

Impact of glucose on the electrochemical performance of nano-LiCoPO₄ cathode for Li-ion batteries

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Abstract LiCoPO₄ nanoparticles were synthesized by standard and glucose-assisted sol–gel methods for use as cathodes in lithium-ion batteries. The effect of glucose on the characteristics of the formed LiCoPO₄ nanoparticles was investigated by TGA, XRD, and FESEM. The TGA results indicated gradual decomposition of glucose in the temperature range 400–700 °C. The XRD results showed olivine phases in addition to small traces of Co₃O₄ for samples calcined at 400 °C while pure olivine phases were confirmed for the 700 °C calcined samples. The addition of glucose strongly suggests promotion of LiCoPO₄ crystallization, as revealed by FESEM studies. The electrochemical measurements pertaining to LiCoPO₄ samples calcined at 400 °C suggested an enhancement of initial discharge capacity from 103.3 to 144.6 mAh/g for the standard and glucose-based electrodes, respectively. Further, the effects of conductive additive and excess lithium on the electrochemical performance of LiCoPO₄ have also been investigated.

Keywords Sol–gel processes · Nanoparticles · Cathode · LiCoPO₄ · Li-ion batteries

Introduction

There has been a recent surge in the development of new electrodes in view of the high energy and power density requirements in Li-ion batteries to meet the demand for

electric vehicles, plug-in hybrid electric vehicles, and power tools. Hence, intense research is aimed at developing efficient cathodes that suit high-power applications and one such promising cathode has been identified as the olivine-type LiFePO₄. The olivine-structured compounds based on stable phosphates are known to be thermally safe though the viability of other transition-metal-based phosphates have yet not been completely examined. In this context, LiCoPO₄ belonging to the olivine family (LiMPO₄, where M = Ni²⁺, Co²⁺, Mn²⁺, or Fe²⁺), form compounds that are generally known to be magneto-electric [1–3]. In general, the olivine structure known as LiMPO₄ consists of a distorted hexagonal close-packed oxygen framework with Li and M in half of the octahedral sites (4a and 4c sites, respectively) and P in one-eighth of the tetrahedral sites. The lattice arrangement of this structure results in a preferential rapid one-dimensional lithium-ion motion along the *b*-axis direction [4]. Due to their high discharge voltages and comparable energy densities to layered LiCoO₂, these phosphor-olivine compounds remain as ideal candidates for new high-voltage and superior-capacity cathode materials [5–18].

The operating voltage of LiCoPO₄ at 4.8 V versus Li/Li⁺ is higher when compared to that of LiFePO₄, which has been successfully optimized for high-power applications. However, a major drawback in this cobalt-based olivine is that its achievable capacity is comparatively low due to its intrinsic limitations of low electronic and ionic conductivities. To overcome these problems, immense efforts have focused on the fabrication of minute, preferably well-dispersed nano-sized LiCoPO₄ particles since it enhances lithium-ion diffusion thereby realizing apparently higher power capacities in view of their reduced dimensions. On the other hand, electrically conductive surface coating of such nanoparticles along the borders of primary crystallites to achieve electronic conductivity enhancement has also been investigated [19–21].

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Therefore, the prospect of obtaining successful particle-size minimization and surface coatings of nanoparticles aimed at subsequent enhancement in corresponding electronic and ionic conductivities, respectively, by adopting various synthetic strategies and/or reaction environments gains utmost significance. Herein, we report an approach toward achieving particle-size minimization by the introduction of an easily available and environmental friendly carbon source namely, glucose. In fact, glucose has recently been identified as a carbon source for the synthesis of LiFePO_4 systems and it was found to play an important role in controlling the size of the particles by preventing them from gaining mass during the formation of carbon, which occurs while calcined under inert atmosphere conditions [21].

The present work describes the introduction of the use of an economical carbon source viz., glucose as one of the starting precursors in order to address the concerns of practical tap density. Glucose was expected to act simply as a physical vesicant thereby controlling the LiCoPO_4 particle size during its calcinations under air. This article reports on the synthesis of LiCoPO_4 via a simple sol–gel route using glucose as an additive and its electrochemical characterization. The reaction conditions and their effects on the products are preliminarily discussed in this study.

