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Effect of LiBOB Additive on the Electrochemical Performance of LiCoPO₄

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Solid-state method is used to synthesize sub-micron size lithium cobalt phosphate, LiCoPO₄ particles. Powder X-ray diffraction pattern reveal the formation of pure phase orthorhombic structure with *pnma* 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 cycleability 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.¹⁻⁵ 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 LiCoO₂.⁶⁻¹³ Among which LiFePO₄ is commercialized by A123 Inc. (with mass production of such power packs by Sony Inc.) due to its advantages such as high thermal stability in both lithiated and de-lithiated state, flat-operating potential because of the distorted arrangement of XO₆ (X = Fe, Mn, Co, Ni, V etc) octahedron and first order phase transition from trypylite to heterosite during Li-insertion etc.,^{7-9,12,13} However, the operating potential is restricted to ~3.4 and 4.1 vs. Li for LiFePO₄ and LiMnPO₄, respectively. In addition, operational potential range of these cathodes falls well within the thermodynamic stability of electrolyte solutions. In contrary, redox couple Co^{2+/3+} in LiCoPO₄ (~4.8 V vs. Li) is noted above the safe operational limitations of the electrolyte (~4.6 V vs. Li) and hence less research work has been reported.¹⁴⁻²⁰ Further, the reactivity of de-lithiated phase toward electrolyte solution is also another problem for LiCoPO₄ electrodes.¹⁶ Amine et al.²¹ first demonstrated the reversible insertion/extraction of Li-ions for LiCoPO₄ in 1 M LiPF₆ in sulfolane based solutions. The Li/LiCoPO₄ cell delivered the initial discharge capacity of 70 mAh g⁻¹. The separated arrangement of XO₆ octahedral units leads to the inferior conducting properties of such polyanion framework materials and thus provides less reversible capacity.²² In order to improve the conducting properties, Yang et al.²³ attempted to make *in-situ* carbon coating over LiCoPO₄ particulates and failed to make such coating due to its peculiar surface properties. However, Li et al.²⁴ succeeded the carbon coating, in which acetylene black was included during synthesis process. To enable such coating, high temperature inert atmosphere sintering is necessary, which in turn provides the secondary phase materials like Co₂P along with native compound.²⁵ Appearance of such secondary phase is mainly because of calcination of carbon or its precursors to enable coating. The presence of carbon provides two important advantages; (i) improve the electronic conductivity and (ii) prevents the unwanted side reaction with electrolyte solutions.^{20,26} Apart from carbon coating, surface modifications of LiCoPO₄ have also been reported, for example Eftekhari²⁷ reported Al₂O₃ coating to improve the cycleability of LiCoPO₄ thin films. In our previous work, we reported LiFePO₄ coating either by dry coating procedure or sol-gel technique over LiCoPO₄ particles to suppress the reactiv-

ity toward electrolyte and thus improving battery performance.^{15,16} The formation of *in-situ* surface film is also possible during electrochemical reaction by adding appropriate amount of additives and this kind of surface film also can effectively suppress the reactivity toward electrolyte. This concept was also successfully employed for LiCoPO₄ cathodes to suppress the reactivity of electrolyte and thereby improving the cycleability, for example Xing et al.²⁸ reported the incorporation of thiophene (TPN) into standard electrolyte solutions and the cell showed capacity retention of 68% after 30 cycles (Li/C-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 In 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) Japan), 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 K α 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 microscope (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

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Figure 1. Rietveld refined powder X-ray diffraction of pattern of synthesized LiCoPO₄ particles.

mesh that served as current collector and subsequently dried at 60°C for overnight before conducting cell assembly in Ar filled glove box (MBraun, Germany). Electrodes in half-cell configurations were separated by microporous glass fiber separator (Whatman, Cat. No. 1825-047, UK). Standard 1 M LiPF₆ in ethylene carbonate (EC)/diethyl carbonate (DEC) (1:1 wt%, DAN VEC) mixture was used as the electrolyte solution. The electrolyte additive, LiBOB has been obtained from Chemetall, Germany and used as such. Cyclic voltammetric (CV) traces were recorded using Solartron, 1470E and SI 1255B Impedance/gain-phase analyzer coupled with a potentiostat in the two electrode configuration with metallic lithium act as both counter and reference electrode. Galvanostatic cycling profiles were recorded using Arbin 2000 battery tester at 0.05 C (1C = 150 mAh g⁻¹) rate between various potential ranges.

