Cr and Si Substituted-LiCo$_{0.9}$Fe$_{0.1}$PO$_4$: Structure, full and half Li-ion cell performance

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HIGHLIGHTS

- The structure of Cr, Si and Fe substituted LiCoPO$_4$ is reported.
- Substitution improves energy storage, cycle life and coulombic efficiency.
- An energy storage capability of 670 Wh per kg of cathode material is demonstrated.

ARTICLE INFO

ABSTRACT

The use of LiCoPO$_4$ as a Li-ion cathode material can enable high energy 5 V batteries. However, LiCoPO$_4$ shows limited cycle life and much less than theoretical energy density. In order to address these shortcomings, Fe, Cr and Si substituted-LiCoPO$_4$ (Cr,Si-LiCo$_{0.9}$Fe$_{0.1}$PO$_4$) was investigated as an improved LiCoPO$_4$ based cathode material. Fe substitution greatly improves the cycle life and increases the energy density. Cr substitution further increases the energy density, cycle life and rate capability. Si substitution reduces the reactivity of the cathode with electrolyte thereby increasing cycle life. In combination, the substituents lead to a LiCoPO$_4$ based cathode material with no capacity fade over 250 cycles in Li/Cr,Si-LiCo$_{0.9}$Fe$_{0.1}$PO$_4$ half cells, a discharge capacity of 140 mAh g^{-1} at C/3 at an average discharge voltage of 4.78 V giving an energy density of 670 Wh per kg of cathode. In graphite/Cr,Si-LiCo$_{0.9}$Fe$_{0.1}$PO$_4$ full Li-ion cells, the cathode material shows an energy density of 550 Wh per kg of cathode material at 1C rate for the initial cycles and 510 Wh per kg of cathode material at the 250th cycle.

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1. Introduction

The development of rechargeable Li-ion batteries operating with a cell voltage near 5 V has attracted much interest over the past decade because of the potential for higher specific energy than the conventional ~4 V Li-ion battery. LiCoPO$_4$ (LCP) has a flat discharge voltage of 4.8 V versus Li and a theoretical discharge capacity of 167 mAh g^{-1} [1]. Therefore, it is an attractive material for enabling high energy Li-ion cells. As a higher energy replacement for LiFePO$_4$, LCP has a more favorable electronic structure for battery use [2] than 4.1 V LiMnPO$_4$ [3] or 5.1 V LiNiPO$_4$ [4] because of its higher d orbital character at the top of the valence band and higher polaronic mobility suggesting better thermal stability and electronic conductivity, respectively. Furthermore, phosphate based cathodes may provide higher abuse tolerance than oxides at a given voltage [5]. The first studies of LiCoPO$_4$ showed that improvements in first cycle discharge capacity were relatively easy to achieve but that capacity fade was the critical problem to solve in order to enable its use as cathode [6–10]. The capacity fade has been proposed to result from instability of the charged structure [11], instability of the electrolyte [11] and nucleophilic attack of fluoride ions on the phosphorus atom of the material [12]. Previous work shows that Fe substitution into LiCoPO$_4$ [11] in conjunction with the use of a voltage stabilizing additive [13], dramatically reduces capacity fade. In addition, progress in reducing LiCoPO$_4$ discharge capacity fade has also been reported through the use of a quartz separator [14] and other electrolyte additives [15].

This work will show that substitutions of Si and Cr into LiCo$_{0.9}$Fe$_{0.1}$PO$_4$ lead to improved electrochemical performance in terms of

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specific energy density, fade and rate capability compared to Fe-only-substituted $LiCoPO_4$. It has been previously reported that the substitution of Co by Fe^{2+}/Fe^{3+} in $LiCoPO_4$ greatly decreases the capacity fade and increases the discharge rate and capacity relative to unsubstituted $LiCoPO_4$ [11]. Furthermore, the Li conductivity is increased for the Fe^{3+} and Fe^{2+} substituted $LiCoPO_4$. The Li conductivity improvement is attributed to increased Li mobility owing to the presence of Li vacancies to charge compensate for Fe^{3+} on the Co^{2+} site [16]. The current study explores using Cr^{3+} and Fe^{2+} substitution for Co^{2+} in $LiCoPO_4$ to determine if a similar electrochemical performance enhancement is found. Furthermore, to reduce the reactivity of the cathode with the electrolyte and thereby improve the coulombic efficiency, Si substitution for Co was performed to introduce strong, less-reactive Si−O bonds. This paper reports the composition, structure, discharge capacity, rate performance and cycle life of Cr, Si and Fe substituted $LiCoPO_4$ cathodes.

2. Experimental

2.1. Powder preparation

For all compositions, the starting components and 5 wt% acetylene black (based on final product mass) were high energy ball milled (Spex SamplePrep 8000 M Mixer/Mill) for 90 min. The milled powders were heated in a tube furnace at a rate of 10 °C per min. to 700 °C under N_2, held at that temperature for 12 h and furnace cooled to room temperature. Initially, samples of starting composition $LiCo_{0.95}Fe_{0.05}PO_4$, $LiCo_{0.90}Fe_{0.10}PO_4$ and $LiCo_{0.85}Fe_{0.15}PO_4$ were prepared from LiH_2PO_4, $Co(OH)_2$ and $FeC_2O_4 \cdot 2H_2O$ to determine the approximate minimal Fe content needed to maintain good cycle life. In subsequent samples, the substitution scheme, $LiCo_{(0.9-y-z)/(1+0.5y)}Fe_{0.1/(1+0.5y)}Cr_{y/(1+0.5y)}Si_zPO_4$ was used to prepare in succession, Cr, Fe substituted LCP and then Si, Cr and Fe substituted LCP. First, Cr substitution into Fe substituted LCP was prepared for optimization of Cr content (y = 0.025, 0.05 or 0.1 and z = 0). Next, two compositions, $LiCo_{0.820}Fe_{0.0976}Cr_{0.0488}Si_{0.00976}PO_4$ and $LiCo_{0.810}Fe_{0.0976}Cr_{0.0488}Si_{0.0195}PO_4$, were prepared for optimization of the Si content (y = 0.05 and z = 0.01 or 0.02, respectively).