Experimental

Synthesis

LiCoPO_4 powders were prepared by sol–gel method without and with glucose additive. For the standard synthesis, 0.01 mol (0.69 g) of analytical grade lithium nitrate (LiNO_3), 0.01 mol (2.49 g) of cobalt acetate tetrahydrate ($\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$), 0.01 mol (0.98 g) of ammonium dihydrogen phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$) and a small amount of citric acid used as a chelating agent were dissolved in distilled water at room temperature. The pH of the resulting solution was maintained below 4 using HNO_3 . Alternatively, the glucose-assisted synthesis was followed by obtaining a similar solution using the starting materials stated above in addition to 0.1 mol (1.8 g) of glucose added as one of the precursors. These two solutions were mixed and heated separately at 70–80 °C to obtain gels which were then dried overnight at 120 °C. The as-prepared standard and glucose-based samples were calcined in air at 400 or 700 °C for 5 hrs to obtain the final powders.

Characterization

Thermogravimetric analysis (TGA) of the samples were performed in the temperature range 30–800 °C in air atmosphere using a TG-50 instrument (Shimadzu Co, Japan)

at a heating rate of 10 °C/min. The crystalline nature of the powders were measured by XRD using a D/MAX Ultima diffractometer (Rigaku, Japan) with $\text{Cu K}\alpha 1$ radiation ($\lambda = 1.54056 \text{ \AA}$). The morphology of the samples was examined by FESEM using a Hitachi S4700 instrument.

Electrochemical measurement

The electrochemical properties of the LiCoPO_4 samples were evaluated with lithium metal as the reference electrode. For the electrochemical measurements, a mixture was obtained by mixing the active material and teflonized acetylene black (TAB) binder with different weight percentage ratios of conductive carbon (Ketjen black). This mixture was then pressed onto a stainless steel mesh before vacuum drying at 120 °C for 12 h and thus formed the cathode. The active mass loading of the electrode was 0.55 mg/cm^2 . A 2032 coin-type cell consisting of the cathode and lithium metal anode separated by a polymer membrane together with glass fiber was fabricated in an Ar-filled glove box and aged for 12 h before actual measurements. The electrolyte employed was a 1:1 mixture of ethylene carbonate and dimethyl carbonate containing 1 M LiPF_6 .

Results and discussion

Characterization of the samples

The thermal behavior of the as-prepared standard and glucose-based samples before calcination was analyzed by TGA and the plots are presented in Fig. 1. The standard sample registered a 32% weight loss for increasing temperatures to

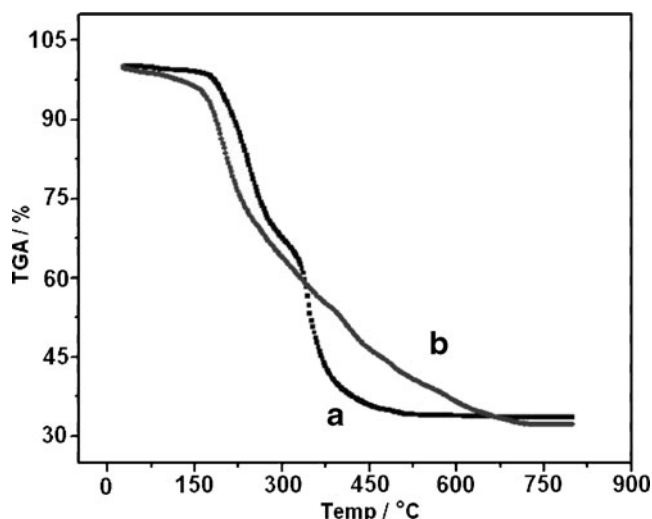


Fig. 1 TGA curves obtained for the as-prepared **a** standard and **b** glucose-assisted LiCoPO_4 at a heating rate of 10 °C/min in air

300 °C. A further decrease of 32% was observed as temperature enhanced to 520 °C and beyond which the mass remains almost constant. By comparison, the glucose-based sample exhibited an initial weight loss of 28% up to 300 °C while an additional decrease of 37% was observed until 710 °C. In other words, glucose appears to continuously decompose during calcination and the decomposition becomes complete at 710 °C, as shown in Fig. 1. Therefore, as glucose is eliminated as CO and/or CO₂ and H₂O in the glucose-based sample, the final sample is expected to become more porous and finer than the powder prepared without glucose. These observations led us to investigate the as-prepared samples calcined at two different temperatures namely, 400 and 700 °C.

