CHAPTER 6

PRISTINE LiCoPO\(_4\) AND LiCoPO\(_4\)/C OLIVINE PREPARED BY CA-ISOL SOLGEL METHOD

6.1 INTRODUCTION

The limitation of LiFePO\(_4\) induced strong interest toward the other members of LiMPO\(_4\), especially LiCoPO\(_4\) thanks to its high theoretical energy density running up to 800 Wh/kg based on its inherently high Co\(^{3+}\)/Co\(^{2+}\) redox potential of 4.8 V vs. Li/Li\(^+\). An early stage of LiCoPO\(_4\) research by Amine et al (2000) showed the evolution of a discharge plateau at 4.8 V accompanied by a capacity of 70 mAh/g, far below its theoretical capacity (167 mAh/g). This degradation of capacity was caused by low electronic conductivity and Li\(^+\) diffusivity of LiCoPO\(_4\). Wolfenstine et al (2004) demonstrated that the enhancement of electronic conductivity by carbon coating on the surface of LiCoPO\(_4\) particles could not make the theoretical capacity of LiCoPO\(_4\) attained. It might stem from its low Li-ion diffusivity. It was also shown by Rabanal et al, (2006) that the improvement of electrochemical performance of LiCoPO\(_4\)/C composite was attributed to the reduced particle size of LiCoPO\(_4\) by high energy ball-milling.

However, because the synthetic process based on a conventional solid-state reaction was very complicated and time-consuming, it was difficult to maintain the reductive atmosphere for preventing the formation of an unwanted by-product during long-term furnace heating.
Besides, unlike the initial intention only to pulverize aggregated particles, the crystallinity of LiCoPO$_4$ was also deteriorated by mechanical milling. Therefore, it is necessary to develop a simple and fast synthetic method for obtaining a LiCoPO$_4$/C composite with a fine particle size and uniform carbon distribution.

Till recently various protocols has been utilized to synthesize LiCoPO$_4$, namely Sol-gel synthesis (Natalia et al 2005, Gangulibabu et al 2009), the Pechini process (Helmut et al 2008, Deniarda et al 2004), hydrothermal method (Xiang et al 2005), ball milling (Rabanal et al 2006) solid state reaction (Wolfenstein 2006, Amine et al 2000, Shigeto et al 2005, Julien et al 2006, Natalia et al 2004) and recently by microwave heating (Li et al 2009, Dong-wook et al 2009) . Inspite of its theoretical prediction of a high storage capacity, the performance of the cathodes are severely limited by issues like rate limitation and low electronic conductivity. The above issues can be addressed via particle size minimization down to nanoscale, as nanosized LiMPO$_4$ showed long-term cyclability. Depositing olivine particles on a conducting support like carbon and metal doping could significantly improve the rate limitation and electronic conductivity of the cathodes (Xie et al 2006).

An approach has been made in this work to synthesize single phase LiCoPO$_4$ (LCP) and carbon coated LiCoPO$_4$/C (LCP/C) particles by CA-ISOL sol-gel method that employs citric acid (CA) as a chelating agent and isopropanol (ISOL) for the solution preparation with the aim of reducing the particle size. This soft chemistry technique offers many advantages such as excellent homogeneity, single heating step, low calcinations temperature, shorter heating time, regular morphology, sub micron sized particles, less impurities, large surface area and good control of stoichiometry.
6.2 EXPERIMENTAL

