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Short communication

Effect of oxygen partial pressure on the discharge capacity of LiCoPO$_4$

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Abstract

The discharge capacity of LiCoPO$_4$, prepared using carbon-containing precursors, heated under different oxygen partial pressures (high-purity argon, air, pure oxygen) was investigated. LiCoPO$_4$ heat-treated under high-purity argon showed a higher discharge capacity over the entire cycle life compared to under air or pure oxygen. No difference in the discharge capacity of LiCoPO$_4$ heat-treated under air or pure oxygen was exhibited. The enhanced discharge capacity of LiCoPO$_4$ heat-treated under argon compared to air/oxygen was a result of its higher electrical conductivity and smaller particle size. The higher electrical conductivity and smaller particle of LiCoPO$_4$ heat-treated under argon is likely do the presence of cobalt phosphides and increased carbon content.
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1. Introduction

Recently, there has been interest in the use of lithium transition metal phosphates with an ordered olivine structure LiMPO$_4$ (M = Fe, Mn, Ni and Co) as potential cathodes for Li-ion batteries [1–6]. Lithium transition metal phosphates suffer from low electrical conductivity and slow Li-ion diffusion which limits rate capability. Past attempts to improve rate by increasing electrical conductivity have focused on coating particles with conductive carbons [7,8] or lattice doping with supervalent cations [9]. Very recently Herle et al. [1] have shown another way to increase electrical conductivity in lithium transition metal phosphates. They observed at least a 2–3 order of magnitude increase in electrical conductivity for LiNiPO$_4$ prepared from carbon-containing precursors when the heat-treatment atmosphere was changed from flowing air to argon. They suggested based on X-ray diffraction and transmission electron microscopy data that the increase in electrical conductivity was a result of the formation of a nano-network of conductive metal phosphides and/or metal phosphocarbides at grain boundaries of the insulating LiNiPO$_4$;

that formed as a result of the reducing conditions under the argon atmosphere. However, no data are presented to determine if this method enhanced electrochemical behavior of LiNiPO$_4$.

It is the purpose of this paper to investigate the effect of heat-treatment under different oxygen partial pressures (pure oxygen, air, high-purity argon) on the discharge capacity of LiCoPO$_4$ prepared using carbon-containing precursors. LiCoPO$_4$ was chosen for the following reasons: (1) it has a higher energy density ($\sim$800 W h kg^{-1} [10]) compared to LiCoO$_2$ ($\sim$540 W h kg^{-1} [11]) and (2) like LiNiPO$_4$ it is stable under high oxygen partial pressures at high temperature [1,10]. Thus, it is possible to observe the affect of heat treatment under a wide oxygen partial pressure, P_{O_2}, range on discharge capacity.

2. Experimental

The LiCoPO$_4$ powders were synthesized using a solid-state reaction method. Stoichiometric amounts of Li$_2$CO$_3$, CoC$_2$O$_4\cdot$2H$_2$O and NH$_4$H$_2$PO$_4$ were mixed in a jar mill for 2 h. These are the same precursors used by Herle et al. [1] except cobalt oxalate was substituted for nickel oxalate. Af-

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ter mixing, the powders were given a two-step heat treatment that was used previously to produce single-phase LiCoPO₄ [12]. In the first step powders were heated at 375 °C for 20 h. They were then crushed and ground and pressed into a pellet. In the second step the pellet was fired at 775 °C for 48 h. The two-step heat treatment was conducted under three different oxygen partial pressures: (1) pure oxygen ($PO_2 = 1$ atm), (2) air ($PO_2 = 0.21$ atm) and (3) high-purity argon ($PO_2 \approx 10^{-5}$ atm).

After heat treatment the powders were crushed and ground. The phases (X-ray diffraction), surface area (Brunauer–Emmett–Teller, BET) and Li and Co content (atomic emission spectroscopy) were then determined. In addition, the elemental carbon content of the oxygen and argon heat-treated powders was determined using combustion analysis.

To get a qualitative indication if the oxidation state of the Co-ion varied as a function of oxygen partial pressure X-ray photoelectron spectroscopy (XPS) was conducted. XPS was conducted using a Mg Kα excitation source. CoO and LiCoO₂ powders were used as reference samples.