The XRD patterns of standard and glucose-based samples calcined at 400 °C are shown in Fig. 2a and b, respectively. The pattern corresponding to the standard and glucose-based samples confirmed the presence of a major LiCoPO₄ phase. Interestingly, the maximum intensity peak corresponded to the (121) diffraction plane around the scan angle, 2θ=37 ° for the standard sample while the maxima peak corresponded to the (311) diffraction plane around 2θ=36 ° in the glucose-based sample. Further, impurity traces of Co₃O₄ were present in both samples though their intensities were apparently lower in the glucose-based sample. The XRD patterns of the standard and glucose-assisted LiCoPO₄ powders calcined at 700 °C were analyzed by the Rietveld refinement technique and the results indicate that both samples possess well-defined orthorhombic olivine-type structures, as shown in Fig. 3a and b respectively. The refined cell parameters evaluated for the LiCoPO₄ powders are summarized in Table 1 and are comparable to that found in the literature [22–24]. The obtained values indicate that the crystal lattice corresponding to the glucose-based sample possessed a unit cell with a slightly higher lattice parameter value along the *x* direction (*a*). The most probable reason for this observation lies in the fact that glucose added as one of the precursors during synthesis consistently provides a reducing environment preventing the oxidation of Co²⁺ to

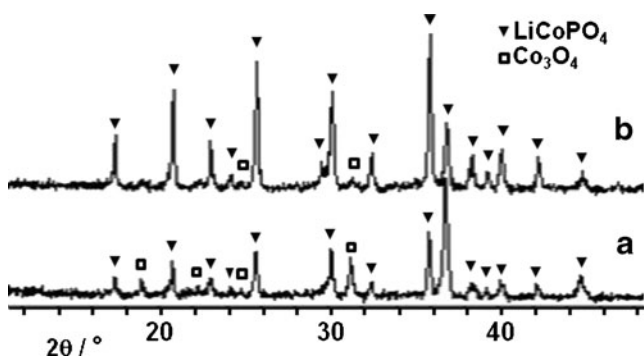


Fig. 2 X-ray diffraction patterns of **a** standard and **b** glucose-assisted LiCoPO₄ samples calcined at 400 °C

