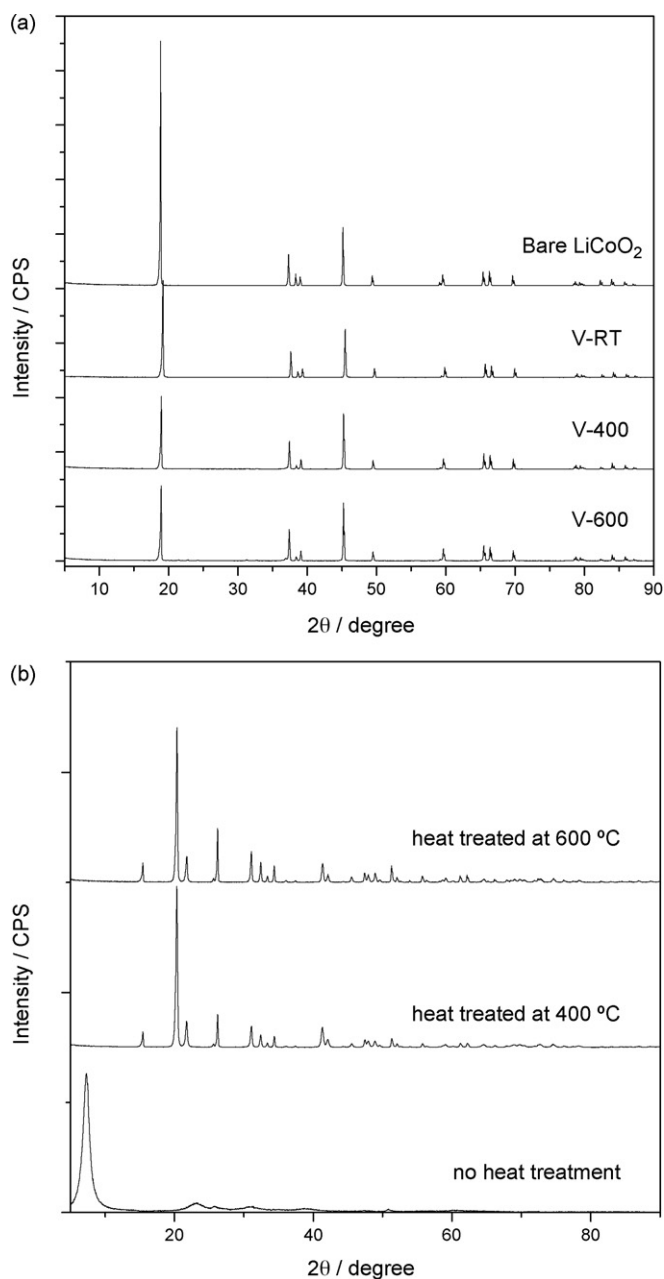


Fig. 1. X-ray diffraction pattern of: (a) bare LiCoO₂ and vanadium oxide-coated LiCoO₂; (b) vanadium oxides calcined at different temperatures.

A coin-cell (CR2016) was used to examine the electrochemical performance of the obtained samples. The positive electrode was made by coating a slurry composed of the active material, Super-P carbon black (MMM, Belgium) and polyvinylidene fluoride (PVdF) binder (Kurea, Japan) at a weight ratio of 80:10:10 on an aluminum foil current-collector. The positive electrodes were prepared by punching and pressing at 1 ton cm⁻², followed by drying at 130 °C for 8 h in a vacuum to remove the adsorbed water. The coin-cells, each of which consisted of a cathode, lithium foil as an anode, a reference electrode and a microporous polyethylene separator, were assembled in an argon-filled glove box. The electrolyte was a 1.0 M LiPF₆ solution in ethylene carbonate/ethyl-methyl carbonate (EC/EMC) (1/1 vol.%) (Cheil Ind., Korea). Galvanostatic charge and discharge cycle tests were carried out at room temperature between 3.0 and 4.4 V.

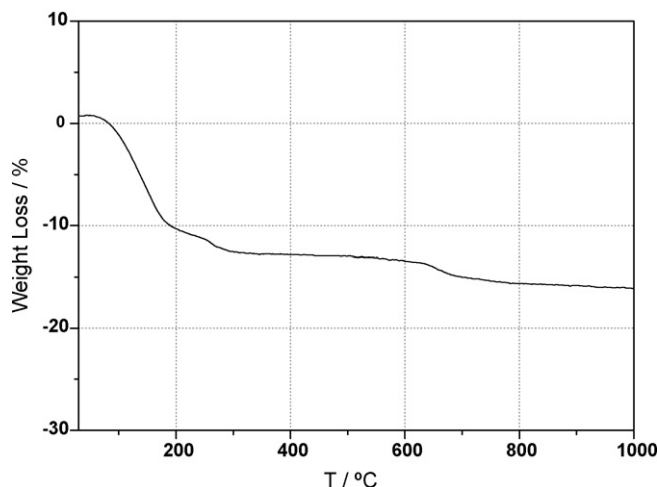


Fig. 2. Thermal gravimetric analysis of vanadium oxides.