The electronic conductivity was measured on sintered and polished disk samples (~12 mm diameter and ~1 mm thickness) using the two-point d.c. method [9,13,14]. The two-point method was chosen over the four-point method for convenience since, good agreement between these two methods was observed for LiFePO₄ [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.

The discharge capacity of the LiCoPO₄ cathode material was determined using coin cells with metallic lithium as the anode. A typical cathode was prepared by mixing 78 wt.% active powders, 12 wt.% carbon and 10 wt.% polyvinylidene fluoride dissolved in *N*-methylpyrrolidinone. The mixture was coated onto an Al substrate. The cathodes were dried under vacuum at 100 °C for 20 h. The electrolyte solution was 1 M LiPF₆:tetramethylene sulfone. Tetramethylene sulfone was used because of its high oxidative stability (around 5.8 V versus Li [15]). The LiCoPO₄ cells were cycled at room temperature between 3.5 and 5.3 V at a constant current density of 50 μA cm⁻² [4].

3. Results and discussion

LiCoPO₄ samples that were heated under air and pure oxygen were purple colored, whereas the sample heated under argon was black. These results are similar to what Herle et al. [1] observed for LiNiPO₄, in that different powder colors were observed for air (yellow) and argon (black). Atomic emission spectroscopy revealed that the Li:Co ratio was close to the expected ratio of 1:1 for all three samples. The carbon content of the oxygen sample was ~0.31 wt.%, whereas for the argon sample it was ~3× higher, ~0.90 wt.%. The carbon content of the air sample was not analyzed by combustion
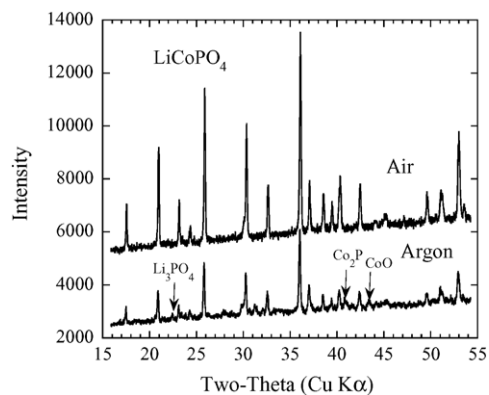

Fig. 1. X-ray diffraction patterns for LiCoPO₄ heated under air or high-purity argon.

synthesis. However, XPS results revealed that the carbon content of the air sample was ~9% higher than that for the pure oxygen sample. Thus, the carbon content of the air sample can be estimated to be ~0.34 wt.%.

X-ray diffraction patterns for LiCoPO₄ heated under air and argon are shown in Fig. 1. The X-ray diffraction pattern for LiCoPO₄ heated under pure oxygen was exactly similar to the one shown for air, in the position and intensity of the peaks. A comparison of the pattern for the air sample with previous LiCoPO₄ X-ray diffraction patterns [3–5,16,17] and JCPDS data file number 32-0552 (LiCoPO₄) reveals that the material is essentially single phase with an ordered olivine structure. From Fig. 1, the X-ray diffraction pattern for the argon sample shows peaks corresponding to single-phase LiCoPO₄ plus additional peaks (shown by arrows) corresponding to Co₂P and second-phase oxides (CoO and Li₃PO₄). The presence of the Co₂P phase in the argon sample is similar to the results of Herle et al. [1], who observed Ni₃P along with Li₄P₂O₇ and Li₂Ni₃P₄O₁₂ in the argon sample where no nickel phosphide phases were present in the LiNiPO₄ sample heated under flowing air. No carbon/carbide phases could be detected in the X-ray diffraction patterns. It should be noted that when the two-step heat treatment was conducted under an Ar + 4% H₂ mixture after heating at 775 °C for 48 h that no LiCoPO₄ peaks could be detected, only peaks corresponding to Co₂P, CoO and Li₂O along with other unidentified peaks were exhibited.