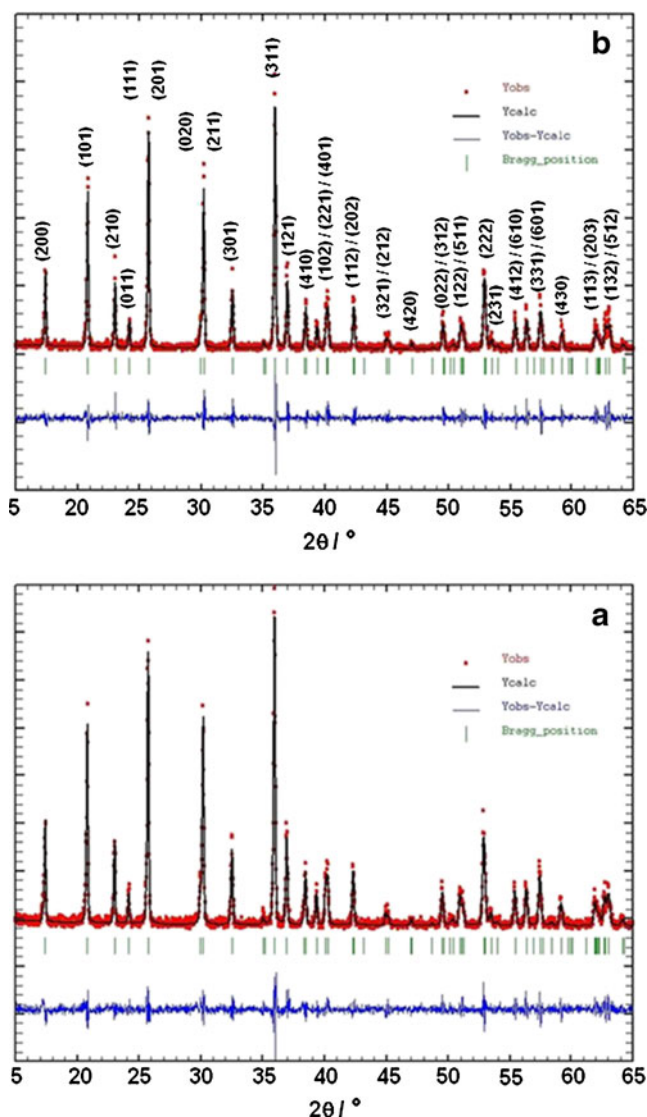


Fig. 3 Rietveld-refined X-ray diffraction patterns of **a** standard and **b** glucose-assisted LiCoPO₄ samples calcined at 700 °C

Co³⁺ to a considerable extent when compared to that in standard synthesis. The slight variation in the lattice parameters is most likely due to the relatively weaker electrostatic repulsive forces between the Co²⁺–Co²⁺ and Co²⁺–Li⁺ ions in the glucose-based powder when compared with that in the standard sample, which is believed to possess apparently higher amounts of Co³⁺. As a consequence, it is highly probable that an apparently lower value in the grain cell volume was observed for the glucose-based sample. In

Table 1 Unit cell parameters of LiCoPO₄ nanopowders synthesized using different routes

Synthesis	<i>a</i> , Å	<i>b</i> , Å	<i>c</i> , Å	<i>V</i> , Å ³
Standard	10.187	5.918	4.696	283.080
Glucose-assisted	10.197	5.915	4.694	282.940

addition, the average particle size, calculated using the Scherrer formula, viz., $d=0.9\lambda/\beta_{1/2}\cos\theta$, where λ is the X-ray wavelength, $\beta_{1/2}$ the corrected width of the main diffraction peak at half-height and θ , the diffraction angle, was determined to be 560 and 450 nm for the standard and glucose-assisted LiCoPO_4 powders calcined at 700 °C, respectively. In fact, a reduction in the primary particle-size is also expected to have a positive effect on the performance of the electrically low conducting olivine family, LiMPO_4 [25, 26].

Therefore, based on the TGA and the XRD results, it is reasonable to conclude that glucose promotes the crystallization of LiCoPO_4 . Moreover, the temperature at which this phase formation occurs is lower than that quoted previously [1–4]. It is generally known that citric acid mainly decomposes at 400 °C and the combustion heat of citric acid is 1960 kJ/mol while the decomposition of glucose can occur until temperatures as high as 710 °C and its combustion heat is 2,804 kJ/mol, thus making it feasible to facilitate LiCoPO_4 crystallization.

The FESEM images in Fig. 4 show that the powders calcined at 700 °C have significantly different morphologies. The standard powder consists of compact secondary highly agglomerated particles while, in contrast, the

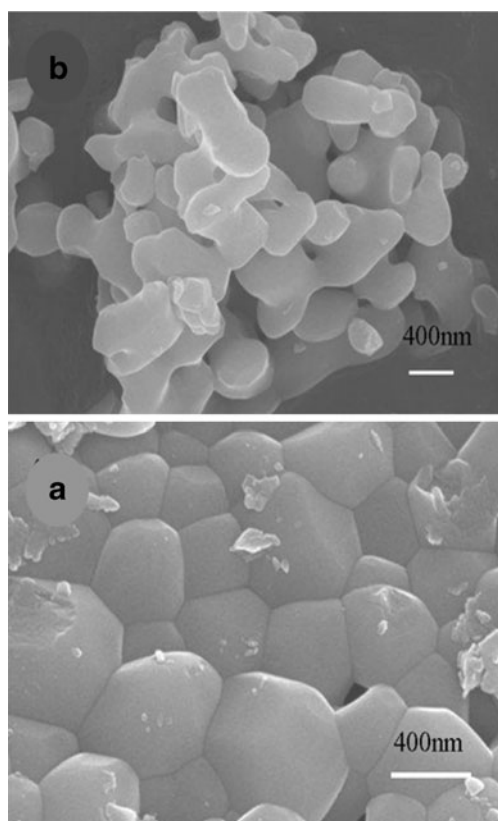


Fig. 4 FESEM images of **a** standard and **b** glucose-assisted LiCoPO_4 samples calcined at 700 °C

