

Short communication

Electrochemical studies on surface coated LiCoVO_4 with Al_2O_3 derived from carboxylate-alumoxane for lithium-ion cells

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Abstract

Various wt.% of Al_2O_3 derived from methoxyethoxy-alumoxane (MEA-alumoxane) were coated by a simple mechano-thermal method on the LiCoVO_4 particles, which were synthesized by a citric acid–urea polymeric method. Powder XRD patterns confirmed that the prepared LiCoVO_4 crystalline sample had an inverse spinel structure when heated at 773 K for 5 h in air and the LiCoVO_4 materials coated with Al_2O_3 showed no evidence of secondary phase peaks. TEM images of LiCoVO_4 identified that the nanosized particles ranged ~ 100 – 120 nm and Al_2O_3 coating had an average thickness of ~ 20 nm over the fine particle of LiCoVO_4 . XPS binding energy data indicated that the presence of two different types O 1s ions corresponds to alumina and core LiCoVO_4 material. The charge and discharge study indicated that the 0.5 wt.% Al_2O_3 derived from MEA-alumoxane coated material delivered an initial discharge capacity of 68 mAh g^{-1} at 3.0–4.5 V and the cycle stability after 20 cycles was stable without any drastic capacity fade normally exhibited by inverse spinel materials. The dQ/dV versus voltage plots revealed that the slower impedance growth for the Al_2O_3 surface coated LiCoVO_4 cathode material.

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1. Introduction

Lithiated transition metal oxides, the layered LiMO_2 ($M \sim \text{Co}$, Ni, Mn) and the spinel LiMn_2O_4 have been widely studied as cathode materials for commercial lithium-ion cells [1,2]. Another new class of inverse spinel structured lithium transition metal vanadate cathode materials was explored by Fey et al. [3], and have attracted the attention of many authors because of high charge voltage. For example, LiCoVO_4 (4.3 V) and LiNiVO_4 (4.8 V) [3–6]. However, cathode materials derived from these inverse spinel vanadates endure several problems such as low discharge capacities, drastic drops in initial capacity, and large capacity fades during continuous cycling. The drawbacks could be associated with the diffusion and dissolution of transition metal ion into the acidic electrolyte. A disproportionate reaction occurs on the surface of the cathode materials, and the high-voltages (>4.5 V) cathode materials were strong oxidizers that may create electrolyte degradation [6–9].

Therefore, in order to develop and achieve high capacity and decrease the capacity fades, many authors attempted to prepare the inverse spinel structure materials as homogenous, uniform nanosized particles through various syntheses techniques and by doping metals and non-metals to the pristine cathode materials [10–13]. Another approach that involved modifying the surface of the cathode material by coating it with electrochemically inactive metal oxides improved the cycle stability and capacity retention. Al_2O_3 [14–18], Co_3O_4 [19], TiO_2 [20], SiO_2 [21] coated to the inverse spinel, the spinel and the layered cathode material enhanced the cycling behavior of the cathode. The electrochemical performance of the coated cathode materials mainly depend on the precursor materials [8,9,14–21], which determined the uniform and well-adhered coating on the surface of the core material. Al_2O_3 as a coating material to improve the cycle stability of the cathode materials has been investigated by several authors [14–18]. In our prior work [17,18], we demonstrated that Al_2O_3 coatings derived from precursors of carboxylate-alumoxanes possess better cycle stability than coatings from other precursor materials. The chemical composition of carboxylate-alumoxanes, $[\text{Al}(\text{O})_x(\text{OH})_y(\text{O}_2\text{CR})_z]_n$, consist of an alumina core surrounded by covalently bonded carboxylate ligands. Hence, in this work, we have attempted to synthesize

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LiCoVO₄ by a citric acid–urea polymeric method and coat the core LiCoVO₄ material with various wt.% of Al₂O₃ derived from MEA-alumoxane by a simple mechano-thermal process and studied their electrochemical behavior.

2. Experiment

LiCoVO₄ cathode material was prepared by a citric acid–urea method using stoichiometric amounts of LiNO₃, Co(NO₃)₂·6H₂O (Merck, >99%), and NH₄VO₃ (Acros Organics, >98%). The precursors were dissolved in the deionized water with constant stirring at 298 K and citric acid in deionized water was added in dropwise, followed an addition of urea. The resultant transparent dark bluish solution was heated gently at 363 K for 6 h to remove excess water and allowed to form a polymeric gel, which was heated at 393 K in an oven for 24 h. The dried polymeric gel precursor was heated at a ramping rate of 4 K min⁻¹ at 773 K for 5 h in air, with intermediate grinding.

