

Short communication

Electrical conductivity of doped LiCoPO₄

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Abstract

The effect of Cr or Cu doping on the electronic conductivity of LiCoPO₄ was investigated. It was observed that neither type of doping for the samples heated under air lead to electronic conductivity values above $\sim 10^{-9}$ S cm⁻¹. Based on these results it is suggested that the room temperature electronic conductivity of LiCoPO₄ is much lower than that for LiFePO₄. For the case of the doped samples heated under argon, they all exhibited an electronic conductivity $\sim 10^{-4}$ S cm⁻¹. It is likely that the enhanced conductivity of the LiCoPO₄ samples heated under argon versus air is a result of conductive Co₂P along LiCoPO₄ particle surfaces that forms as a result of carbothermal reduction during heat-treatment. The electronic conductivity of the LiCoPO₄ samples heated under high-purity argon is essentially independent of dopant type and concentration. This is because it is the conductive Co₂P layer that controls the electronic conductivity of the doped samples overriding any possible dopant effects.

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1. Introduction

In recent years there has been a lot of interest in orthophosphates (LiMPO₄, where M=Fe, Mn, Co and Ni) as cathodes for use in Li-ion batteries [1–4]. They offer the advantages of a stable structure on charging/discharging, thermal stability and flat voltage profile. However, they suffer from poor rate capability as a result of both low electronic and ionic conductivity [1,5–14]. For the case of LiFePO₄ several methods have been used to increase the electronic conductivity by a factor of 10⁶ or more compared to that for the un-treated LiFePO₄. These involve carbon coating of the particles [7,8], aliovalent doping on Li⁺ sites (i.e., Cr⁺³) [11] and aliovalent (i.e., Zr⁺⁴) and isovalent (i.e., Mg⁺²) on Fe⁺² sites [12,13] and formation of an iron phosphide (i.e., Fe₂P) layer along LiFePO₄ particle surfaces/grain boundaries, that forms as a result of the reduction of carbon-based precursors during the heat-treatment(s) used to form crystalline LiFePO₄ [14]. For the case of LiCoPO₄ it has been shown that the electronic conductivity can be increased from $\sim 10^{-9}$ S cm⁻¹ or lower to $\sim 10^{-4}$ S cm⁻¹, when the heat-treatment atmosphere was changed from air to high-purity argon

when carbon-containing precursors were used [6]. It was suggested that the higher electrical conductivity of LiCoPO₄ heat-treated under argon is most likely due the presence of Co₂P, similar to the results of Herle et al. [14] for the case of LiFePO₄. It is of interest to determine if doping on Li⁺ or Co⁺² sites can also be used to increase the electrical conductivity of LiCoPO₄, as is the case for LiFePO₄.

It is the purpose of this paper to investigate: (1) if aliovalent doping on Li⁺ or Co⁺² sites can be used as methods to increase the electronic conductivity of LiCoPO₄ and (2) gain insight into the mechanism of electrical conduction of orthophosphates since, there is some controversy on the effect of dopants on electronic conductivity [9,10,14].

2. Experimental

Two different doped LiCoPO₄ powders were prepared: (1) Cr-doped LiCoPO₄, and (2) Cu-doped LiCoPO₄. Both types were prepared using a solid-state reaction method. Stoichiometric amounts of Li₂CO₃, CoC₂O₄·2H₂O and NH₄H₂PO₄ along with correct precursors were mixed in a jar mill for two hours. After mixing, the powders were given a two-step heat-treatment. In the first step, powders were heated at 375 °C for 10 h. They were then crushed and ground and pressed into a pellet. In the second step, the pellet was fired at 675 °C for 24 h. To investigate