glucose-based sample consists of porous nanoparticles with considerable particle-dispersion. The latter morphology appears to be attributed to the continuous decomposition of the glucose during the calcining stage, as analyzed from the TGA results. The average particle sizes of the standard LiCoPO_4 samples were observed to be in the range 500–600 nm while that of the glucose-assisted sample appears to be slightly lower, as confirmed from the particle-size estimation in the XRD studies.

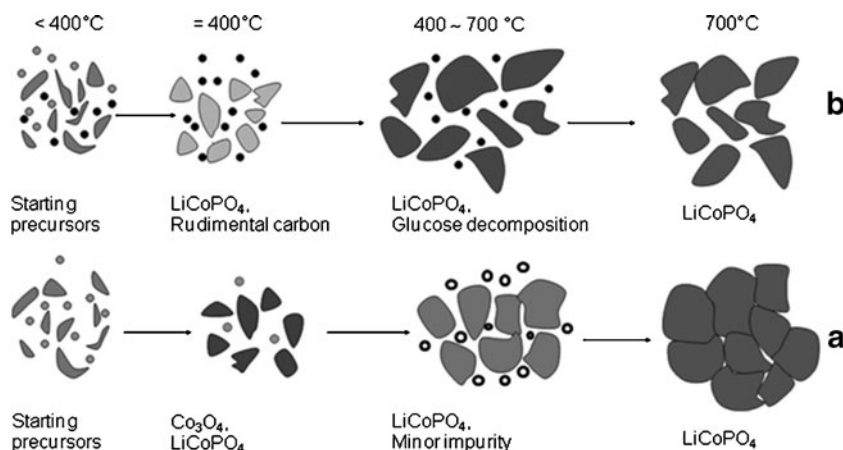
In fact, a mixture of glucose and citric acid heated separately under the same experimental conditions, described in “Synthesis” section, resulted in its complete disappearance during calcination. This observation can be considered as further evidence for the total conversion of glucose to carbon oxides and vapor during the thermal treatment at 700 °C in air. Therefore, it can be argued here that significant difference in morphologies of the calcined powders is most probably due to the effect of the addition of glucose during the synthesis. These morphology variations are expected to influence the electrochemical properties.

In the light of the above discussions, we propose a possible mechanism toward LiCoPO_4 formation based on the standard and glucose-assisted methods as shown in Figs. 5a and b, respectively. The initial step in the standard method indicates the concerned precursors containing gray dots that represent citric acid. After being calcined at 400 °C, the citric acid completely decomposes and impurities in addition to olivine are formed in the sample as shown in Fig. 5a. At elevated temperatures of 700 °C, the grains tend to agglomerate to form compact but large phase-pure secondary olivine particles. However, in the glucose-assisted method, while citric acid vaporizes on being calcined at 400 deg glucose, represented by black dots in Fig. 5b decomposes gradually within the temperature range of 400–700 °C. The slow decomposition of glucose is expected to facilitate pore-like formations ultimately causing a variation in the particle morphology of the final sample, as observed from the FESEM studies. The particle morphologies obtained were similar to that obtained by using carbon black as a precursor during synthesis, as proposed by Lloris et.al [3].

Electrochemical characterization

The charge–discharge profiles of standard and glucose-based electrodes based on LiCoPO_4 powders calcined at 400 °C in the voltage range 3.0–5.1 V under current density 0.1 mA/cm² are presented in Fig. 6. These electrodes were prepared by mixing active material and TAB binder with 33 wt.% conductive carbon. Such high percentages of carbon black has been introduced to understand the true properties of the active material and measurements per-

Fig. 5 Schematic representation of the possible mechanism for the formation of **a** standard and **b** glucose-assisted LiCoPO_4 samples with their morphologies



formed by employing decrementing amounts of conductive carbon content is also described later in this section. The standard and glucose-based Li/LiCoPO_4 cells delivered initial discharge capacities of 103.3 (ca. 62% of the theoretical capacity) and 144.6 mAh/g (ca. 87% of the theoretical capacity) respectively. Further, the profile of glucose-based electrode exhibits an apparently gradual sloping during lithium insertion when compared to that of the standard electrode. It is possible that the addition of glucose seem to influence the discharge capacity to a significant extent when compared to that of the standard electrode.