6.2.1 Synthesis of pristine LiCoPO$_4$

Stoichiometric amounts of lithium nitrate (Aldrich), cobaltous nitrate (Aldrich) and ammonium dihydrogen phosphate (Merck) were used as starting materials in our modified synthesis protocol namely citric-acid/isopropanol assisted (CA-ISOL) sol-gel method to obtain single phase products of pristine LiCoPO$_4$. The stoichiometric quantities of the above starting materials were dissolved in appropriate quantity of de-ionized water/iso-propanol mixtures (4:1) separately. They were sonicated using an ultrasonic processor (UP200S 200 watts, 24kHz Hielscher Ultrasonics GmbH, Germany) for 10 min. The sonochemical reaction and synthesis is a process in which an ultrasound at fixed frequency and pulse power is used for chemical reactions and processes. This causes sonochemical effects in liquids, the phenomenon called acoustic cavitation. The acoustic cavitation develops a turbulence facilitating the dispersion and homogenization in the mixture solution. Cobalt (II) nitrate and Ammonium dihydrogen phosphate solutions were mixed together and kept in the magnetic stirrer till they were mixed uniformly. Stoichiometric amounts of Lithium nitrate were added to the above solution of CoPO$_4$. The specific quantity of citric acid required for the process is 100 ml saturated. It is added to the above solution of LiCoPO$_4$. Citric acid acts not only as a chelating reagent but also as a carbon source, which improves the Li ion diffusion in the electrode reaction and hinders the growth of LiCoPO$_4$ particles. The methnolic solution (isopropanol) acts as a handle for solution homogenization and the citric acid saturated solution as chelating agent favours the complexation inducing the molecular level mixing of the mixture solution comprising of the starting materials. This is a vital process in obtaining the uniform nanoparticles of the final product. The resulting purple color total clear solution was stirred continuously at 80 °C until a sticky paste-
like substance was obtained and later the temperature was increased to 300 °C to favour decomposition of the organic moieties.

This process thus produced the as-prepared oxide product which was further annealed in a programmed tubular furnace (Carbolite, U.K) further at 600 °C, 700 °C and 800 °C for about 6 hr at 10°C/min rate of heating and cooling to ensure uniform distribution of particles and to avoid surface cracking. This kind of synthesis allows a better control of the morphology and texture of solid particles.

6.2.2 Preparation of LiCoPO$_4$/C

On the other hand, owing to poor electronic conductivity of LiCoPO$_4$ (LCP), the renowned in-situ carbon coating was attempted successfully utilizing sucrose as carbon source. Pristine LiCoPO$_4$ annealed at 700 °C was chosen for carbon coating. A little amount of sucrose which yields 7.5 wt% of carbon was grinded with synthesized LiCoPO$_4$ powders and kept in the tubular furnace for 2 hrs in argon atmosphere to synthesize LiCoPO$_4$/C. Coating procedure is given in detail below.
6.2.3 Coating Procedure

We have carefully chosen the sucrose/LCP ratio in order to obtain actual carbon content as in bulk composite electrode preparation to increase the surface electronic conductivity. Thus, we determined the carbon content with our preliminary carbon formation of mere sucrose treated in a furnace and assessed that 1 g of sucrose yields 0.18 g of carbon by controlled heating with continuous purging of purified argon/H$_2$ (95:5) gas mixture. Our present synthesis protocol aimed at producing in-situ carbon content equivalent to an amount of 7.5 wt% of acetylene black being used as conductive additive in composite electrode preparation technique to increase the overall electronic conductivity. Accordingly, the active material (LCP) content/sucrose was initially ground in the ratio of 0.1 g/0.052 g respectively and the mixture was heat treated in a tubular furnace at 600 °C for 2 hr under flowing Ar/H$_2$ gas mixture. Care must be exercised to purge the tubular furnace column with Ar/H$_2$ gas prior to avoid any residual O$_2$ left in the furnace tube.

6.2.4 Characterization

The products thus obtained were subjected to physical and electrochemical technique as below. In order to confirm the completion of the phase formation of the as-prepared final product, the thermal analyses techniques such as thermo-gravimetric (TG) and DTA (differential scanning analysis) were carried out by employing a thermal analyzer SDTA FRS2 METTLER TOLEDO to elucidate the phase formation temperature. Powder XRD was obtained using X’pert PRO MPD (Pan Analytical instrument) equipped with CuKα radiation. Preliminary refinements of lattice parameters were performed by using X’Pert HighScore Plus software. Fourier transform infrared (FTIR) spectroscopy was performed on samples using a Spec Horiba Jobin Yvon spectrofluorimeter (F-311). The grain size, morphology, microstructure and composition (EDX) were examined employing a field
emission scanning electron microscopy (FESEM) and scanning transmission electron microscopy (STEM) (FEI Quanta 400F, The Netherlands). Cyclic voltammetry studies have been carried out using a Versastat3 potentiostat (AMETEK, USA).