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the effects of aliovalent doping on the Li^+ site Cr_2O_3 powder was added to the above powders to form $\text{Li}_{0.99}\text{Cr}_{0.01}\text{CoPO}_4$ and $\text{Li}_{0.97}\text{Cr}_{0.03}\text{CoPO}_4$. Cr_2O_3 (Cr^{+3}) was chosen because it has been shown at these dopant levels it increased electronic conductivity at room temperature from $\sim 10^{-9}$ to $\sim 10^{-1}$ S cm^{-1} compared to undoped LiFePO_4 [11]. To investigate the effect of aliovalent doping on the Co^{+2} site Cu_2O (Cu^+) powder was mixed in with the above powders to form $\text{LiCo}_{0.99}\text{Cu}_{0.01}\text{PO}_4$ and $\text{LiCo}_{0.97}\text{Cu}_{0.03}\text{PO}_4$. Cu_2O was chosen because, based on ionic size it is expected to occupy the Co-ion site and when it occupies this site it would be expected that for charge compensation for each Cu^+ added a Co^{+2} ion will change to Co^{+3} , increasing the hole concentration and hence, electronic conductivity. For both types of doped LiCoPO_4 samples the two-step heat-treatment was conducted under two different oxygen partial pressures: (1) air ($P_{\text{O}_2} = 0.21$ atm) and (2) high-purity argon ($P_{\text{O}_2} \approx 10^{-5}$ atm).

All samples were first characterized by X-ray diffraction using Cu K alpha radiation. The amount of any second phase(s) was estimated using Rietveld refinement (RIQAS software). The electronic conductivity was measured on sintered and polished disk samples (~ 12 mm diameter and ~ 1 mm thickness) using the two-point dc method [9,11,12]. The two-point method was chosen over the four-point method for convenience since, good agreement between these two methods was observed for LiFePO_4 [9]. Silver paste electrodes were applied to the top and bottom surfaces of the disk. A high impedance multimeter was used to measure the resistance at room temperature. Conductivity was calculated from the resistance and specimen dimensions.

3. Results and discussion

All samples that were heated under air were purple colored, whereas all samples heated under argon were black. X-ray diffraction patterns for $\text{LiCo}_{0.99}\text{Cu}_{0.01}\text{PO}_4$ heated under air and argon are shown in Fig. 1. The diffraction patterns for the following samples: $\text{Li}_{0.99}\text{Cr}_{0.01}\text{CoPO}_4$, $\text{Li}_{0.97}\text{Cr}_{0.03}\text{CoPO}_4$, and $\text{LiCo}_{0.97}\text{Cu}_{0.03}\text{PO}_4$ heated under air are similar to that shown in Fig. 1(air). A comparison of these patterns with previous X-ray

diffraction patterns for LiCoPO_4 [4,15–17] heated under air and JCPDS data file numbers 32–552 (LiCoPO_4) suggests that all these materials are single-phase with an ordered olivine structure. Rietveld refinement revealed no second phase(s). A slight shift in the LiCoPO_4 peak positions for the doped samples compared to undoped LiCoPO_4 was observed, suggesting that all the dopants were in solid solution (within the limits of X-ray resolution), in agreement with previous studies on doped- LiFePO_4 at similar dopant levels [9,11–13].

A comparison of the X-ray diffraction pattern for $\text{LiCo}_{0.99}\text{Cu}_{0.01}\text{PO}_4$ heated under high-purity argon (argon) with that for the sample heated under air reveals the presence single phase LiCoPO_4 plus additional peaks, indicated by dots above these peaks in Fig. 1. These extra peaks correspond to Co_2P . X-ray diffraction patterns for $\text{Li}_{0.99}\text{Cr}_{0.01}\text{CoPO}_4$, $\text{Li}_{0.97}\text{Cr}_{0.03}\text{CoPO}_4$, and $\text{LiCo}_{0.97}\text{Cu}_{0.03}\text{PO}_4$ heated under high-purity argon all revealed the presence of second phase Co_2P in addition to the majority LiCoPO_4 phase. The amount of Co_2P for all samples was estimated to be between 1 and 3 vol.% using Rietveld refinement. These results are in good agreement with previous results on the heat-treatment of undoped LiCoPO_4 prepared using the same precursors and heated under high-purity argon, where the presence of second phase Co_2P (~ 2 vol.%) was observed [6]. They are also in agreement with the results of Herle et al. [14], who observed Ni_3P along with $\text{Li}_4\text{P}_2\text{O}_7$ and $\text{Li}_2\text{Ni}_3\text{P}_4\text{O}_{12}$ in samples prepared from similar precursors used in this study except Ni compounds instead of Co compounds were used and heated under argon, where as no nickel phosphide phases were present in the LiNiPO_4 sample heated under flowing air.