3. Results and discussion

Fig. 1(a) shows the XRD patterns of bare and vanadium oxide-coated LiCoO₂. The peaks for V₂O₅ or V₂O₅·xH₂O were not observed in the pattern due to the thin coating and the relatively low degree of crystallinity of V₂O₅ or V₂O₅·xH₂O compared with LiCoO₂. The XRD patterns of V₂O₅ or V₂O₅·xH₂O prepared using the melt-quenching method are also shown in Fig. 1(b) for reference. The V₂O₅ was obtained in hydrate form after drying the gel, and was converted to the anhydrous form after heat treatment. The results of thermogravimetric analysis are given in Fig. 2. The reference V₂O₅ hydrate sample was analyzed from room temperature to 1000 °C. The water in V₂O₅·xH₂O was removed gradually from 70 to 300 °C with a weight loss of 13%, which corresponds to approximately $x = 1.5$, and no distinct change was observed up to 600 °C.

The surfaces of the bare and V₂O₅-coated LiCoO₂ are given in Fig. 3. V₂O₅ or V₂O₅·xH₂O are clearly observed on the surface. The sample coated with V₂O₅·xH₂O and not calcined (designated as V-RT) appears to be covered with a film-like layer. The surfaces of V-400 and V-600 are somewhat different from that of V-RT. The proportion of the coated surface appears to be less than that of V-RT. The morphology and crystal structure of the coating layer of V-RT changes at the same time as the water in V₂O₅·xH₂O is released. Vanadium was mapped using energy dispersive X-ray spectroscopy (EDS); the results are shown in Fig. 4. Vanadium is distributed uniformly over the film-like layer on the surface. The overall molar ratio of vanadium oxide to LiCoO₂ is estimated to be 1.5%, which corresponds to 1.6 wt.% of V₂O₅·xH₂O.

A TEM image of the V₂O₅ coating layer of sample V-400 is given in Fig. 5. Nanoparticle aggregates of V₂O₅ are observed on the surface. The surface is partially covered, which corresponds to the SEM images.

The initial charge and discharge profile is presented in Fig. 6. The capacities of V-400 and V-600 are similar to that of the bare LiCoO₂ without significant capacity loss from the oxide coating. By contrast, the capacity of V-RT is much lower than that of the other V₂O₅-coated samples and bare LiCoO₂. The potential on the first charge of V-RT is higher than that of the other samples, but lower from the second cycle. It appears that the resistance at the interface between V₂O₅·xH₂O and LiCoO₂ is higher than for the V₂O₅-coated sample, which results in high polarization at the first charge and a lower specific capacity.

The cycleability of the samples when charged to 4.4 V is shown in Fig. 7. V-400, the sample calcined at 400 °C, gives the best cycle-

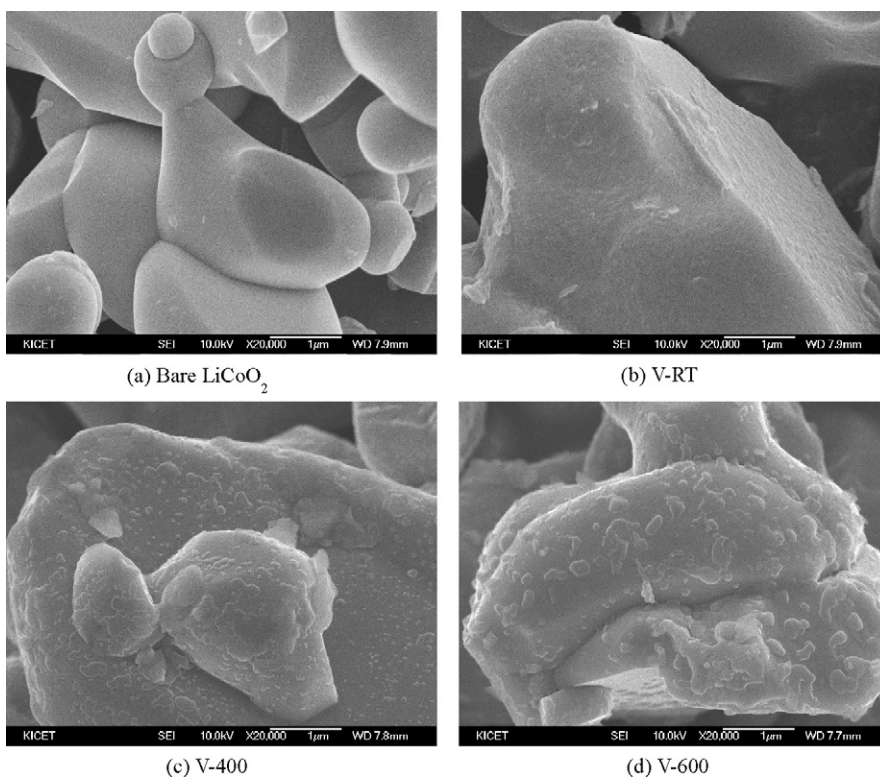


Fig. 3. Scanning electron microscope images of: (a) bare LiCoO_2 , (b) V-RT, (c) V-400, (d) V-600.