MEA-alumoxane was synthesized from pseudo-boehmite, [Al(O)(OH)]_n (Plural SB) and methoxyethoxy acetic acid (Aldrich) as described in our prior work [17,18]. The calculated wt.% of MEA-alumoxane was dispersed in double distilled water for 10 h and sonicated for 30 min with the above-prepared LiCoVO₄ powder and stirred for 10 h at 298 K. Subsequently, the mixture was heated at 323 K to eliminate excess water by slow evaporation and obtain a thick slurry that was further dried in an oven at 383 K for 24 h. The resultant was a black dry mass of MEA-alumoxane coated LiCoVO₄ particles. The obtained powder was calcined at 723 K in air for 10 h, when MEA-alumoxane decomposed to yield an adherent coating of Al₂O₃ on the LiCoVO₄ particles [22]. The weight ratios of Al₂O₃ to LiCoVO₄, formed during calcination, were 0.1:99.9, 0.5:99.5 and 1.0:99.0.

A powder X-ray diffractometer (XRD), Siemens D-5000, Mac Science MXP18, equipped with a nickel-filtered Cu K α radiation source ($\lambda = 1.5405 \text{ \AA}$) was used to study the structure and phase purity. The diffraction patterns were recorded between scattering angles of 15° and 80° in steps of 0.05°. The microstructures of the particles were examined by a JEOL JEM-200FXII transmission electron microscope (TEM) equipped with a LaB₆ gun. X-ray photon spectroscopy (XPS) were recorded by a XPS analyzer, Fisons instrument, with monochromatic Mg K α radiation 1523.6 eV and the spectra were scanned in the range of 0.00–1400.00 eV binding energy (BE) in 1.00 eV steps.

The cathodes for electrochemical studies were prepared by a doctor-blade coating method as described elsewhere [18]. The electrochemical performance was carried out with coin type cells of the 2032 configuration that were assembled in an argon-filled VAC MO40-1 glove box. The above prepared circular disk was used as the cathode, lithium metal (Foote Mineral) as the anode and a 1 M LiPF₆ in 1:1 by volume ethylene carbonate (EC)/diethyl carbonate (DEC) (Tomiya Chemicals) as the electrolyte with a Celgard membrane as the separator. The cells charge–discharge cycles were preformed at a 0.1 C rate between 3.0–4.5 V in a multi-channel battery tester (Maccor 4000) at 298 K.

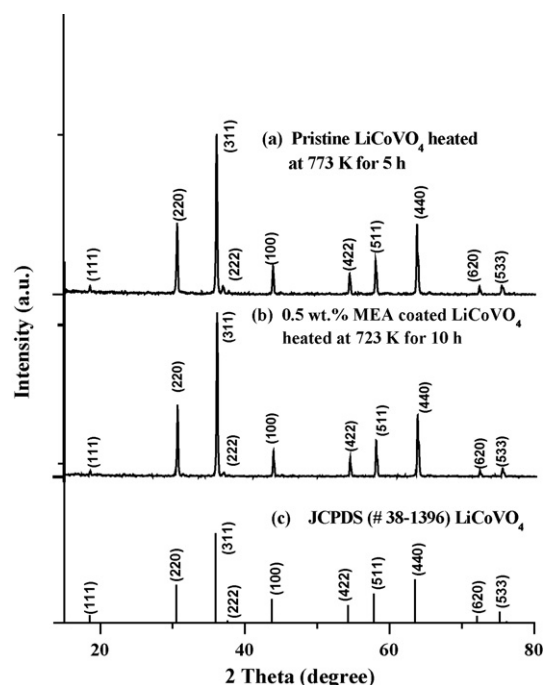


Fig. 1. XRD patterns for (a) pristine LiCoVO₄, (b) 0.5 wt.% Al₂O₃ coated LiCoVO₄ and (c) JCPDS (#38-1396) LiCoVO₄.