The results of the X-ray diffraction studies reveal that for $\text{LiCo}_{0.99}\text{Cu}_{0.01}\text{PO}_4$, $\text{Li}_{0.99}\text{Cr}_{0.01}\text{CoPO}_4$, $\text{Li}_{0.97}\text{Cr}_{0.03}\text{CoPO}_4$ and $\text{LiCo}_{0.97}\text{Cu}_{0.03}\text{PO}_4$ heated under air form single phase LiCoPO_4 with an ordered olivine structure where as the same materials heated under high-purity argon in addition to LiCoPO_4 revealed the presence of a second phase Co_2P (1–3 vol.%). This is most likely a result of the carbothermal reduction of the LiCoPO_4 at particle surfaces during high-temperature heat-treatment, as suggested by Herle et al. [14] and Barker et al. [18] for orthophosphates heated under low oxygen partial pressures in the presence of carbon that comes from the precursors or intentionally added.

Before discussing the electronic conductivity results it should be noted that with our experimental set-up and sample size that the lower limit of electronic conductivity which can be accurately measured is $\sim 10^{-9}$ S cm^{-1} . The electronic conductivity of the $\text{LiCo}_{0.99}\text{Cu}_{0.01}\text{PO}_4$, $\text{Li}_{0.99}\text{Cr}_{0.01}\text{CoPO}_4$, $\text{Li}_{0.97}\text{Cr}_{0.03}\text{CoPO}_4$, and $\text{LiCo}_{0.97}\text{Cu}_{0.03}\text{PO}_4$ samples heated under air were all below the lower limit of the experimentally measurable value. Thus, it can be concluded that the electronic conductivity of all these materials was $< 10^{-9}$ S cm^{-1} . As a result the effect of doping on the electronic conductivity for LiCoPO_4 heated under air can not be evaluated. However, several important points can be obtained from this data. Firstly, it has been shown the electronic conductivity of undoped LiCoPO_4 heated under air using the same precursors was $< 10^{-9}$ S cm^{-1} [6]. Thus, it can be seen that Cr-doping of LiCoPO_4 does

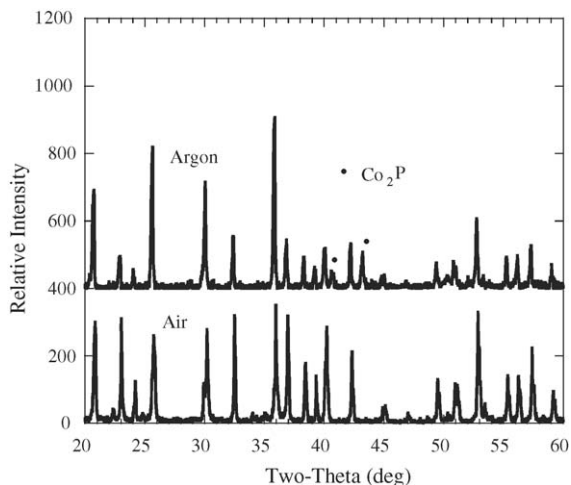


Fig. 1. X-ray diffraction patterns for $\text{LiCo}_{0.99}\text{Cu}_{0.01}\text{PO}_4$ heated under air and argon.