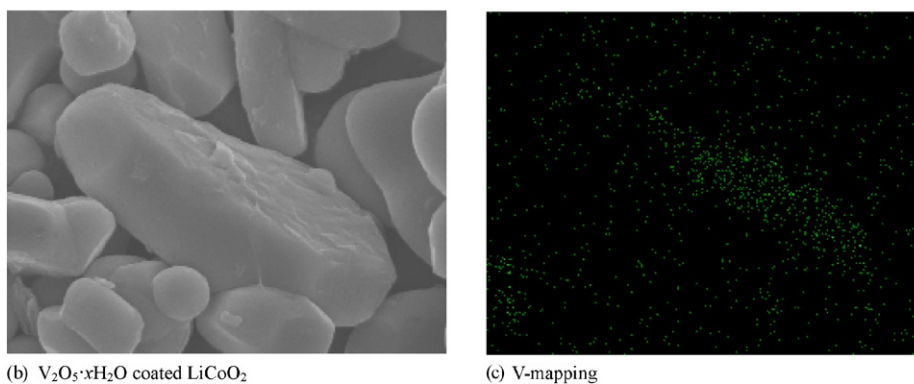
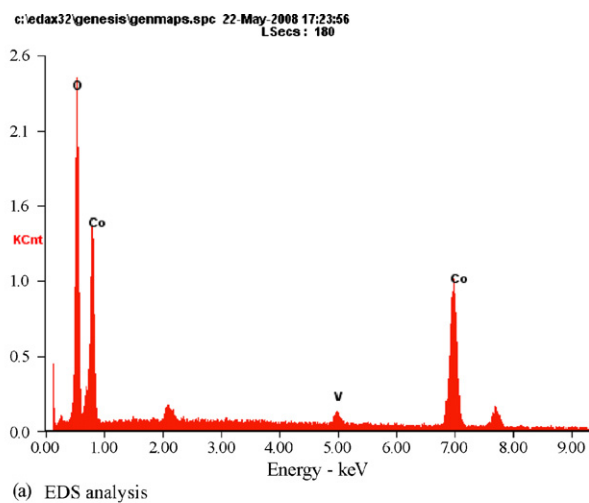


Fig. 4. Energy dispersive X-ray spectrometer analysis: (a) EDS spectrum of V-RT; (b) SEM image of V-RT; (c) EDS dot-mapping for V.

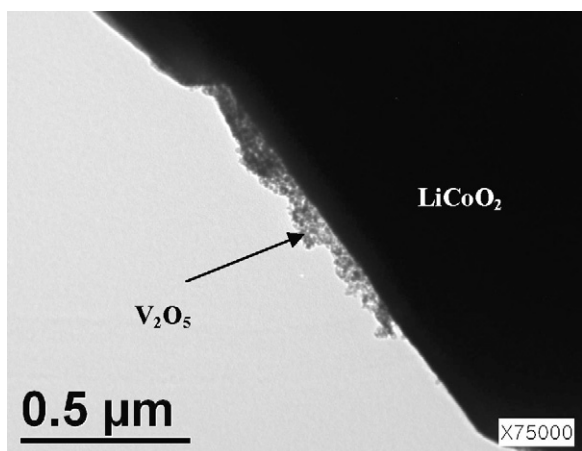


Fig. 5. Transmission electron microscope image of vanadium oxide-coated LiCoO₂.

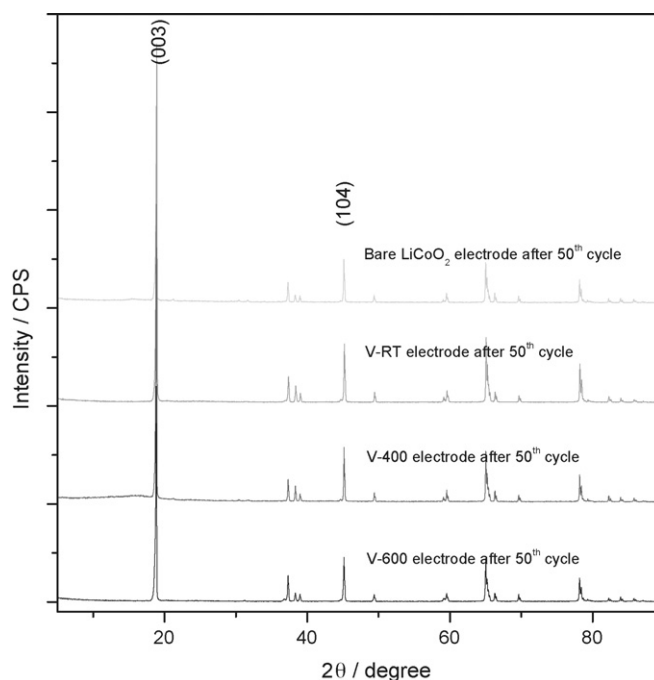


Fig. 8. X-ray diffraction pattern of electrodes after 50th cycle.