6.2.5 Electrode Preparation

Electrodes for electrochemical testing were prepared by a well established casting procedure. The composite mixture slurry consists of active materials, acetylene black (in the case of non-carbon coated sample), additive carbon (Timcal carbon) and PVDF binder added to a N-methyl pyrrolidone (NMP) solvent. The composite coating thus comprised of LiCoPO$_4$: AB: AC: PVdF (75:10:10:5) and the slurry mix was coated onto thin aluminum foil (Delker, USA) which was used as a current collector and dried at 120 °C under vacuum.

6.2.6 Cell Assembly

The coin type (CR2032) cells were assembled in an argon gas filled glove box (mBruan, Germany) using Li metal foil as the counter electrode and an aprotic organic electrolyte containing 1M LiPF$_6$ dissolved in a mixture solvent of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 by volume) as liquid electrolyte (Merck, LP30) with a micro porous polymer separator (Celgard 2400™).

6.3 RESULTS ANS DISCUSSION

6.3.1 Thermal Analysis

Figure 6.2 shows the thermal decomposition profile of gel precursor. The precursor sample was analyzed from 25 (room temperature) up to 800 °C at a heating rate of 10 °C min$^{-1}$. About 73 % weight loss is observed during the temperature sweep to 800 °C. Since the gel precursor has been taken it can be seen that in the first weight loss range of 25–200 °C, the
weight loss is about 57 wt% resulted from the evaporation of NH₃ and water. It can be observed that in the second weight loss region of 200–400 °C, the weight loss is around 11 wt% which is due to the decomposition of organic moieties. Subsequently, about 5 wt% weight loss is shown due to pyrolysis of the remaining organic compounds occurs in the temperature range from 400 to 800 °C. The final product remains at about 27 wt% LiCoPO₄ composite cathode material, which was consistent with the theoretical yield of LiCoPO₄ measured by elementary analysis. The weight loss which occurs between 300 and 600 °C in the TG curve can be ascribed to the formation of crystalline LiCoPO₄. The reaction stopped at around 600 to 700 °C. Absence of strong exothermic peak in DSC profiles proves the thermal stability of the compound formed. According this result, we choose 600, 700 and 800 °C as heating temperature.

![Figure 6.2 TG-DSC curve of LiCoPO₄](image-url)
### 6.3.2 Structural Analysis

Figure 6.3 shows the X-ray diffraction pattern of the LiCoPO$_4$ calcined at 600 °C (a), 700 °C (b), and 800 °C (c) for 6 hours and LiCoPO$_4$/C, reflecting the amorphous phase of the sample. LiCoPO$_4$ adopt an olivine related structure having a hexagonal closed packed (hcp) oxygen array occupied by P$^{5+}$ from PO$_4$ tetrahedral oxo-anions at tetrahedral. It has orthorhombic symmetry with alternate a-c planes of Li and Co occupying the octahedral sites, which makes it possible for there to be two dimensional Li diffusion paths between the hcp oxygen layers.

The diffraction patterns of LiCoPO$_4$ and LiCoPO$_4$/C, indicates the formation of well ordered olivine structures with space group Pnma with no new phase formation. The profiles of the reflection peaks are quite narrow and symmetric. The diffraction peaks of the samples were indexed as per the ICSD file number 89-6192. Thereby, a pure homogeneous and well crystallized product corresponding to single-phase material is indicated. The carbon is in amorphous form, as there are no additional peaks on the XRD patterns belonging to its crystal modification, it is believed that the effect of carbon coating has restricted the undesirable conversion of cobalt and hence resulted in the phase pure formation of samples. Otherwise, the carbon is not detected because the residual carbon is amorphous.
Figure 6.3  XRD patterns of LiCoPO₄ heated at (a) 600 °C (b) 700 °C (c) 800 °C d) Carbon coated