3. Results and discussion

Fig. 1a–c shows the XRD patterns for pristine LiCoVO₄ heated at 773 K for 5 h in air, 0.5 wt.% Al₂O₃ derived from MEA-alumoxane coated LiCoVO₄ at 723 K for 10 h in air and JCPDS #38-1396 of LiCoVO₄, respectively. From Fig. 1a, it is observed that phase pure crystalline LiCoVO₄ was obtained when calcined at 773 K for 5 h in air. The pure single-phase synthesized LiCoVO₄ compound has been indexed to the JCPDS #38-1396 pattern (Fig. 1c), which has an inverse spinel structure with $Fd\bar{3}m(O_h^7)$ space group symmetry [23]. In Fig. 1b, the observed XRD reflection positions remained same as pristine LiCoVO₄ for the 0.5 wt.% Al₂O₃ coated LiCoVO₄ cathode material and there was evidently no appearance of any secondary phase peaks corresponding to Al₂O₃. Therefore, from the XRD results, it is concluded that the surface coated Al₂O₃ was of a very low concentration and so did not reveal any corresponding peaks.

Fig. 2a and b shows the TEM images of the pristine LiCoVO₄ and the 0.5 wt.% Al₂O₃ coated LiCoVO₄ cathode materials, respectively. In Fig. 2a, it is noticeable that the synthesized LiCoVO₄ crystalline sample was nanosized spherical particles with an average particle size range ~100–120 nm. The particles shown in Fig. 2a have a unique nanosized spherical shape that is attributed to the action of the chelating agent assisted with urea to form unidentate bonded complexes between the metallic cations and citric acid that make it easy to obtain homogeneous and nanosized particles. From Fig. 2b, it is clearly observed that a compact thin translucent layer (Al₂O₃ particles) with a thickness of ~20 nm covered the surface of the core LiCoVO₄ material. Therefore, the formed thin layer of Al₂O₃ coating demonstrated a good additive property through physiochemi-

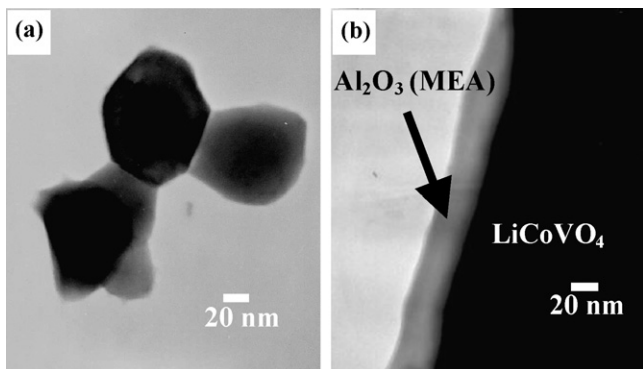


Fig. 2. TEM images of (a) pristine LiCoVO_4 , and (b) 0.5 wt.% Al_2O_3 coated LiCoVO_4 cathode material.

cal interaction between the core and coating material, which improved the adhesiveness of the coating.

Fig. 3 shows the XPS spectrum of O 1s for the 0.5 wt.% Al_2O_3 coated LiCoVO_4 sample. From Fig. 3, it is observed that the O 1s spectrum shows an unsymmetrical peak in the region 528–534 eV. The fitted O 1s peak of Al_2O_3 -coated LiCoVO_4 revealed two bands, one centered at 530.6 eV and another at 531.9 eV, which clearly indicates two different environmental oxygen ions could be observed. The various depth level XPS data have revealed only a single symmetrical band centered at 530.6 eV. A low intensity band centered at a BE of 531.9 eV corresponds to the Al_2O_3 , whereas the high intensity band centered at 530.6 eV corresponds to O 1s bonded with ions in the lattice of the core material [14,24]. The BE 530.6 eV value does not change even after coating the core sample with Al_2O_3 [24]. It could be concluded that the coating did not affect chemical state or binding energies of the different ions in the LiCoVO_4 material, because the Al_2O_3 coating material remained on the surface and there was no interaction with the core material to form an inter-oxide solid-solution.

Fig. 4 shows the charge and discharge capacity data of pristine LiCoVO_4 and 0.1, 0.5 and 1.0 wt.% Al_2O_3 coated LiCoVO_4 . The initial charge and discharge capacity of pristine LiCoVO_4 were 71 and 61 mAh g^{-1} , respectively. After 20 cycles, the discharge capacity was 18 mAh g^{-1} and the coulombic efficiency 30% for the first 20 cycles. The capacity fading increased with continuous