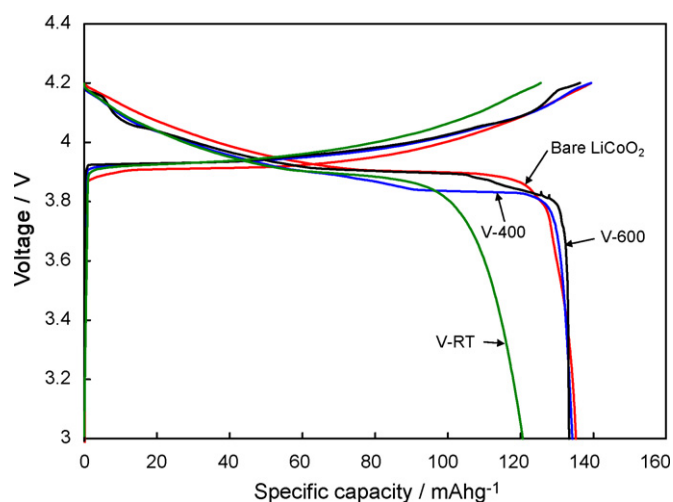


Fig. 6. First charge and discharge curves of samples with a cut-off voltage ranging from 3.0 to 4.2 V.

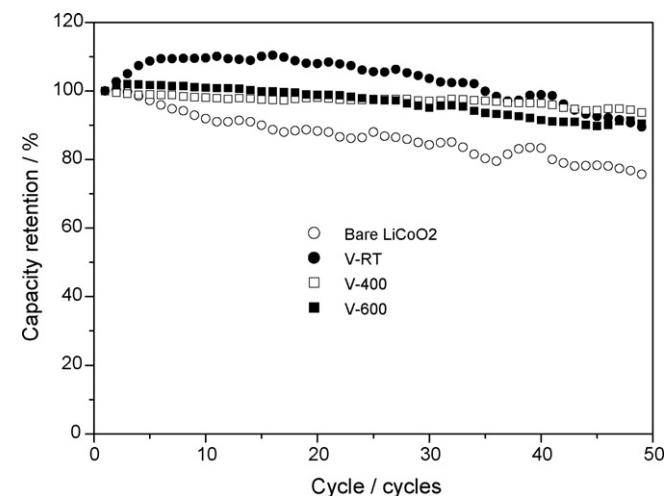


Fig. 7. Cycle-life performance of samples with cut-off voltage ranging from 3.0 to 4.4 V.

life performance. V-RT shows an increase in capacity at the initial stage but steep capacity fading after reaching a maximum value. All V₂O₅-coated samples are superior to the bare LiCoO₂ in terms of the cycle-life performance. The electrodes were analyzed by XRD

after the 50th cycle, and the peak patterns are shown in Fig. 8. Li et al. [16] reported a relationship between the relative peak intensity and cation mixing of LiCoO₂. The relative peak intensity ratio between the (003) and (104) planes of the electrodes was estimated after the 50th cycle. The ratio for the bare LiCoO₂, V-RT, V-400 and V-600 is 3.184, 4.054, 4.900, and 5.220, respectively. The intensity ratios of the V₂O₅-coated electrodes are greater than that of the bare LiCoO₂ electrode. This means that the degree of cation mixing during cycling can be mitigated by a V₂O₅ coating on LiCoO₂. Consequently, better cycleability can be achieved from the coating.

4. Conclusions

LiCoO₂ is coated with vanadium oxides using a sol-gel process to enhance the cycleability at high voltage. Investigations by SEM and TEM confirm that nanoparticles of vanadium oxides coat the LiCoO₂ surface uniformly. The vanadium oxides on LiCoO₂ are distributed uniformly and are identified as V₂O₅ or V₂O₅·xH₂O by XRD, TG-DTA and EDS analysis. By adjusting the calcination temperature, the coating effect can be controlled and the best performance is achieved with a sample calcined at 400 °C. The coating of vanadium oxides imparts a better cycle performance at a high-charge cut-off voltage than the bare LiCoO₂ electrode by preventing cation mixing during cycling and reducing the active surface area that contacts the electrolyte.

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