not lead to high (compared to the undoped) values of electronic conductivity of $\sim 10^{-1}$ S cm $^{-1}$ observed for LiFePO $_4$ at similar Cr $^{+3}$ doping levels (1 and 3 vol.%) on the Li $^{+}$ site heated under an argon (92%) + hydrogen (8%) atmosphere [11]. Secondly, Cu-doping of LiCoPO $_4$ does not lead to the electronic conductivity values of $\sim 10^{-5}$ to $^{-4}$ S cm $^{-1}$ observed for Mg $^{+2}$ -doped (0.5–2 vol.%) LiFePO $_4$ on the Fe $^{+2}$ site heated under argon [12]. X-ray diffraction revealed that for the case of Cu $_2$ O heated under air that a majority of the Cu $_2$ O transformed to CuO thus, it is expected that a majority of Cu enters the LiCoPO $_4$ lattice in this case as Cu $^{+2}$ and hence, the results for the Cu-doped LiCoPO $_4$ are justified in being compared to those for LiFe $_{1-x}$ Mg $_x$ PO $_4$. In summary, doping LiCoPO $_4$ with either Cr or Cu and then heated under air does not lead to the high values of electronic conductivity observed for LiFePO $_4$ doped with similar impurities and concentration levels. This difference may be a result of the heat-treatment atmospheres (argon or argon/hydrogen versus air), or the result of an intrinsic property difference between LiFePO $_4$ and LiCoPO $_4$, which causes the electronic conductivity of LiCoPO $_4$ to be much lower than that for LiFePO $_4$ making it very difficult to measure any change in conductivity with doping since, even with doping the conductivity will still be below the experimental measurable value.

It may be possible that the conductivity difference between doped LiCoPO $_4$ and doped LiFePO $_4$ is a result of the difference in heat-treatment atmospheres (air versus argon). Herle et al. [14] have suggested that for both pure and Zr-doped LiFePO $_4$ formed from carbon-containing precursors heated under argon that the increase in electronic conductivity to $\sim 10^{-2}$ S cm $^{-1}$ was attributed to the formation of iron phosphide along the LiFePO $_4$ surfaces based on X-ray diffraction and transmission electron microscopy. Since, the Mg and Cr-doped LiFePO $_4$ materials were prepared from carbon-containing precursors and heat-treated under argon [12] or argon (92%) + hydrogen (8%) [11] it is possible that the increase in conductivity seen in these materials may also be a result of the formation of iron phosphides during heat-treatment. However, if iron phosphide was controlling the conductivity of the doped samples one would expect that the conductivity would be independent of doping concentration. Both the Mg and Cr-doped LiFePO $_4$ materials show an increase in conductivity with an increase in dopant concentration suggesting that it is the doped impurities that causes the conductivity increase. This would suggest that the difference the conductivity difference between doped LiCoPO $_4$ heated under air versus doped LiFePO $_4$ heated under argon is not related to the difference in heat-treatment atmosphere. However, to conclusively confirm this, very detailed microstructural analysis must be conducted on the samples to examine for the metal phosphide formation.

Another possibility is that the conductivity difference between the two is a result of an intrinsic property difference between LiFePO $_4$ and LiCoPO $_4$, which causes the electronic conductivity of LiCoPO $_4$ to be much lower than that for LiFePO $_4$ making it very difficult to measure any change in conductivity with doping since even with doping the conductivity will still be below the experimental measurable value. For example, extrapolation of the conductivity data for LiMnPO $_4$

