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<td>Author(s)</td>
<td>Aravindan, Vanchiappan; Cheah, Yan Ling; Wong, Chui Ling; Madhavi, Srinivasan</td>
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Effect of LiBOB Additive on the Electrochemical Performance of LiCoPO₄

V. Aravindan, a Yan L. Cheah, b W. Chui Ling, a and S. Madhavai, a,b,c,z

a Energy Research Institute @ NTU (ERI@N), Nanyang Technological University, Singapore 637553
b School of Materials Science and Engineering, Nanyang Technological University, Singapore 639798
c TUM-CREATE Center for Electromobility, Nanyang Technological University, Singapore 637553

Solid-state method is used to synthesise sub-micron size lithium cobalt phosphate, LiCoPO₄ particles. Powder X-ray diffraction pattern reveal the formation of pure phase orthorhombic structure with puna space group. Electrochemical properties of LiCoPO₄ are evaluated in half-cell configurations with conventional 1 M LiPF₆ ethylene carbonate (EC): diethyl carbonate (DEC) electrolyte solution. Interestingly, increasing charging potential leads to the decrease in re-insertion potential as is confirmed by cyclic voltammetric (CV) measurements. Galvanostatic studies corroborated CV analysis and suggest that higher charge potential delivers maximum discharge capacity, but with severe capacity fade upon cycling. Incorporation of lithium bis(oxalato)borate (LiBOB) in conventional electrolyte solutions certainly enhances the cyclability of LiCoPO₄ electrode, for example 3 wt% of LiBOB comprising electrolyte shows capacity retention of 74% of its initial discharge capacity after 25 cycles. The present study elucidates LiBOB addition is one of the unique approaches to alleviate the capacity fade of LiCoPO₄ during cycling.

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Recently, research focus is devoted to the development of high voltage cathodes for lithium–ion batteries with much more safety features than LiCoO₂, LiMn₂O₄ and its derivatives. 1-3 Lithium cobalt phosphate, LiCoPO₄ belongs to the olivine family and is one of the high voltage candidates (~4.8 V vs. Li) with highest theoretical energy density of 800 Wh kg⁻¹. Other candidates from olivine family LiFePO₄ and LiMnPO₄ have been extensively studied and reported as alternative cathodes for the place of LiCoO₂. 4-13 Among which LiFePO₄ is commercialized by A123 Inc. (with mass production of conducting properties, Yang et al. 23 attempted to make in-situ carbon coating, in which acetylene black was included during in-situ atmosphere sintering is necessary, which in turn provides the secondary phase materials (LiCoPO₄). The electrolyte containing 1% tris(hexafluoroisopropyl) phosphate (HFIP) additive showed the capacity retention of ~85% after 10 cycles reported by Allen et al. 19 This line, an attempt has been made to study the influence of lithium bis(oxalato)borate (LiBOB) concentration toward LiCoPO₄, obtained by solid-state reaction. The inclusion of LiBOB into electrolyte provides many fold advantages like increase in Li⁺ ion mobility thereby enhancing ionic conductivity, over charge tolerance, formation of stable and robust semi-carbonate type solid electrolyte interphase (SEI) layer etc. 26 The semi-carbonate type SEI is expected to provide the necessary protection for LiCoPO₄ particles from the nucleophilic attack of F⁻ ions from HF present in the electrolyte. Further, the prepared LiCoPO₄ has been subjected to various cutoff potentials in conventional 1 M LiPF₆ EC:DEC 1:1 wt% solution and the obtained results are described in detail.

Experimental

Solid-state procedure was adapted to synthesis LiCoPO₄ powders under the optimized conditions stated below. In a typical synthesis procedure, stoichiometric amounts of LiOH·H₂O (Aldrich, USA), CoO (Aldrich, USA) and NH₄H₂PO₄ (Sigma-Aldrich, USA) were used. First, the starting materials were finely ground, made into a pellet, and calcined at 400 °C for 10 h to decompose hydroxyl and ammonia moieties present in the source. Then, the intermediate product was finely ground again, placed in a tubular furnace and heated at 800 °C for 10 h to yield the resultant LiCoPO₄ powders.

Crystal structural diffraction studies were carried out using Bruker AXS, D8 Advance X-ray diffractometer equipped with Cu Kα radiation. Rietveld refinement was conducted for the obtained X-ray diffraction patterns (XRD) using Topas V3 software. Morphological features and internal structure of the powders were studied by transmission electron microscopy (TEM, JEOL 2100F). The electrochemical properties were evaluated in standard two electrode CR 2016 coin-cell configurations at ambient temperature conditions. All the composite electrodes were formulated with 20 mg of active material (LiCoPO₄), 3 mg of super P, and 3 mg of binder (Teflonized acetylene black, TAB-2). It was pressed on a 200 mm² stainless steel
Figure 1. Rietveld refined powder X-ray diffraction pattern of synthesized LiCoPO₄ particles.