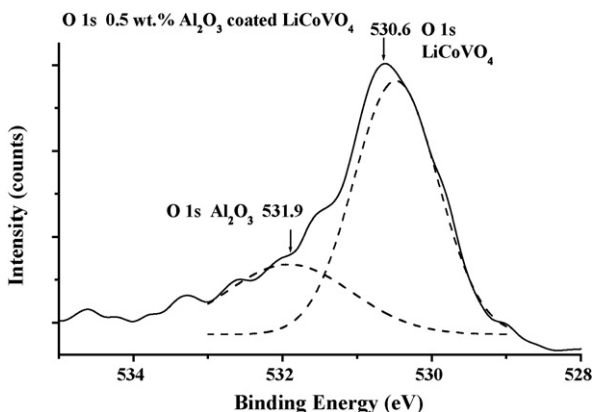


Fig. 3. XPS O 1s spectrum of 0.5 wt.% Al_2O_3 coated LiCoVO_4 .

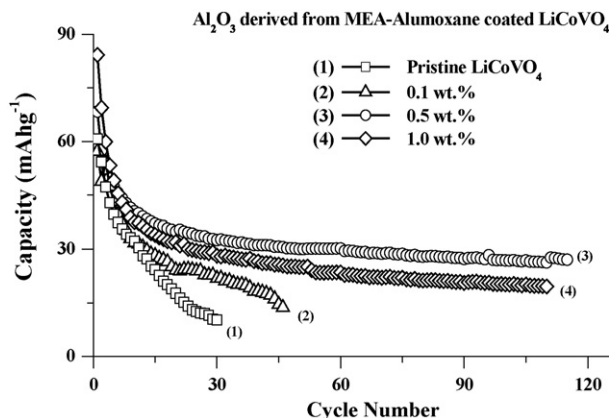


Fig. 4. Cycling behavior of the pristine LiCoVO_4 and the various wt.% Al_2O_3 coated LiCoVO_4 cathode materials. Charge–discharge: 0.1 C rate between 3.0 and 4.5 V.

cycling and exhibited 10 mAh g^{-1} for 30 cycles. In Fig. 4, the charge and discharge capacity data for 0.1, 0.5 and 1.0 wt.% Al_2O_3 coated LiCoVO_4 were 71, 77 and 108 mAh g^{-1} and 57, 68 and 84 mAh g^{-1} , respectively. After 20 cycles, the discharge capacity of the 0.1, 0.5 and 1.0 wt.% Al_2O_3 coated samples was 24, 35 and 32 mAh g^{-1} and coulombic efficiency was 42%, 51% and 38% for first 20 cycles, respectively. Thus, better discharge capacity and cycle stability was achieved by the Al_2O_3 coated cathode materials compared to the pristine cathode.

From Fig. 4, the 0.5 wt.% Al_2O_3 coated sample initially showed a fall in the capacity for 20 cycles and thereafter, it retained cycle stability with a slope of -0.083 for about 115 cycles. A practical assessment of 0.1, 0.5 and 1.0 wt.% of coating levels show a lower coating level of 0.1 wt.% was advantageous, but resulted in an insufficient compact coating on the core material. Hence, the cycle stability and initial capacity declined drastically. However, when the coating level was increased to 0.5 and 1.0 wt.%, cycle stability was much better after 20 cycles with coulombic efficiency of 80%. Among 0.5 and 1.0 wt.% Al_2O_3 coated LiCoVO_4 samples, 0.5 wt.% exhibited a better discharge capacity, as well as cycle stability. The improved cycle stability of the cathode showed that the Al_2O_3 coating on the surface shielded the core material from direct contact with the acidic electrolyte at a high voltage of 4.5 V. Thackeray et al. [25] reported that ZrO_2 coated LiMn_2O_4 showed enhanced cycle stability, since an amphoteric ZrO_2 formed on the surface protected the acidic LiPF_6 liquid electrolyte from direct contact with the core material. In the present study, the Al_2O_3 coating material is an amphoteric oxide that protects the surface of the cathode material from harmful side reactions, dissolution of Co ions and direct contact of the cathode particles with the acidic electrolyte solution. The results obtained with our coating technique agree well with existing literature [14–21]. Apart from the improved cycle stability of the coated materials, a coating process based on MEA-alumoxane is more attractive and its importance was reported in our prior studies [18].