data from Delacourt et al. [19] to room temperature predicts a value of $\sim 10^{-17}$ S cm $^{-1}$. This value is $\sim 10^8$ times lower than for LiFePO $_4$ ($\sim 10^{-9}$ S cm $^{-1}$ [9,11–14]). Thus, even if doping increased the electronic conductivity of LiMnPO $_4$ by a factor of 10^6 this would only increase the electronic conductivity to a value of $\sim 10^{-11}$ S cm $^{-1}$, a value still below the measurable limit of the current set-up. A very low room temperature electronic conductivity value for LiCoPO $_4$ similar to LiMnPO $_4$ is possible since, it is believed that the electronic conduction mechanism in orthophosphates is related to the same mechanism (i.e., polaron hopping between transition metal ions) that controls electronic conductivity in FeO, CoO and MnO [9,11,20–22]. It is known that the room temperature conductivity of FeO is ~ 10 S cm $^{-1}$, CoO is $\sim 10^{-13}$ S cm $^{-1}$ and MnO is 10^{-15} S cm $^{-1}$ [22]. From this, it is expected that the room temperature electronic conductivity of LiCoPO $_4$ would be similar to that for LiMnPO $_4$ and would be orders of magnitude lower than for LiFePO $_4$ hence, making determination of the electronic conductivity of undoped and doped LiCoPO $_4$ not possible with the current experimental set-up.

The electronic conductivity of the LiCo $_{0.99}$ Cu $_{0.01}$ PO $_4$, Li $_{0.99}$ Cr $_{0.01}$ CoPO $_4$, Li $_{0.97}$ Cr $_{0.03}$ CoPO $_4$, LiCo $_{0.97}$ Cu $_{0.03}$ PO $_4$ along with data for undoped LiCoPO $_4$ [6] all heated under high-purity argon are shown in Fig. 2. The data in Fig. 2 are plotted as logarithm of conductivity versus dopant concentration. From Fig. 2, several important points are noted. Firstly, the electronic conductivity of all samples heated under argon is $\sim 10^{-4}$ S cm $^{-1}$. This is an increase of at least 10^5 times in electrical conductivity compared to similar LiCoPO $_4$ samples and undoped LiCoPO $_4$ heated under air. These results are in good agreement with the results of Herle et al. [14] for LiNiPO $_4$, who observed a $\sim 10^2$ – 10^3 increase in electrical conductivity for LiNiPO $_4$ heated under argon compared to air. It is highly likely that the enhanced conductivity of the LiCoPO $_4$ samples heated under argon versus air is a result of conductive Co $_2$ P (Fig. 1, argon) along particle surfaces that forms in-situ as a

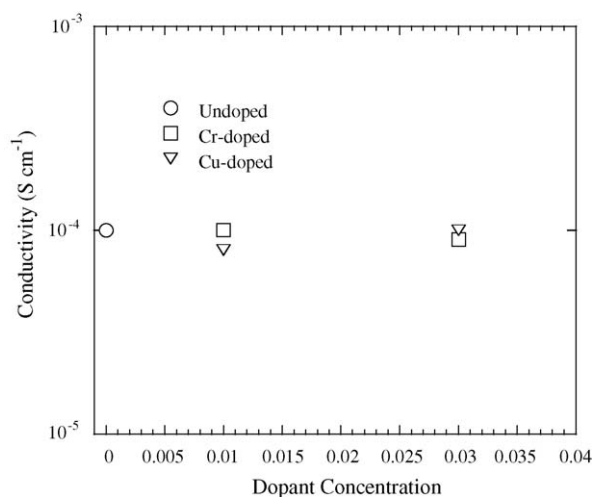


Fig. 2. Electronic conductivity of LiCo $_{0.99}$ Cu $_{0.01}$ PO $_4$, Li $_{0.99}$ Cr $_{0.01}$ CoPO $_4$, Li $_{0.97}$ Cr $_{0.03}$ CoPO $_4$, LiCo $_{0.97}$ Cu $_{0.03}$ PO $_4$ along with data for LiCoPO $_4$ [6] all heated under high-purity argon.

result of carbothermal reduction at high-temperature under low oxygen partial pressure atmospheres when carbon-containing precursors are used. After heat-treatment we have a composite material consisting of a highly restive interior (LiCoPO₄) with a highly conductive surface coating (Co₂P). This is similar to what Herle et al. [14] proposed for the increase in conductivity of LiNiPO₄ heated in argon versus air based on X-ray diffraction and transmission electron microscopy data. It is possible that the enhanced conductivity could be a result of residual carbon from the carbon-containing precursors used as starting materials. However, based on previous work [6] where the effect of heat-treatment atmospheres (argon versus air) on the electrical conductivity of undoped LiCoPO₄ using the same carbon-containing precursors as used in this study showed that the most likely cause for the increase in conductivity was a result of the Co₂P formation rather than residual carbon thus, it is most likely that this is the also the case for doped LiCoPO₄.