Results and Discussion

Powder X-ray diffraction pattern of synthesized LiCoPO₄ is given in Figure 1 with Rietveld refinement. The obtained patterns clearly indicate the formation of native compound without any impurity traces like, Co₃O₄, Li₃PO₄ etc. The Rietveld refinement has been carried out using Topas V3 software based on orthorhombic structure with pnma space group. The observed lattice parameter values, a = 10.211 (6), b = 5.924 (8) and c = 4.703 Å are consistent with the literature values (JCPDS #89-6192). The average crystallite size is also calculated during refinement from Scherrer formula and found to be 86 nm. The cell parameters are indexed for bright spots.

The LiCoPO₄ particle size distribution is similar to its counterparts LiFePO₄ and LiMnPO₄. The Rietveld refinement has been carried out using Topas V3 software based on orthorhombic structure with pnma space group. The obtained patterns clearly indicate the formation of native compound without any impurity traces like, Co₃O₄, Li₃PO₄ etc. The Rietveld refinement has been carried out using Topas V3 software based on orthorhombic structure with pnma space group. The observed lattice parameter values, a = 10.211 (6), b = 5.924 (8) and c = 4.703 Å are consistent with the literature values (JCPDS #89-6192). The average crystallite size is also calculated during refinement from Scherrer formula and found to be 86 nm. The cell parameters are indexed for bright spots.

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Figure 2. (a) Transmission electron microscopic (TEM) picture of LiCoPO₄ particles and (b) high-resolution TEM pictures with selected area electron diffraction pattern.

Family of cyclic voltammograms (CV) for LiCoPO₄ particles in half-cell configuration (Li/LiCoPO₄) comprising the conventional electrolyte (1 M LiPF₆ EC:DEC 1:1 wt%) with various charging potential limits (3.5–5 V, 3.5–5.05 V, 3.5–5.1 V, 3.5–5.15 V and 3.5–5.2 V) is described in Figure 3a–3e. For the CV measurements, metallic lithium acts as both counter and reference electrode. Impedance/gain-phase analyzer coupled with a potentiostat in the two electrode configuration with metallic lithium as act as both counter and reference electrode. Galvanostatic cycling profiles were recorded using Arbin 2000 battery tester at 0.05 C (1C = 100 mAh g⁻¹) rate between various potential ranges.

The strong P–O covalent bond in LiCoPO₄ polyanion framework is expected to translate high thermal and electrochemical stability, which is obvious to notice all the test cells showed the open circuit voltage (OCV) of ∼3 V vs. Li and cells were first charged to extract lithium from the lattice. All the cells showed the oxidation of Co²⁺ to Co³⁺ couple occurred above ∼4.8 V vs. Li. Increasing cutoff potential results increase in peak current, which in turn provides higher reversible capacity and clearly evident from Figure 3f. Surprisingly, all the cells showed the different re-insertion potentials. More clearly, increasing the upper-cut off potential from 5 to 5.2 V results shifting the re-insertion potential toward lower voltage from 4.67 to 4.59 V with linear decrease and illustrated in Figure 3f (inset). According to Aurbach et al.,¹⁷,¹⁸ decrease in re-insertion potential results the depletion of undamaged active mass on the surface of electrode and not due to the growth of surface resistance. Further, area under the CV curve is also decreased during subsequent cycling irrespective of the cutoff potentials. Decrease in the area under the curve is found more severe in the case of 3.5–5.2 V potential windows, whereas minimum for 3.5–5 V. The observed CV traces and decrease in area under the curve is consistent with Aurbach et al.¹⁷ report. This clearly reveals the capacity fading upon cycling and correlating the following side reaction with HF present in the electrolyte solutions.

PO₄⁻ + HF + H⁺ ↔ POF₂⁻ + H₂O
PO₄F⁻ + HF + H⁺ ↔ POF₂F₂ + H₂O
PO₄F⁺ + HF + H⁺ ↔ POF₃ + H₂O

Moreover according to the above mechanism, presence of trace amount of water molecules start a chain process that leads to the full degradation of the cathode material due to the formation of difluorophosphate lithium salts. Interestingly, the difluorophosphate lithium salts also dissolves in the electrolyte solutions. Mainly, the nucleophilic attack of F⁻ ions from HF on phosphorus atoms from (PO₄)³⁻ group occurred in the de-lithiated phase of LiCoPO₄. Since, Co³⁺ exists in high-spin configuration in the de-lithiated phase (CoPO₄) unlike that of other de-lithiated olivine phases MnPO₄ and FePO₄. This leads to the degradation of the active material near its surface, accompanied by the dissolution of the product in to the electrolyte solution.