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 structure of the LiCoPO₄ is described to the hexagonal close-packing of oxygen with Li and Co ions located in half of the octahedral sites and P atom lays in one eight of the tetrahedral positions. The [CoO₆] octahedra share four corners in the *cb*-plane being cross-linked along with *a*-axis by the PO₄ groups. While Li ions are occupied in rows, running along *a*, of edge-shared LiO₆ octahedra which appeared between two consecutive [CoO₆]_∞ layers lying on the *cb*-plane.^{15,21,29} The strong P–O covalent bond in LiCoPO₄ polyanion framework is expected to translate high thermal and electrochemical stability, which is similar to its counterparts LiFePO₄ and LiMnPO₄.

Morphological features of the synthesized LiCoPO₄ powders were analyzed through transmission electron microscopy (TEM) and presented in Figure 2a. Formation of sub-micron size particles with irregular shape with particle size in the range from ~500–700 nm was observed. The obtained particulate morphologies are expected, since the LiCoPO₄ powders are synthesized at high temperature with longer sintering duration, which in turn provides the aggregation of crystallites in to relatively bigger size crystals. High-resolution TEM picture of the LiCoPO₄ is illustrated in Figure 2b with selected area electron diffraction (SAED). The *d*-spacing value is found 3.869 Å and it corresponds to the (1 2 0) Bragg line. The SAED pattern clearly reveals the highly crystalline nature of the powder synthesized and *hkl* values are also indexed for bright spots.

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 with the scan rate of 0.1 mV s⁻¹ in room temperature. All the test electrodes were formulated with accurately weighed 20 mg of active mass. It 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.

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 LiCoPO₄.¹⁷ 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, an 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

Figure 3. Cyclic voltammograms (CV) of Li/LiCoPO₄ half-cells cycled between (a) 3.5–5.0 V, (b) 3.5–5.05 V, (c) 3.5–5.10 V, (d) 3.5–5.15 V and (e) 3.5–5.20 V in room temperature. For the CV measurements metallic lithium acts as both reference and counter electrode with the scan rate of 0.1 mV s⁻¹ (f) comparison of the second CV traces of Li/LiCoPO₄ half-cells with different cutoff potentials. Inset: plot of upper-cutoff potential vs. re-insertion potential of lithium and it was extracted from the above measurements.

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^{15,16} and other reports as well.^{20,21,28} 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.³⁰ 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 LiPF₆ 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 report²⁶ and elsewhere.^{31,32} 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.^{33,34} The cycling profiles of the above cells are

Figure 4. (a) Galvanostatic charge-discharge curves of Li/LiCoPO₄ 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.

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 25th cycles the cell comprising 3 wt% of LiBOB showed a discharge capacity of 83 mAh g^{−1} which

Figure 5. (a) Galvanostatic charge-discharge curves of Li/LiCoPO₄ 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.

Figure 6. Plot of capacity retention vs. lithium bis(oxalato)borate (LiBOB) concentration after 25 cycles.

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,²⁸ HFIP incorporation¹⁹ and LiFePO₄ coating as well.¹⁵ Above results establishes the incorporation of LiBOB certainly improves the cycling profiles of LiCoPO₄ electrodes. Further studies are in progress to improve the cycleability of LiCoPO₄ 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 LiCoPO₄ particles. X-ray diffraction pattern reveal the formation of pure phase orthorhombic structure with *pnma* space group. Cyclic voltammogram (CV) of Li/LiCoPO₄ indicated that increasing the upper-cut off potential tends to decrease the re-insertion potential in conventional 1 M LiPF₆ EC:DEC 1:1 wt% electrolyte solutions. Galvanostatic cycling studies well supported 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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