Figure 6.4  XRD patterns of LiCoPO₄ and LiCoPO₄/C
It is found that crystalline phase of the samples heat treated at 700°C are in good agreement with the TG/DSC result shown in Figure 6.1. Table 6.1 shows the lattice parameters and the particle size of LiCoPO₄ and LiCoPO₄/C powder, calculated from the powder X-ray pattern using the Debye–Scherer equation. Thus the formation of nanosize LiCoPO₄ particles by this new synthesis route has been confirmed. Figure 6.4 shows the X-ray diffraction pattern of the LiCoPO₄/C. Then the embedding of LiCoPO₄ grains in the carbon matrix was clearly confirmed by relatively large particle size of LiCoPO₄/C composite than pure LiCoPO₄. This is further evidenced by scanning electron micrographs (SEM) images of LiCoPO₄ and LiCoPO₄/C which has particles distributed uniformly.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Lattice constants (Å)</th>
<th>Cell Volume (Å³)</th>
<th>Average particle size(nm)</th>
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</thead>
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<tr>
<td>LiCoPO₄(JCPDS-89-6192)</td>
<td>a 10.202  b 5.923  c 4.700</td>
<td>284.0</td>
<td>-</td>
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<tr>
<td>LiCoPO₄-600°C</td>
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<td>LiCoPO₄-700°C</td>
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<td>LiCoPO₄-800°C</td>
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<tr>
<td>LiCoPO₄/Carbon</td>
<td>a 10.196  b 5.919  c 4.699</td>
<td>283.6</td>
<td>47</td>
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</table>

### 6.3.3 Vibrational Studies

Figure 6.5 shows the Fourier transform infrared (FTIR) spectra of LiCoPO₄ and LiCoPO₄/C material confirming the purity of LiCoPO₄ and LiCoPO₄/C composites. The curve shows three broadly distributed peaks around 1050, 600 and 450 cm⁻¹ which corresponds to vibrational modes of tetrahedral AB₄ molecules. The spectra are dominated by the internal
vibrations ($v_1$-$v_4$) of the PO$_4^{3-}$ units which involve the displacement of oxygen atoms of the tetrahedral PO$_4^{3-}$ anions and present frequencies closely related to those of the free molecule. For olivine’s, these are a singlet (A1) at a frequency $v_1=965$ cm$^{-1}$; a doublet (E) at $v_2=465$ cm$^{-1}$ and two triply degenerate (F2) modes, $v_3$ in the region 1050-1140 cm$^{-1}$ and $v_4$ in the range 500-560 cm$^{-1}$. $v_1$ and $v_3$ involve the symmetric and antisymmetric mode of the P-O bonds, whereas $v_2$ and $v$ involve mainly O-P-O symmetric and antisymmetric bending mode with a small contribution of P vibration. These groups correspond to the internal stretching, internal bending and external oscillations modes of PO$_4$, respectively. The bands in the spectral range 400–550 cm$^{-1}$ are sensitive to the local lithium environment.

The complex pattern of bands in the region 400-700 cm$^{-1}$ corresponds to the bending motion of the tetrahedral group and to the external modes. The appearance of bands between 900-1200 cm$^{-1}$, relates to stretching vibrations of the tetrahedral anion i.e. PO$_4^{3-}$. The complex pattern of bands in the region 400-700 cm$^{-1}$ corresponds to the bending motion of the tetrahedral group and to the external modes. With reference to vibrational modes of tetrahedral XO$_4$ molecules having four fundamental vibrations of PO$_4^{3-}$ such as a symmetric stretching mode around $v_1$–967-1146 cm$^{-1}$, a symmetric bending mode doublet $v_2$ around 466-644 cm$^{-1}$, two triplets $v_3$ corresponding to antisymmetric stretching vibration at 1058 cm$^{-1}$, and an antisymmetric bending mode ($v_4$) at 644 cm$^{-1}$ region confirms the formation of impurity free LiCoPO$_4$. Comparison of FTIR spectral data for LiCoPO$_4$ and LiCoPO$_4$/C were given in Table 6.2. Absence of any additional peaks for LiCoPO$_4$/carbon composites compared with the peaks in LiCoPO$_4$ clearly indicates the insignificant level of carbon doping into LiCoPO$_4$ matrix.
Figure 6.5 FTIR spectra of (a) LiCoPO$_4$ and (b) LiCoPO$_4$/C