However, a discharge plateau was not detectable for LiCoPO_4 synthesized by both methods and since plateau formation remains to be a strict control parameter for electrode quality evaluation [20], the effect of conductive carbon content on the electrochemical performance of the electrode was examined. Figure 7 displays the performance of the

glucose-based LiCoPO_4 calcined at 400°C when three different weight percentages, namely, 33, 14, and 0 wt%, of conductive carbon was employed for electrode fabrication. A decrease in the conductive carbon content from 33 to 0 wt.% led to significant decrease in capacities, as expected, but with fairly defined 4.7 V discharge plateaus. In fact, the cell based on conductive carbon-free electrode exhibited a well-defined discharge plateau at 4.7 V characteristic of the typical $\text{Co}^{2+}/\text{Co}^{3+}$ redox couple with a capacity value of 100 mAh/g. This weight percentage ratio of active materials and binder viz., 90:10 with no additional conductive carbon was chosen as the stoichiometric composition for the glucose-based electrode fabrication for further electrochemical measurements. Figure 8 presents initial discharge curves for the glucose-based (calcined at 400 and 700°C) and standard (calcined at 700°C) LiCoPO_4 samples. It should be mentioned here that the stoichiometric weight percentage ratio for the standard

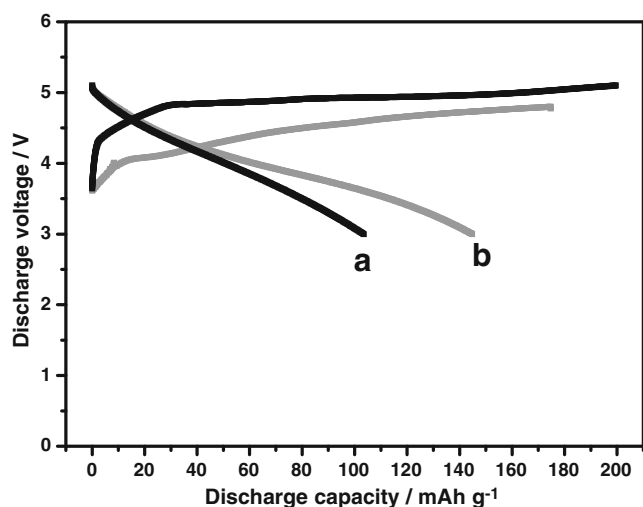


Fig. 6 Charge–discharge profiles of Li/LiCoPO_4 cells prepared using LiCoPO_4 samples from **a** standard and **b** glucose-assisted methods calcined at 400°C

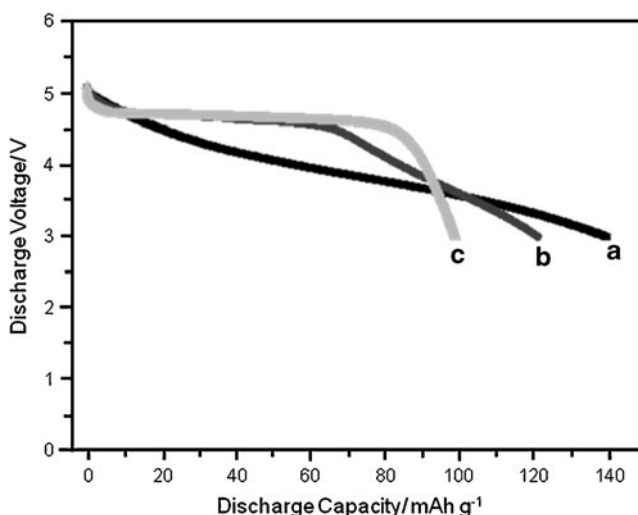


Fig. 7 Initial discharge profiles for the Li/LiCoPO_4 cells based on the glucose-assisted LiCoPO_4 calcined at 400°C (optimized sample) fabricated using **a** 33, **b** 14 and **c** 0 wt.% conductive carbon content