Fig. 5a shows the dQ/dV versus voltage plot of pristine LiCoVO_4 when the charge–discharge was between 3.0 and 4.5 V

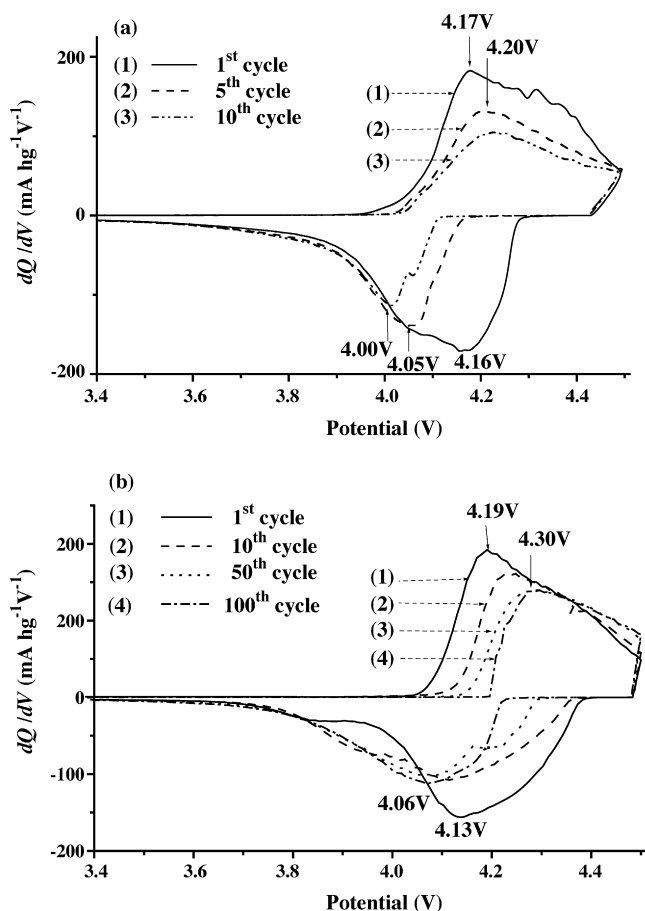


Fig. 5. The dQ/dV vs. voltage curves charge–discharge at 3.0–4.5V; 0.1 C rate for (a) pristine LiCoVO_4 and (b) 0.5 wt.% Al_2O_3 coated LiCoVO_4 .

at 293 K for 1st, 5th and 10th cycles. Fig. 5b shows the dQ/dV versus voltage plot of 0.5 wt.% Al_2O_3 coated LiCoVO_4 for 1st, 10th, 50th and 100th cycles. In Fig. 5a, the charge and discharge peaks (oxidation and reduction) centered at ~ 4.17 V and ~ 4.16 V, respectively, were broader. The peaks correspond to the redox couple of $\text{Co}^{2+}/\text{Co}^{3+}$ of the LiCoVO_4 material, accompanied by (de)intercalation of Li^+ ions in the matrix. There is a shift in the charge–discharge peak potentials and the area under the peaks decreases with 10 cycles, which corresponds to faster capacity fade. In Fig. 5b, the 0.5 wt.% Al_2O_3 coated sample showed the peak potentials of oxidation and reduction were centered at ~ 4.19 V and ~ 4.13 V, respectively. There was a slight shift with the relative peak intensities and slight decrease in the area under the peaks upon cycling to 100 cycles, which indicates the reversibility and slow capacity fading attributable to slower impedance growth on the surface of the coated samples compared to the pristine LiCoVO_4 cathode material. Edstrom et al. [26] from the XPS analysis concluded that the cathode material surface is formed of organic species and their reactions with the lithium-salt anion are more dependent on electrode material type. It is especially important to reduce the impact of the PF_6 anion and its related contaminants (HF and PF_5) on electrode surface chemistry through the implementation of more stable salts.

4. Conclusions

The surface of the LiCoVO_4 cathode, synthesized through a citric acid–urea polymeric method, was coated with 0.1, 0.5 and 1.0 wt.% of Al_2O_3 by a polymeric process. TEM images exposed that the coated layer formed a thick kernel of ~ 20 nm on the LiCoVO_4 material. In addition, XPS results confirmed that the coated Al_2O_3 remained on the surface of the core material by two different types of O 1s ions. The cell performance of 0.5 wt.% Al_2O_3 coated LiCoVO_4 retained 27 mAh g^{-1} for 110 cycles with better cycle stability. The dQ/dV versus voltage plots of the cathode materials suggest there was slower impedance growth on the surface of the 0.5 wt.% Al_2O_3 coated LiCoVO_4 compared to the pristine LiCoVO_4 cathode material.

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