Table 6.2 FTIR spectral data of LiCoPO$_4$ and LiCoPO$_4$/C

<table>
<thead>
<tr>
<th>LiCoPO$_4$-700 °C (Cm$^{-1}$)</th>
<th>LiCoPO$_4$/C (Cm$^{-1}$)</th>
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<tr>
<td>466</td>
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6.3.4 Morphology Studies

Figure 6.6 (a to d) shows the typical FE-SEM images of pure LiCoPO$_4$ calcined at different temperatures and LiCoPO$_4$/C powders. The powders are composed of well-dispersed secondary particles which are slightly agglomerated and show a small quantity of fragments, where the residual carbon introduced by the decomposition of sucrose is distributed around the powders. The powders are composed of agglomerated crystallites of 200 nm in average. As expected, the smaller particle size has been achieved, because the fine particle size shortens the path of Li$^+$ diffusion and improves the Li$^+$ diffusion rate. The reduction of particle size can be related to the nanocrystalline precursor materials produced by sol–gel route and in situ introduced carbon which can interfere with the coalescence of the grains. The particle size increased with increasing heating temperature and time in synthesis, which was in good agreement with the results of XRD analysis.

In the case of pure LiCoPO$_4$, orthorhombic shaped particles with large size distribution were observed. However in the case of LiCoPO$_4$/C, particles were more uniform with narrow size distribution. Though the samples were calcined at relatively higher temperature, carbon as an additive inhibits the particle growth yielding a homogeneous particle size distribution.
Figure 6.6  FE-SEM images of LiCoPO$_4$ heated at (a) 600 °C (b) 700 °C (c) 800 °C d) carbon coated
Figure 6.7  EDAX Spectra of LiCoPO$_4$ heated at (a) 600°C (b) 700°C (c) 800°C
This is because the undesirable growth of the crystals has been reduced by the carbon precursor and carbon coating during the active material processing. Then, the LiCoPO$_4$/C composites are expected to have a microstructure where each carbon particles with a size of approximately 50 nm would be covered with LiCoPO$_4$ layer or inserted in LiCoPO$_4$ aggregates. Figure 6.6(d) shows that the LiCoPO$_4$/C particles separated apart could be connected through the nano-sized carbon and the surface of the particle is wrapped with a carbon layer of few nanometer thicknesses. These typical nano-carbon webs can provide good electronic contact between intra- and inter-particles so as to improve surface electrical conductivity. It was believed that the optimized surface morphology and the small size of the particles are favorable for the intercalation/de-intercalation process. Spot EDX analysis in the FE-SEM is shown in Figure 6.7.

In order to further check carbon distribution in the powders, STEM images were applied. Some morphology like a nanometer sized web was found around the particles. Figure 6.8 shows the results of Scanning Transmission Electron Microscopy (STEM), which clearly indicates the existence of carbonaceous film, confirming the carbon coating of the LiCoPO$_4$ nanopowders. This image displays representative primary particles with a network of carbon in the interstitial grain-boundary region. In the micrograph, the LiCoPO$_4$ crystallites appear as the darker regions, while the carbon coating surrounds the primary particle as the grayish region. The morphology of the samples appears more compact with agglomerated particles and wider grain size distribution with carbon coating.
Figure 6.8 STEM images of LiCoPO4/C

Spot EDX analysis in the STEM (Figure 6.9) confirmed that the outside layers are amorphous carbon and the inside crystalline region is Lithium cobalt phosphate. The powders have primary crystal size ranging from 40 nm to 150 nm, and the crystals form loose agglomerates. The small crystallinity and porous agglomerate structure allow easy penetration of the electrolyte and provide a short pathway for lithium diffusion in the active material crystals. Because the individual lithium cobalt phosphate crystals are wired together by the coated carbon layer, it was expected that the carbon coating on the lithium cobalt phosphate crystals would dramatically increase the electronic conductivity of the electrodes. We pressed the lithium cobalt phosphate crystals with and without carbon coating into disk shaped pellets.
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6.3.5 Electrochemical Redox properties