2.2. Structural characterization

Phase purity was initially evaluated using X-ray powder diffraction. Data were collected using a Rigaku Ultima III diffractometer. Lattice constants were calculated from peak positions using Rietveld refinement of the pattern collected in a parallel beam geometry using Riqas software (Materials Data Inc.). More detailed structural information was obtained from a combined neutron and synchrotron X-ray Rietveld refinement of diffraction data. Time of flight neutron powder diffraction data were collected at the POWGEN beamline at the Spallation Neutron Source (SNS), Oak Ridge National Laboratory (ORNL) with center wavelengths of 1.066 Å at 298 K to obtain diffraction patterns that spans from d-spacing of 0.35–4.6 Å. High resolution synchrotron powder diffraction data were collected using beamline 11-BM at the Advanced Photon Source (APS), Argonne National Laboratory (ANL) using wavelength of 0.414 Å at 300 K to obtain diffraction patterns that spans from d-spacing of 0.7 Å to 9 Å. Rietveld structural refinements of the synchrotron X-ray and neutron diffraction data were performed using GSAS with EXPGUI [17,18].

2.3. Electrochemical characterization

For electrochemical testing, a composite electrode was fabricated by a slurry coating method. Using N-methylpyrrolidone (NMP) as solvent, the slurry was coated onto an Al foil substrate

after which the solvent was evaporated by heating at 80 °C in a drying oven to produce a composite electrode of 80 wt% carbon containing active (contains 5 wt% C), 10 wt% polyvinylidene fluoride (PVDF) and 8 wt% super-P carbon and 2 wt% conductive carbon nanotube composite (CheapTubes.com). The total carbon content of the composite electrode was thus 14 wt%. The active loading for the cathode was on average about 4–5 mg cm^{-2}. In a dry room (Dew point < −40 °C), the electrode film was cut into small discs and dried at 100 °C under vacuum before use. Electrochemical testing for capacity, rate and cycle life was performed using a Maccor Series 4000 tester. For calculation of C-rate, a capacity of ~130 mAh g^{-1} was used for the substituted $LiCoPO_4$. This value is based on measurement of the average half cell cycling capacity of initially synthesized material and was used throughout the study to maintain consistency although as the synthesis was optimized a higher half cell cycling capacity was measured.

The electrolyte for both half and full cell data reported here was a 1.2 M $LiPF_6$ solution in a 3:7 (wt.%) mixture of ethylene carbonate (EC) and ethyl methyl carbonate (EMC) electrolyte with 2 wt% tris (trimethylsilyl) phosphite, a known high voltage stabilizing additive [19–25].

Li/active half cells (Hohsen Al-clad CR2032) were assembled using Asahi ceramic coated polypropylene as the separator. After cell assembly, the half cells were rested for 12 h. In the first cycle, the half cells were charged to 5 V and then discharged to 3.5 V at a constant C/10 current. In subsequent cycles, the half cells were charged at a C/3 constant current to 5.0 V, charged at a constant 5 V until the current was less than C/15 and then discharged at a C/3 constant current to 3.5 V.

Graphite/active full cells (Hohsen Al-clad CR2032) were assembled using Whatman quartz microfiber (QM) as the separator. The negative to positive electrode capacity ratio was 1.2. The graphite negative electrodes were supplied by Saft America. QM separator was used owing to the reported favorable properties as an HF scavenger in LCP cells [14]. After cell assembly, the full cells were rested for 30 min. In the first cycle, the full cells were charged to 4.85 V and then discharged to 3.0 V at a constant C/20 current. In subsequent cycles, the full cells were charged at a C/2 constant current to 4.85 V, charged at a constant 4.85 V until the current was less than C/15 and then discharged at a 1C constant current to 3.5 V.

3. Results and discussion

3.1. Composition

Since the average discharge voltage and therefore the energy density increases with higher Co content, the minimal amount of Fe^{2+} substitution for Co^{2+} needed to maintain good cycle life was determined. Samples with 5, 10 and 15 atom % Fe^{2+} substitution for Co^{2+} were prepared and tested. From analysis of the fade rate of cells built from these compositions, Fe^{2+} substitution for Co at approximately the 10 atom % level was found adequate to maintain good cycle life. For example, at 5% Fe substitution for Co, 93% of the initial discharge capacity was retained after 25 cycles. By comparison 99% of the discharge capacity was retained at 10% Fe. No further benefit was found at 15% Fe.

Subsequently, in order to further improve properties in terms of discharge capacity, Cr^{3+} substitution into $LiCo_{0.9}Fe_{0.1}PO_4$ was screened based on the idea that the introduction of Cr^{3+} might lead to improved discharge capacity while maintaining cycle life using the nominal substitution scheme: $Li_{1+0.5y}Co_{0.9-y}Fe_{0.1}Cr_y(PO_4)_{1+0.5y}$. It was found that Cr^{3+} substitution at y = 0.025, 0.05 and 0.10 according to the nominal stoichiometry $Li_{1+0.5y}Co_{0.9-y}Fe_{0.1}Cr_y(PO_4)_{1+0.5y}$ was particularly effective to improve the discharge capacity. This substitution scheme rewritten based on the olivine framework is $LiCo_{(0.9-y)/}$