BET analysis yielded a surface area, S, of 1.2, 1.3 and 6.0 m² g⁻¹ for the oxygen, air and argon samples, respectively. Using these surface areas, a density, ρ, of 3.76 g cm⁻³ for LiCoPO₄ [2] and assuming spherical particles ($d = 6/S\rho$, where d is the particle diameter [18]) yields particle sizes of 1.3, 1.2 and 0.27 μm respectively, for the oxygen, air and argon samples. The particle size of the argon sample is ~6× smaller than that for the air/oxygen samples. The smaller particle size of the argon sample versus the air/oxygen samples is probably due to the presence of second phases (i.e., Co₂P) and higher carbon content. It is known that impurities and/or second phases restrict particle growth thus, creating a high surface area material [19,20]. The air and oxygen sam-

ples exhibited a similar particle size, which is a result of the fact that they both have nearly the same impurity content ($\sim$0.31 wt.% versus $\sim$0.34 wt.% carbon) and amount of second-phase material (i.e., both are essentially single-phase, second phases < 2% for both).

XPS of the LiCoPO$_4$ samples revealed the following: (1) a majority of the Co-ion was in the +2 oxidation state. This result is in agreement with the magnetic measurements of Okada et al. [21] and X-ray absorption spectroscopy results of Nakayama et al. [22]. There was no change in the amount of Co^{2+} as the heat-treatment atmosphere varied from air to pure oxygen. (2) There was about a $\sim$5% decrease in the relative amount of Co^{2+} as the heat-treatment atmosphere was changed from air/oxygen to argon. At present it is not known what oxidation state of cobalt this change is associated with however, based on the X-ray diffraction results shown in Fig. 1 it is likely that this change is associated with the formation of Co$_2$P.

The room-temperature d.c. electrical conductivity of LiCoPO$_4$ heated under air was $\sim$10^{-9} S cm^{-1}. This is in agreement with value of 10^{-10} S cm^{-1} measured using a d.c. method for LiCoPO$_4$ prepared by a solution method and heat treated under air [16]. No difference could be detected in the electrical conductivity values for air versus oxygen. In contrast, the room-temperature electrical conductivity of LiCoPO$_4$ heated under argon was between 10^{-5} and 10^{-4} S cm^{-1}. This is an increase of $\sim$10^4 to 10^5 in the electrical conductivity for LiCoPO$_4$ samples heated under argon compared to under air or oxygen. The conductivity results for LiCoPO$_4$ are in good agreement with the results of Herle et al. [1] for LiNiPO$_4$, who observed a $\sim$10^2 to 10^3 increase in electrical conductivity for LiNiPO$_4$ heated under argon compared to air. They attributed the increase in conductivity to presence of conductive metal phosphides and/or metal phosphocarbides along boundaries of the insulating LiNiPO$_4$ which formed as a result of carbothermal reduction at high temperature when carbon-containing precursors were used [1]. Since, the LiCoPO$_4$ samples used in this study prepared from carbon-containing precursors heat treated under argon also revealed the presence of a metal phosphide (Co$_2$P), whereas no metal phosphides were present in the air and oxygen samples, it is likely that the enhanced conductivity of LiCoPO$_4$ heated under argon versus air/oxygen is do to the presence of conductive metal phosphides along boundaries in the argon sample. On the other hand, because the carbon concentration of the argon sample was $\sim$3$\times$ higher than that for the air/oxygen samples it is also possible that the increased carbon content has contributed to the enhanced electrical conductivity observed. The carbon content was not reported by Herle et al. [1] for LiNiPO$_4$ heated under either flowing air or argon.

It has been shown by Dominko et al. [23] that as the carbon content varied from $\sim$0.3 to 1 wt.% (similar to this study) for LiMn$_2$O$_4$ that the electrical conductivity increased only by $\sim$10^1. Chung et al. [8,24] have suggested that for LiFePO$_4$ doped with supervalent cations containing carbon contents

($\sim$0.3–1.5 wt.%) similar to those observed in the present studies, that the major reason for the $\sim$10^6 increase in the electrical conductivity of the doped versus the undoped samples has do with lattice doping rather than the background carbon impurity. In addition, it has been shown that the incorporation of low levels (amount not reported) of conductive Fe$_2$P increased the conductivity of LiFePO$_4$ by $\sim$10^6 [25], similar to the value observed in this study ($\sim$10^4 to 10^5). Thus, it is tempting to suggest that the major cause of the increase in electrical conductivity of argon sample versus the air/oxygen samples is a result of metal phosphide phases rather than from impurity carbon. However, confirmation of this suggestion would require detailed experiments, in any case it is important to note whatever is the reason (metal phosphides and/or carbon) that $\sim$10^4 to 10^5 in the electrical conductivity for LiCoPO$_4$ samples heated under argon compared to under air or oxygen was observed.