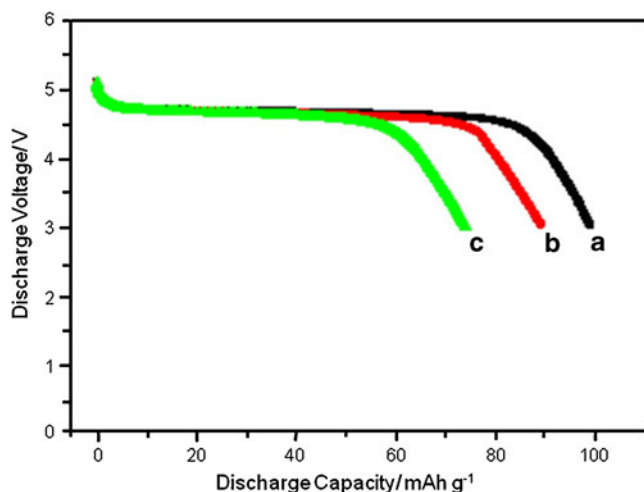


Fig. 8 The initial discharge profiles for the Li/LiCoPO₄ cells comprised of electrodes fabricated from glucose-assisted LiCoPO₄ calcined at a 400, b 700 °C and standard LiCoPO₄ calcined at c 700 °C

electrode preparation using active material, conductive carbon and binder was 70:20:10 while that for glucose-based electrode using active material and binder was 90:10, respectively. On comparing the profiles of 700 °C pure olivine samples, the glucose-based LiCoPO₄ shows apparently higher capacity values though distinct 4.7 V discharge plateaus were observed for all the samples. This improved performance in glucose-based sample most probably lies in the influence of glucose to facilitate pore-like sample morphology. Therefore, it is reasonable to suggest that the enhanced electrochemical performance is most probably influenced by the significant particle morphology variation and possibly in combination with the particle size in the glucose-based sample, as discussed in the FESEM studies. In other words, the considerably well-dispersed and porous particles appear to provide better lithium-ion and electron transport across the slightly greater cathode/electrolyte interface area of contact. Additionally, the reducing atmosphere provided by glucose tends to inhibit the oxidation of Co²⁺ to Co³⁺ and hence these factors possibly contribute towards enhanced capacities. However, among the profiles, the longest discharge plateau and hence highest capacity of 100 mAh/g could be achieved for the glucose-based LiCoPO₄ sample calcined at 400 °C. This trend is most likely due to the carbon arising as a result of incomplete glucose decomposition. It is possible that the formed carbon facilitates effective electronic transport between the active materials and the current collector thereby influencing electrochemical performance. The discharge capacities observed for the present samples under study are fairly comparable to that found in literature [27–29].

However, subsequent cycling of the optimized sample viz., glucose-based LiCoPO₄ calcined at 400 °C led to considerable capacity fading. As seen from Fig. 9a, a 20%