CV technique is one of the absolute electrochemical means to confirm the reversibility of cathode materials (positive electrodes). In the present study, due to limitations involved with aprotic organic electrolytes, we restricted our measurements within 5 V vs. Li/Li\(^+\) owing to electrolyte’s (1M LiPF6 in EC/DMC 50/50) electrochemical oxidation stability. LiCoPO\(_4\) is one the renowned high voltage materials amongst the olivine family and hence we restricted our studies to slow scan cyclic voltammetry to prove the presence of electron transfer reaction facilitated by the redox couple due to cobalt (Co\(^{2+}/^{3+}\)) which is clearly exemplified in the voltammogram reported

![Figure 6.9 EDAX Spectra of LiCoPO4/ carbon](image)

(a)

(b)

Figure 6.9 EDAX Spectra of LiCoPO\(_4\)/ carbon
The electronic conductivities of LCP/C was $10^{-1}$ S/cm at room temperature. Such a high electronic conductivity mainly comes from the carbon coating. The electronic conductivity of the compressed pellets is probably dominated by the carbon network.

Figure 6.10 shows the initial cyclic voltammograms curves of LiCoPO$_4$ and LiCoPO$_4$/C electrodes. During the anodic sweep, lithium ions are extracted from the LiCoPO$_4$ structure. An oxidation peak is located at 4.92 and 4.89V versus Li/Li$^+$ for LiCoPO$_4$ and LiCoPO$_4$/C respectively, but the peak intensity is notably higher for the later. When the potential was scanned from 5 V to 3 V, a reduction peak occurred at 4.58 and 4.51V for LiCoPO$_4$ and LiCoPO$_4$/C respectively, corresponding to lithium insertion into the LiCoPO$_4$ structure. The sharp lithium insertion and extraction peaks in the CV curves indicated high reactivity of the carbon-included LiCoPO$_4$ electrode. This confirms the reversibility of the electrode reaction and the improvement in lithium ion diffusion due to carbon coating and suggests that LiCoPO$_4$ and LiCoPO$_4$/C will have capacity on discharge with a plateau voltage around 4.5V. This result is attributed to the high quality of the synthesized LiCoPO$_4$ and carbon coated LiCoPO$_4$ impurity free materials used as positive electrodes. Given that the experimental conditions were identical for both electrodes, the higher redox peak intensities indicate an enhanced electrochemical reactivity of the carbon coated compared to the pure LiCoPO$_4$. Thus the role of carbon addition in improving the electrode reaction is confirmed. Figure 6.11 shows the first charge-discharge profile of LiCoPO$_4$/C. This clearly confirms the electrolyte decomposition at the higher voltage as the present electrolyte cannot sustain at high voltage due to time consuming constant current technique.
Figure 6.10  Cyclic voltammograms of (a) LiCoPO$_4$ (b) Carbon coated LiCoPO$_4$

Figure 6.11  First charge-discharge profile of LiCoPO$_4$/ carbon
6.4 CONCLUSION

CA-ISOL sol-gel method is an easy and effective method to synthesis olivine compounds. LiCoPO$_4$ and LiCoPO$_4$/C composite was successfully synthesized by CA-ISOL sol-gel method. Sucrose being the carbon source is one of the suitable precursors for in-situ carbon coating on the active materials grains in order to enhance the bulk electronic conductivity of olivine compound studied. Sucrose, used as the carbon source for carbon coated LiCoPO$_4$ avoids the formation of the impurity phase. XRD and FTIR results indicate that the perfect olivine phase LiCoPO$_4$ could be prepared by this new method. This method exhibits excellent particle size reduction up to 40nm which had significant effect in the reversibility of the electrode material. STEM study clearly reveals that a thin layer of unorganized carbon is coated on the surface of the LiCoPO$_4$ crystals.

Electrode active characteristic of the synthesized olivine (both pristine and coated materials) was successfully tested using CV studies as exemplified by the clear near mirror symmetric redox peaks due to Co. Given that the experimental conditions were identical for both electrodes, the higher redox peak intensities indicate an enhanced electrochemical reactivity of the carbon coated compared to the pure LiCoPO$_4$. With the suitable high voltage stable electrolyte (at least up to 5.1 V vs. Li/Li$^+$), LiCoPO$_4$/C composite would be an excellent candidate for the cathode of next generation of high capacity material for lithium-ion batteries.