The first cycle discharge curves for LiCoPO$_4$ heated under argon and air are shown in Fig. 2. From Fig. 2 several important points are noted. First, the discharge plateau for the air and argon samples is about 4.7–4.8 V. The plateau of 4.7–4.8 V is in good agreement with previous results for the Co^{3+}/Co^{2+} redox couple in LiCoPO$_4$ [3–5,16,17,21,22].

Second, the discharge capacity of the air sample is $\sim$72 mAh g^{-1}. The first cycle discharge capacity for the air sample is in good agreement with previous first cycle results for LiCoPO$_4$ prepared by a solid-state reaction method and heat treated under air, which range from 60 to 72 mAh g^{-1} [3–5]. However, the result of this study is lower than the $\sim$100 mAh g^{-1} obtained by Okada et al. [21] and the value of $\sim$120 mAh g^{-1} obtained by Nakayama et al. [22], where both studies also used powders prepared by a solid-state method and heated under air. Since, the heat-treatment temperatures used by Nakayama et al. [22] were lower than those used in the present study, it is likely that their material had a smaller particle size and hence, higher capacity is expected and was observed. The precursors, heat-treatment temperatures and times used by Okada et al. [21] were similar to those used in the present study thus; it is surprising why such a large difference in discharge capacity was observed between the two
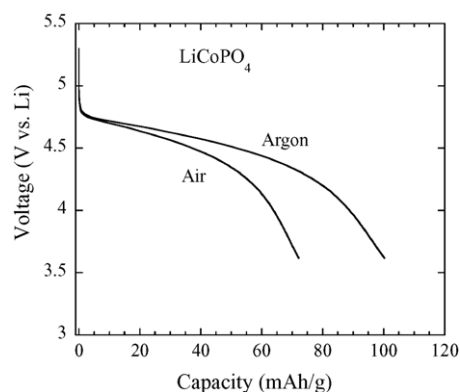

Fig. 2. First cycle discharge curves for LiCoPO$_4$ heated under air or high-purity argon.

studies. Since, no X-ray diffraction, chemistry or particle size data was given in the study by Okada et al. [21] to compare to the present results it is difficult to suggest what causes the difference in discharge capacity. The first cycle discharge capacity for the oxygen sample was $\sim$70 mAh g^{-1}. This is nearly the same value as for the air sample. Similar values of discharge capacity would be expected for the air and oxygen samples since, the chemistry, phases, particle size and electrical conductivity of both samples was nearly identical.

Third, the discharge capacity for the argon sample is higher than that for the air sample. The discharge capacity for the argon sample ($\sim$101 mAh g^{-1}) is $\sim$1.4 $\times$ that for the air sample ($\sim$72 mAh g^{-1}). This is most likely a result of the higher electrical conductivity and smaller particle size in the argon sample which results from the different phases present (i.e., Co$_2$P) and chemistries (i.e., higher carbon concentration) between the two samples. The increase in LiCoPO$_4$ discharge capacity with increasing electrical conductivity is in agreement with the results for LiFePO$_4$ and LiMnPO$_4$, where an increase in discharge capacity was observed as the electrical conductivity of these materials was increased by using a conductive coating [6–8] or lattice doping [9]. The increase in LiCoPO$_4$ discharge capacity with decreasing particle size, leading to enhanced Li-ion diffusion, is in agreement with results for LiMnPO$_4$ [26] and LiFePO$_4$ [27].