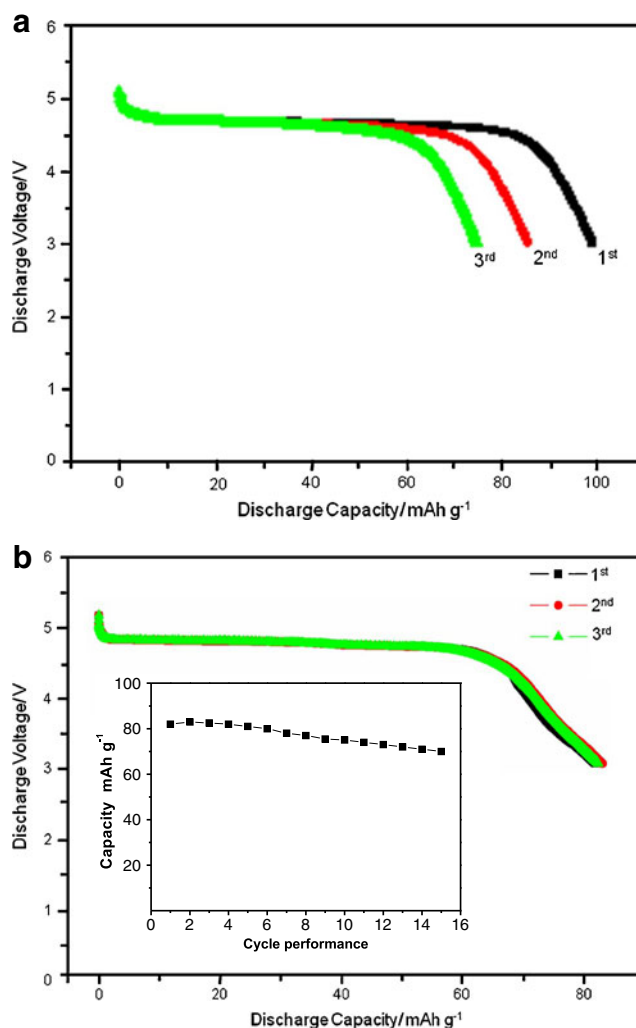


Fig. 9 The initial three voltage profiles of a glucose-based LiCoPO₄ and b excess lithium inserted glucose-based Li_{1.4}CoPO₄ samples calcined at 400 °C

reduction in the discharge capacity (80 mAh/g) was observed in just the third cycle. To circumvent these problems, the strategy to introduce excess lithium into the optimized sample was adopted to arrive at the possible best performing LiCoPO₄. This Li-rich sample, Li_{1.4}CoPO₄ was prepared by the glucose-assisted sol-gel method mentioned earlier using 0.01 M Co(CH₃COO)₂·4H₂O, 0.01 M NH₄H₂PO₄, 0.1 M glucose, and 0.14 M LiNO₃ that corresponds to 40% excess lithium as the starting materials. The initial three discharge profiles of such a Li-rich based cell, i.e., Li/Li_{1.4}CoPO₄, wherein active material:binder weight percentage ratio of 90:10 was employed for electrode fabrication, is displayed in Fig. 9b. It is evident from Fig. 9b, that a clear distinction in the capacity retention capability is achieved when compared to that of optimized LiCoPO₄. Precisely, reversible discharge capacities of 80 mAh/g were maintained until three initial cycles for Li_{1.4}CoPO₄ though a 20% decrease in the overall

discharge capacity was observed when compared to the optimized sample. Interestingly, subsequent cycling of the prepared Li-rich electrode led to capacity retentions until 15 discharge cycles, as shown in the inset of Fig. 9b, and is consistent with that in literature [29].

Conclusions

In conclusion, olivine-structured LiCoPO_4 nanoparticles were prepared via standard and glucose-assisted sol-gel routes. The TGA plot of the as-prepared glucose-based sample indicated complete glucose decomposition occurs approximately at 700 °C. The XRD studies on LiCoPO_4 powders calcined at 400 °C showed olivine phases in addition to impurity traces of Co_3O_4 while the samples calcined at 700 °C confirmed presence of pure olivine phases. The FESEM studies of the 700 °C calcined LiCoPO_4 nanoparticles obtained by the standard and glucose-assisted method exhibited contrasting morphologies viz., large agglomeration and considerably dispersed porous-like morphologies respectively while the average particle sizes was estimated to be in the range of 400–600 nm. These results lead one to argue that glucose promoted the crystallization of LiCoPO_4 during calcination since glucose possessed elevated combustion heat and decomposition temperatures. The glucose-based LiCoPO_4 calcined at 400 °C, identified as the optimized sample, in combination with 33 wt.% conductive carbon exhibited initial discharge capacity of 144.6 mAh/g, an enhancement of 40% when compared to 103.3 mAh/g registered by the standard sample. Interestingly, a well-defined 4.7 V discharge plateau with a still lower capacity of 100 mAh/g (c.a. 60% of its theoretical capacity) was observed when no conductive carbon content was added to the optimized LiCoPO_4 (active material) during electrode fabrication. However, on subsequent cycling, the optimized electrode experienced severe capacity fading and the capacity retention was considerably sustained on adopting the strategy of incorporating excess lithium into the optimized LiCoPO_4 .

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