Secondly, the electronic conductivity of the LiCoPO₄ samples heated under high-purity argon is essentially independent of dopant type and concentration. This is because it is the conductive Co₂P layer that dominates electronic conductivity of the doped and undoped LiCoPO₄ material. If the conductive Co₂P layer controls the electronic conductivity it would be expected that electronic conductivity would be independent of dopant type and concentration, in agreement with the data shown in Fig. 2. Thirdly, the electrical conductivity value of $\sim 10^{-4}$ S cm⁻¹ for all samples shown in Fig. 2 is within the conductivity range of cathodes (LiCoO₂ $\sim 10^{-3}$ S cm⁻¹ [23] and LiMn₂O₄ $\sim 10^{-5}$ to 10^{-4} S cm⁻¹ [24]) used for Li-ion batteries. It has been shown for both undoped and doped LiCoPO₄ formed by heating carbon-based precursors under high-purity argon leads to formation of a Co₂P layer along LiCoPO₄ particle surfaces that increases the electronic conductivity to $\sim 10^{-4}$ S cm⁻¹, within the range of values for cathodes used for Li-ion batteries.

Even though the LiCoPO₄ offers both the advantages of higher voltage and capacity and safety compared to the current LiCoO₂ the above results suggest there are some major disadvantages if it is to be used as a cathode in practical applications. For example, the fact that the room temperature intrinsic electrical conductivity is very low and doping followed by heat-treatment under air does not attain the required conductivity level, suggests that in order for LiCoPO₄ to be used as a cathode in this case requires a high percentage of carbon be added to the electrode to get the needed conductivity, which in turn will reduce energy density. For heat-treatment under argon the enhanced conductivity that results from the formation of a Co₂P layer is at near the bottom of the electronic conductivity levels required for the cathode to get reasonable rates. Thus, additional procedures maybe required to increase the electronic conductivity, which in turn will increase cost and reduce energy density. Even though high-voltage/capacity orthophosphates such as; LiCoPO₄ and LiNiPO₄ offer the advantages of increased energy density compared to what is currently available they have many disadvantages (i.e., electronic conductivity) that must be overcome before they can be used as cathodes in Li-ion batteries.

4. Conclusions

The effect of doping Cr or Cu in LiCoPO₄ or varying stoichiometry using carbon-based precursors and heating under air or argon on electronic conductivity was investigated. It was observed that neither doping nor vary stoichiometry for the samples heated under air lead to electronic conductivity values above $\sim 10^{-9}$ S cm⁻¹. Any possible dopant effects could not be measured. Based on the air results it is suggested that room temperature electronic conductivity of LiCoPO₄ is much lower than that for LiFePO₄. For the case of the doped samples heated under argon they all exhibited an electronic conductivity $\sim 10^{-4}$ S cm⁻¹. It is highly likely that the enhanced conductivity of the LiCoPO₄ samples heated under argon versus air is a result of conductive Co₂P along particle surfaces that forms in-situ as a result of carbothermal reduction at high-temperature under low oxygen partial pressure atmospheres when carbon-containing are used. The electronic conductivity of the LiCoPO₄ samples heated under high-purity argon is essentially independent of dopant type and concentration. This is because it is the conductive Co₂P layer that controls the electronic conductivity of the doped samples overriding any possible dopant effects. For LiCoPO₄ formed from carbon-based precursors and heat-treated under air or argon, doping had no effect on enhancing the electronic conductivity to values required for Li-ion cathodes.

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