The discharge capacity versus cycle number as a function of heat treatment under the three different oxygen partial pressures is shown in Fig. 3. From Fig. 3 several important points are noted. First, the discharge capacity for all three samples decreases with increasing cycle number. The results for the LiCoPO$_4$ sample heat treated under argon shown in Fig. 3 are in good agreement with studies on LiCoPO$_4$ by Tadanaga et al. [16], prepared by a solution method and heat treated under air, and Bramink et al. [28], prepared using excess LiOH and heat treated under flowing argon, where discharge capacity as a function of cycle life was investigated. Tadanaga et al. [16] recorded an initial discharge capacity of $\sim$85 mAh g^{-1}, while Bramnik et al. [28] observed $\sim$92 compared to $\sim$101 mAh g^{-1} in this study. After 10 cycles

the capacity had decreased to $\sim$41 mAh g^{-1} for Tadanaga et al. [16] and $\sim$54 mAh g^{-1} for Bramink et al. [28] compared to $\sim$54 mAh g^{-1} for this study. Based on X-ray diffraction studies Tadanaga et al. [16] suggested that the loss of capacity is not a result of the destruction of the LiCoPO$_4$ structure but resulted from electrolyte decomposition, whereas in contrast Bramnik et al. [28] suggest that irreversible structural transformation of LiCoPO$_4$ is responsible for capacity fade. It is of interest to note both studies used similar electrolytes (1 M LiPF$_6$: EC/DMC) and tested to the same upper voltage limit $\sim$5–5.1 V. Current work is underway to determine if LiCoPO$_4$ structural changes are responsible for capacity fade.

Second, a higher discharge capacity is exhibited by the argon sample over the entire cycle range tested compared to the air/oxygen samples. Third, the discharge capacity as function of cycle number for the air and oxygen samples are in excellent agreement over the entire cycle range tested. Both of these observations have been explained previously.

Fourth, the relatively low discharge capacity ($\sim$50–100 mAh g^{-1}) at low rates ($\sim$C/5) exhibited by LiCoPO$_4$ heat treated under an argon atmosphere compared to the theoretical value ($\sim$170 mAh g^{-1} [2–4]) over the cycle life tested is in contrast to the results for LiFePO$_4$ prepared with either a conductive coating or lattice doping, where at similar rates near theoretical (>90% theoretical) capacity is obtained over a similar cycle life [8,9,27]. This suggests for LiCoPO$_4$ that heating under an argon atmosphere does not provide sufficient enough electrical conductivity and a small enough particle size required to achieve a high discharge capacity for LiCoPO$_4$ to be used as a cathode in Li-ion batteries. Additional procedures such as adding a conductive coating and/or lattice doping and reducing the particle size to the nanoscale are needed.

4. Conclusions

The results of this study reveal that the discharge capacity of LiCoPO$_4$ prepared using carbon-containing precursors is affected by heat-treatment under different oxygen partial pressures. LiCoPO$_4$ heat treated under low oxygen partial (high-purity argon) exhibited a higher discharge capacity compared to under air or pure oxygen over the cycle range tested. The enhanced discharge capacity of the argon sample compared to the air/pure oxygen samples was a result of its higher electrical conductivity and smaller particle size. The enhanced conductivity and smaller particle size of the argon sample are likely do the presence of cobalt phosphides and increased carbon content. No difference in the discharge capacity of LiCoPO$_4$ heat treated under air or pure oxygen was observed. This is expected since the air and oxygen samples had nearly identical chemistry, phases, particle size and electrical conductivity. In order to obtain high discharge capacities needed for LiCoPO$_4$ to be as a cathode in Li-ion
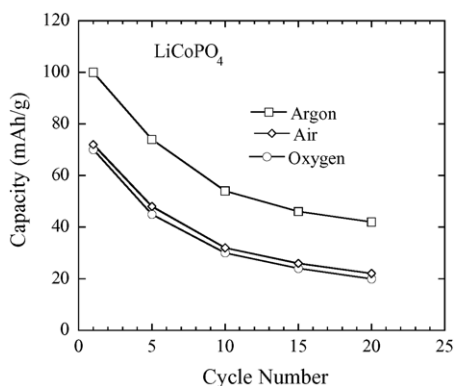

Fig. 3. Discharge capacity vs. cycle number curves for LiCoPO$_4$ heated under pure oxygen or air or high-purity argon. The cells were cycled between 3.5 and 5.3 V at a constant current density of 50 μA cm^{-2}.

batteries, in addition to heat treatment under reducing conditions, additional procedures such as adding a conductive coating and/or lattice doping and/or reducing particle size to the nanoscale are also needed.

Acknowledgement

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