In order to complement the results obtained in the CV analysis, galvanostatic charge-discharge studies were conducted in the half-cell configuration (Li/LiCoPO₄) for different potential limits (3.5–5 V, 3.5–5.1 V and 3.5–5.2 V) using same 1 M LiPF₆ EC:DEC 1:1 wt% electrolyte solution at 0.05 C rate in room temperature. Figure 4a shows the typical galvanostatic charge-discharge curves of
Li/LiCoPO4 half-cells with superimposed region of discharge curves. The shifting of re-insertion potential toward lower voltages, while increasing charging potential is clearly observed. The superimposed portion clearly distinguishes the shifting of potential toward lower voltage and corroborates well with CV measurements. At the same time, there is no deviation in the charging curves are noted. The Li/LiCoPO4 cell delivered the initial discharge capacity of 96, 111 and 115 mAh g\(^{-1}\) for 5, 5.1 and 5.2 V cutoff potentials, respectively. Increasing the potential to 5.2 V leads to the extraction of more number of lithium ions, which in turn provides the higher capacity. Nevertheless, the charge capacity exceeds the theoretical capacity of the LiCoPO4 when charging beyond 5 V and obtained extra capacity is also due to the decomposition of electrolyte solution along with lithium extraction. The cycling performances of the Li/LiCoPO4 cells with different potentials are given in Figure 4b. As expected, the discharge capacity tends to decreased with cycle number in all the three cases. The capacity fading is severe in the case of 3.5–5.2 V range when compared to the rest and observed fading is consistent with our previous reports and other reports as well. It is believed that, at higher potentials the reactivity of HF is accelerated toward de-lithiated phase. To suppress the capacity fading at high potentials, lithium bis(oxalato) borate (LiBOB) has been incorporated as an additive into the electrolyte solutions to form solid electrolyte interphase (SEI) over the active particulates and thereby reducing the reactivity toward electrolyte. Hence, the electrochemical properties were evaluated only in the 3.5–5.2 V potential windows with different weight ratios of LiBOB in standard solution.

Figure 5 represents the galvanostatic cycling profiles of Li/LiCoPO4 cells comprising different ratios of LiBOB as additive with 1 M LiPF\(_6\) EC:DEC 1:1 wt% solution. The cells were cycled between 3.5–5.2 V at 0.05 C rate in room temperature. The advantage of using LiBOB as an additive/electrolyte salt for lithium battery applications has been described in our previous report and elsewhere. Apparent to see the discharge traces, there is no big differences in the initial discharge capacities were noted. The discharge capacities of 115, 110, 109, 113 and 112 mAh g\(^{-1}\) were obtained for 0, 0.1, 0.5, 1 and 3 wt% concentrations of LiBOB inclusion, respectively. Owing to the restricted solubility of LiBOB in linear carbonates, it is very difficult to make concentration of beyond 3 wt% LiBOB in electrolyte solution. The cycling profiles of the above cells are
Figure 4. (a) Galvanostatic charge-discharge curves of Li/LiCoPO$_4$ half-cells between 3.5–5.0 V, 3.5–5.10 V and 3.5–5.20 V at 0.05 C rate in room temperature with super imposed region of discharge curves and (b) Cycling profiles of above half-cells.

Figure 5. (a) Galvanostatic charge-discharge curves of Li/LiCoPO$_4$ half-cells cycled between 3.5–5.2 V with various concentrations of lithium bis(oxalato)borate (LiBOB) at 0.05 C rate in room temperature and (b) Cycling profiles of above half-cells.

Illustrated in Figure 5b. It is obvious to notice increasing LiBOB concentration in the electrolyte leads to improved capacity retention. The increase in capacity retention is mainly ascribed to the reduced reactivity of de-lithiated phase that hampers the dissolution of phosphate group/breaking of P–O bonds during nucleophilic attack of F$^-$ ions from HF at higher potentials. After 25$^{th}$ cycles the cell comprising 3 wt% of LiBOB showed a discharge capacity of 83 mAh g$^{-1}$ which corresponds to 74% of capacity retention and ~50% of theoretical capacity. Similarly, the other concentrations (except 0.1 wt%) of LiBOB indicates improved capacity retention as compared to standard electrolyte solution. Figure 6 shows the discharge capacity vs LiBOB concentration after 25 cycles. The obtained capacity retention is comparable/better than the previous work on TPN in to the solutions, HFIP incorporation$^{19}$ and LiFePO$_4$ coating as well.$^{15}$ Above results establishes the incorporation of LiBOB certainly improves the cycling profiles of LiCoPO$_4$ electrodes. Further studies are in progress to improve the cycleability of LiCoPO$_4$ by utilizing HF free electrolytes such as LiBOB in conventional linear carbonates, ionic liquids etc.

Conclusions

A solid-state method has been used to synthesize the LiCoPO$_4$ particles. X-ray diffraction pattern reveal the formation of pure phase orthorhombic structure with $pqnm$ space group. Cyclic voltammogram (CV) of Li/LiCoPO$_4$ indicated that increasing the upper-cut off potential tends to decrease the re-insertion potential in conventional 1 M LiPF$_6$ EC:DEC 1:1 wt% electrolyte solutions. Galvanostatic cycling studies wellsupported CV measurements with higher cutoff potential delivering the maximum discharge capacity. Various concentrations of lithium bis(oxalato) borate (LiBOB) has been incorporated in to standard electrolyte solution and 3 wt% of LiBOB comprising cell showed good cycling profile as compared to the other concentrations. The 3 wt% cell retained 74% of initial discharge capacity after 25 cycles, which is almost 50% of theoretical capacity.

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References